COAL MINE WATERS IN SOUTH AFRICA: THEIR GEOCHEMISTRY, QUALITY AND CLASSIFICATION

VOLUME 1

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CHAPTER 1

Introduction

1.1 Overview

South Africa is thought to be one of the few water-scarce countries in the world in which coal mining has been, and still is, extensively performed. Parts of Australia and the U.S.A. (specifically Wyoming and Montana) are also water-scarce coal-mining regions. In the past, mining has impacted heavily on the South African environment (Funke, 1983). In recent years, however, individual mines have been striving to ensure that the negative impacts of their operations are kept within acceptable limits, especially in terms of water conservation.

Numerous problems are known to exist specifically in the coal mining industry where water is required for underground and surface operations. In these operations it is used for drilling, dust suppression, environmental cooling, as an energy source in hydropower and as a transport medium for backfilling. In addition, potable water is required for drinking purposes.

Large volumes of water are affected by chemical contaminants in the coal mines (Azzie, 1999). These contaminants vary significantly depending on the coal seam mined, the mining method employed, the area, size and purpose of the infrastructure used. The water management structures in place around the seam, the chemistry of the rock sequence in which the coal is found and the quality and quantity of the natural groundwater also play a role (Kempe, 1983).

In many coal mines, such as those studied by Bell and Bullock (1996), Bullock and Bell (1997), Bullock *et al.* (1997), Geldenhuis and Bell (1998), Hobbs (1998), and Bell *et al.* (2001), acid mine drainage (AMD) arises when sulphide minerals contained in coal and associated rocks are exposed to oxidation and the products are flushed by water. The oxidation rate is dependent on temperature, pH, oxygen concentration, chemical composition of the pore water and microbial population (Ritchie, 1994). The process of AMD creates saline drainage water, which is normally strongly acidic (pH less than 3) unless it has been neutralized by contact with alkaline or calcareous rocks (Skousen, 1996; Gray, 1997) as was observed in the collieries studied by Azzie (1999). The affected mine water often resides in surface containment structures and in storage dams in underground workings.

Although acid mine drainage and salinity are the two most serious threats posed to the environment by coal mining (Rikard and Kunkle, 1990), water in many mines has potential for re-use in agriculture (irrigation and livestock watering) and industry (steam generation, cooling, processing, and washing) (Azzie, 1999). Occasionally it has potential for domestic and recreational use. For the most part, the quality can often be improved through appropriate treatment. A number of treatment options are discussed in the literature including both physical and chemical processes (Buehrer and Reitmeier, 1940; Vermeiren, 1958; Loewenthal *et al.*, 1986; Maree *et al.*, 1986; Wagner and van Niekerk, 1987; Friend, 1990; Coetzee *et al.*, 1996 and Pulles *et al.*, 1996).

Despite the fact that a great deal is known about water and the absence thereof in South Africa, it is clear that water resources have been poorly managed in the mining industry for years. This is believed to be due to a general lack of knowledge in terms of its character and re-use potential. A systematic approach to managing the water is needed in order to conserve this resource.

In a recent study by Azzie (1999), the chemical data for a limited number of water bodies in selected South African collieries was assessed. Although some correlations were noted between major constituents in these waters, only a narrow range of pH conditions (6.4 to 8.5) was encountered. The pH of a water body is the result of complex acid-base equilibria of various dissolved compounds (mainly the CO_2–HCO_3^-–CO_3^{2-} equilibrium system), which are also affected by temperature. Under extreme pH conditions, adverse effects result from the dissolution of toxic heavy metals and the protonation and deprotonation of other ions. Therefore, further studies were required in order to gain a comprehensive perspective of the full extent of the impact of varying pH conditions. In addition, a better understanding of the factors causing the noted correlations, and those still to be observed, is crucial as they are invaluable in predicting the behaviour of other similar water bodies and their environmental impacts.

The main thrust of this research was to develop a systematic strategy to identify and explain the relationships between constituents of mine waters and associated, undisturbed groundwaters. By covering a wider study area than the previous one (Azzie, 1999), it will include most of the major South African coal mining regions. It is expected that this will provide a suitable framework for the design of an information system to make water use more effective in the mining industry. The essence of this information system will be a geochemically based classification of the water bodies on the coal mines, with due recognition also being given to technical criteria which are practically relevant to water quality. It is anticipated that the chemical characterization, classification and subsequent treatment of affected water will help optimize reclamation and re-use, and reduce pollution and waste.

1.2 Coal in South Africa

Coal is one of the major primary energy resources in South Africa and the world; it is the backbone of the metallurgical industry where it is used as a reducing agent in the manufacture of iron and steel, ferro-alloys and many non-ferrous metals, and it also constitutes a major feedstock for the chemical industry (Snyman, 1998).

The world oil crisis of 1973 stimulated an overseas interest in South Africa's coal. Competitive production costs and a sound infrastructure permitted South Africa to successfully penetrate the international coal market. Furthermore, it currently houses approximately 90% of the known coal resources of Africa. The recoverable reserves put South Africa in the fifth position in the world, with 10.9% of the world reserves of hard coal. South Africa also ranks fifth in terms of coal production and second in terms of coal exports (Clifford, 2000).

Bituminous coal comprises the predominant coal resource in the country. These coals form the core of the South African resources and reserves. They are present in all the coalfields of the central and northern regions of what was the old "Transvaal" and in the Free State. In general the coal increases in rank from west to east across the country. Thermal metamorphism has reduced the majority of coals in the most eastern coalfields (such as Vryheid) to anthracite and low volatile bituminous coals (Barker, 1999).

1.2.1 Environmental setting

In Southern Africa the major period of coal formation commenced about 260Ma in the southern and eastern Mpumalanga region and northern Natal (Ecca Group, Vryheid Formation). From this central region of the main Karoo basin, coal development radiated outwards in all directions over the ensuing period. It finally died out during the Upper Permian (Beaufort group) in the centre of the "Transvaal Craton", in the Northern Province and in the north-eastern Kwazulu-Natal (KZN) and the Eastern Cape (Barker, 1999).

Southern hemisphere, and in particular South African, coals were formed in a cool temperate climate and post glacial environment, hence both the vegetation sources and the depositional conditions were distinctly different from those in which the Carboniferous coals of Laurasia were produced. The coal bearing basins were formed in a relatively stable continental region in a fluviatile, lacustrine or deltaic environment. Gondwanan coals formed from the *Glossopterid* flora which, although growth was rapid over a short growing season, degraded relatively slowly (Falcon, 1986).

1.2.2 Distribution and quality

South African coal deposits are confined to an area east of 26°E. Three coal-bearing intervals are recognized. These are in: the Vryheid Formation (Low to Middle Ecca Group), the Lower Beaufort Group or upper Ecca Group (Faure *et al.*, 1996) coal "zones" in disconnected and, in part, widely separated fields, and in the lower Beaufort Group. All those considered in this study are derived from the Vryheid Formation. The sulphur content of the unwashed coals of eastern regions of South Africa is generally higher than that in the central and western coalfields. The washability of the coals in the Witbank and Highveld coalfields with regard to sulphur is generally better than the coals in the eastern regions (Barker, 1999).

According to Barker (1999), fairly good quality steam coals and some metallurgical coals are developed in the Highveld Coalfield, and even higher quality steam and metallurgical coals in the Witbank Coalfield. High quality bituminous steam, coking and anthracitic coals are developed in the KZN fields (including the Vryheid coalfield).

Anthracite is developed in selected South African coalfields entirely as a result of heating due to dolerite sill and dyke intrusions during the late Jurassic. The deposits are thus erratic in development and grade laterally through low volatile bituminous coals into unmetamorphosed coals, often of high rank. Such deposits are widespread in the coalfields of KZN.

1.3 Geology

The South African coal measures form part of the Ecca Group of the Karoo Sequence. Most of the deposits are found in the Vryheid Formation (Figure 1.1), which is economically the most important formation in the Sequence (Stratten, 1986). Coal seams also occur locally in beds of both the Molteno Formation and the Beaufort Group. The Vryheid Formation has a maximum thickness of 500m and consists of sandstone or conglomerate, shale, and the coal beds (SACS, 1980).

SUPERGROUP	AGE (Ma)		GROUP	FORMATION
KAROO SEQUENCE	Jurassic	140	Drakensberg	Drakensberg
		195		Clarens
	Triassic	225		Elliot
	Upper Permian	230	Beaufort	Adelaide Subgroup
	Middle Permian	260	Ecca	Volksrust Formation
				Vryheid Formation
				Pietermaritzburg Formation
	Lower Permian	300	Dwyka	

Figure 1.1: Lithostratigraphic nomenclature for the Karoo Sequence in South Africa (After Barker, 1999).

The Vryheid Formation occurs as a sequence of coarse clastic sediments between the overlying, Volksrust, and underlying, Pietermaritzburg, shale formations. It is composed mainly of coarse-grained arkose, conglomerate, micaceous siltstone, carbonaceous shale, coal seams, and thin layers of limestone. It has abundant sedimentary structural features such as large-scale planar and trough cross-bedding, indicating the presence of channel bars, ripple marks, scour channels, and slump structures. This implies deposition by shifting variable currents in shallow water; a predominantly fluvial-deltaic environment. The fact that marine transgressions took place are indicated by an extensive glauconite-rich sandstone immediately overlying the No. 4 Coal Seam and the discovery of marine microfossils in thin carbonaceous shale beds (Hart, 1964).

Nineteen coalfields are recognized in South Africa, covering a surface area in excess of 9.7M ha (Barker, 1999). Of these, samples were taken from five coalfields, covering an area of 4.1M ha. These include the Free State, Sasolburg/Vereeniging, Witbank, Highveld and Vryheid coalfields (Figure 1.2). The boundaries between the individual coalfields are largely based on historical and geographical considerations and not necessarily on pronounced geological differences.

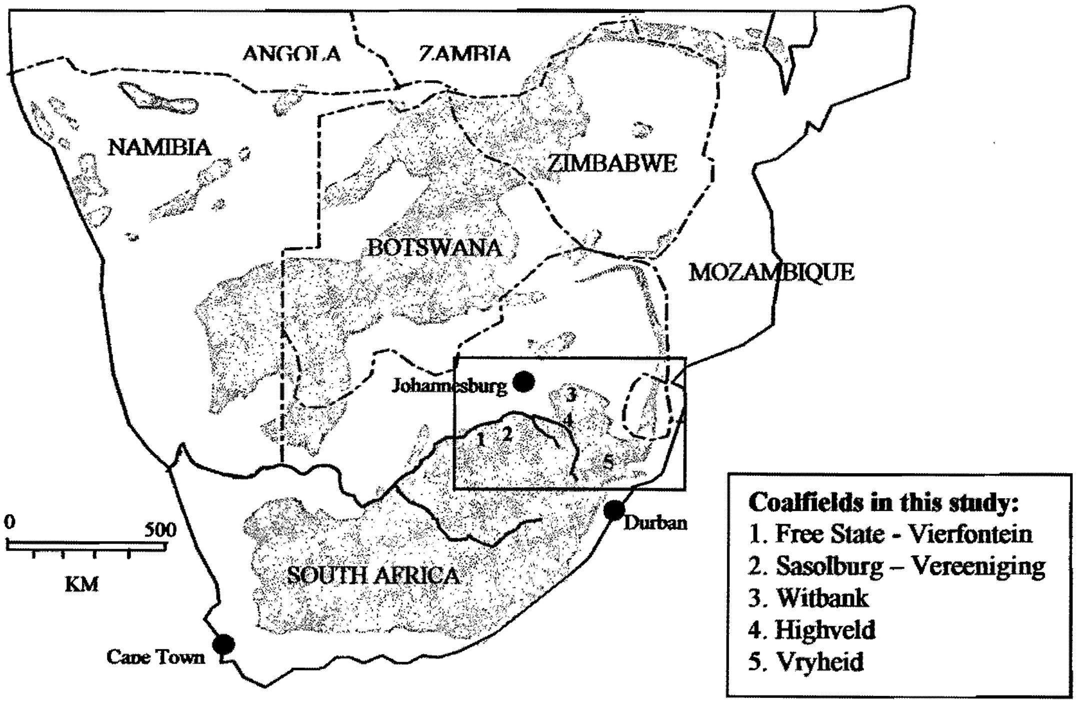

Figure 1.2: *Coalfields in this study and general distribution of Karoo rocks (shaded areas) in Southern Africa (After Barker, 1999).*

Almost 59% of the mines are currently concentrated in the Witbank and Highveld coalfields. The mines in the Vryheid and Sasolburg / Vereeniging coalfields add a further 10% to this total. The Witbank, Highveld and Mpumalanga coalfields account for almost 90% of the coal production in South Africa (SACR, 1998). Further details will be presented in Chapter 4.

1.4 Climate

Most of the mines are situated in the Eastern Plateau Highveld climate zone, which is characterized by relatively warm wet summers (October to March) and cool to cold dry winters (April to September). The rain occurs almost exclusively as showers (mild to heavy) and thunderstorms occur mainly in summer, with the maximum in December to February. The mean annual number of thunderstorms on the Highveld is approximately 75. Heavy falls (+100 mm) in a single 24-hour period are rare.

Detailed climatic records have not been kept for a number of the collieries. Therefore, data presented in Table 1.1 are calculated from monthly averages, as supplied by the National Weather Bureau, for the nearest district, over the past 10 - 15 years. It is important to note, however, that where seasonal sampling was undertaken, the rainfall during the summer was well in excess of the average.

Table 1.1: *Climatic data, obtained from the South African Weather Bureau, for districts in the study area.*

District	**Mean Max Temp (°C)**		**Mean Min Temp (°C)**		**Mean Annual Rainfall (mm)**	**Mean Annual Evaporation**
	Summer	*Winter*	*Summer*	*Winter*		
Klerksdorp	28.8	20.5	16.1	2.3	499	178 (Potchefstroom)
Vereeniging	27.6	20.0	15.0	1.4	604	178 (Potchefstroom)
Witbank	25.9	19.2	14.8	4.9	649	147 (Hendrina)
Hendrina / Carolina	24.3	18.5	13.2	2.3	653	147 (Hendrina)
Standerton	26.2	18.9	14.0	1.2	655	148 (Standerton)
Vryheid	26.6	20.8	16.1	5.9	834	139 (Newcastle)

1.5 Classification of mine waters

The following quote is from a 1937 report on the pollution of streams, in the Ohio Basin, by coal mine drainage: "..... the water caused excessive corrosion of the federal navigation locks and dams, ships and barges, bridges and culverts, pipelines and plumbing. The acid, iron sulphate, and iron oxide (red water) often destroyed all fish and aquatic life, interfered with nature's self-purification of the streams sometimes perhaps favourably, in other cases detrimentally, made water unfit for drinking or household purposes, and caused unsightly reddish brown spots on fabrics in laundries and textile factories and scum in washbowls, sinks and tubs. The water was destructive, scale forming, and unsuitable for use in locomotive and power plant boilers, in manufacturing industries, and in municipal waterworks…." (Hodge, 1937).

From this it is clear that mining activities result in a variety of chemical impacts on nearby water bodies. Mine drainage is chemically unstable and continually changing in character. Its composition reflects not only its origin, but also what it encounters along its flow path. Treatment of water supplies is becoming more difficult, more time consuming, and more expensive depending on what its proposed use is. Although numerous uses exist, the three main classes of use are domestic (household), agricultural and industrial (Driscoll, 1986). A supply intended for municipal use may include all three classes and accordingly require a standard of quality that is generally higher than that needed for any one class. On the other hand, water for use in a particular industry may require a quality that is substantially higher than the one considered acceptable for a municipal supply.

There are numerous individual criteria by which water can be classified on an *ad hoc* basis either in terms of quality (e.g. hardness, scaling or corrosion potential, irrigation suitability, potability) or geochemical origin (e.g. mineral saturation indices, ionic ratios or products). Some parameters (e.g. sodium adsorption ratio and calcite saturation index) are both geochemically revealing and empirically valuable as indices of quality for specific purposes. Although numerous classifications exist, five major hydrochemical schemes have been employed to classify mine water discharges. Details of these can be found in Chapter 2 suffice to say that none is hydrogeochemically useful in terms of the genesis of the water and addresses the question of quality.

1.6 Objectives

The classification of waters, whether natural or contaminated by various human activities, is usually designed to suit specific purposes. These purposes include improved geochemical understanding and water use within agricultural and industrial processes. Is it then possible to develop a classification system that satisfies all or most of these different objectives simultaneously ?

> i.e. *Can a classification system have a sound geochemical basis and at the same time be useful in the evaluation of water for a wide spectrum of applications in the mining industry and in agriculture* ?

In order to integrate the geochemical and technical criteria required for such a classification, a link is sought between those constituents which characterize a water body as a result of its genesis and those responsible for limiting its use (e.g. alkalinity, salinity and sodicity).

As the composition of a water body may be affected by its interactions with the local geology, it is necessary to determine to what extent the surrounding rock, specifically the shales, affects the composition of the water. Furthermore, these water-rock interactions may be useful for predicting whether acidification or neutralization is the primary process responsible for the characterization of a particular water body and indicating whether is it likely to last. In addition, one wonders whether it is possible to gain a better understanding of the evolution of mine waters by including the natural salinity levels, local climate and soil type in the characterization of the water ?

As already noted, some interesting correlations were found to exist between major chemical constituents in previous studies of colliery waters. It would be interesting to determine whether similar correlations could be found in other South African colliery waters. What conclusions can be drawn from these correlations and how can these be used to predict the future behaviour of the particular water bodies ?

The main aim of this study is to classify water in the South African collieries by integrating geochemical and technical criteria. Could economic factors relating to water treatment costs be added to these geochemical and technical criteria ? Regardless of whether economic factors are included or not, such a classification would be invaluable if it could be applied to coalfields worldwide despite the differences between host rocks, minerals and *in situ* conditions.

Despite the fact that large quantities of information are already housed in institutional databases in South Africa, it is uncertain whether this is sufficient to allow such a system to be designed without having to resort to additional sampling and analysis. Could a simple, yet effective, means of assessing the water quality, based on a few ideal analyses, be developed such that potentially usable sources of water could be identified without having to perform a multitude of expensive and time-consuming analyses ?

CHAPTER 2

Geochemistry, quality and classification of colliery waters – A Review

2.1 Introduction

South Africa possesses abundant mineral resources which have been mined for over a century, but it has limited water resources. Water is a fundamental necessity for mining, in terms of both quantity and quality. The use of water in coal mining covers a variety of processes, from potable water to cooling water to acting as a transport medium, with many uses in between. Unfortunately coal mining activities can result in contamination of surface and groundwater by the addition of salinity, acidity and suspended sediment load. This review addresses the major influences on the geochemical evolution of mine waters, the criteria used for assessing its quality and re-use potential, and critically examines the progress which has been made in the development of classification systems for mine waters.

2.2 Geochemical evolution of mine waters

2.2.1 Geochemistry of acid mine waters

2.2.1.1 Formation of acid mine waters

The chemical reaction responsible for the formation of acid mine waters requires three basic ingredients: pyrite (or other sulphide minerals), oxygen, and water. The overall reaction is often written as:

$$FeS_2\,(s) + 15/4\ O_2\,(g) + 7/2\ H_2O\,(l) \rightarrow Fe(OH)_3\,(s) + 2\ H_2SO_4\,(aq) \qquad [1]$$

Although this gives the correct picture in that oxygen is the ultimate driving force for the oxidation of pyrite and the final products are an insoluble form of oxidized iron and an aqueous sulphuric acid solution, it is an oversimplification of the process. It fails to explain geochemical mechanisms or rates and it does not reflect the slow oxidation of aqueous ferrous iron in acid solutions that often results in high ferrous iron concentrations in acid mine waters. Furthermore, factors such as microbial catalysis, neutralization reactions, sorption reactions, and climatic effects have an important influence on pyrite weathering, but are not considered explicitly in the above equation (Nordström and Alpers, 1999a).

In addition, there is no simple, single test to assess metal and acid mobility in the mining environment because of the numerous variables that affect contaminant transport. The problem is multi-faceted and it must be emphasized that acid mine drainage forms within a complex system for which several factors need to be considered by the disciplines of inorganic and organic chemistry, geology and mineralogy, hydrology and microbiology. Recently, the geochemistry of acid mine waters was reviewed by Nordström and Alpers (1999a), a summary of which is presented here in Section 2.2.1 (Geochemistry of acid mine waters).

2.2.1.2.1 Stoichiometry and kinetics of abiotic pyrite oxidation

The voluminous literature on pyrite oxidation has been reviewed by Lowson (1982) with regard to abiotic chemical oxidation and by Nordström (1982a) with regard to biotic and abiotic geochemical oxidation. More recent contributions can be found in Goldhaber (1983), McKibben and Barnes (1986), Moses *et al.* (1987), Moses and Herman (1991), and Evangelou (1995). When pyrite oxidizes there are two components that can oxidize, the ferrous iron and the sulphidic sulphur. It has also been recognized that iron easily leaches out of pyrite but tends to stay in the ferrous state in acid solutions. Hence, another common representation of the pyrite oxidation reaction is:

$$FeS_2\,(s) + 7/2\ O_2\,(g) + H_2O\,(l) \rightarrow Fe^{2+}\,(aq) + 2\ SO_4^{2-}\,(aq) + 2\ H^+\,(aq) \qquad [2]$$

As the sulphur in pyrite oxidizes more rapidly than the iron, it will transfer a larger number of electrons. Consequently, a number of possible side reactions and sulphur intermediates may occur during oxidation. One side reaction is the formation of elemental sulphur during oxidation (Stokes, 1901; Bergholm, 1955; Clark, 1966). Another side reaction, or group of reactions, is the formation of intermediate sulphoxyanions of lower oxidation state than that found in sulphate: i.e. thiosulphate ($S_2O_3^{2-}$), polythionates ($S_nO_6^{2-}$), and sulphite (SO_3^{2-}).

These intermediate sulphoxyanions are an excellent source of energy for chemoautotrophic bacteria of the *Thiobacillus* genus and may be rapidly biodegraded before detectable concentrations can accumulate (Gould *et al.*, 1994). The degradation of intermediate valence sulphur species can also occur rapidly through abiotic processes.

It has long been known that ferric iron rapidly oxidizes pyrite (Stokes, 1901). Experiments carried out by Garrels and Thompson (1960) and McKibben and Barnes (1986) have confirmed the reaction stoichiometry:

$$FeS_2\,(s) + 14\,Fe^{3+}\,(aq) + 8\,H_2O\,(l) \rightarrow 15\,Fe^{2+}\,(aq) + 2\,SO_4^{2-}\,(aq) + 16\,H^+\,(aq) \qquad [3]$$

for the oxidation of pyrite by ferric ions. Reaction [3] is considerably faster than the reaction with oxygen as the oxidant, but significant concentrations of oxidized iron only occur at low pH values because of the low solubility of hydrolyzed ferric iron at near-neutral pH values. Hence, it is thought that pyrite oxidation is initiated by oxygen at near-neutral pH (Equation [2]) but as pH values reduce to about 4, the rate of oxidation becomes governed by equation [3]. Oxygen is still required to replenish the supply of ferric iron according to:

$$Fe^{2+}\,(aq) + \tfrac{1}{4}\,O_2\,(g) + H^+\,(aq) \rightarrow Fe^{3+}\,(aq) + \tfrac{1}{2}\,H_2O\,(l) \qquad [4]$$

The oxygen, however, does not have to diffuse all the way to the pyrite surface. It is quite possible for the pyrite to oxidize in the absence of dissolved oxygen. Nevertheless, the overall rate of pyrite oxidation in a tailings pile, in a mine, or in a waste rock pile will largely be determined by the overall rate of oxygen transport. Furthermore, the oxidation of pyrite by O_2 is mediated by the Fe(II)/Fe(III) system; pyrite is oxidized by Fe (III), which forms a surface complex with pyrite (Stumm and Morgan, 1981).

Considerable speculation can be found in the literature on the question of the initiation and propagation of pyrite oxidation. Undoubtedly, during the initiation of pyrite oxidation, there are complex chemical and microbiological processes occurring in microenvironments (Williams *et al.*, 1982). The existence and importance of these microenvironments is well illustrated by the formation of jarosite, a mineral that can only form under acid conditions but has been found by Carson *et al.* (1982) in soil waters of near-neutral pH.

Nitrate reduction coupled with pyrite oxidation in aquifers has been reported by Van Beek *et al.* (1988, 1989) and Postma *et al.* (1991). This process involves the oxidation of both sulphur and Fe (II) and can be described by the reactions:

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 5Fe^{2+} + 10SO_4^{2-} + 2H_2O \qquad [5]$$

and

$$10Fe^{2+} + 2NO_3^- + 14H_2O \rightarrow 10FeOOH + N_2 + 18H^+ \qquad [6]$$

As in the case of pyrite oxidation by oxygen, the energy of sulphide oxidation yields Fe^{2+}-rich waters. Inorganic oxidation of pyrite by nitrate seems not to be possible in anaoxic systems (Appelo and Postma, 1996). The sulphide in pyrite, however, is apparently oxidized by *Thiobacillus denitrificans* (Kölle *et al.,* 1987) while the Fe^{2+} subsequently is oxidized by nitrate with *Gallionella ferruginea* (Gouy *et al.*, 1984). The additional presence of oxygen in field situations may furthermore generate complex reaction sequences.

The oxidation of at least 18 different sulphide minerals has been investigated by Nordström and Southam (1997). Most of these have been studied with and without microbial catalysis by *Thiobacillus ferrooxidans*. The microbial oxidation rate is usually greater than the abiotic rate, all other conditions being equal. Furthermore, there are numerous reports on the oxidation rates of pyrite and marcasite (and other sulphide minerals) by oxygen, by ferric iron, and by hydrogen peroxide. Nordström and Alpers (1999a) compared the oxidation rate of pyrite by ferric iron and found that it can be 2 – 3 orders of magnitude faster than by oxygen, that some minerals oxidize more rapidly than pyrite and some more slowly, and that oxidation rates can range over three orders of magnitude. These rates are demonstrably faster than the dissolution rates for aluminosilicate minerals (White and Brantley, 1995) by one to several orders of magnitude.

As the oxidation rate for pyrite by Fe^{3+} *(aq)* is faster than that by oxygen, it is important to know the oxidation rate for ferrous to ferric iron according to equation [4]. Numerous studies on the ferrous iron oxidation rate show that, under acid conditions, the rate becomes very slow and independent of pH. Singer and Stumm (1968) reported an abiotic rate of 2.7×10^{-12} mol/L at pH values below 4. Similar rates have been reported elsewhere. Such rates are considerably slower than the rate of oxidation of pyrite by Fe^{3+} *(aq)*; hence, equation [4] would be the rate-limiting step were it not for the catalytic effect of bacteria.

2.2.1.2.2 Microbial oxidation

Micro-organisms are abundant in natural waters containing acid mine drainage. In many cases, they are the only form of life under such conditions. As early as 1919, Powell and Parr suggested that pyrite oxidation and the consequent acid mine drainage from coal deposits may be catalyzed by bacteria. Lackey (1938) observed flagellates, rhizopods, ciliates, and green algae in 62 West Virginian steams. Joseph (1953) found gram-positive and gram-negative bacilli and cocci, fungi, green algae, diatoms, and actinomyces in acidified surface waters and soils in West Virginia and Pennsylvania. Two acidophilic bacteria, *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans*, were also isolated and identified and it was shown that microbial degradation of pyrite was an important factor in the production of acid mine waters. The nutritional requirements for *T. ferrooxidans* are ubiquitous. Nitrogen and carbon dioxide are available in the atmosphere. Sulphur is readily available in mined environments, and only small amounts of phosphorus are needed. Furthermore, Thiobacilli have several adaptive techniques that permit them to tolerate low pH and high metal concentrations (Tuovinen *et al.*, 1971; Kushner, 1978).

T. thiooxidans oxidizes elemental sulphur but not iron, *T. ferrooxidans* oxidizes both iron and sulphur compounds, and a third species *Leptospirillum ferrooxidans*, behaves metabolically like *T. ferrooxidans* although it has a different morphology, which was first described by Markosyan (1972). Nevertheless, it is now thought to be as important as the other two bacilli (Sand *et al.*, 1992). In addition, there are probably numerous other bacteria, yet to be identified or characterized, that also oxidize Fe and S.

2.2.1.2 Redox chemistry and mineral solubility

2.2.2.3.1 Eh-pH diagrams and redox chemistry

The traditional graphical method of delineating the stabilities of reduction-oxidation (or redox) species in geochemical systems (and in corrosion systems) has been through the use of Eh-pH (or pe-pH) diagrams. These are a type of master variable diagram where the independent or master variable is pH. Although originally developed by Pourbaix in 1945, they were introduced and championed in the geochemical literature by Garrels and Christ (1965) and Hem (1961, 1985), who used the concepts of Eh and pH as a convenient means of representing redox relationships for ions and minerals.

These pe-pH diagrams can be very useful in showing the general stability relations among redox-sensitive ions and minerals, but their limitations must be clearly understood:

1) The redox chemistry of a solution or a natural water cannot be measured by a simple "Eh" parameter. There is no such thing as a single representative redox potential or an Eh of a water. Hence, Eh measurements must be quantitatively correlated to a specific redox couple such as Fe (II/III), otherwise they are of little use.

2) Redox couples rarely, if ever, reach equilibrium at temperatures below 100°C. This is why a single Eh cannot be assigned to a water sample. Furthermore, when different redox couples are present in the same water sample, none of them appear to be in equilibrium. Multiple redox couples present in individual samples have been known to yield computed Eh values spanning as much as 1000 millivolts. Not only do computed Eh values not agree with each other, but they do not agree with a single "master" value measured in the field with a platinum electrode (Lindberg and Runnells, 1984).

3) Redox potential measurements respond to electroactive aqueous ions. To be electroactive an ion must have a sufficiently high exchange current density (Bricker, 1982) so that there is no kinetic hindrance to the transfer of electrons. The only elements or ions which commonly meet this requirement in mine drainage are iron (II/III) and sulphur (sulphide / sulphate).

4) The redox conditions of a water sample are best characterized analytically by determining the concentrations of multiple redox species for each redox-active element in the sample. For example, acid mine waters are easily analyzed for Fe (II) and Fe (total) by visible spectrophotometry using a ferroin reagent, such as orthophenanthroline. Acid mine waters and other types of surface waters are usually of a mixed redox chemistry and only by determining relevant redox species can the redox chemistry of the water be interpreted.

2.2.2.3.2 Iron photo-reduction

Iron (II) concentrations in oxygenated surface waters have not only been detected but have been found to vary from night to day. The concentrations of Fe (II) reach a peak during the middle of the day, at the peak of insolation. The solar radiation reduces both dissolved Fe (III) and colloidal ferric hydroxide in natural waters (Waite and Morel, 1984). The same effect has been found for acid mine waters that have < 5 mg/L dissolved iron (McKnight *et al.*, 1988; McKnight and Bencala, 1988). McKnight *et al.* (1988) found the day-time production of Fe (II) to be nearly 4 times faster than the night-time oxidation of Fe (II). These results might also be enhanced by light inhibition of iron- and sulphur-oxidizing bacteria (le Roux and Marshall, 1977). The continual exposure of acid mine waters to the sun promotes recycling of the iron between dissolved and particulate phases and may have important consequences for the sorption of metals. It is uncertain whether temperature as well as light play a role, but it is expected that, indirectly, both do as they are likely to be at their maximum at the peak of solar insolation.

2.2.2.3.3 Saturation indices and mineral solubilities

Although not always the case (Azzie, 1999), acid mine waters are often characterized by low pH, high concentrations of iron, aluminium, other metals, and sulphate. Compounds that might be stable under these conditions include jarosite, alunite, barite, anglesite, gypsum, and a suite of ferric- and aluminium-hydroxysulphates.

The saturation index (SI) for an aqueous solution with respect to a particular mineral describes the thermodynamic tendency of that solution to precipitate or to dissolve that mineral. If equilibrium solubility is achieved and if it exerts the dominant control on the concentration of one or more elements, then the SI values should show a linear and horizontal trend close to zero. In other words, such a pattern on a plot of SI (gypsum) vs sulphate concentration signifies that the water chemistry reflects the stoichiometry of gypsum, indicating that it may have reached equilibrium. One would expect the values to plateau with the appropriate stoichiometry of the mineral, generally in the region of supersaturation, due to the particle size effect on solubility. This is because the solubility product constant usually refers to a coarse-grained, well-crystallized material. It might also be due to solid solution substitution of trace components (Nordström and Alpers, 1999a). In general, the stoichiometry of a phase controlling the solubility of an aqueous constituent can be derived from an appropriately selected ion-activity plot.

2.2.1.3 Secondary minerals

Acid mine waters are highly reactive solutions that can dissolve most primary minerals and induce the formation of a variety of secondary minerals. For the most part, secondary minerals are those that form during weathering. Insoluble secondary minerals with large surface areas can effectively immobilize many of the major contaminants in acid mine waters, providing an important attenuation and detoxifying mechanism.

Mining tends to cause a dramatic increase in the rate of sulphide oxidation reactions because of exposure of large volumes of reactive material to atmospheric oxygen. Blasting and crushing of ores and waste material leads to a considerable increase in the available surface area of reactive minerals. Hydrologic changes caused by mine dewatering in both underground and open-pit mines may expose large volumes of rock to atmospheric oxygen.

According to Nordström and Alpers (1999a), four important processes lead to the formation of secondary minerals from acid mine waters:

1) iron oxidation and hydrolysis;
2) reaction of acid solutions with sulphides, gangue minerals and country rock;

3) mixing of acid mine waters with more dilute waters;
4) evaporation of acid mine waters.

A suite of Fe (III) minerals can form from iron oxidation and hydrolysis. Many of these minerals have very low solubility, fall in the colloidal size range (< 1.0 μm), and can adsorb or co-precipitate significant quantities of trace elements. Reaction of acid mine waters with country rock and some gangue minerals, such as calcite and dolomite, will cause neutralization and precipitation of metals. Evaporation concentrates the acid, sulphate, and metals found in acid mine waters, which may reach mineral saturation, forming efflorescent sulphate salts, a common feature associated with oxidizing sulphide-bearing mine wastes. These processes are thought to be instrumental in the evolution of many of the mine waters in this study, and will be discussed further in Chapter 5 (Modelling water-rock interactions).

2.2.1.3.1 Metal oxides, hydroxides and hydroxysulphates

Most divalent and trivalent metals exhibit amphoterism, i.e., they produce a solubility minimum at near-neutral pH values with enhanced solubilities under both acidic and basic conditions. Different metals reach their minimum solubility at different pH values. This phenomenon provides the basis for removal of metals during rapid neutralization of acid mine drainage by alkaline treatment (lime, limestone, or sodium hydroxide). The pH-specific solubility minimum varies for each metal, causing a different efficiency of metal removal for neutralization to a given pH (Barton, 1978).

Nordström and Alpers (1999a), Bigham and Nordström (2000) and Jambor *et al.* (2000) give a comprehensive overview of the iron, aluminium and other metal oxides (such as copper, nickel and manganese), which are known to be associated with acid mine drainage, and specifically the jarosite-alunite group of minerals. Common iron oxide, hydroxide and hydroxysulphate minerals include hematite, magnetite, goethite, lepidocrocite, ferrihydrite, schwertmannite and jarosite. Common aluminium oxide, hydroxide and hydroxysulphate minerals include boehmite, gibbsite, alunite, jurbanite and basaluminite. The reader is referred to the above-mentioned publications for details.

According to Nordström and Alpers (1999a), and Bigham and Nordström (2000), ferrous hydroxide is considerably more soluble than its ferric equivalent at a given pH and the former appears only rarely in nature. $Fe(OH)_2$, when slightly oxidized, takes on a green appearance and is also known as "green rust". Ferrihydrite is a poorly crystalline form of hydrous ferric oxide/hydroxide that seems to be the first phase to form upon neutralization of Fe(III)-bearing solutions at low temperature, surficial conditions. Ferrihydrite in mining environments is associated with waters having pH values of 5 to 8 (Bigham, 1994). Hematite (Fe_2O_3) and goethite ($FeO(OH)$) are the most common and most stable forms of ferric oxide and oxyhydroxide. Therefore, it is not surprising that ferrihydrite is known to convert to hematite if conditions are maintained between pH 5 and 9. Outside of this range, most of the ferrihydrite dissolves and reprecipitates as goethite (Schwertmann and Murad, 1983).

In acid mine waters, aluminium-sulphate and -hydroxysulphate minerals become more stable than common soil minerals such as gibbsite and kaolinite. Depending on sulphate and potassium activities, at pH < 5.5, gibbsite becomes unstable relative to alunite (Nordström, 1982b). At pH < 4, jurbanite becomes more stable. Despite its apparent thermodynamic stability, jurbanite only rarely occurs as post-mining efflorescence (Anthony and MacLean, 1976), and has not been found commonly as a mineral precipitate from acid mine waters.

The behaviour of aluminium in acid mine waters has been described by Nordström and Ball (1986). For waters with pH values less than 4.5 to 5.0, dissolved aluminium tends to behave as a conservative ion in surface waters, whereas for waters with pH > 5.0, solubility control of dissolved aluminium by microcrystalline to amorphous $Al(OH)_3$ is apparent. Such control may be caused by equilibrium solubility or by a surface reaction involving the exchange of Al^{3+} for $3H^+$ on an aluminous surface.

2.2.1.3.2 Soluble sulphates

Soluble sulphate minerals, often occurring as efflorescent salts, are common in mines, on mine tailings and waste rock dumps, and on sulphide mineralization exposed to the air. These phases store metals and sulphate during dry periods and dissolve readily during flushing events, a process that has an important influence on temporal variations of metals in surface waters affected by mine wastes.

The most common efflorescent minerals are hydrated iron sulphate salts. Examples, in paragenetic sequence, include melanterite ($Fe^{II}SO_4 \cdot 7H_2O$), copiapite ($Fe^{II}Fe^{III}_4(SO_4)_6(OH)_2 \cdot 20H_2O$), roemerite ($Fe^{II}Fe^{III}_2(SO_4)_4 \cdot 14H_2O$) and rhomboclase $(H_3O)Fe^{III}(SO_4)_2 \cdot 3H_2O$. The formation of melanterite as the first phase to precipitate from the evaporation of many acid mine waters is consistent with the preponderance of aqueous ferrous iron in these waters. Reactions [2] and [3] above indicate that aqueous ferrous iron and sulphate are the initial products of pyrite oxidation, and it is these ions that combine to form melanterite. The remaining iron sulphates form in a sequence as the solutions evaporate and the ferrous iron oxidizes to ferric iron. A simple progression of ferrous to ferric salts is, however, not observed because of differences in solubility among the various salts and the influence of other major elements which substitute to a variable degree for divalent and trivalent iron.

Another important role of the soluble iron sulphates is to store acidity and oxidation potential in the form of hydronium and ferric ions. The mineral rhomboclase is essentially a solid form of sulphuric acid plus ferric sulphate. Although generally considered rare, large quantities of rhomboclase and other iron sulphate salts were found at Iron Mountain, California, in inactive underground mine workings within a volcanogenic massive sulphide deposit (Alpers and Nordström, 1991). The salts were observed to be actively forming from waters with pH values from 1 to less than –3 (Nordström *et al.*, 1991; Alpers *et al.*, 1991; Nordström and Alpers, 1999b). Other ferric-sulphate and mixed ferrous-ferric-sulphate salts have been found associated with mine wastes and spoils in numerous localities including coal and metal mines (e.g. Zodrov and McCandlish, 1978a, b; Zodrov *et al.*, 1979; Cravotta, 1994; Plumlee *et al.*, 1995).

There are a large number of additional metal sulphates that occur as efflorescent minerals in weathered mineral deposits and mining environments. Some of the more common ones include epsomite ($MgSO_4 \cdot 7H_2O$), goslarite ($ZnSO_4 \cdot 7H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$). It is important to note that these salts, like the metal hydroxides, hydroxysulphates and sulphates, will dissolve during the next major rainfall event and be transported to a drainage system.

2.2.1.3.3 Less soluble sulphates

Although a large number of metal sulphate minerals of low solubility are known to occur, the most common ones are barite ($BaSO_4$), celestite ($SrSO_4$) and anglesite ($PbSO_4$). These are likely to provide solubility controls for barium, strontium and lead. Their low solubilities tend to immobilize these elements in the environment and make them less bioavailable than many of the other metals at mine sites (Nordström and Alpers, 1999a).

2.2.1.3.4 Carbonates

Many carbonate minerals occur as either primary or secondary minerals in mine wastes, such as calcite, magnesite, siderite, rhodocrosite and strontianite. Carbonates may originate as an accessory gangue mineral that accompanies the mineral deposit and mine waste, as an amended material for neutralization, or as a secondary product from weathering of wastes or amendments. Carbonate minerals are important as neutralizers of acid mine drainage (Blowes and Ptacek, 1994). Siderite forms as a secondary phase in tailings impoundments where calcite reacts with Fe(II)-rich solutions (Ptacek and Blowes, 1994).

2.2.1.3.5 Summary of mineralogic controls on metal concentrations

As a guide to the aqueous geochemistry of acid mine waters Nordström and Alpers (1999a) compiled a list of minerals (Table 2.1) that might be important in governing metal concentrations. This list, based on modelling and interpretation of mine water chemistry, is intended as a guide rather than a strict protocol. The two columns show those minerals most likely to have a solubility control and those less likely but possible.

Perhaps the most important factors affecting the production of acid mine waters are the amount, concentration, grain size, and distribution of pyrite present in a mine, tailings, or waste pile. The rate of oxidation can vary depending on the accessibility of air, moisture, and microbes to the pyrite surfaces and the neutralizing capacity of available buffering materials (Nordström and Alpers, 1999a). These complex geochemical processes can be modelled with either equilibrium or kinetic principles to estimate the result of pyrite oxidation, carbonate buffering, and silicate hydrolysis. Modelling calculations of this type have been done for pyritic rocks and waters of different initial compositions (e.g. Lichtner, 1994). Modelling calculations, however, are well-educated guesses. There will always be inadequate data and contentious ambiguities in the conclusions. The advantage of modelling is that it can take into account some of the complex interaction between hydrology, geochemistry, geology, and other site characteristics as well as performing database management. This advantage is a major step beyond various acid-base accounting, static and kinetic tests for which comparison, evaluation, and agreement is lacking (White and Jeffers, 1994).

Table 2.1: *Minerals whose solubilities might control metal concentrations in mine waters (After Nordström and Alpers, 1999a).*

Solubility equilibrium likely	Solubility equilibrium less likely, but possible
Alunogen	Alunite
Anglesite	Ankerite
Barite	Antlerite
Basaluminite (amorphous)	Atacamite, paratacamite
Calcite	Azurite
Cerrusite	Bronchantite
Chalcanthite	Chrysocolla
Epsomite	Goethite
Ferrihydrite	Hemimorphite
Gibbsite (amorphous to microcrystalline)	Hematite
Goslarite	Hydrozincite
Gypsum	Jarosite
Halotrichite-pickeringite	Kaolinite
Jurbanite	Kutnohorite
Manganese oxides	Malachite
Melanterite	Natroalunite
Otavite	Natrojarosite
Rhodocrosite	
Schwertmannite	
Scorodite	
Siderite	
Silica (microcrystalline)	
Smithsonite	
Witherite	

2.2.2 Static test methods commonly used to predict acid mine drainage

Since acid mine drainage can produce effluent containing acid- and heavy-metal concentrations that exceed water quality standards, and is perceived as irreversible once started, it is one of the more vexing environmental problems facing the minerals industry today. Consequently, reliable prediction tools that quantify the risk for a particular mine waste to produce acid mine drainage are actively sought by the minerals industry and regulators. Various laboratory "static"- and "kinetic"-predictive tests are available.

Static tests are short-term (usually measured in hours or days) and relatively low cost per sample. Their objective is to provide an estimate of a mine waste's capacity to produce acid and to neutralize acid. Unfortunately, static tests measure only the capacities for acid production and consumption and do not consider the differences between the respective dissolution rates of acid-producing and acid-consuming minerals. Another potential source of error inherent to static-test-data interpretation is the assumption that all acid-producing and acid-consuming minerals present will react completely. Clearly, this assumption ignores the influence of mineral particle size and morphology (White *et al.*, 1999).

Kinetic tests are long-term (usually measured in months and sometimes years) and expensive per sample. Lapakko and Wessels (1995) report that it is not uncommon for these tests to continue for at least 20 weeks. The objectives of kinetic tests are to confirm or reduce uncertainty in static-test classification, identify dominant chemical-weathering reactions, and determine acid-generation rates and temporal variations in leachate water quality. This is accomplished by accelerating the natural weathering rate of a mine-waste sample under closely controlled laboratory conditions (Lapakko, 1988; Lawrence, 1990; White and Jeffers, 1994).

2.2.2.1 Mine waste dissolution: Sources of acid and neutralization

2.2.2.1.1 Sources of acid

The dissolution of iron sulphide minerals, such as pyrite and pyrrhotite, is responsible for the majority of acid produced by mine waste (Stumm and Morgan, 1981). Consider the weathering of these two minerals:

$$FeS_2\,(s) + 7/2\ H_2O + 15/4\ O_2\,(g) \rightarrow Fe(OH)_3\,(s) + 4\ H^+\,(aq) + 2\ SO_4^{2-}\,(aq) \qquad [8]$$

$$FeS\,(s) + 5/2\ H_2O + 9/4\ O_2\,(g) \rightarrow Fe(OH)_3\,(s) + 2\ H^+\,(aq) + SO_4^{2-}\,(aq) \qquad [9]$$

These reactions produce acidic, iron- and sulphate-rich aqueous water.

Hydrated iron-sulphate minerals precipitate during the evaporation of acidic, iron- and sulphate-rich water within mine waste materials and store (for potential subsequent release) acid generated by iron sulphide mineral oxidation. The more common hydrated iron sulphate minerals that occur as efflorescent salts on the surfaces of weathering pyrite have already been mentioned in Section 2.2.1.3 (Secondary minerals). According to Nordström (1982a) and Cravotta (1994), these sulphate salts are highly soluble and provide an instant source of acidic water upon dissolution and hydrolysis. They are partially responsible for increased acidity and metal loading in the receiving environment during rain events.

Nordström (1982a) suggests that the formation of hydrated iron sulphates is an important intermediate step that precedes the precipitation of the more common insoluble iron minerals such as goethite and jarosite. Jarosite is, however, slightly soluble (Alpers *et al.*, 1994) and can, therefore, contribute acid according to equation [10].

$$KFe_3(SO_4)_2(OH)_6\,(s) \rightarrow K^+ + 3\ FeOOH\,(s) + 2\ SO_4^{2-}\,(aq) + 3\ H^+\,(aq) \qquad [10]$$

Note that because of its relatively low solubility, the acid contributed by jarosite dissolution may be small relative to that by dissolution of more soluble hydrated iron sulphates.

2.2.2.1.2 Sources of neutralization

The balance between the rates of acid production by iron sulphide mineral oxidation and host rock buffering determines the overall acidity of mine waste drainage. The most effective minerals for neutralizing acid are those containing calcium carbonate and magnesium carbonate. Examples include calcite ($CaCO_3$), magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)$) and ankerite ($CaFe(CO_3)_2$). Equation [11] represents the dominant dissolution reaction of calcite ($CaCO_3$) with iron-sulphide generated acid (H^+) above pH 6.4, while equation [12] is the dominant reaction below pH 6.4 (Drever, 1997):

$$CaCO_3\ (s) + H^+\ (aq) \rightarrow HCO_3^-\ (aq) + Ca^{2+}\ (aq) \qquad [11]$$

$$CaCO_3\ (s) + 2\ H^+\ (aq) \rightarrow H_2CO_3\ (aq) + Ca^{2+}\ (aq) \qquad [12]$$

The dissolution rates for the calcite reactions in equations [11] and [12] are relatively rapid. Dissolution rates, however, are not the same for all carbonates. Rauch and White (1977) and Busenberg and Plummer (1986) have reported that the rates of magnesite and dolomite dissolution are substantially slower than that of calcite. Furthermore, iron carbonates do not provide for net acid neutralization under oxidizing conditions, due to oxidation of the ferrous iron released, subsequent precipitation of ferric hydroxide, and the consequent acid production (White *et al.*, 1999).

Dissolution of silicates such as plagioclase (e.g. anorthite) and olivine (e.g. forsterite) can also neutralize acid, but their dissolution rates (and subsequent acid neutralization) are slow relative to the carbonate minerals (Busenberg and Clemency, 1976; Hem, 1970). The effectiveness of silicate-mineral neutralization is thought, by Morin and Hutt (1994), to be optimized by the fact that:

- the acid-production rate is relatively slow;
- feldspar minerals comprise a significant percentage of the overall mineralogy; and
- the available silicate-mineral surface area is large.

2.2.2.2 Acid-base accounting

The most commonly used static test is known as acid-base accounting (ABA) (Ferguson and Erikson, 1988). Several variations of ABA are in use in the United States and Canada (Lapakko, 1992a). They include standard ABA (Sobek *et al.*, 1978), the B.C. Research Initial Test (BCRI) (Bruynesteyn and Duncan, 1979), modified ABA (Reclamation Research Unit and Schafer and Associates, 1987; Coastech Research Inc., 1989; Lawrence, 1990), and the NP (pH6) Test (Lapakko, 1994). Protocols of these can be found in White *et al.* (1999).

The Net Acid Production (NAP) (Coastech Research Inc., 1989) and Net Acid Generation (Miller *et al.*, 1990) tests are based on the principle that hydrogen peroxide accelerates the oxidation of iron sulphide minerals. The acid consequently produced dissolves neutralizing minerals present, and the net result of the acid production and neutralization can be measured directly. This test does not require sulphur determinations and is, therefore, more readily conducted in a field laboratory than other static tests. Problems associated with this type of test and a modification of the protocol are presented elsewhere (Lapakko, 1992a, 1993; Lapakko and Lawrence, 1993).

2.2.2.2.1 Principles

Although now used to evaluate both coal- and metal-mine wastes, the ABA test was originally designed to evaluate the acid-producing capacity of coal mine wastes. ABA measures the balance between the acid-producing potential (AP) and acid-neutralizing potential (NP) of each mine-waste rock sample. AP is determined by sulphur assay and represents the sulphur contained in acid-generating iron-sulphide minerals, which are present in the sample. NP is determined by subjecting the mine-waste sample to some form of acid digestion and represents the amount of acid-neutralizing carbonate minerals present in the sample.

Net-neutralizing potential (NNP), which is the difference between these two values (NP – AP = NNP), is one of the measurements used to classify a mine-waste rock sample as potentially acid or non-acid producing. The NNP is often called the "acid-base account" of the sample. If NP is greater than AP, NNP is positive; and vice versa.

Recent ABA classifications for mine-waste samples are based on both NNP and the NP/AP ratio. Three categories comprise the ABA classification ("high", "uncertain", and "low" acid-producing potential). The ranges of NNP and NP/AP values defining each of the three categories have been described by Day (1989), Brodie *et al.* (1991), Ferguson and Morin (1991), and Morin and Hutt (1994).

2.2.2.2.2 Sources of error

The commonly used static tests quantify acid producing potential (AP) using either total sulphur or sulphide-sulphur content to estimate the quantity of acid-producing minerals. The total sulphur content will overestimate the actual AP of samples containing substantial non-acid producing sulphate minerals (e.g. barite or gypsum). On the other hand, the sulphide-sulphur measurement will underestimate the actual AP of samples containing substantial acid-producing sulphate minerals (e.g. melanterite or jarosite). Knowledge of the mine waste sulphate mineralogy will indicate whether the sulphate minerals present, if any, are acid producing and, thereby, allow selection of the more appropriate AP quantification.

Different static-test methods can produce markedly different NP values for the same sample (Lapakko, 1992a; 1992b; 1994). Protocol variables which may contribute to these differences include mine-waste particle size; "digestion" variables such as the acid used, amount of acid added (i.e. digestion pH), temperature, and duration; and the endpoint pH of the "back titration", if a back titration is used. According to White *et al.* (1999), the most influential of the protocol variables are particle size, extent of acid addition, and the back titration endpoint. The extent to which protocol variables will affect the measured NP is dependent on the sample mineralogy (including carbonate and feldspar content). Studies in which the extent to which these variables may be affected have been reviewed in detail by White *et al.* (1999).

2.2.3 Geochemical modelling of water-rock interactions in mining environments

Geochemical modelling is a powerful tool for evaluating geochemical processes, particularly in mining environments. When properly constrained and judiciously applied, modelling can provide valuable insights into processes controlling the release, transport, and fate of contaminants in mine drainage (Alpers and Nordström, 1999). Modelling, however, is not an exact science and its application has numerous pitfalls, uncertainties and limitations.

Three general strategies used to interpret water-rock interactions are statistical analysis, "inverse" modelling, and "forward" modelling:

- Statistical analysis can be a useful tool in organizing complex geochemical data for interpretation. Multivariate correlation analysis, factor analysis, cluster analysis, and other statistical techniques can group water chemistry data into sets that may relate to hydrogeochemical processes (Puckett and Bricker, 1992; Drever, 1997).
- Inverse modelling uses field data to interpret water analyses in terms of water-rock interactions. Chemical and isotopic data for water and rocks along a known flow path are used to test hypotheses regarding geochemical processes using mass-balance considerations. Several possible combinations of geochemical reactions are considered simultaneously to narrow the choice to a minimum number of feasible reactions (Alpers and Nordström, 1999).
- Forward modelling predicts or simulates the consequences of particular geochemical reactions given assumptions regarding the initial state of a system and its boundary conditions. From user-supplied reactions with associated thermodynamic data and assumptions regarding equilibrium, the consequences of specific geochemical reactions can be computed. Reactions that may be modelled include mineral dissolution and precipitation, oxidation-reduction, gas evolution, and sorption (Alpers and Nordström, 1999).

Alpers and Nordström (1999) remind us that it is possible to use the modelling approach to gain considerable insight into processes that may be occurring at a contaminated mine site, to test hypotheses regarding major controls on the mobility of selected contaminants, and to assess the probable consequences of various remediation strategies without costly field experiments, as long as we are aware of the inherent limitations and uncertainties of the geochemical models in use.

While it has been suggested that MINTEQA2 is the best modelling program for metal speciation of mine waters (due to its large database for metals), speciation modelling and the determination of saturation indices, of a wide range of minerals, in the waters in this study, was performed using PHREEQC. The PHREEQC program has numerous capabilities, which are outlined in Chapter 3, suffice it to say here that it was specifically selected as it can use redox couples to distribute redox elements among their valence states in speciation calculations. The database that was used, in the PHREEQC calculations, was that of WATEQ4F. According to Bird *et al.* (1994), the WATEQ4F and MINTEQA2 thermodynamic databases have the largest quantity of thermodynamic data for speciation modelling, including many trace metals appropriate to mine water quality modelling. The WATEQ4F database, however, has been updated (Nordström *et al.,* 1990) and re-developed with an emphasis on trace metals and redox-sensitive species; such that the user may now designate redox disequilibrium among the redox-sensitive elements, if desired. Redox disequilibrium is common in acid mine waters, but has often been ignored in aqueous speciation calculations. Most commonly this was due to a lack of analytical data for individual redox-active species (Alpers and Nordström, 1999).

In this study, an attempt was made to use the Fe(II)/Fe(III) redox couple (and WATEQ4F), and PHREEQC, to interpret the geochemistry of the waters accurately. Inverse (mass-balance) modelling, using NETPATH, was utilized to establish the processes responsible for the chemistry of the mine waters. Whilst PHREEQC has been used to model numerous water bodies in South Africa, very few of these were mine waters. Furthermore, no record of mass-balance modelling NETPATH has been found for any waters.

2.2.3.1 Aqueous speciation modelling

Aqueous speciation is the distribution of dissolved constituents among various complexes and individual free ions. The speciation results are needed to compute the degree of saturation of an aqueous solution with respect to various minerals. Speciation calculations can provide some bounding constraints on water-rock interactions, but mostly they indicate which reactions are possible thermodynamically, and not necessarily which reactions are likely to occur. It should be noted that the accuracy with which aqueous speciation calculations describe a natural water depends on the completeness of the chemical analysis used by the model (inorganics, organics, dissolved gases, etc.).

Kinetic barriers may inhibit many mineral precipitation or dissolution reactions from occurring. Numerous minerals simply do not reach solubility equilibrium in natural waters at temperatures of 0–100°C. Minerals with slow precipitation rates are unlikely to control the aqueous concentrations of the relevant ions (Alpers and Nordström, 1999). Furthermore, quantitative knowledge of aqueous speciation is important for evaluating bioavailability and toxicity because, as discussed in Section 2.3.3 (Abundance, mobility, bioavailability and toxicity of metals), certain aqueous species of a given element are much more toxic than others (Smith and Huyck, 1999). Other useful results from speciation modelling include the elemental molalities needed as input for mass-balance and reaction-path models and the aqueous activities of individual ions.

2.2.3.1.1 Speciation calculation

Speciation and mineral saturation are calculated by a sequence of steps containing both thermodynamic quantities and numerical approximations. For ion association models, the ionic strength, I, is computed from

$$I = \frac{1}{2} \Sigma m_i z_i^2 \qquad [13]$$

where m_i and z_i are the molality and charge, respectively, of the ith ion. The ionic strength is then used to calculate the activity coefficient of each ion, γ_i, according to the extended Debye-Hückel equation, the Davies equation, or a Brønsted-Guggenheim equation (e.g. Nordström and Munoz, 1994). The activity of each ion is then computed with the equation

$$a_i = \gamma_i m_i \qquad [14]$$

After one iteration, through a numerical approximation, a first estimate of speciation is made.

Alpers and Nordström (1999) suggest an alternative approach to calculating activity coefficients, which uses the Pitzer equation (Pitzer, 1973; 1979; 1987). This approach is known as the specific-ion interaction method because all ions are assumed to interact to some degree and these interactions are incorporated into terms that are added to an electrostatic Debye-Hückel term. The power of this approach is that activity coefficients can be fit to experimental data for ionic strengths up to 10 molal and higher in some chemical systems, whereas with the ion-association model, good fits to experimental data are limited to considerably lower ionic strengths.

There are two main drawbacks with application of the Pitzer approach to acid mine waters (Alpers and Nordström, 1999). One is that insufficient data are available to model the activity coefficients for all the principal trace elements found in acid mine waters. The other is the necessity to refit the interaction parameters for all elements whenever new data are added, so that consistency is maintained.

Once the speciation calculation has been made then the ion activity product (*IAP*) can be compared to the solubility product (K_{sp}) to test for mineral saturation. The saturation index, *SI*, is computed for each mineral in the database from

$$SI = \log\left(\frac{IAP}{K_{sp}}\right) \qquad [15]$$

The SI for an aqueous solution with respect to a particular mineral describes the thermodynamic tendency of that solution to precipitate or to dissolve that mineral. Positive values of SI indicate supersaturation and the tendency of the water to precipitate that mineral. Negative values of SI indicate undersaturation and the tendency of the water to dissolve a certain mineral. A value of SI = 0 indicates apparent equilibrium, a balance between the thermodynamic driving forces of dissolution and precipitation.

2.2.3.1.2 Uncertainties and limitations

As mentioned, speciation modelling programs can provide useful information concerning the geochemistry of water. Provided that a complete analysis of the water is available and that errors in analytical and thermodynamic data are minimal, it may be possible to determine which minerals are likely to dissolve or to precipitate in water of a given composition. Analysis of several water samples from one field area may provide support for a hypothesis, that the solubility of a certain mineral or group of minerals, controls the concentrations of other minerals. The correctness of such an interpretation, however, depends largely on the knowledge and experience of the modeller (Alpers and Nordström, 1999).

The application of chemical models and their computer codes is limited to certain water compositions. Waters with high ionic strength such as brines should be modelled where possible with the specific-ion interaction (Pitzer) approach. Critical data, however, are not yet available for certain trace elements or for Fe (III), a major constituent of many acid mine waters with pH values below 3 (Alpers and Nordström, 1999).

As already mentioned, individual redox species should be measured if at all possible, and a modelling program that can handle independent couples should be used. Otherwise, Alpers and Nordström (1999) suggest that interpretations concerning the geochemistry of redox-active metals such as Fe, As and Mn are subject to extreme uncertainty and error.

2.2.3.2 Inverse modelling: Mass balance

Inverse modelling which uses the mass-balance approach is one of the most powerful tools available for identifying the processes responsible for the chemistry of surface and groundwater. Inverse modelling as a general approach to problem-solving refers to a problem where final results of a process are known and it is either the initial conditions or the nature of the processes themselves that are unknown. The basic goal of mass balance modelling is to determine one (or more) set(s) of reactions that are sufficient to account for known changes in water composition caused by mineral-water interactions (Alpers and Nordström, 1999).

The mass-balance approach does not depend on thermodynamics or kinetics, *per se*. The user must, however, be prepared to rule out unreasonable models that are inconsistent with the thermodynamics or kinetics of hydrogeochemical processes. With regard to the kinetics, it is necessary to use caution when invoking the participation of phases with very slow rates of precipitation or dissolution under the conditions being considered (Alpers and Nordström, 1999).

The program NETPATH (Plummer *et al.*, 1991, 1992, 1994) represents a significant enhancement of its predecessor, BALANCE (Parkhurst *et al.*, 1982), which was the first inverse geochemical modelling program to be applied widely to groundwater problems. The NETPATH program allows the user to consider more phases than the number of known compositional parameters by computing every possible combination of the correct number of phases. The user can streamline the process by indicating that certain phases should be allowed only to dissolve or precipitate, and can force the model to include certain phases in all possible solutions which can reduce considerably the number of possible combinations. The program PHREEQC (Parkhurst, 1995) also has inverse modelling capabilities similar to those in NETPATH, v2.0.

2.2.3.3 Uncertainties and limitations of geochemical modelling

A number of critical assumptions are made in geochemical modelling and careless application may lead to erroneous results and unreasonable models. Alpers and Nordström (1999) report that a central assumption in applying inverse modelling to groundwater compositions is that both initial and final water samples are along a single flow path. In the absence of confirmation of such information, one must consider the apparent success of a mass-balance model to be qualitative or semi-quantitative at best, despite its exactness. Another critical assumption with inverse modelling is that the chemistry of the system being modelled is in a steady-state condition. Transient behaviour of either flow or chemistry, if not recognized, can cause erroneous results in mass-balance modelling.

Furthermore, reactions hypothesized in mass-balance models must be feasible, both thermodynamically and kinetically. Thermodynamic feasibility can be established with saturation indices, by ensuring that only phases that are saturated or supersaturated are allowed to precipitate, and that only phases that are undersaturated are allowed to dissolve. It is also up to the user to determine independently whether or not there are any kinetic barriers to hypothetical reactions, including mineral precipitation and dissolution, ion exchange, and isotope exchange. Wherever possible mass-balance modelling should be accompanied by detailed mineralogical and geochemical characterization of aquifer material.

Knowledge of the flow system and the effects of sampling on the system are important with regard to interpreting the chemistry of groundwater samples and using this type of data to determine boundary conditions for geochemical models, both inverse and forward.

Many of the limitations and uncertainties described with regard to inverse modelling also pertain to forward modelling. Assumptions are often made as to what are the reactive minerals, which minerals reach equilibrium and which do not, and what the relative reaction rates are. Detailed mineralogic characterization can provide valuable constraints on forward modelling (e.g. Lichtner and Waber, 1992), but even the most sophisticated of the models presently available will only approximate the complexitiy of the natural systems. Another important limitation, emphasized by Bethke (1992), is that geochemical computations may be non-unique in the sense that a particular geochemical condition may be achieved by more than one possible equilibrium system.

Alpers and Nordström (1999) suggest that all of these limitations to geochemical modelling can be reduced to two main sources of uncertainty:

- the input data (thermodynamic data, kinetic data, water compositions, mineral compositions, surface areas); and
- the user's knowledge of hydrogeochemical processes, both in general and with specific reference to the real system being modelled.

2.2 Criteria for assessing mine water quality

2.3.1 Industrial use

Water quality requirements for industry are almost impossible to summarize except very superficially. The requirements vary considerably between countries, industries, and processes, and will be specific to a particular product. Quality tolerances for a range of industrial process waters are given in Section 2.4.1.3.2 (Industrial use). In South Africa, the water quality requirements are governed by the Department of Water Affairs guidelines (DWAF, 1995b). One of the main problems of industrial water quality is related to boiler feed waters in which waters are heated up to considerable temperatures normally under high pressure. Under these conditions carbonate hydrochemistry, and to a lesser extent sulphate hydrochemistry, are particularly important. Changes in chemistry associated with the temperature and pressure changes can be assessed thermodynamically. Garrels *et al.* (1960) and Loewenthal and Marais (1976) discuss the problem of carbonate chemistry at length, while Denman (1961) has examined sulphate hydrochemistry over a range of temperatures. These publications provide charts for the calculation of mineral stability.

In the construction industry, groundwater and soil are normally analyzed for sulphates and chloride that can cause deterioration of concrete. To combat the problem, sulphate-resisting cements have been developed to suit a range of sulphate concentrations (Lloyd and Heathcote, 1985). For this particular work the sulphate salt is normally quoted as sulphur trioxide (SO_3).

2.3.1.1 Corrosion in cooling systems

Refined metals have a tendency to revert to a more natural and stable thermodynamic form; as a result, in the right environment oxidation of the metal occurs, metal is lost from the fabric, and usually passes into solution and may be re-deposited. The removal of the metal is termed corrosion (Lloyd and Heathcote, 1985).

It has been established that the mechanisms of the corrosion process in aqueous solutions are electrochemical. Details on the process of corrosion can be found in most water chemistry textbook (e.g. Snoeyink and Jenkins, 1980; Stumm and Morgan, 1981).

2.3.1.1.1 Role of bacteria

Corrosion can be accentuated by the metabolic process of bacteria under both aerobic and anaerobic conditions (Lloyd and Heathcote, 1985):

Aerobic bacteria: Many of the common bacteria present in groundwaters such as *Aerobacter aerogenes*, *Escherichia coli*, the *Pseudomonas* family, and *Proteus vulgaris* utilize hydrogen and can therefore take part in the cathodic reaction in a galvanic cell. On the other hand, iron bacteria such as *Gallionella, Clonothrix, Crenothrix* and *Leptothrix* which are active in the oxidation of ferrous iron to ferric iron, are probably more problematical and cause more difficulties. While these bacteria are prolific in promoting iron hydroxide scaling, this can only be excessive if iron concentrations are high as a result of extensive anodic attack and therefore corrosion. Iron bacteria grow best at low temperatures and are commonly found in groundwaters. They have a wide range of oxygen tolerance and will live in water containing 0.3 – 9.0mg/L dissolved oxygen.

Anaerobic bacteria: The action of aerobic bacteria can cause local anaerobic microenvironments and allow the growth of anaerobic bacteria adjacent to aerobic bacteria. More generally, however, such bacteria are prevalent in the truly reducing conditions of confined groundwater systems. Sulphate-reducing bacteria are reported to be the most active participants in the corrosion of well installations (Lloyd and Heathcote, 1985). *Desulfovibrio desulfuricans* and *Clostridium nigrificans* are examples that utilize sulphate as their primary oxygen source in the presence of enzymes and other compounds. *D. desulfuricans* will grow at temperatures up to 50°C, and develop at pH values between 5.5 and 9.0 although it prefers a neutral pH. *C. nigrificans* grows mainly in water with a temperature in excess of 35°C.

2.3.1.1.2 Corrosion environments

Moss (1964) listed a number of chemical parameters that can be used to indicate corrosion potential. These are pH, dissolved oxygen (DO), hydrogen sulphide, total dissolved solids (TDS), carbon dioxide, chloride and temperature. Several other factors can be added including fluid velocity, bacterial activity, and the presence of heavy metals. Most of these are discussed by Lloyd and Heathcote (1985). While each parameter can be considered separately, the chief problem is the complex interdependence of a number of them.

2.3.1.1.3 Assessing corrosion potential

A variety of methods are available to assess corrosion potential. Firstly, the significant chemical parameters listed in Section 2.3.1.1.2 (Corrosion environments) can serve as indicators (Table 2.2). Although these may be difficult to interrelate, their assessment is important in that no bulk chemical appraisal is really possible. For this reason, Eh-pH relationships should be considered as an alternative. These come nearest to providing a bulk assessment in that many of the individual parameters, listed in Table 2.2, control or are controlled by the redox environment.

***Table 2.2:** Chemical parameters indicating corrosion potential and general individual effects in groundwaters (mainly applicable to iron and iron-based materials). (After Lloyd and Heathcote, 1985).*

Parameter	Comment
pH	As pH decreases below 7, corrosion increases.
DO	Accelerates corrosion in acid, neutral, and slightly alkaline waters.
H_2S	As concentration increases, corrosion increases.
TDS	As salinity increases, particularly over 1000 mg/L, corrosion increases.
CO_2	Accelerates corrosion particularly if concentration greater than 50 mg/L.
Cl^-/CO_3^{2-}	As (logarithm of) ratio increases, corrosion increases.
Temperature	Corrosion is accelerated at higher temperatures.
Eh	Indicator of reducing conditions and an important parameter in metal speciation stability.

Owing to the difficulties of reliably assessing corrosion by chemical means many industries make direct measurements of metal loss by corrosion probes. As described by Barnes and Clarke (1969) such probes can be exceptionally valuable in water wells and have been applied to a number of deep-well studies.

2.3.1.1.4 Prevention and control of corrosion

Once an assessment of the corrosion potential has shown that it is detrimental, then either corrosion-resistant materials should be used or measures have to be taken to combat corrosion in materials that are prone to corrosion. Where possible it is preferable to use corrosion-resistant materials at the outset, as these will reduce the ongoing costs usually associated with control techniques.

Corrosion-resistant metals and alloys can be very expensive and so their use tends to be very restricted. Campbell and Lehr (1973) have graded the commonly used metals and alloys in order of decreasing corrosion resistance (Table 2.3).

Table 2.3: *Corrosion resistance of metals and alloys in decreasing order (after Campbell and Lehr, 1973).*

Metal or alloy	Composition
Monel metal	70% Ni, 30 % Cu
Stainless steel	74% low carbon steel, 18% Cr, 8% Ni
Everdur metal	96% Cu, 3% Si, 1% Mn
Silicon red brass	83% Cu, 1% Si, 16% Zn
Anaconda red brass	85% Cu, 15% Zn
Common yellow brass	67% Cu, 33% Zn
Low carbon steel	-

In the past, the cost of stainless steel was about 6 times that of ordinary steel plus galvanizing (Johnson, 1966). Many different types of stainless alloys are available today. Normal stainless steel with its chromium and nickel content has an excellent corrosion resistance. Its low carbon content is important with respect to its good weldability. Everdur is normally more corrosion resistant to sea water than is stainless steel. Swan (1982), however, indicates that the copper based steels are substantially more expensive than carbon steels and that their anticorrosive performance is no better. In many groundwater environments non-metallic materials such as epoxy resins (fibre glass) and various plastics (i.e. polyvinylchloride) are replacing the corrosion resistant metals and alloys.

Under circumstances where corrosion resistant materials are not used certain methods can be adopted to combat corrosion. The general methods listed by Lloyd and Heathcote (1985) include:

- the use of coated metals or alloys
- the injection of chemicals (eg. $Ca(OH)_2$) into the device
- cathodic protection.

2.3.1.2 Scaling in pipes and machinery

Scaling is the deposition of precipitate from groundwater onto material surfaces. The most serious results of scaling are the reduction in diameter of pipes and the loss of temperature in heating elements. Scaling relates directly to the supersaturation of a groundwater with respect to a certain compound, usually calcite. Other compounds that are of importance include other carbonate minerals, and iron and manganese compounds. As already discussed, supersaturation with respect to a compound can be calculated thermodynamically.

For practical engineering purposes, carbonate scaling has been extensively examined. An index developed by Langelier (1936) for calcium carbonate is in common use for interpretations. The equation used is:

$$\mathrm{pH_s} = (\mathrm{p}K_2\text{-}\mathrm{p}K_s) + \mathrm{pCa} + \mathrm{pAlk} \qquad [16]$$

where pHs is the pH at which calcite is in equilibrium with the solution (applicable in the range pH 6.5 – 9.5), K_2 and K_s are equilibrium constants, pCa is the negative logarithm of the calcium ion concentration (in mol/L), and pAlk is the negative logarithm of the total alkalinity (in $\mathrm{mmol_c/L}$).

The saturation index (SI) determined is:

$$\mathrm{SI} = \text{actual pH} - \mathrm{pHs} \qquad [17]$$

If SI is positive there is a tendency for the water to scale. The measurements required to determine the index are pH, Ca^{2+}, alkalinity and TDS. Although in general use, the Langelier index can be misleading in that it is only an approximate method of calculating calcite saturation.

Another index, which is widely used as an indicator of both scaling and corrosion is that of Ryznar (1944). Ryznar modified the Langelier index to provide an empirical stability index defined as:

$$\text{Stability index} = 2\mathrm{pH_s} - \mathrm{pH} \qquad [18]$$

Scaling is likely to occur for a stability index below 7; whilst above 7, corrosion becomes progressively more severe.

2.3.2 Irrigation water

The most extensive use for groundwater in the world is for the irrigation of crops, which are dependent on an adequate water supply of usable quality. Water quality refers to the characteristics of a water supply that will influence its suitability for a specific use, and is defined by certain physical, chemical and biological characteristics. The concentration and composition of dissolved constituents in water determine its quality for irrigation use. Quality of water is an important consideration in any appraisal of salinity or alkali conditions in an irrigated area (Richards, 1954). Only the hydrochemical factors pertinent in irrigation water suitability will be considered here. It must be stressed however, that other criteria are also important, such as the soil and crops to be irrigated, local climate, and management of irrigation and drainage, before any final decisions should be made with respect to water use.

2.3.2.1 Water quality problems

The characteristics of an irrigation water that appear to be most important in determining its quality are: (1) Total concentration of soluble salts; (2) relative proportion of sodium to other cations; (3) concentration of boron or other elements that may be toxic; and (4) under some conditions, the bicarbonate concentration as related to the concentration of calcium plus magnesium (Richards, 1954; Ayers and Westcot, 1985).

2.3.2.1.1 Electrical conductivity

Osmotic processes form the most important life function in plants so that any changes in osmotic conditions in the root zone can automatically change the rate of water flow to a plant. Osmotic effects are usually caused by total salt concentrations and therefore, the osmotic pressure of soil waters relates directly to electrical conductivity (Lloyd and Heathcote, 1985). Nearly all irrigation waters that have been used successfully for a considerable time have conductivity values less than 2.25mS/cm. Waters of higher conductivity have been used, but except in unusual situations, crop production was not satisfactory (Richards, 1954).

Richards (1954) found that the conductivity of the saturation extract of a soil, in the absence of salt accumulation from groundwater, usually ranges from 2 to 10 times higher than the conductivity of the applied irrigation water. Furthermore, the use of waters of moderate to high salt content may result in saline conditions, even where drainage is satisfactory.

The United States Salinity Laboratory has established guide groupings of waters based on the conductivity (Richards, 1954). In general, waters with conductivity values below 0.75mS/cm are satisfactory for irrigation insofar as salt content is concerned, although salt-sensitive crops may be adversely affected by the use of irrigation waters having conductivity values in the range 0.25 to 0.75mS/cm. Waters in the range of 0.75 to 2.25mS/cm are widely used, and satisfactory crop growth is obtained under good management and favourable drainage conditions, but saline conditions will develop if leaching and drainage are inadequate. Use of waters with conductivity values above 2.25mS/cm is the exception, and very few instances can be cited where such waters have been used successfully. Only the more salt tolerant crops can be grown with such waters and then only when the water is used copiously and the sub-soil drainage is good.

Lloyd and Heathcote (1985) remind us that although the salinity of irrigation water is of major importance, the evolution of salinity within the root zone is the controlling factor on plant growth and crop yield. Thus, it is essential to consider the leaching status of the soil. The steady-state leaching requirement for soils where no precipitation of salts occurs is directly related to the electrical conductivity of the irrigation water and the permissible conductivity of the water draining from the root zone. The leaching requirements for specified electrical conductivity values of irrigation and drainage waters, calculated by the United States Salinity Laboratory (Richards, 1954) are given in Table 2.4.

Table 2.4: *Leaching requirement as related to the electrical conductivities of the irrigation and drainage waters (After Richards, 1954).*

Electrical conductivity of irrigation waters (mS/cm)	**Leaching requirement for the indicated maximum values of the conductivity of the drainage water at the bottom of the root zone**			
	4 mS/cm	*8 mS/cm*	*12 mS/cm*	*16 mS/cm*
	%	%	%	%
0.10	2.5	1.2	0.8	0.6
0.25	6.2	3.1	2.1	1.6
0.75	18.8	9.4	6.2	4.7
2.25	56.2	28.1	18.8	14.1
5.00	-	62.5	41.7	31.2

Clearly, the water transmission and drainage properties of the soil and the salt tolerance of the crop to be grown are important factors in appraising irrigation waters from the standpoint of total salt concentration.

2.3.2.1.2 Specific ion effects

Specific ion effects in waters used for irrigation are very important. Owing to its effects on both soil and plants, sodium is one of the governing specific ions. Boron, magnesium and chloride are other ions that can affect the growth of plants adversely.

Sodium

The sodium adsorption ratio (SAR) of a soil solution is concerned with the adsorption of sodium by the soil; consequently, this ratio has certain advantages for use as an index of the sodium or alkali hazard of the water. This ratio is defined by the equation:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \qquad [19]$$

where Na^{+}, Ca^{2+} and Mg^{2+} represent the concentrations in $mmol_c/L$ of the respective ion (McBride, 1994).

After the SAR value of an irrigation water is determined, it is possible to estimate the exchangeable sodium percentage (ESP) value of a soil that is at equilibrium with the irrigation water, using a nomogram (Ayers and Westcot, 1985, p11). It is, however, unlikely that the equilibrium condition will occur in the field because the soil solution is nearly always appreciably more concentrated than the irrigation water. The relation between SAR and ESP is, nevertheless, given by:

$$ESP = \frac{100\left(-0.0126 + 0.01475 \times SAR\right)}{1 + \left(-0.0126 + 0.01475 \times SAR\right)} \qquad [20]$$

or

$$\frac{ESP}{100 - ESP} = 0.015 \times SAR \qquad [21]$$

It should be noted that this is an approximation only, and the coefficient varies depending on the soil type.

As the quantity of salt absorbed by plants is relatively small, the solution remaining in the soil is more concentrated than the applied irrigation water. At the next irrigation this more concentrated solution may be displaced downward or diluted, and so the concentration of the solution in contact with the soil varies with time and location in the profile. Therefore, leachate from a contaminated soil with respect to a specific ion may not show any concentration of that ion until supersaturation is met (pers. comm. Alex Campbell, 2001).

Bicarbonate

In waters containing high concentrations of bicarbonate, there is a tendency for calcium and magnesium to precipitate as carbonates as the soil solution becomes more concentrated. This reaction does not go to completion under ordinary circumstances; insofar as it does proceed, the concentration of calcium and magnesium are reduced and the relative proportion of sodium is increased. Based on the assumption that all calcium and magnesium would precipitate, Eaton (1950) devised an empirical parameter to quantify the effects of bicarbonate. The parameter, which is termed the residual sodium carbonate (RSC), is given by:

$$RSC = (CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+}) \qquad [22]$$

In these relations the ionic constituents are expressed in $mmol_c/L$.

On the basis of data obtained in a bicarbonate study at the U.S. Salinity Laboratory (Richards, 1954) and using the "residual sodium carbonate" concept of Eaton (1950), it is concluded that waters with more than $2.5 mmol_c/L$ "residual sodium carbonate" are not suitable for irrigation purposes. Waters containing 1.25 to $2.5 mmol_c/L$ are marginal, and those containing less than $1.25 mmol_c/L$ are probably safe. It is believed that good management practices and proper use of amendments might make it possible to successfully use some of the marginal waters for irrigation.

Adjusted SAR

Bower *et al.* (1968) combined the sodium adsorption ratio (SAR) with a carbonate saturation assessment to produce an index referred to as the adjusted SAR (adj. SAR). This was because the carbonate dissolution-precipitation conditions clearly related to sodium concentrations in both the irrigation water and the soil. The adj. SAR is defined as:

$$\text{Adj. SAR} = \text{SAR}\,[1 + (8.4 - pH_c)] \qquad [23]$$

where SAR is the SAR for the irrigation water, 8.4 is the approximate pH of a non-sodic saline soil in equilibrium with $CaCO_3$, and pH_c is the pH for carbonate saturation of the irrigation water. According to Lloyd and Heathcote (1985), the adjusted SAR now often supersedes SAR and is used in combination with the exchangeable sodium percentage (ESP) of a soil for classification.

Boron

Boron is a constituent of all natural waters, the concentration varying from traces to several mg/L. It is essential to plant growth, but is exceedingly toxic at concentrations only slightly above optimum. A deficiency of boron produces striking symptoms in many plant species with yellowing or spotting being observed on the edges and tips of older leaves first, progressing towards the centre between veins. Richards (1954) reports that the concentrations which may injure more sensitive plants, are often approximately that required for normal growth of very tolerant plants. The occurrence of boron in toxic concentrations in certain irrigation waters makes it necessary to consider this element specifically, in assessing the water quality.

Boron frequently occurs in toxic concentrations along with other salts that are present in saline soils. It can be leached from the soil but, if concentrations are high initially, a quantity of boron sufficient to cause trouble may remain after the concentration of other salts is reduced to a safe level (Richards, 1954). The criteria adopted for boron are given in Tables 2.5 and 2.6 and are based on work by Richards (1954) and Wilcox (1960).

Table 2.5: *Permissible limits of boron in irrigation waters (After Wilcox, 1960).*

Class of water	**Limit (mg/L)**		
	Sensitive crops	**Semi-tolerant crops**	**Tolerant crops**
Excellent	< 0.33	< 0.67	< 1.00
Good	0.33 – 0.67	0.67 – 1.33	1.00 – 2.00
Permissible	0.67 – 1.00	1.33 – 2.00	2.00 – 3.00
Doubtful	1.00 – 1.25	2.00 – 2.50	3.00 – 3.75
Unsuitable	> 1.25	> 2.50	> 3.75

Table 2.6: *Relative tolerance of plants to boron. Tolerance increases in each column from top to bottom (After Richards, 1954 and Wilcox, 1960).*

Excellent water:	*< 0.33mg/L*	*< 0.67mg/L*	*< 1.0mg/L*
Unsuitable water:	*> 1.25mg/L*	*> 2.50mg/L*	*> 3.75mg/L*

	Sensitive	**Semi-tolerant**	**Tolerant**
	Lemon	Lima bean	Carrot
	Grapefruit	Sweet potato	Lettuce
	Advocado	Bell pepper	Cabbage
	Orange	Pumpkin	Turnip
	Apricot	Zinnia	Onion
	Peach	Oats	Broadbean
	Cherry	Maize	Gladiolus
	Persimmon	Milo	Alfalfa
	Kadota fig	Corn	Gardenbeet
	Grape	Wheat	Mangel
	Apple	Barley	Sugarbeet
	Pear	Olive	Dare palm
	Plum	Field pea	Asparagus
	Navy bean	Radish	Athel *(Tamarix aphylla)*
	Jerusalem artichoke	Sweet pea	
	Walnut	Tomato	
		Cotton	
		Potato	
		Sunflower	

Chloride

Chloride absorbed by plants can adversely affect growth. Adsorption during irrigation can be either through the leaves or through the roots with varying effects. An assessment of the hazard is difficult and needs to be made on a local basis and for specific crops (Lloyd and Heathcote, 1985).

2.3.2.1.3 Other trace elements

Branson *et al.* (1975) have carried out an exhaustive study of plant tolerance to trace elements and provide a useful guide, which is summarized in Table 2.7.

***Table 2.7:** Recommended maximum concentrations of trace elements in irrigation water (After Branson et al., 1975).*

Elements[1]	**For waters used continuously on all soil (mg/L)**	**For use up to 20 years on fine-textured soils at pH 6.0 to 8.5 (mg/L)**
Aluminium	5.00	20.0
Arsenic	0.10	2.00
Beryllium	0.10	0.50
Boron	0.75 [2]	2.0 – 10.0
Cadmium	0.01	0.05
Chromium	0.10	1.00
Cobalt	0.05	5.00
Copper	0.20	5.00
Fluorine	1.00	15.0
Iron	5.00	20.0
Lead	5.00	10.0
Lithium	2.50	2.50 [3]
Manganese	0.20	10.0
Molybdenum	0.01	0.05 [4]
Nickel	0.20	2.00
Selenium	0.02	0.02
Vanadium	0.10	1.00
Zinc	2.00	10.0

1. No data are available for mercury, silver, tin, titanium, or tungsten.
2. No problem with less than 0.75mg/L; increasing problem with between 0.75 and 2.0mg/L; severe problem with greater than 2.0mg/L.
3. Recommended maximum concentration for citrus is 0.75mg/L.
4. Only for fine-textured acid soils, or acid soils with a relatively high iron oxide content.

2.3.2.2 Infiltration problems

An infiltration problem occurs if the irrigation water does not enter the soil rapidly enough during a normal irrigation cycle to replenish the soil with water needed by the crop before the next irrigation. The reduced infiltration rate, if due to quality of applied water, is generally a problem within the upper few centimetres of soil but occasionally may occur at greater depths. The end result is a decrease in water supply to the crop, similar to the reduction due to salinity, but for a different reason. (A water infiltration problem reduces the quantity of water put into the soil for later use by the crop while salinity reduces the availability of the water in storage.)

The infiltration rate generally increases with increasing salinity and decreases with either decreasing salinity or increasing sodium content relative to calcium and magnesium (the SAR). Therefore, the two factors, salinity and SAR, must be considered together for a proper evaluation of the ultimate effect on water infiltration rate. Figure 2.1 shows that both salinity (EC) and the sodium adsorption ratio (SAR) of the applied water affect the rate of infiltration of water into surface soil.

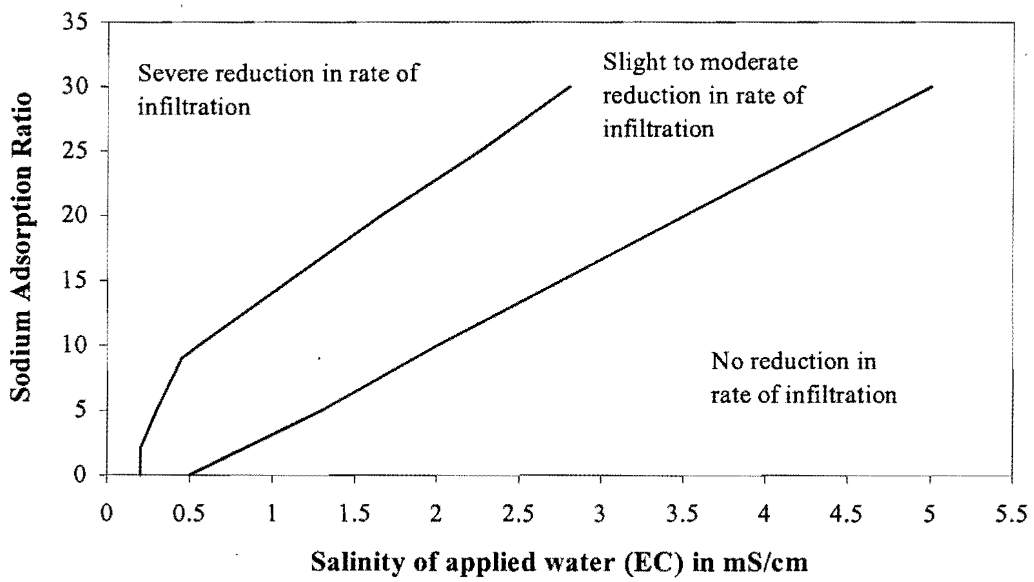

Figure 2.1: *Relative rate of water infiltration into soil as affected by salinity and sodium adsorption ratio (Adapted from Oster and Schroer, 1979).*

Low salinity water (< 0.5mS/cm and especially below 0.2mS/cm) is corrosive and tends to leach surface soils free of soluble minerals and salts, especially calcium, reducing their strong stabilizing influence on soil aggregates and soil structure. Without salts and without calcium, the soil disperses and the dispersed finer soil particles fill many of the smaller pore spaces, sealing the surface and greatly reducing the rate at which water infiltrates the soil surface. Soil crusting and crop emergence problems often result, in addition to a reduction in the amount of water that will enter the soil in a given amount of time and which may ultimately cause water stress between irrigations.

Very low salinity water (EC < 0.2mS/cm) almost invariably results in water infiltration problems, regardless of the relative sodium ratio (or SAR). Rainfall is a very low salinity water and irrigated areas frequently experience exceptionally low rates of infiltration or rainfall resulting in excessive runoff (Oster and Schroer, 1979; Ayers and Westcot, 1985).

Excessive sodium in irrigation water also promotes soil dispersion and structural breakdown but only if sodium exceeds calcium by more than a ratio of 3:1. Such a relatively high sodium content (> 3:1) often results in a severe water infiltration problem due to soil dispersion and plugging and sealing of the surface pores, in much the same way as does the very low salinity water. This is due to a lack of sufficient calcium to counter the dispersing effects of the sodium. Excessive sodium may also make it extremely difficult to supply enough water to meet the crop water demand (Ayers and Westcot, 1985).

2.3.3 Abundance, mobility, bioavailability and toxicity of metals

To adequately assess the impact of human activities on metals in the environment, one must consider both the geological / geochemical / physical aspect as well as a biological / biochemical / toxicological perspective.

2.3.3.1 Abundance of elements

There are numerous compilations of estimates of the average abundance of elements within the Earth's crust (Rickwood, 1983). These compilations tend to vary due to the different approaches, methods and assumptions used to derive estimates of crustal abundance. Our knowledge of the crustal abundance of most rock types (and hence their associated elements) is inadequate because the Earth's crust is so variable and, in many parts, poorly exposed. Rose *et al.* (1979) summarized the geochemical characteristics of a number of trace elements. Although somewhat dated, they have outlined the ranges and / or average composition of these elements in different environments in their unusually complete review. Those relative to this study are outlined in Table 2.8. More recent data has been published by Steinnes (1995), but is not available in South Africa.

Table 2.8: Means and ranges of selected elemental concentrations in sedimentary rocks, soil and water. Data are in ppm, except water, which are in ppb (After Rose et al., 1979).

Element	Sedimentary Rocks			Soil	Water
	Sandstones	Shales	Black shales		
Antimony	1	3			
Arsenic		4	75 – 225	1 – 50	1 – 30
Barium	100 – 500	300 – 600	450 – 700	100 – 3000	4 – 35
Beryllium	< 1	1 – 6	1	~ 6	Order of 0.1
Boron	155	130		~ 10	1 – 10000
Cadmium		0.3		~ 0.5	
Chromium	10 – 100	100 – 400	10 – 500	5 – 1000	0.5 – 40
Cobalt	1 – 10	10 – 50	5 – 50	1 – 40	0.03 – 10
Copper	10 – 40	30 – 150	20 – 300	2 – 100	0.3 – 30
Fluorine	290	590		~ 200	50 – 1000
Iron	3.1 %	4.3 %		1.4 – 4.0 %	40 – 1500
Lead	10 – 40	20	20 – 400	2 – 200	0.3 – 3
Lithium	7 – 29	50	17	5 – 200	0.3 – 3
Manganese	385			200 – 3000	0.3 – 300
Mercury	0.03 – 0.1	0.4		0.03 – 0.3	0.01 – 0.1
Molybdenum	0.1 – 1	1	10 – 300	0.2 – 5	0.05 – 3
Nickel	2 – 10	20 – 100	20 – 300	5 – 500	0.02 – 10
Selenium	1	0.5 – 1		0.1 – 2	
Silver	0.4		5 – 50	~ 0.1	0.01 – 0.7
Sulphur	2200	1100		100 – 1500	~ 5 500
Tin		40		~ 10	
Titanium	3000	4400		1000 – 10000	0.2 – 30
Uranium	0.45	4.1	2 – 300	~ 1	0.05 – 1
Vanadium	10 – 60	50 – 300	50 – 2000	20 – 500	
Zinc	5 – 20	50 – 300	100 – 1000	10 – 300	1 – 200

Concentrations of trace elements in surface waters are still a matter of debate and uncertainty because water samples can be easily contaminated during collection or analysis, analytical detection limits are sometimes greater than the natural concentrations and few pristine surface waters have been analyzed cleanly for trace elements (Martin *et al.*, 1980). Table 2.9 lists concentrations of dissolved constituents in surface waters complied by various authors. The values listed in this table are meant only as a rough guide.

Table 2.9: Summary of the average elemental composition of dissolved and suspended matter in surface water from a variety of sources and various authors.

Element	Martin & Whitfield (1983) Dissolved [1] (µg/L)	Martin & Whitfield (1983) Suspended [1] (µg/g)	Meybeck (1988) Dissolved [2] (µg/L)	Hem (1985) Dissolved [3] (µg/L)
Aluminium	50	94 000	40 ± 20	
Antimony	1	2.5		0.1 – 1s
Arsenic	1.7	5	1 ± 0.5	0.1 – 1s
Barium	60	600	1 ± 0.5	10s
Beryllium				0.1s
Boron	18	70	30 ± 20	
Cadmium	0.02	(1)		0.1 – 1s
Calcium	13 300	21 500		
Chlorine				
Chromium	1	100	0.8 ± 0.3	0.1 – 1s
Cobalt	0.2	20	0.1 ± 0.05	0.1s
Copper	1.5	100	2 ± 1	1 – 10s
Fluorine			100 ± 20	
Iron	40	48 000	50 ± 30	
Lead	0.1	100		0.1 – 1s
Lithium	12	25		
Magnesium	3 100	11 800		
Manganese	8.2	1 050	10 ± 5	
Mercury				0.1s
Molybdenum	0.5	3	0.8 ± 0.4	0.1 – 1s
Nickel	0.5	90	0.4 ± 0.3	0.1 – 1s
Potassium	1 500	20 000		
Selenium				0.1s
Silver	0.3	0.07	0.4 ± 0.2	0.1s
Sodium	5 300	7 100		
Tin				
Titanium	10	5 600		
Vanadium	1	170		1s
Zinc	30	250	10 ± 5	1 – 10s

1. Data from Martin and Whitfield (1983): Values are based on analytical results from world rivers.
2. Data from Meybeck (1988): Ranges are based on more than ten rivers and represent an estimate of world averages.
3. Data from Hem (1985): Values are based on a variety of literature citations for element concentrations in a variety of water sources, including groundwater.

2.3.3.2 Factors affecting mobility and dispersivity

2.3.3.2.1 Chemical and physical properties of elements

Elements have certain inherent chemical and physical properties that influence their behaviour in the environment (Nordström, 1999). The chemistry of the elements is determined by how atoms exchange, interchange, and share the electrons that occupy their "outermost orbits" (valence electrons). A short summary of the properties of elements, which can influence their mobility and dispersivity, can be found in Smith and Huyck (1999).

2.3.3.2.2 General characteristics of elements in aqueous systems

Minerals in the Earth's crust are the ultimate source of metals. Metals are redistributed by several different kinds of mechanisms in the environment. Consequently, metals are not distributed uniformly in the Earth's crust or among the various earth materials (e.g. rocks, soils, sediments).

According to Smith and Huyck (1999), minerals formed in deep-seated environments are unstable to varying degrees in the surficial environment, and elements contained in these minerals may be released, transported, and redistributed in the surficial environment. A wide variety of minor and trace elements can be found in common rock-forming minerals. When these minerals weather, these elements are expected to be released from the mineral matrix. Thus, using Bowen's or Goldich's reaction series (found in many earth science texts), one may be able to predict which elements may be most readily remobilized in the surficial environment based on the ease of weathering of the minerals in which they occur. Minerals crystallized at higher temperatures are less stable in the surficial environment and minerals formed at lower temperatures are more stable in the surficial environment. One exception to this rule is calcite.

2.3.3.2.3 Metal mobility in the surficial environment

Mobility refers to the capacity of an element to move within fluids after dissolution. It is difficult to predict element mobility quantitatively in surficial environments. Instead it should be considered in a relative sense by empirically comparing the behaviour of elements under changing environmental conditions, such as at geochemical barriers. The relative mobility of selected elements in weathering are indicated qualitatively by Rose *et al.* (1979), and the principal limiting factors controlling their mobility are mentioned in Table 2.10.

Table 2.10: *Relative mobility of selected elements in weathering environments (After Rose et al., 1979).*

Element	Mobility
Antimony	Probably low.
Arsenic	Generally low, limited by co-precipitation as AsO_3^{3-} with hydrated ferric oxide and as $FeAsO_4$ (scorodite); in iron-poor environments, As becomes more mobile and may even form detectable dispersion trains in stream waters.
Barium	Probably high (limited primarily by solubility of Ba sulphate), but may be low in mine drainage environments due to the high concentrations of sulphate.
Beryllium	Probably low, limited by insolubility of beryl in weathering.
Boron	Extremely high, except for B in stable silicates, particularly in tourmaline.
Cadmium	Cd usually follows Zn in weathering. During the oxidation of zinc sulphide, however, the secondary Cd sulphide has been found in some cases to remain behind after the Zn sulphide has been solubilized by oxidation.
Chromium	Generally low, except for conditions of high pH and Eh where the mobile CrO_4^{2-} chromate ion is stable.
Cobalt	Probably moderately high, limited in early stages by co-precipitation with hydrated ferric oxide and MnO_2.
Copper	High where pH < 5.5, low at neutral to alkaline pH; mobility limited primarily by pH, to a lesser extent by co-precipitation with hydrated ferric oxide and by sorption to organic matter and clay minerals.
Fluorine	Not highly mobile; limited by abundance of phosphate.
Iron	Fe^{2+} moderate; Fe^{3+} low, limited by precipitation of limonite, but under some conditions colloidal suspensions of undissociated hydrous Fe oxides or Fe-bearing organic complexes may be stable.
Lead	Generally low, in part limited by precipitation with organic matter and hydrated ferric oxide, but probably higher in chloride (semi-arid) environment.
Lithium	Probably high.

Element	Mobility
Manganese	Very low, limited by low solubility of Mn^{4+} oxides at normal pH; in acid pH range, Mn may be mobile as Mn^{2+} ion.
Mercury	Probably low in water; apparently very high in vapour phase.
Molybdenum	Extremely high to moderate, limited by (i) rate of solution of primary MoS_2, (ii) sorption on hydrated ferric oxide to form ferrimolybdite at pH 2.5 – 7.0 and to a less extent on clay minerals at pH 2 – 4 (Jones, 1957), and (iii) precipitation in carbonate-rich environments; otherwise, mobility of Mo is independent of pH variations.
Nickel	Moderately high, limited by co-precipitation with hydrated ferric oxide, and hydrolysis above pH 6.5.
Selenium	Se is highly mobile under oxidizing, alkaline conditions, and apparently highly immobile under reducing and neutral to acid conditions; the mobility is limited by the stability fields of the soluble SeO_4^{2-} ion and of the insoluble native Se and selenites.
Silver	Possibly fairly low, limited by low solubility of AgCl.
Sulphur	As sulphate, extremely high, limited only by the Eh at which sulphate is reduced to sulphide, and the solubility of saline minerals, principally gypsum.
Tin	Generally low, limited by high stability of primary cassiterite; may be relatively high after liberation of ionic Sn from primary minerals.
Titanium	Low, limited by stability of both primary and secondary minerals.
Uranium	Extremely mobile under alkaline, oxidizing conditions; limited by Eh of reduction of UO_2^{2+}, and by tendency to be either precipitated with solid organic matter or by solubility of organic complexes.
Vanadium	Probably very low, limited by reaction and precipitation with organic matter.
Zinc	Moderately high, limited by organic activity and co-precipitation with hydrated ferric oxide.

Smith and Huyck (1999) have compiled a series of shaded periodic tables, which illustrate the generalized relative mobility of elements expected under changing environmental conditions. The figures take into account the tendency of the elements to sorb onto hydrous oxides or precipitate. By comparing these periodic tables, one may make qualitative statements about the behaviour for a given element under changing conditions, such as geochemical barriers.

Although Smith and Huyck's (1999) figures provide a general guide or first approximation to predict metal behaviour in the surficial environments, this approach does not substitute for in-depth field studies and topical research. It may, however, help to determine which elements could be mobile in a given environment and could be used to anticipate the effects of various geochemical barriers. It should be kept in mind that there was a great degree of subjectivity in assigning the elements to the various categories in their figures.

The rates of geochemical and biological reactions also can impact on metal mobility, as many reactions involving metals are kinetically controlled and biologically mediated. This rate dependence makes reactions difficult to predict (e.g. Langmuir and Mahoney, 1984).

2.3.3.2.4 Metal dispersivity in the surficial environment

Atmospheric deposition of metals may impact the chemistry of soils, rivers, lakes, estuaries, and oceans. Metals enter the atmosphere as gases, vapours, aerosols, and particles originating from a variety of anthropogenic sources. Pacyna (1996) provides an in-depth discussion of trace metal emissions into the atmosphere. He states that trace metals emitted into the atmosphere can be transported a long distance and that atmospheric deposition is an important pathway for worldwide metal contamination of terrestrial and aquatic ecosystems.

Residence times of metals in the atmosphere are fairly short - generally on the order of days to weeks (Salomons and Forstner, 1984). The distance of airborne transport depends on the source, size, shape, and density of the particles, on changes in particle characteristics during transport and on meteorological conditions. Particles in the atmosphere can undergo diffusion, coagulation, condensation, sedimentation, scavenging by precipitation, and reaction with atmospheric gases. Deposition varies with particle-size distribution, ground cover, and meteorological conditions.

Physical transport of sediments is related to hydrologic and geomorphologic processes such as erosion, vertical and horizontal transport, sediment deposition, and compaction. In general, to transport sediment, flow rate of water must exceed a certain critical velocity, which depends on grain size, shape and density; for deposition, the flow must decrease below another critical value. In the water column, metals are commonly associated with suspended particulates. This suspended load can transport significant quantities of metals during spring run-off and storm events when the suspended load is highest (Smith and Huyck, 1999).

Metals are not homogenously distributed among the various grain-size fractions in sediments. Generally, the finer-grained clay-sized fractions have the highest metal concentrations due to large specific surface areas and to the presence of metal-oxide and organic coatings on mineral surfaces that tend to sorb metals. In the silt and sand-sized fractions, metals concentrations generally decrease due to the greater abundance of quartz and lower oxide and organic content. The coarse fractions either may increase in metal concentrations, if they include metal-containing minerals (e.g. sulphide minerals), or may decrease in metal concentrations (Smith and Huyck, 1999). Filipek and Owen (1979) discuss the influence of grain size on metal distribution in lacustrine sediments.

2.3.3.3 Factors affecting bioavailability and toxicity

Biologically related factors, such as mode of exposure, cumulative residence time in the host, ability of the host to absorb a particular size or compound, presence of other metals in the host, genetics, host species, and age and development of the host, affect the bioavailability of a particular metal. Host-related factors are important to metal bioavailability and toxicity, and are also very complex. A brief discussion of these factors can be found in Smith and Huyck (1999).

2.3.3.3.1 Chemical, geochemical and geological factors

Most metals cannot be considered solely detrimental because they commonly are also essential micronutrients for plants and animals. Uptake and accumulation of metals by organisms provides an essential link between the types, concentrations, forms, and species of metals in the environment and the effects that these have on living systems.

Chemical factors, such as water composition (e.g. pH, hardness) and chemical and physical properties of elements (e.g. oxidation state), can influence element bioavailability in aquatic systems. The pH of a system is often a master variable that governs reactions and processes in the system (Smith and Huyck, 1999); this, in turn, will influence bioavailability. For example, the bioavailability of cationic metals to aquatic organisms is generally greater in the acidic pH range than in the alkaline range.

Water hardness may affect the toxicity of some metals. Water hardness refers to the concentration of calcium and magnesium ions, as well as other polyvalent metals such as manganese, iron, and aluminium (Smith and Huyck, 1999). In general, most metals are more toxic to aquatic life in soft (total hardness < 75mg/L) water rather than hard water (Zitko and Carson, 1976). According to Sprague (1985), heavy metals are an order of magnitude more toxic to aquatic life in very soft water than in very hard water. He attributed this increased toxicity to increased membrane permeability due to low calcium concentrations. Oxidation state also influences toxicity of metals. Molybdenum (VI) and chromium (VI), for example, are much more toxic than molybdenum (II) (commonly occurring as a sulphide mineral) or chromium (III) (Smith and Huyck, 1999).

Simple relationships between metal concentrations in organisms and total metal concentrations in the food, water, or sediment to which the organisms are exposed, are seldom found in natural systems (Jenne and Luoma, 1977). Consequently, it is not sufficient to determine total metal concentrations in earth materials if the ultimate goal is to estimate bioavailability of the metals. The total metal concentrations do, however, place an upper limit on metal bioavailability.

Aquatic organisms may accumulate metals from the dissolved phase, suspended particulates, bottom sediments and prey or food sources (Smith and Huyck, 1999). Numerous detailed studies have been done on individual species for specific metals, showing the primary route of exposure to natural systems. In some cases, this primary route is water, whilst in others it is particulate material or a food source. Details of these are beyond the scope of this study.

In a study on ingested lead in lab rats, Mahaffey (1978) noted that mineralogy and mode of occurrence can affect bioavailabilty of metals. Furthermore, the bioavailability of soil-bound metals is related to the physicochemical form of the metal in the soil. Ingestion of soil by animals and humans can be an important route of exposure for metals. Generally, the more soluble a metal is, the more bioavailable it is (Sheppard *et al.*, 1995). Ruby *et al.* (1992)

demonstrate that dissolution kinetics must be considered when assessing metal availability from minerals or soils.

Sediment texture can play a role in metal bioavailaibility. For example, Pesch and Morgan (1978) showed that a polychaete (a type of worm) exhibited greater bioaccumulation when exposed to water mixed with sandy sediment than when exposed to water mixed with fine-grained sediment. Smith and Huyck (1999) suggest that this is probably due to the higher metal-binding capacity of fine-grained sediment.

2.3.3.3.2 Metal speciation

The speciation of an element, rather than its total concentration, influences its effects on an organism. Smith and Huyck (1999) list the factors that affect speciation. These include pH and redox conditions, the solubility of solid compounds, the oxidation state of the element, the availability and type of complexing agents, complex and ion-pair formation, sorption-desorption reactions, and biochemical processes.

The bioavailabiltiy and toxicity of metals may be strongly modified by the chemical partitioning of metals in food components (e.g. Luoma and Jenne, 1977), the speciation of metals in solution (Driscoll *et al.*, 1980), and the speciation of metals in sediments and soils (Luoma and Jenne, 1977).

Smith and Huyck (1999) report that metal concentrations in soils and sediments are commonly several orders of magnitude greater than those found in associated waters. Metals can partition among various components of soils and sediments and may be (1) sorbed on hydrous metal oxides, organic matter, or clays, (2) present in the lattice of primary or secondary minerals, or (3) occluded in amorphous materials or remains of organisms. Salomons (1995) relates metal speciation to potential relative mobility with the following distinctions:

Exchangeable cations .... High mobility
Metals assoc. with iron and manganese hydroxides .... Medium mobility
Metals bound or fixed inside organic substances ....Medium mobility
Metals bound or fixed inside mineral particles .... Low mobility

Metals assoc. with a sulphidic phase.......... Depends on environmental conditions

The composition of the suspended phase influences the physicochemical form in which a metal is transported, which in turn influences bioavailability (e.g. Luoma and Bryan, 1979). Bioavailability also can be affected by the preferential partitioning of metals to the suspended sediment and consequent removal from the dissolved phase, since metals are generally more bioavailable when dissolved (Smith and Huyck, 1999).

2.4 The classification of waters

2.4.1 Classification types

Matthess (1982) proposes that for groundwater classification purposes genetic, chemical, and hydrological viewpoints are the major items of geological and geochemical interest. In water supply studies, the physical and chemical properties are incorporated into classifications for assessment of possible applications and exploitation of the water. In general, Matthess (1982) classifies waters on the basis of origin, dissolved constituents and potential use. The last two of these will be discussed in further detail.

2.4.1.1 Classification on basis of dissolved constituents

The simplest classification depends on the total concentration of dissolved constituents. Davis and De Wiest (1967) have proposed the following classification on this basis:

	Concentration of Total Dissolved Solids (mg/L)
Fresh water	0 – 1 000
Brackish water	1 000 – 10 000
Saline Water	10 000 – 100 000
Brines	> 100 000

This classification has the disadvantage that a salty taste is already noticeable below 1 000mg/L. Richter and Wager (1969) therefore consider Cl^- contents above 350mg Cl^-/L as saline water. In mining terminology, waters with more than 40 000mg/L, and in German mineral water terminology (Quentin, 1969) waters with at least 14 000mg/L of dissolved salts, are called brines.

A classification based on chemical composition is widely used, in which the percentage fraction of dissolved ions is reported either in mg % following the model of Clarke (1924), or in meq % following that proposed by Palmer (1911). Palmer (1911) uses the concepts of salinity and alkalinity as the basis of his classification, in which salinity is caused by non-hydrolyzed salts, and alkalinity by free alkaline bases, through the hydrolysing effect of water on solutions of bicarbonates or on solutions of salts of other weak acids. All cations including hydrogen can contribute to salinity, but among anions only those of the strong acids can act in a similar way. Since salinity depends on the combined effects of the equivalent values of anions and cations, its extent is limited only by the amounts of strong acid present, the value of which must be multiplied by 2. On the other hand, complete alkalinity can be calculated by doubling the amount of cations that exceeds the content of strong acids. It should be noted that alkalinity can only be calculated from the difference between cations and anions if a complete and accuarte analyses has been performed.

Thus, ions can be grouped as follows:

A	Alkali ions ($Na^+ + K^+ + Li^+$) meq %
B	Alkaline earth ions ($Ca^{2+} + Mg^{2+}$) meq %
C	Hydrogen ion (H^+) meq %
D	Strong acids ($Cl^- + SO_4^{2-} + Br^- + NO_3^-$) meq %
E	Weak acids ($HCO_3^- + CO_3^{2-}$) meq %

Salinity and alkalinity can now be further classified:

1. Primary salinity (alkali salinity) is salinity that does not exceed twice the sum of the alkali ions.
2. Secondary salinity (non-carbonate hardness) is the excess of salinity over the primary salinity; it does not exceed twice the total of the alkaline earths.
3. Tertiary salinity (acidity) is the excess of salinity over the primary and secondary salinities.
4. Primary alkalinity is the excess of twice the total of alkalis over the salinity.
5. Secondary alkalinity is the excess of twice the sum of the alkaline earths over the secondary salinity.

Palmer has proposed five classes, as follows:

			Possible types of salinity or alkalinity
Class 1	$D < A$	2D	Primary salinity
		2(A-D)	Primary alkalinity
		2B	Secondary alkalinity
Class 2	$D = A$	2A or 2D	Primary salinity
		2B	Secondary alkalinity
Class 3	$A + B > D > A$	2A	Primary salinity
		2(D-A)	Secondary salinity
		2(A+B-D)	Secondary alkalinity
Class 4	$D = A + B$	2A	Primary salinity
		2B	Secondary salinity
Class 5	$D > A + B$	2A	Primary salinity
		2B	Secondary salinity
		2(D-A-B)	Tertiary salinity or acidity

Palmer's method groups together substances that could be of quite different origin and have been subject to different diagenetic processes. Schoeller (1956) sought to avoid this in his classification by considering several viewpoints, given below in order of decreasing importance:

1. Differentiation according to chloride concentration.
2. Differentiation according to sulphate concentration.
3. Differentiation according to concentration of hydrogen carbonate + carbonate ions.
4. Indices of chloride-alkali unbalance or base exchange.
5. Differentiation on basis percentage anions and cations.

Alekin's (1962) classification differentiates waters into three classes based on the dominant anions: bicarbonate and carbonate waters ($HCO_3^- + CO_3^{2-}$), sulphate waters (SO_4^{2-}), and chloride waters (Cl^-). Each class is subdivided into three groups according to the dominant cation: Ca, Mg, and Na groups. Each group is broken down on a basis of ionic ratios (in meq/l) into three or four water types:

Type I $HCO_3^- > (Ca^{2+} + Mg^{2+})$.

Type II $HCO_3^- < (Ca^{2+} + Mg^{2+}) < (HCO_3^- + SO_4^{2-})$.

Type III $(HCO_3^- + SO_4^{2-}) < (Ca^{2+} + Mg^{2+})$ or $Cl^- > Na^+$.

Type IV $HCO_3^- = 0$, which of course does not occur in the class of carbonate waters.

Each class is denoted by the chemical symbol for the anion concerned (C, S, Cl). To characterize the group, the chemical symbol of the anion is placed as a superscript to the right of the class symbol. The type membership is given by a Roman numeral subscript. Thus a water type in the hydrogen carbonate class, calcium group, of the second type is described by the symbol C^{Ca}_{II}.

In addition, the total dissolved solids (to an accuracy of up to 0.1mg/kg) is added before this symbol, and before the group symbol the total hardness (to whole number accuracy in meq/L). If the second most abundant anion or cation is not more than 5 meq % below the concentration of the dominant ion, the symbol for this anion or cation is included in the index.

2.4.1.2 Classification on basis of potential use

Waters can be classified with regard to their suitability for a proposed use. The three main classes of use considered here are domestic (household), industrial, and agricultural. A supply intended for municipal use may include all three classes and accordingly require a standard of quality that is generally higher than that needed for any one class. On the other hand, water for use in a particular industry may require a quality that is substantially higher than the one considered acceptable for a municipal supply. For many applications, it is economically acceptable to process the naturally available water.

2.4.1.2.1 Potable water

In 1995 the South African Department of Health proposed guidelines for Drinking Water Quality (DWAF, 1995a). In conjunction with the Department of Water Affairs and Forestry (DWAF) and the Water Research Commission (WRC), the first combined South African Water Quality Guidelines were published in 1996 (Anon., 1999). The maximum contaminant levels suggested assume that an individual consumes 2 litres of water per day. Although consumption in certain regions may be higher, the safety factor built into the maximum contaminant levels provides good protection for all consumers regardless of the amount of water ingested. The current primary drinking water guidelines, which are provided by the regulating authorities, for various inorganic substances are presented in Table 2.11. These are based on health requirements, which are affected by a number of factors, including climate, weight and age of persons, and individual eating and drinking habits.

Secondary contaminant levels are set for aesthetic reasons. Contaminants covered by these regulations are those that may adversely affect the aesthetic qualities of drinking water, such as taste, odour, colour and appearance and which thereby may deter public acceptance of drinking water provided by municipalities. At considerably higher concentrations, these contaminants may also be associated with adverse health implications. The secondary contaminant levels are not shown here but can be found in Anon. (1999).

To facilitate easy interpretation and reporting of water quality information, the South African water quality guidelines (Anon., 1999) are presented in terms of a simple colour-coded classification system. The suitability for domestic use of each of the 21 key substances, is expressed in terms of the following colour-coded classes:

🟦	**Class 0**	**Ideal** water quality – suitable for lifetime use
🟩	**Class I**	**Good** water quality – suitable for use, rare instances of negative effects *
🟨	**Class II**	**Marginal** water quality – conditionally acceptable. Negative effects may occur in more sensitive groups
🟥	**Class III**	**Poor** water quality – unsuitable for use without treatment
🟪	**Class IV**	**Dangerous** water quality – totally unsuitable for use. Acute effects may occur

* Potential negative effects include:

Health effects: Illnesses

Aesthetic effects: Changes in water colour, taste or odour; staining of laundry and household fixtures

Economic effects: Increased soap consumption and scaling and corrosion of household pipes

Table 2.11: Guidelines for South African drinking water quality, based on health effects. Concentrations expressed in mg/L unless otherwise specified (After Anon, 1999).

	Class 0	Class I	Class II	Class III	Class IV
pH	5 – 9.5	4.5 – 5 9.5 - 10	4 – 4.5 10 – 10.5	3 – 4 10.5 – 11	< 3 > 11
Electrical conductivity (mS/m)	< 70	70 – 150	150 – 370	370 – 520	> 520
Total Dissolved Solids	< 450	450 – 1000	1000 – 2400	2400 – 3400	> 3400
Turbidity range (NTU)	< 0.1	0.1 – 1	1 – 20	20 – 50	> 50
Faecal coliforms range (counts / 100mL)	0	0 – 1	1 – 10	10 – 100	> 100
Total coliforms range (counts / 100mL)	0	0 – 10	10 – 100	100 – 1000	> 1000
Free available chlorine (residual)	0.3 – 0.6	0.2 – 0.3 0.6 – 0.8	0.1 – 0.2 0.8 – 1.0	0.05 – 0.1 1.0 – 1.5	< 0.05 > 1.5
Arsenic	< 0.010	0.010 – 0.050	0.050 – 0.20	0.20 – 2.0	> 2.0
Cadmium	< 0.003	0.003 – 0.005	0.005 – 0.020	0.020 – 0.050	> 0.050
Calcium	< 80	80 – 150	150 – 300	> 300	
Chloride	< 100	100 – 200	200 – 600	600 – 1200	> 1200
Copper	< 1	1 – 1.3	1.3 – 2	2 – 15	> 15
Fluoride	< 0.7	0.7 – 1	1 – 1.5	1.5 – 3.5	> 3.5
Iron	< 0.5	0.5 – 1	1 – 5	5 – 10	> 10

	Class 0	Class I	Class II	Class III	Class IV
Total Hardness	< 200	200 – 300	300 – 600	> 600	
Magnesium	< 70	70 – 100	100 – 200	200 – 400	> 400
Manganese	< 0.1	0.1 – 0.4	0.4 – 4	4 – 10	> 10
Nitrate + nitrite (as N)	< 6	6 – 10	10 – 20	20 – 40	> 40
Nitrate	< 26	26 – 44	44 – 89	89 – 177	> 177
Potassium	< 25	25 – 50	50 – 100	100 – 500	> 500
Sodium	< 100	100 – 200	200 – 400	400 – 1000	> 1000
Sulphate	< 200	200 – 400	400 – 600	600 – 1000	> 1000
Zinc	< 20	> 20			

Bacteriological quality of a water supply is determined by analysing for coliform bacteria. The coliform group of organisms is used as an indicator of dangerous contaminant levels because some of these bacteria are excreted from the human intestinal tract. Study of these organisms is advantageous because they are non-pathogenic, do not multiply outside the human body, and are easily identified and counted (Driscoll, 1986).

2.4.1.2.2 Industrial use

Quality requirements for industrial waters vary widely according to potential use (DWAF, 1995b). For example, salt and brackish waters are commonly used as cooling water, particularly when they are used only once (not recycled) and can be disposed of without polluting the environment. Disposal of these waters is a major problem; deep-well injection may provide the best, or often the only, disposal method available (Driscoll, 1986).

Industrial process waters must be of much higher quality than cooling waters. Municipal supplies are generally good enough to satisfy the quality requirements of most process waters, with the exception of those waters used in boilers. About 60% of the water used by industry must be treated to meet quality standards (Fair *et al.*, 1971). Sanitary requirements for waters used in processing milk, canned goods, meats, and beverages exceed even those for drinking water.

In many cases, groundwater may be desirable for particular uses because of its low, relatively constant temperature. In other cases, groundwater may be suitable because of its natural hardness, since distilleries, bakeries, and breweries prefer hard water. On the other hand, even small amounts of iron, manganese, or calcium can cause great harm in paper-making processes (Driscoll, 1986). Table 2.12 lists some typical quality tolerances for industrial process water, as specified by the American Society for Testing Materials (1960).

***Table 2.12:** Quality tolerances for industrial process waters* (After American Society for Testing Materials, 1960; Fair et al., 1971).*

Industry	**Turbidity**	**Colour**	**Hardness** (as mg/L of $CaCO_3$)	**Alkalinity** (as mg/L of $CaCO_3$)	**Fe + Mn** (mg/L)	**Total Solids** (mg/L)	**Other**
Food products							
Baked goods	10	10	#		0.2		*a*
Beer	10			75 – 150	0.1	500 – 1000	*a, b*
Canned goods	10		25 – 75		0.2		*a*
Confectionery					0.2	100	*a*
Ice	5	5		30 – 50	0.2	300	*a, c*
Laundering			50		0.2		
Manufactured products							
Leather	20	10 – 100	50 – 135	135	0.4		
Paper	5	5	50		0.1	200	*d*
Paper pulp	15 – 50	10 – 20	100 – 180		0.1 – 1	200 – 300	*e*
Plastics, clear	2	2			0.02	200	
Textiles, dyeing	5	5 – 20	20		0.25		*f*
Textiles, general	5	20	20		0.5		

* Stated values are general averages only; there is much local variance.
# Some hardness is desirable.
a. Must conform to standards for potable water.
b. NaCl no more than 275mg/L.
c. SiO_2 no more than 10mg/L; Ca and Mg bicarbonates are troublesome; sulphates and chlorides of Na, Ca, and Mg each no more than 300mg/L.
d. No slime formation.
e. Non-corrosive.
f. Constant composition; residual alumina no more than 0.5mg/L.

2.4.1.2.3 Water for agriculture

Despite its generally dry climate, the present South Africa has its origins in agriculture. Most of its inhabitants are not more than a generation or two removed from an agricultural livelihood and still maintain some contact with their agricultural roots. Three agricultural water users can be identified in the country: irrigation, livestock watering and freshwater aquaculture. Only the first two will be discussed here. Of these, irrigation accounts for almost

50% of the water used in South Africa (DWAF, 1993), and is expected to remain the main water user for the foreseeable future. By comparison, livestock watering requires very little water, but is nonetheless equally, if not more, dependent on an adequate supply of water of an acceptable quality. The primary livestock industry accounts for almost 50% of the gross agricultural product (compared to 25 – 30% for irrigation) and is thus most important in the agricultural economy of the country (DWAF, 1993). Obviously, irrigation and livestock watering have different requirements in terms of water quality.

Requirements for livestock watering

For livestock, fundamentally the same requirements hold as for human consumption. Animals can, however, drink water with moderately high dissolved solids (about 10g/L) when NaCl is the chief constituent, but the concentrations should not exceed 5000mg/L as far as possible. Poisonous substances that occur particularly in polluted waters can cause injury to livestock, although it is often found that the poisoning has been caused by ingestion of plants, in which the poisons are enriched, and less often through water (Lloyd and Heathcote, 1986).

Table 2.13: *Upper limits of total dissolved solids in water for livestock use (After Hem, 1970).*

Livestock	Upper limit (mg/L)
Poultry	2 860
Pigs	4 290
Horses	6 435
Dairy cattle	7 150
Beef cattle	10 100
Lambs (fattening)	12 900

Most of the current South African guidelines for livestock watering have been adapted from international guidelines. One should note that the use of water for livestock production depends on several factors, such as the type of production system in use (i.e. intensive to extensive), the type of livestock and the type of livestock products. Therefore, the suggested target ranges given in Table 2.14 are only guidelines, and as such vary depending on a number of factors (such as stage of physiological development, gestation, lactation, physical exertion, type of ration and dry matter intake, inorganic salt intake and ambient temperature-humidity indices, among others).

Table 2.14: *Summary of water quality guidelines for livestock watering (After DWAF, 1995b).*

Water quality constituents	Target guideline range (mg/L)	
Potentially hazardous constituents with a high incidence of occurrence		
Arsenic	0 – 1.0	
Calcium	0 – 1000	
Chloride	0 – 1500	Non-ruminants
	0 – 3000	Ruminants
Copper	0 – 0.5	Sheep
	0 – 1	Cattle
	0 – 5	Horses, pigs and poultry
Fluoride	0 – 2	Non-ruminants and dairy cattle
	0 – 6	Ruminants
Molybdenum	0 – 0.01	
Magnesium	0 – 500	
Nitrate	0 – 100	
Nitrite	0 – 10	
Salinity	TDS: 0 – 1000	
	EC (mS/m): 0 – 154	
Sodium	0 – 2000	
Sulphate	0 – 1000	
Toxic algae *	No visible blue-green scum	
	< 6 colonies of blue-green algae / 0.5mL	
	< 2000 Microcystis cells/mL	
Potentially hazardous constituents with a low incidence of occurrence		
Aluminium	0 – 5	
Boron	0 – 5	
Cadmium	0 – 0.01	
Chromium (VI)	0 – 1	
Cobalt	0 – 1	
Iron	0 – 10	
Lead	0 – 0.1	
Manganese	0 – 10	
Mercury	0 – 0.001	

Water quality constituents	Target guideline range (mg/L)
Nickel	0 – 1
Pathogens	1000 / 100mL faecal coliforms 5000 / 100mL total bacteria
Pesticides	Depends on type of pesticide
Selenium	0 – 0.05
Vanadium	0 – 1
Zinc	0 – 20

* Specialist advice should be sought.

Classification of irrigation waters

Water quality, soil types, and cropping practices all play a role in successful irrigation. Good quality water permits maximum yields consistent with proper soil and water management. Study of soil types determines the infiltration rates that can be expected for certain soils, thereby providing some guides to the amount of leaching of mineral salts that can be anticipated; leaching is essential to reduction of salinity in topsoils. Equally important, the tolerance for certain elements must be determined before specific crops can be selected. Table 2.15 gives the guideline concentrations for evaluating a particular water for irrigation purposes.

Table 2.15: *Guidelines for evaluating water quality for irrigation purposes (from Ayers and Westcot, 1985).*

Potential irrigation problem	Units	Degree of Restriction on Use		
		None	Slight to moderate	Severe
Salinity *(affects crop water availability)*				
EC	mS/cm	< 0.7	0.7 – 3.0	> 3.0
TDS	mg/L	< 450	450 – 2000	> 2000
Infiltration *(affects infiltration rate of water into the soil. Evaluate using EC and SAR together)*				
SAR = 0 – 3 and EC =		> 0.7	0.7 – 0.2	< 0.2
SAR = 3 – 6 and EC =		> 1.2	1.2 – 0.3	< 0.3
SAR = 6 – 12 and EC =		> 1.9	1.9 – 0.5	< 0.5
SAR = 12 – 20 and EC =		> 2.9	2.9 – 1.3	< 1.3

Potential irrigation problem	Units	Degree of Restriction on Use		
		None	Slight to moderate	Severe
SAR = 20 – 40 and EC =		> 5.0	5.0 – 2.9	< 2.9
Specific Ion Toxicity *(affects sensitive crops)*				
Sodium (Na)				
Surface irrigation	SAR	< 3	3 – 9	> 9
Sprinkler irrigation	mmol$_c$/L	< 3	> 3	
Chloride (Cl)				
Surface irrigation	mmol$_c$/L	< 4	4 – 10	> 10
Sprinkler irrigation	mmol$_c$/L	< 3	> 3	
Boron (B)	mg/L	< 0.7	0.7 – 3.0	> 3.0
Trace Elements (See Table 2.16)				
Miscellaneous Effects *(affects susceptible crops)*				
Nitrogen ($NO_3 - N$)	mg/L	< 5	5 – 30	> 30
Bicarbonate (HCO_3) *(overhead sprinkling only)*	mmol$_c$/L	< 1.5	1.5 – 8.5	> 8.5
pH		Normal range 6.5 – 8.4		

1. The guidelines are based on the following assumptions:
2. EC is the electrical conductivity (measure of the water salinity) reported in mS/cm at 25°C. TDS is the Total Dissolved Solids, reported in mg/L.
3. SAR is the Sodium Adsorption Ratio. Concentrations are in mmol$_c$/L.

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}}$$

4. At a given SAR, infiltration rate decreases as water salinity decreases.
5. For surface irrigation, the guideline values are acceptable for most tree crops and woody plants which are sensitive to sodium and chloride. Most annual crops are not sensitive, however, and Ayers and Westcot (1985) should be consulted for the relevant salinity tolerance figures.
6. $NO_3 - N$ is the nitrate nitrogen reported in terms of elemental nitrogen. $NH_4 - N$ and Organic – N should be included when wastewater is being tested.

As already mentioned, trace elements occur in almost in all water supplies but at very low concentrations, usually less than a few mg/L, with most less than 100μg/L. Not all trace elements are toxic, and, in small quantities, many are essential for plant growth (Fe, Mn, Mo, Zn). Table 2.16 gives some recommended concentrations for trace elements in irrigation waters. The maximum concentration is based on a water application rate which is consistent with good irrigation practice (i.e. 1000 mm/yr).

Table 2.16: *Recommended maximum concentrations of selected trace elements in irrigation water (from Ayers and Westcot, 1985).*

Element	Recommended max conc. (mg/L)	Remarks
Al	5.0	Can cause non-productivity in acid soils (pH < 5.5), but more alkaline soils at pH > 7.0 will precipitate the ion and eliminate any toxicity.
Cr	0.10	Not generally recognized as an essential growth element. Conservative limits recommended due to a lack of knowledge on its toxicity to plants.
Cu	0.20	Toxic to a number of plants at 0.1 to 1.0mg/L in nutrient solutions.
F	1.0	Inactivated by neutral and alkaline soils.
Fe	5.0	Not toxic to plants in aerated soils, but can contribute to soil acidification and loss of availability of essential phosphorus and molybdenum. Overhead sprinkling may result in unsightly deposits on plants, equipment and buildings.
Li	2.5	Tolerated by most crops up to 5mg/L; mobile in soil. Toxic to citrus at low concentrations (< 0.075mg/L).
Mn	0.20	Toxic to a number of crops at a few tenths to a few mg/L, but usually only in acid soils.
Ni	0.20	Toxic to a number of plants at 0.5 mg/L to 1.0 mg/L; reduced toxicity at neutral or alkaline pH.
Zn	2.0	Toxic to many plants at varying concentrations; reduced toxicity at pH > 6.0 and in fine textured or organic soils.

Ground waters tend to be much more variable in composition than surface waters. With few exceptions, it is not always possible to select ground waters that are typical of an area or to generalize about the groundwaters of a given basin, as one could with surface waters. Water quality problems in irrigation, in general, have already been discussed in Section 2.3.2 (Irrigation water) and will not be discussed further.

In classification of irrigation waters, it is assumed that the water will be used under average conditions with respect to soil texture, infiltration rate, drainage, quantity of water used, climate, and salt tolerance of crop. Large deviations from the average for one or more of these variables may make it unsafe to use what, under average conditions, would be a good water;

or may make it safe to use what, under average conditions, would be a water of doubtful quality.

A diagram for classifying irrigation waters was suggested by Wilcox (1948), and this was subsequently modified by Thorne and Thorne (1951) for the classification of irrigation waters of Utah. Both diagrams have been widely used (Figure 2.2). In the classification, the SAR value rather than soluble sodium percentage is taken as the index of sodium status or sodium hazard.

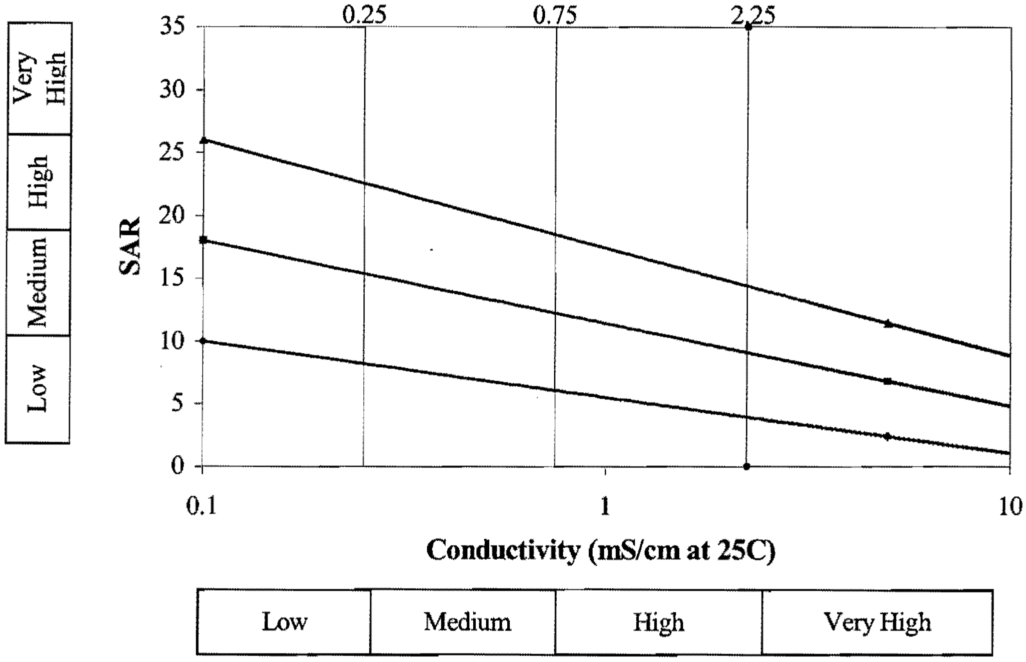

Figure 2.2: Wilcox classification of irrigation waters based on sodium adsorption ratio (SAR) and conductivity.

Salinity hazard: Waters are divided into four classes with respect to conductivity, the dividing points between classes being at 0.25, 0.75 and 2.25mS/cm. These class limits were selected in accordance with the electrical conductivity of saturation extracts.

Sodium hazard: The establishment of water quality classes from the standpoint of the sodium hazard is more complicated than for the salinity hazard. The problem can be approached from the point of view of the probable extent to which soil will adsorb sodium from the water and the rate at which adsorption will occur as the water is applied.

Interpretation of quality-class ratings in the Wilcox classification of water for irrigation purposes is as follows:

Conductivity (Salinity)

Low-salinity water can be used for most crops and soils with little likelihood that soil salinity will develop. Some leaching is required, but this occurs under normal irrigation on all but the tightest of soils.

Medium-salinity water can be used where a moderate amount of leaching occurs. Plants with moderate salt tolerance can be grown in most cases without special practices for salinity control.

High-salinity water cannot be used on soils that have restricted drainage. With adequate drainage, special management for salinity control may be required and plants with good salt tolerance should be selected.

Very-high-salinity water is not suitable for irrigation under ordinary conditions. If used the soils must be permeable, drainage must be adequate, considerable excess irrigation water must be applied, and very tolerant crops should be selected.

Sodium Adsorption Ratio

Low-sodium water can be used with little danger on nearly all soils. Sodium-sensitive crops such as stone-fruit trees and avocados may accumulate injurious concentrations of sodium.

Medium-sodium water is hazardous for use on fine textured soils that have high cation-exchange capacity. This water may be used on coarse-textured or organic soils with good permeability.

High-sodium water may be harmful to most soils and thus requires special soil management: good drainage, high leaching, and addition of organic matter. Chemical amendments may be necessary except for gypsiferous soils.

Very-high-sodium water is generally unsatisfactory for irrigation purposes, except at low salinity and where calcium from the soil or use of gypsum or other mineral additions may make these waters usable.

2.4.2 Classifications used for mine waters

Five major hydrochemical schemes have been employed to classify mine water discharges. Although the simpler schemes are described in many standard textbooks, they are included here as part of a critique to determine their usefulness beyond being standard hydrochemical graphical methods. Therefore the basis of each will be explained briefly and their shortcomings outlined. In Section 6.3 (Application of existing classification systems) an attempt will be made to apply these schemes to the mine waters sampled in this study.

2.4.2.1 Piper classification and hydrochemical facies

The Piper diagram (Piper, 1944) has become universally used and is shown in Figure 2.3. Major ions are plotted in the two base triangles of the diagram as cation and anion percentages of $mmol_c$/L. Total cations and total anions are each considered as 100%. The respective cation and anion locations for an analysis are projected into the parallelogram, which represents the total ion relationships. The Piper diagram allows comparisons to be made between a large number of analyses, but has the drawback that all trilinear diagrams have in not portraying actual ion concentrations. The distribution of ions within the main field rectangle is unsystematic in hydrochemical process terms so that the diagram lacks a certain logic. Furthermore, the large amount of line work is a hinderance.

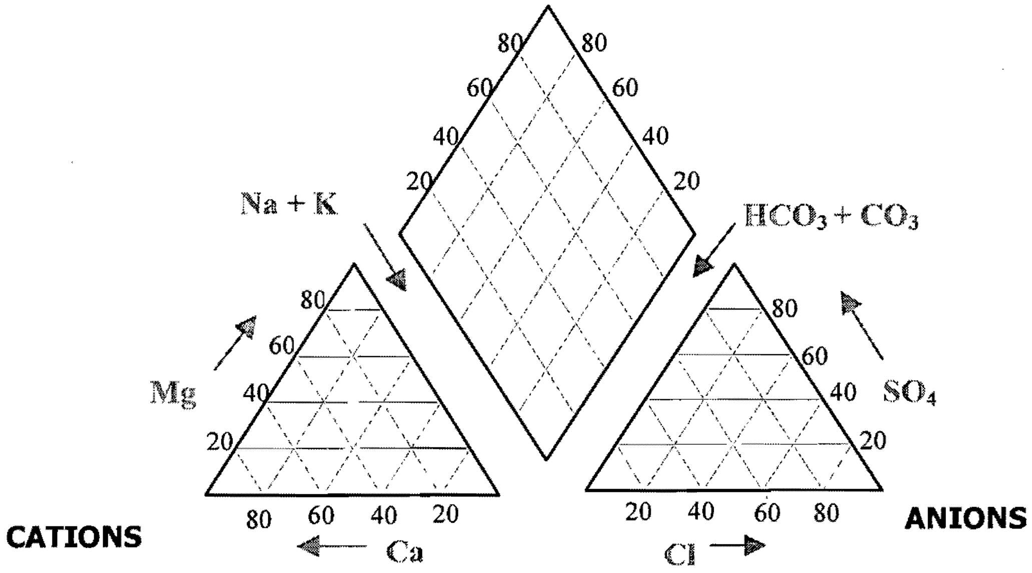

Figure 2.3: Trilinear diagram of major ions (After Piper, 1944).

An alternative diagram to that of Piper has been devised by Durov (1948) and is shown in Figure 2.4. As with the former diagram it is normally based upon percentage major ion mmol$_c$/L values, but in this case the cations and anions together total 100%. The cation and anion values are plotted in the appropriate triangle and projected into the square main field. An expanded version of the Durov diagram was developed by Burdon and Mazloum (1958) and Lloyd (1965). The expanded Durov diagram has a distinct advantage over the Piper diagram in that it canbe extended to include a seventh parameter, it provides a better display of hydrochemical types and some processes, and in practical terms has less line work in the main field.

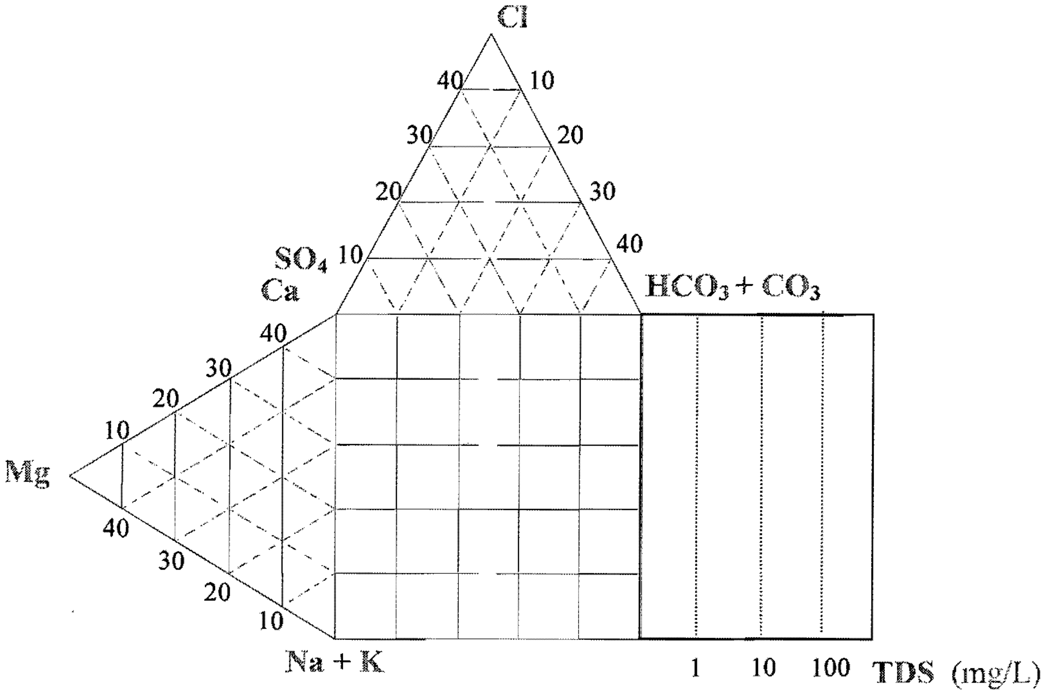

Figure 2.4: *The original type of Durov diagram (After Durov, 1948).*

The Piper and Durov classifications consider the major ions that dominate groundwater chemistry in most natural environments but they omit metals dominating acidic milieux such as Fe and Al, and therefore have limited application to mine waters. Furthermore, salinity and pH can only be represented by various inconvenient approaches such as adjusting the size of plotted points diagrammatically. The cognate Durov diagram (Lloyd and Heathcote, 1985) is more amenable to such modifications, but comparability with non-coalfield groundwaters is compromized once plots become highly customized.

2.4.2.2 Scheme of Glover (1975)

Glover (1975) presented a scheme specifically for mine waters based primarily on Fe and pH. Therefore it does not suffer from the limitations of Piper-type approaches. Five groups of waters were recognized depending on the valence state of dissolved iron, presence of suspended iron and 'degree of acidity' (i.e. pH). The groups are as follows:

- Acidic with low total Fe concentration
- Acidic with high Fe^{3+} concentration
- Acidic with high Fe^{2+} concentration
- Neutral with high Fe^{2+} concentration
- Suspended ferric hydroxide (combined with dissolved Fe^{2+} or Fe^{3+})

The practical application of this scheme is hindered by the difficulty of obtaining reliable determinations of Fe^{2+} and Fe^{3+}. Direct sampling and analysis of waters for these species is troublesome and geochemists prefer to analyze total Fe and infer the distribution of Fe^{2+} and Fe^{3+} by speciation modelling, with redox equilibria calculated from concentrations of other redox couples or measured Eh values (Appelo and Postma, 1993).

Furthermore, the scheme was based on the composition of waters from working mines, which generally differs from that of waters flowing from abandoned mines (Younger 1994). The focus on pH and Fe as key classification parameters limits the geochemical usefulness of the scheme, for the other major ions (which are well represented in Piper and Durov diagrams) are neglected. This limits the assessment of both genesis and quality of a given mine-water.

2.4.2.3 Ficklin's trace metal classification system

A classification was developed by Ficklin *et al.* (1992) in order to show the geological controls that affect the acidity and concentration of metals in mine drainage across a broad spectrum of mineral deposits, each with characteristic ore and gangue minerals, trace metals, host rocks, wallrock alteration, and structural features. They suggest then that the pH and trace metal (Zn, Cu, Cd, Ni, Co and Pb) composition were sufficient to summarize the major attributes of the waters (Figure 2.5).

In a study done on the Colorado Mineral Belt, Ficklin *et al.* (1992) found that the most acidic drainage originated in mines rich in pyrite or pyrite-alunite and quartz pyrite veins. Other mines located in host rocks that can buffer the acid, produce drainage water with near-neutral pH values but high metal concentrations. The near absence of pyrite in some mines results in near-neutral, low metal mine drainage waters. Natural drainage in mineralized areas produce waters that are chemically similar to mine drainage water. Since this scheme is concerned primarily with trace metals, it largely neglects the major ions that are important in governing quality.

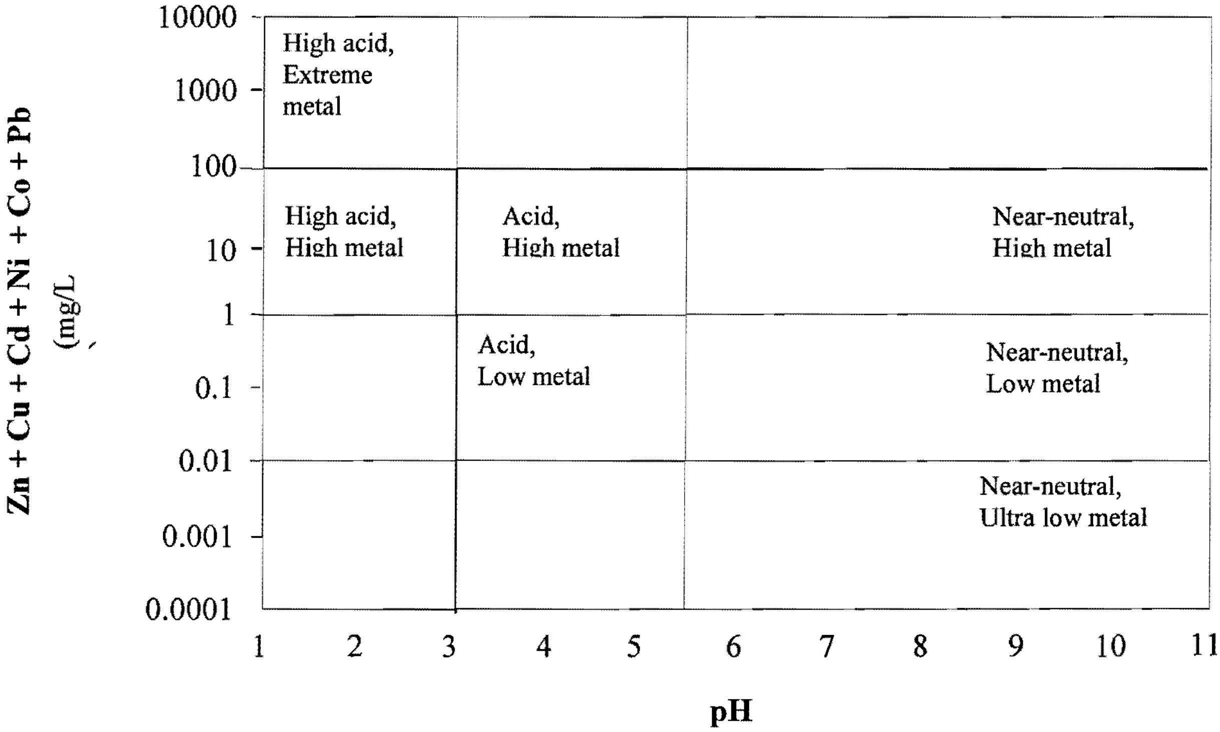

Figure 2.5: *Trace metal classification system for diverse ore deposit types (After Ficklin et al., 1992).*

2.4.2.4 Scheme of US Bureau of Mines

The US Bureau of Mines' system was developed by Hedin *et al.* (1994) to classify mine waters with respect to their treatability, using different treatment technologies. Any water can, in theory, be classified under this scheme on the basis of acidity and alkalinity. By convention, results are reported as mg/L $CaCO_3$ equivalent (though it should be acknowledged that it would be in many ways preferable to report results in mmol$_c$/L or mmol/L). For most acidic or circum-neutral groundwaters, alkalinity is dominated by the bicarbonate content of the water (Hem, 1985), though other species may be significant in mine waters (such as S_2^- or HS^- where sulphate reduction is active). Acidity is a reflection of both hydrogen ion activity but also of the mineral acidity arising from the capacity of metals such as iron, manganese and aluminium to undergo hydrolysis reactions that release protons.

Thus these two properties of the water, acidity and alkalinity, relate to different interacting components of the dissolved load, including HCO_3^-, HS^-, pH, Fe, Al and Mn. It should also be noted that there is no contradiction when a mine-water with high alkalinity concentrations possesses a pH substantially below 6.5. With these definitions, Hedin *et al.* (1994) classify mine waters into two groups:

- Net alkaline mine waters (i.e. alkalinity > acidity)
- Net acidic mine waters (i.e. acidity > alkalinity)

This scheme summarizes the relative importance of six important parameters and is a useful means of classifying waters with respect to their amenability to different treatment technologies. Unfortunately, it completely neglects those aspects of quality related to the presence of Cl^-. For mine drainage environments, it only partially ignores the presence of SO_4^{2-} since the degree of acidity will probably correlate with SO_4^{2-} as both are derived from the oxidation of pyrite.

2.4.2.5 Younger's Scheme

Younger (1995) extended the US Bureau of Mines' classification scheme by considering how Cl^- and SO_4^{2-} concentrations might be incorporated, since these provide clues to the evolution of mine water. He proposed the following:

> As alkalinity and acidity are both expressed in units of mg/L $CaCO_3$ equivalent, the net alkalinity or net acidity of a solution can be quantified by calculating the alkalinity or acidity as a percentage of the total $CaCO_3$ equivalent species (i.e. alkalinity + acidity).
>
> The major anions other than bicarbonate (i.e. sulphate and chloride) are clues to the genesis of a given mine water. The processes which favour dominance of one over the

other represent opposite ends of a hydrogeological spectrum ranging from undisturbed coal measures (high chloride from brines; Edmunds (1975)) to extensively mined coal measures in which pyrite oxidation dominates water quality evolution (leading to high sulphate concentrations). It is thus logical to plot the ratio of sulphate to chloride (% total meq) on a single axis).

With a diagram of this type (Figure 2.6), basic geochemical process interpretations are feasible. Unfortunately, it does not address the question of quality.

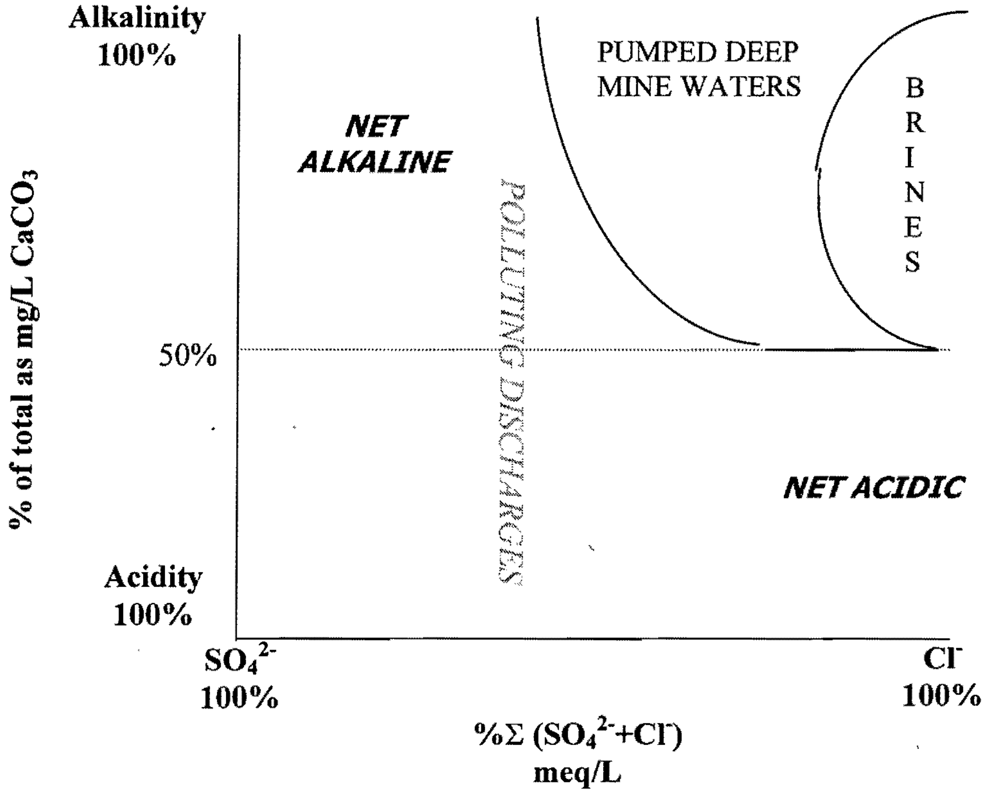

Figure 2.6: Younger's classification scheme for mine waters indicating fields in which mine waters of different origins and affinities plot (After Younger, 1995).

There are, of course, numerous individual criteria by which water can be classified on an *ad hoc* basis either in terms of quality (e.g. hardness, scaling or corrosion potential, irrigation suitability, potability) or geochemical origin (e.g. mineral saturation indices, ionic ratios or products). Some parameters (e.g. sodium adsorption ratio and calcite saturation index) are both geochemically revealing and empirically valuable as indices of quality for specific purposes.

2.5 Conclusions

In coal mining, many affected waters have a tendency to turn acidic over time. The most important factors affecting the production of acid mine waters are the amount, concentration, grain size, and distribution of mainly pyrite present in a mine, tailings, or waste pile. The rate of oxidation can vary depending on the accessibility of air, moisture, and microbes to the pyrite surface and the neutralizing capacity of available buffering materials. These complex geochemical processes can be modelled with either equilibrium or kinetic principles to estimate the result of pyrite oxidation, carbonate buffering, and silicate hydrolysis. Modelling calculations of this type have been done for pyritic rocks and waters of different initial compositions.

If used with proper caution, geochemical models can be powerful tools for interpreting the processes that affect water quality. As with any tool, however, the potential for misuse is high and it is the responsibility of the user to bring to each modelling application an adequate knowledge of the thermodynamic and kinetic behaviour of phases to be modelled, as well as appreciation of uncertainties in the input data. The advantage of modelling is that it can take into account some of the complex interactions between hydrology, geochemistry, geology, and other site characteristics as well as performing database management. This advantage is a major step beyond various acid-base accounting, static, and kinetic tests for which comparison, evaluation, and agreement is lacking .

The water quality requirements, for industry, vary considerably depending on the processes and products being produced. One of the main problems is related to waters used for heating or cooling, as this is subject to major pressure and temperature changes. Scaling relates directly to the supersaturation of a water with respect to carbonate minerals, and iron and manganese compounds. Scaling can cause a reduction in the diameter of pipes and the loss of temperature in heating elements. Corrosion results from electrochemical processes in which oxidation of the metal takes place. Corrosion can be accentuated by the metabolic processes of bacteria.

If all of the irrigation hazard indices are considered then conflicting conclusions may be drawn or, on the other hand, specific hazards may indicate the need for soil management or cropping of particular plant species. Certain of the hazard parameters do not pose major difficulties, for example the magnesium hazard, while others are less reliable such as the residual sodium carbonate index. The indices used will depend on the water analyses available or may be specified because a particular soil type predominates or cropping pattern is required. For general assessment, the Food and Agriculture Organization have emphasized that EC, adj. SAR, and certain specific ions should be considered.

Metals can be both essential and toxic to humans. The natural cycles of metals can be disturbed by human activities, which redistribute them throughout the various reservoirs of natural systems. The metal content of biota is often influenced by the geochemical nature of their habitat. The bioavailability and toxicity of metals are influenced by the speciation and physicochemical forms in which metals are present in waters, sediments and soils. It is important to combine physicochemical, geochemical, geological, and biological information in the study of metal bioavailability and toxicity.

A number of systems have been employed to classify waters. Some of these have been on the basis of origin, while others depend on the quantity or quality of dissolved constituents. More commonly, waters have been classified on the basis of their potential use (e.g. drinking water, industrial water, and irrigation waters). The advantages and disadvantages of five classification systems, used specifically on mine waters in the past 50 years, were examined. It was found that some of these systems consider the major ions that dominate water chemistry in natural environments but they omit metals dominating acidic milieux such as Fe and Al. Others are based primarily on pH (in some cases acidity / alkalinity) and Fe, thereby neglecting the major ions. Only one was concerned with trace elements. All these schemes are hydrogeochemically useful but none adequately addresses the question of quality.

CHAPTER 3

Geochemical characterization of colliery waters

3.1 Introduction

Some 260 water samples were taken from 13 Anglo Coal collieries and 1 other abandoned colliery. Many of the samples were taken from underground workings, while others were taken from opencast operations and surface streams. A few of the collieries in this study have already closed down, or are in the process of closure. These include New Largo, the Vryheid collieries (Natal Anthracite and Vryheid Coronation), Transvaal Natal & Delagoa Bay Collieries (TNDBC) and Vierfontein. Extensive analyses covering a wide range of analytical techniques were conducted, followed by speciation modelling using PHREEQC. This chapter presents and describes how they have been used to better understand the geochemical nature and origin of the water. Furthermore, correlations between major chemical constituents are presented in the hope that these may be useful for predicting future behaviour of the water bodies. Considerations relating to the geochemistry of the adjacent sediments are dealt with in Chapter 4.

3.2 Materials and methods

3.2.1 Sampling

Duplicate water samples, of approximately 1 litre, were collected at various locations within the fourteen collieries. Due to the need to respect confidentiality and information supplied by the mine owners, only a regional locality map could be supplied (Figure 3.1). Prior to sampling, each high density polyethylene sample bottle was rinsed several times at the site in order to equilibrate it with the water to be collected. Where possible, samples were collected from approximately mid-depth within each of the water bodies, taking care to avoid disturbing the substrate in the immediate vicinity of the sampling site. Due to the circumstances under which this study was conducted the author was not able to spend a great deal of time at each of the sample sites, and it is for this reason that on-site observations were limited.

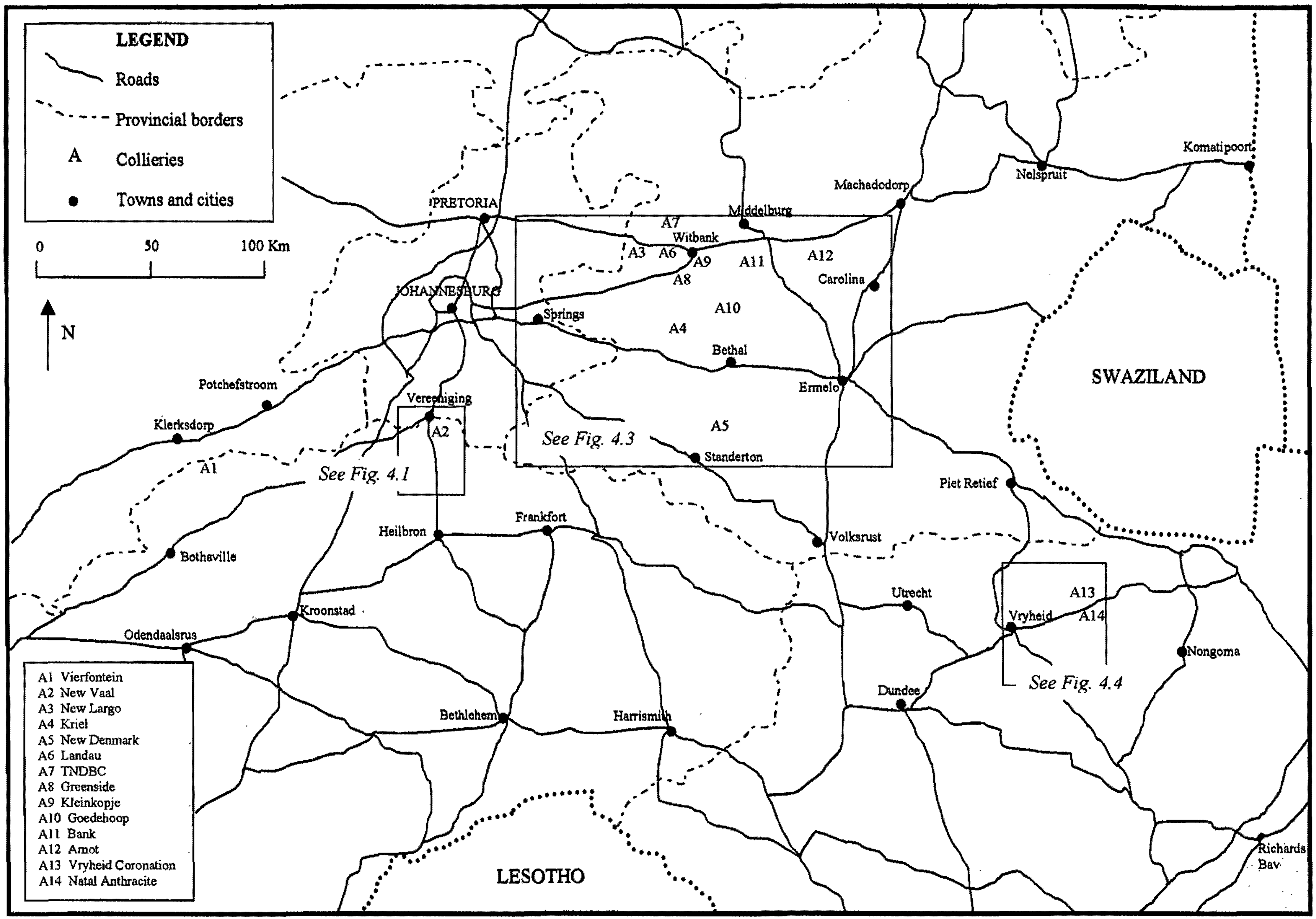

Figure 3.1: Regional locality map of collieries investigated (Adapted from Barker, 1999).

Sample bottles were completely filled and sealed in order to exclude air. Prior to being transported for analysis, the samples were split and refrigerated. The samples were divided as follows: (1) an unfiltered, unacidified sample was kept for pH, EC, alkalinity / acidity and major ion determinations, (2) a filtered (0.45μm), acidified (2mL 6M HCl/250mL) sample for iron determinations, and (3) a filtered (0.45μm), acidified (1mL conc. HNO_3/100mL) sample for trace element determinations. The maximum holding time for the water-sample splits was 24 hours. The unacidified samples taken at six of the collieries (viz. Kriel, New Denmark, Greenside, Goedehoop, Bank and Arnot), as well as all the acidified samples were transported to the University of Cape Town for analysis. Unacidified samples taken from the other seven collieries were transported to Pretoria for analysis at the Institute for Soil, Climate and Water. All of the samples were stored at 4°C so as to minimize the risk of chemical interaction (solute precipitation and/or adsorption) with the sample container. No major precipitates were observed in the sample containers prior to analysis.

Field measurements were taken for all samples using a Ciba Corning M90 microprocessor based pH and EC meter, with temperature compensator. The meter was calibrated using pH 4 and 7 buffers and a 1413μS standard solution. Dissolved Oxygen readings were also taken at approximately half of the study sites, using a Yellowstone DO meter, fitted with a membrane electrode, and calibrated for 1600m altitude. Unfortunately the instrument was later found to give spurious readings due to an electrical fault and therefore the data could not be utilized.

3.2.2 Chemical analysis

A brief description of the methods used to analyze the colliery water samples will be given here; further details, including an assessment of analytical accuracy and precision, are outlined in Appendix 1. The author performed the majority of water analyses in the Department of Geological Sciences at the University of Cape Town. Samples were initially analyzed for pH and electrical conductivity (EC) using an automated Metrohm 691 pH meter and an automated CRISON microCM 2201 conductivity meter, respectively. Alkalinity was determined by potentiometric titration to a pre-selected pH of 4.5 using 0.01M HCl and an automated Radiometer DTS 800 multi-titration system fitted with glass and saturated calomel reference electrodes. Acidity was determined via a method of potentiometric titration to a pre-selected pH of 8.3 using 0.02M NaOH and an automated Radiometer DTS 800 multi-titration system with a glass and calomel reference electrode pairs. The method used to determine iron was the phenanthroline colorimetric method (Method number 3500-Fe D), as described in Eaton *et al.* (1995; p3-67).

The water samples were then filtered through 0.2μm Millipore filters prior to analysis for their various constituents. The majority of the cation (Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) and anion (F^-, Cl^-, NO_2^-, NO_3^-, Br^-, PO_4^{3-}, and SO_4^{2-}) data were obtained by ion chromatography (IC) using a Dionex 300 ion chromatograph. The samples were refiltered using the 0.2μm Millipore as a precautionary measure to minimize colloidal contamination of the IC, which often occurs during the analysis of acid mine waters. The water samples were also analyzed on an ELAN 6000 inductively coupled plasma-mass spectrometer (ICP-MS) for a pre-selected range of elements. (Only those elements expected to be of any concern in this study either as a result of their influence in assessing re-use potential or because of their magnitude were measured.) Iron was measured by colorimetry, using the phenanthroline method. Dissolved organic carbon (DOC) was determined using a variation of the persulphate-ultraviolet oxidation method, at the CSIR in Stellenbosch. Pre-treatment for DOC analysis required only that the samples be passed through a 0.45μm Millipore filter.

3.2.3 Statistical methods

All statistical calculations and graphics were carried out using the STATISTICA computer programme version 5.5 (Statsoft Inc., 2000). Non-parametric statistics were chosen for interpretation because the data, for the majority of variables, do not conform to a normal distribution and because of the relatively small sample sizes being evaluated.

Descriptive statistics were calculated separately for each variable, and these provide such basic information as the mean, median, minimum and maximum values, different measures of variation, as well as data about the shape of the distribution of the variable (Table 3.1). The measures of variation included the standard deviation and the standard error (the standard error is the standard deviation of the sampling distribution of a mean). Some of the results are presented graphically with box and whisker plots which show the median, inter-quartile range (box), non-outlier maximum and minimum values (whiskers), outliers and extremes.

Outlier values are defined as follows:

> [75th percentile + 1.5(inter-quartile range)], or
< [25th percentile - 1.5(inter-quartile range)].

Extreme values are defined as:

> [75th percentile + 2(inter-quartile range)], or
< [25th percentile - 2(inter-quartile range)].

In order to assess for which variables there was a significant difference between the summer and winter seasons, the Mann-Whitney U test was employed. This is the non-parametric equivalent of the t-test and is approximately 95% as efficient. The statistic consists of assigning ranks to median values for all cases, summing the ranks of each group and comparing the summed ranks between groups. Statistical significance is assessed by p-values, which indicate the probability of error in accepting the test result. Mann-Whitney U results are also presented graphically with box and whisker plots.

Correlation between variables was assessed with the Spearman's correlation coefficient (r_s values), which consisted of ranking raw data values independently for each variable comprising a data set for the *n* cases consisting of *n* pairs of ranks. The squared differences in the ranks was summed and used to calculate r_s. Spearman's correlation co-efficient is the non-parametric equivalent of Pearson's r and is approximately 90% as efficient.

3.3 Results and discussion

3.3.1 Chemical composition

Detailed results of chemical analyses are presented in Appendix 2. Descriptive statistics for the mine waters as a whole are presented in Table 3.1. The total number of samples used for the statistical analysis was 167, and this included both summer and winter samples but only one from each locality. Summaries for each colliery can be found in Figures 3.2 through 3.36. Those samples which are considered to be outliers have been excluded from the initial plots as the range shown is meant to be representative of typical concentrations for each colliery, so that comparisons can be made. Furthermore, where a particular colliery appears to be an outlier, the figures have been reprinted excluding the outlier colliery, also to facilitate comparison (e.g. Figure 3.4a includes all collieries, Figure 3.4b excludes the outliers).

Table 3.1: *Descriptive statistics for each constituent measured in the mine waters. Concentrations reported in mg/L.*

	No. of cases	Mean	Median	Minimum	Maximum	Standard Deviation	Standard Error	Skewness	Kurtosis
pH	167	6.57	7.34	2.37	9.91	1.92	0.15	-0.92	-0.56
Temp. (°C)	69	18.6	18.5	6.10	29.8	3.75	0.45	-0.96	3.65
EC (mS/cm)	167	2.48	1.74	30.0	13.7	2.43	1.88	2.24	5.86
Na	167	186	56.0	1.60	1 890	362	28.0	3.09	9.41
NH_4	12	7.03	4.80	0.44	46.0	12.5	3.61	3.24	10.9
K	167	7.25	5.27	0.36	40.0	6.76	0.52	1.99	4.62
Mg	167	102	62.6	0.72	838	115	8.92	2.61	10.8
Ca	167	230	175	1.90	839	186	14.4	0.76	-0.19
F	101	2.25	0.43	0.01	43.4	5.41	0.54	5.58	37.0
Cl	167	67.8	14.8	2.14	1 538	183	14.2	5.23	32.4
NO_2	6	2.01	2.07	0.90	3.34	0.87	0.36	0.33	-0.26
NO_3	105	8.90	2.63	0.06	107	17.5	1.71	3.86	17.5
SO_4	167	1 849	850	0.59	23 711	3267	253	4.48	23.0
HCO_3	129	194	148	2.44	1 214	181	16.0	2.40	8.17
DOC	166	25.5	2.85	1.00	176	41.7	3.24	1.43	0.40
Li	121	0.64	0.08	0.001	9.20	1.58	0.14	3.97	17.0
B	115	0.34	0.11	< 0.001	4.20	0.64	0.06	4.14	20.6
Al	145	12.2	0.05	0.001	341	43.0	3.57	5.45	33.7
SiO_2	164	12.5	10.5	0.12	75.9	9.38	0.73	2.29	11.9
P	7	8.51	0.44	0.11	30.4	13.9	5.26	1.25	-0.73

Table 3.1 cont.: *Descriptive statistics for each constituent measured in the mine waters. Concentrations reported in mg/L.*

	No. of cases	Mean	Median	Minimum	Maximum	Standard Deviation	Standard Error	Skewness	Kurtosis
Cr	117	0.05	0.008	< 0.001	0.90	0.131	0.012	4.92	26.1
Mn	167	4.15	0.45	< 0.001	224	18.7	1.44	10.3	118
Fe(II)	41	527	26.8	0.010	5621	1345	210	3.20	9.57
Fe(III)	70	67.1	1.33	0.003	1406	236	28.2	4.85	23.8
Fe_{Total}	75	351	12.9	0.003	5865	1135	131	3.98	15.4
Co	166	0.11	0.008	< 0.001	3.94	0.36	0.03	8.09	81.4
Ni	155	1.24	0.03	< 0.001	20.2	3.93	0.32	3.39	10.4
Cu	131	0.02	0.003	< 0.001	0.75	0.08	0.007	7.69	66.8
Zn	159	0.26	0.09	0.001	3.63	0.49	0.04	3.86	18.3
As	152	0.002	0.001	< 0.001	0.06	0.006	0.001	6.46	51.6
Se	140	0.01	0.002	< 0.001	0.88	0.07	0.006	11.7	138
Rb	166	0.02	0.01	0.001	0.11	0.02	0.001	2.25	7.45
Sr	166	1.89	1.48	0.003	9.29	1.86	0.14	1.61	2.87
Cd	144	0.002	< 0.001	< 0.001	0.12	0.01	0.001	8.61	83.8
Cs	162	0.005	0.001	< 0.001	0.12	0.02	0.002	5.15	26.3
Ba	166	0.07	0.05	0.009	0.51	0.06	0.005	3.38	17.4
Pb	134	0.009	0.002	< 0.001	0.10	0.02	0.001	3.66	14.4
U	161	0.007	0.001	< 0.001	0.44	0.04	0.003	10.13	111

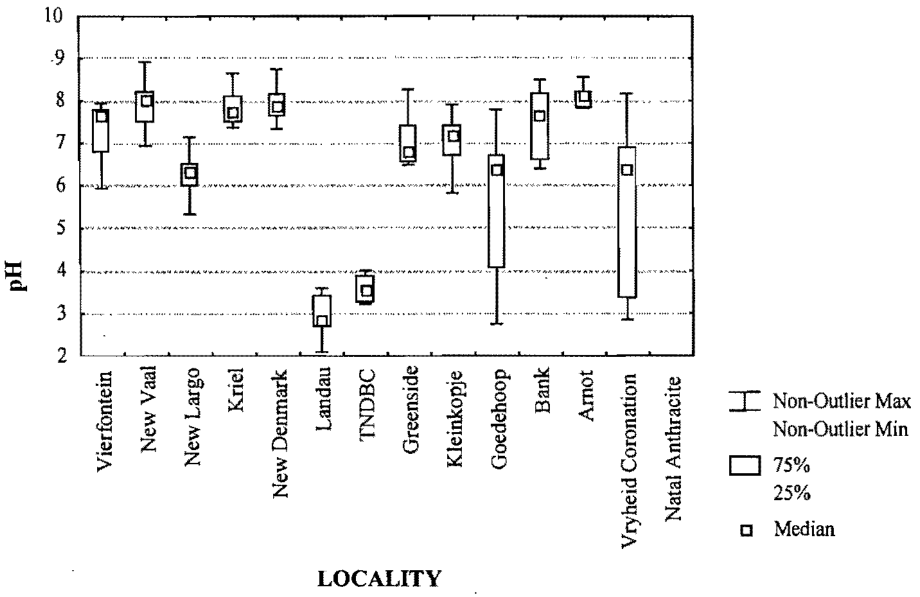

Figure 3.2: pH of water samples from Highveld collieries (n=167).

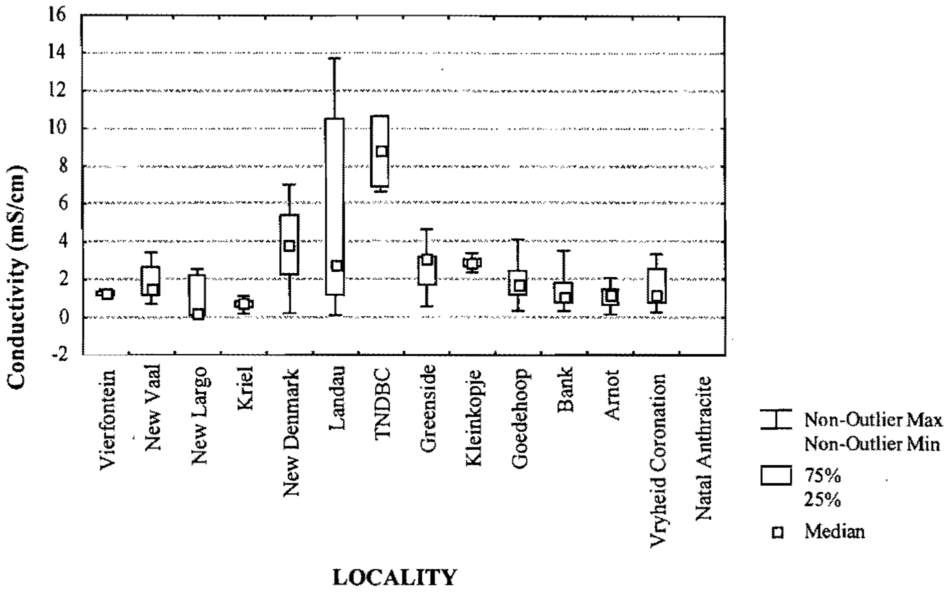

Figure 3.3: Electrical conductivity of water samples from Highveld collieries (n=167).

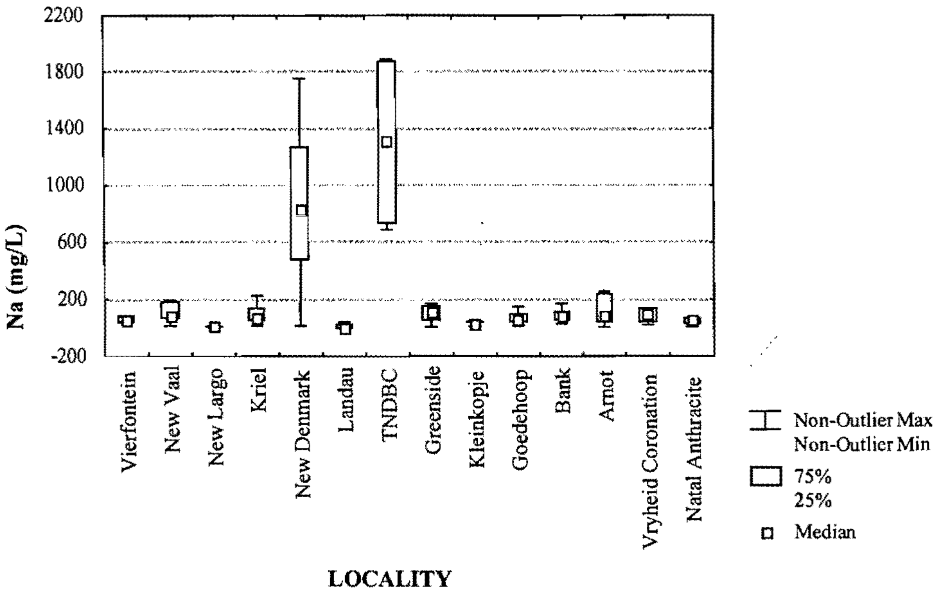

Figure 3.4a: Sodium concentration of water samples from Highveld collieries (n=167).

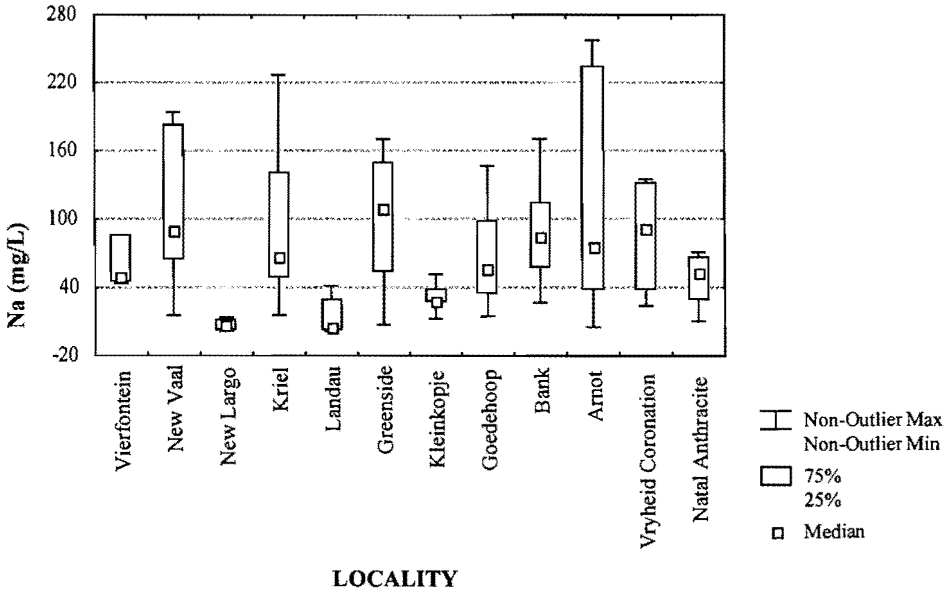

Figure 3.4b: Sodium concentration of water samples from Highveld collieries, excluding New Denmark and TNDBC.

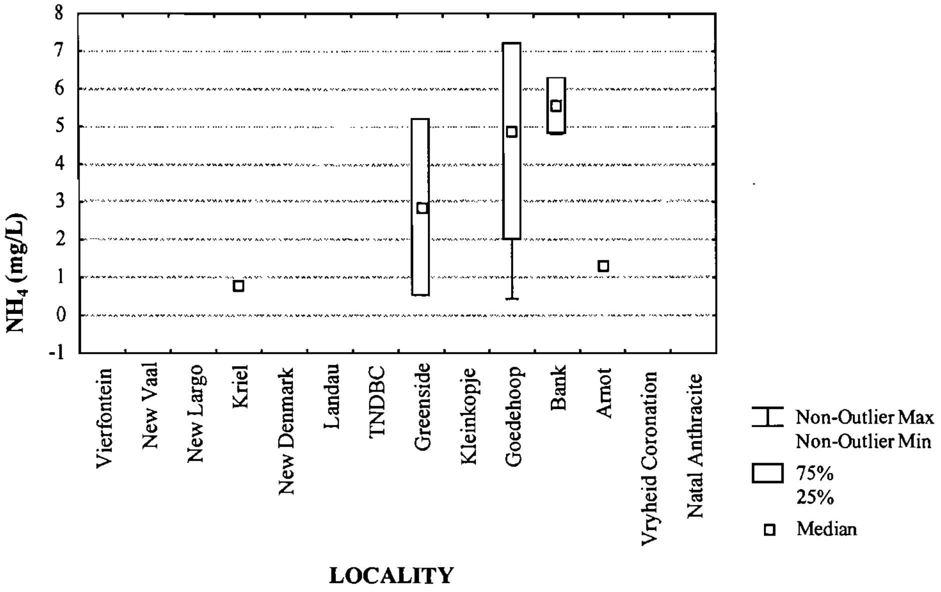

Figure 3.5: Ammonium concentration of water samples from Highveld collieries (n=12).

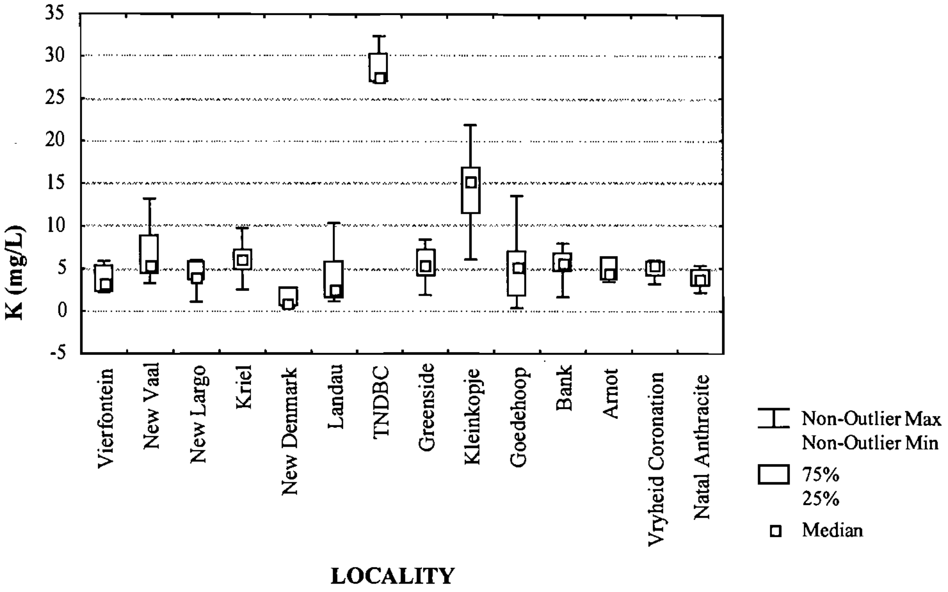

Figure 3.6: Potassium concentration of water samples from Highveld collieries (n=167).

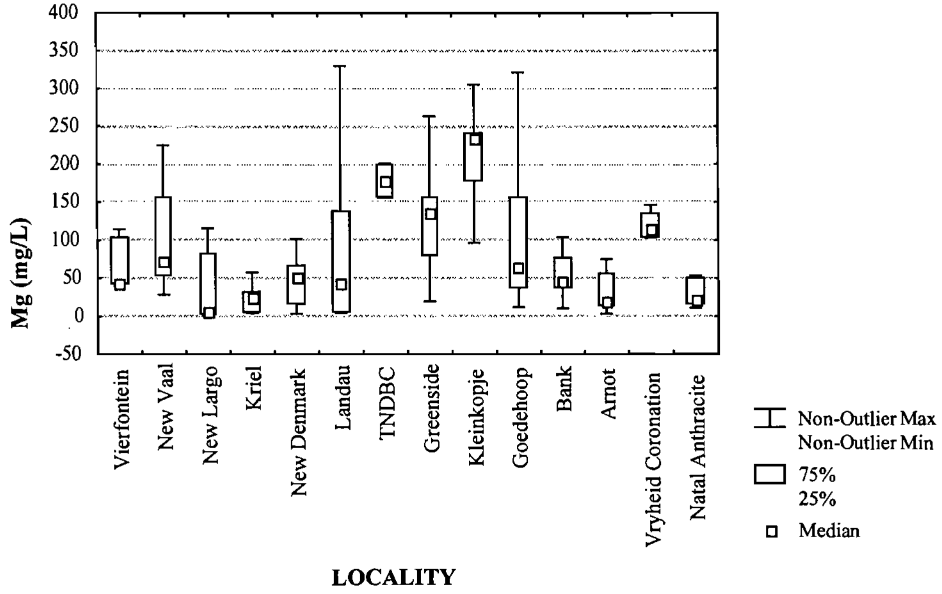

Figure 3.7: Magnesium concentration of water samples from Highveld collieries (n=167).

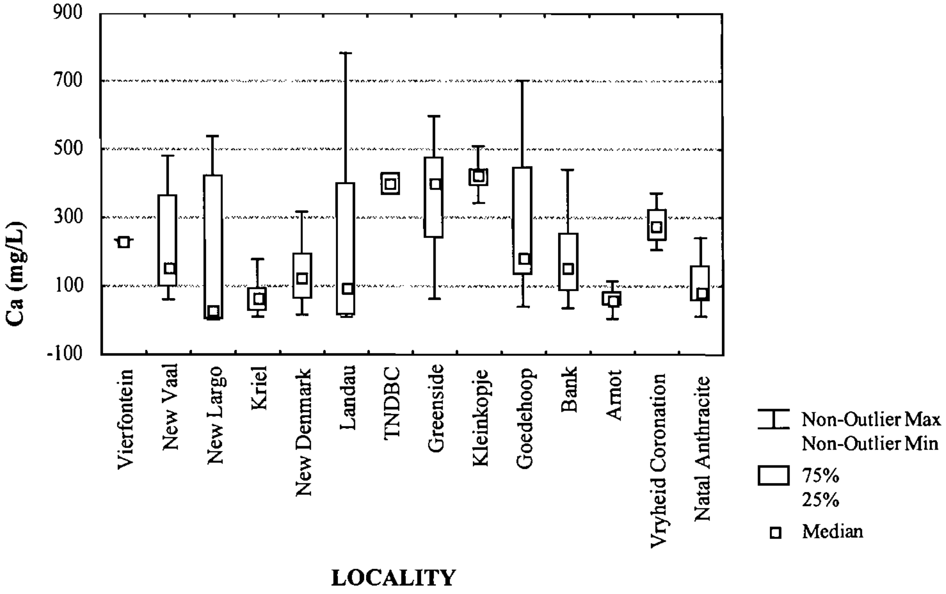

Figure 3.8: Calcium concentration of water samples from Highveld collieries (n=167).

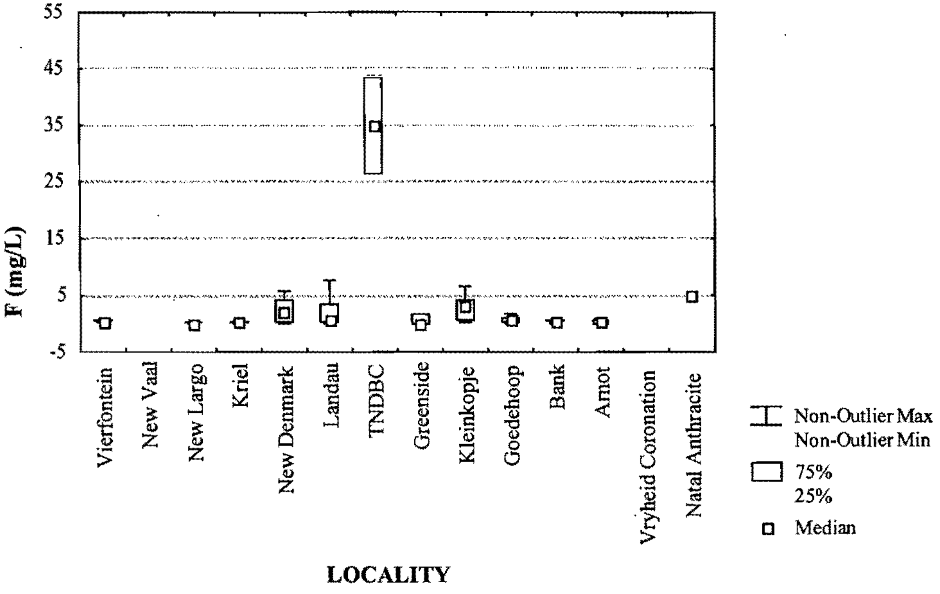

Figure 3.9a: *Fluoride concentration of water samples from Highveld collieries (n=101).*

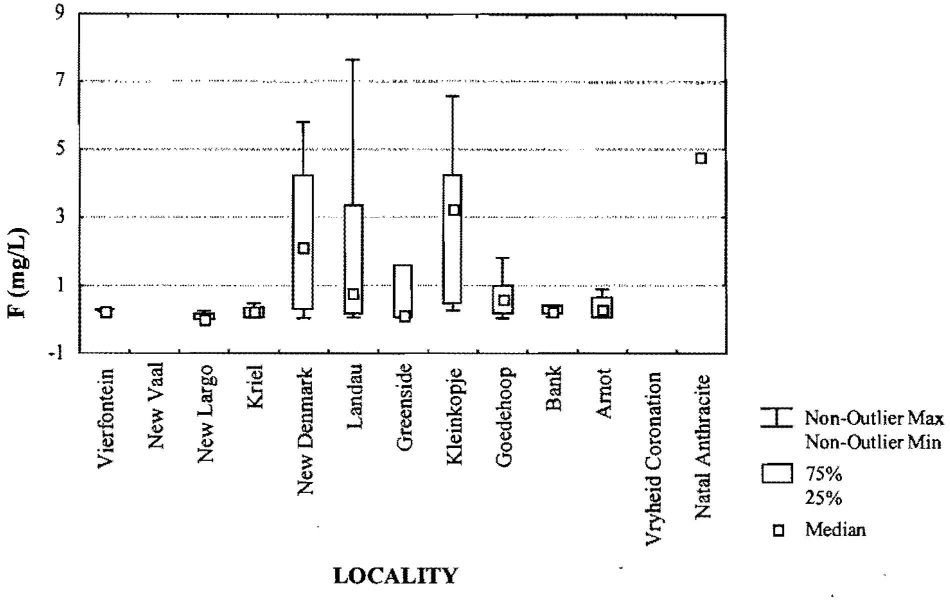

Figure 3.9b: *Fluoride concentration of water samples from Highveld collieries, excluding TNDBC.*

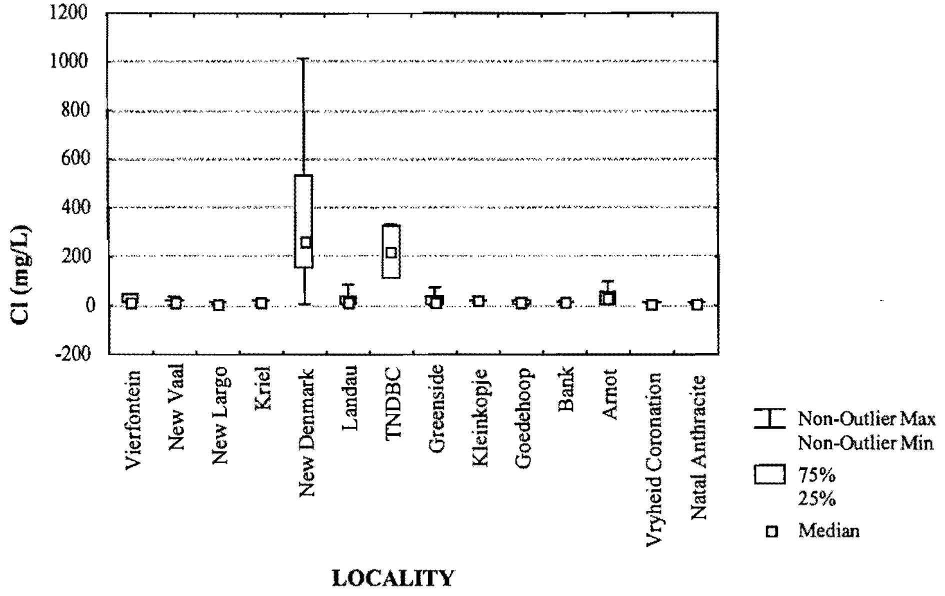

Figure 3.10a: *Chloride concentration of water samples from Highveld collieries (n=167).*

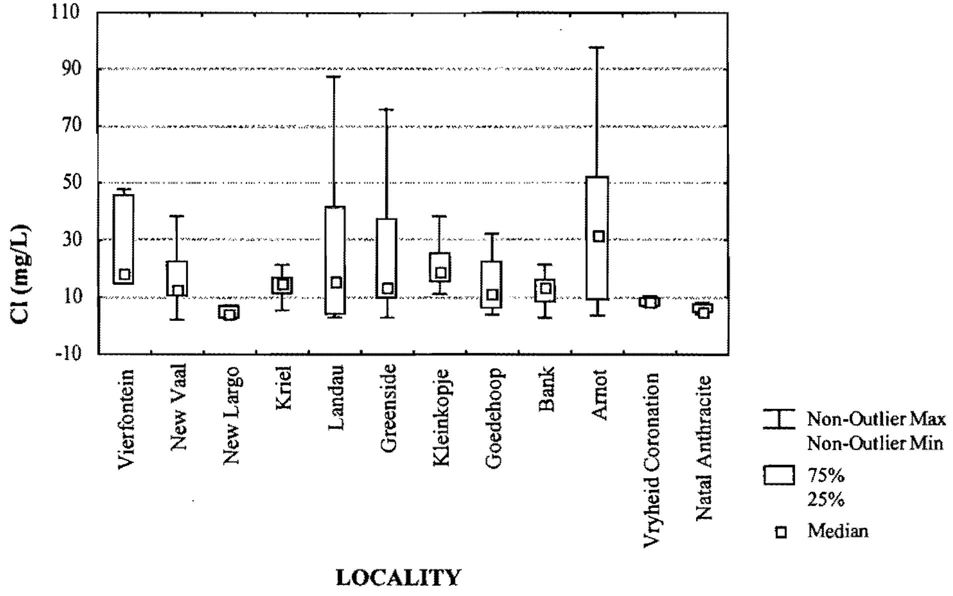

Figure 3.10b: *Chloride concentration of water samples from Highveld collieries, excluding New Denmark and TNDBC.*

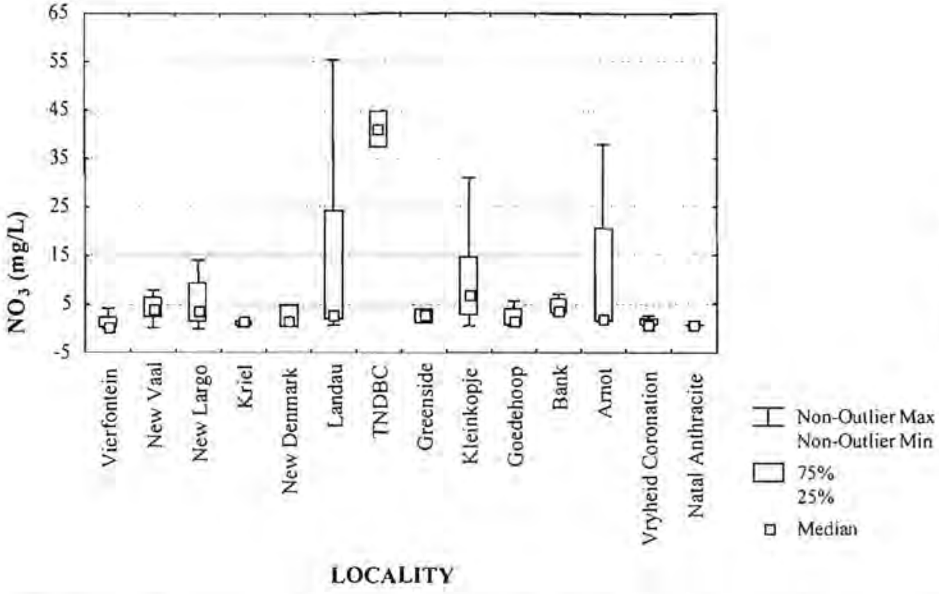

Figure 3.11a: *Nitrate concentration of water samples from Highveld collieries (n=105).*

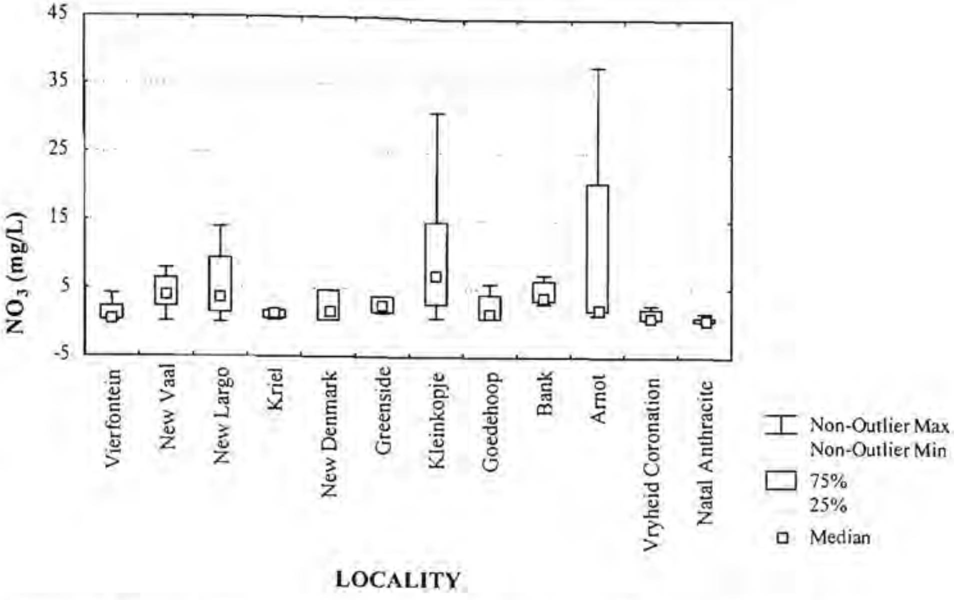

Figure 3.11b: *Nitrate concentration of water samples from Highveld collieries, excluding Landau and TNDBC.*

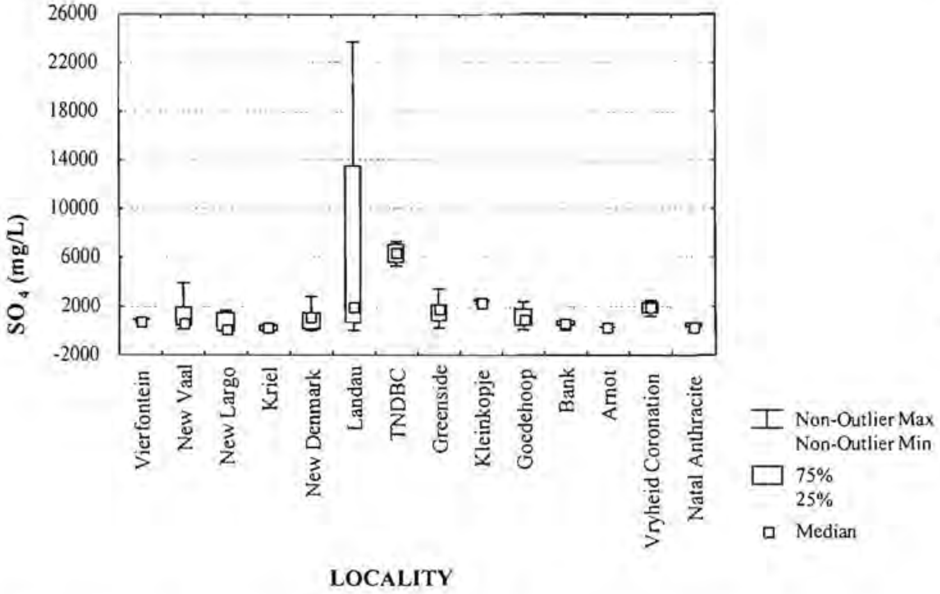

Figure 3.12a: *Sulphate concentration of water samples from Highveld collieries (n=167).*

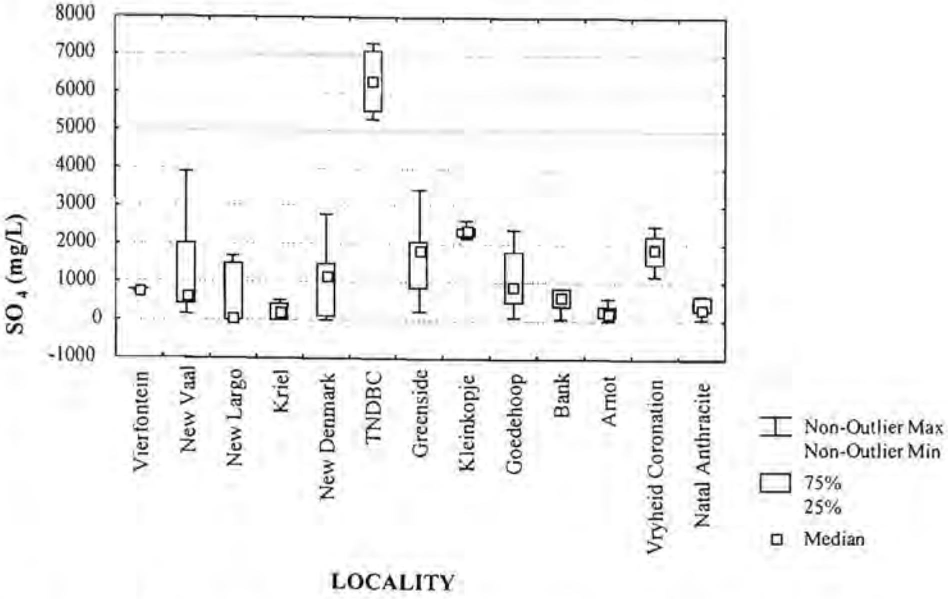

Figure 3.12b: *Sulphate concentration of water samples from Highveld collieries, excluding Landau.*

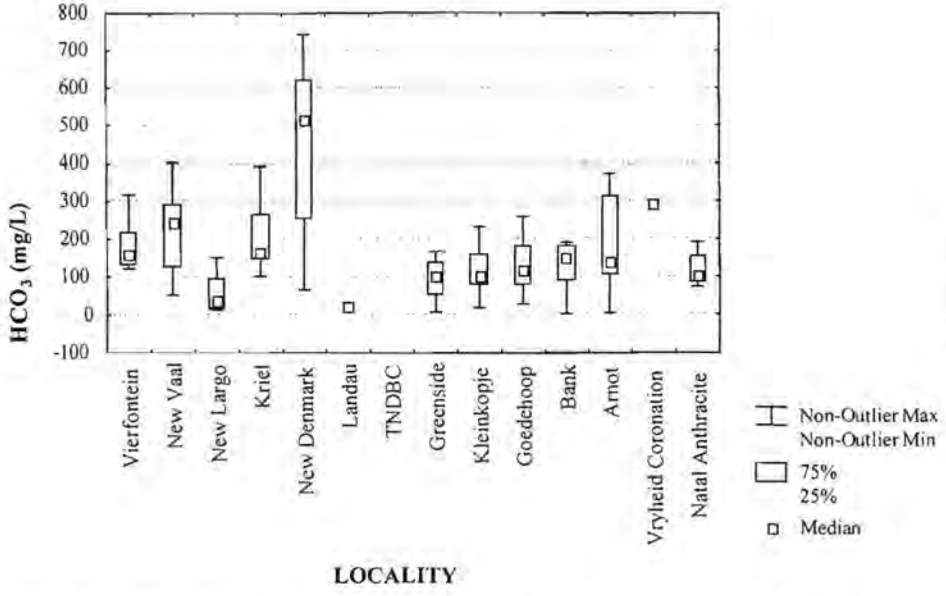

Figure 3.13a: Bicarbonate concentration of water samples from Highveld collieries (n=129).

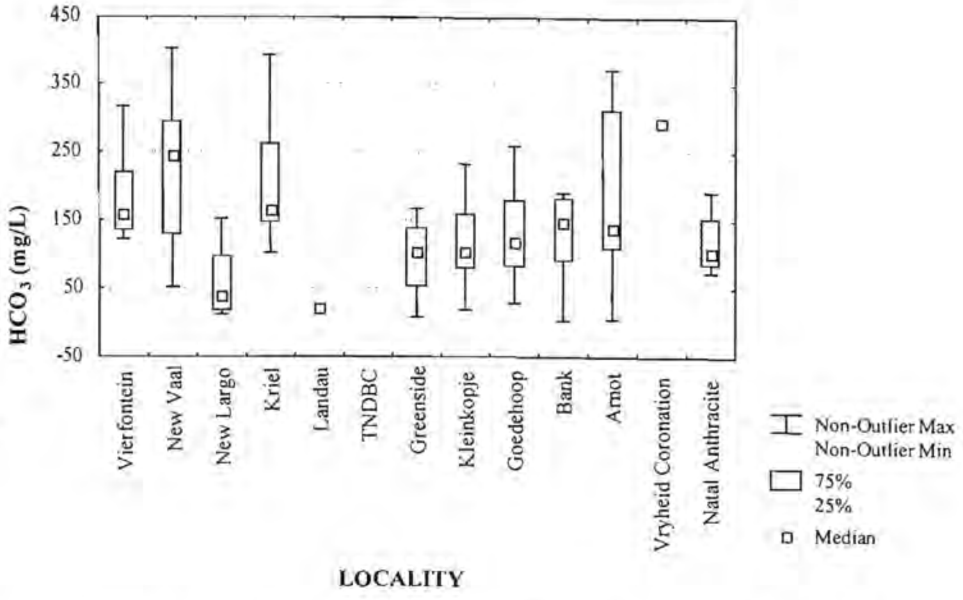

Figure 3.13b: Bicarbonate concentration of water samples from Highveld collieries, excluding New Denmark.

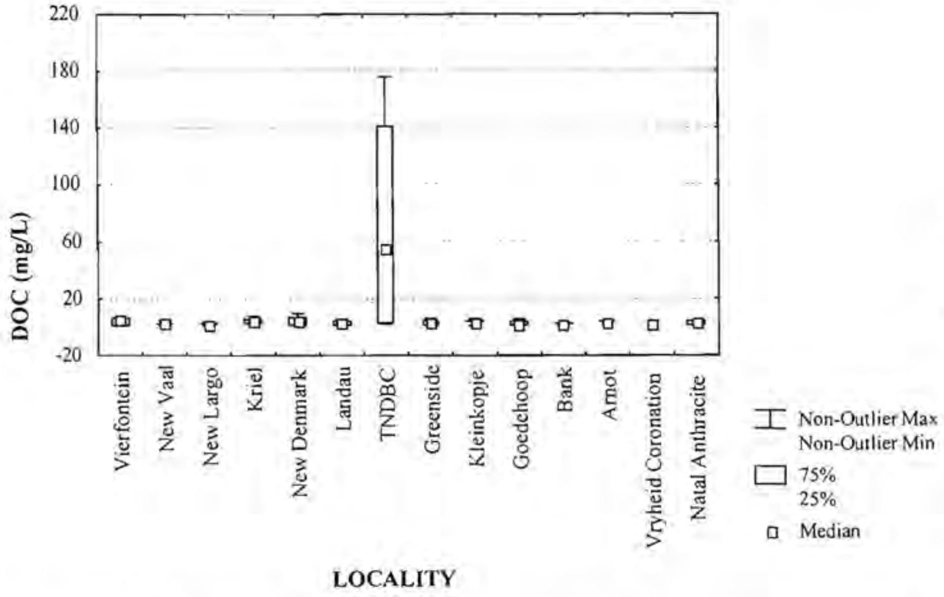

Figure 3.14a: Dissolved organic carbon concentration of water samples from Highveld collieries (n=131).

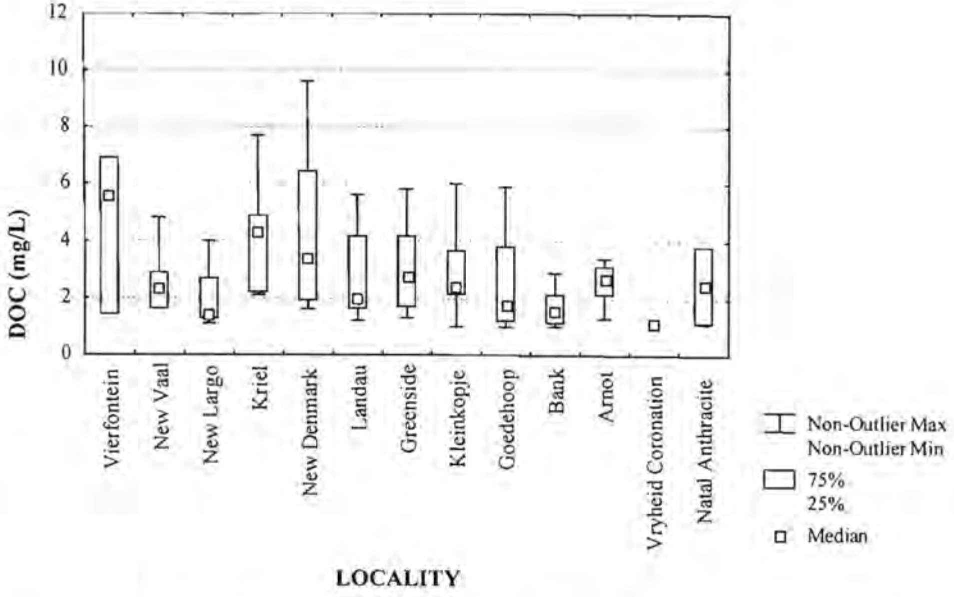

Figure 3.14b: Dissolved organic carbon concentration of water samples from Highveld collieries, excluding TNDBC.

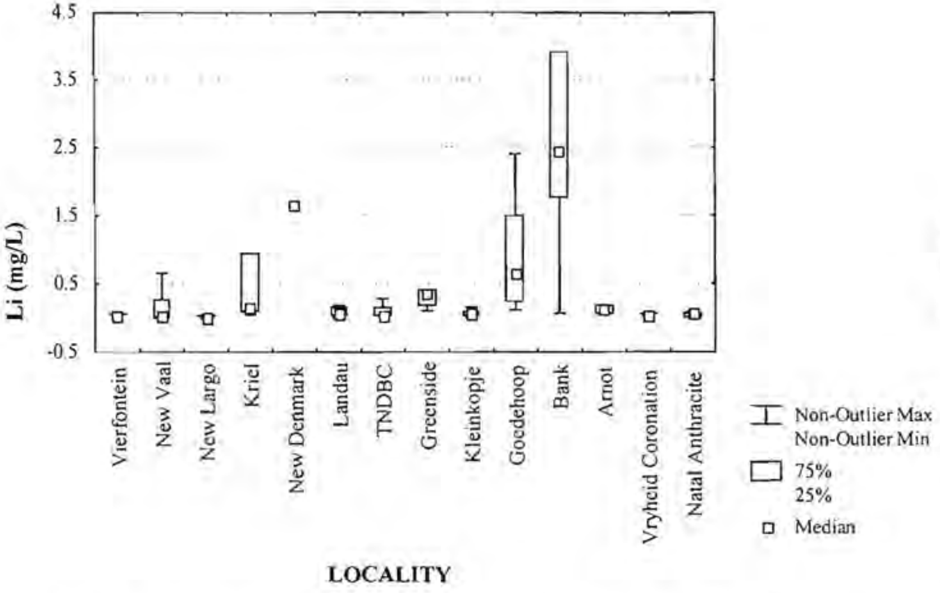

Figure 3.15a: Lithium concentration of water samples from Highveld collieries (n=121).

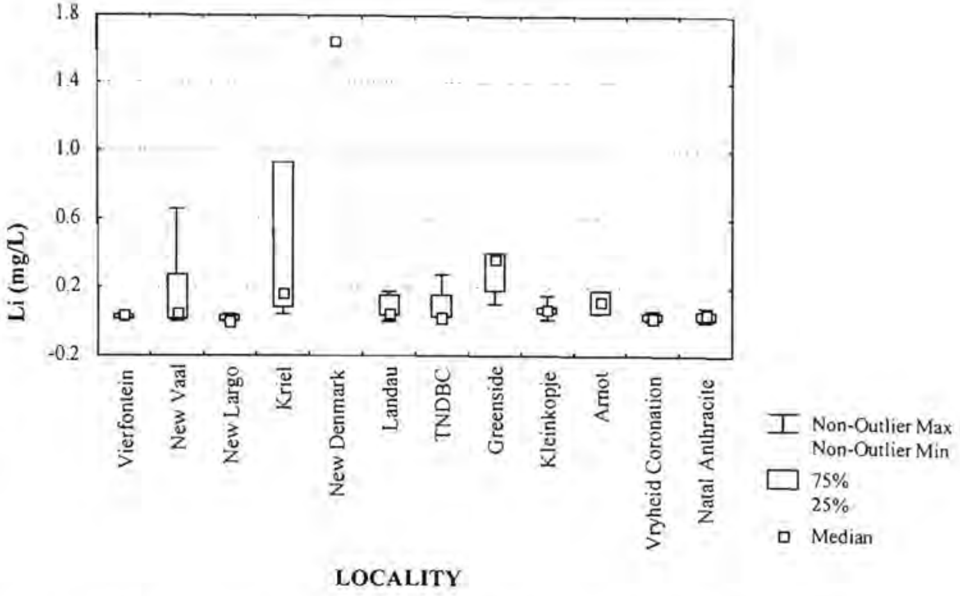

Figure 3.15b: Lithium concentration of water samples from Highveld collieries, excluding Goedehoop and Bank.

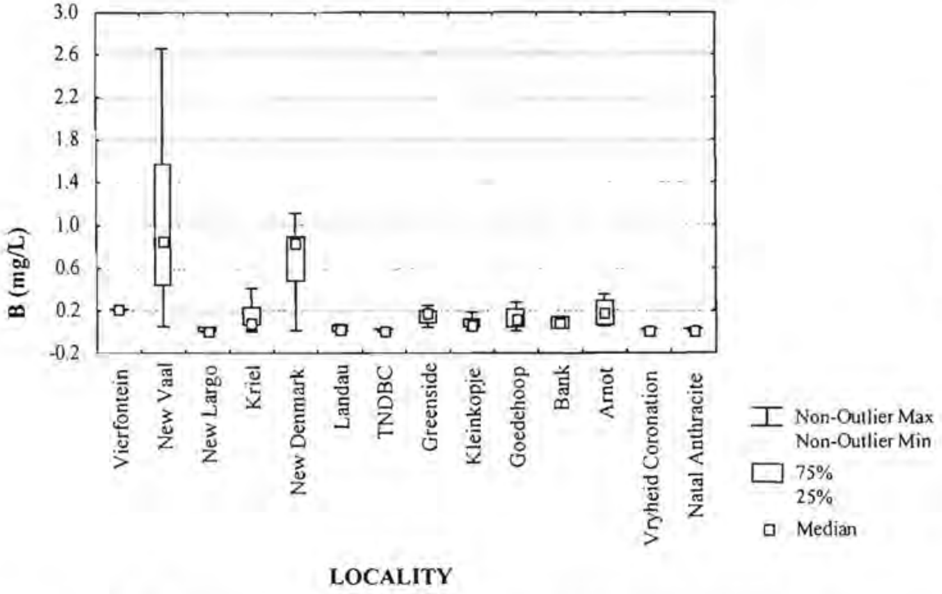

Figure 3.16a: Boron concentration of water samples from Highveld collieries (n=115).

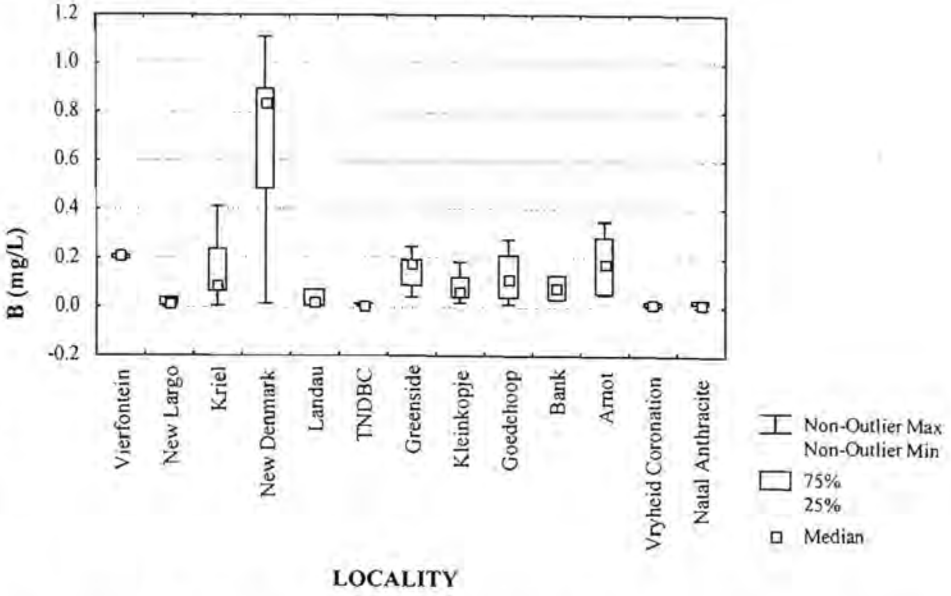

Figure 3.16b: Boron concentration of water samples from Highveld collieries, excluding New Vaal.

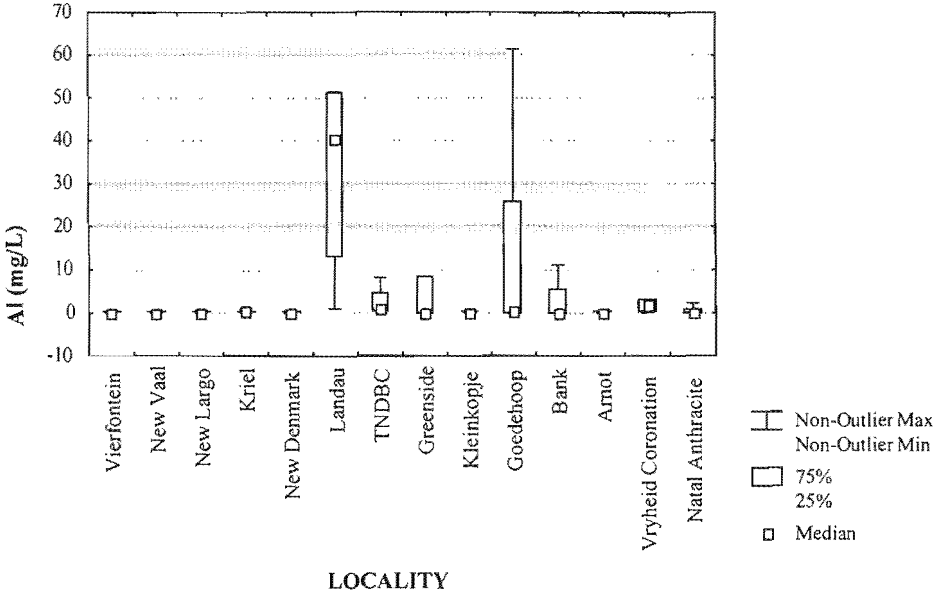

Figure 3.17a: Aluminium concentration of water samples from Highveld collieries (n=145).

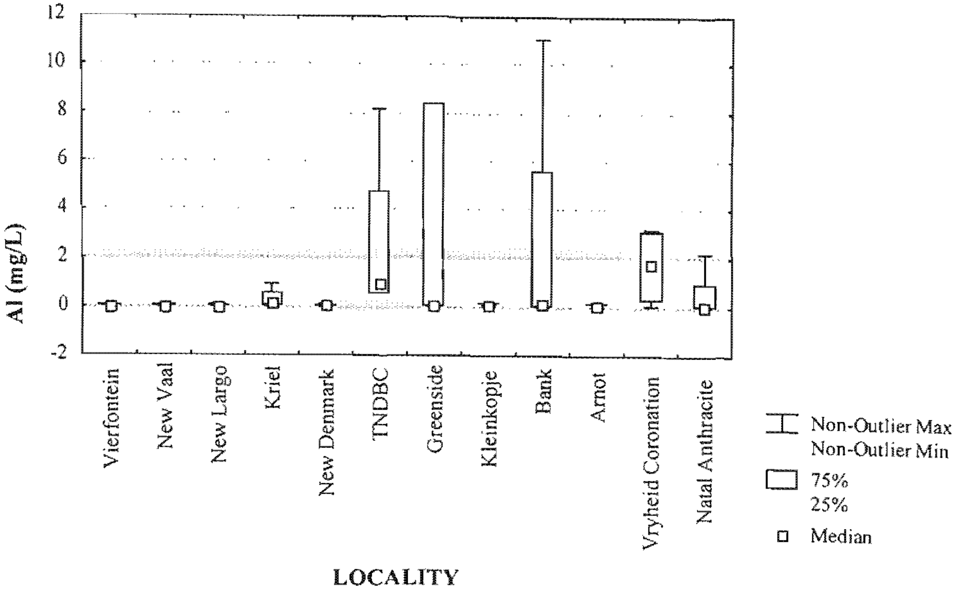

Figure 3.17b: Aluminium concentration of water samples from Highveld collieries, excluding Landau and Goedehoop.

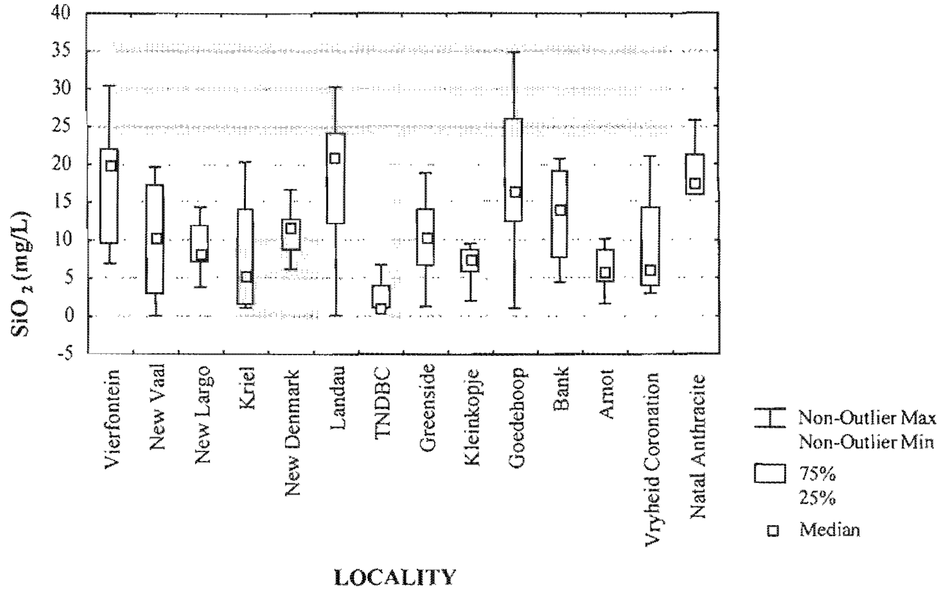

Figure 3.18: Silica concentration of water samples from Highveld collieries (n=164).

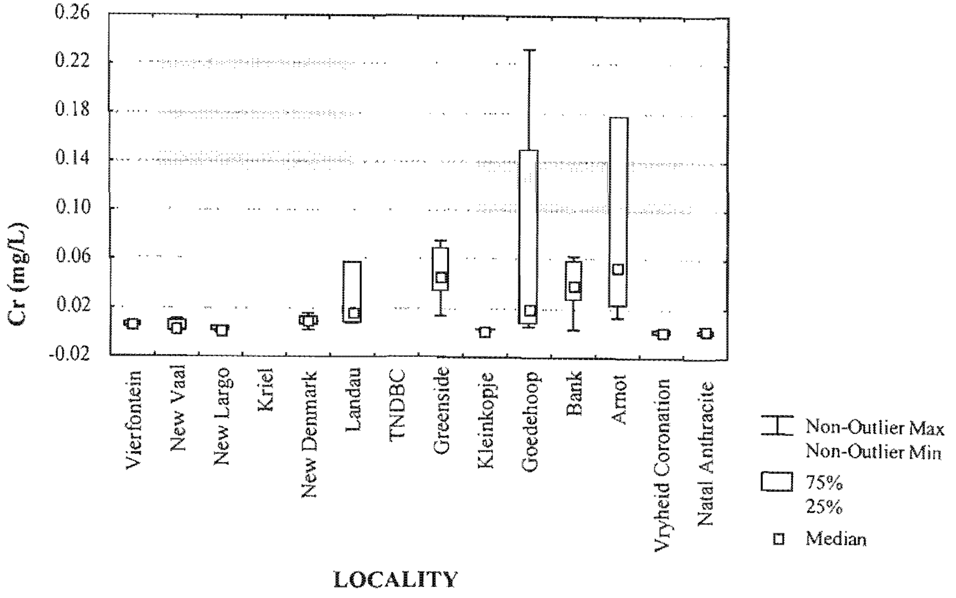

Figure 3.19: Chromium concentration of water samples from Highveld collieries (n=117).

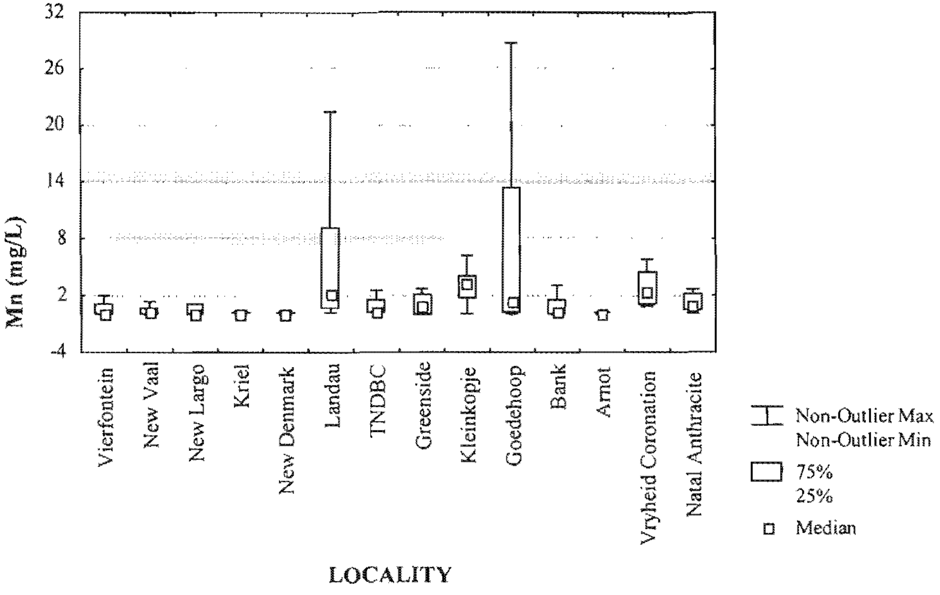

Figure 3.20a: *Manganese concentration of water samples from Highveld collieries (n=167).*

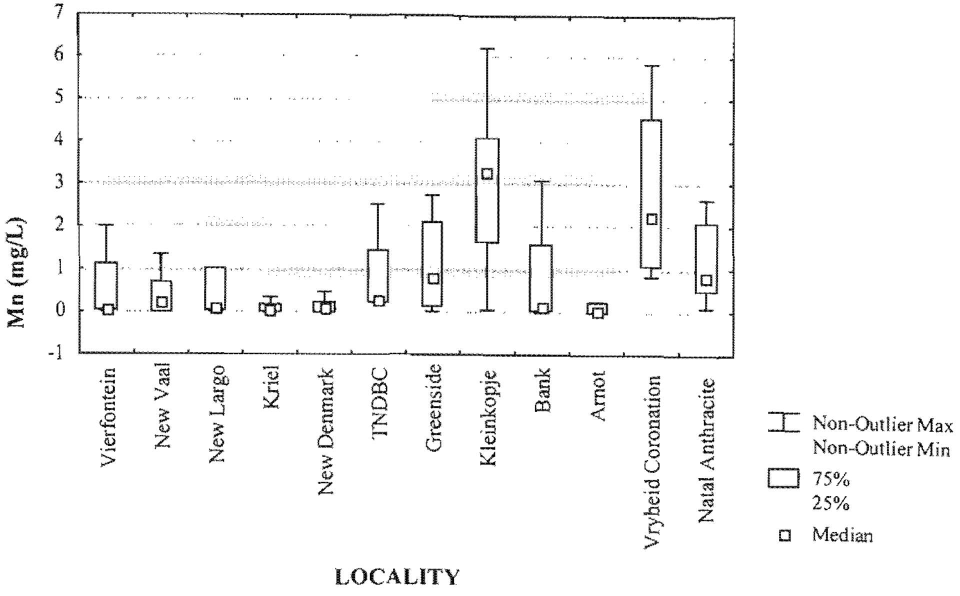

Figure 3.20b: *Manganese concentration of water samples from Highveld collieries, excluding Landau & Goedehoop.*

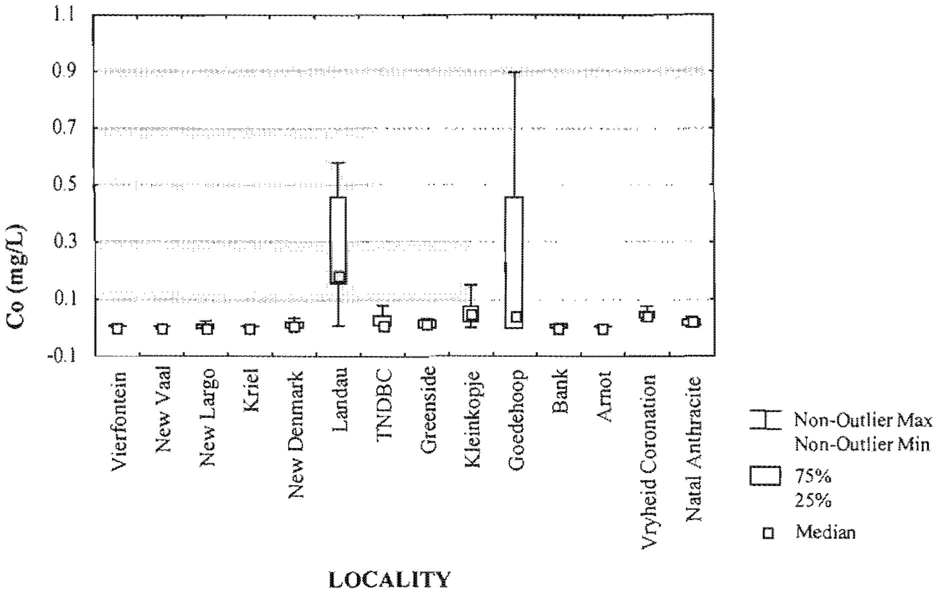

Figure 3.21a: *Cobalt concentration of water samples from Highveld collieries (n=166).*

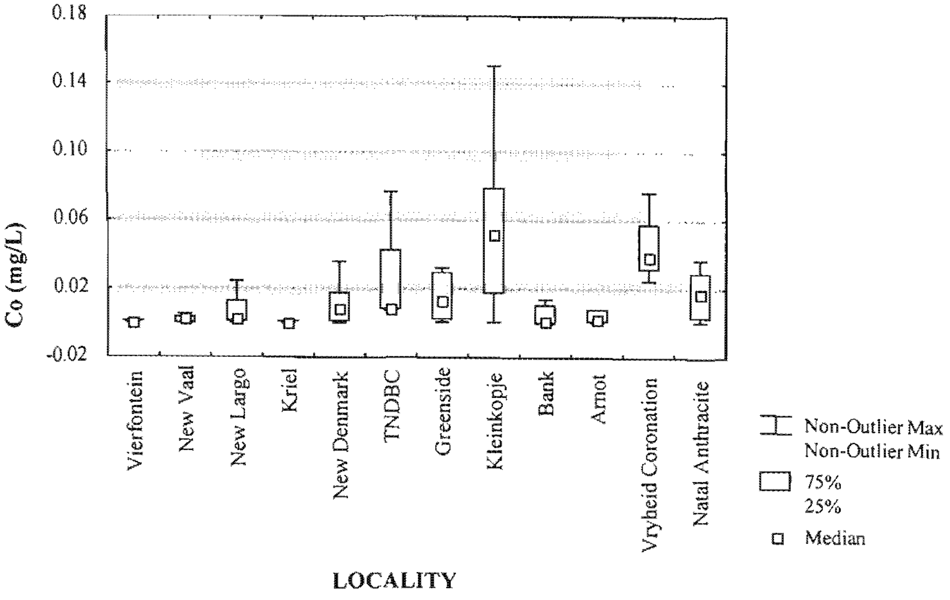

Figure 3.21b *Cobalt concentration of water samples from Highveld collieries, excluding Landau and Goedehoop.*

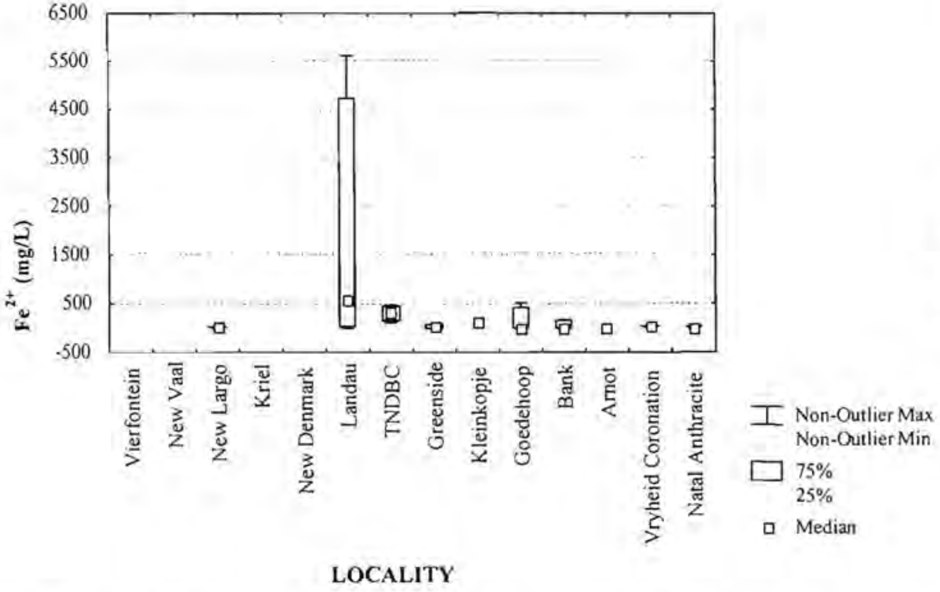

Figure 3.22a: *Iron (II) concentration of water samples from Highveld collieries (n=41).*

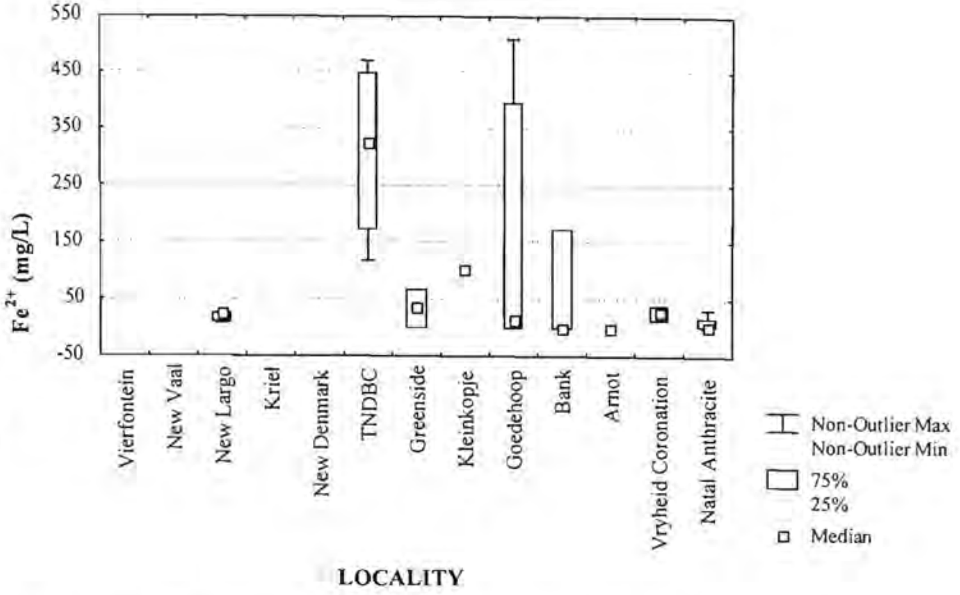

Figure 3.22b: *Iron (II) concentration of water samples from Highveld collieries, excluding Landau.*

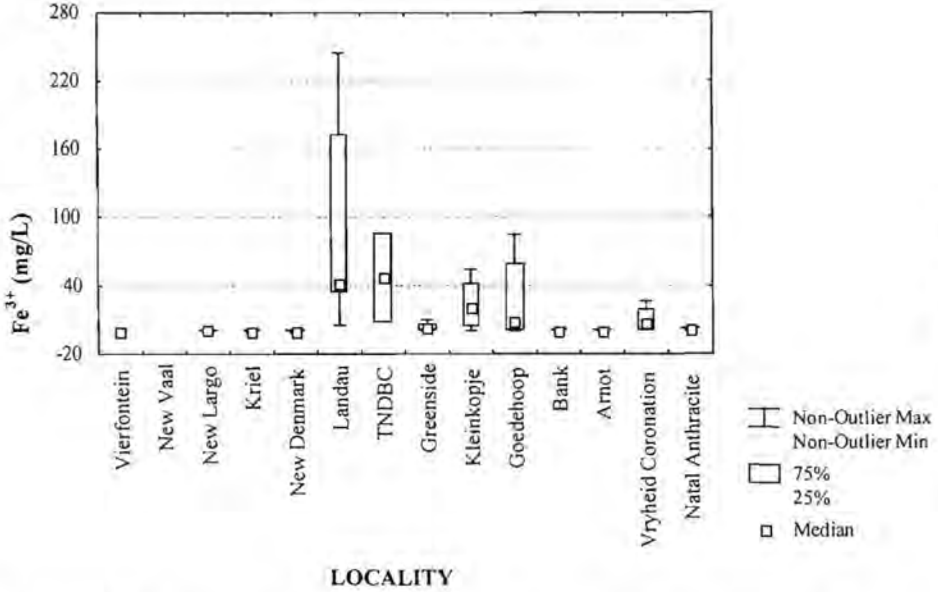

Figure 3.23a: *Iron (III) concentration of water samples from Highveld collieries (n=70).*

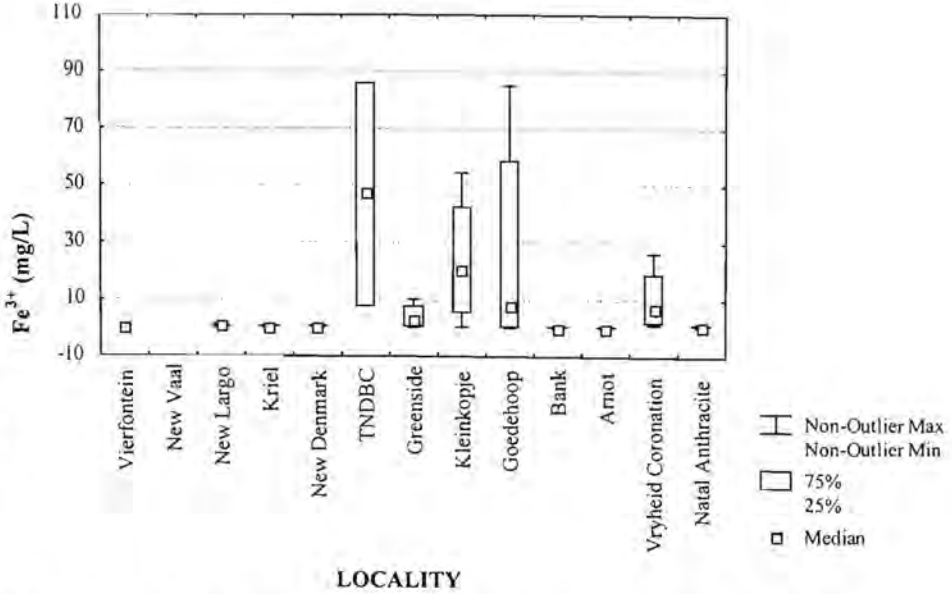

Figure 3.23b: *Iron (III) concentration of water samples from Highveld collieries, excluding Landau.*

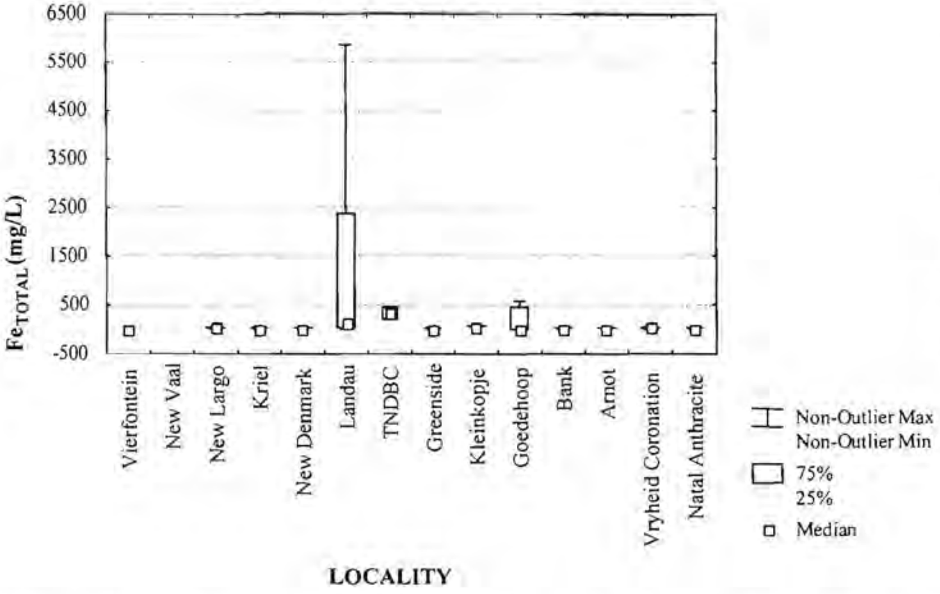

Figure 3.24a: *Total iron concentration of water samples from Highveld collieries (n=75).*

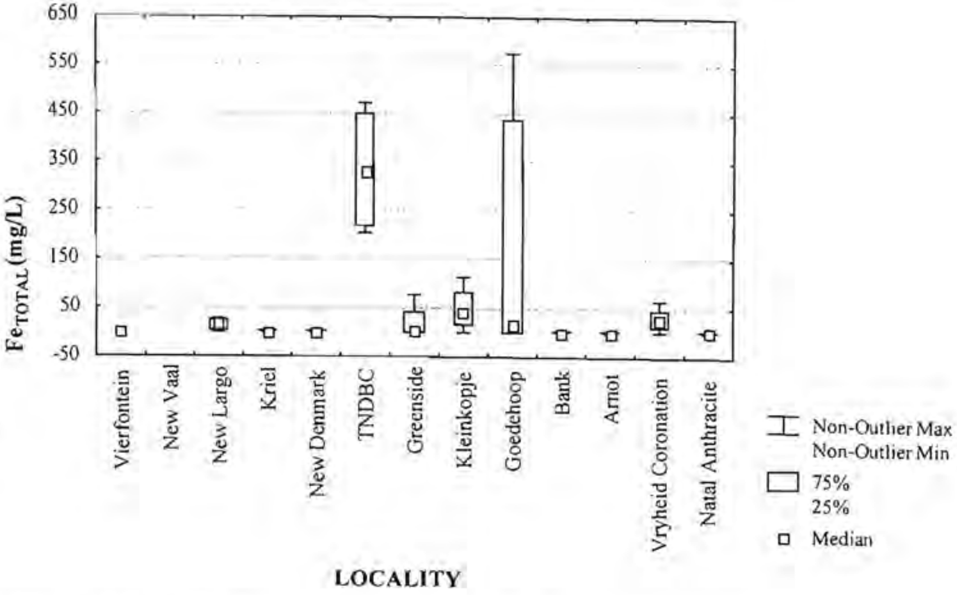

Figure 3.24b: *Total iron concentration of water samples from Highveld collieries, excluding Landau.*

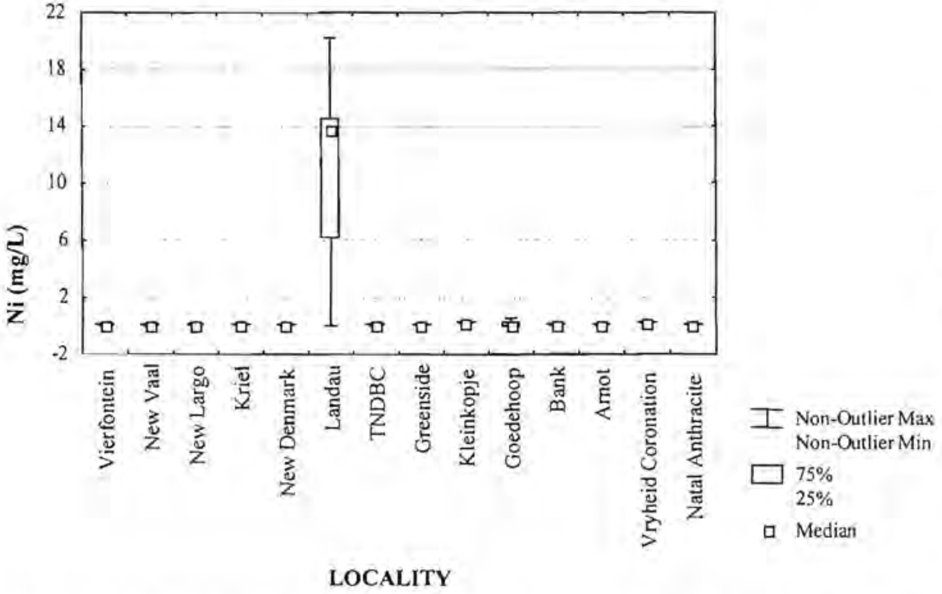

Figure 3.25a: *Nickel concentration of water samples from Highveld collieries (n=155).*

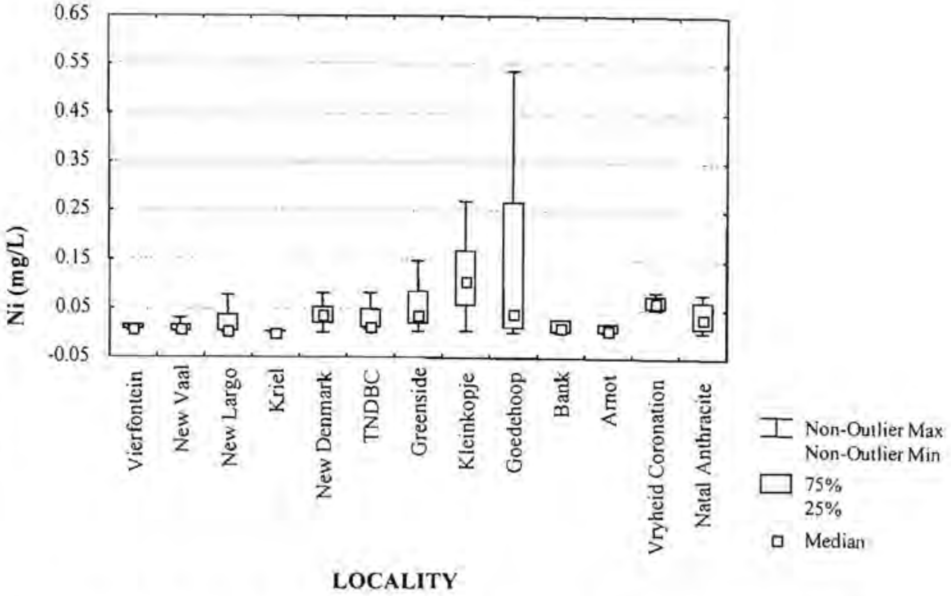

Figure 3.25b: *Nickel concentration of water samples from Highveld collieries, excluding Landau.*

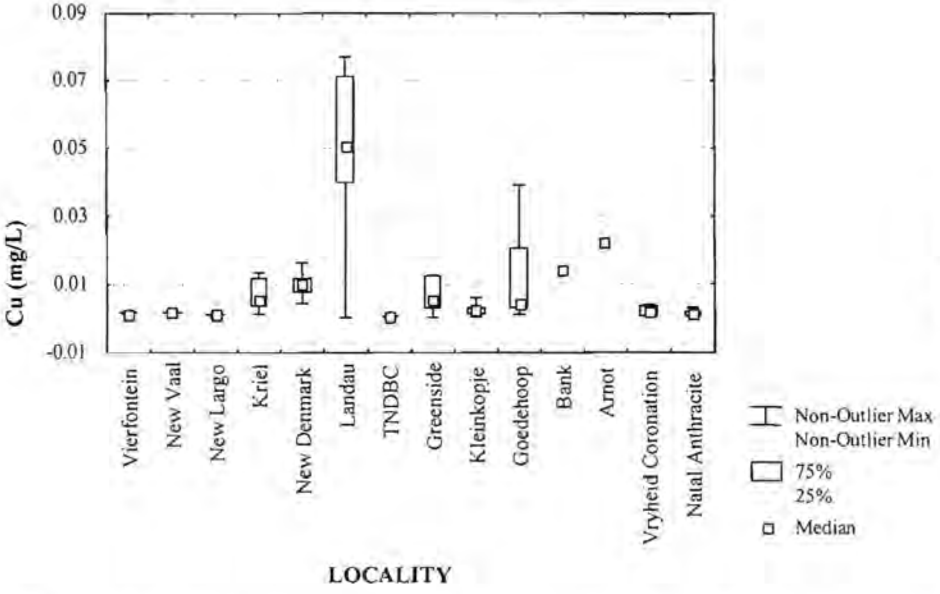

Figure 3.26a: *Copper concentration of water samples from Highveld collieries (n=131).*

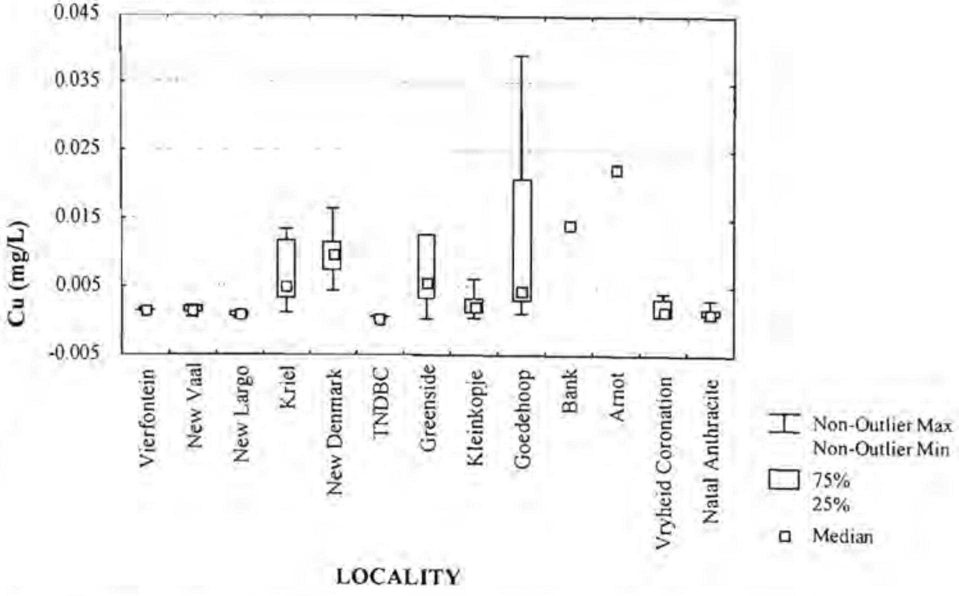

Figure 3.26b: *Copper concentration of water samples from Highveld collieries, excluding Landau.*

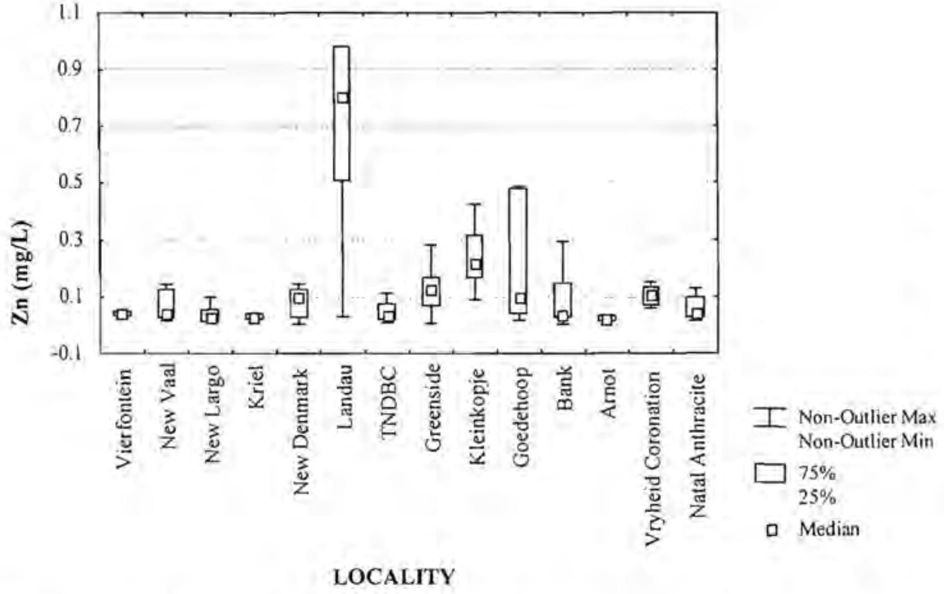

Figure 3.27a: *Zinc concentration of water samples from Highveld collieries (n=159).*

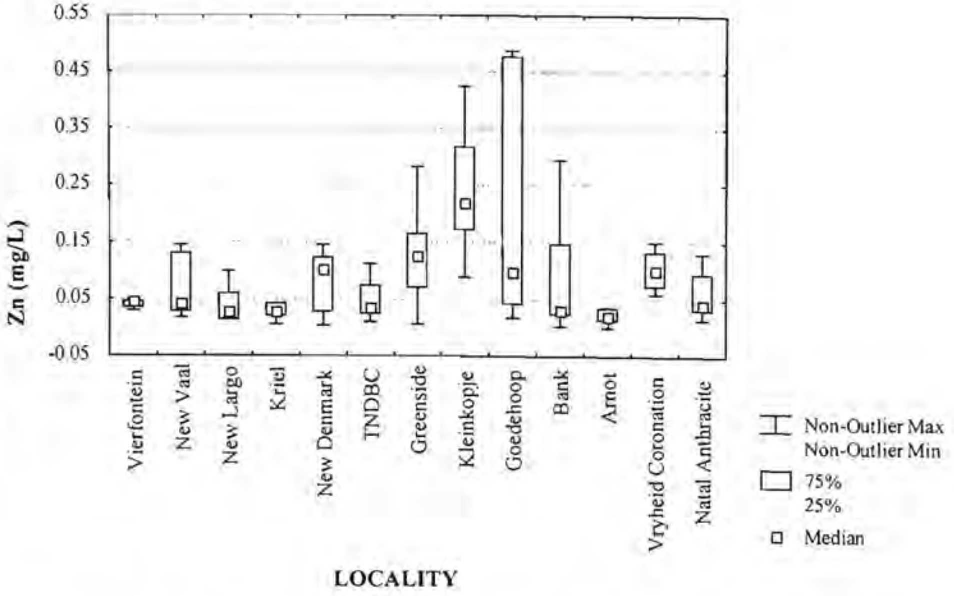

Figure 3.27b: *Zinc concentration of water samples from Highveld collieries, excluding Landau.*

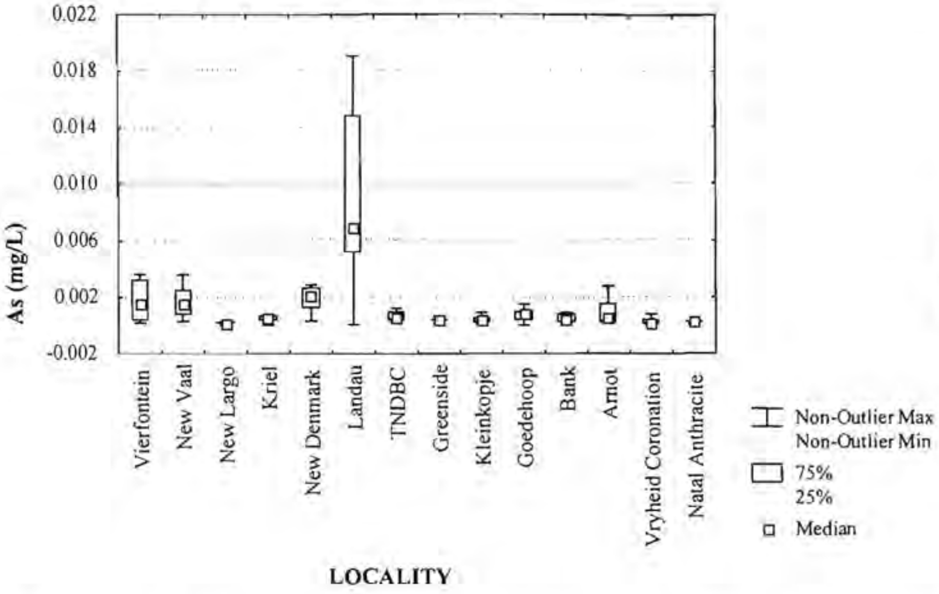

***Figure 3.28a:** Arsenic concentration of water samples from Highveld collieries (n=152).*

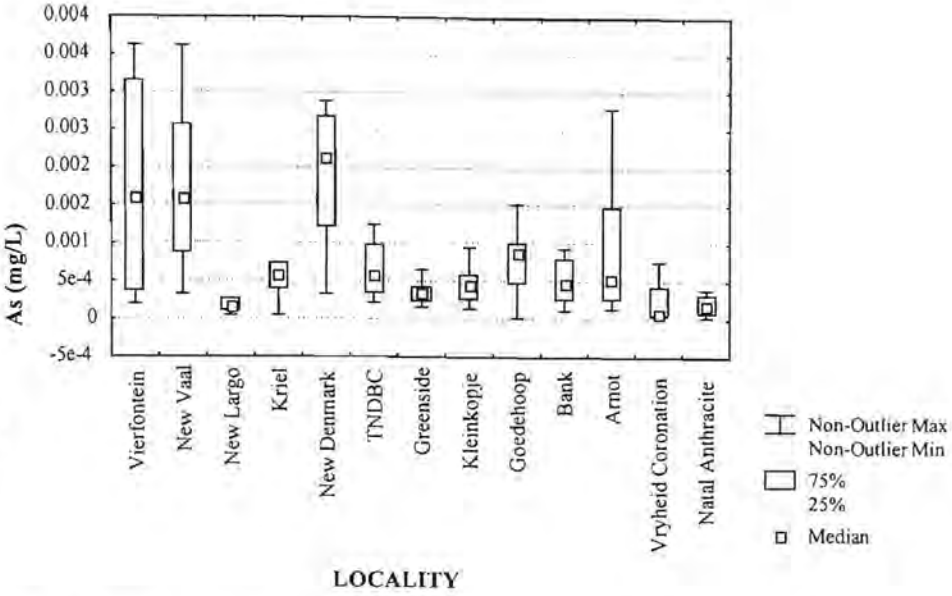

***Figure 3.28b:** Arsenic concentration of water samples from Highveld collieries, excluding Landau.*

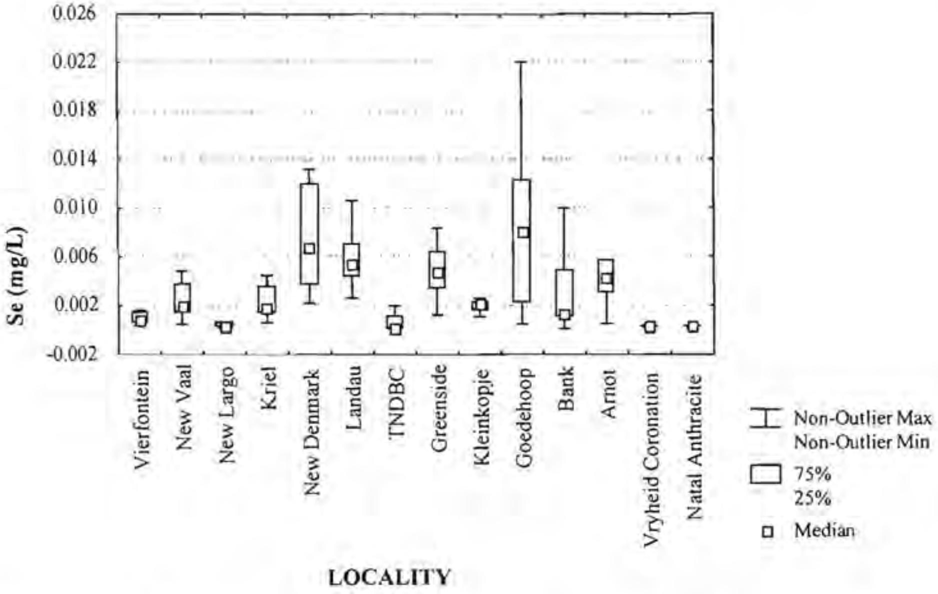

***Figure 3.29:** Selenium concentration of water samples from Highveld collieries (n=140).*

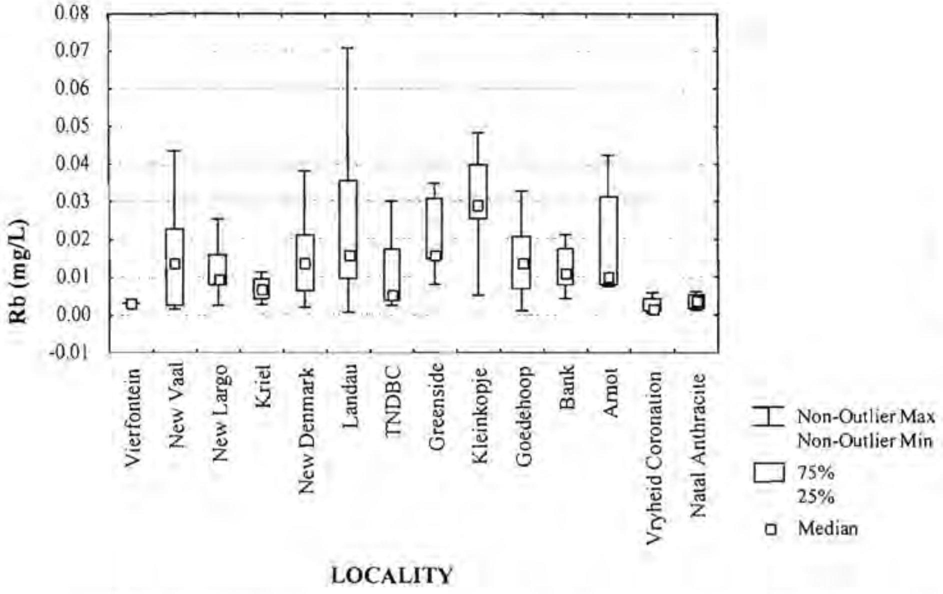

Figure 3.30: *Rubidium concentration of water samples from Highveld collieries (n=166).*

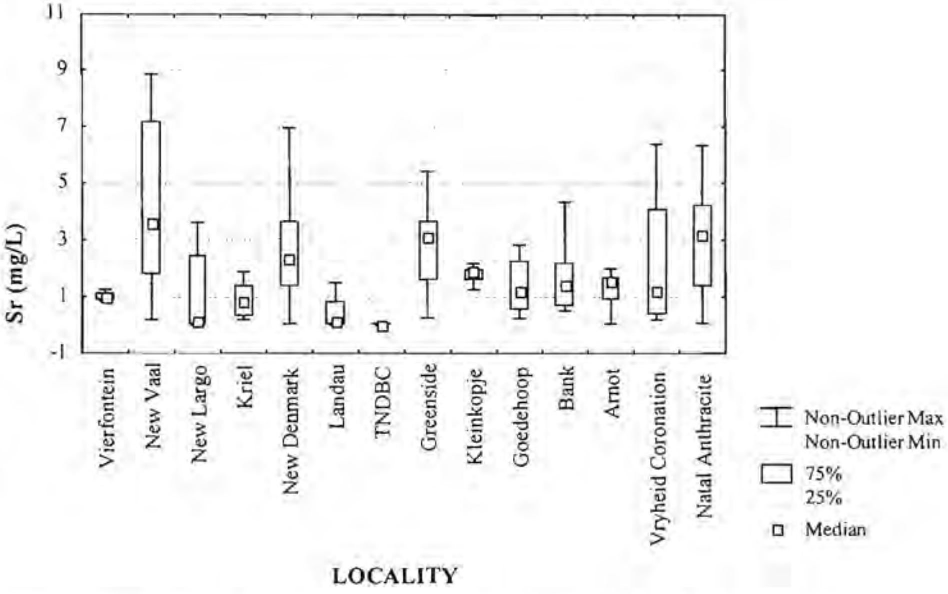

Figure 3.31: *Strontium concentration of water samples from Highveld collieries (n=166).*

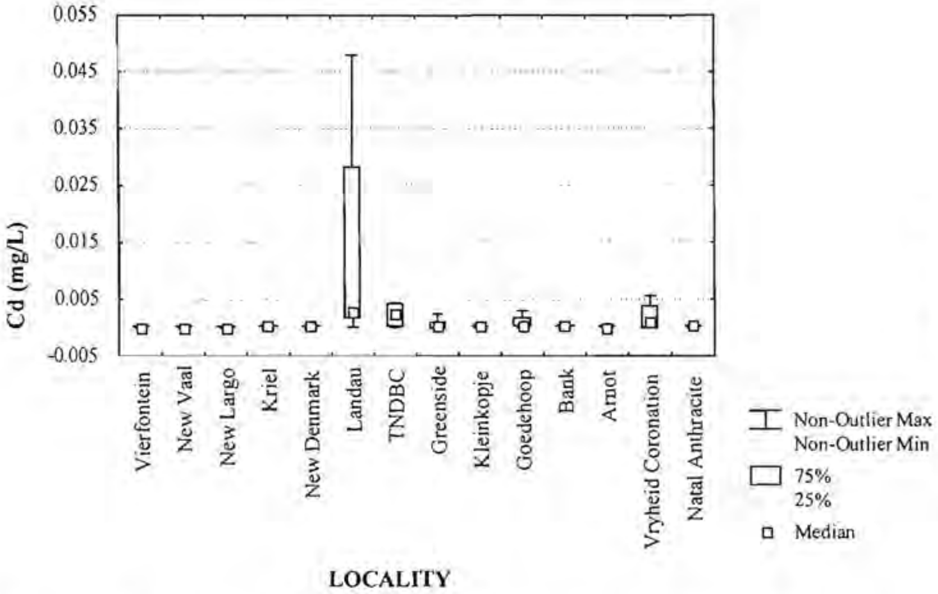

Figure 3.32a: *Cadmium concentration of water samples from Highveld collieries (n=144).*

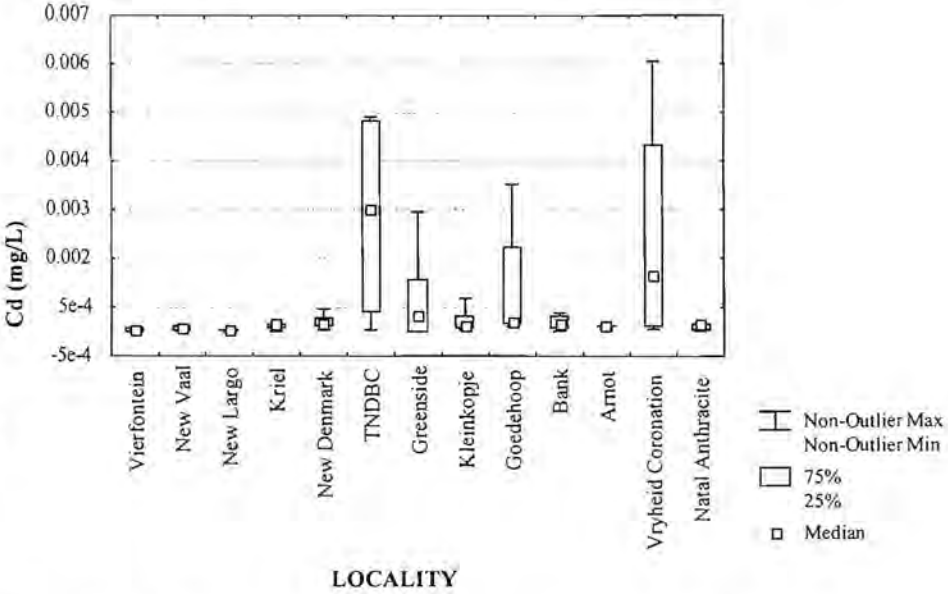

Figure 3.32b: *Cadmium concentration of water samples from Highveld collieries, excluding Landau.*

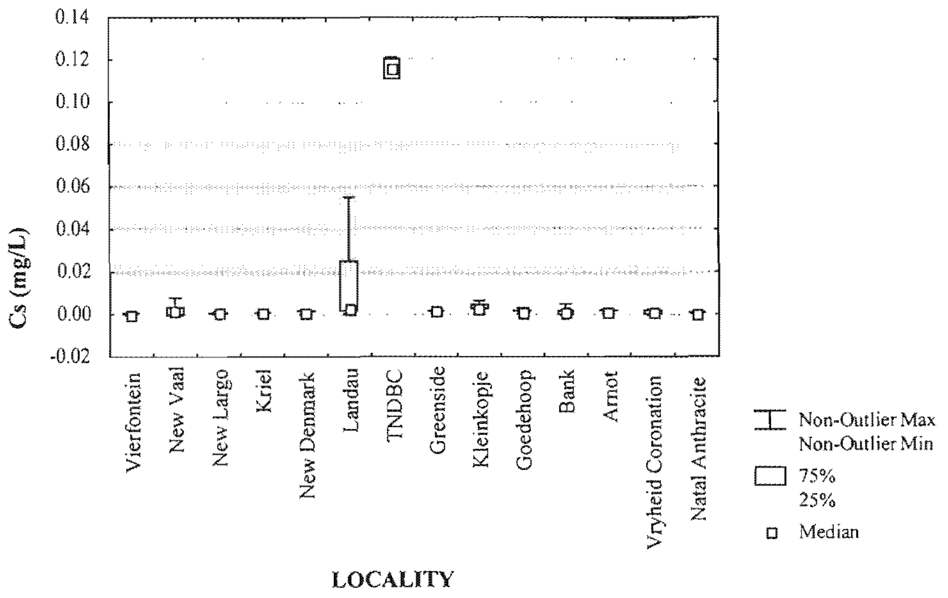

Figure 3.33a: *Cesium concentration of water samples from Highveld collieries (n=162).*

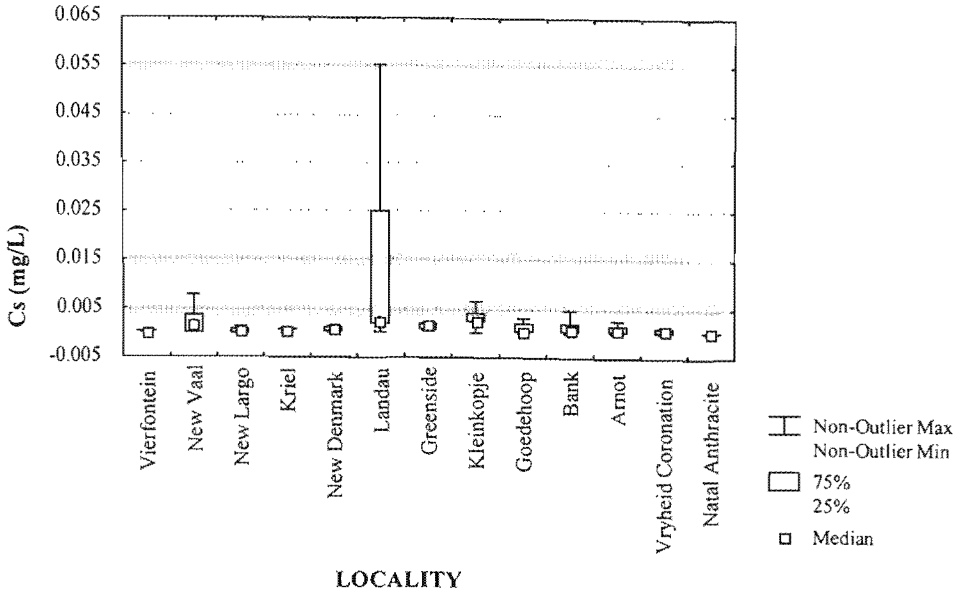

Figure 3.33b: *Cesium concentration of water samples from Highveld collieries, excluding TNDBC.*

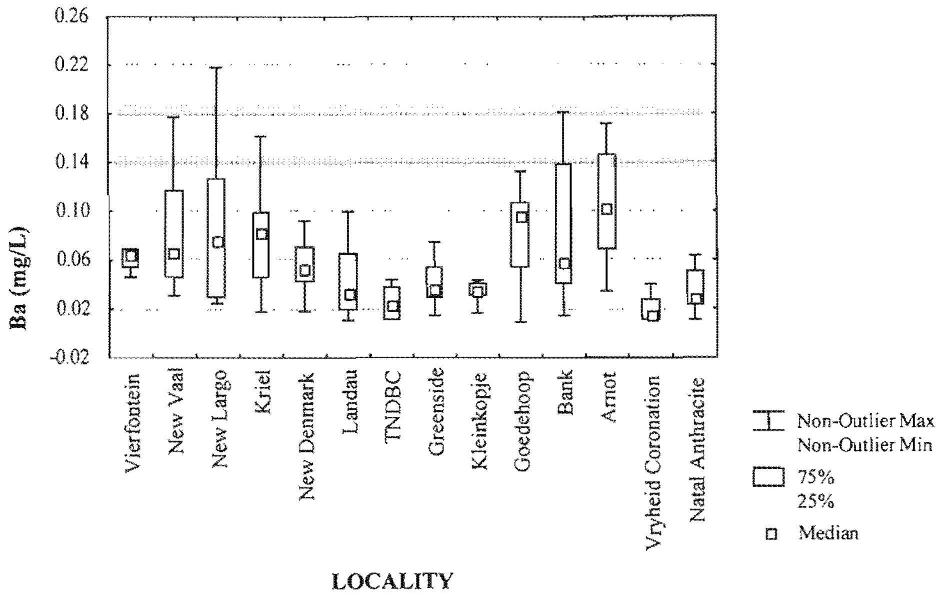

Figure 3.34: *Barium concentration of water samples from Highveld collieries (n=166).*

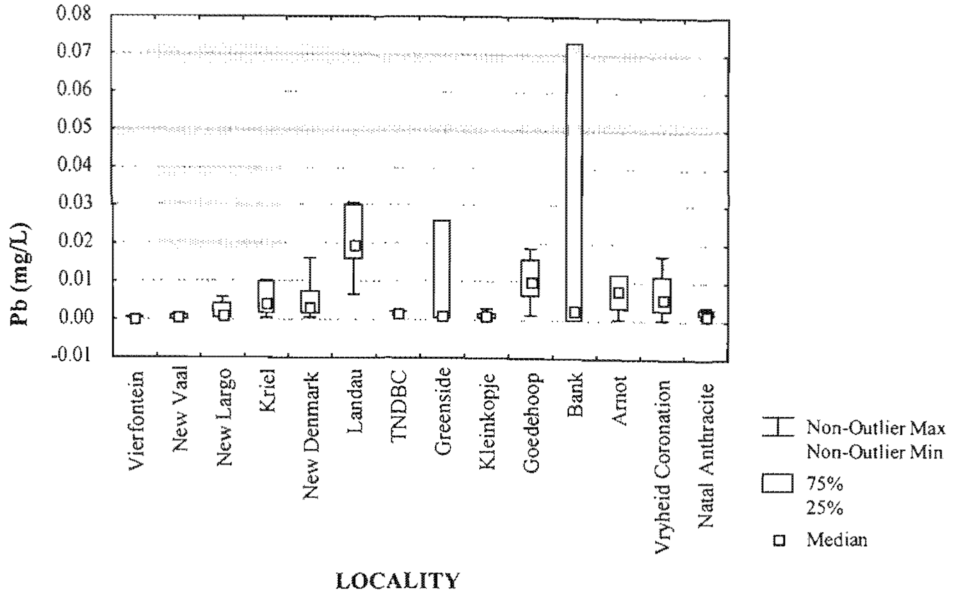

Figure 3.35: *Lead concentration of water samples from Highveld collieries (n=134).*

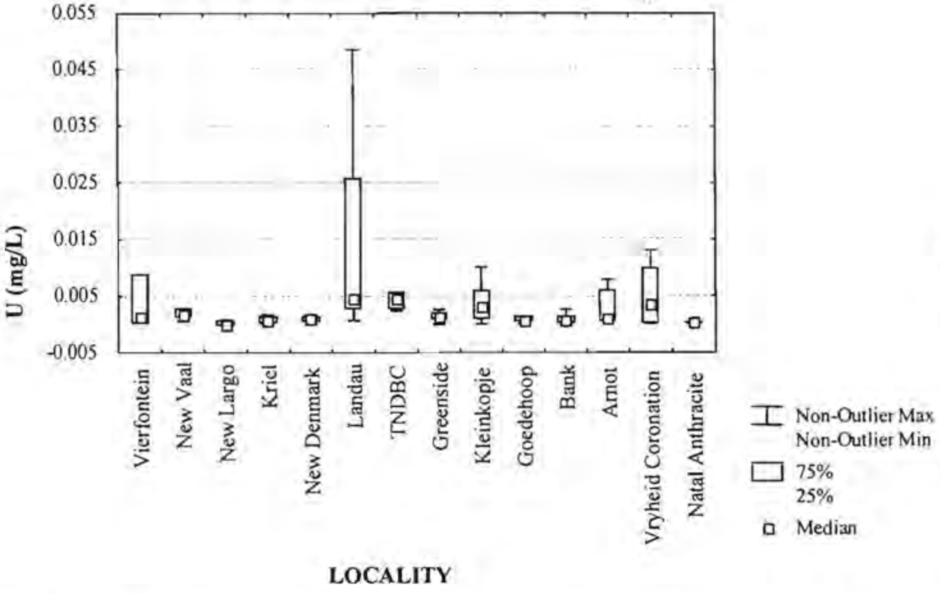

Figure 3.36a: *Uranium concentration of water samples from Highveld collieries (n=161).*

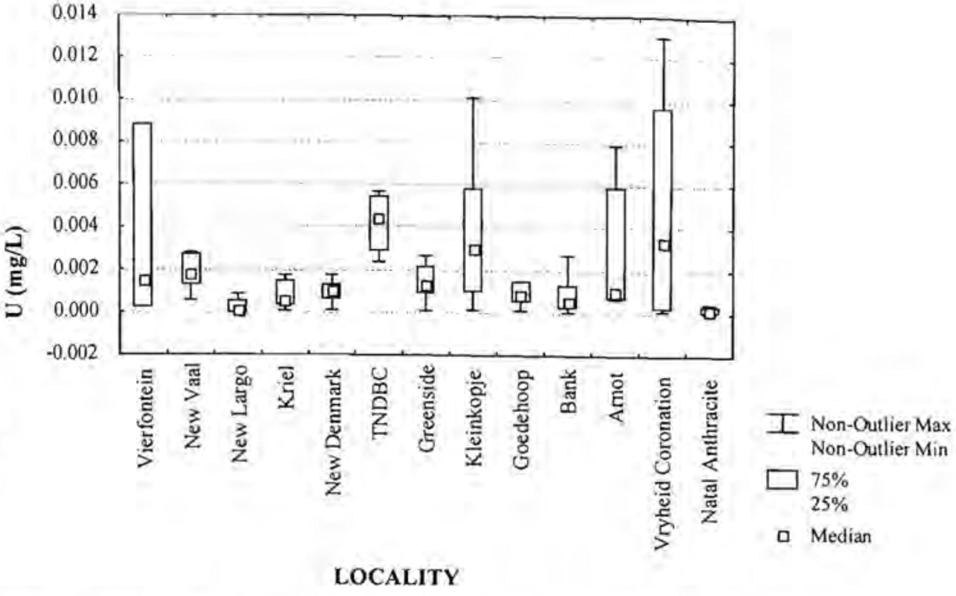

Figure 3.36b: *Uranium concentration of water samples from Highveld collieries, excluding Landau.*

The broadest range in pH is observed in the Goedehoop samples (2.8 to 7.8), though this may be because more samples were taken at Goedehoop than any of the other collieries studied. There appears to be a bimodal distribution in the pH with some collieries being acidic (average pH ~ 3.5) and the rest near-neutral (average pH ~ 7.5), with relatively few samples having pH values between 4 and 6 (Figure 3.37).

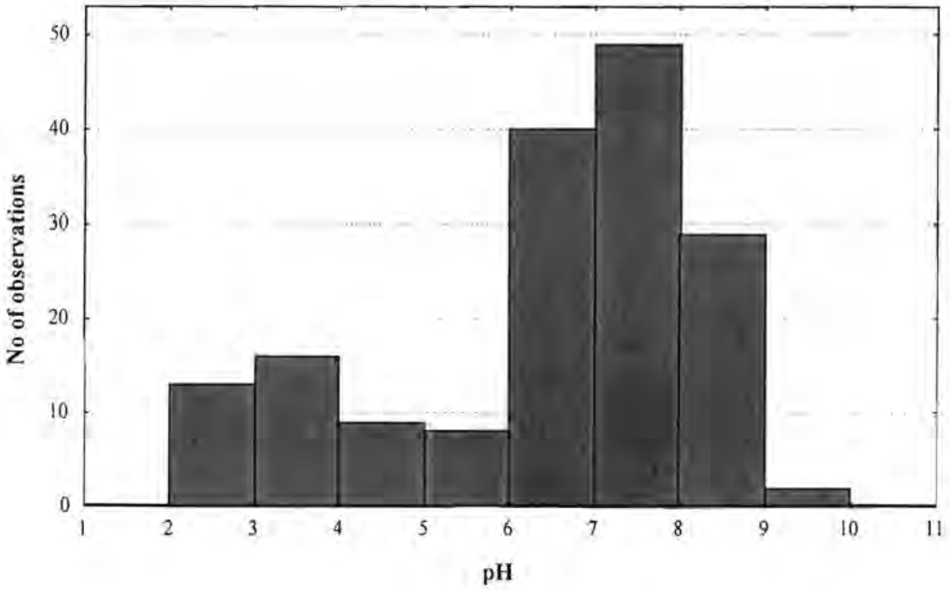

Figure 3.37: *Bimodal pH distribution of water samples from 167 sites on 14 Highveld collieries.*

A bimodal distribution in pH of coal mine water, with modes at pH 2.5 to 4 (acidic) and pH 6 to 7 (near neutral), has been observed in Pennsylvania by Cravotta *et al.* (1999) and by Rose and Cravotta (1998). Although pyrite and calcareous minerals are believed to comprise only a few percent, or less, of the coal-bearing rock, these minerals are highly reactive and are mainly responsible for the bimodal pH distribution. Field and laboratory studies and computer simulations by Cravotta *et al.* (1999) indicate that pH will be driven toward one mode or the other depending on the relative abundance and extent of weathering of pyrite (FeS_2; acid forming) and calcite ($CaCO_3$; acid-neutralizing). The pH values in the near-neutral mode result from carbonate buffering and imply the presence of calcareous minerals; acid produced by pyrite oxidation is therefore neutralized. The pH values in the acidic mode result from pyrite oxidation and imply a deficiency of calcareous minerals and the absence of carbonate buffering. Cravotta *et al.* (1999) note that the oxidation of only a small quantity of pyrite can acidify pure water (0.012g/L FeS_2 may produce up to about 0.5mmol/L acidity with 20mg/L

SO_4^{2-}, and pH ~ 4 (pers. comm. Dick Loewenthal, 2001)); however, because of the log scale for pH and proton buffering (SO_4^{2-}/HSO_4^- and $Fe^{3+}/FeOH^{2+}$), an order of magnitude greater oxidation is required to produce pH < 3.

In contrast to the bimodal pH, the acidity (or net alkalinity, equal to alkalinity-acidity) is unimodal, with a peak between -2000 and +2000mg/L as $CaCO_3$ (Figure 3.38a). The net alkalinity usually decreases with decreasing pH, but in a non-linear manner (Figure 3.38b). This phenomenon was also observed in Pennsylvania by Cravotta *et al.* (1999) and by Rose and Cravotta (1998).

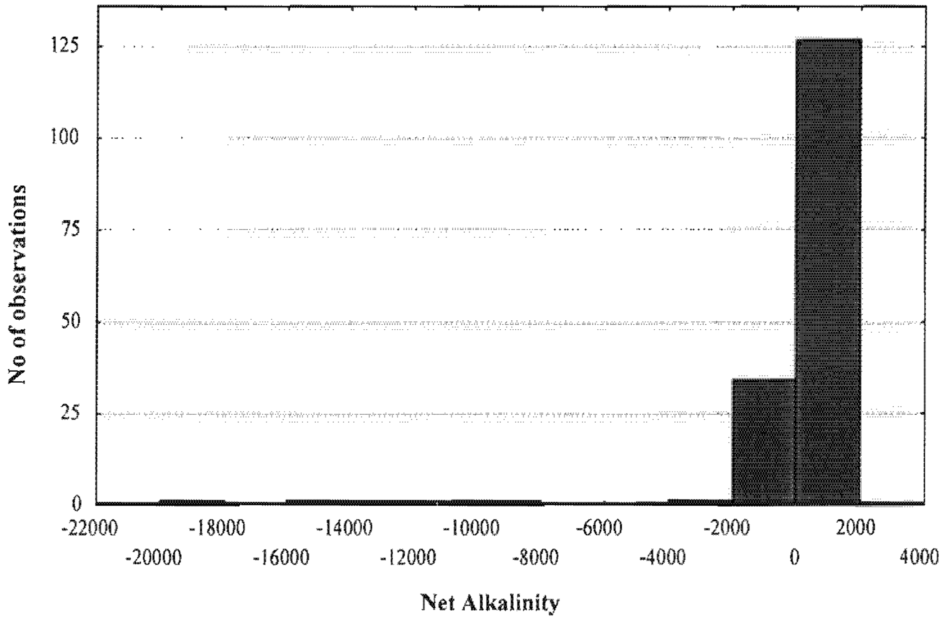

Figure 3.38a: *Unimodal net alkalinity distribution of water samples from 167 sites on Highveld collieries.*

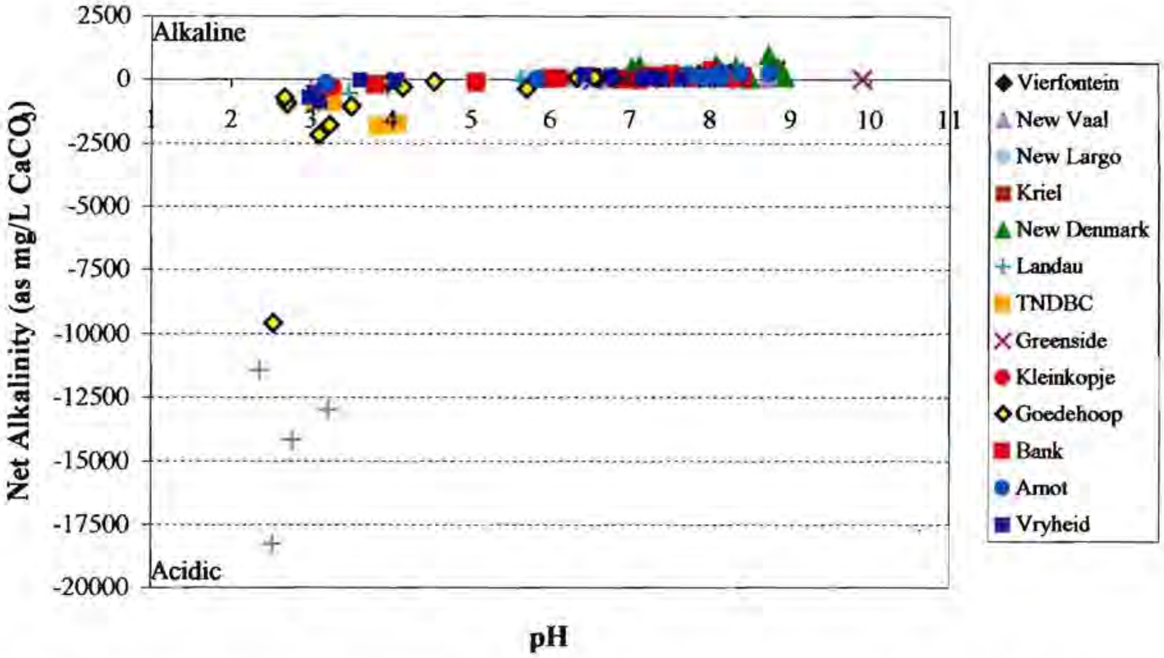

Figure 3.38b: *Net alkalinity (alkalinity - acidity) relative to pH for water samples from all the collieries.*

Most of the collieries exhibit an electrical conductivity (EC) below 4.0mS/cm. Exceptions include New Denmark (up to 7.01mS/cm), TNDBC (ranging between 6.6 and 10.6mS/cm) and Landau (up to 13.7mS/cm). Even though the elevated EC measurements throughout the collieries correlate positively with sulphate concentrations (Figure 3.39), as predicted by Rikard and Kunkle (1990), New Denmark is the only non-acidic colliery mentioned in the three with the highest conductivity. In this case, it is evident from Figures 3.4 and 3.13 that sodium and bicarbonate are the major contributors to the EC. Similar basic drainage has been observed in Wasatch Plateau, Utah, USA (Mayo *et al*., 2000) where the coal is also mined by longwall methods at a depth of approximately 300m below land surface. In longwall mining, the rock immediately above the coal seam collapses within hours to days after coal is mined, forming roof-rock rubble composed of coal, sandstone and mudstone. This exposes greater surfaces of alkaline material, which buffers the immediate formation of acid through pyrite oxidation. The sediments in the New Denmark Colliery have been chemically analyzed and the water-rock interactions anticipated in this colliery will be discussed later (Section 5.4.1).

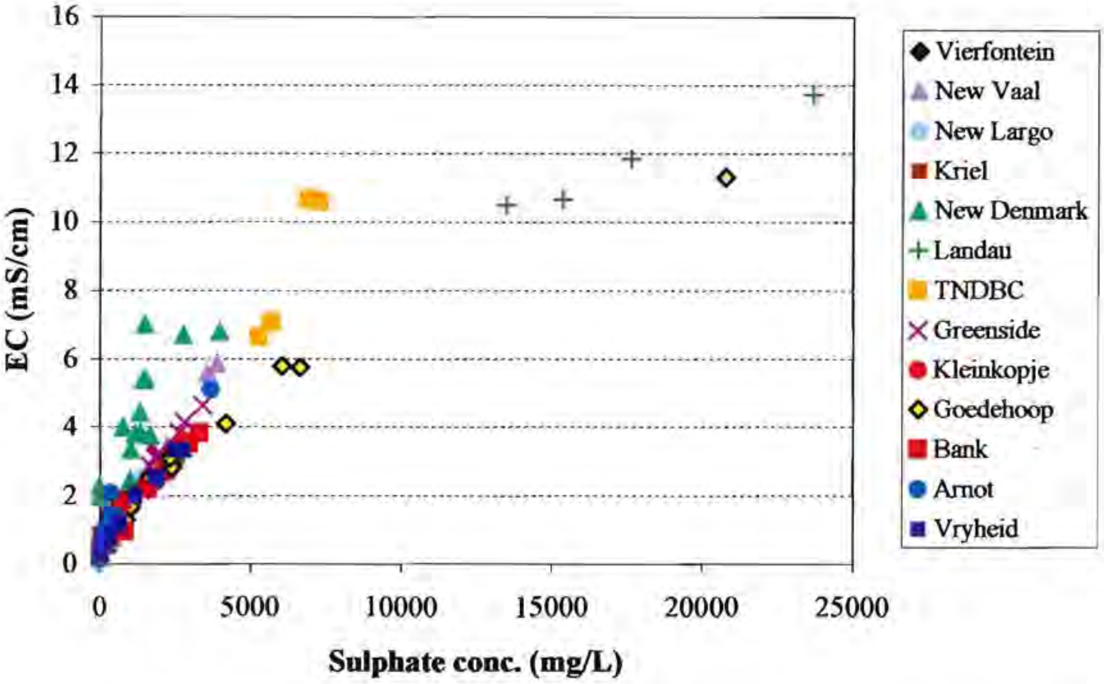

Figure 3.39: *Relationship between conductivity and sulphate concentration for each colliery.*

In addition, the steeper slope for the New Denmark and most Arnot waters, as compared to the others, in Figure 3.39 is interesting. Richards (1954) report that the curves for the chloride salts and Na_2SO_4 solutions (e.g. New Denmark and Arnot waters) almost coincide, but $MgSO_4$, $CaSO_4$ and $NaHCO_3$ have lower conductivities than the other salts at equivalent concentrations. These trends are very obvious in the mine waters as a whole.

3.3.1.1 Major solutes

The major contributors to the reported EC values throughout the collieries include Na^+, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-} and in some cases Cl^-. In the acidic waters, Al, Mn and Fe were also present as major ions. For consistency, however, they will be discussed with the trace elements. The proportions of the major cations and anions in each of the samples are plotted in the Piper trilinear diagram in Figure 3.40. A comparison of the samples indicates that there is no dominant cation type in most of the collieries. Exceptions include New Denmark and some of the Arnot waters, which are dominated by Na^+, and New Largo, which is dominated by Ca^{2+}. In terms of the major anions, there is a distinct trend in all the collieries, except New Denmark, Arnot and New Largo, to be SO_4^{2-} dominated. For the most part, the exceptions mentioned do not show any dominant anion (HCO_3^- is a significant anion along with SO_4^{2-}).

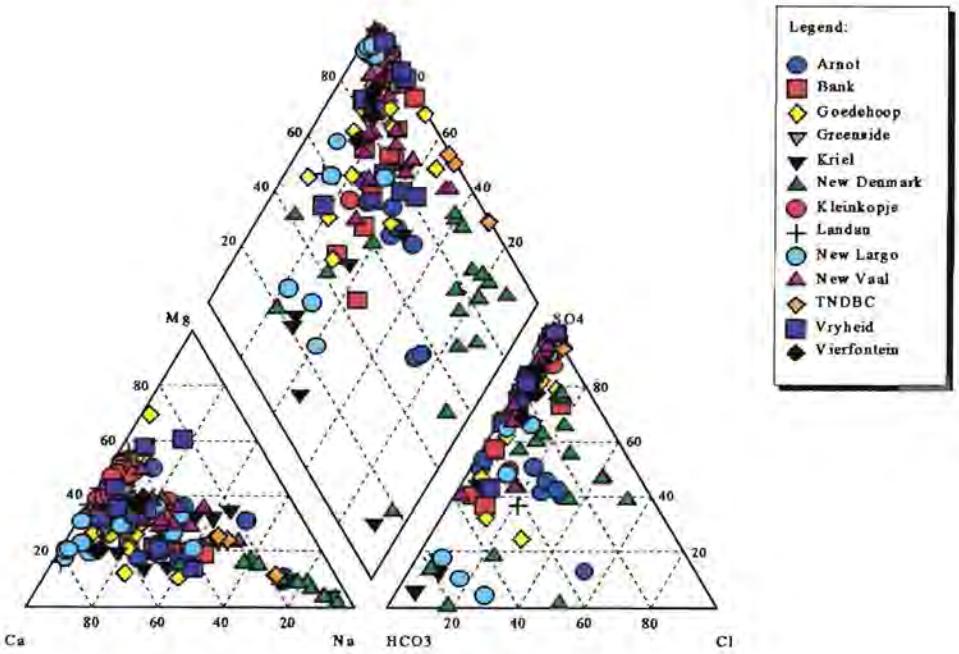

Figure 3.40: Piper trilinear diagram showing chemical composition of colliery waters.

From the box and whisker plots in Figures 3.2 to 3.14, some trends are obvious. Firstly, although TNDBC is not Na-Cl dominated, it does contain similar proportions of these constituents to those in New Denmark (up to 1755mg/L Na^+ and up to 1538mg/L Cl^-). Secondly, as one moves from west to east across the coalfields the Ca and Mg concentrations decrease first in the Free State and Vereeniging-Sasolburg coalfields, then start to increase as one moves into the Highveld and the Witbank coalfields, from where they start to decrease again into the Vryheid coalfield. It is difficult to ascertain whether similar trends occur in the HCO_3^- concentration since the oxidation of pyrite and subsequent generation of SO_4^{2-}, which consumes the alkalinity, is highly variable. Nevertheless, all but two of the collieries have high SO_4^{2-} concentrations (ranging between 314mg/L and 2267mg/L). The two exceptions, Landau and TNDBC, contain exceptionally large SO_4^{2-} concentrations, of up to 23 711mg/L.

Though not excessive, the K^+ concentration at TNDBC (26.9 - 32.4mg/L) is substantially higher than at any of the other collieries (Figure 3.6). Similarly, a surplus of F^- (26.4 - 43.4mg/L) is observed in the samples from TNDBC (Figure 3.9), although this may be erroneous due to the high dilutions (up to 100x) which had to be made for IC analysis. No fluoride was detected at the New Vaal or Vryheid Coronation collieries.

3.3.1.2 Minor elements

Trace element concentrations at Landau, and in many cases at Goedehoop, exceed those at the other collieries (Figure 3.15 to 3.36). This is due to the lower pH observed in these waters. Elements of particular interest include Al, Mn, Fe, Cu and Co. It is therefore surprising that similar concentrations of these elements, are not found in the acidic TNDBC waters, which are only enriched in Cs. Overall, the Al, Fe and Mn concentrations tend to be elevated in the Witbank coalfield only.

The Zn concentrations tend to fluctuate across all the coalfields, with the maximum (0.983mg/L) being observed in the Witbank coalfield, specifically at Landau. Zinc has been found to influence the growth of $CaCO_3$ crystals during the scaling process (Coetzee *et al.*, 1996; Coetzee *et al.*, 1998) and is therefore used as an anti-corrosion agent by the metal industry.

The Encyclopaedia Britannica (www.britannica.com, 2001) defines stainless steel as an "alloy steel usually containing 10 to 30 percent chromium. In conjunction with low carbon contents, chromium imparts remarkable resistance to corrosion and heat. Other elements such as nickel, molybdenum, titanium, aluminium, niobium, copper, nitrogen, sulphur, phosphorus, and selenium may be added to increase corrosion resistance to specific environments, enhance oxidation resistance, and impart special characteristics". Some of the elevated metal concentrations, such as Cr, Al, Cu and Se, in the collieries near Witbank (specifically Landau, Greenside, Kleinkopje, Goedehoop, Bank and even Arnot) may be attributable to a steel and/or ferrometal processing plant situated just north of Witbank. No direct link can, however, be proven.

The SiO_2 concentrations seem to fluctuate from west to east across all the coalfields, as does Rb, Sr and Ba. Neither Sr nor Rb are toxic and are thought to be present as a result of isomorphous substitution of calcium and magnesium in the 2:1 clay mineral structure. Likewise, Rb substitutes for K in the clay mineral structure. Two of the collieries, New Vaal and New Denmark, show elevated concentrations of B (~ 1mg/L). Both of these collieries also exhibit relatively high HCO_3^- concentrations. Although essential to plant growth, boron can be highly toxic if the water is used for irrigation. Bester (1993) reported that sunflower, maize and sorghum, which are grown in the vicinity of the collieries, were all semi-tolerant to boron and could tolerate between 1.0 and 2.0mg/L before the first visual signs of toxicity were observed.

3.3.1.3 Temporal variations

Waters were sampled during both the winter and summer seasons at six of the collieries (Kriel, New Denmark, Greenside, Goedehoop, Bank and Arnot) and annually at two of the collieries (Landau and TNDBC). The suffixes 'w' and 's' in the sample no's in Appendix 2 denote 'winter' and 'summer' sampling, and 'a' and 'b' denote '1999' and '2000' sampling. A total of 96 samples were taken during the winter of 1999, and 88 during the summer of 2000. A further 79 samples were taken during the winter of 2000. A statistical analysis was performed to determine whether any significant difference occurs in the chemistry of the waters over time, followed by some consideration of the effect of evaporation during the dry winter months. It is important to reiterate that where seasonal sampling was undertaken, the rainfall during the summer was well in excess of the average.

3.3.1.3.1 Statistical analysis

The Mann-Whitney U statistical test was employed to determine whether significant variations occurred in the composition of the waters over time (i.e. seasonally and annually). In terms of the seasonal sampling, significant differences were observed, at the 95% confidence level in almost all variables at all the collieries. The fluoride concentration is the only variable that appears to remain consistent throughout the year (Table 3.2). It is important to note that fluoride measurements were done by ion chromatography, which may involve substantial sample dilutions. This may affect the accuracy and precision of the analytical results, especially since fluoride is present in exceptionally small concentrations relative to sulphate. The chloride, cadmium and chromium concentrations are also relatively constant.

Table 3.2: *Variables measured seasonally and found not to be significantly different at the 95% confidence limit.*

Colliery	Variables not significantly different
Kriel	F, Cl, Ni, Cd
New Denmark	K, F, Al, Fe (total), Cu, Zn, Cd, Pb
Greenside	F, B, Cr, Cd
Goedehoop	F, Cl, Li, B, Cr, Fe (total), Se
Bank	F, Cl, Li, Cr
Arnot	DOC, F, Cr, Se

As with the seasonal sampling, most variables were significantly different at the 95% confidence limit from one winter (1999) to the next (2000). At Landau, only two samples were repeated annually and all the variables changed significantly during this time period. At TNDBC, three sample points were visited annually. Six constituents showed no significant concentration difference during this period: Na, Ca, SO_4, Li, $Fe_{(total)}$ and Zn.

In spite of the significant difference obtained for most variables between the summer and winter, it was not possible to use only those samples taken in the winter for this study. The reason for this is that for some of the samples, only Fe_{total} was determined as opposed to Fe(II) and Fe(III). Therefore, all further discussions will be based on those samples (167 in number) for which both Fe(II) and Fe(III) were measured.

3.3.1.3.2 Evaporation

In considering seasonal variations in the chemistry of the water, chloride was chosen as a reference ion to demonstrate the effects of evaporation. As chloride is generally not removed or supplied significantly by interaction with rocks, and is not precipitated as a salt until very high salinities are reached, the chloride concentration in the water forms some indication of the amount of evaporation that has taken place since the water started out as rainfall. An exception to this was noted in the case of one particular colliery, New Denmark, where a double aquifer rich in fossil salts is thought to occur.

From both the plots of EC and sodium against chloride concentration (Figures 3.41 and 3.42), it is clear that in the winter, the points fall closer to the 1:1 line over a concentration range of three orders of magnitude. Calcium and magnesium (Figure 3.43 and 3.44) show the

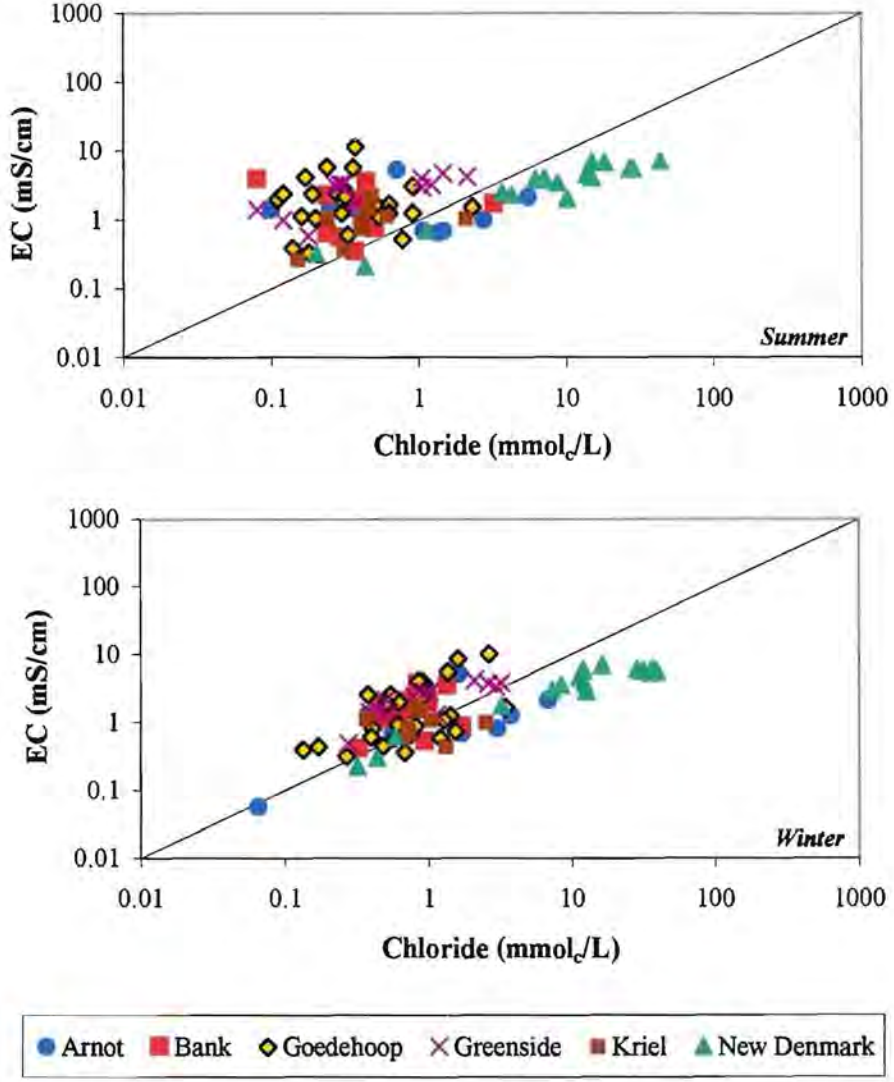

Figure 3.41: Seasonal variation in EC with chloride concentration, relative to the 1:1 simple evaporation line.

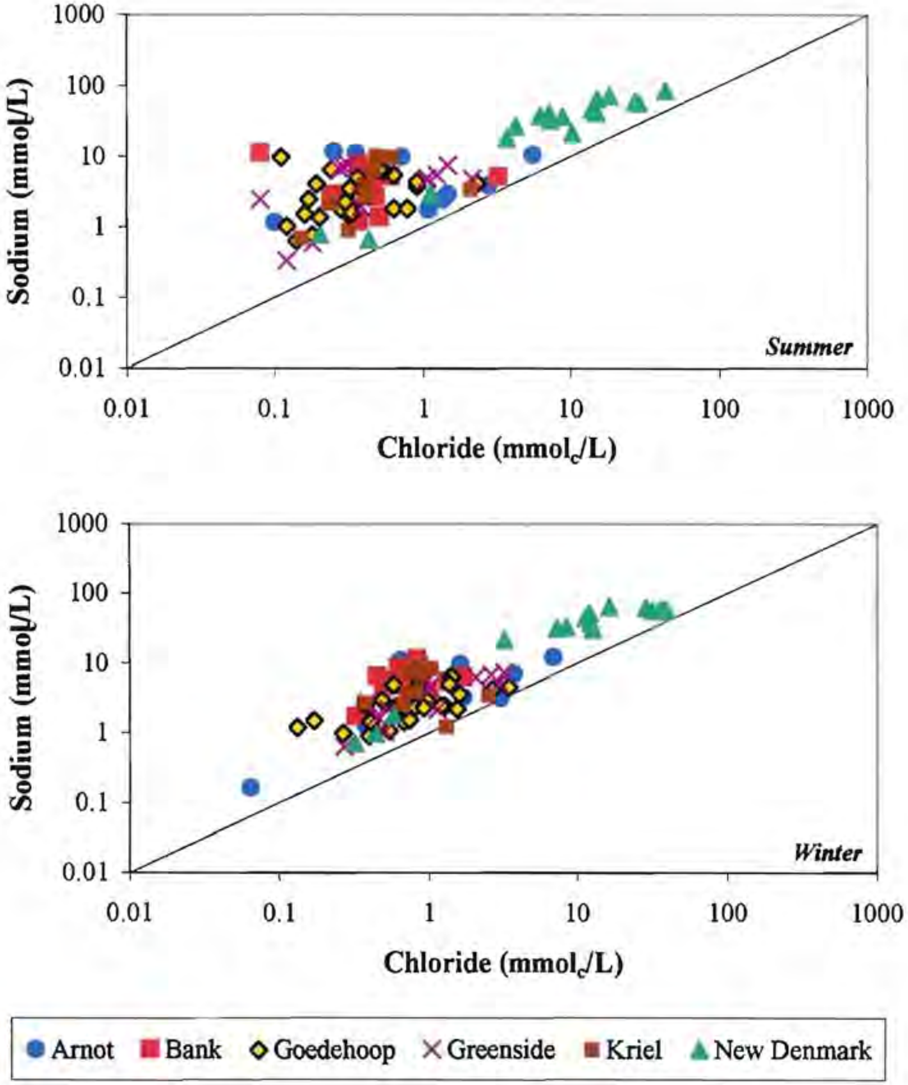

Figure 3.42: Seasonal variation in sodium with chloride concentration, relative to the 1:1 simple evaporation line.

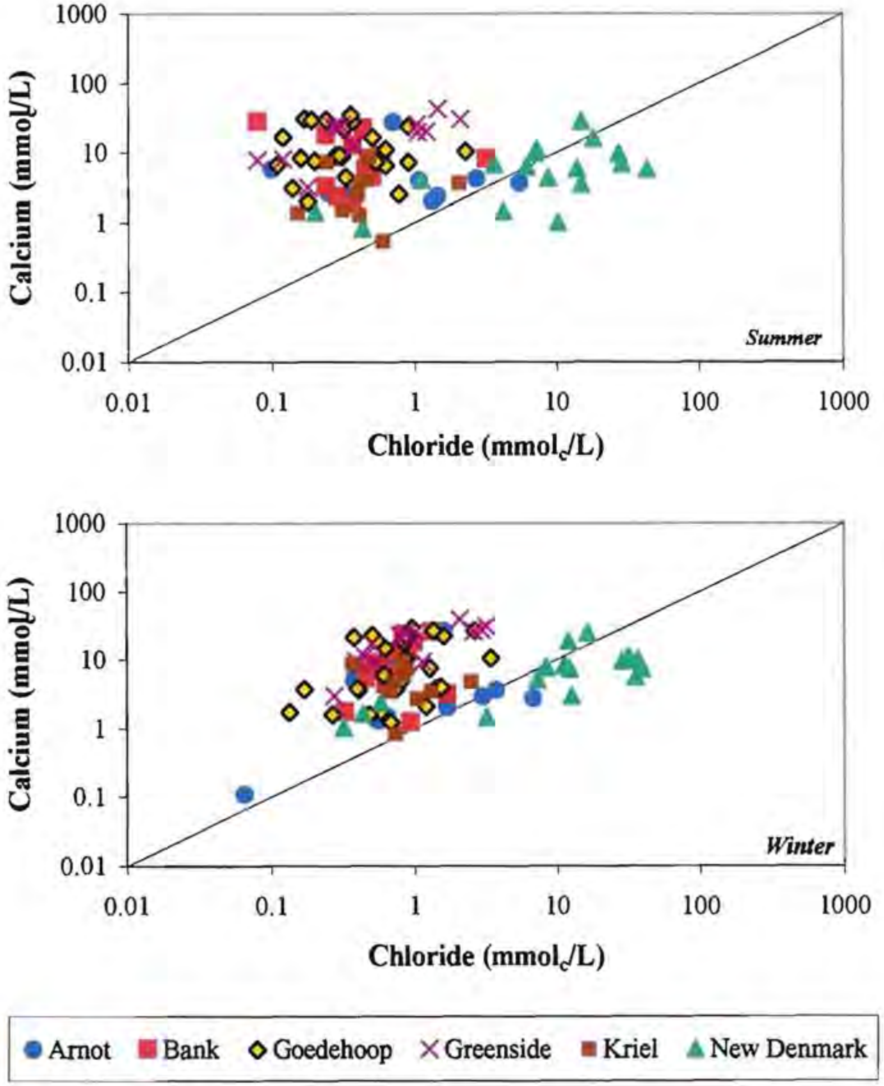

Figure 3.43: *Seasonal variation in calcium with chloride concentration, relative to the 1:1 simple evaporation line.*

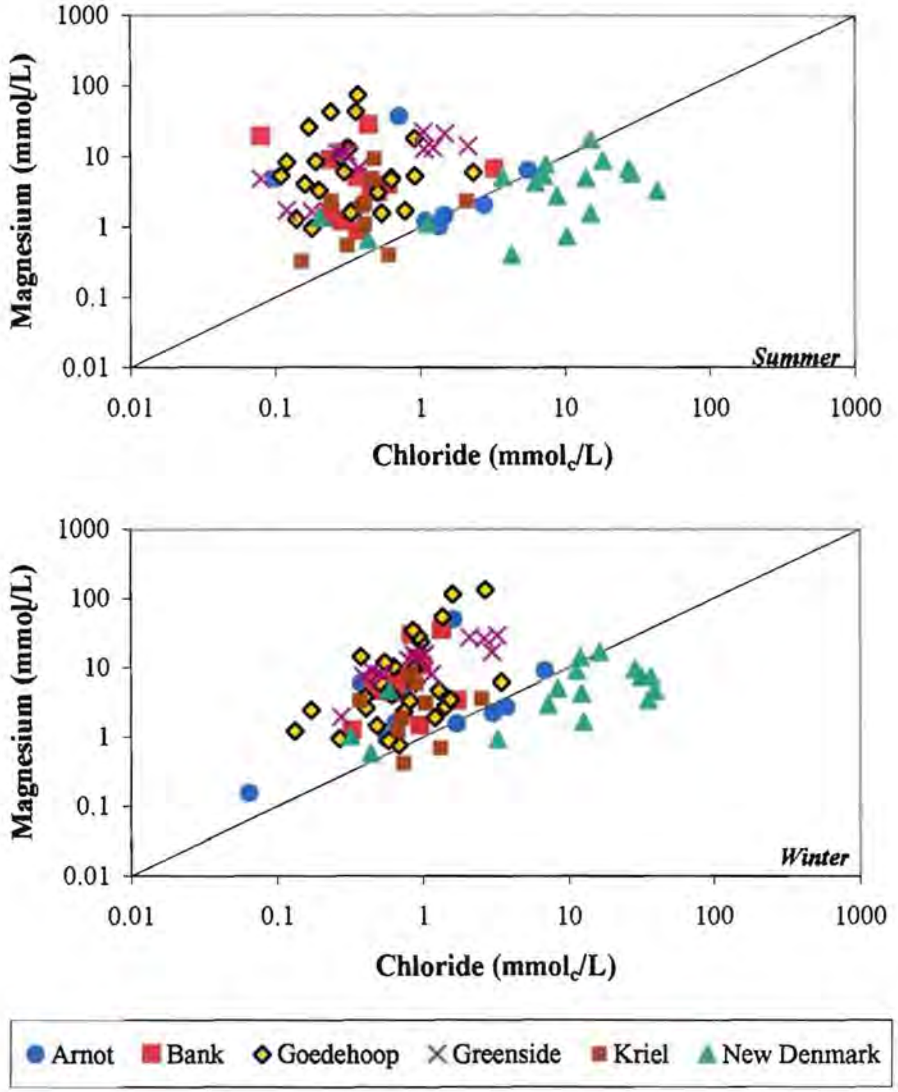

Figure 3.44: *Seasonal variation in magnesium with chloride concentration, relative to the 1:1 simple evaporation line.*

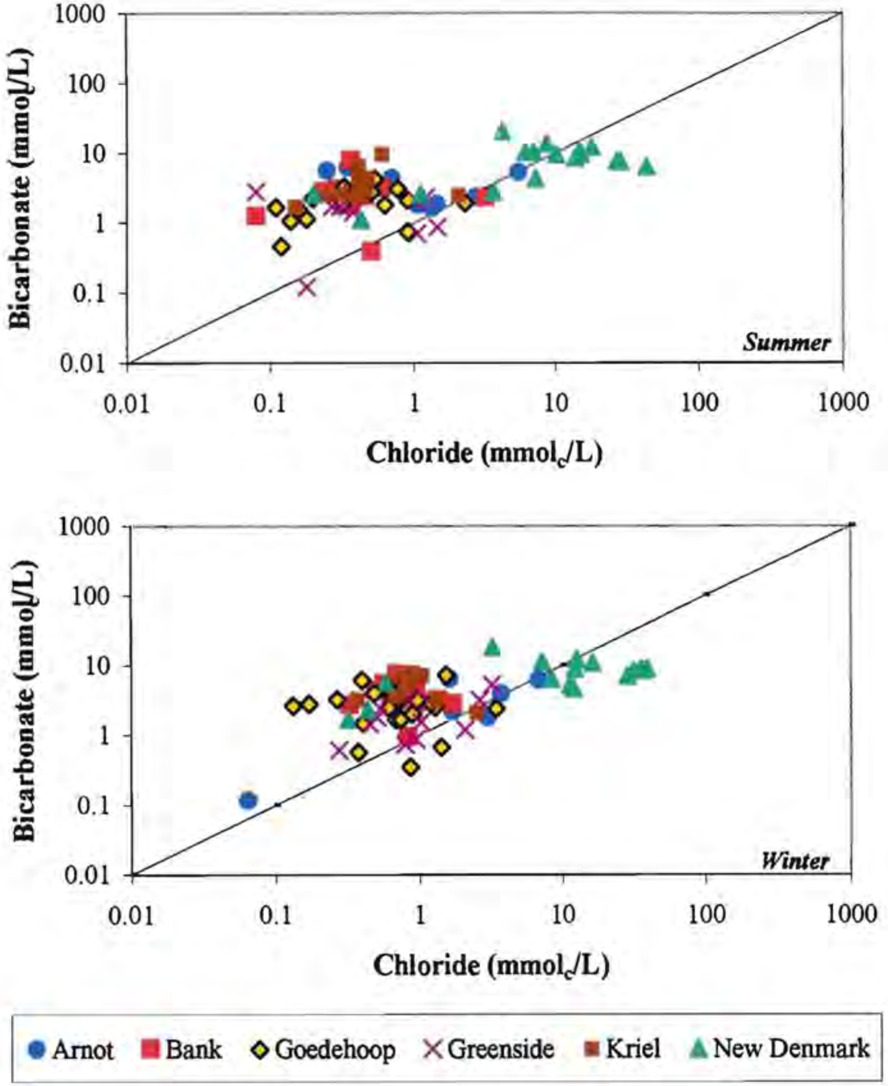

***Figure 3.45:** Seasonal variation in bicarbonate with chloride concentration, relative to the 1:1 simple evaporation line.*

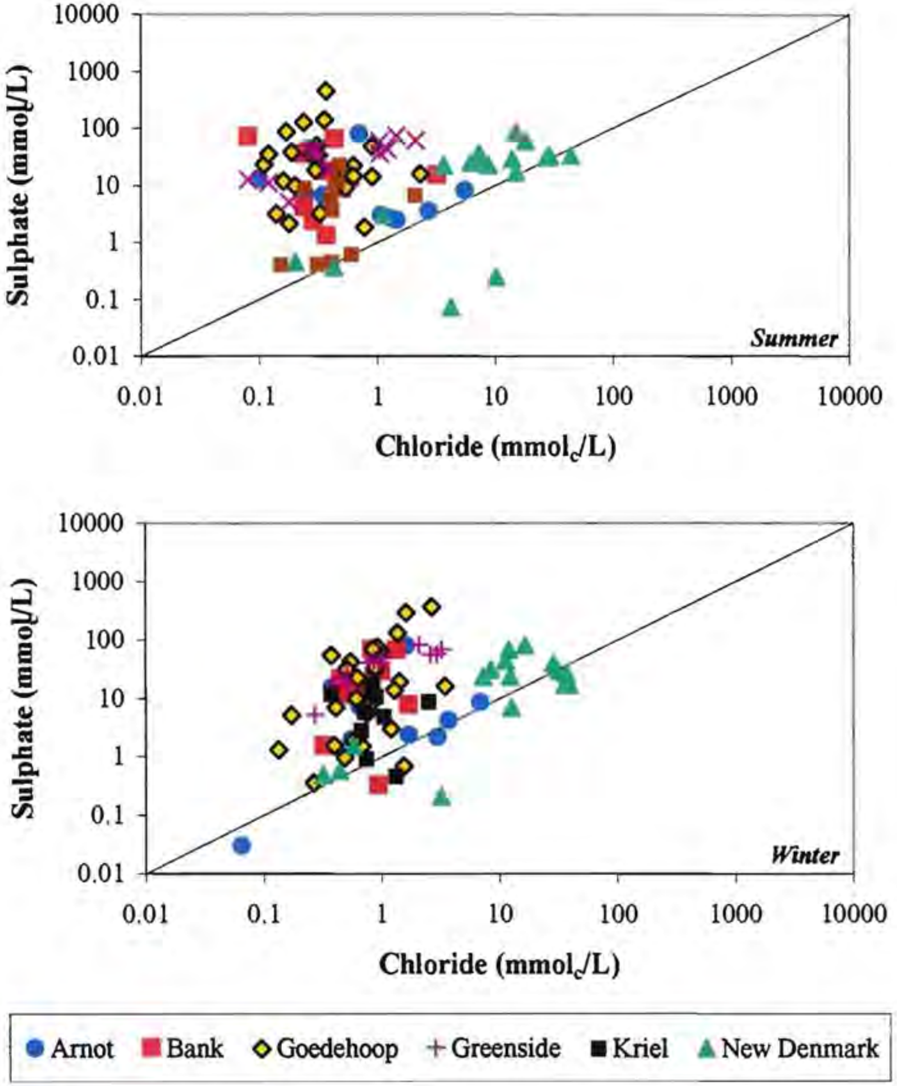

***Figure 3.46:** Seasonal variation in sulphate with chloride concentration, relative to the 1:1 simple evaporation line.*

behaviour predicted by the Hardie-Eugster (1970) model, which interprets the chemistry of waters undergoing evaporation in terms of a succession of chemical divides. As chloride concentration increases, the concentration of both calcium and magnesium decrease. They are both expected to precipitate as carbonates, or possibly silicates. There is no distinct difference in the concentration of bicarbonates (Figure 3.45) during the summer and winter months, reinforcing the idea that carbonate species are removed from solution on a continual basis. On the other hand, the sulphate concentration during both the summer and winter months appears to remain steady (Figure 3.46). One would expect this to increase as a result of continuous pyrite oxidation, however, it is likely that the sulphate is constantly precipitating out as gypsum. On the whole, no <u>major</u> seasonal variations as a result of evaporation are obvious in the colliery waters. This may, however, be due to the flushing of salts which resulted from excessive rainfall, as experienced during summer sampling.

3.3.1.4 Comparison with natural waters

There is apparently a great variation in water supplies in different localities underlain by the Ecca series. Some 2500 boreholes were critically examined, by the Geological Survey of South Africa (Frommurze, 1937). Frommurze (1937) points out that in the North-West Cape the yield is often in an inverse ratio to the rainfall, and that everywhere the yields are much affected by the presence or absence of dolerite sills and dykes which tend to dam up the water. These intrusions also have an appreciable effect on the chemical characteristics of the water.

The geology of the study area will be discussed in more detail later. Suffice it to say that the Ecca series in the north and eastern parts is arenaceous, being mainly composed of sandstones, with some softer sandy shales, whereas in the south and west, it is argillaceous. Bond (1946) collected and analysed 30 samples of water from Kwazulu-Natal, Mpumalanga and the Northern Free State. He found that these parts of the Ecca do not yield a characteristic water (Figure 3.47). All types except the extremely saline are encountered, so it is not possible to allocate these waters to any one group. Furthermore, the rainfall is much the same over all the areas in question, with only a slight increase further to the east, so it is necessary to look for other reasons than climatic ones. One probable cause is the variation of the rock from argillaceous to purely arenaceous. Another cause is the large number of dolerite dykes

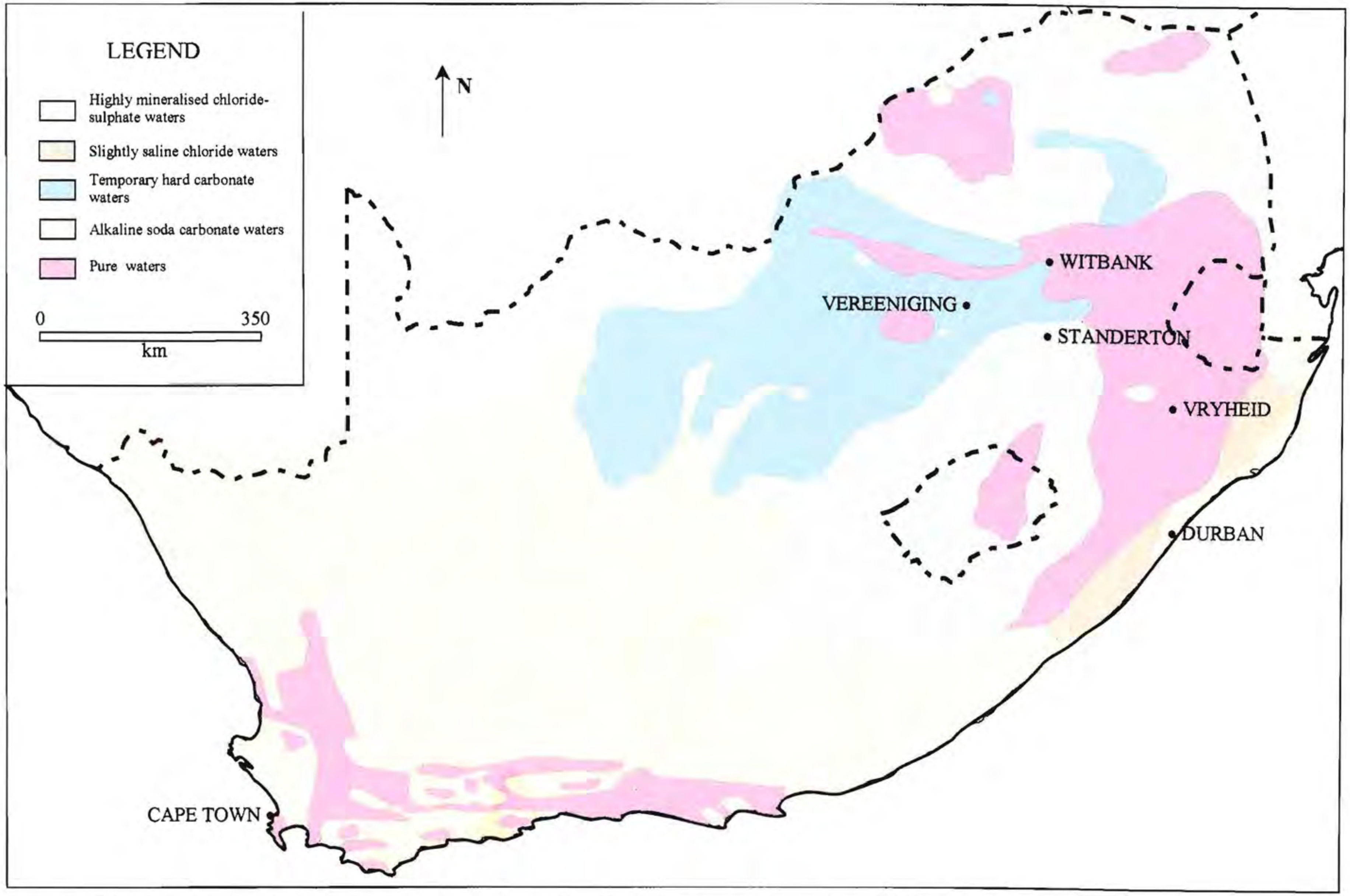

Figure 3.47: *Water map of the Union of South Africa showing baseline water compositions. Compiled by Bond (1943).*

and sills, which traverse the Ecca beds in these regions, and affect considerably the chemical characteristics of the waters.

In summary, Bond (1946) found that although the concentrations vary greatly, the waters as a whole do not carry excessive solids in solution (seldom over 5mg/L). The pH value shows a considerable variation but remains in the near-neutral range. There is nearly always slightly more calcium than magnesium present, but this is not so marked as in the waters of the western and southern parts of South Africa, where calcareous concretions and layers are apparently common. Silica varies greatly but is, on average, considerably higher than in the Ecca waters elsewhere and this is to be expected since the waters are of non-saline types. Fluoride is negligable in the Kwazulu-Natal and Mpumalanga areas, while only very small amounts are found in the Free State and all under the maximum permissible for potable purposes. Chlorides vary a lot but are very seldom above 11% of total salts. This is very different from the Cl content of the Dwyka and the Ecca waters in the west and south of the country. Sulphates are generally present in traces or small amounts (1.8mg/L), but occasionally high values are obtained. This may be due to pyritic dolerite dykes or to pyritic segregations in the sandstones (Bond, 1946). Soda alkalinity is sometimes present, generally in small amount, but occasionally in appreciable amount. This may be due to a feldspathic sandstone in the vicinity or to a dolerite dyke. The total scale-forming salts vary a lot but are generally fairly high.

From the results of Bond's analyses, it would appear that the Ecca sediments in the study area were laid down in fresh water and that the region did not suffer any subsequent transgression by the sea. This, however, contradicts later investigations by Cairncross *et al.* (1990) who revealed that coal-peat deposition was associated with both marine and non-marine palaeodepositional events. At the terminal stage of peat accumulation, they report that swamps were inundated by marine transgressions which deposited mud and silt above the peat (coal) and these overlying sediments contain typical marine features, such as glauconite associated with marine ichnofossil assemblages. Nevertheless, the waters are entirely suitable for domestic supply, irrigation and livestock watering, but as regards utilization for cooling and other industrial purposes, the variation is too great to make generalizations, each water having to be treated on its own merits.

Although extensive groundwater sampling programmes have been implemented at almost all of the collieries in this study, these have only been in place for a few years. Therefore it is almost impossible to obtain comprehensive information on the quality of water in the pre-mining environment. It was for this reason that, wherever possible, a sample was taken from a water body believed to be unaffected by mining activities, at each of the collieries. It was hoped that the composition of this water would give an indication of the background level of constituents one would expect to find in the study area. The chemical composition of the major ions in the waters are plotted in Figure 3.48, and given in Table 3.3. Trace element compositions can be found in Appendix 2.

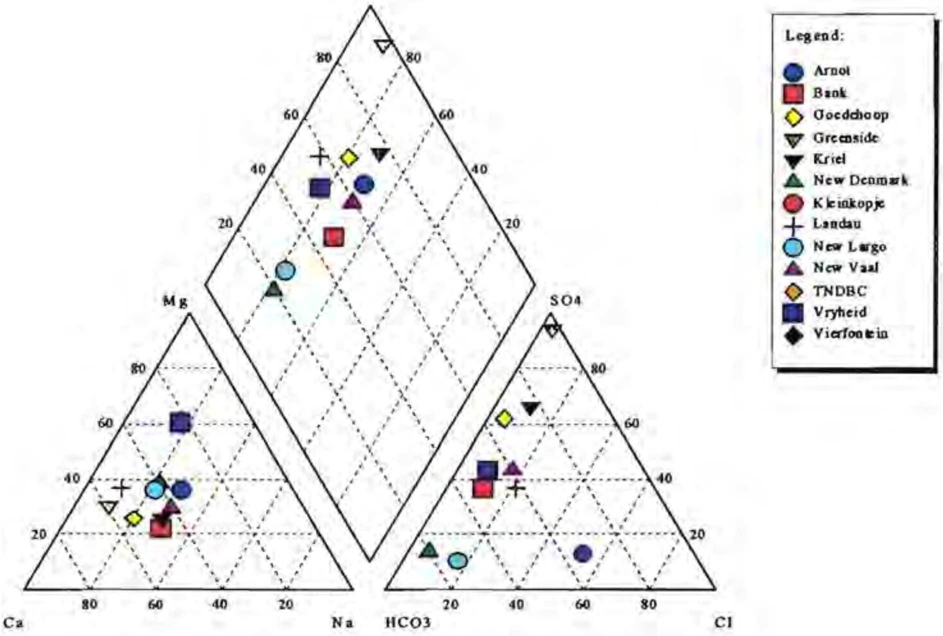

Figure 3.48: *Piper trilinear diagram showing chemical composition of those waters "unaffected" by mining operations.*

Many of the natural waters in the study area show no dominant cation or anion. Most of the samples taken from collieries in the Witbank region are slightly Ca-dominated, whereas the water from the Vryheid district is Mg-dominated. In terms of the anions, the waters from New Largo and New Denmark tend to be enriched in HCO_3^-, whilst that from Arnot is Cl^-dominated. The waters taken from Greenside, Kriel and Goedehoop are all enriched in SO_4^{2-}, indicating that they have probably been affected by mining activities, although a SO_4^{2-} signature may evolve from the weathering of pyrites associated with dolerite intrusions (Bond, 1946), or the pyrite associated with the Ecca sediments (see Chapter 4).

Table 3.3: *Chemical composition (in mg/L) of selected waters at the collieries. These are believed to be unaffected by mining operations.*

Sample	AC 6	BC 9	GH 8	GS 12	KC 9	ND 16	LN 2	NLC 5	NVC 11	NAC 1
pH	5.6	8.4	6.2	6.8	7.6	7.3	5.7	6.3	7.8	7.4
EC (mS/cm)	0.141	0.340	0.336	0.575	0.860	0.318	0.120	0.070	0.720	0.260
SAR	0.432	1.00	0.631	0.367	1.92	0.655	0.16	0.23	1.40	0.43
Na^+	5.10	26.7	17.6	13.0	71.2	17.7	2.40	2.40	53.5	10.3
NH_4^+			0.44	0.54						
K^+	3.60	3.20	6.96	3.90	16.8	0.75	1.27	1.63	6.49	2.14
Mg^{2+}	3.28	10.3	11.7	19.5	33.3	16.6	4.18	2.11	28.2	19.5
Ca^{2+}	5.18	36.6	40.5	63.1	97.0	28.1	9.80	4.10	64.1	12.2
Mn^{2+}	0.041	0.004	0.271	2.12	0.014	0.003	0.172	0.055	0.133	0.106
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.431
Fe^{3+}	0.037	< 0.001	0.129	< 0.001	< 0.001	0.136	< 0.001	< 0.001	< 0.001	< 0.001
Al^{3+}	< 0.001	< 0.001	0.116	< 0.001	0.038	0.065	0.958	0.052	0.012	0.036
F^-	< 0.01	0.37	0.58	0.05	0.48	0.072	0.18	< 0.01	< 0.01	< 0.01
Cl^-	3.84	13.1	6.29	6.41	38.2	7.09	6.34	2.84	45.2	8.07
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	26.1	2.83	0.54	< 0.01	1.43	< 0.01	4.03	14.1	0.23	1.15
PO_4^{3-}	< 0.01	< 0.01	1.35	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	1.24	59.9	102	233	314	21.1	14.6	2.35	158	51.6
HCO_3^-	4.21	108	69.8	7.38	138	157	21.4	21.4	186	73.2
Si	3.94	9.52	3.15	1.13	1.98	7.79	2.95	3.82	4.30	9.92
B	< 0.001	< 0.001	< 0.001	< 0.001	0.089	0.014	0.072	0.002	0.051	0.011

3.3.1.5 Comparison with other coal mining regions

Studies of the world-wide abundance of coal-bearing sedimentary material (Ronov *et al.*, 1974; Bluth and Kump, 1991) demonstrate that vast amounts of coal are preserved in late Carboniferous and Early and middle Permian sedimentary rock. Major coalfields of Late Permian age are found in Australia, South Africa, Antarctica and South America (Faure *et al.*, 1995). These were formed in Gondwanaland. Precise ages of Southern African coals suggest that the Permian coals vary in age from late Sakmarian to mid-Tartarian (about 270 to 248 Ma) (Harland *et al.*, 1990). Age estimates of the other Permian coalfields in Australia (Hobday, 1987), Brazil (Petrobras, 1991), Antarctica (Balme and Playford, 1967), India (Krishnan, 1961), and China (Zhang and Zhen, 1991) also indicate minimum ages of mid-Tartarian.

Unfortunately, the author experienced great difficulty in obtaining detailed information on the quality of the waters from mines in these countries. Therefore, occasional comparisons have been made with waters from Laurasian coal mining districts (Europe, Asia and North America). These were formed during the hot, humid Carboniferous period, and are thus slightly older, as well as being produced from another flora in a different depositional environment (Falcon, 1986; Barker *et al.*, 1999).

3.3.1.5.1 The Witbank Coalfield

A disused colliery in the northern part of the Witbank coalfield was studied by Bullock and Bell (1997) from 1990 to 1996, and again during 1997 by Bullock, Bell and Marsh (1997). The disused colliery is not unique in that the waters are characterized by low pH (1.8 to 3.0) and high EC (283 to 471mS/m), indicating high levels of contamination. Although many of the collieries in this study do not exhibit extensive acid mine drainage, two of those which do, TNDBC and Landau, occur within the same region as the disused colliery.

The generally near-neutral pH of the currently mined collieries in the southern part of the Witbank coalfield ensures that metals, for the most part, have not dissolved and therefore their concentrations in the solutions remain low. The low pH values observed in the disused colliery, can be attributed to the formation of sulphuric acid as a product of reactions involving the oxidation of pyrite. This is supported by the high sulphate concentrations in the waters there (1440 to 3250mg/L). Similarly, high sulphate concentrations (average ~ 1850mg/L) were observed in the waters from most of the collieries presently being studied. Those two which occur near the disused colliery, however, reported substantially higher (~ 5380mg/L) sulphate concentrations, indicating either that pyrite oxidation has not occurred to the same extent in the disused colliery, or that the acidity has already been at least partly neutralized.

The TDS of the waters at the disused colliery are generally higher (2082 to 4844mg/L) than at Landau colliery (average ~ 1621mg/L), which contains the highest sulphate concentrations of the collieries being studied. From this, it is concluded that although the acidity produced by oxidation has already been neutralized, the pyrite in the collieries currently being studied has not oxidized to the same extent as in the disused colliery. Furthermore, the calcium and magnesium concentrations at Landau are similar to those encountered at the disused colliery, but the sodium concentrations (65 to 399mg/L) are higher than at Landau colliery. In addition, the chloride concentrations at Landau are substantially lower than in the disused colliery (84 to 611mg/L). The calcium, magnesium and sodium concentrations at the TNDBC site are higher than for the disused colliery, and the sodium and chloride concentrations are approximately the same.

Between March 1990 and February 1992, Geldenhuis and Bell (1998) assessed the acid mine drainage problem at the Loubert Mine, which lies south-east of Ermelo, in the Witbank coalfield. Here, contaminated water seeps into a nearby stream from overfull reservoirs in backfilled workings. The coal here is particularly high in sulphide content (1.01 - 3.26%), primarily associated with pyrite, and therefore it is not surprising that over 75% of the samples taken from the central reservoir have a sulphate content of 3000mg/L and above. The pH at both the central and mine return reservoirs was always below 2.8 and the EC between 228 and 584mS/m, indicating that the water quality is generally quite similar to that found at Landau colliery and the abovementioned disused colliery.

3.3.1.5.2 The Damodar River basin, India

Coal mining activities in the Damodar River basin in India has also caused significant degradation in ground water quality. Tiwary and Dhar (1994a; 1994b) report that the mine water in this region, for the most part, does not have an acid mine drainage problem. This is thought to be because the coal deposits are not associated with pyrite. The sulphur content in the coal is also low (~ 1%). The pH values recorded were in the range of 6.5 to 9.2 in different coalfields within this basin. Those waters with a pH below 7.0 were reported to cause leaching, and as a result elevated TDS levels (200 to 860mg/L) were found in the water. Similar TDS concentrations were noted in the waters from many of the Highveld collieries in this study, especially those with near-neutral pH.

The sulphate concentrations in many of the Highveld colliery waters (exceptions include Landau and TNDBC) were similar to most of the Indian coalfields, indicating a similar degree of pyrite oxidation. As in the Highveld collieries, the resulting acidity from this oxidation has been neutralized largely by carbonate dissolution. In this process, large concentrations of calcium and magnesium are brought into solution. The concentrations of these cations (as expressed by the hardness) at the Greenside and Vierfontein collieries are similar to those in the Karanpura, Bokaro and Ramgarh coalfields; whereas those in the Bank and New Denmark collieries are similar to the lower concentrations observed in the Raniganj coalfield. The very hard waters of Jharia coalfield are analogous to those at Kleinkopje. Chloride concentrations in most of the Highveld colliery waters fall within the bottom of the range expressed for the Indian coalfields (20 to 1009mg/L). The chloride concentrations in many of the New Denmark waters, however, were similar to those observed in the Jharia coalfield (< 1010mg/L). Finally, the nitrate concentration detected at TNDBC is similar to those observed in the Jharia coalfield (40.8 to 58.0mg/L), and those found in the Karanpura, Bokaro and Ramgarh coalfields (0.11 to 4.6mg/L) comparable to many of the other Highveld collieries (exceptions include, New Largo, Landau, TNDBC, Kleinkopje and Arnot).

3.3.1.5.3 The Sydney Basin, Australia

The characteristics of mine waters associated with coal seams in the Illawarra coal measures of New South Wales, were assessed by Judell and Anderson (1988). Although pyrite-rich seams do occur in New South Wales, those in this study contained between 0.38 and 0.69%

total sulphur. The three seams considered include the uppermost Katoomba, the Lithgow (which lies about 100m below) and the Bulli seam (Southern coalfield equivalent of the Katoomba).

Waters entering the Katoomba seam contain low quantities of dissolved solids (0.04 - 0.07mS/cm, TDS: 30 - 32mg/L) and alkaline salts (1.0 - 1.9mg/L Mg, 0.3 - 22.7mg/L Ca and 15mg/L HCO_3). Acidic solutions, formed by the chemical reaction with oxidized pyrite within the mines, when waters percolate through fractured rocks and coal in goafed areas, are consequently not neutralized and become progressively more acidic as bacterial reactions occur. Consequently, iron, manganese and zinc, contained in the sedimentary rocks, are dissolved in the mine waters. The resulting goaf waters vary in pH from 3.0 to 4.2 and the EC increases to 0.127 - 0.789mS/cm. Calcium and Mg concentrations range between 3.8 - 4.1mg/L and 3.0 - 16.0mg/L, respectively. No alkalinity was measured in the waters, but acidity ranged between 19 and 169mg/L as $CaCO_3$. Up to 8.3mg/L Zn, 8.1mg/L Fe and 6.3mg/L Mn did, however, appear. Even at its worst, the contaminated mine waters from Katoomba are purer, in terms of major constituents, than any of the waters in this study which have been affected by mining activities. Zinc concentrations, however, are far in excess of those observed in Highveld mine waters. Similar amounts of iron have been observed at most of the Highveld collieries, and manganese at Landau and Goedehoop.

Waters entering the Lithgow seam mines differ from those of the Katoomba Seam in that dissolved minerals are in much higher concentrations. The waters entering these mines contain TDS within the range 216 to 358mg/L. Furthermore, the alkalinities are substantially higher (248 - 359mg/L HCO_3), and therefore acid formation is inhibited at most mines. Water in the goafed areas is similar in composition to many waters on the Highveld collieries, with pH ranging from 7.0 to 8.4, 32 - 68mg/L Ca, 16 - 28mg/L Mg and 16 - 24mg/L Na. No unusual amounts of Fe or Zn were found. Phosphorus was detected in the waters associated with both the Katoomba (< 2 - 35mg/L) and Lithgow seams (4 - 22mg/L). On the Highveld, phosphorus was barely detected, and only in a few of the waters.

An exception to the generally near-neutral Lithgow seam waters is Wallerawang colliery (pH 3.2), where the presence of acidic water is attributed to (1) the relatively thin cover of roof strata (30-40m as opposed to 50-200m); (2) the existence of a confined aquifer containing water of low alkalinity above the Lithgow seam; and (3) the rapid ingress of surface water through joints, fractures and faults permitting insufficient contact with carbonaceous sediments in the overlying strata. The Wallerawang waters are similar to waters found in a few Highveld collieries (e.g. Goedehoop) in that they contain an average of 73mg/L Ca, 46mg/L Mg, 31mg/L Na, 530mg/L SO_4 and 28mg/L Fe.

Non-acidic waters (pH 6.6 - 7.9) occur along the Bulli Seam and are caused by reactions of the varying amounts of carbonaceous rocks with the natural surface and groundwaters prior to their entry into the mines. These alkaline waters (433 - 3360mg/L HCO_3) neutralize acids formed by reaction of water with pyrite thereby preventing significant reduction in pH. The alkalinity and associated pH results in a lower solubility of ferric iron, which removes the pyrite-oxidation pathway utilized by bacteria which may catalyze the oxidation process. The waters associated with the Bulli Seam are similar to those from New Denmark in that they contain large quantities of Na (27 - 1120mg/L), although their Cl concentrations are not unusual (21.3 - 51mg/L). The waters are definitely HCO_3-dominated, with only 0.8 - 25mg/L SO_4. Other constituents occur in typical amounts.

The characteristics of mine waters encountered in collieries around Gondwanaland are highly variable. They appear to be dependent on the paleoenvironments of the different coal seams, the topography of the area in which each mine is located, the depth of each mine, the tectonic movements which have caused faulting and fractures, the volumes and characteristics of groundwaters which occur and the subsidence which has resulted from the mining operations.

3.3.2 Ion speciation

The distribution, mobility and biological availability of chemical elements depends on their concentration and on their chemical and physical associations in natural systems. Changes in environmental conditions may strongly influence the behaviour of both essential and toxic elements by altering the forms in which they occur. Some of the more important controlling factors include pH, redox potential and availability of 'reactive species' such as complexing ligands (both organic and inorganic), particle surfaces for adsorption, and colloidal matter (Ure and Davidson, 1995).

Speciation modelling provides constraints on whether plausible reactant phases potentially are dissolving or precipitating, or are inert. These models calculate thermodynamic properties of aqueous solutions, including the molalities and activities of aqueous species and saturation indices of minerals. The modelling code used here, PHREEQC, is based on an ion-association approach which attempts to account for much of the non-ideality of aqueous solutions by ion association, that is, the formation of complexes from the hydrated individual ions in solution (Parkhurst and Plummer, 1993). PHREEQC has capabilities for (1) speciation and saturation index calculations, (2) reaction-path and advective transport calculations involving specified irreversible reactions, mixing of solutions, mineral and gas equilibria, surface complexation reactions, and ion exchange reactions, and (3) inverse modelling which finds sets of mineral and gas mole transfers that account for composition differences between waters, within specified compositional uncertainties (Parkhurst, 1995).

According to Parkhurst and Plummer (1993), the main advantage of the ion-association approach is that it is relatively easy to modify the model to include new species and new elements. They also point out that there are three major deficiencies: (1) the original Debye-Hückel theory only applies at very low ionic strengths (< 0.01 mol/L), and extensions of the theory are only applicable to selected solution compositions of moderate ionic strengths approaching sea-water concentrations (ionic strength of 0.7); (2) insufficient work has been done to ensure that the model adequately reproduces experimental solution properties such as mineral solubilities and mean-activity coefficients; and (3) whereas attractive forces among aqueous species can be accounted for by ion association, there is no mechanism to account for repulsive forces in mixed electrolyte solutions.

The WATEQ4F.DAT thermodynamic database that is supplied with the PHREEQC package was used for the calculations discussed here. The water quality data were input to the PHREEQC model without modification, except that non-detect data were entered as zero. Where the water temperature was recorded at the time of sampling it was used as input to PHREEQC. Otherwise the water temperature was set at 25°C, the temperature at which analyses were performed. The temperatures that were measured in the field ranged from 13.1°C to 29.8°C, with a mean of 18.6°C.

Acid mine waters, and other types of surface waters, are usually of a mixed redox chemistry and only by determining relevant redox species can one interpret the redox chemistry of the water. Nordström *et al.* (1979) showed that acid mine drainage waters typically have sufficient iron concentrations to give an equilibrium potential at the platinum electrode for the Fe(II)/Fe(III) redox couple but that the O_2/H_2O redox couple was far from equilibrium with respect to the iron couple. A comparison between measured and calculated Eh in acid mine waters from the Leviatha/Bryant Creek system showed that the Fe(II)/Fe(III)redox couple reflects the bulk pe of water for high total iron concentrations (i.e. $Fe_{TOTAL} > 10^{-5}$m). Other redox couples, however, becaome equally, or more, important at lower total iron concentrations (i.e. $Fe_{TOTAL} < 10^{-6}$m). Therefore, estimates based on Fe(II)/Fe(III) ratios at these lower concentrations may be meaningless (Nordström and Alpers, 1999a).

Thirty-nine of the samples in this study contained both Fe (II) and Fe (III), and as no other relevant redox pair data (specifically Mn) was available, this redox couple formed the basis for calculating pe using PHREEQC. The relationship between these pe values and the pH (Figure 3.49) was then used to estimate a pe value for those samples that contained an undetectable iron concentration. It is important to note that this calculated pe value is only an estimate, and as such the modelling results are not exact. They are, however, more accurate than if the default pe value, of 4, was utilized for all waters, especially the more acidic ones.

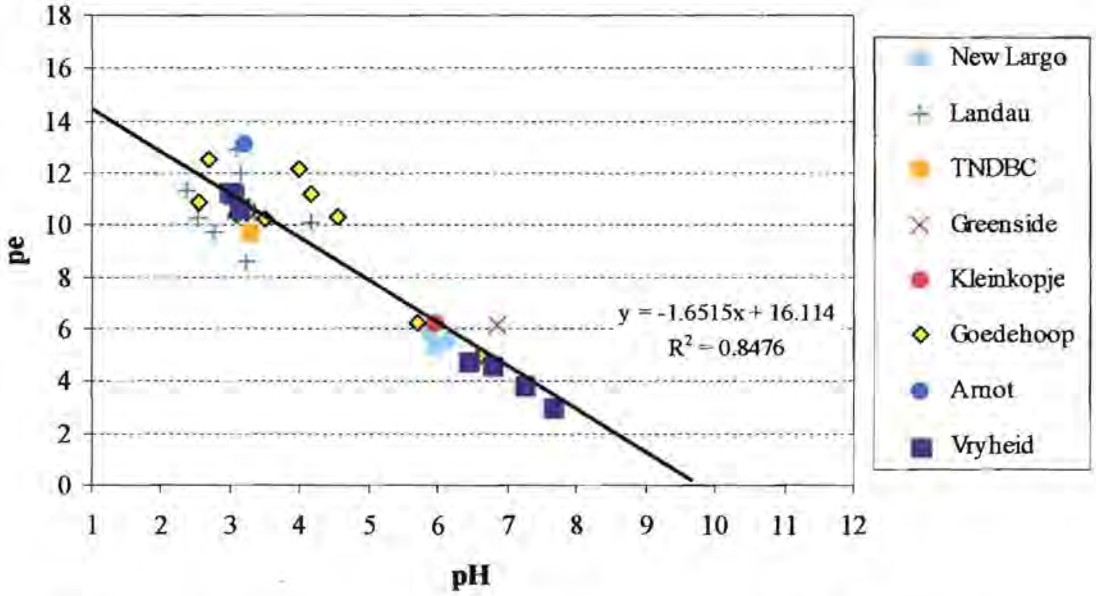

Figure 3.49: *Relationship between pe and pH for waters containing the Fe(II) / Fe(III) pair.*

The speciation of ions in the colliery water is complex and in view of the fact that it has little direct bearing on purely geochemical characterization of waters, will not be discussed at length. Although the primary purpose of the speciation modelling in this study was to calculate mineral saturation indices, which are indicators of the saturation state of a mineral with respect to a given water composition, it is important to remember that a knowledge of the chemical speciation of a water system is essential in order to understand the behaviour of the water (Kerr and Buckley, 1994; Kot and Namiesńik, 2000). It is only then that predictions can be made about how the water would behave if the chemistry or the environment changed. The detailed relative distributions of specific dissolved ionic species, within each of the water samples in this study have been calculated. The results for aluminium, iron and sulphate speciation are presented in Appendix 3, and only a summary is given here.

Waters show different speciation depending on whether they are acidic, or near-neutral. Firstly, we consider those waters falling in the lower pH range ($2.5 < pH > 5$). Then we will consider those waters falling in the upper pH range ($5 < pH > 9$) of the bimodal pH distribution noted.

In terms of aluminium, the acidic waters tend to be dominated (up to 60%) by $AlSO_4^+$, with 5 – 20% of the aluminium occurring as $Al(SO_4)_2^-$, due to the presence of sulphate arising from the oxidation of pyrite. Al^{3+} is usually present, though seldom exceeds 20% of the total aluminium. Where fluoride is present, some of the aluminium is predicted to exist as aluminium fluoride complexes (AlF^{2+} and/or AlF_2^+) rather than the expected aluminium sulphate complexes. The presence of aluminium hydroxide complexes, particularly $Al(OH)^{2+}$, are only noted as pH increases (> pH 4.5). As with the aluminium, the bulk of the complexed iron occurs as $Fe(SO_4)_2^-$, $FeSO_4$ and $FeSO_4^+$ ($pH < 4$). In many cases, 20 – 50% of the iron in the water is present as free Fe^{2+} and/or Fe^{3+}. The formation of iron hydroxide complexes, particularly $Fe(OH)^{2+}$ and $Fe(OH)_2^+$, commences above pH 3.5, which is a lower threshold than that for aluminium. Overall, the bulk of the sulphate (~ 60%) is present as free SO_4^{2-}. At $pH > 2.5$, 10 - 12% and 5 - 15% of the sulphate is complexed with magnesium and calcium, respectively. At lower pH, the presence of $CaSO_4$ and $MgSO_4$ complexing is negligible since the bulk of the sulphate is locked into aluminium and iron complexes. Furthermore, in this low pH region the bisulphate ion (HSO_4^-) competes for sulphate.

In the neutral to alkaline pH range, almost all of the aluminium occurs as aluminium hydroxide complexes, with approximately 60 – 90% as $Al(OH)_4^-$, the remainder being $Al(OH)_3$ ($pH > 6.5$) or $Al(OH)_2^+$ and $Al(OH)^{2+}$ ($pH < 6.5$). In some of the samples, particularly where $pH < 6.5$, aluminium fluoride complexes (AlF^{2+}) were calculated by PHRREQC. Whether these complexes exist or not is debatable, since the fluoride concentrations of the waters were determined by ion chromatography, which required substantial dilutions (up to 100x) in many of the samples. Up to 70% of the iron in the near-neutral waters, occurs in the free ion state, exclusively as Fe^{2+}. In these waters, a small portion of the iron complexes with sulphate ($FeSO_4^+$ and $FeSO_4$) and bicarbonate ($FeHCO_3^+$). In some of the waters, all of the iron was present as hydroxides, with $Fe(OH)_3$ dominating and the remainder occurring as $Fe(OH)_2^+$ and $Fe(OH)_4^-$. The occurrence of free sulphate ions (SO_4^{2-}) is slightly higher (> 70%) in the near-neutral waters. The remainder of the sulphate is locked into $MgSO_4$ (5 - 10%) and $CaSO_4$ (15 - 20%) complexes. No significant aluminium or iron sulphate complexes were found in these waters.

The speciation trends, over the full pH range, for a water sample from Kriel colliery (KC8s) is depicted in Figure 3.50. This sample was assumed to be representative as a result of its heterogenous composition and the presence of both Fe(II) and Fe(III). As already suggested, it is interesting to note that the bisulphate ion (HSO_4^-), and probably metal bisulphate complexes, compete for sulphate at pH values < 2.

3.3.3 Major ion coherence

Rikard and Kunkle (1989) conducted a water quality assessment on three Appalachian streams polluted by coal mining at the Big South Fork National River and Recreation Area in Tennessee and Kentucky. Their results showed that although the determined sulphate concentrations were less than 90mg/L and the EC less than 0.40mS/cm, both sulphate and EC were excellent parameters for detecting the effects of coal mining. They also found that hardness is a good indicator of mining impacts and relates closely to the sulphate concentration. In the current study, the Spearman's correlation coefficient was calculated in order to assess correlations between concentrations of all variables.

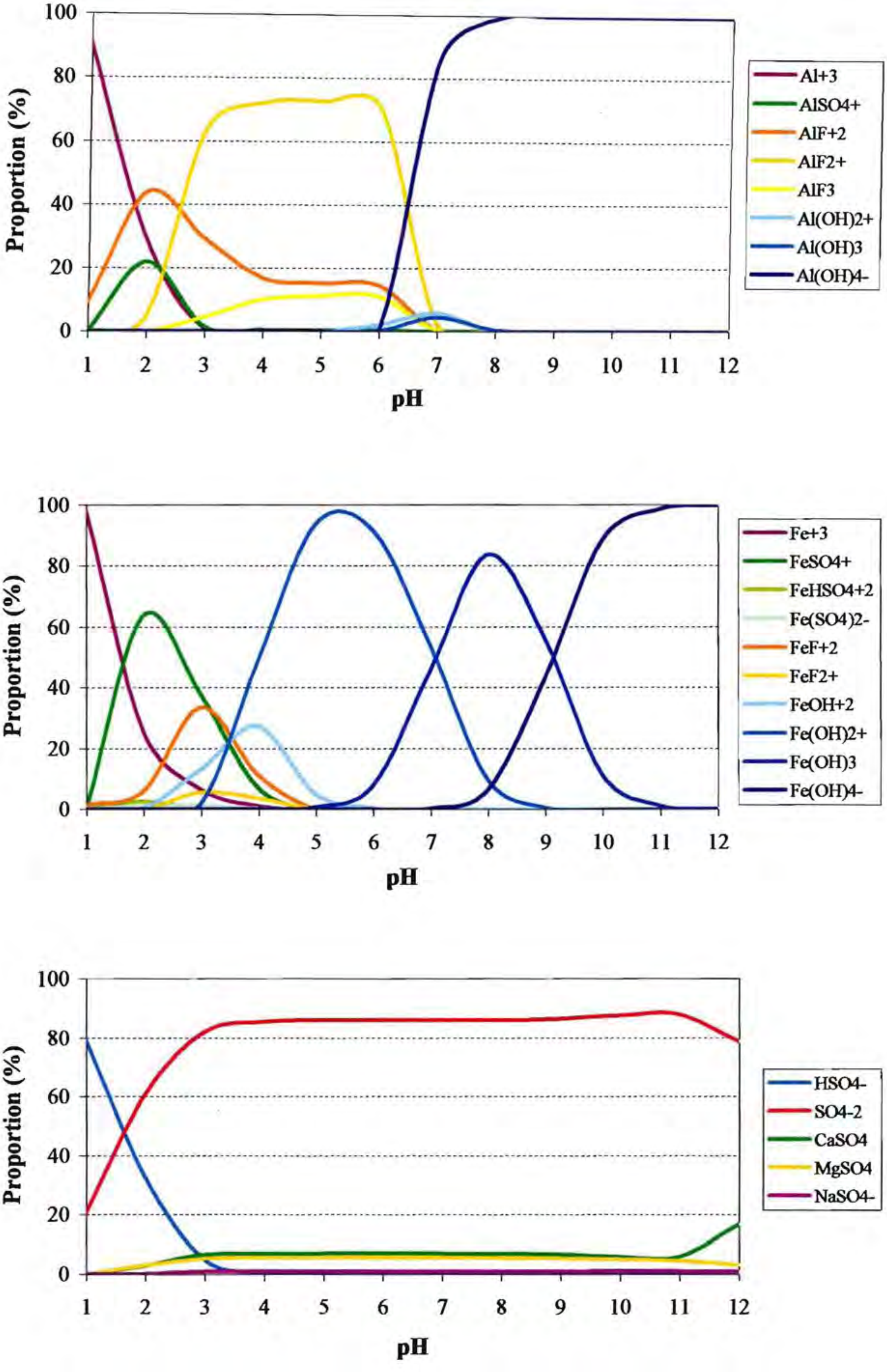

Figure 3.50: *Ion speciation changes as a function of pH for a sample from Kriel colliery (KC8s).*

Figure 3.39 shows that a strong overall correlation exists between conductivity and sulphate (r_s= 0.93), reinforcing Rikard and Kunkle's discovery and suggesting that either could be used to detect water pollution associated with coal mining. It should be noted, however, that EC cannot discriminate between ion species. Many groundwater and surface water bodies will show spatial trends in EC that relate to a variety of processes, for example, evaporation, water-rock interaction, ion exchange, etc.

A correlation was also observed between hardness and sulphate (r_s=0.91) (Figure 3.51). Furthermore, magnesium correlates slightly better with sulphate (r_s=0.91) than does calcium (r_s=0.89). A similar relationship was observed by Azzie (1999), in which the correlation between hardness and sulphate (r_s=0.85) suggested the existence of an affinity in the colliery waters between magnesium and calcium, and sulphate. It is important to note that Azzie (1999) only considered 20 samples, all of which contained <1800 mg/L sulphate and an EC < 5.3mS/cm. Detailed investigations also showed that magnesium correlated slightly better with sulphate (r_s=0.94) than did calcium (r_s=0.91).

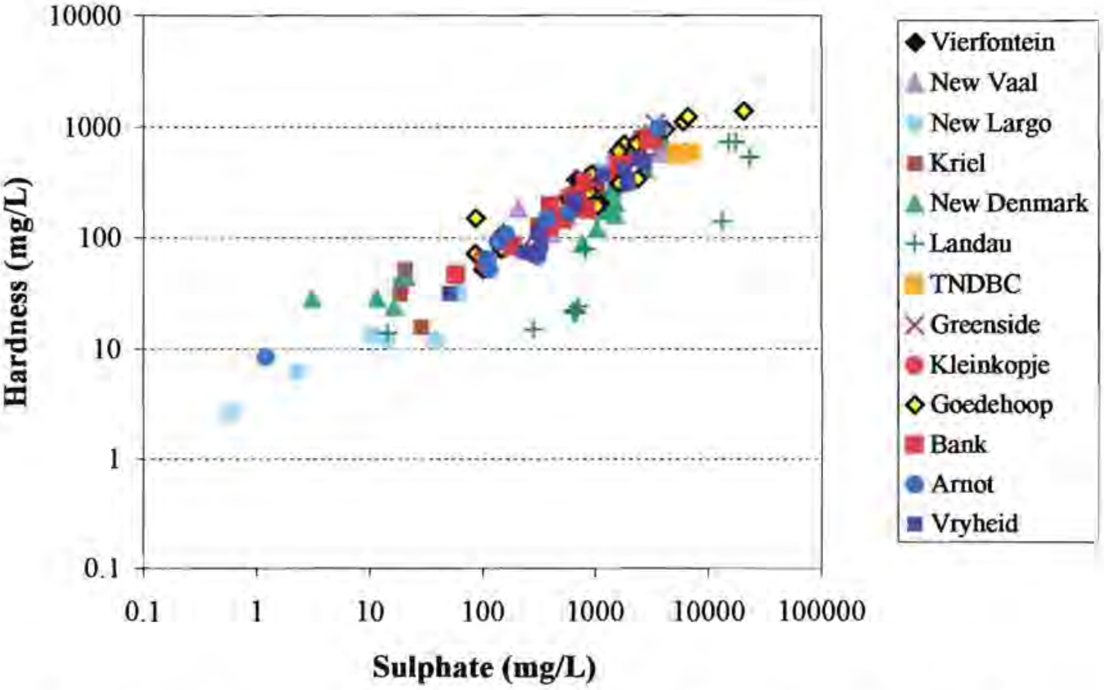

Figure 3.51: *Correlation observed between hardness (Ca + Mg) and sulphate concentration (r_s=0.907).*

Furthermore, although no correlation was evident, between sodium and sulphate concentrations, in Azzie (1999), a very weak correlation did exist between sodium and bicarbonate (r_s=0.46). Again, no correlation is evident between sodium and sulphate concentrations, but a slight correlation is noted between sodium and bicarbonate (r_s=0.66) as compared to the previous study. In addition, a stronger correlation is observed between sodium and bicarbonate + chloride (r_s=0.68) (Figure 3.52).

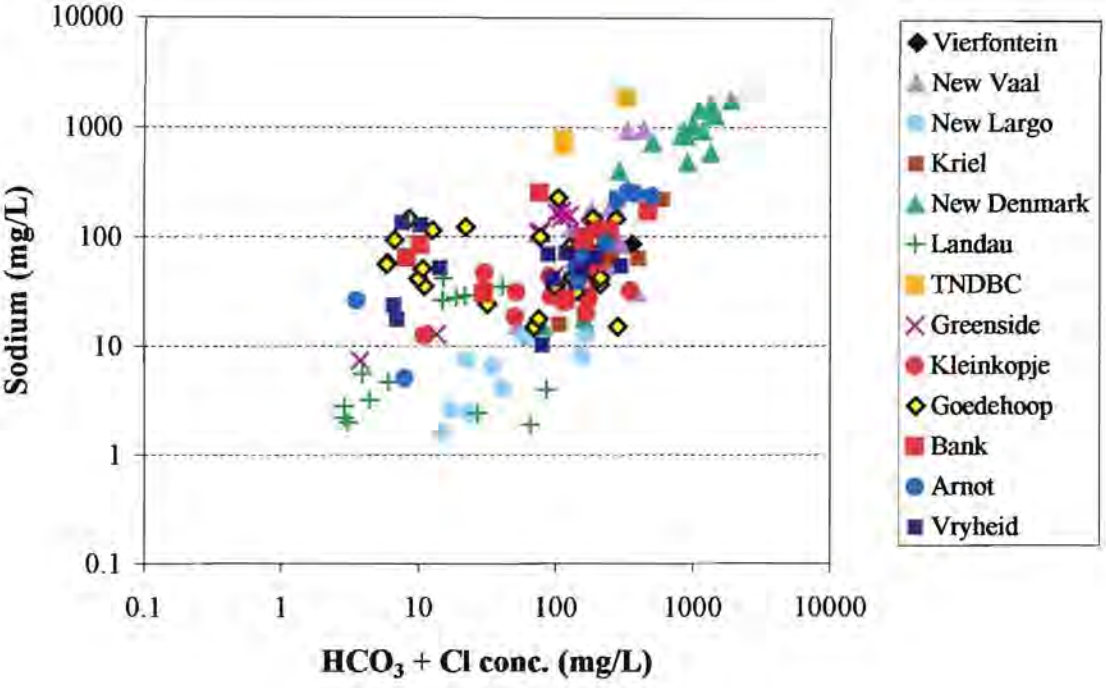

__Figure 3.52:__ Correlation observed between sodium and HCO_3^- + Cl^- concentration (r_s=0.693).

The relationship between hardness and sulphate suggests that an affinity exists between the major divalent cations and sulphate. Fey (pers. comm., 1999) suggested that the correlation of Na^+ concentration with univalent anions (HCO_3^- + Cl^-) is the result of less sulphate, on a geochemically equivalent basis, being generated through pyrite oxidation in some waters than that of calcium plus magnesium associated with the clay mineral surfaces in the host rocks. Since both Ca and Mg, but not Na, exhibit a strong tendency for ion pair formation with sulphate, these divalent cations will be preferentially stripped from cation exchange surfaces by H_2SO_4 (derived from pyrite oxidation). Under these circumstances of an excess of exchangeable Ca and Mg relative to sulphate in solution, Na will only dissociate substantially if some other acid (e.g. H_2CO_3) is available to protonate the exchange sites and provide an accompanying anion (HCO_3^-) in solution. The result is that solution concentrations of sulphate exhibit coherence with those of Ca and Mg, while bicarbonate concentration exhibits coherence with that of Na.

Other strong correlations observed in the data are presented in Table 3.4. The coherence between pH and Fe(III) is not surprising since all species that can coexist in a range of oxidation states are likely to show a correlation of speciation with pH. It is, however, interesting to note the coherence between EC and Fe(II) and, also the appearance of some form of interdependence between Co, Ni, and Zn, but not Cu.

Table 3.4: *Spearman's correlation coefficients of selected variables, which show strong interdependence.*

	No. of cases	r_s
pH & Fe(III)	70	-0.87
EC & NH_4	12	0.93
EC & Mg	167	0.83
EC & Ca	167	0.79
EC & Fe (II)	41	0.82
NH_4 & Mg	12	0.94
NH_4 & Ca	12	0.88
NH_4 & SO_4	12	0.89
NH_4 & Al	9	0.92
NH_4 & Cu	7	0.86
NH_4 & U	11	0.85
F & NO_2	4	-0.80
NO_3 & Fe(II)	23	0.82
SO_4 & Fe(II)	41	0.82
B & P	3	-1.00
P & Cr	4	0.80
P & $Fe_{(total)}$	4	0.80
Mn & Co	166	0.83
Co & Ni	155	0.92
Co & Zn	159	0.81
Ni & Zn	153	0.89

3.3.4 Mineral solubility equilibria

The saturation index is a convenient parameter for evaluating the proximity to equilibrium for various solubility reactions, for aqueous systems that show a range of solution compositions. It is important to note that the saturation index only indicates what should happen thermodynamically; it does not indicate the rate at which the process will proceed. In many cases, a mineral having a saturation index less than zero may dissolve very slowly or not at all, depending on the kinetics of the reaction. A more definitive conclusion can be drawn if the mineral saturation index is less than zero; that is, the mineral cannot precipitate from the water concerned. This conclusion is qualified only by the accuracy of the chemical analysis and the aqueous model, not by rates of reaction (Parkhurst and Plummer, 1993). By similar reasoning, if the saturation index is greater than zero, the mineral might precipitate but cannot dissolve. If the saturation index is close to zero, the mineral may not be reacting at all or may be reacting reversibly, in which case the mineral could be dissolving or precipitating. The concept therefore represents a powerful tool for the geochemical interpretation of water quality.

The saturation indices of all the potential minerals were calculated by PHREEQC using the formula:

$$SI = \log\left(\frac{IAP}{K_{eq}}\right)$$

where *IAP* is the ion activity product determined from observed solution concentrations after appropriate activity and speciation calculations are performed, and K_{eq} is the equilibrium constant.

The Davies equation was used to compute the activity coefficients. On the whole, a large proportion of the colliery waters were found to be supersaturated with respect to the carbonate minerals, specifically calcite and dolomite (Figure 3.53), as well as quartz and $ZnSiO_3$. The waters are, however, invariably undersaturated or, in some cases, in equilibrium with strontianite. Note that the SI of these carbonate minerals are plotted against sulphate rather than pH or alkalinity, since sulphate concentration is an indicator of oxidative alteration which is important in assessing evolution of mine waters. Most of the samples are undersaturated with respect to gypsum and celestite (Figure 3.54), but supersaturated with

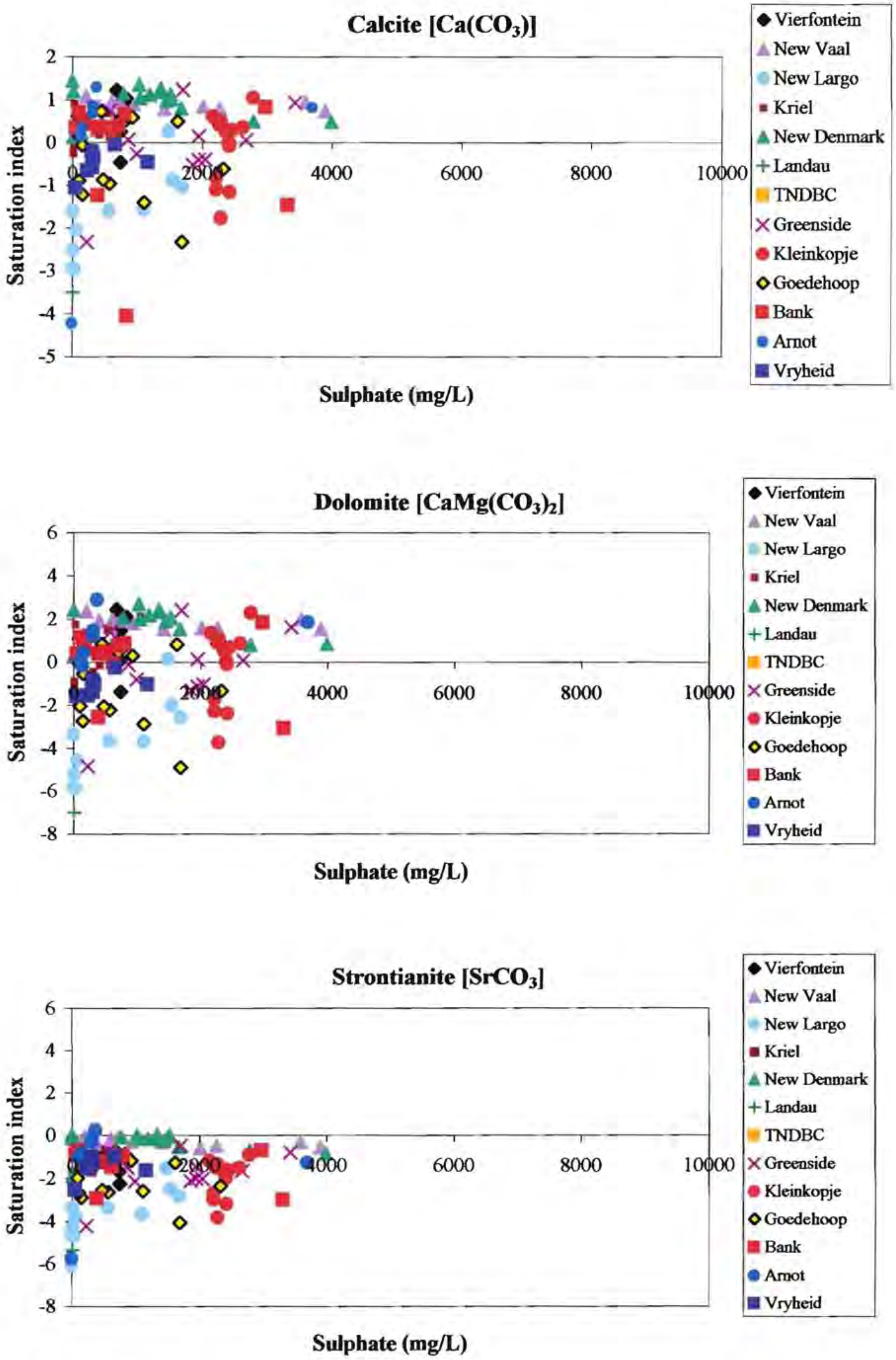

***Figure 3.53:** Saturation indices for calcite, dolomite and strontianite as a function of sulphate concentration for the colliery waters.*

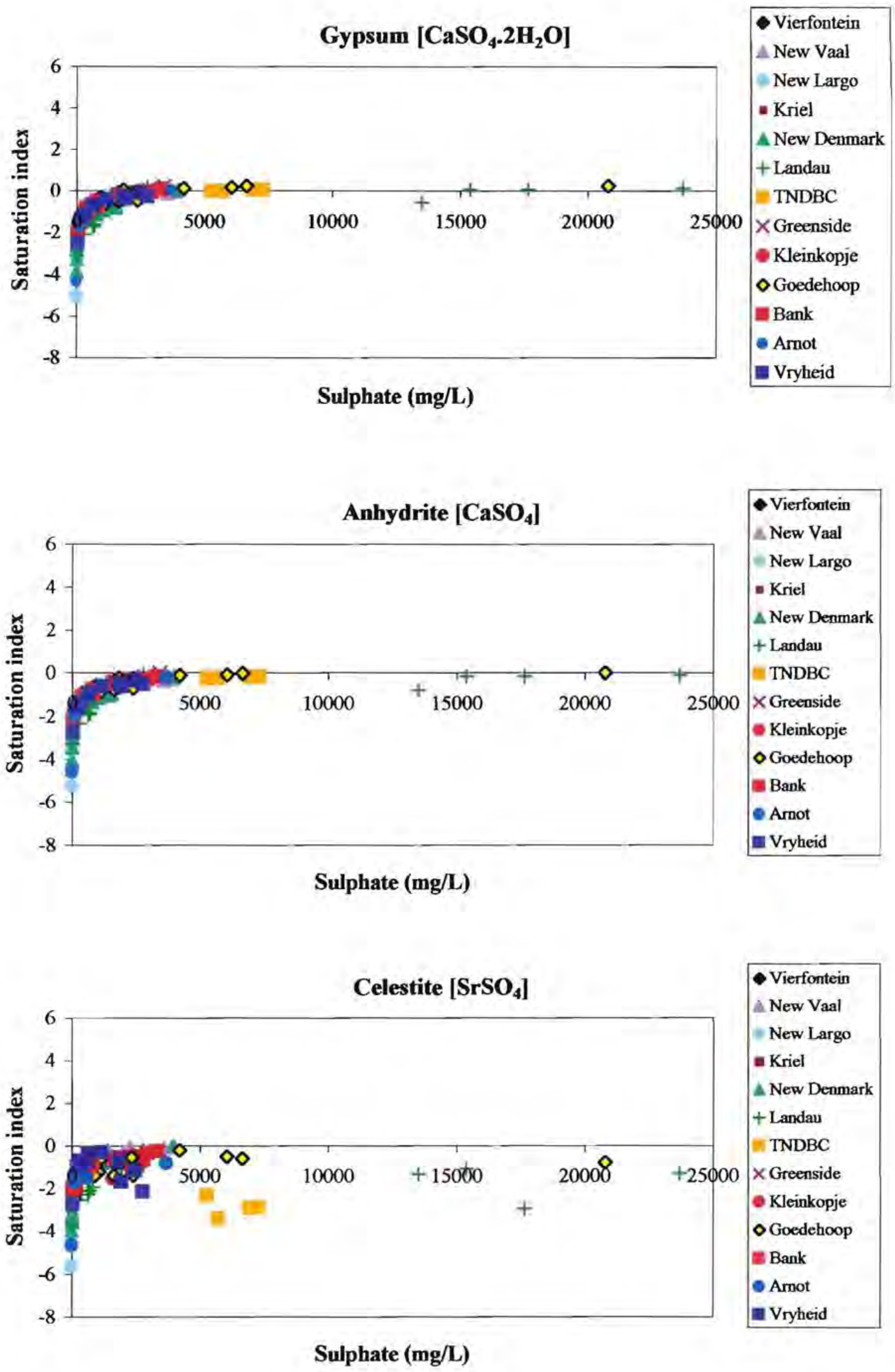

Figure 3.54: *Saturation indices for gypsum, anhydrite and celestite as a function of sulphate concentration for the colliery waters.*

respect to other sulphate minerals, such as barite (Figure 3.59). Many of the mineral saturation indices exhibit interesting relationships when considered for the collection of waters as a whole. These will be discussed in the next section (Section 3.3.4.1).

According to Parkhurst and Plummer (1993), the interpretation of saturation indices requires knowledge of the aqueous model, the mineral stability and stoichiometry, and the kinetics of reactions. For low temperature calculations such as these, the number of minerals for which meaningful saturation indices can be calculated is relatively small. Saturation indices usually are meaningful for carbonate, sulphate and chloride minerals because these minerals tend to react rapidly. Saturation indices for sulphides are useful if the environment is reducing and sulphide is measured. Under conditions where ferric iron can be measured, the saturation indices of ferric hydroxides are meaningful. Saturation indices also are meaningful for aluminium oxides and hydroxides (provided accurate dissolved aluminium data are available), pure silicate phases, and some minerals that contain trace elements. Except for kaolinite, saturation indices for most clays, feldspars, and other aluminosilicate minerals are at best qualitative because of uncertainties in the thermodynamic data and dissolved aluminium measurements (Parkhurst and Plummer, 1993).

Nordström and Alpers (1999) suggest that hydrolysed iron- and aluminium-sulphate minerals, as well as insoluble metal sulphate minerals should be stable in a mining environment. Prime candidates include jarosite, alunite, barite, anglesite, gypsum, and a suite of ferric- and aluminium-hydroxysulphate compounds. The saturation indices of some of the minerals likely to affect the potential of the water to be used in mining-related activities are presented here.

3.3.4.1 Equilibrium trends for calcium, alkalinity, fluoride and sulphate

Calcium and carbonate alkalinity are typically major solutes in the alkaline colliery waters. In most natural waters with near-neutral to alkaline pH, Ca and carbonate alkalinity concentrations are affected by the solubility of calcite [$CaCO_3$]. In these colliery waters the SI values for calcite show an increase over the pH range of 5 – 9 and slight flattening (Figure 3.55). Waters with a pH > 7 generally have calcite SI values > 0, indicating that conditions of oversaturation are typical. The apparent oversaturation with calcite is common in natural aqueous systems and is often attributed to slow precipitation kinetics (Herman and Lorah, 1988; Suarez, 1983).

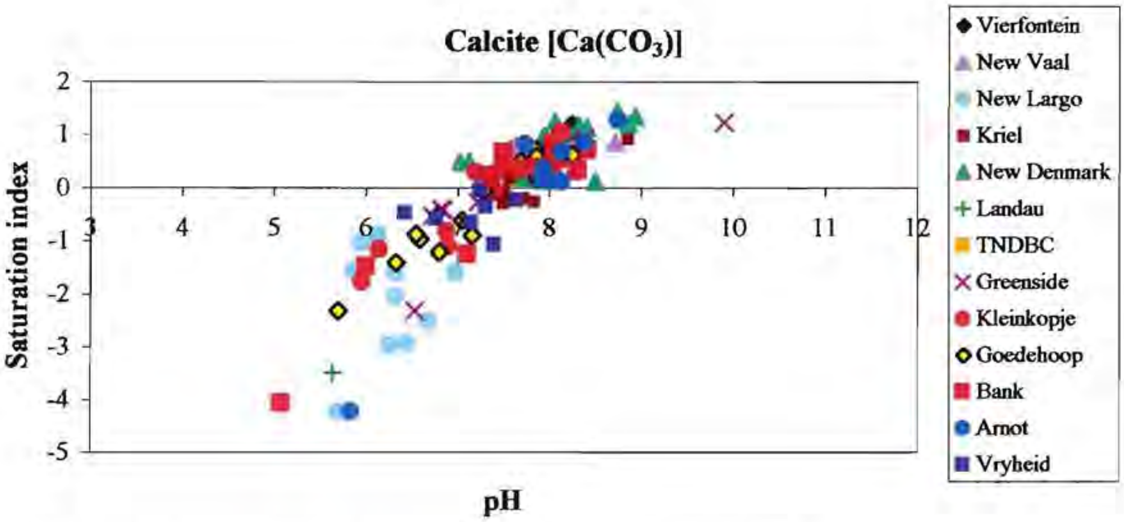

Figure 3.55: *Saturation index of calcite as a function of pH for the colliery waters.*

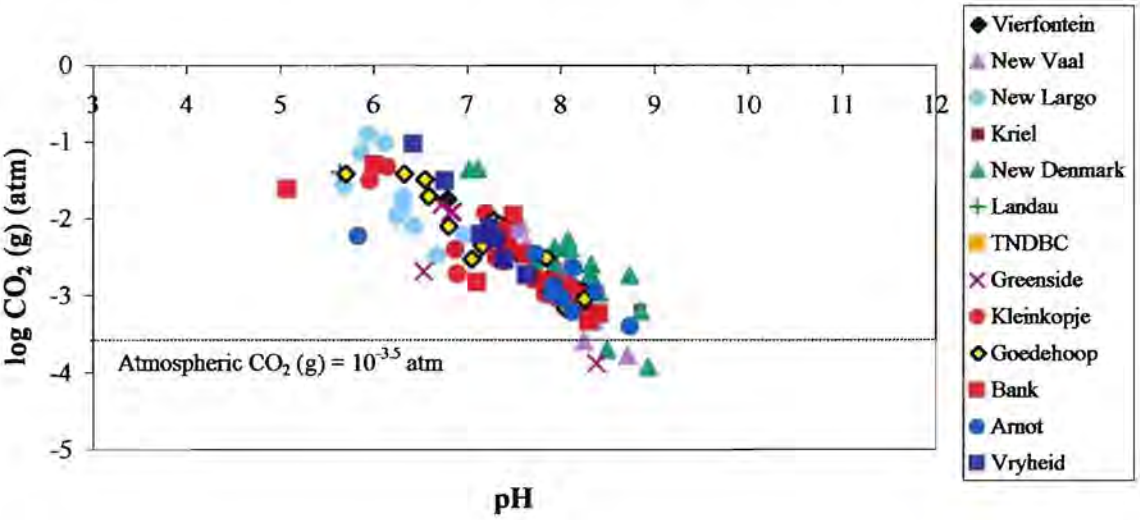

Figure 3.56: *Equilibrium partial pressures of CO_2 (g) as a function of pH for the colliery waters.*

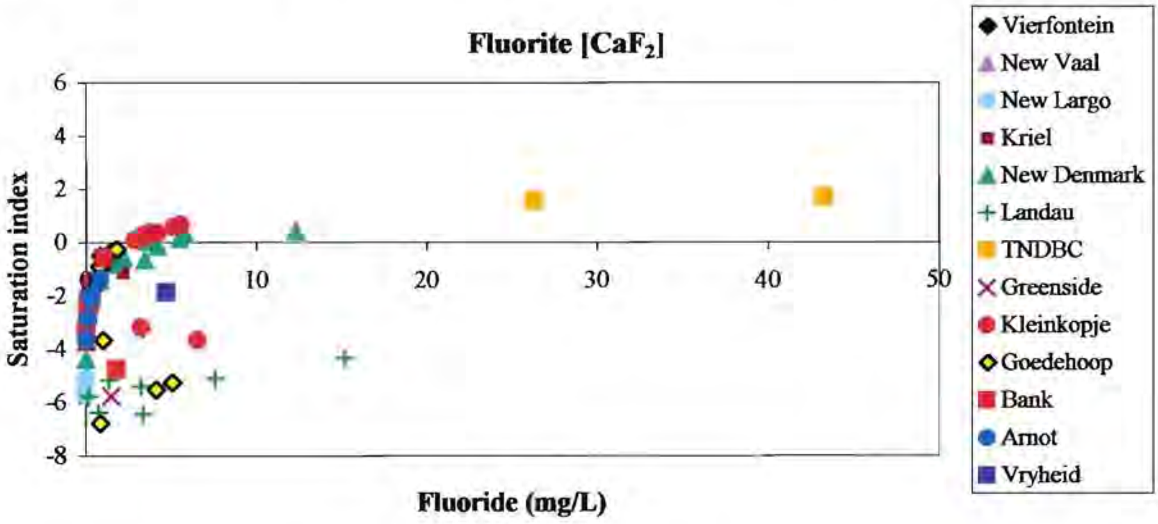

Figure 3.57: *Saturation index of fluorite as a function of the fluoride concentration of the colliery waters.*

The degree of calcite saturation is also related to the solubility of $CO_2(g)$ in solution and the rate of $CO_2(g)$ loss or gain by the solution (Langmuir, 1997). The equilibrium partial pressures were calculated by PHREEQC, based on measured pH and alkalinity values. The results of these show that the colliery waters are oversaturated with $CO_2(g)$ compared to the atmospheric level of $10^{-3.5}$atm, ranging up to levels of $10^{-1.0}$atm. The degree of oversaturation decreases with increasing pH (Figure 3.56). This decrease may be related to the increase in solubility of $CO_2(g)$ in water with increase in pH. In a temperature sensitivity test for oversaturation of CO_2 it was found that for samples of near-neutral pH (i.e pH = 7-8), an increase of 0.135atm was calculated over the temperature range 5°C to 30°C for the log CO_2. In other words, there was an increase in log CO_2 of 0.0054atm/°C.

The dissolution of fluorite [CaF_2] and some layer silicates, such as biotite, can release F. Fluorite is the least soluble F-containing mineral that might be expected to form and limit F concentrations in low temperature systems (Eary, 1999). Values for fluorite in the colliery waters show a pattern that is similar to that observed for gypsum, with an increase from negative values at low F concentrations to values near or above zero at F concentrations greater than about 2mg/L (Figure 3.57). This pattern indicates that fluorite solubility is a reasonably effective control for F concentrations in colliery waters, although conditions of slight oversaturation typically occur.

Note that although the saturation indices recorded for calcite are, for the most part, greater than zero no obvious calcite precipitates were observed in the water. This may be attributed to slow precipitation coupled with insufficient opportunity for samples to equilibrate with atmospheric CO_2. Other possible explanations include pressure effects on the activities of species, variations in calcite stability caused by incorporation of sulphate in the mineral structure, or possibly CO_2 de-gassing during the measurement of pH. The largest contributor to the uncertainty in SI is thought to be some uncertainty in pH. pH measurements were taken at almost all sites and repeated in the laboratory over a few weeks. From Figure 3.58, it can be seen that a strong correlation was observed between those measurements taken in the field and the first laboratory readings ($r_s = 0.95$). Selected data are presented in Appendix 1, where a comparison indicates that the relative standard deviation was less than 5% for most samples.

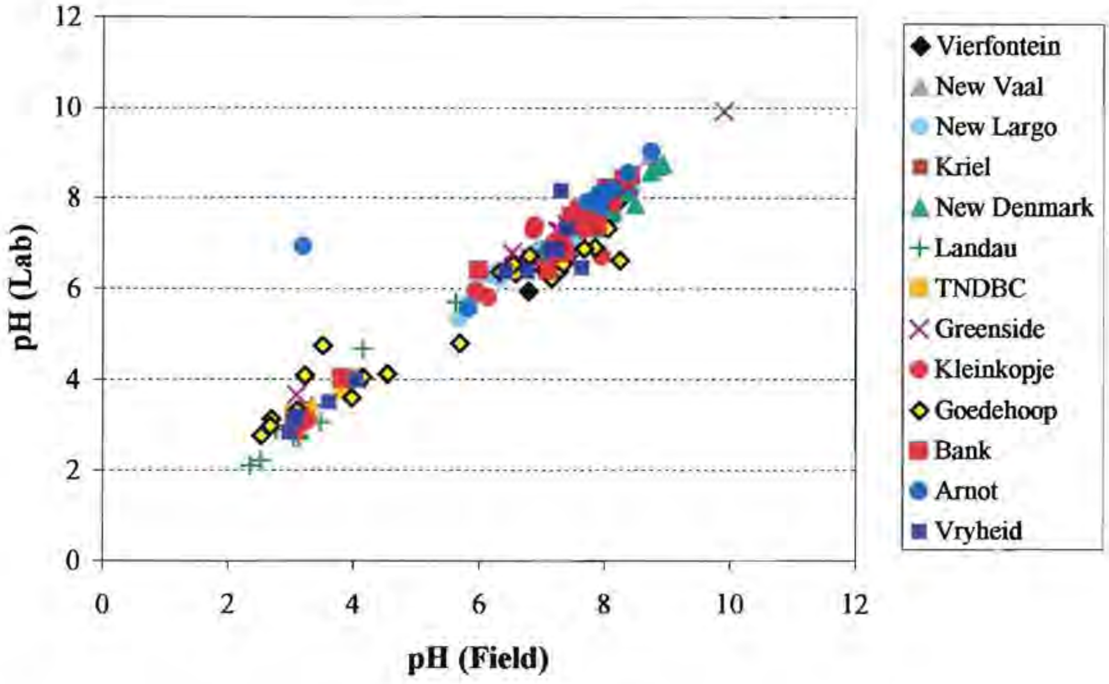

Figure 3.58: *Correlation between measurements of laboratory pH and field pH.*

As we have seen, under both acidic and alkaline pH conditions, SO_4 is typically the major anion solute in colliery waters. This is believed to be the result of both the oxidation of Fe-sulphides after exposure to the atmosphere, as well as evapoconcentration. In many aqueous systems, gypsum [$CaSO_4 \cdot 2H_2O$] solubility may be the only limiting factor for SO_4 concentration (Drever, 1988; Langmuir, 1997). This appears to be true for the colliery waters in that SI values for gypsum increase from negative values at low SO_4 concentrations to values that approximate zero with increasing SO_4 concentration (Figure 3.54). This result combined with the flattening of the SI curve with increasing SO_4 concentration could indicate that gypsum solubility provides an upper limit to SO_4 concentrations in these waters. This, however, is probably not the case as SO_4 is generally present in much higher concentrations then Ca. Thus, the combination of high sulphate concentrations ($\geq$ 2000mg/L) and gypsum saturation will limit Ca and not SO_4.

3.3.4.2 Equilibrium trends for barium and strontium

Barium and Sr are typically present in low concentrations in the colliery waters. Saturation indices show that most of the waters are slightly oversaturated with respect to barite [$BaSO_4$]and undersaturated with witherite [$BaCO_3$] (Figure 3.59). The tendency for oversaturation with barite increases slightly with increased Ba concentration, but SI values generally remain between 0 and 1. The flattened trend in SI values for barite indicates that barite may be a reasonable solubility control for representing Ba concentrations in colliery waters with excess SO_4 relative to alkalinity. Barite is generally thought to be a primary control for Ba concentrations in low temperature systems (Hem, 1985; Jenne *et al.*, 1980). In strongly alkaline mine waters, conditions of saturation with witherite may be reached eventually as a result of increased concentration through evaporation, although the existing waters are clearly undersaturated.

Most natural waters are undersaturated with respect to celestite and strontianite (Hem, 1985). Strontium concentrations in the mine waters range from 0.01 to 9.29mg/L. SI values for celestite [$SrSO_4$] and strontianite [$SrCO_3$] indicate that conditions of undersaturation prevail (Figure 3.60). It is interesting to note that a similar trend towards equilibrium to that observed for gypsum, is seen for celestite. As the concentration range of Sr in solution is < 10mg/L, and that of SO_4 is up to nearly 25 000mg/L, it is possible then that celestite precipitation will provide a likely upper limit to Sr solubility.

3.3.4.3 Equilibrium trends for aluminium

The behaviour of aluminium as reflected in the saturation indices of some aluminium-bearing minerals can be seen in Figure 3.61. A plateau in the SI values for microcrystalline gibbsite [$Al(OH)_3$] and kaolinite [$Al_2Si_2O_5(OH)_4$] is seen at pH values above about 4.5. At pH values above 4.5, solubility equilibrium is apparently reached and seems to be maintained, for the most part, at all higher pH values. This relationship, for gibbsite, is seen more clearly in Figure 3.62, where at lower pH values, a distinct deviation from this trend is observed.

Additional research into this deviation is currently being conducted at the University of Stellenbosch. From this work, it would appear that Al-organic, or Al-coal, complexes and jurbanite or related more soluble basic Al-sulphates (such as basaluminite) are responsible for

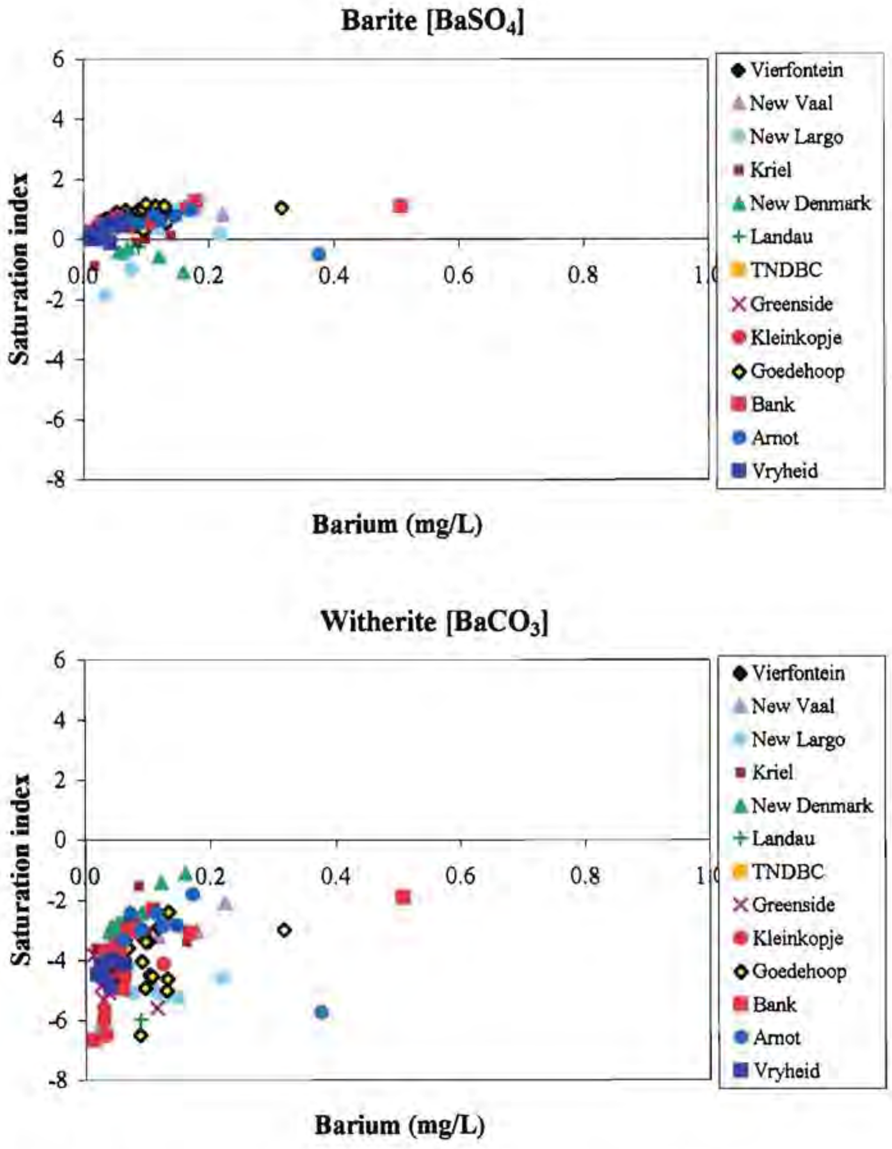

Figure 3.59: *Saturation indices for barite and witherite as a function of barium concentration for the collierv waters.*

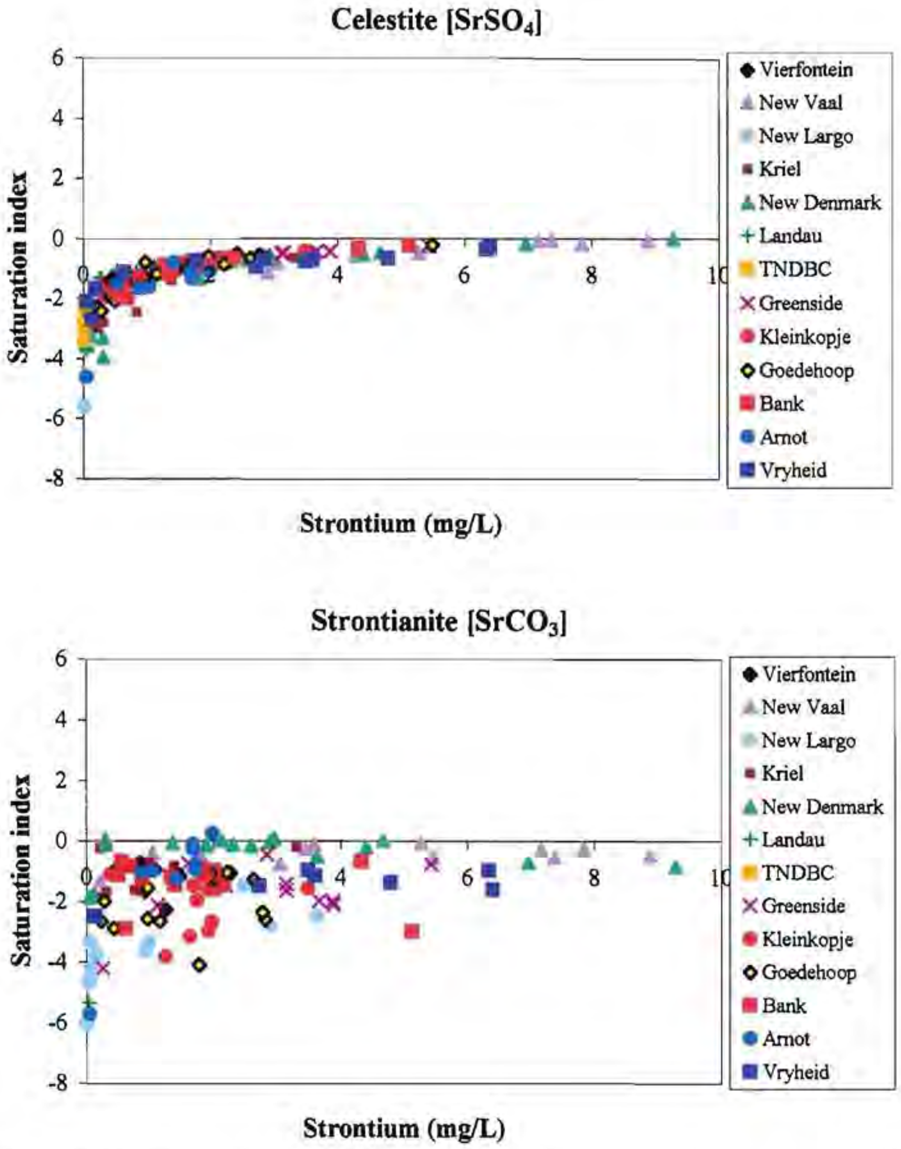

Figure 3.60: *Saturation indices for celestite and strontianite as a function of strontium concentration for the colliery waters.*

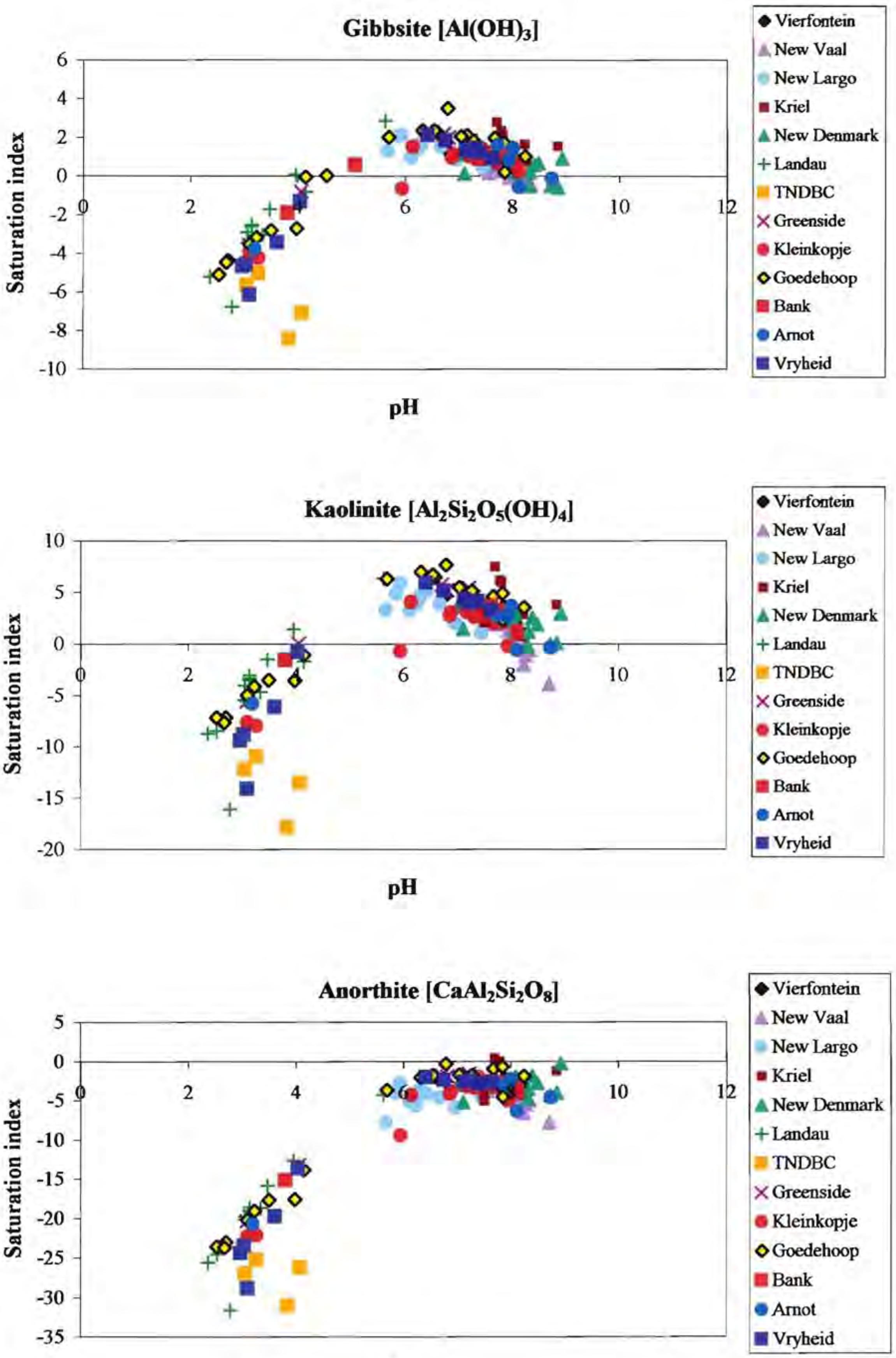

Figure 3.61: *Saturation indices for selected aluminium-bearing minerals as a function of pH for the colliery waters.*

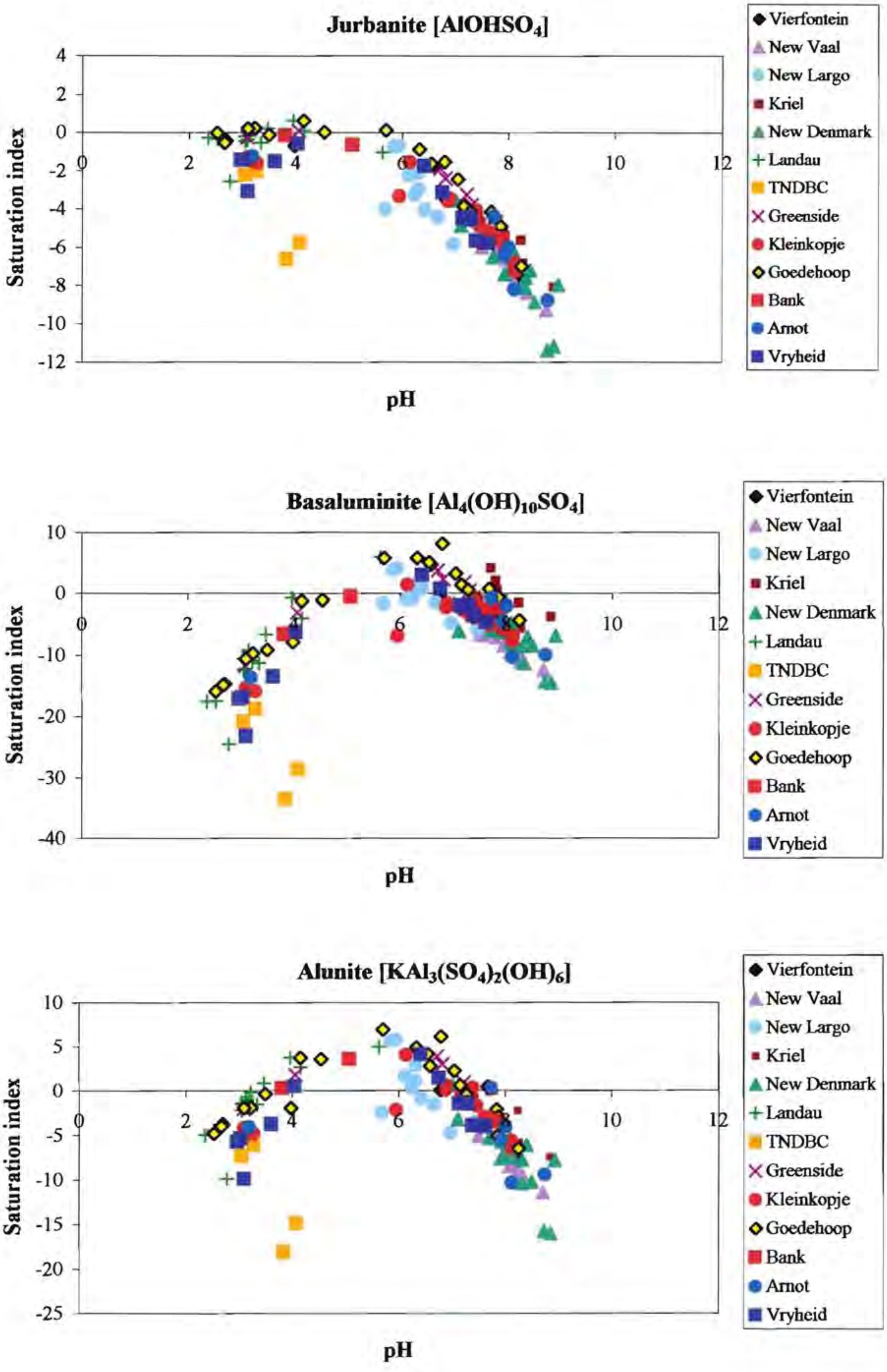

Figure 3.61 cont.: *Saturation indices for selected aluminium-bearing minerals as a function of pH for the colliery waters.*

the shallower trendline at low pH. At these low pH's, the aluminium is substituted for by hydrogen ions. Furthermore, experiments indicate that the same trend appears regardless of whether Al-saturated or Al/Fe-saturated coals are used, although a different amount of sulphate was measured as compared to that expected in acid mine drainage.

In a similar discovery, using water samples over a wide range of pH, Al and sulphate concentrations, Nordström and Ball (1986) showed that two trends are apparent, with a change in slope close to the first hydrolysis constant for Al ($pK_1 = 5.0$) as shown in Figure 3.62. When the pH is significantly less than pK_1 then hydrolysis is insignificant; the Al is little affected by geochemical reactions, and it travels in surface water systems as if it were a conservative constituent. Once the pH of the water reaches the pK_1, hydrolysis causes the Al to become insoluble and precipitate. They also reported that the rate of aluminium leaching from common minerals at low pH is not generally fast enough relative to the flow rate of surface and ground waters to reach equilibrium with gibbsite. Furthermore, gibbsite and kaolinite solubility is very high at low pH and it becomes an unstable or metastable phase with respect to other aluminous minerals, especially in the presence of high sulphate concentrations (Nordström, 1982).

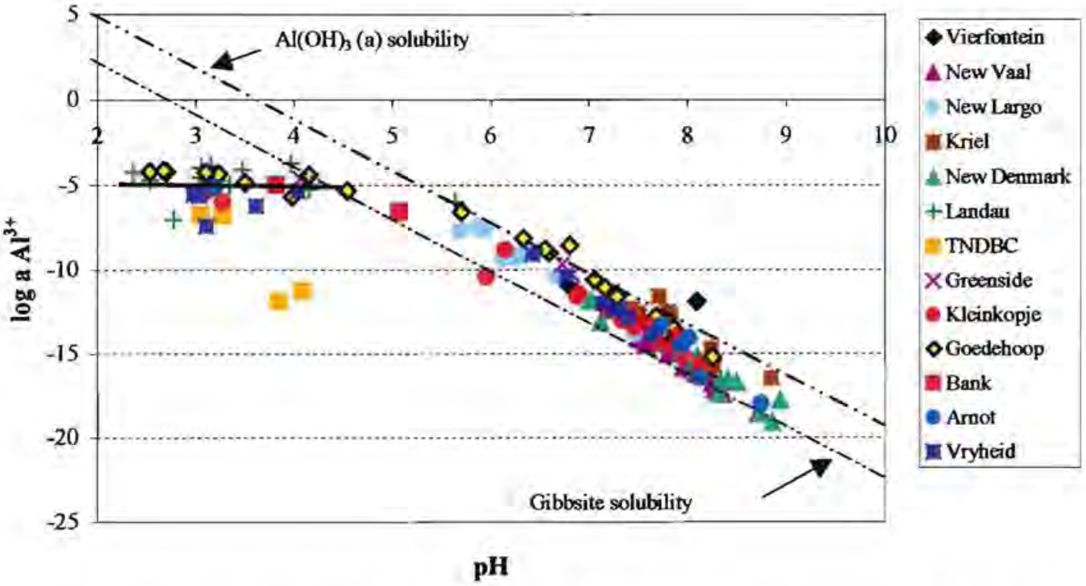

Figure 3.62: Plot of the log Al^{3+} activity against pH for the colliery waters. Dashed lines show equilibrium solubilities of microcrystalline and amorphous $Al(OH)_3$ to which the data fits well, suggesting an equilibrium solubility control.

According to Nordström and Alpers (1999), when acid mine drainage is diluted by neutral surface waters, the pH and aluminium concentrations eventually reach the gibbsite solubility curve and aluminium concentrations become controlled by one of 3 possibilities: (1) solubility of a solid phase, such as gibbsite; (2) a surface coating control with a stoichiometry similar to gibbsite; or (3) a common aluminosilicate mineral with an exchange ratio of Al^{3+} to H^+ of 1:3. As already mentioned, a pH of 5 is also equal to the pK_1, the negative logarithm of the first hydrolysis constant for aluminium, and without hydrolysis the precipitation of hydrolysed aluminium would not be possible. In addition, Hem and Robertson (1990) have shown that the rate of aluminium hydrolysis increases as pH values rise to about 5 so that the hydrolysis kinetics for dissolved aluminium favour the tendency towards equilibrium.

Since gibbsite and kaolinite are not stable in acid sulphate waters, it has been suggested by Nordström (1982) that the mineral jurbanite [$AlOHSO_4$] may control aluminium concentrations. Fillipek *et al.* (1987) indicate that at low pH, it is also possible that water may tend towards equilibrium with alunite [$KAl_3(SO_4)_2(OH)_6$]. In this study, Figure 3.61 shows that most waters having a $pH > 4$ are saturated or supersaturated with respect to gibbsite and kaolinite, whereas the lower pH waters are undersaturated with respect to these minerals. The waters at almost all of the sites in the drainage area are undersaturated with respect to the major plagioclase feldspars, both anorthite [$CaAl_2Si_2O_8$] and albite [$NaAl_2Si_3O_8$]. Some of the waters at $pH < 4$ appear to be close to equilibrium or slightly supersaturated with respect to jurbanite and alunite, and highly undersaturated with respect to basaluminite [$Al_4(OH)_{10}SO_4$]. Nordström and Ball (1986) found that acid streams with $pH < 4.6$ transported aluminium in a conservative manner and any resemblance to mineral solubility was coincidental.

3.3.4.4 Equilibrium trends for iron

Comparable diagrams to those for aluminium, are shown for iron in Figure 3.63. Apparent supersaturation with respect to ferric hydroxide or ferrihydrite occurs at pH values above about 4. The supersaturation may possibly be explained by substitution of sulphate for hydroxide ions in the ferrihydrite and the formation of a more soluble, schwertmannite-like phase. Schwertmannite [$Fe_8O_8(OH)_6(SO_4)$] was described by Bigham *et al.* (1990) and is discussed in more detail, later. The apparent supersaturation with respect to ferric hydroxide

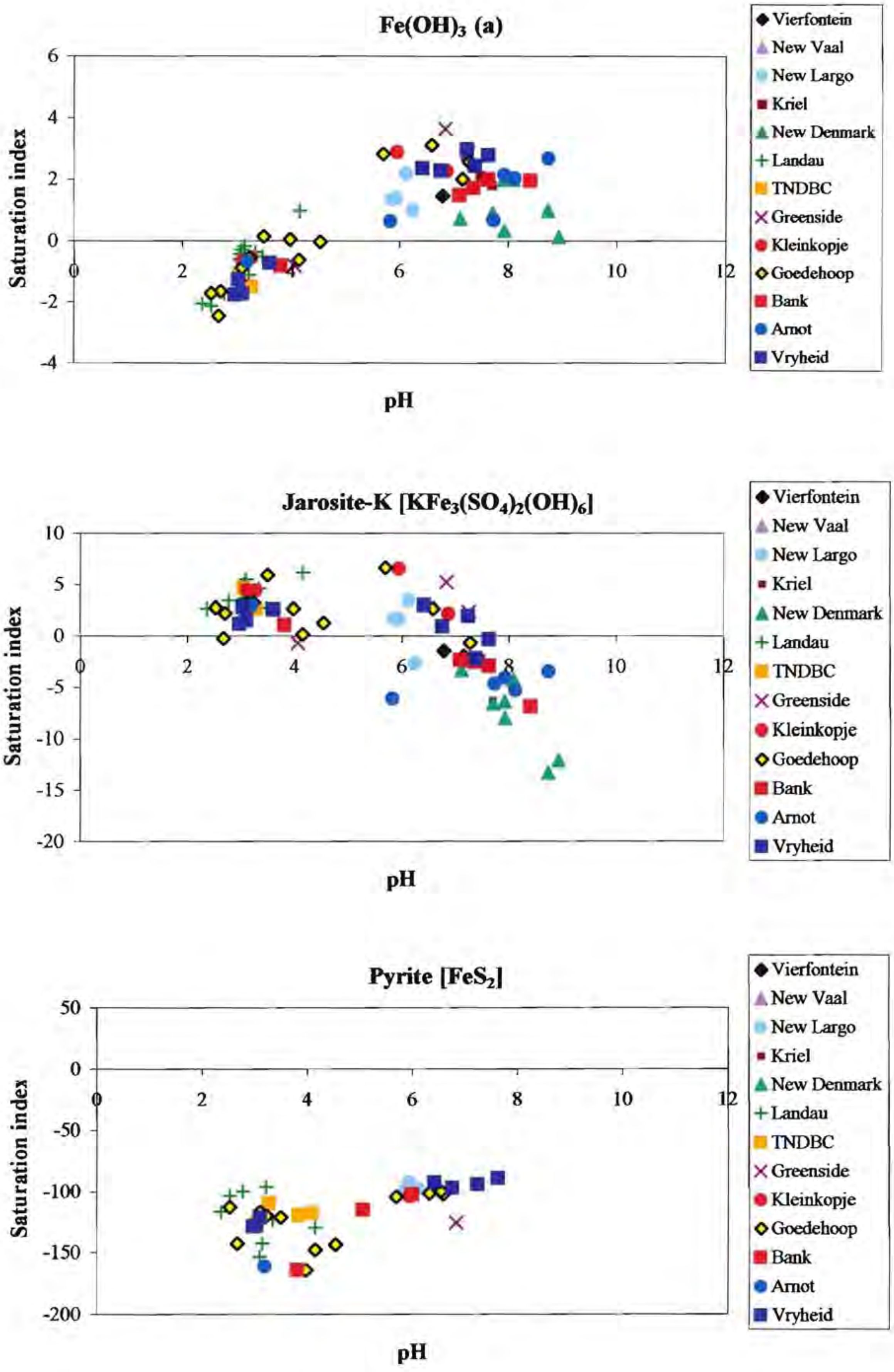

Figure 3.63: Saturation indices of selected iron-bearing minerals a function of pH for the colliery waters.

might also be explained by the formation of colloidal iron particles that were not filtered out by the 0.2μm pore size membranes prior to conducting solution analyses, by incorrect identification of the solid phase, or by sampling artifacts.

The stoichiometry of the phase controlling the solubility of Fe can be predicted from an appropriate ion-activity plot. If pure ferric hydroxide were controlling the solubility of ferric iron, the reaction

$$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$$

and its log equilibrium constant expression

$$\log K = \log Fe^{3+} + 3pH$$

would indicate that a plot of Fe^{3+} activity versus pH should have a slope of –3. The observed slope of –3.2 is fairly consistent with solubility control by pure ferric hydroxide having a molar Fe:OH ratio of 1:3 (Nordström, 1991).Bigham (1994) reported that schwertmannite is associated with mine drainage ranging in pH from about 2.5 to 6, and is most commonly associated with mine effluents with pH from 3 to 4. Bigham (1994) also noted that ferrihydrite is associated with mine drainage in the pH range of about 5 to 8. Therefore, the relation at the lower end of the pH scale in Figure 3.64 could be caused by a reaction involving a sulphate-substituted ferric hydroxide, such as schwertmannite.

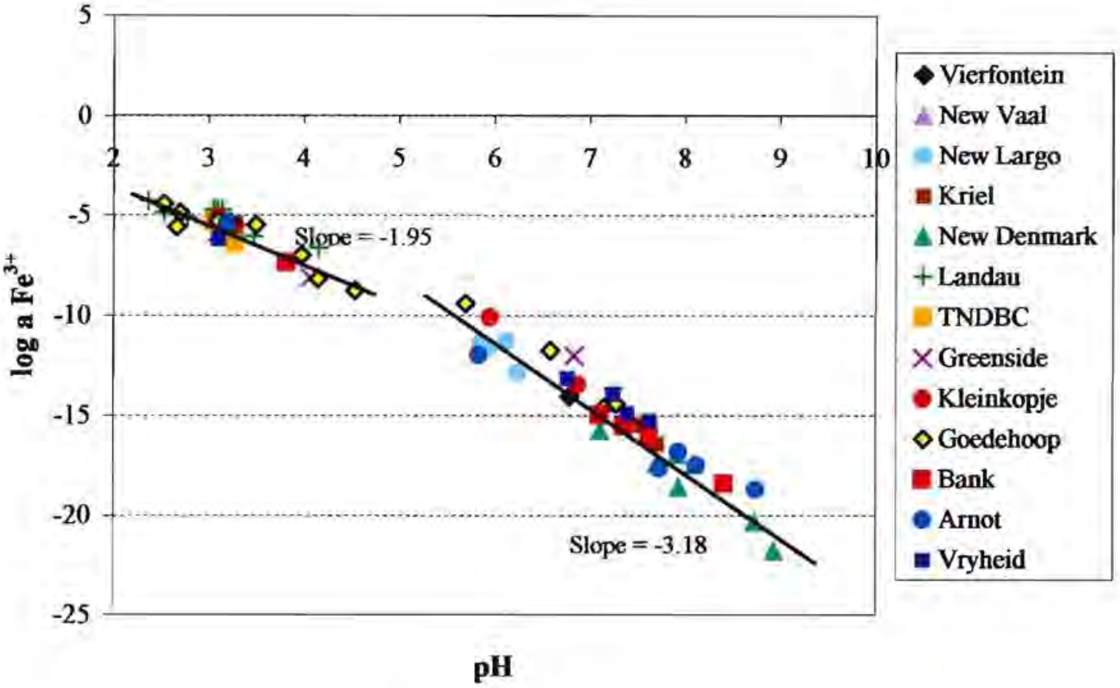

Figure 3.64: *Plot of the log Fe^{3+} activity against pH for the colliery waters. The solid lines show best fit of data between pH of 2 and 5, and pH between 5 and 9.*

On the basis of mineralogical and chemical analyses of ochreous precipitates and associated waters from Ohio mine drainage, Bigham *et al.* (1996) proposed a solubility "window" of log IAP = 18.0 ± 2.5 for schwertmannite dissolution according to the reaction:

$$Fe_8O_8(OH)_{8-2x}(SO_4)_x + (24-2x)\ H^+ = 8\ Fe^{3+} + x\ SO_4^{2-} + (24-2x + 8-2x)/2\ H_2O$$
$$\text{where } 1 \leq x \leq 1.75$$

for which the solubility product would be defined by

$$\log K = 8 \log Fe^{3+} + x \log SO_4^{2-} + (24-2x)\ pH$$

Clearly, the data in this range do not indicate solubility with schwertmannite of the composition reported by Bigham *et al.* (1990), since the expected slope on a plot of log Fe^{3+} vs pH showing schwertmannite solubility equilibrium would be in the range of –2.75 to –2.56. Instead, it suggests the stoichiometry is more likely to represent a sulphate-substituted ferrihydrite, schwertmannite-like phase, or other hydrous ferric oxide with a molar Fe:OH ratio of 1:1.95, such as jarosite [$KFe_3(SO_4)_2(OH)_6$], or a mixture of different iron minerals which precipitate over the pH range represented by the acid sulphate waters, so that the line is not resolvable into one particular reaction.

Consider the reaction

$$KFe_3(SO_4)_2(OH)_6 + 6\,H^+ \;=\; K^+ + 3\,Fe^{3+} + 2SO_4^{2-} + 6\,H_2O$$

and its log equilibrium constant expression

$$\log K \;=\; \log K^+ + 3\,\log Fe^{3+} + 2\,\log SO_4^{2-} + 6\,pH$$

This indicates that a plot of Fe^{3+} activity versus pH should have a slope of –2. The observed slope of –1.95 is therefore more consistent with solubility control by jarosite-K rather than schwertmannite. It is important to reiterate that mixtures of different iron mineral phases are likely to be precipitating from these waters over this pH range and thus the line is not clearly resolvable into any one particular reaction.

Bigham *et al.* (1996) suggested that the discrepancy between observed and calculated slopes in pH vs log Fe^{3+} plots for acid sulphate waters was because the data define at least three slopes corresponding to the precipitation of different minerals over the full pH range examined. Figure 3.65 indicates that those data in the pH range below 3 are influenced by the formation of jarosite-K, those above pH 5.5 by ferrihydrite and those at intermediate pH values by schwertmannite.

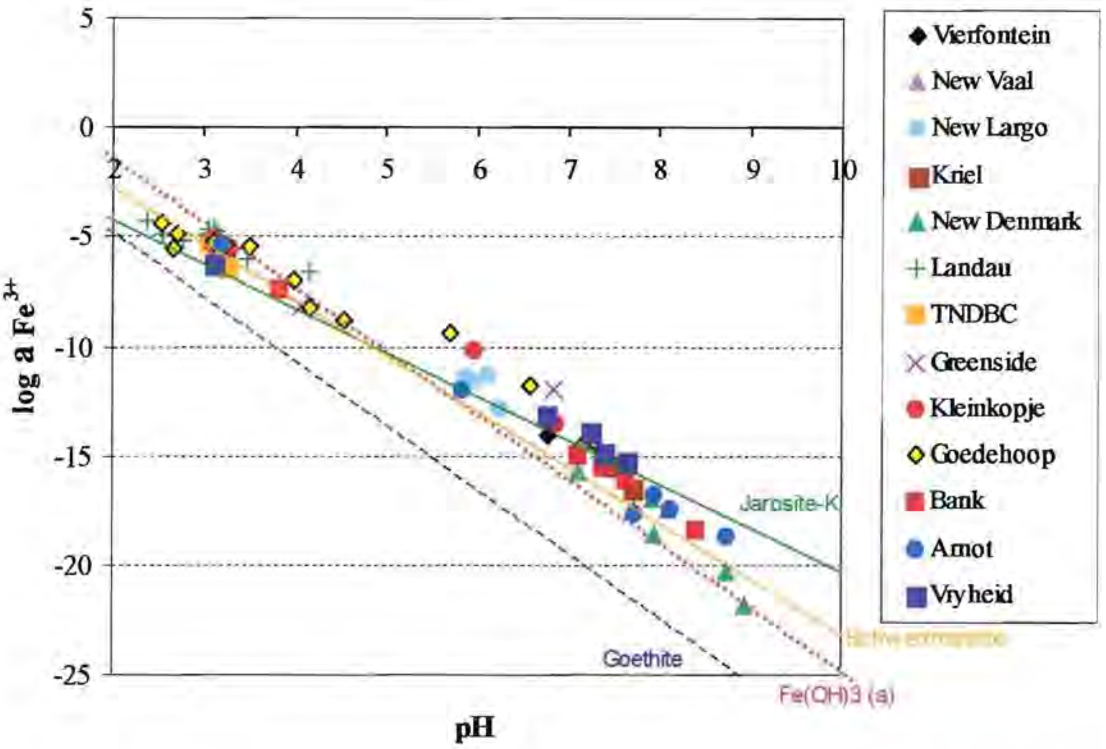

Figure 3.65: *Plot of* Fe^{3+} *activity against pH for the colliery waters with solubility lines for goethite, jarosite-K, ferrihydrite and schwertmannite.*

It is well known that the first hydrolysis constant greatly affects the chemical behaviour and separation of metals (Hem and Robertson, 1990; Baes and Mesmer, 1976; and Rubin, 1974). This explained the tendency in the previous section for the separation of Al ($pK_1 = 5.0$) and could be used here to explain the first separation of Fe^{3+} ($pK_1=2.2$).

3.3.5 Mineral stability patterns: Implications for predicting evolution of colliery waters

By identifying mineral stability patterns, which are consistent for all collieries, it is anticipated that the stage of geochemical evolution of a particular water can be determined.

Al mineral stability:

As shown in Figure 3.61, the waters reach supersaturation with respect to gibbsite (crystalline) at pH ~ 4.5 but become undersaturated again at pH ~ 8 i.e. at low pH, they are undersaturated.

$$Al(OH)_{3\ (crystalline)} + 3H^+ = Al^{3+} + 3H_2O \ldots\ldots\ldots\ldots\ldots \log K_{cg} = 8.11 \qquad [1]$$

Similarly, amorphous $Al(OH)_3$, which is also undersaturated at low pH, reaches equilibrium at pH ~ 6.5, then returns to a state of undersaturation at higher pH.

$$Al(OH)_{3\ (amorphous)} + 3H^+ = Al^{3+} + 3H_2O \ldots\ldots\ldots\ldots\ldots \log K_{ag} = 10.8 \qquad [2]$$

Therefore, depending on the crystallinity the solubility product varies, as does the pH at which the solution becomes supersaturated with respect to gibbsite.

Furthermore, the waters become undersaturated with respect to jurbanite (Figure 3.61) at pH ~ 4.5

i.e. at low pH, they are supersaturated.

$$Al(SO_4)(OH)\cdot 5H_2O + H^+ = Al^{3+} + SO_4^{2-} + 6H_2O \ldots\ldots\ldots\ldots \log K_j = -3.23 \qquad [3]$$

So,

by subtracting [2] from [3],

$$Al(SO_4)(OH)\cdot 5H_2O + 2H_2O = Al(OH)_3 + 2H^+ + SO_4^{2-} + 5H_2O \ldots\ldots\ldots \log K = -14.03$$

Then,

$$\log K = 2 \log H^+ + \log SO_4^{2-}$$

Thus,

$$\log SO_4^{2-} - 2pH = -14.03$$

In conclusion,

jurbanite is eclipsed by $Al(OH)_3$ at $pH_2SO_4 = 14.03$ (Figure 3.66a).

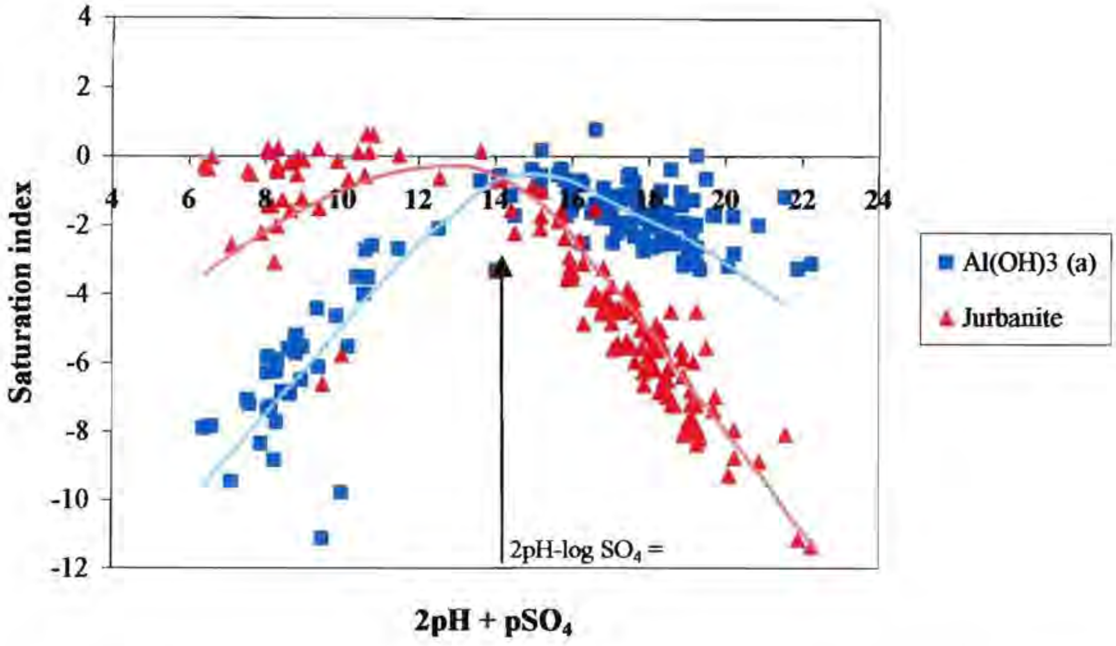

Figure 3.66a: Saturation indices for selected aluminium-bearing minerals in the colliery waters, as a function of 2pH + pSO$_4$. (or 2pH-log SO$_4$)

The reason for apparent solubility equilibrium with respect to jurbanite for acid sulphate waters with pH generally less than 4.5 originated with the publications of van Breemen (1973) and Nordström (1982). Van Breemen (1973) found good agreement between ion-activity products calculated from speciation computations of acid sulphate waters and an unidentified mineral that had the equilibrium stoichiometry of $Al(OH)SO_4$. Nordström (1982), noting that there was a mineral with the same stoichiometry, whose solubility had been measured by Bassett and Goodwin (1949), reduced the solubility data to a solubility-product constant. Many investigators have used this information for chemical speciation modelling and the calculation of saturation indices.

The agreement between the IAP for jurbanite and the K_{sp}, however, should be considered fortuitous and not indicative of solubility equilibrium for the following reasons. Jurbanite is a rare very soluble efflorescent mineral. Bassett and Goodwin (1949) found that it was at equilibrium with a solution containing 15-20 wt% sulphate which would be equivalent to pH values of 0.0 or less, not pH values of 1 to 4.5. Thus, there must be some error in the K_{sp} value reported by Nordström (1982) that shows its stability in pH values of 4 or less, depending on sulphate concentrations. The solubility data of Bassett and Goodwin (1949) should then be re-evaluated using the Pitzer approach (confirmed by Kirk Nordström, pers. comm., 2001). The fortuitous coincidence between the IAP and the K_{sp} most likely reflects the well-behaved correlation of increasing sulphate with increasing Al and with decreasing pH for pH < 4.5, the pH below which Al behaves conservatively (Nordström and Ball, 1986). In other words, for pH values below the first hydrolysis constant for Al (pK = 5.0), Al remains predominantly dissolved and any changes in concentration are caused by dilution in an identical manner as changes in sulphate concentration (Bigham and Nordström, 2000).

Fe mineral stability:

In light of the relationship between $Al(OH)_3$ and jurbanite, it would be interesting to ascertain whether a ferri-hydroxysulphate similarly eclipses ferrihydrite [$Fe(OH)_3$]. The range of log K_{sp} values reported by Nordström *et al.* (1990) for ferrihydrite solubility (amorphous to microcrystalline) range from 3.0 to 5.0 based on several other reported literature studies. For consistency, an amorphous form will be considered here.

$$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O \text{ .... } \log K_{af} = 4.89 \qquad [4]$$

As jurbanite contains 5 waters of crystallization, the equivalent equally soluble Fe-mineral would be fibroferrite [$Fe(SO_4)(OH)\cdot5H_2O$]. Fibroferrite, however, like butlerite, is only stable between pH –1 to 1, which is too low for it to be considered a likely solid limiting Fe solubility in the pH range in this study. Furthermore, as there are no reliable solubility data available for fibroferrite (pers. comm. Kirk Nordström, 2001), one would then have to consider jarosite and/or schwertmannite.

Schwertmannite has the ideal formula $Fe_8O_8(OH)_6SO_4\cdot nH_2O$, which implies an Fe/S molar ratio of 8 and a composition that is intermediate between those of jarosite (Fe/S = 1.5) and the common iron oxides (no S) with which it is generally associated. In fact, the sulphate content is somewhat variable, and natural samples are best described by the formula $Fe_8O_8(OH)_{8-2x}(SO_4)_x\cdot nH_2O$ where $1 \leq x \leq 1.75$ and Fe/S ranges from 8 to 4.6 (Bigham *et al.*, 1996).

Ferrihydrite can sorb enough sulphate to approximate the composition found for schwertmannite (Smith, 1991), making it difficult to distinguish between hydrous ferric oxides with sorbed sulphate and schwertmannite. In addition, jarosites have been produced in the laboratory when the $FeSO_4$ solutions contained Na, K, or NH_4 and an excess of sulphate at pH 2.5. Without these cations, an "amorphous" ferric hydroxysulphate was produced that was indistinguishable from precipitates collected from acid mine waters (Lazaroff *et al.*, 1982, 1985). In light of these complications, a "schwertmannite-like" phase has been used here.

$$Fe(SO_4)(OH) + H^+ = Fe^{3+} + SO_4^{2-} + H_2O \text{ ...... } \log K_s = ? \qquad [5]$$

From Figure 3.63, it can be seen that the waters reach saturation with respect to ferrihydrite at pH ~ 3.5. The spread seen in the data is possibly due to interference from colloids, which passed through the 0.2μm filter, or may be a result of using an "estimated pe" for those waters for which no redox couple was measured.

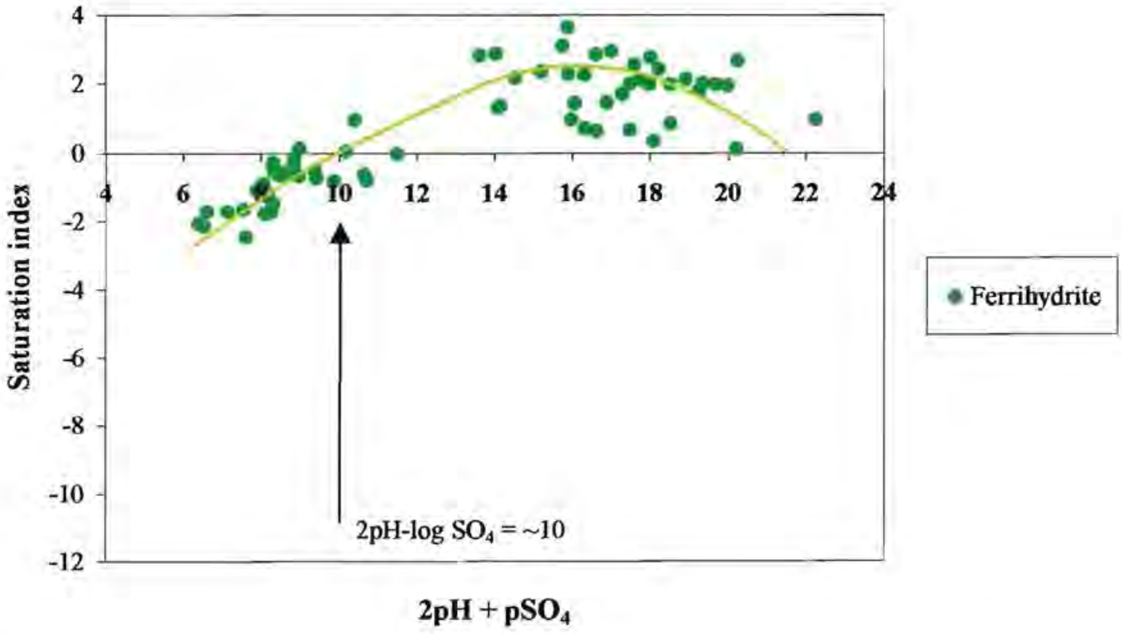

Figure 3.66b: *Saturation index for ferrihydrite in the colliery waters, as a function of 2pH + pSO_4.*

By subtracting ferrihydrite [4] from the "schwertmannite-like" phase [5] we get

$$FeOHSO_4 + 2H_2O = Fe(OH)_3 + 2H^+ + SO_4^{2-} \ldots\ldots\ldots \log K = x - 4.89$$

and the equilibrium constant expression

$$\log K = 2 \log H^+ + \log SO_4^{2-}$$

That is,

$$\log K = \log SO_4^{2-} - 2pH$$
$$= -pH_2SO_4$$

From inspection of Figure 3.66b, we can derive a log K_s for the "schwertmannite-like" phase:

$$pH_2SO_4 = -(x - 4.89)$$
$$10 = 4.89 - x$$

So,

$$\log K_s = -5.11$$

This estimated value falls slightly below the solubility product of schwertmannite indicated by dissolution experiments conducted by Kawano and Tomita (2001). For an average chemical composition of $Fe_8O_8(OH)_{5.9}(SO_4)_{1.05}$ they estimated a log K_s of 7.06 ± 0.09 at 30°C. The value presented by Kawano and Tomita (2001) falls well short of estimates by Yu *et al.* (1999) and Bigham *et al.* (1996). Yu *et al.* calculated a log K_s value of 10.5 ± 2.5 for a composition of $Fe_8O_8(OH)_{4.4}(SO_4)_{1.8}$, and Bigham *et al.* etimated a value of 18.0 ± 2.5 for a composition of $Fe_8O_8(OH)_{4.8}(SO_4)_{1.6}$.

It is important to note that jurbanite and fibroferrite are both very soluble salts, whereas jarosite, ferrihydrite and schwertmannite are insoluble salts (pers. comm. Kirk Nordström, 2001). Therefore, although this may appear to be an effective method for estimating the unknown solubility product of a mineral phase, which may be utilized in geochemical modelling, particularly for acidic waters, it shouldn't be used as such. Nevertheless, it can be seen that the waters conform to a relationship between the saturation index of key minerals (gibbsite, jurbanite, ferrihydrite) and pH (more strictly, pH_2SO_4). This may suggest a unique relationship between pH and SO_4 activity for ALL mine waters, allowing the degree of evolution to be compared between mines. Further investigations are, however, required before any conclusions can be drawn.

3.4 Conclusions

A bimodal distribution occurs in the pH with some collieries being acidic (average pH ~ 3.5) and the others near-neutral (average pH ~ 7.5). Relatively few samples have pH values between 4 and 6 since the pH will be driven toward one mode or the other depending on the relative abundance and extent of weathering of pyrite (FeS_2; acid-forming) and calcite ($CaCO_3$; acid-neutralizing). Most of the collieries exhibit an electrical conductivity (EC) below 4mS/cm. Exceptions include New Denmark (up to 7.01mS/cm), TNDBC (ranging between 6.6 and 10.6mS/cm) and Landau (up to 13.7mS/cm).

A comparison of the samples indicates that there is no dominant cation type in most of the collieries. Exceptions include New Denmark and some of the Arnot waters, which are dominated by Na^+, and New Largo, which is dominated by Ca^{2+}. In terms of the major anions, there is a distinct trend in all the collieries, except New Denmark, Arnot and New Largo, to be SO_4^{2-} dominated. For the most part, the exceptions mentioned do not show any dominant anion (HCO_3^- is a significant anion along with SO_4^{2-}).

Some trends are obvious in the data. Firstly, although TNDBC is not Na-Cl dominated, it does contain similar proportions of these constituents to New Denmark (up to 1890mg/L Na^+ and up to 1013mg/L Cl^-). Secondly, as one moves from west to east across the coalfields the Ca and Mg concentrations decrease first in the Free State and Vereeniging-Sasolburg coalfields, then start to increase as one moves into the Highveld and the Witbank coalfields, from where they start to decrease again into the Vryheid coalfield. It is difficult to ascertain whether similar trends occur in the HCO_3^- concentration since the oxidation of pyrite and subsequent generation of SO_4^{2-}, which consumes the alkalinity, is highly variable. Nevertheless, all but two of the collieries have high SO_4^{2-} concentrations (ranging between 314mg/L and 2267mg/L). The two exceptions, Landau and TNDBC, contain phenomenal SO_4^{2-} concentrations, of up to 23 711mg/L.

Trace element concentrations at Landau, and in many cases at Goedehoop, exceed those at the other collieries, due to the lower pH observed in these waters. Elements of particular interest include Al, Mn, Fe, Cu and Co. Similar concentrations of these elements, are not found in the acidic TNDBC waters, which are only enriched in Cs. Overall, the Al, Fe and Mn concentrations tend to be elevated in the Witbank coalfield only.

Seasonal sampling was carried out and significant differences were observed, at the 95% confidence level, in almost all variables at all the collieries. Furthermore, most variables were significantly different at the 95% confidence limit from one winter (1999) to the next (2000). Furthermore, no major seasonal variations as a result of evaporation are obvious in the colliery waters, though they may be masked by the flushing of salts, due to excessive rain, during the summer sampling season.

Many of the natural waters in the study area show no dominant cation or anion. Most of the samples taken from collieries in the Witbank region are slightly Ca-dominated, whereas the water from the Vryheid district is Mg-dominated. In terms of the cations, the waters from New Largo and New Denmark tend to be enriched in HCO_3^-, whilst that from Arnot is Cl-dominated. The waters taken from Greenside, Kriel and Goedehoop are all enriched in SO_4^{2-}, indicating that they have probably been affected by the mining activities, although a SO_4^{2-} signature may evolve from the weathering of pyrites associated with dolerite intrusions or the Ecca sediments.

Furthermore, comparisons were made with a disused colliery in the Witbank area in which acid mine drainage has manifested itself, and with mines in the coalfields of the Damodar River basin (India) and the Sydney coalfield (Australia) in which calcite dissolution has invariably neutralized the acid produced by pyrite oxidation.

The waters show different speciation depending on whether they are acidic, or near-neutral. At lower pH, the major cations (i.e. Na, Ca, Mg, Al and Fe) tend to form complexes with sulphate, whereas at near-neutral pH, hyroxide complexing is more prevalent.

The electrical conductivity and hardness correlate positively with SO_4 concentration, implying that they are both good indicators of mining impacts. The correlation between hardness and SO_4 suggests that an affinity exists in the colliery waters between Mg and Ca, and SO_4. No correlation was evident between Na and SO_4, although a weak correlation exists between Na and HCO_3. For the most part, solution concentrations of SO_4 exhibit coherence with those of Ca and Mg while HCO_3 concentration exhibits coherence with that of Na. In addition, some coherence between pH and Fe (III) and between EC and Fe (II) was found, as well as some form of interdependence between Co, Ni, and Zn, but not Cu.

The SI values for calcite show an increase over the pH range of 5 – 9, with supersaturation being reached at a pH of about 7. Furthermore, the waters are oversaturated with $CO_2(g)$ compared to the atmospheric level of $10^{-3.5}$atm, ranging up to levels of $10^{-1.0}$atm. As dissolved sulphate increases the colliery waters approach sulphate mineral saturation. Gypsum SI values increase from negative values at low SO_4 concentrations to values that approximate zero with increasing SO_4 concentration. Saturation indices show that most of the waters are slightly oversaturated with respect to barite and undersaturated with respect to witherite and strontianite. Although undersaturated, celestite shows a similar trend towards equilibrium, to that observed for gypsum. This indicates that both are factors limiting the SO_4 concentration.

Most waters having a pH > 4 are saturated or supersaturated with respect to gibbsite and kaolinite, whereas the lower pH waters are undersaturated with respect to these minerals. Both anorthite and albite are undersaturated at almost all sites. Some of the waters at pH < 4 appear to be close to equilibrium or slightly saturated with respect to jurbanite and alunite, and highly undersaturated with respect to basaluminite. Apparent supersaturation with respect to ferric hydroxide or ferrihydrite occurs at pH values above about 4. At lower pH, iron mineral solubility is most likely to be controlled by jarosite-K. It is possible that mixtures of different iron mineral phases are likely to be precipitating from these waters.

All waters conform to one relationship between the saturation index of key minerals (calcite, gibbsite, jurbanite, ferrihydrite) and pH (more strictly, pH_2SO_4). This suggests a unique relationship between pH and SO_4 activity for all mine waters, allowing the degree of evolution to be compared between mines.

CHAPTER 4

Geochemistry and mineralogy of the Ecca sediments

4.1 Introduction

One of the main objectives of this study is to determine the extent to which the surrounding rock, specifically the coal and shales, affects the composition of the water. Furthermore, the author wanted to ascertain whether these water-rock interactions could be used to predict the primary processes (i.e. acidification or neutralization) responsible for the characterization of a particular water body, and as an indication of whether this condition is sustainable. In light of this, sections of selected borehole cores were sampled at four Anglo Coal collieries. The collieries sampled include New Vaal, Kriel, Goedehoop and New Denmark. Extensive X-ray fluorescence (XRF) and X-Ray diffraction (XRD) was performed on the samples, in order to model the water-rock interactions using NETPATH. This chapter presents an overview of the geochemistry and mineralogy of the sediments, so that the interaction between the water and sediments can be used to better understand the geochemical nature and origin of the waters.

4.2 Geology of regional coalfields

4.2.1 Free State

The Free State coalfield stretches from the Vaal River in the north to Theunissen in the south. The coal zone is between 25 and 50m thick and occurs at a depth of 50-100m in the north and 320-360m near Welkom. It contains the Bottom and Top Seams in the north (Gilligan, 1986) whilst in the south, Stavrakis (1986) distinguished two additional seams, viz. a Middle Seam and a seam directly above the Dwyka tillite, which he called the "Dwyka Seam". These additional seams can probably be ascribed to seam splitting.

The coal seams

Distribution of the coal is determined by the pre-Karoo topography; the Bottom Seam is more widely distributed than the Top Seam, which is more patchy. At Vierfontein the Top Seam is encountered approximately 85m from surface. In the north the Bottom Seam is some 2.5m thick, but in the south it may reach a thickness of 8m; the Top Seam is generally less than 2m thick. Both seams are in fact coal zones and are frequently interlaminated with either mudstone or sandstone. Dolerite sills, up to 150m in thickness, affect the coal seams in places (Barker, 1999; Snyman, 1998). Stavrakis (1986) estimated that up to 40% of the coal resources in this field have been affected by these intrusions. The coal is generally dull and rich in mineral matter.

In 1985 Vierfontein Colliery supplied 1230 kt of coal to Eskom by means of pillar extraction, but production ceased in 1988. At present no coal is produced from the Free State coalfield. The significant factors which could hinder development of new mines are: dolerite which has rendered up to 50% of the coal resources in the Free State unmineable; and the relation of seam depth to coal seam thickness with respect to the opencastable potential of the region. The coals are too thick in some cases to mine economically underground (Snyman, 1998; Barker, 1999).

4.2.2 Vereeniging-Sasolburg

At present only two mines are operating in this field, viz. the Sigma and New Vaal Collieries (Figure 4.1). Typical stratigraphic columns from this coalfield are shown in Figure 4.2. The coal zone in this coalfield is about 40m thick and contains three coal units:

- No. 3 Seam, or No. 3 Lower and Upper Seams (Top Seam),
- No. 2 Seam, or No. 2A and 2B Seams (Middle Seam, or Lower Middle and Upper Middle Seams), and
- No. 1 Seam (Bottom Seam).

Many of the mines, which operated in this coalfield have closed down. As in the Free-State coalfield, the significant factors which could hinder development of new mines are: dolerite which has rendered up to 50% of the coal resources unmineable; and the relation of seam depth to coal seam thickness with respect to the opencastable potential of the region. In some cases, the coals are also too thick to mine economically underground (Barker, 1999).

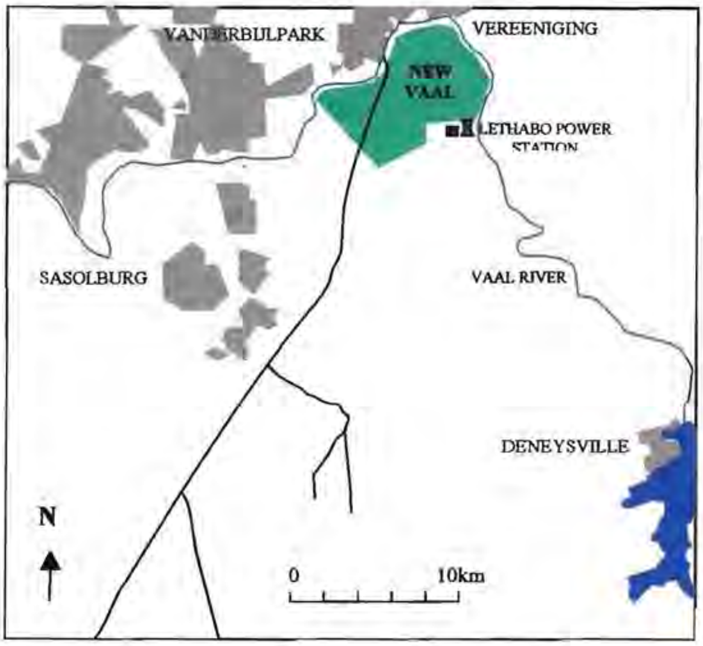

Figure 4.1: *Vereeniging - Sasolburg coalfield, showing location of New Vaal Colliery (After Barker, 1999).*

The coal seams

The top coal unit comprises the No. 3 Seam and the Coal Marker Seam. On its own the Marker seam is not mineable. In places the Top Seam is about 130m from surface and is generally about 5-7m thick. The Top Seam is a poor quality coal interlaminated with carbonaceous mudstone towards the top of the seam zone. A 12-15m section of mudstone separates the Top from the Middle Seam. The Middle Seam has a maximum width of just over 10m and is split. The middle coal unit consists of the No. 2A and 2B Seams and their correlates (each up to 8m thick). The lower coal unit varies in thickness between 0 and 5m with an average of 3m. In places the No. 1 Seam is split into up to three benches by sandstone partings. All the seams consist predominantly of dull coal and are not amenable to dense medium beneficiation (Barker, 1999; Snyman, 1998).

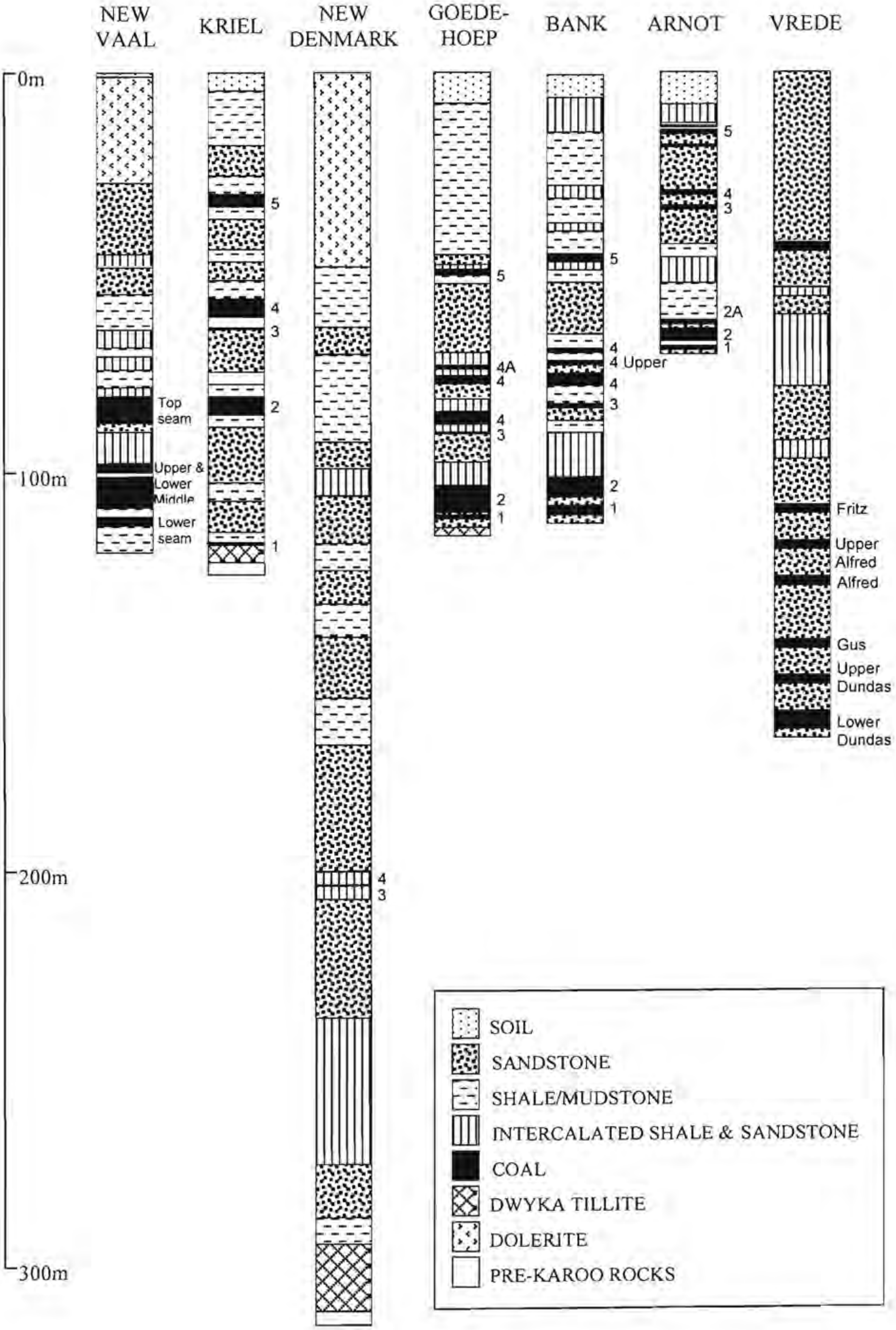

***Figure 4.2:** Generalized stratigraphic columns for selected collieries in the study area.*

4.2.3 Highveld

The Highveld Coalfield extends from the Smithfield basement ridge southwards to beyond Standerton (Figure 4.3). Its eastern boundary is formed by a straight line through Hendrina, Davel and Morgenzon (Jordaan, 1986). It covers an area in excess of 11M hectares. Until the capacious coal-fired powers stations of Matla (3600MW) and Kriel (3000MW) were built in the mid-1970's, this coalfield lay virtually dormant. In 1976 the SASOL Colliery conurbation of four mines (now at least seven) was established. This was followed by the New Denmark Colliery, which was established in 1982 (Barker, 1999).

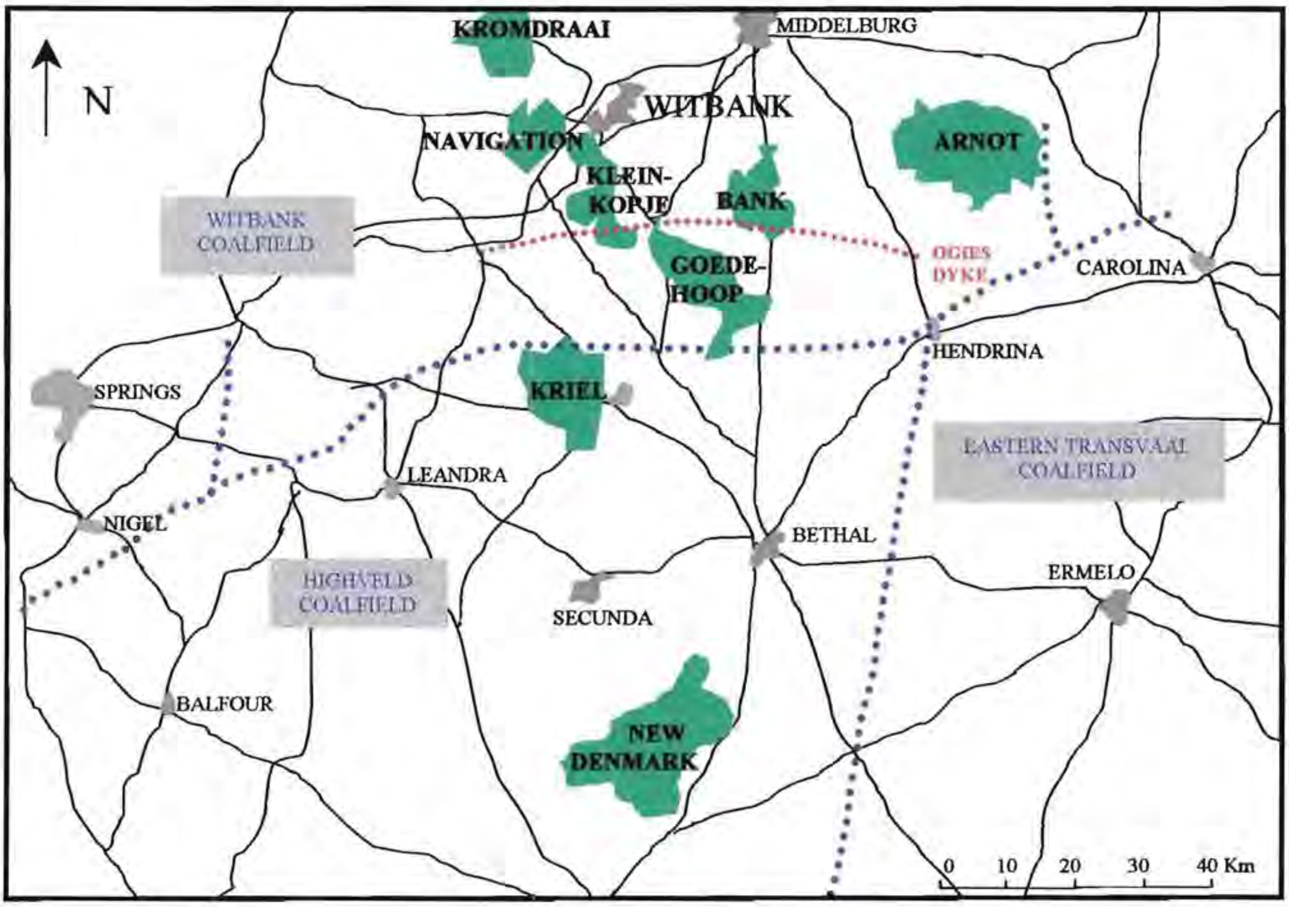

Figure 4.3: Highveld and Witbank coalfields, showing location of the New Largo, Kriel, New Denmark, Landau (Navigation + Kromdraai), TNDBC, Greenside, Kleinkopje, Goedehoop, Bank and Arnot collieries (After Barker, 1999).

The coal seams

There are five seams in this field, numbered from the No. 1 Seam at the base to the No. 5 Seam at the top. (Figure 4.2). The lower two coal seams, however, are absent over the southern and eastern parts of the coalfield, and the parting thicknesses between the seams are more variable than in the Witbank field, though the structure of the seams is similar. The No. 4 seam, like its Witbank counterpart, is divided into an Upper and Lower Seam. According to Barker (1999), both are widely developed but it is the Lower, No. 4L, which is the prime target of this field. Dolerite sills and dykes are also much more common than in the Witbank field, with the concomitant structural complications and devolatilization of the coal (Snyman, 1998).

The Nos. 1, 3 and 4A Coal Seams are thin and discontinuous; the No. 4 Upper Seam is generally also thin and of low grade. The No. 4 Seam is laterally continuous and is economically the most important. The No. 2 Seam varies from 1.5 to 4m in thickness where it is laterally continuous, but locally in the west and northeast it may be up to 8m thick. It consists mainly of dull coal. The average thickness of the No. 4 Seam is 4m, but it varies from less than 1m up to 12m. Shale intercalations are common in the upper part of the seam, which consists mainly of dull coal (Snyman, 1998).

The No. 4 Upper Seam only reaches a mineable thickness in the western part of the field, where its thickness varies between 1.5 and 3.4m, averaging about 2m. The parting between the No. 4 Upper and No. 4 Seam is thin (1-5m), which enhances the danger of collapse of the interseam parting where both seams are mined (Jordaan, 1986). The No. 5 Seam, present over most of the area, only attains a mineable thickness in the northern and western parts of the field. It consists mainly of bright coal, but does not have coking potential (Snyman, 1998).

In general the *in situ* coal qualities are lower in the Highveld seams than those in the Witbank Coalfield and for export purposes will have to be considerably beneficiated. Furthermore, all the mines in this field have encountered mining development problems due to dolerite intrusions (Barker, 1999). Both sills and dykes are present in numbers throughout the basin. Sills have probably caused the most significant regional disturbances and destruction of coal, whereas on the mine scale, dykes are a constant sources of seam disturbance where they are associated with not only seam destruction by burning (Hagelskamp, 1987) but vertical movements as well as geotechnical problems. The latter include poor hanging wall conditions and groundwater on occasions.

Production from the Kriel and Matla collieries is supplied to the adjacent power stations, Kriel and Matla respectively. Coal from the New Denmark colliery is supplied to the Tutuka Power Station. Apart from the opencast section at Kriel Colliery, coal in the other cases is mined mainly by bord-and-pillar, longwall and shortwall methods.

4.2.4 Witbank

The Witbank Coalfield extends from the Brakpan / Springs area in the west to Belfast in the east and covers an area in excess of 568 000 ha in size (Figure 4.3). The southern boundary is formed by a series of inliers of Rooiberg felsite, known as the Smithfield ridge (Smith and Whittaker, 1986). The main areas of operation at present lie to the south of Ogies, Witbank, Middelburg, to Belfast, although some reclamation (pillar extraction) mining is taking place along the northern margin of the basin, such as at the Kromdraai (Landau) colliery. The Highveld seam nomenclature is also applied to the Witbank coalfield (i.e. the seams are numbered (1-5) from the base upwards in chronological order).

The coal seams

The five coal seams are contained in a 70m thick succession, consisting predominantly of sandstone with subordinate siltstone and mudstone (Figure 4.2). Snyman (1998) reports that the partings between seams are remarkably constant. Seam splits are, however, fairly common, with the parting between the splits being about 8m thick in places. The distribution and attitude of the Nos. 1 and 2 Seams are largely determined by pre-Karoo topography, and the distribution of the Nos. 4 and 5 Seams is controlled by the present-day surface, parts of these seams having been eroded away. The No. 3 Seam is usually less than 0.5m thick and is generally considered uneconomical to mine.

Dykes and sills are ubiquitous. The Ogies dyke is about 15m thick and can be followed for about 100km along strike (Figure 4.3). It devolatilized the coal on either side over a distance of up to 300m, suggesting that it probably acted as a magma conduit for a considerable length of time (Snyman, 1998). To the north of the Ogies dyke, small dykes are less common than to the south. The non-porphyritic dolerite sills attain a thickness of 50m and the porphyritic sills a thickness of about 15m. Both of these devolatilize the coal and displace the seams where they are transgressed by the sills (Smith and Whittaker, 1986).

The No. 1 Seam is about 1.5 to 2m thick near the Arnot Colliery; elsewhere it is patchily developed and therefore only represents about 2% of the *in situ* demonstrated resources in the coalfield. It mainly consists of dull coal and is often indistinguishable from the No. 2 Seam with which it is sometimes combined in opencast mines. According to Barker (1999), the No. 1 Seam has been important to the development of the low cost Ferro-Chrome industry in South Africa.

The No. 2 Seam has been the backbone of the South African coal industry for over 110 years. It is on the No. 2 seam that South Africa's export coal industry was founded. The seam contains some 69% of the *in situ* demonstrated resources in the coalfield. In the central part of the field it averages 6.8m in thickness, and may consist of up to 5 benches of different appearance and quality. Snyman (1998) notes that the lowest three benches can be mined separately for the production of low-ash metallurgical coal and steam coal for export. The seam has been mined extensively and is nearing its limit (Barker, 1999). It is currently being mined in reclamation at several collieries by opencast methods along both its northern and southern boundaries. The seam is clearly defined from Delmas eastwards through towards Carolina. On the flanks of the basin it is both relatively thin (± 2m) and variable in width as at Arnot Colliery with numerous sandstone and shale partings. It reaches its maximum development south, east and west of Witbank where it exceeds 6m in width (e.g. Greenside Colliery).

Barker (1999) reaffirms that with possible local exceptions in some open pit mines, the No. 3 Seam, which seldom exceeds 0.5m, is not likely to be mined viably due to inconsistent development and narrowness.

The No. 4 Seam is generally of poor quality (predominantly dull), variable in thickness (2.5 to 6.5m) and is often split into a number of sub seams with a variety of partings often comprised of sandy mudstones and siltstones. The partings are seldom thick enough to allow the coals to be mined selectively. Where the coals are thick enough to mine selectively underground, such as at Goedehoop Colliery, the seam has a yield of about 60% for washed steam coal with less than 14% ash. For these reasons, it has until more recently been ignored in the underground mines of the Witbank region. Since the 1980's the No. 4 Seam has been used to bulk out the No. 2 Seam, even though it has a much lower yield (Barker, 1999; Snyman, 1998).

Whereas the No. 4 Seam accounted for about 26% of the *in situ* demonstrated resources in the field, the No. 5 Seam accounts for about 4%. It consists predominantly of bright coal, and has an average thickness of about 1.8m.

4.2.5 Vryheid

The coalfields of Kwazulu-Natal are situated in the northern part of the province. They are developed in the various and sometimes non-contiguous blocks in the region extending from the Mpumalanga border in the north near Volksrust, east to the Swaziland border and then southwards to a point 25km north-west of Richards Bay and west to Ladysmith (Figure 4.4). The Kwazulu-Natal Coalfields include the Utrecht, Vryheid, Klip River, Nongoma and Somkele coalfields. These are characterized by thin seams and numerous structural problems. By contrast the coals mined are generally of high quality. Consequently, the region has become renowned for its thin seam mining and ability to achieve high levels of extraction under difficult mining conditions (Barker, 1999; Snyman, 1998).

The Vryheid Coalfield covers 2 500km^2 in area, 15% of which is underlain by coal seams. It forms part of a highly dissected plateau, on which the present-day topography is markedly affected by dolerite sills, the oldest being the predominantly concordant Zuinguin sill. Younger sills, viz. the Ngwibi, Matshongololo, Nyembi and Enyati sills, mentioned in order of decreasing age, are more transgressive, and in general have a detrimental effect on the coal properties and the mineability of the seams, due to devolatilization and displacement. In 1975 the Vryheid coalfield was considered a major anthracite producer in South Africa, with an output of some 1 500kt of anthracite and 900 kt of bituminous coal, from nine collieries. Since then the production has decreased considerably due to the depletion of reserves (Snyman, 1998).

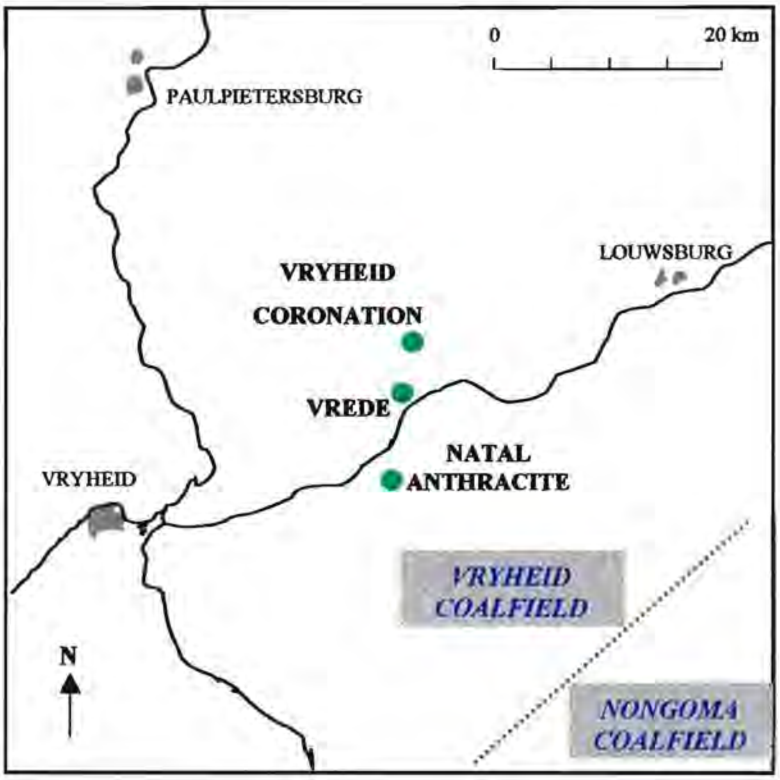

Figure 4.4: *Vryheid coalfield, showing location of Vryheid Coronation Colliery (including Vrede section) and Natal Anthracite Colliery (After Barker, 1999).*

The coal seams

A typical stratigraphic column from the Vrede section of this coalfield is shown in Figure 4.2. A number of coal units occur in the Vryheid coalfield, including:

- Bonas seam
- Fritz seam
- Alfred seam (Alfred and Upper Alfred)
- Gus seam
- Dundas seam (Lower Dundas and Upper Dundas)
- Coking seam

The Coking Seam seldom exceeds 1m in thickness. It is a high-grade, predominantly bright coal, however, with excellent coking properties at medium rank. The Lower Dundas Seam may be up to 2.5m thick and consists of interbedded bright and dull coal. It is a source of coking coal or steam coal. The Upper Dundas Seam is generally too thin to be mined on its own, but at Vryheid Coronation Colliery it reaches a thickness of 1 to 1.2m, and was mined as a straight coking coal. The Gus Seam varies from 0.5 to about 2m in thickness and it consists predominantly of bright coal. The Alfred Seam tends to be of lower grade than the other seams. Its thickness rarely exceeds 1m. Of the minor seams, only the Fritz Seam may be of economic importance if mined together with other seams by opencast methods. Although of fairly high grade and predominantly bright, it rarely exceeds 0.5m in thickness. The coals are frequently gassy. Due to a combination of westerly inclined dips and deeply incised topography the seams rapidly deepen from surface away from the outcrop. The average depth of the coal is thus about 15m (Snyman, 1998; Barker, 1999).

The Bonas seam is inconsistently developed in the Vryheid coalfield. The Targas Seam, below the Coking Seam, is also uneconomical. In-seam partings lead to seam splits, e.g. Upper and Lower Dundas, and Upper Alfred Seams. The Gus Seam is the most important in the area, and where it is of medium volatile bituminous rank it is a good coking coal. Where it has been partially devolatilized it is a high-grade anthracite (Bell and Spurr, 1986).

The coalfield is extensively intruded by dolerite sills. The sills, up to 100m or more in thickness, often form major topographical features and have been individually named in some places. They have either produced anthracite or raised the rank at best, or have totally destroyed the coal. Between these two extremes lie a whole spectrum of coal types. Not only do the sills cause quality problems, they also have a profound effect on the geotechnical/rock mechanics aspects of mining. Faulting caused by dolerite intrusion and of post-dolerite age is an additional hazard, compounding an already complicated structural environment. Throws of 15m or more are common (Barker, 1999).

4.3 Materials and methods

4.3.1 Sampling methods

The boreholes sampled were part of the regular borehole drilling programme on the respective mines. The depth of the holes drilled varied depending on the position of the lowermost coal seam. (i.e. holes were drilled to intersect the bottom of the lowermost mineable seam.) The core was logged by the Mine Geologist before the samples were collected and dispatched to the author, for analysis at the University of Cape Town. The borehole logs can be found in Appendix 4.

Each sample comprised a 20-30cm long section of the core. The sections were taken from major lithological units, usually in excess of 50cm in thickness and labelled by the Mine Geologist. The numbers pertaining to each sample can be found on the borehole logs in Appendix 4. Where a marked change occurred in the sample, for example due to a nodule horizon, the sample was sub-divided and the subsections numbered with a subscript.

4.3.2 Analytical methods

A brief outline of the methods used to analyze the core samples will be given here; further details are given in Appendix 1. Samples were crushed and milled to 300#, before being dried overnight in an oven at 110ºC. Dr Dave Reid determined the chemical composition, using a Philips PW 1480 wavelength dispersive X-ray fluorescence (XRF) spectrometer. The mineral component of the rocks was identified by the author, using a Philips PW 1130/90 X-ray diffractometer (XRD). Selected samples were re-run after low temperature ashing at the United States Geological Survey in Reston, Virginia so as to determine the clay mineral composition more accurately. Some XRD sample traces were also sent to the School of Earth Sciences at the University of New South Wales for SIROQUANT analysis.

Although XRD typically cannot detect minerals present in amounts much below 5% (which is where many of the trace metals are found), optical microscopy was not utilized in this study as it has limitations for fine-grained samples (such as shales) and the optical properties of some of the more commonly occurring minerals (viz. quartz, kaolinite and feldspar) are very similar. Furthermore, the geochemical character of the waters is largely governed by major ions, and not the trace elements. Both the XRD and XRF were housed in the Department of Geological Sciences, at the University of Cape Town. The total cation exchange capacity (CEC), as well as the exchangeable cations, were measured, by uptake and release of ammonium ions from 1M ammonium acetate solution at pH 7.0, by Bemlab, in Somerset West. No precise grain-size analyses of the sediments were attempted.

4.3.3 Normative mineral calculations

Quantitative determination of mineral abundances in these sediments by point counting techniques would be extremely difficult, if not impossible. The irresolvable mineralogy of many lithic fragments and matrix components, especially in the organic-rich units, and the similarity between the optical properties of quartz, kaolinite, and feldspar are a major hindrance. X-ray diffraction methods are capable of identifying minerals present in a representative rock powder, but variations in mineral crystallinity, mixed-layering in phyllosilicates, spectral interferences, and high background counts in the case of organic-rich samples (low mass absorption coefficients) generally allow only limited use of XRD as a quantitative analytical method.

An alternative to these methods is the calculation of a normative mineral composition, similar to CIPW norm calculations applied to igneous rocks. Normative methods for sedimentary rocks have been proposed by Nicholls (1962), and Garrels and Mackenzie (1971), and it is on the basis of their rationale, with a few modifications to suit the range of minerals in the Vryheid Formation, that a computer program was used to calculate the normative mineralogy of the rocks from whole-rock chemical compositions. The program used, SEDNORM, calculates a normative mineralogy specifically designed for sedimentary rocks, based on the chemical analyses. The sequence of allocating elements (oxides) to various minerals is a function of observed sedimentary mineral assemblages, mineral stabilities in surficial environments, and the restriction of certain elements to specific minerals, for example phosphorous is completely contained in apatite (Cohen and Ward, 1991). For the most part, elements have been assigned to minerals on the basis of data from the XRD analyses.

In deriving a sedimentary norm from oxide percentage data, the following principles or procedures have been applied:

1. Phosphorus is assumed to be present in apatite. Although a number of other phosphorus-bearing minerals such as goyazite-gorceixite and crandallite may be present, apatite is the dominant phosphate mineral in most types of sedimentary deposits. Excess P_2O_5 is assumed to be organically bound.
2. Calcium is assigned first to apatite and the remainder to calcite. Montmorillonite is not calculated because its exact composition, which probably occurs as a mixed-layer clay with illite, was not known.
3. Sulphur, where present, is assumed to occur as pyrite. Gypsum was observed in only one sample, KRL-5. In some samples there may be an excess of S and this is assumed to be organically bound.

4. Excess iron that remains after allocating S to Fe as pyrite, is assigned to siderite.
5. Either muscovite or illite may be dominant as the potassic layer silicate, depending on the degree of weathering. The degree of difference between cation proportions in these two minerals is, however, not great. The distribution of potassium between K-feldspar, muscovite and illite was fixed, and any excess potassium remaining after the clays or muscovite are formed was assigned to feldspar.
6. Although there are two K-bearing minerals (illite and microcline) in the Vryheid Formation, only normative illite has been calculated, since no Vryheid cores were utilized. Microcline was detected by XRD in only a few samples. In the samples that do contain microcline the normative illite concentration will be exaggerated. Microcline, however, is assumed to alter to a mixture of illite, smectite, kaolinite and quartz and therefore the normative illite concentration will be a good indicator of the degree of alteration of feldspars.
7. The Al and Si left over after calculation of the illite percentage are assigned to kaolinite, and any remaining SiO_2 is expressed as quartz. If Al_2O_3 rather than SiO_2 is left after the kaolinite calculation, it is expressed as gibbsite.
8. The carbonates permitted are siderite, calcite and magnesite. The effective dolomite content can be derived by combination of the calcite and magnesite contents. Calcite forms in preference to siderite, with excess iron eventually being assigned to hematite.
9. Manganese is assumed to be associated with iron in hematite (in the form of pyrolusite inclusions). This is consistent with many of the sediments and soils found in eastern Australia (Cohen and Ward, 1991), however, some manganese may be present in either montmorillonite or siderite, replacing Fe^{2+}.
10. Smectites are difficult minerals to handle in normative calculations due to the highly variable cation contents in dioctahedral, trioctahedral or cation exchange sites. Similarly, the water content may vary greatly, with 2 structural H_2O groups but up to 15% adsorbed or non-structural water (hence the term "swelling clays"). For these reasons it has been excluded from the normative calculations.

As only total C was determined by XRF, it was suggested (pers. comm. David Cohen, 2001) that the system be allowed to add sufficient CO_2 to form calcite / dolomite and siderite. Any excess CO_2 at the end of the calculation could be ignored. The difference between the total mineral composition and 100% could then be taken as organic C.

4.3.4 Rietveld-based interpretations

Another approach to quantitative mineralogy is the Rietveld technique. Ward *et al.* (2001) explain that the full profile of an XRD pattern provides considerably more information for mineral quantification than the integrated intensities of particular diffractogram peaks. Rietveld (1969) developed a formula to give the intensity at any point in the scan of a single mineral, with information on how to refine relevant crystal structure and instrumental parameters by least-squares analysis of the profile. This approach has been extended to quantify mixtures of minerals using the full XRD profile by authors such as Taylor (1991), Taylor and Matulis (1991), and Bish and Post (1993). Such an extension allows a calculated XRD profile of each mineral to be generated from its known crystal structure, and the sum of all calculated patterns to be fitted to the observed XRD profile of a multi-mineral sample by iterative least-squares analysis, to find the optimum individual phase scales. These are then used to determine the mineral percentages in the sample.

One of the more recent methods for the use of X-ray diffractometry, and the one used in this study, is SIROQUANT™. This is a personal computer software system, which was initially described by Taylor (1991), and which allows the proportions of up to 25 different minerals in a mixture to be quantified from a conventional X-ray powder diffractometry pattern using Rietveld techniques. Corrections are incorporated into the standard mineral patterns used in the process to allow for absorption contrasts between the elements involved (Brindley, 1945), preferred orientation (March function) and amorphicity effects.

As well as computation of standard XRD patterns from crystallographic and chemical data, reference patterns can be developed for use in SIROQUANT directly from measured XRD traces of the mineral in question (Taylor and Zhu, 1992; Taylor and Matulis, 1994). These allow minerals having imperfectly known or poorly developed crystal structures to be incorporated in the analysis, with data derived from the measured patterns refined and quantified along with those for the other reference components using the Rietveld technique. Such a capability is particularly relevant to the clay minerals, which might otherwise limit the applicability of the Rietveld approach in dealing with both sediments and coal samples.

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The raw diffraction data from approximately half of the XRD traces run at the University of Cape Town were sent to the School of Geology at the University of New South Wales for SIROQUANT analysis. Details of the method used are given in Appendix 1. For many of the minerals indicated by SIROQUANT to be present in low concentrations (<1%), the estimated error is of magnitude similar to, if not greater than, the actual determination. These minerals represent components for which a small proportion is indicated by the diffractogram but quantification is below the resolution of the Rietveld technique. The minerals in question could have been omitted from the analysis in each case and the remaining components normalized to 100%, but they are included in the tabulations to ensure that their presence is not completely overlooked.

4.4 Results and discussion

4.4.1 Chemical composition

The major and trace element distributions in sedimentary rocks are controlled by several factors such as: source rock compositions (provenance), intensity of the weathering process, which is mainly related to tectonics and climate; sedimentation rates and depositional environments; and post-depositional changes (Taylor and McLennan, 1985). The composition of the Vryheid Formation coal seams, and the overlying sediments, will be discussed with respect to these controlling parameters. The minimum, maximum and means of the major and trace element values are presented in Table 4.1 and all the whole-rock data are presented in Appendix 2. In calculating the mean concentrations in Table 4.1, it was decided to exclude values that were below detection limits. Note that there is no difference between SO_3 and S. They both pertain to total sulphur, but are just expressed differently.

Several studies on coal, which usually have <15 wt % mineral matter, have tried to ascertain whether trace elements occur predominantly in the organic fraction (either bonded, adsorbed or merely associated) or in the mineral fraction (for a useful review see Swaine, 1990). The majority of elements in coal tend to be associated with the mineral fraction but there are coals in which certain elements do have a predominantly organic association, for example Mo, S, Cu, Cr, V, etc. (Swaine, 1990). For some elements there is no universal predominantly organic or inorganic association in carbonaceous sediments. In this study it has been assumed

Table 4.1: *The mean, minimum and maximum concentrations of oxides and LOI's in weight %, and trace elements in ppm.*

	Coal				Dolerite				Shale			
	Valid N	*Mean*	*Minimum*	*Maximum*	*Valid N*	*Mean*	*Minimum*	*Maximum*	*Valid N*	*Mean*	*Minimum*	*Maximum*
SiO_2	12	16.7	3.06	43.3	2	47.3	40.6	54.1	11	48.7	27.6	60.3
TiO_2	12	0.32	0.12	0.75	2	0.83	0.81	0.85	11	0.77	0.44	1.03
Al_2O_3	12	6.94	2.45	15.2	2	13.5	12.1	14.9	11	17.5	9.91	22.4
Fe_2O_3	12	1.21	0.04	4.08	2	10.1	9.93	10.2	11	3.51	0.74	7.33
MnO	12	0.01	0.00	0.02	2	0.15	0.15	0.16	11	0.04	0.00	0.16
MgO	12	0.29	0.14	0.56	2	4.63	3.27	5.98	11	0.95	0.11	1.98
CaO	12	1.48	0.15	5.28	2	8.24	8.00	8.47	11	0.42	0.07	1.25
Na_2O	12	0.12	0.00	0.31	2	2.88	2.72	3.05	11	0.26	0.07	0.74
K_2O	12	0.28	0.03	1.84	2	0.65	0.52	0.78	11	1.85	0.51	2.53
P_2O_5	12	0.11	0.00	0.64	2	0.12	0.12	0.12	11	0.07	0.03	0.20
SO_3	12	1.73	0.28	5.83	2	0.16	0.05	0.28	11	0.50	0.13	1.16
Cl	12	0.00	0.00	0.00	2	0.00	0.00	0.00	11	0.00	0.00	0.00
H_2O	12	1.91	1.38	2.38	2	1.65	1.54	1.75	11	1.24	0.00	2.38
C	12	68.9	32.5	87.5	2	9.38	0.00	18.8	11	23.7	7.50	55.0
Mo	6	2.49	1.25	4.95	0				10	1.67	1.04	2.61
Nb	12	10.1	4.31	21.6	2	5.02	4.03	6.01	11	20.3	13.9	28.2
Zr	12	138	44.7	288	2	101	93.0	109	11	260	164	650
Y	12	24.5	12.1	47.9	2	24.9	22.3	27.5	11	41.0	15.3	59.6
Sr	12	467	57.8	1925	2	250	155	346	11	139	24.7	355
U	12	3.58	2.45	5.69	0				10	7.70	2.19	11.8
Rb	12	19.0	1.39	123	2	15.9	14.8	17.0	11	112	25.5	146
Th	11	11.3	0.00	29.9	1	3.56	3.56	3.56	11	23.0	11.6	31.3
Pb	12	38.0	0.00	324	1	6.19	6.19	6.19	11	30.4	13.5	49.9
Ba	12	317	111	970	2	260	244	276	11	498	117	795
Sc	12	8.46	3.51	17.6	2	29.3	27.3	31.2	11	16.9	4.08	24.0
Zn	12	15.0	1.51	43.8	2	78.7	78.3	79.2	11	98.6	23.7	133
Cu	12	7.35	3.16	16.8	2	80.6	78.0	83.2	11	27.5	3.46	59.3
Ni	12	17.2	2.83	65.2	2	86.7	46.3	127	11	41.1	13.4	63.0
Co	8	4.89	1.94	11.6	2	12.5	7.21	17.8	8	15.6	4.36	27.6
Mn	12	36.7	12.8	72.5	2	774	772	776	11	207	27.5	734
Cr	12	42.3	12.2	97.7	2	288	120	456	11	101	63.7	130
V	10	24.4	1.73	161	2	71.0	67.5	74.6	11	47.5	4.20	163
S	12	8127	1268	27141	2	799	299	1300	11	2304	610	5353

Table 4.1 cont.: The mean, minimum and maximum concentrations of oxides and LOI's in weight %, and trace elements in ppm.

	Silt				**Silt / Sandstone**				**Sandstone**			
	Valid N	*Mean*	*Minimum*	*Maximum*	*Valid N*	*Mean*	*Minimum*	*Maximum*	*Valid N*	*Mean*	*Minimum*	*Maximum*
SiO_2	5	45.4	33.1	51.8	5	50.3	43.1	59.6	19	65.7	41.4	86.5
TiO_2	5	0.81	0.76	0.89	5	0.82	0.74	0.97	19	0.52	0.14	1.34
Al_2O_3	5	17.8	14.8	23.1	5	16.4	15.2	17.5	19	11.8	5.27	23.8
Fe_2O_3	5	5.86	2.69	9.15	5	6.06	2.75	8.73	19	4.44	0.40	21.5
MnO	5	0.05	0.01	0.08	5	0.05	0.02	0.08	19	0.04	0.00	0.31
MgO	5	1.54	1.00	1.91	5	1.56	0.75	2.49	19	0.76	0.08	3.00
CaO	5	0.36	0.30	0.51	5	0.36	0.27	0.42	19	1.74	0.04	10.5
Na_2O	5	0.80	0.57	1.16	5	0.82	0.24	1.13	19	0.81	0.01	1.78
K_2O	5	2.22	1.51	2.92	5	2.62	2.05	3.10	19	2.95	0.23	4.50
P_2O_5	5	0.06	0.04	0.09	5	0.06	0.02	0.09	19	0.06	0.01	0.45
SO_3	5	0.35	0.13	0.62	5	0.60	0.06	2.57	19	0.39	0.01	2.91
Cl	5	0.00	0.00	0.01	5	0.00	0.00	0.01	16	0.00	0.00	0.00
H_2O	5	1.93	1.25	2.38	5	1.73	1.25	2.38	19	1.41	0.00	2.25
C	5	22.5	16.3	33.8	5	17.8	15.0	22.5	19	9.13	0.00	32.5
Mo	4	1.85	1.13	2.60	4	2.05	1.46	2.83	14	1.78	0.96	3.15
Nb	5	19.6	17.6	22.8	5	18.6	14.3	22.4	19	11.5	3.86	25.8
Zr	5	242	92.8	318	5	286	213	340	19	200	83.4	526
Y	5	34.9	11.9	45.9	5	28.6	11.2	45.6	19	14.3	3.28	29.2
Sr	5	132	74.5	186	5	126	61.2	201	19	110	23.6	235
U	4	5.53	4.40	7.44	5	4.83	2.56	7.44	7	3.49	1.94	4.91
Rb	5	149	96.7	178	5	145	93.2	191	19	112	11.36	265
Th	5	15.6	7.75	19.9	5	14.9	9.41	21.3	19	8.94	3.06	20.2
Pb	5	31.8	20.8	46.9	5	28.3	16.5	39.2	19	22.4	5.40	32.7
Ba	5	559	490	663	5	600	364	711	19	638	111	1025
Sc	5	19.1	15.4	26.2	5	15.6	12.1	17.2	19	10.7	3.43	25.3
Zn	5	157	104	301	5	100	26.2	158	19	42.7	18.8	70.6
Cu	5	18.7	10.2	25.6	5	12.7	7.30	18.9	12	8.04	1.56	25.7
Ni	5	47.3	30.1	70.6	5	31.3	19.5	45.5	19	20.6	4.48	59.5
Co	3	16.6	4.10	33.1	1	2.49	2.49	2.49	7	5.72	1.85	16.9
Mn	5	267	94.0	450	5	282	115	384	19	209	16.4	1505
Cr	5	116	77.8	148	5	101	75.4	147	19	78.8	22.5	223
V	5	37.1	22.4	52.7	5	22.1	12.2	30.2	18	13.9	2.63	56.8
S	5	1617	605	2852	5	2740	294	11675	19	1818	40.9	13381

Table 4.1 cont.: The mean, minimum and maximum concentrations of oxides and LOI's in weight %, and trace elements in ppm.

	Sandstone / Shale			
	Valid N	*Mean*	*Minimum*	*Maximum*
SiO_2	8	45.1	34.5	50.7
TiO_2	8	0.77	0.58	0.95
Al_2O_3	8	17.1	13.6	20.1
Fe_2O_3	8	6.03	0.43	10.9
MnO	8	0.08	0.00	0.25
MgO	8	1.12	0.09	1.73
CaO	8	0.91	0.07	3.30
Na_2O	8	0.54	0.08	1.00
K_2O	8	1.80	0.17	2.72
P_2O_5	8	0.05	0.03	0.08
SO_3	8	0.88	0.07	4.63
Cl	8	0.00	0.00	0.00
H_2O	8	1.64	0.00	2.25
C	8	23.9	12.5	42.5
Mo	3	2.03	0.93	2.93
Nb	8	18.1	11.9	27.7
Zr	8	295	193	530
Y	8	25.4	15.9	39.4
Sr	8	111	26.6	171
U	5	3.72	2.53	5.63
Rb	8	103	12.7	150
Th	8	14.2	10.0	23.8
Pb	8	24.2	15.9	38.3
Ba	8	443	124	683
Sc	8	15.5	3.78	30.1
Zn	8	90.2	28.6	147
Cu	8	17.7	4.16	66.7
Ni	8	40.4	15.6	130
Co	3	8.72	3.23	11.6
Mn	8	393	8.98	1223
Cr	8	126	59.2	343
V	8	29.0	4.26	97.6
S	8	4021	342	21085

that the major proportion of all the elements that were determined (C, H, and N were not determined) were associated with the mineral fraction.

The overlying sediments consist predominantly of the two oxides SiO_2 and Al_2O_3. The sandstones (including the glauconitic layers) have between 41 and 87 wt % SiO_2, the shales, siltstones and dolerite have between 27 and 61 wt %, and the coals usually less than 40 wt % SiO_2. Al_2O_3 was highest in the silts, shales and dolerite (9 – 23 wt %), followed by the sandstones (5 – 24 wt %), and then the coal (2 – 15 wt %). C (including organic-C and CO_2) makes up the bulk of the coal samples (32 – 88 wt %) and is usually less than 30% in the other rock types studied, being particularly low in the sandstones (and glauconite) where it makes up only 32 wt %.

Fe_2O_3, CaO, MgO, Na_2O and K_2O are present in smaller concentrations than SiO_2 and Al_2O_3 in the horizons that were sampled. The dolerite sills sampled contain far more CaO (~ 8.2 %), MgO (~ 4.6 %) and Na_2O (2.9 %) than the other rock types. The glauconitic sandstone is enriched in Fe_2O_3 (~ 9 wt %), K_2O (~ 4.2 wt %) and CaO (~ 2 wt %) compared to the other rock types. On the whole, the sandstone layers tend to have slightly higher concentrations of CaO (~ 1.7 wt %) and K_2O (~ 2.9 wt %); whilst the coal appears to be depleted in MgO, Na_2O and K_2O (all < 1.9 wt %). Fe_2O_3 and MnO are also lower in the coals than the other rocks (< 4 and < 0.02 wt %, respectively). TiO_2 concentrations were lowest in the glauconitic sandstones (~ 0.2 wt %) and the coal (~ 0.3 wt %); and SO_3 concentrations were highest (~ 1.5 and ~ 1.7 wt %, respectively). P_2O_5, MnO and Cl, particularly, were barely present at all in any of the rocks.

4.4.2 Mineralogical composition

XRD patterns of the major lithological units, ordered according to depth, are presented in Appendix 5. Qualitative results of the XRD analyses are as follows:

1. Kaolinite and quartz are the main mineral constituents in all the rocks, including many of the coals.
2. Illite was observed in many sediment samples in major to minor amounts.
3. Felspars, including microcline, occur in many of the sandstones, shales and silts in major to minor proportions, and in minor proportions in a few of the coals.

4. Siderite is present in some samples in major to minor proportions.
5. Pyrite, calcite and magnesite are present intermittently in minor to trace proportions in the shales and siltstones; and minor proportions in the coals.

Table 4.2: *Average mineral compositions of the 4 coal-bearing sequences as determined by normative calculations.*

Core	No. samples	Detrital components				Clay minerals					
		Quartz		Feldspar		Illite		Kaolinite		Anatase	
		% n	Ave %	% n	Ave %	% n	Ave %	% n	Ave %	% n	Ave %
NVC	18	94.4	27.9	83.3	9.29	100	8.03	94.4	40.2	100	0.87
KRL	18	100	26.8	83.3	14.4	100	11.9	94.4	31.4	100	0.78
GHC	11	100	31.9	81.8	7.01	100	9.35	100	44.5	100	1.05
ND	15	100	34.5	93.3	19.0	100	14.0	80.0	18.9	100	0.72

Core	No. samples	Authigenic components									
		Calcite		Siderite		Magnesite		Pyrite		Apatite	
		% n	Ave %	% n	Ave %	% n	Ave %	% n	Ave %	% n	Ave %
NVC	18	100	3.62	88.9	10.7	100	2.72	100	2.56	72.2	0.31
KRL	18	100	4.26	94.4	8.29	100	2.86	83.3	2.95	72.2	0.98
GHC	11	54.5	2.03	90.9	3.50	100	1.31	81.8	1.41	45.5	1.12
ND	15	100	4.77	100	8.37	100	3.35	53.3	0.50	60.0	0.19

% n = Percentage of samples containing that mineral.
Ave % = Average percentage of the mineral contained in the sample population (n).

Mineral concentrations used in these discussions were obtained from both XRD analysis of the coals and argillaceous sediments, and normative calculations based on compositions determined by XRF. This is because variable amounts of organic matter in the coal often prevent the accurate determination of mineral concentrations by XRD only. The organic matter causes a broadening of peaks and an increase in background intensities. A low temperature ashing technique to remove the organic portion of carbon-bearing rocks, with minimal thermal effect upon the inorganic minerals, was made available by the USGS in Virginia, for selected samples in this study. The results of further XRD analyses performed at the USGS on the ashed samples, however, proved to be solely qualitative and could only be used as confirmation of the minerals determined by other methods. For this reason normative mineral proportions were calculated from whole-rock chemical compositions for all the rock samples. In addition, SIROQUANT analysis was performed on approximately half the XRD traces of the unashed samples. A summary of the results is presented in Table 4.2 and 4.3, whilst the full results can be found in Appendix 5. The mineral data are recalculated to 100%.

Table 4.3: *Average mineral compositions of the 4 coal-bearing sequences as determined by SIROQUANT analysis.*

Core	**No. sam-ples**	**Detrital components**				**Clay minerals**					
		Quartz		**Feldspar**		**Illite**		**Kaolinite**		**Anatase**	
		% n	**Ave %**	**% n**	**Ave %**	**% n**	**Ave %**	**% n**	**Ave %**	**% n**	**Ave %**
NVC	18	100	26.6	61.1	6.94	66.6	17.4	100	37.1	11.1	2.55
KRL	8	100	29.8	50.0	18.2	25	13.3	100	27.3	25.0	1.35
GHC	4	100	37.2	50.0	10.9	25	14.2	100	39.5	50.0	2.10
ND	6	100	42.0	83.3	36.1	33.3	18.0	100	12.9	16.7	1.50

Core	**No. sam-ples**	**Authigenic components**									
		Calcite		**Siderite**		**Dolomite**		**Pyrite**		**Apatite**	
		% n	**Ave %**	**% n**	**Ave %**	**% n**	**Ave %**	**% n**	**Ave %**	**% n**	**Ave %**
NVC	18	72.0	8.71	77.7	3.66	72.2	0.54	77.7	3.84	0	
KRL	8	75.0	2.75	100	10.6	100	2.84	100	8.24	25	13.2
GHC	4	50.0	8.00	75.0	6.03	100	2.75	75	2.70	50	< 0.1
ND	6	100	2.87	50.0	2.73	100	2.47	66.7	3.10	0	

% n = Percentage of samples containing that mineral.
Ave % = Average percentage of the mineral contained in the sample population (n).

4.4.2.1 Clay mineral fraction

XRD diffractograms demonstrated that the principal clay mineral present was kaolinite. They also revealed that "illite" is present in random argillaceous sediments, and occasionally in the sandstones. It was not established whether predominantly mixed-layer clays were present or whether mixtures of discrete montmorillonite and illite were present. Coarse-grained mica, a few millimetres in diameter, is commonly observed in hand-specimen of all cores investigated and indicates a detrital origin.

Bühmann and Bühmann (1988), in a comparative study of four borehole cores from the Witbank, Eastern Transvaal and Vryheid coalfields, found that fundamental differences occurred in the nature of the clay minerals, both within one core and between the cores. Insufficient detailed data was available in this study, however, to investigate such a possibility suffice it to say that generally, the core from Goedehoop has substantially more kaolinite than New Denmark, whilst the reverse is true for illite.

4.4.2.2 Non-clay fraction

XRD analyses of the whole-rock powder showed that the qualitative composition of the non-clay fraction is similar in all four cores and each lithologic facies investigated, thus confirming the findings of Ryan (1967), Tavener-Smith (1986), and Willis and Hart (1986), that the sediments in the three coalfields were derived from source rocks of similar composition. Quartz is ubiquitous and feldspars (K-feldspar and plagioclase) are abundant (Table 4.2 and 4.3). Accessory minerals that may, however, constitute the main component in some samples, include carbonates, pyrite and apatite. Carbonates comprise siderite, calcite and magnesite in order of decreasing abundance (Table 4.2 and 4.3). Aragonite is absent. The occurrence of more than one carbonate mineral within the same sample is not uncommon (Appendix 5).

Differences exist in the relative proportions of the non-clay minerals, both within and also between the various localities.

1. The quartz content is very similar in all cores investigated, with values peaking in the sandstones. Absence, or trace quantities, of quartz in some of the coal sub-units (e.g. NVC-13) is correlated with high proportions of either carbonate, clay minerals or gypsum (Appendix 5).
2. Feldspar contents are highest in Core ND, both in terms of prevalence as well as abundance, and lowest in Core GHC.
3. Siderite is the overall dominant carbonate mineral in all the argillaceous and arenaceous rocks, though it occurs in much higher concentrations in the NVC core, particularly in the sandstones. Calcite and magnesite are the dominant carbonate phases in the coals at all the collieries.

4. Pyrite is generally a minor constituent in the sediments overlying the coal in all four cores. It does, however, play a significant role in the composition of most of the coal seams.
5. Apatite contents are lowest in Core GHC and highest in the NVC and KRL cores, where 72% of all samples contain traces of this phosphate mineral. Concentrations of apatite are highest in the coal units.

Ankerite, microcline and anatase were also identified by XRD analysis. Microcline was commonly detected in samples from the upper sediment units of the cores, but not at all at New Vaal; and anatase throughout the cores, though elevated in samples from the base of the formation. In general, no characteristic differences were found to exist in the non-clay mineral content between the four sequences. This is in keeping with studies by Bühmann and Bühmann (1988).

4.4.3 Comparison of SIROQUANT- and SEDNORM-determined mineralogy

A comparison of the mineral percentages calculated by SEDNORM and SIROQUANT is given in Figure 4.5.

4.4.3.1 Quartz and feldspar

The correlation line between the proportions of quartz has a slope of around 1.2, a high correlation coefficient (r_s=0.87), and a small intercept (Figure 4.5a). Both SIROQUANT and SEDNORM therefore provide very similar estimates of quartz content, even though completely different principles are involved.

The proportion of K-feldspar indicated by SEDNORM depends on the option chosen to distribute the K_2O content. The option selected in this study was to distribute K_2O equally between feldspar and illite. The alternative options were to exclude feldspar and allocate all K_2O to illite, or exclude illite and allocate all K_2O to feldspar. The points plotted in Figure 4.5b (which includes both K-feldspar and plagioclase) do not show a particularly good correlation. When only K-feldspar from the SIROQUANT analyses is plotted against feldspar from the SEDNORM calculations the correlation does not improve, the slope, however, does

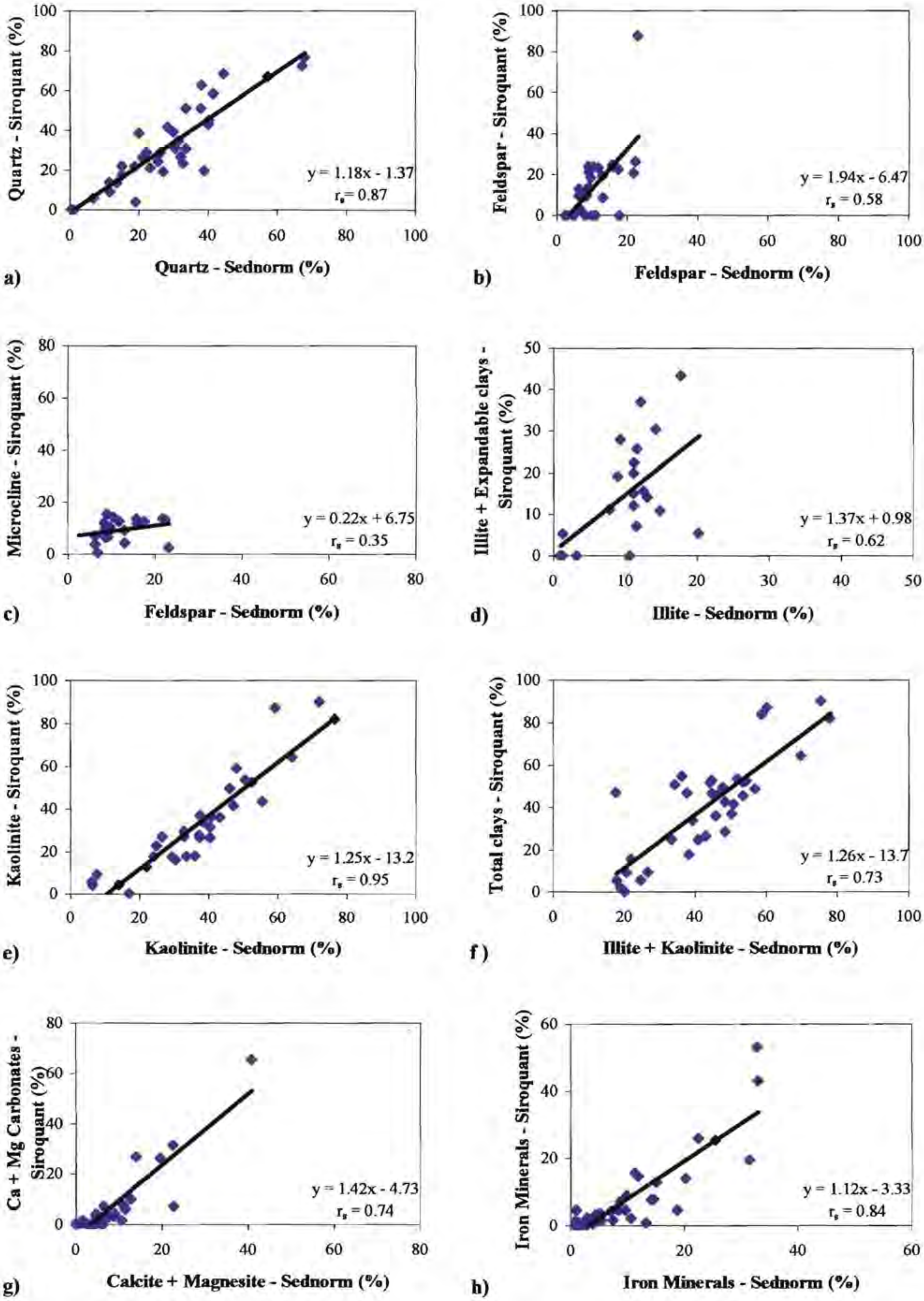


Figure 4.5: *Comparison between percentages of different minerals indicated by SEDNORM and SIROQUANT. (a) Quartz, (b,c) Feldspar, (d) Illite and expandable clays, (e) Kaolinite, (f) Total clays, (g) Ca and Mg carbonates, and (h) Iron minerals.Thin dashed line is 1:1 correlation, while thick solid line is the actual correlation.*

change substantially (Figure 4.5c). The allocation of 50% of the K_2O to feldspar is probably inappropriate, and most (but not all) of the K_2O would have been better allocated to illite. Furthermore, the absence of more specific information regarding the composition of the feldspars from SEDNORM, make it difficult to make any comparison between the plagioclase concentrations found in the SIROQUANT analysis and normative calculations.

4.4.3.2 Clay minerals

As with K-feldspar, the proportion of normative illite depends in large part on the method chosen for K_2O distribution in the SEDNORM calculation. For the present study the comparison is also affected by the inclusion of interstratified illite / smectite with illite in the SIROQUANT data (Figure 4.5d), but computation of illite alone with SEDNORM. A combination of both factors means that no useful correlation is obtained between the SIROQUANT and the SEDNORM data.

By contrast, a reasonably good correlation (slope=1.25 and r_s=0.95) is observed for kaolinite (Figure 4.5e). In the normative calculation, kaolinite represents the balance of the Al-bearing components after allocation of Al_2O_3 to illite and feldspar. Therefore, in spite of the misallocation of K_2O to feldspar and illite, SEDNORM was still able to estimate the proportion of kaolinite in the samples quite well. The sum of illite and kaolinite (Figure 4.5f) shows an overall agreement (slope = 1.26, r_s=0.73) between the two analytical methods.

4.4.3.3 Other minerals

Figure 4.5g shows the comparison between SEDNORM and SIROQUANT for the calcium and magnesium carbonate minerals identified by the different techniques. For SIROQUANT these represent the sum of calcite and dolomite; for SEDNORM they represent the sum of the normative calcite and magnesite components. A correlation based on the individual carbonate minerals was not attempted because of the mixed mineralogy.

Good agreement is indicated between SEDNORM and SIROQUANT in Figure 4.5g. SIROQUANT, however, indicates a slightly higher overall proportion of carbonate minerals than SEDNORM for equivalent samples. This may be because a large proportion of the CO_2

in the SEDNORM calculations is allocated to siderite, which is not included in this correlation.

Good agreement is also indicated between SEDNORM and SIROQUANT for the different iron minerals in the sample suite (Figure 4.5h). These are represented by siderite, pyrite and hematite (albeit in miniscule amounts) in the SEDNORM output, and by siderite and pyrite in SIROQUANT. This suggests that, for the most part, the Fe in the samples is mainly in carbonate or sulphide form, and that only minor proportions, if any, occur in the clay minerals.

4.4.4 Relationship between chemical composition and mineral matter

A knowledge of the concentration and distribution of trace elements in coals is vital from ana economic and, more importantly in the study, environmental point of view. Environmentally important trace elements include As, Cd, Pb, Mo, Se and, to a lesser extent, Cu, Ni, Zn, V, U, Cr and F. Other elements, such as Cl, the alkalies, S, Pb, Zn and Mn may cause large-scale problems in coal utilization, including boiler fouling, corrosion and catalyst poisoning in conversion technology (Spears and Zheng, 1999). As virtually no information is available on the geochemistry of the sediments associated with the Highveld coals, the main objectives of this section are to: 1) present trace element analyses of the Highveld coals and associated sediments; and 2) determine the association of the trace elements with specific mineralogical components in the coals and sediments.

Computer-based techniques for the interpretation of XRD results (Taylor, 1991; Ward and Taylor, 1996) and procedures for normative interpretation of chemical analysis data (Cohen and Ward, 1991) allow the relations between trace elements and minerals in sedimentary rocks to be explored more fully. Due to the discrepancies resulting from the incorrect allocation of K_2O in the normative calculations, the relationships considered here are based on the results of the SIROQUANT analysis. Although the trends were similar in most cases, the correlation is not as good using the SIROQUANT data, since only about half the original number of samples was used. Authors such as Gluskoter *et al.* (1977), Finkelman (1982, 1994), Swaine (1990), Spears and Zheng (1999), and Ward *et al.* (1999) have identified minerals in coal, in particular, as the prime source for many of the trace elements present.

Statistical correlation coefficients (i.e. Spearman's r) were obtained between all pairs of components (including individual major, trace element and mineral concentrations), using STATISTICA. Concentrations below the detection limits of the XRF instrument were regarded as zero values and excluded for the purposes of this computation.

4.4.4.1 Titanium, kaolinite and quartz

Titanium in the coals ranges from 0.12 to 1.34 wt %, with most samples having less than 0.45 wt %. A reasonably good correlation (r_s=0.75) is seen in all lithological types for TiO_2 and Al_2O_3 (Figure 4.6). Aluminium occurs in kaolinite, feldspars and the clay fraction. Of these, a moderate correlation is observed between Al_2O_3 and kaolinite (Figure 4.7), suggesting that some of the Ti is associated with the very abundant kaolinite in the sediments (r_s=0.82), but not as significantly in the coal (r_s=0.44), as was found by Ward *et al.* (1999).

Finkelman (1993) reports that coal represents the ultimate organic-inorganic interactions. For many elements, coal and the precursor organic matter in peats and plants provides a chemical framework for attachment. Therefore, at some time in the coalification process most elements will experience some degree of organic complexing. Titanium in coal is reported to occur in oxides, clays and complexed with organic matter (Finkelman, 1982; Ward *et al.*, 1999). In this study, it is thought that the TiO_2 in the coal occurs with quartz (r_s=0.81) (Figure 4.8) and, to some degree, complexed with organic matter.

Niobium is a minor but significant element associated with TiO_2 in the sample suite. The graphic representation, in Figure 4.9, of their relationship indicates an overall steadily increasing concentration with TiO_2 abundance (r_s=0.79). Finkelman (1982) suggests that Nb is most likely to be present in oxides. Figure 4.10 shows a good correlation between Nb and quartz (r_s=0.75) in the coals. In addition, positive correlations exist in the coals for TiO_2 and Nb (r_s=0.80), Zr (r_s=0.86), Y (r_s=0.79), Th (r_s=0.94), Sc (r_s=0.78) and Cu (r_s=0.73) (Figure 4.11). No explanation can be given for these associations, especially since their probable modes of occurrence, as reported by Finkelman (1982), are highly variable.

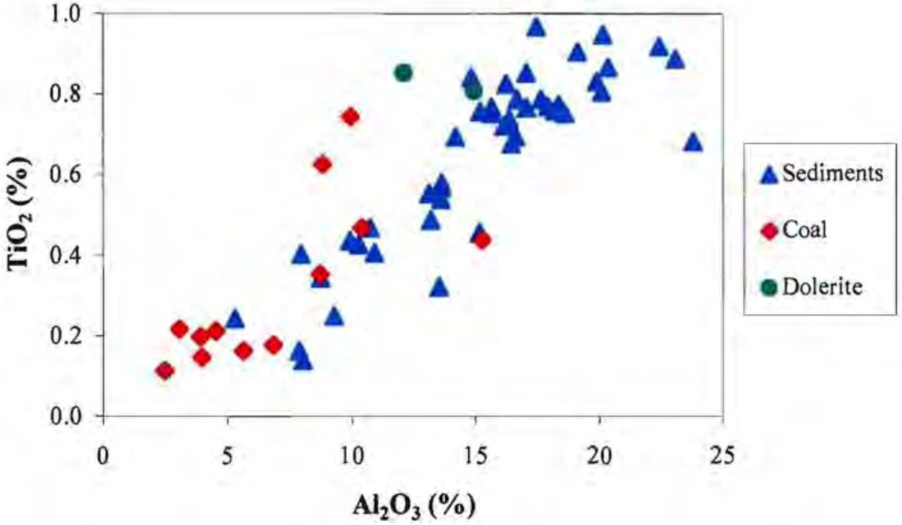


Figure 4.6: Relationship between titanium and aluminium concentrations in selected lithological units.

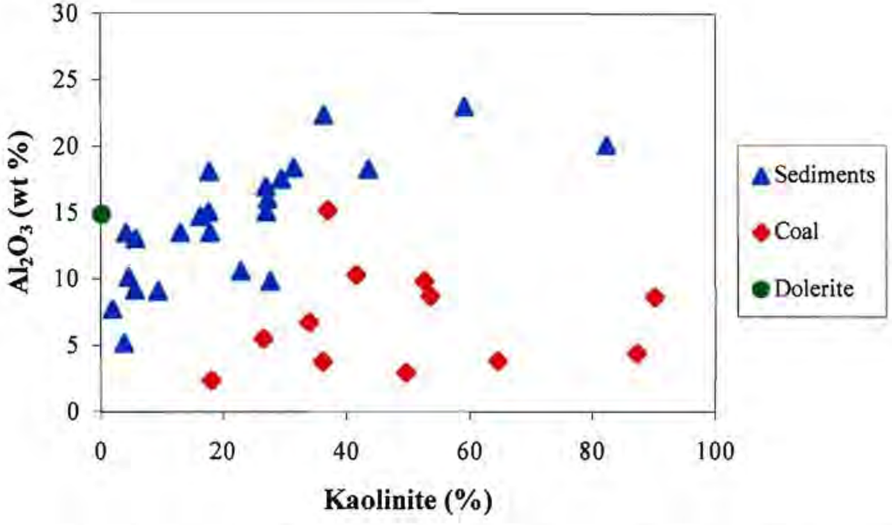


Figure 4.7: Relationship between aluminium concentration and kaolinite composition in selected lithological units.

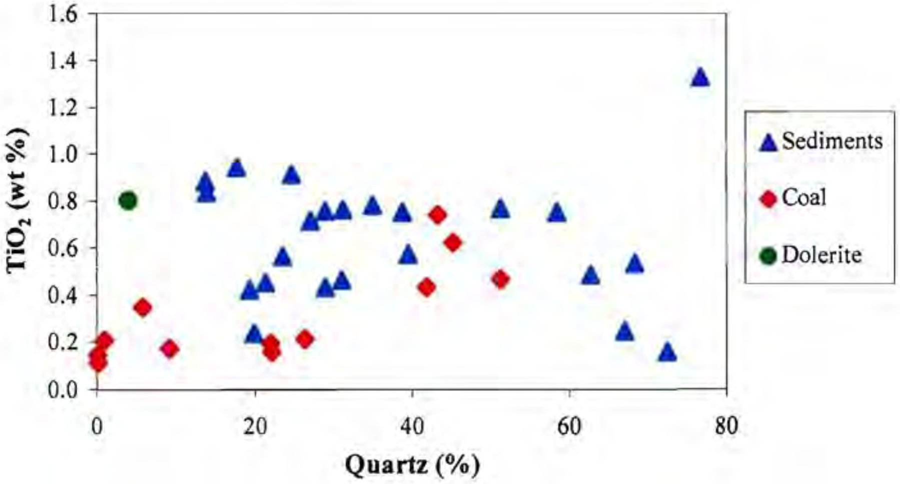


Figure 4.8: Relationship between titanium concentration and quartz composition of selected lithological units.

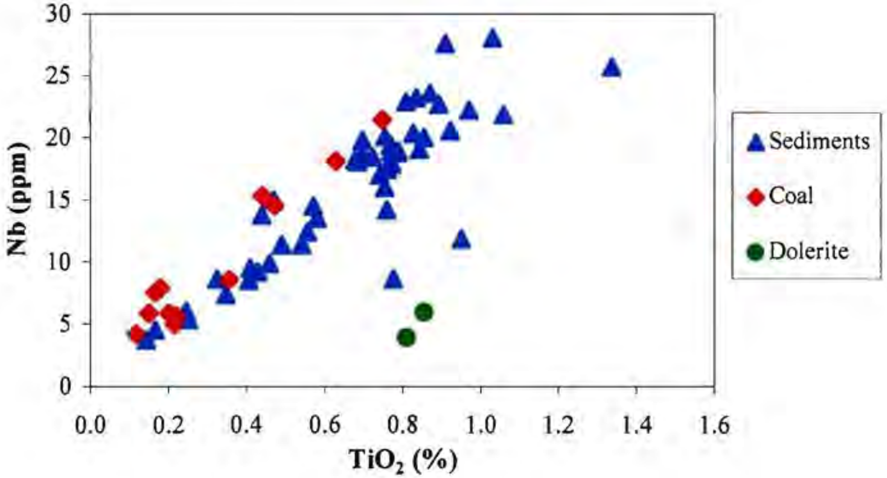


Figure 4.9: Relationship between niobium and titanium concentration in selected lithological units.

4.4.4.2 Iron, sulphur and pyrite

Total sulphur in the samples, as indicated by XRF analysis of the powder briquettes, ranges from 0.005 to 5.83 wt % oxide SO_3 equivalent. By far the majority of the samples have less than 1.5% SO_3 (wt %). A plot of total sulphur, as SO_3, against pyrite (Figure 4.12) shows a linear relationship with a reasonably good correlation for the sediments (r_s=0.68). The trend intersects the *y*-axis (SO_3) close to zero, indicating that the amount of organic sulphur present in the sediments is negligible. The slope of the line, however, indicates slightly less than the approximately 2:1 ratio between pyrite and sulphur expected from the mineral's composition. This may be due to oxidation of the pyrite with storage prior to analysis. The uncertainty in the y-intercept value of the regression, however, is 1.01. Therefore, the presence of other sulphide minerals, in addition to pyrite, that might be below the detection limit of XRD, and which could provide a slope of less than 2, cannot be ruled out.

In the coals, specifically, the correlation between SO_3 and pyrite is also quite good (r_s=0.87). Pyrite formation depends on the availability of Fe and the bacterial reduction of SO_4 in the pore waters during or shortly after deposition in the original peat accumulation (cf. Williams and Keith, 1963; Chou, 1990).

A plot of the relation between iron and sulphur is given in Figure 4.13. A reasonably good correlation (r_s=0.76) is observed between iron and sulphur for the coal samples. This trend is consistent with iron and sulphur occurring together, in approximately equal proportions, as pyrite in the coal samples. Furthermore, the y-intercept of the coal trendline, at 0.16% sulphur, indicates that practically no organic sulphur is present. No correlation is evident in the sediment samples.

As can be seen in Figure 4.14, the iron in the sediment samples is largely present as siderite (r_s=0.76), which was probably formed by interaction of Fe and CO_2 under reducing conditions in the absence of a significant SO_4 concentration. It is interesting to note the poor correlation (r_s=0.30) between iron and siderite, in the coal samples.

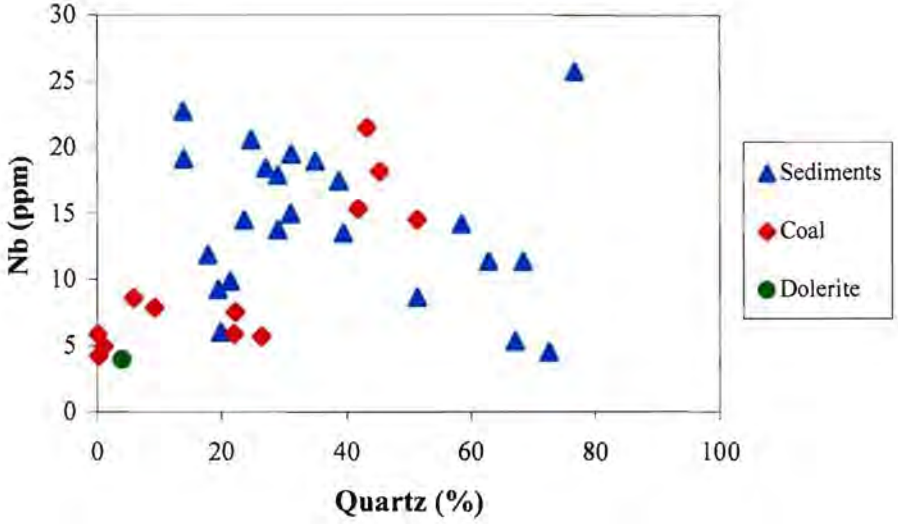


Figure 4.10: *Relationship between niobium concentration and quartz composition in selected lithological units.*

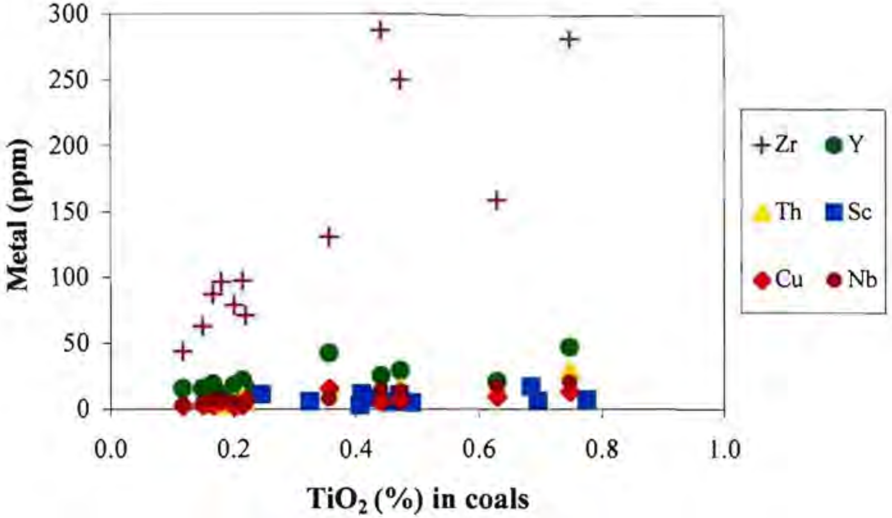


Figure 4.11: *Relationship between various metals and titanium in selected lithological units.*

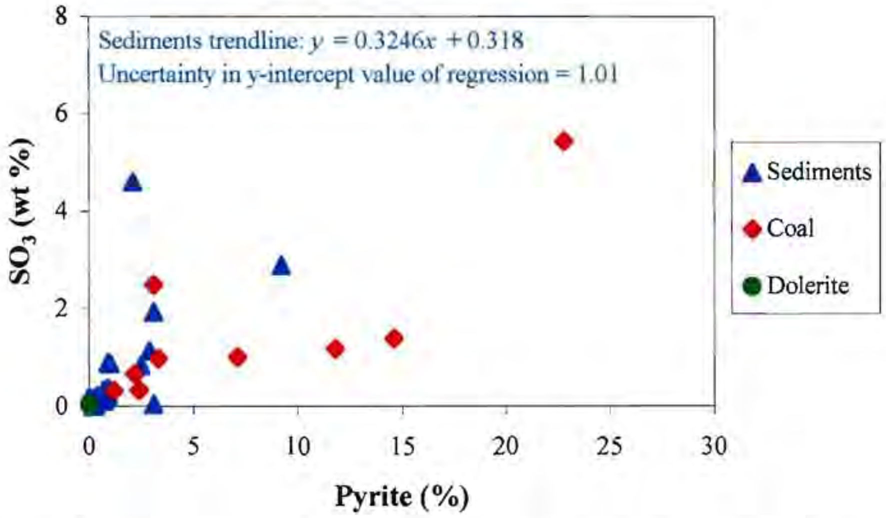


Figure 4.12: *Relationship between total sulphur concentration and pyrite composition of selected lithological units.*

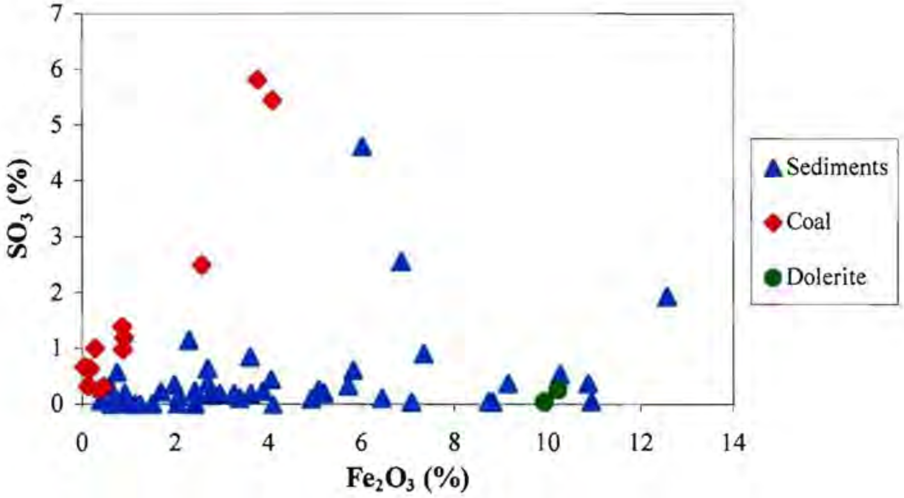


Figure 4.13: *Relationship between total sulphur and iron concentration in selected lithological units.*

4.4.4.3 Calcium, magnesium, strontium and barium

Calcium and magnesium occur in the samples mainly, if not entirely, as carbonate minerals. The correlation between CaO and calcite yields a coefficient of 0.71 (Figures 4.15). The results of the SIROQUANT analysis indicate that calcite and dolomite are present in substantial quantities in selected samples. Furthermore, some of the XRD patterns show traces of ankerite, which were not determined by SIROQUANT. Most samples have relatively low concentrations of Ca and Mg and a poor correlation (r_s=0.40) exists between these elements for the whole sample suite (Figure 4.16). Of the two sample groups, a stronger correlation (r_s=0.61) is evident in the sediments, indicating that more dolomite is likely to be present than in the coals where calcite is abundant. It can be seen on some of the XRD patterns that both calcite and dolomite occur together in the coals, and this would obviously affect the poor correlation coefficient (r_s=0.29) found here.

In the coals, Sr exhibits a reasonably strong correlation with Ca (r_s=0.83), but a weak correlation with Mg (r_s=0.47). Barium exhibits very poor correlations with Ca and Mg, with coefficients of 0.27 and 0.50, respectively. Strontium exhibits poor correlations with calcite and dolomite, and Ba exhibits no correlation at all with either calcite or dolomite. The relation of Sr to CaO and MgO in the coals is illustrated in Figure 4.17.

The existence of both Sr and Ba (as well as Ca) as aluminophosphate minerals of the goyazite-gorceixite-crandallite group was proposed by Ward and Taylor (1996). No such minerals, however, have been identified in this study as the techniques used are unlikely to detect trace quantities of aluminophosphate minerals. Reasonably good correlations of these elements with P_2O_5 in the coals of this study (r_s=0.67 and r_s=0.85) suggest that they are likely to occur in some phosphatic mineral. This, however, could not be confirmed as the sample groups were too small. Similarly, insufficient data was available to show a reliable correlation between P_2O_5 and apatite.

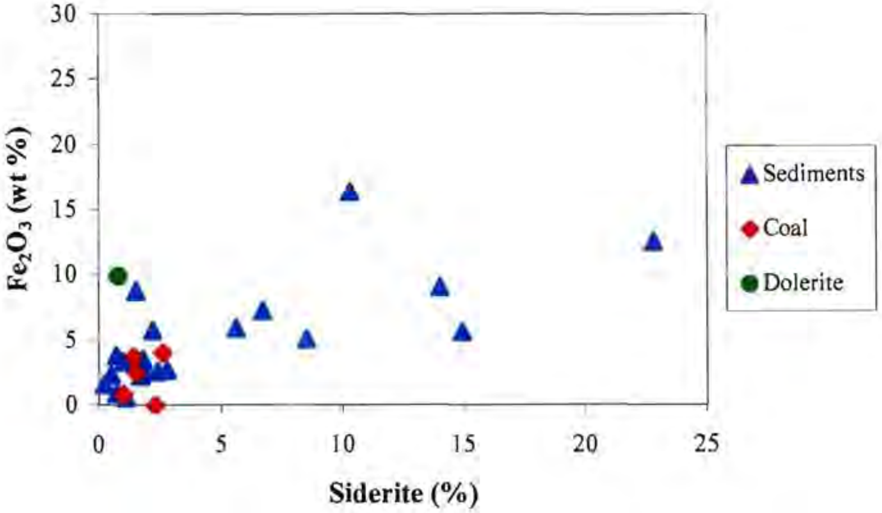


Figure 4.14: Relationship between iron concentration and siderite composition in selected lithological units.

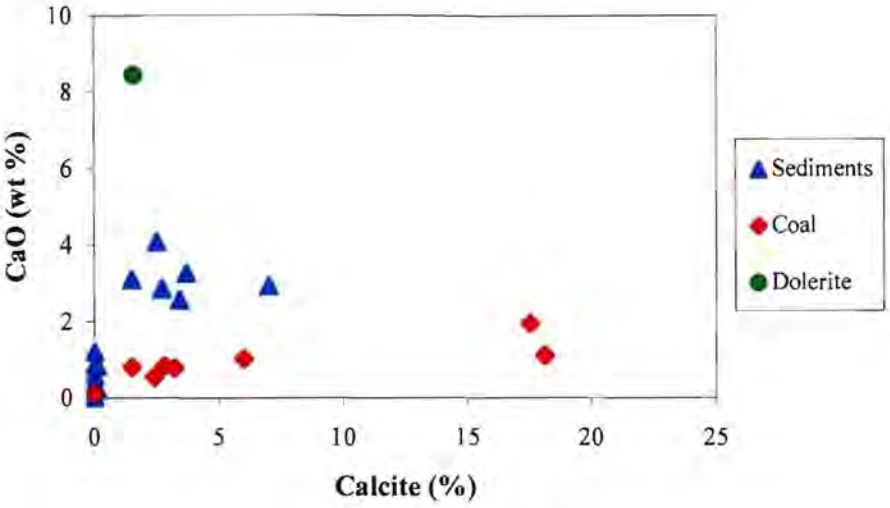


Figure 4.15: Relationship between calcium concentration and calcite composition of selected lithological units.

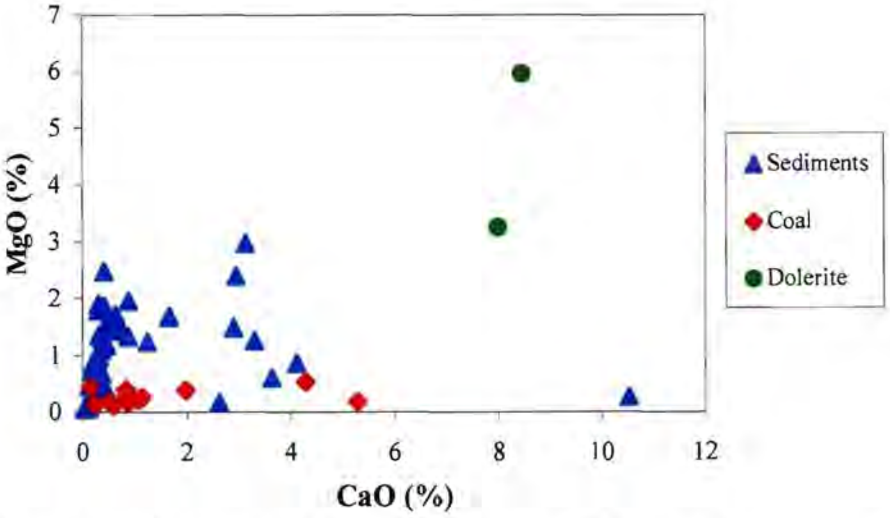


Figure 4.16: Relationship between magnesium and calcium concentration in selected lithological units.

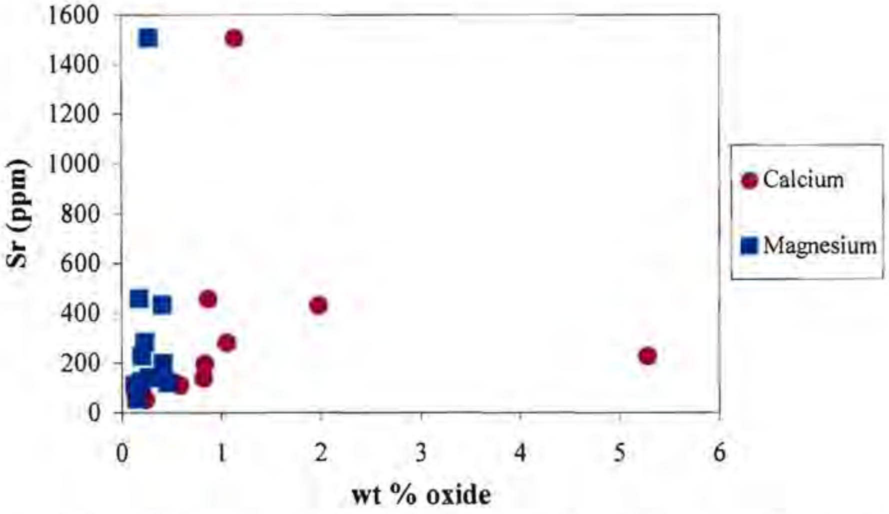


Figure 4.17: Relationship between calcium and magnesium, and strontium in selected lithological units.

4.4.4.4 Sodium, feldspar and halite

Small amounts of feldspar are present in a number of coal samples from various parts of Australia (Ward, 1978), the Illinois basin (Harvey *et al.*, 1983) and in bituminous coals from other areas as well. Much of this material is probably of epiclastic or pyroclastic origin, washed or blown into the swamp during peat accumulation (Ward, 1989). In the sediments, reasonable correlations (r_s=0.55) were observed between Na_2O and albite (r_s=0.55), and between Na_2O and microcline (r_s=0.60) (Figure 4.18 and 4.19). Insufficient data was available to indicate a correlation between CaO and anorthite, and plagioclase was not detected in the coal samples.

Halite was not found to occur although it is thought to exist, particularly at New Denmark colliery, as a result of marine transgressions. Furthermore, no correlation could be determined for Na_2O and Cl, as Cl was below detection limits in most of the samples. In a detailed study on the forms of chloride in Illinois Basin coals, Chou (1991) concluded that Cl occurs as NaCl dissolved in pore water and adsorbed on the inner surfaces of micropores in macerals. Similarly, much of the U in coal appears to be organically bound (Finkelman, 1993).

4.4.4.5 Potassium and rubidium

A number of different potassium minerals occur in the sample suite, including illite, muscovite, glauconite and feldspar. A weak correlation was found in the sediments (r_s=0.20) for K_2O and illite (Figure 4.20), and a slightly stronger correlation for K_2O and the mixed layer clays (r_s=0.50). The second correlation, however, was based on too few samples to be certain. Due to insufficient information, no reliable correlation could be determined for K_2O and feldspar in the sediments, though it is almost certain that one does exist. The reasonably good correlation seen in the sediments for K_2O and Ba (r_s=0.82) is therefore not unexpected (Figure 4.21), since both show promising correlations with the mixed layer clays. This may imply that Ba is ultimately substituting for divalent cations, such as Ca and Mg, in the clay mineral lattice. Although no correlations were found between either Ca or Mg and Ba, reasonably good correlations were found between Ba and Sr, particularly in the coals (r_s=0.65); as well as Sr and Ca (r_s=0.83).

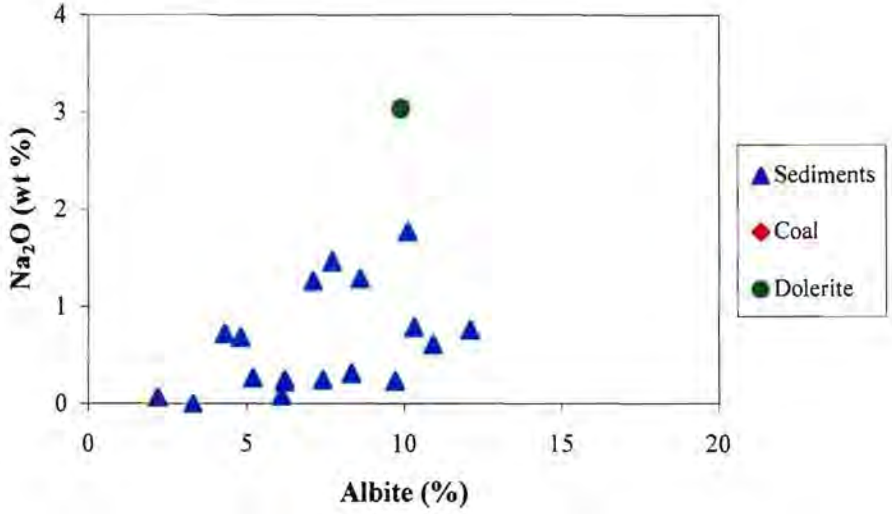


Figure 4.18: *Relationship between sodium concentration and albite composition of selected lithological units.*

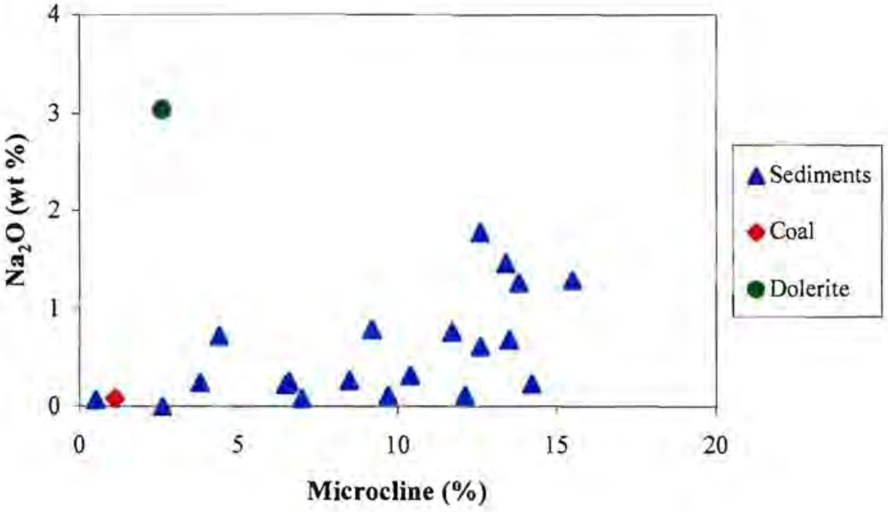


Figure 4.19: *Relationship between sodium concentration and microcline composition in selected lithological units.*

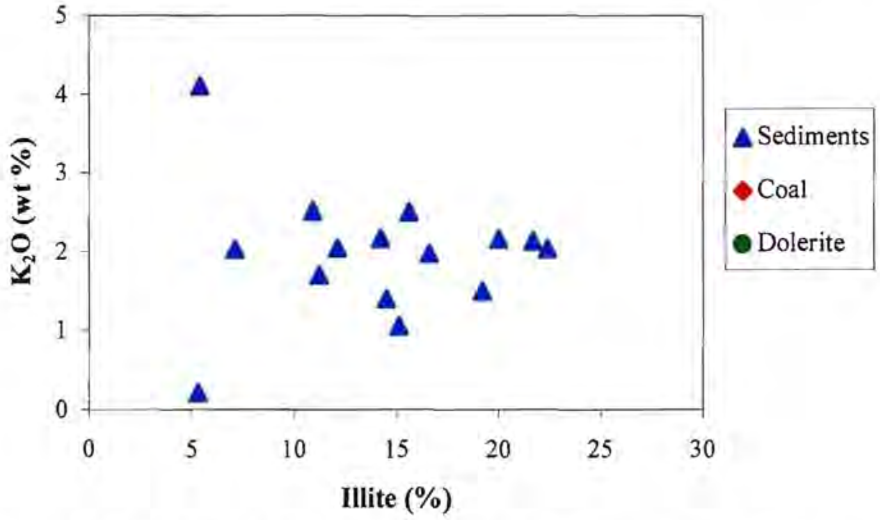


Figure 4.20: *Relationship between potassium concentration and illite composition in selected lithological units.*

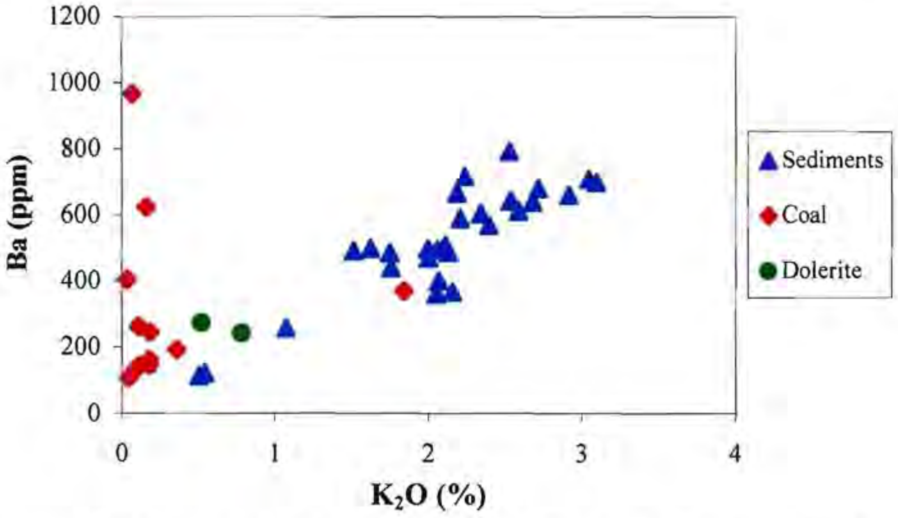


Figure 4.21: *Relationship between barium and potassium concentration in selecetd lithological units.*

Rubidium exhibits a very strong correlation with K_2O in the coals (r_s=0.93), and a weaker correlation in the sediments (r_s=0.82). All the coal samples studied plot close to the correlation line, regardless of the K-bearing minerals involved. This suggests that the Rb is intimately related to the K itself, and not any particular mineral component. From Figure 4.22, it can be seen that two sediment trends exist, almost parallel to each other. The lower trend comprises mostly arenaceous material whilst the upper trend is mostly argillaceous material. The argillaceous trend is not as tightly constrained as the coal trend, but follows the same line, intersecting the axes at the origin, indicating similar behaviour to the K_2O in the coal. The arenaceous trend, however, in spite of having an identical slope, cuts the K_2O axis at approximately 1.75 wt %. This would intimate that 1.75 wt % of the K_2O is probably bound in feldspar, which occurs only rarely, and in very small quantities, in the coal.

Figure 4.23 shows a mild correlation (r_s=0.57) between Rb and illite, indicating that Rb does substitute for K_2O, to a small extent, in the clay mineral lattice. This is confirmed by Finkelman (1982), who reports that the most probable mode of occurrence of Rb is in illite.

4.4.4.6 Manganese, molybdenum and siderite

According to Finkelman (1995), although few Mn minerals occur in coal, most of the Mn, especially in bituminous coals, occurs in solid solution in the carbonate minerals siderite and ankerite. The correlation coefficient for MnO and siderite (r_s=0.60) in this study, suggest that it substitutes partially for iron in this mineral throughout the sample suite (Figure 4.24). A weaker correlation was observed, for MgO and siderite (r_s=0.47), though this is largely influenced by the sediments. This is not unexpected, especially since Finkelman (1982) suggests clays as the most probable mode of occurrence for magnesium.

Like nickel, there is very little consensus in the literature as to the mode of occurrence of Mo. The strong chalcophile tendencies of Mo (Goldschmidt, 1954) indicate that a sulphide association, perhaps solid solution in pyrite, may be a likely mode of occurrence (Finkelman, 1995). The correlation between Mo and pyrite in the coals of this study is 0.90 (Figure 4.25), as is the correlation between Mo and siderite, in spite of the small number of samples. Incidentally, apart from those discussed, no other correlations were found in this study for chalcophile elements and S. Because of the relative abundance of pyrite in these samples, the

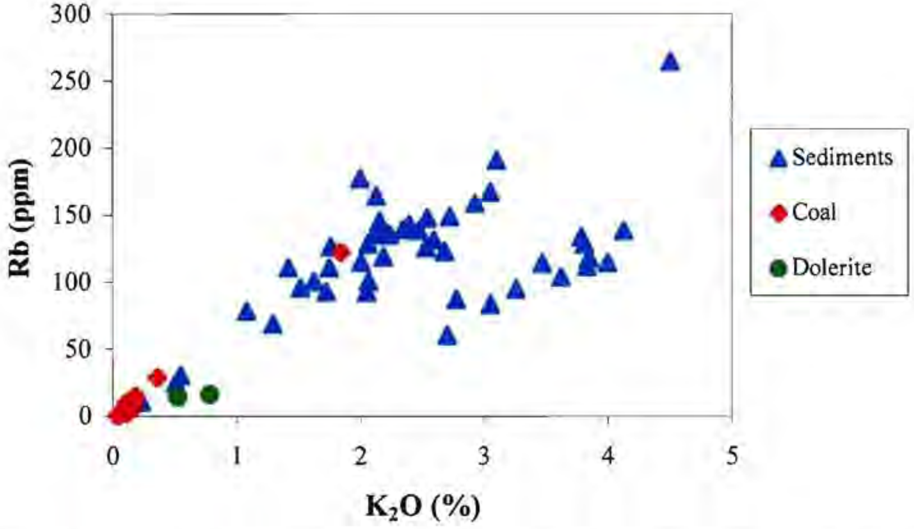


Figure 4.22: *Relationship between rubidium and potassium concentration in selected lithological units.*

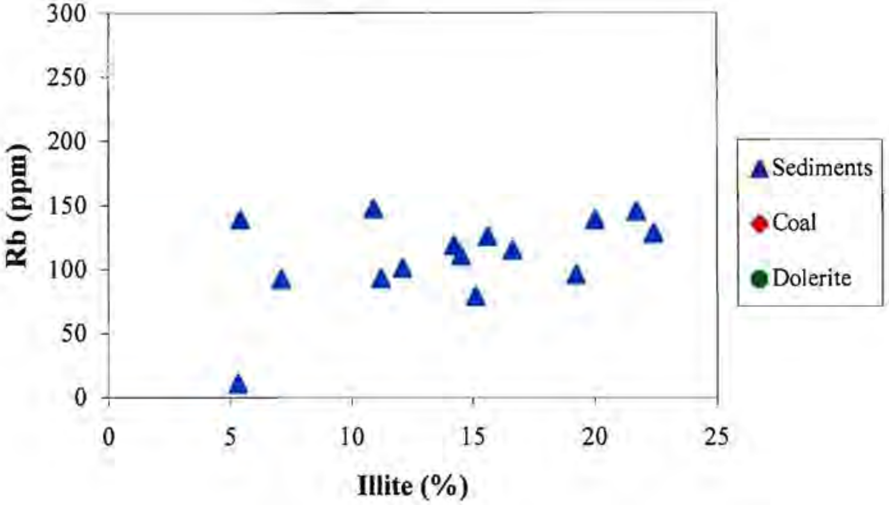


Figure 4.23: *Relationship between rubidium concentration and illite composition of selected lithological units.*

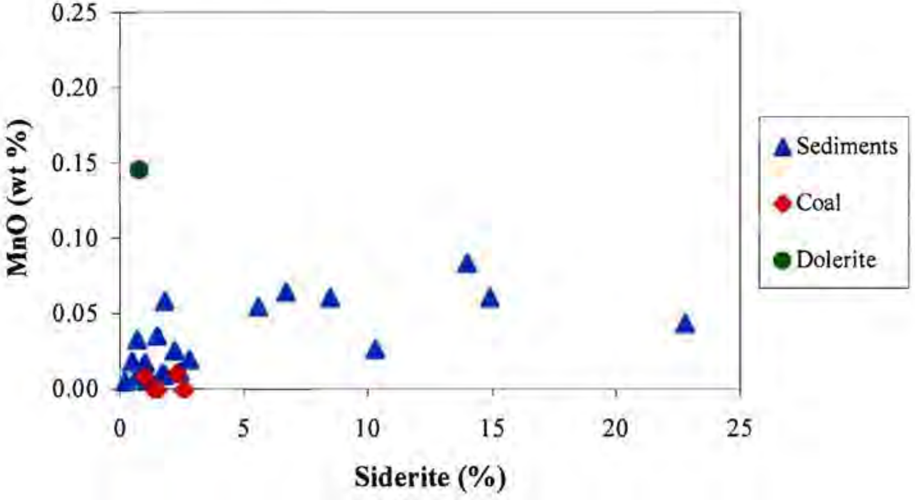


Figure 4.24: *Relationship between manganese concentration and siderite composition in selected lithological units.*

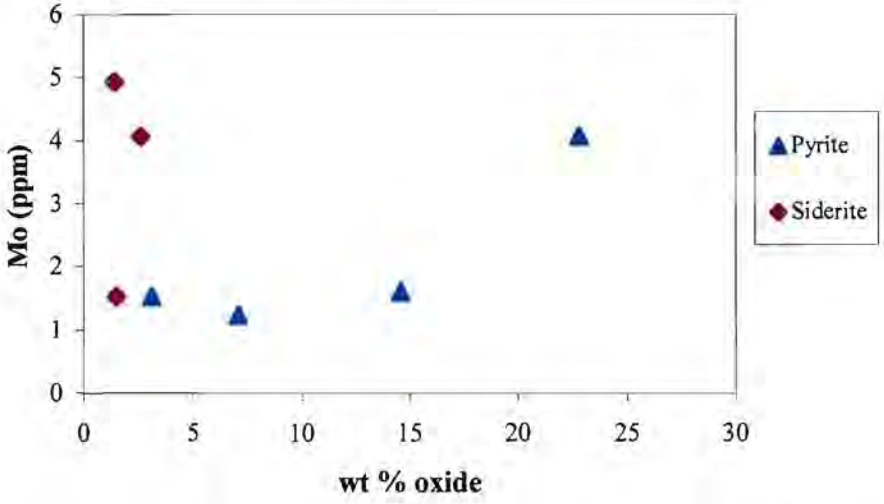


Figure 4.25: *Relationship between molybdenum concentration, and pyrite and siderite in selected lithological units.*

lack of, or limited correlation of other chalcophile elements with S really says little about the actual mineralogical hosts of these metals.

4.4.4.7 Zirconium and related elements

Zirconium is a relatively abundant trace element in the sample suite, with concentrations ranging from around 45 to almost 650 ppm. In the coals, however, Zr concentrations do not exceed 300ppm. Such concentrations are unusually high relative to British coals (Spears and Zheng, 1999), but are similar to those reported by Swaine (1990) and Ward *et al.*, (1999) in Australian coals. The occurrence of Zr is usually ascribed to the presence of discrete zircon grains (Swaine, 1990; Finkelman, 1994). These may in turn be derived from input of igneous material (Cook and Kirk, 1991) into the peat swamp. Zircon is also reported to occur commonly as rounded detrital grains in sands and sandstones (Cook and Kirk, 1991). No zircon was detected in the XRD study of these samples.

The only mineral with which Zr exhibits a reasonably strong correlation is quartz (r_s=0.74), and this is only in the coals (Figure 4.26). Petrographic studies on Australian coals (Kemezys and Taylor, 1964) suggest that some of the quartz in bituminous coals occurs as silt-sized, probably detrital grains, washed or blown into the swamp in conjunction with peat accumulation. The association between Zr and quartz therefore coincides with similar modes of occurrence in the coal.

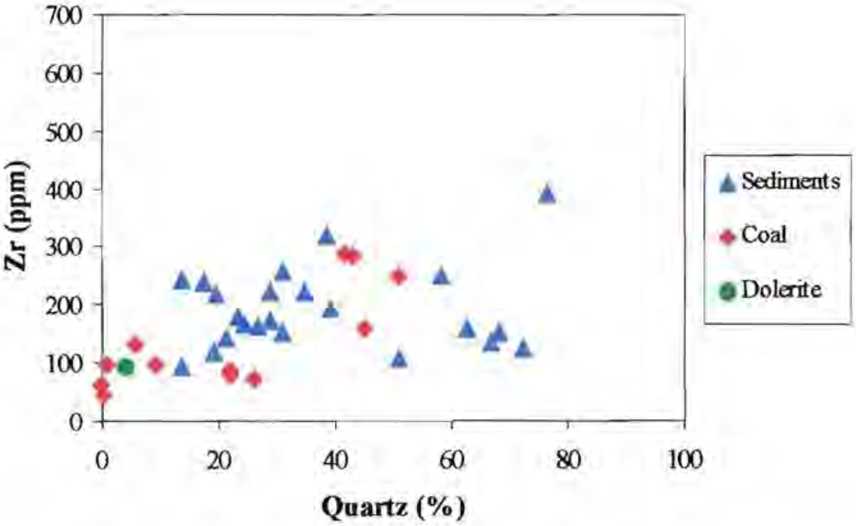


Figure 4.26: *Relationship between zirconium concentration and quartz composition of selected lithological units in the Vryheid Formation.*

Zirconium correlates fairly well with Nb (r_s=0.71) in all the samples. It also correlates well with Y (r_s=0.80), Rb (r_s=0.70), Th (r_s=0.76), Sc (r_s=0.80) and Cr (r_s=0.80) in the coals. Finkelman (1982) suggests the following modes of occurrence for these elements in coal: Nb = oxides, Y = rare earth phosphates, Rb = probably illite, Th = rare earth phosphates, Sc = unclear: clays, phosphates or organics, and Cr = clays (?). A very strong correlation can also be seen between Th and Y (r_s=0.83) confirming that these elements may be affiliated with a rare earth phosphate. No correlation, however, could be found with either of these and P_2O_5.

The reasonably strong correlations (r_s>0.70) that were found between almost all the above-mentioned elements (viz. Nb, Zr, Rb, Y, Th, Sc, and in some cases, Cr and V) is perhaps a reflection of a common igneous source. Based on the information available in this study, no further explanation can be given.

4.4.5 Ion exchange

Exchangeable cations are those that can be exchanged by a cation of an added solution. Thomas (1982) reports that in many cases, the definition of an exchangeable cation is straightforward, i.e. any added cation will exchange the soil (sediment) cation. In other cases, the definition is less sure. Examples of quasi-exchangeable cations are K^+ in micaceous ground, Al^{3+} in acid ground, and H^+ in practically all ground. Cation exchange capacity, the suite of exchangeable cations, and the nature of the measured exchangeable cations are dependent to a large extent on the chemical and mineralogical make-up of the ground (Thomas, 1982).

Clay minerals all exhibit ion exchange behaviour to some degree, as do zeolites, colloidal oxyhydroxides, and natural organic compounds. Adsorption capacity is therefore linked to clay content (< 2μm fraction), clay minerals, organic matter (%C), and oxide or hydroxide content. An empirical formula which relates cation exchange capacity (CEC) to percentage clay (2μm) and organic carbon is:

$$CEC(meq/100g) = 0.7 \times (\%clay) + 3.5 \times (\%C)$$

Some commonly reported cation exchange capacities (CEC) are shown in Table 4.4.

Table 4.4: *Cation exchange capacities of common soil and sediment materials (after Appelo and Postma, 1996).*

	CEC ($cmol_c$/kg)
Kaolinite	3 – 15
Halloysite	5 – 10
Montmorillonite	80 – 120
Vermiculite	100 – 200
Glauconite	5 – 40
Illite	20 – 50
Chlorite	10 – 40
Allophane	< 100
Goethite & Hematite	< 100
Organic matter (C)	150 – 400 (at pH 8)

It should be noted that CEC in clay minerals is not a very precise or fundamental quantity. It varies as a function of pH and as a function of the nature of the ions occupying the exchange sites. In general, we would expect cations located in the Gouy layer to exchange rapidly, whereas cations in the Stern layer might exchange rapidly or slowly depending on their bonding to the particle surface. Oxides and organic matter, which commonly form coatings on clay minerals (Jenne, 1977), often have high exchange capacities; thus specific values must be interpreted with caution because the surface charge (and hence CEC) of such material is strongly dependent on pH (Drever, 1997). Ion exchange reactions will exert an important control on water chemistry whenever water is in contact with sediments. For this reason, both the exchangeable cations and the CEC was determined for selected samples.

4.4.5.1 Vertical variation within a borehole

In an attempt to ascertain the vertical variation in CEC through the overlying sediments, all the lithological units from the most comprehensive borehole core (that from New Vaal colliery) were analysed. The results are presented in Table 4.5:

Table 4.5: *Exchangeable cations and CEC (both in cmol$_c$/kg) of sampled lithologies in a borehole at New Vaal Colliery.*

Sample No.	Lithology	Na	Mg	K	Ca	CEC (pH 7)
NVC-1	Weathered sst	0.911	19.4	2.80	24.6	32.3
NVC-2	Shale	0.762	20.2	1.88	22.3	25.5
NVC-3	Shale	0.795	14.5	1.53	17.7	22.4
NVC-4	Sandstone	0.373	7.58	1.71	15.3	11.3
NVC-5	Sst / shale	0.207	15.3	0.897	32.7	9.09
NVC-6	Shale	0.634	11.9	1.60	9.80	14.7
NVC-7$_A$	Sandstone	0.471	8.08	2.25	21.1	11.3
NVC-7$_B$	Glauconitic sst	0.626	10.2	5.22	26.3	13.6
NVC-8	Silt / sst	0.412	5.56	1.56	7.29	13.8
NVC-9$_A$	Coal	0.593	3.13	0.082	39.7	13.3
NVC-9$_B$	Coal	1.83	6.59	0.258	9.54	16.2
NVC-10	Silt	10.7	4.61	1.32	6.43	19.5
NVC-11	Silt	11.7	4.19	1.38	6.81	19.1
NVC-12	Shale	11.7	3.23	1.46	5.78	19.7
NVC-13	Coal	9.90	4.16	0.054	11.7	5.76
NVC-14$_A$	Sst / shale	4.28	1.04	0.295	2.40	11.9
NVC-14$_B$	Sandstone	2.04	0.707	0.207	1.55	8.18
NVC-15	Coal	5.65	1.73	0.211	11.8	16.0

In the sediments overlying the Top Seam (NVC-9) calcium and magnesium are the dominant exchangeable cations. In these units, the exchangeable magnesium trend correlates well with the overall CEC trend. The exchangeable calcium, however, fluctuates wildly with major peaks being observed in the sandstone and, lower down, with the coal seams. It is evident from the fact that the exchangeable calcium peaks exceed the total CEC, that a substantial amount of free calcium is available in these sediments. As anticipated, an increase in exchangeable potassium is observed in the glauconitic sandstone (NVC-7$_B$). It is interesting to note the increase in exchangeable sodium just below the Top Seam (NVC-9) and the resulting contribution this makes to the total CEC (Figure 4.27). It is well-known that Na, due to its lower valence and atomic radius, is far more readily exchanged from the clay mineral surface than either magnesium or calcium (McBride, 1994).

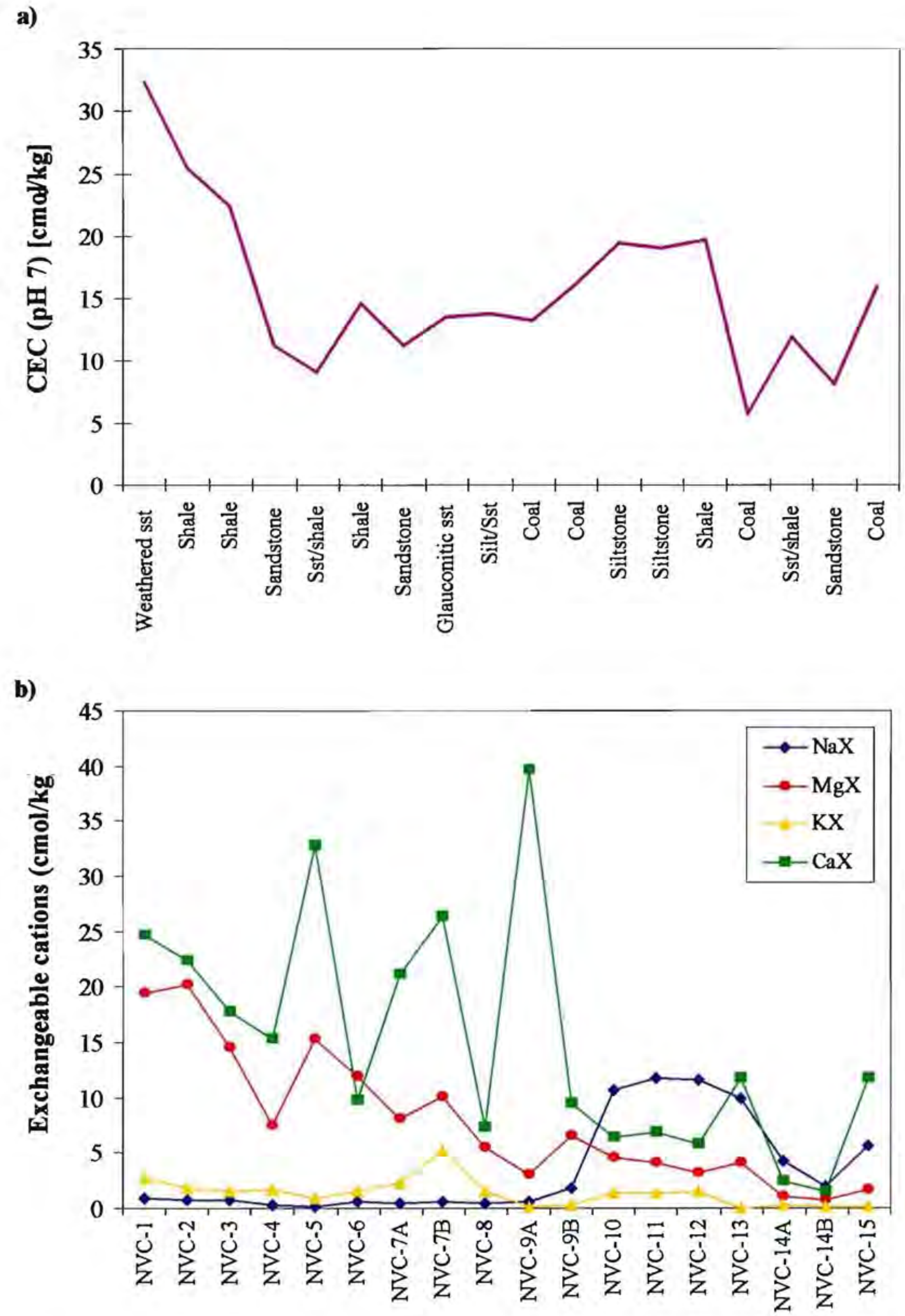


Figure 4.27: ***(a)*** *Cation exchange capacity, expressed in cmol$_c$/kg and measured at pH; and* ***(b)*** *Exchangeable cation concentrations, expressed in cmol/kg, for descending lithological units at New Vaal colliery.*

4.4.5.2 Horizontal variation across coalfields

Where possible, one representative sample of each of the following lithologies was selected from each borehole: shale, sandstone, glauconitic sandstone, siltstone and coal and analysed to see the variation across the coalfields. A sample from a dolerite sill was also included out of interest. The results are presented in Table 4.6, and Figures 4.28 and 4.29.

Table 4.6: *Exchangeable cations (in cmol/kg) and CEC (in cmol$_c$/kg) for selected lithological units across the coalfields.*

Sample No.	Lithology	Na	Mg	K	Ca	CEC (pH 7)
NVC-3	Shale	0.795	14.5	1.53	17.7	22.4
NVC-7$_B$	Glauconitic sst	0.626	10.2	5.22	26.3	13.6
NVC-8	Silt / Sandstone	0.412	5.56	1.56	7.29	13.8
NVC-11	Silt	11.7	4.19	1.38	6.81	19.1
NVC-13	Coal	9.90	4.16	0.054	11.7	5.76
KRL-K	Shale	0.507	8.81	1.23	15.8	19.9
KRL-F	Sandstone	0.453	1.69	0.682	11.2	4.53
KRL-D	Silt	2.96	3.40	1.257	3.14	10.0
KRL-4	Coal	3.76	3.93	0.142	23.3	14.7
GHC-B	Coal	0.186	3.16	0.400	5.77	9.55
GHC-D	Sandstone	0.079	0.442	0.866	0.779	6.20
GHC-F	Shale	0.558	2.90	0.978	3.46	8.91
ND-1	Dolerite	4.33	4.19	0.522	3.73	8.81
ND-5	Silt	5.14	3.26	2.10	2.11	15.8
ND-6	Glauconitic sst	2.79	1.43	3.46	2.17	9.94
ND-D$_1$	Sandstone	0.084	0.435	0.851	0.755	5.52
ND-G	Coal	2.77	2.70	0.103	13.5	10.9

Generally, the exchangeable cations Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} occur in the lithologies sampled, in the order listed. In most cases, Ca^{2+} occurs in larger quantities than all the other bases combined. Occasionally, more Mg^{2+} is exchangeable than Ca^{2+} (i.e. KRL-D and NVC-6). Thomas (1982) reports that this occurs in soils formed from serpentine, and in acid subsoils on older landscapes. No serpentine, however, was detected in these argillaceous units. Neither are they believed to be any more acidic than the coals.

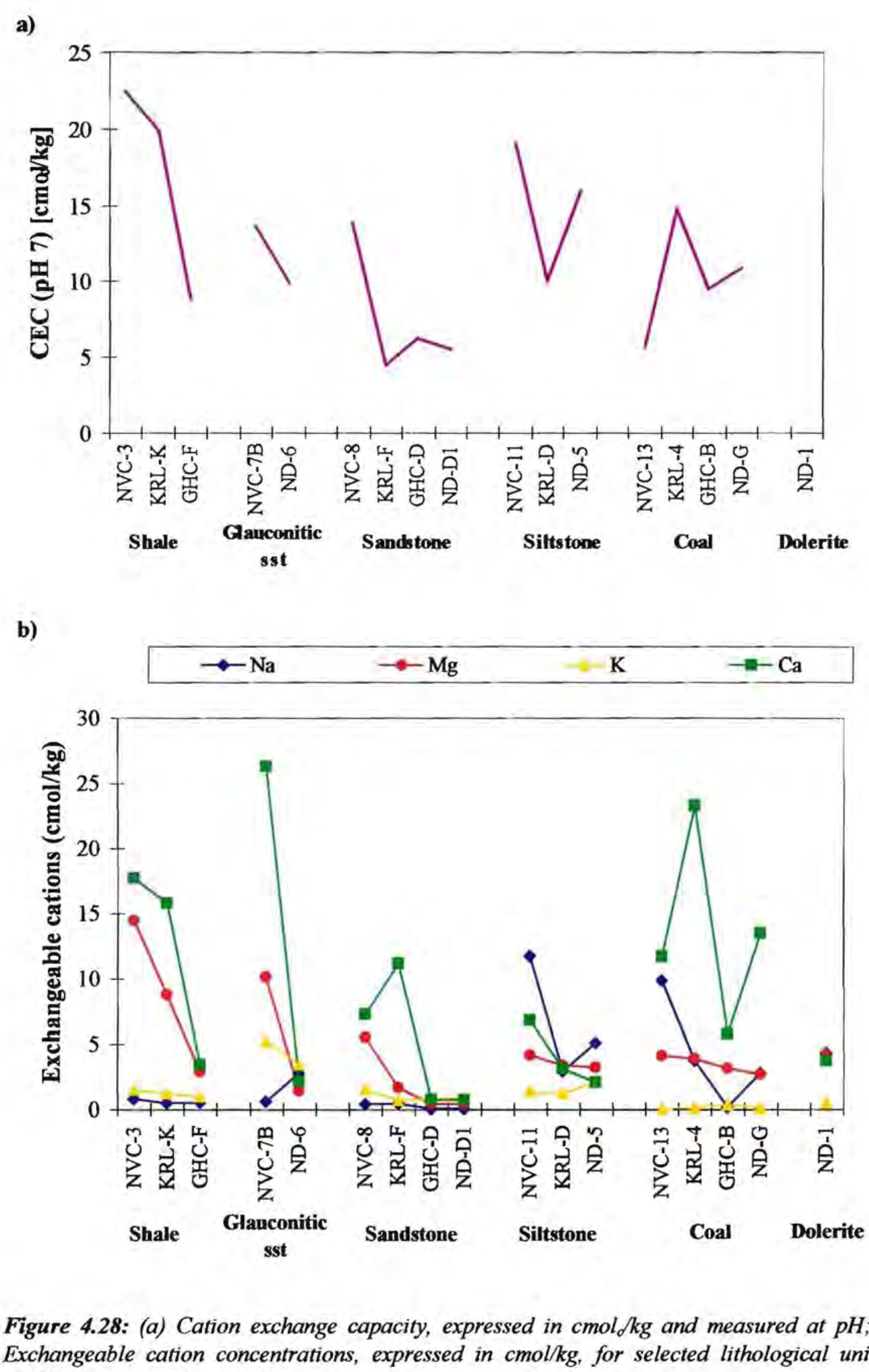


Figure 4.28: *(a) Cation exchange capacity, expressed in cmol$_c$/kg and measured at pH; and (b) Exchangeable cation concentrations, expressed in cmol/kg, for selected lithological units in the coalfields.*

Potassium is the third most abundant exchangeable base and its quantity varies depending on the feldspar and clay composition of the rock. In two of the sandstones, K^+ occurs in higher quantities than any other exchangeable cation: GHC-D and ND-6. The second of these is one of the few glauconitic sandstones that were sampled. Exchangeable sodium in most samples was very low. Thomas (1982) notes that in nitric soils, Na^+ may be present at a concentration of several centimoles charge per kilogram, although rarely is it present in as high a concentration as Ca^{2+}. In some of the silts and coals, however, these supposedly rare high concentrations were observed at all the collieries, except Goedehoop. Furthermore, the silts in which they occur, are usually overlying but close to the coal seams.

Furthermore, it was observed that except for the coal seams, the total CEC was highest at New Vaal for each of the lithologies analysed. This is thought to be a result of the relatively higher concentration of exchangeable Ca and Mg in almost all of the lithologies sampled. Apart from the increased exchangeable Na observed in the lower horizons at New Vaal (see previous section, Figure 4.27), the exchangeable Na concentrations in three of the lithological types at New Denmark are also elevated relative to the other collieries.

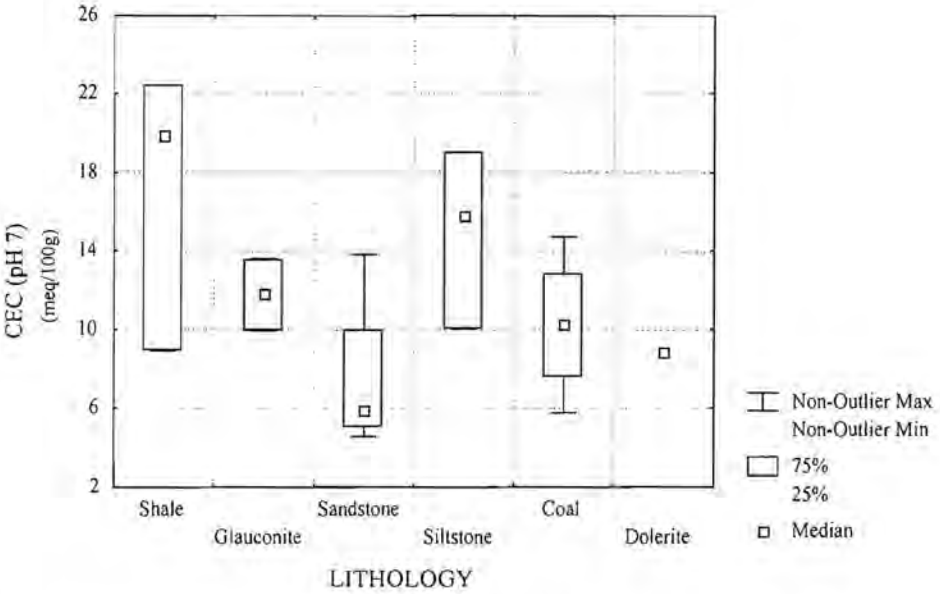


Figure 4.29: *Summary of variation in CEC of different lithologies of the coalfields.*

The highest overall CEC's were recorded in the shales and siltstones and the lowest in the sandstone and dolerite. Whereas the CEC in the shales is dominated by exchangeable Ca and Mg, in the siltstones it is attributable to Na, Ca and Mg. As anticipated, almost all the exchangeable K in the area comes from the glauconitic sandstones. These are also rich in exchangeable Ca and Mg. The coal is dominated by exchangeable Ca, with some exchangeable Na and Mg occurring.

4.5 Conclusions

The coal deposits are located in the Vryheid Formation of the Ecca group. The main lithological units include sandstones, shales, siltstones and coal. These sediments consist of varying proportions of two major oxides SiO_2 and Al_2O_3. C makes up the bulk of the coal, but is usually less than 30 wt% in the other rock types studied. In addition, Fe_2O_3, CaO, MgO, Na_2O are present in minor concentrations. Numerous trace elements were also detected. P_2O_5, MnO and Cl were barely present at all in any of the rocks.

The mineral matter in these sediments is dominated by silicates, carbonates, sulphides, phosphates and other crystalline mineral groups. In the coals, these are present in various forms including bands and laminae associated with organic matter as well as lenses, nodules and aggregates which indicate concurrent formation with the peat bed. Other minerals occur as veins or cleat and fracture fillings, indicating precipitation after compaction. Some of the mineral matter is of detrital origin, representing epiclastic or pyroclastic particles washed or blown into the peat swamp whilst other mineral matter, including most of the pyrite, quartz, siderite and kaolinite appears to have been formed by precipitation processes either within the swamp waters or in the pores of the peat deposit. Some pyrite, formed by bacterial reduction of dissolved sulphate ions, seems to be related in abundance to marine trangressions, which allowed permeation of sea water into the swamp and through the peat bed beneath. Siderite formed in the absence of sulphate-rich sea water, probably from CO_2 released during organic decay.

The clay fraction of the non-coal rocks is dominated by illite or interstratified clay minerals and kaolinite, with feldspar still present to a variable extent. Although perhaps modified by chemical reactions or ion-exchange mechanisms in the peat swamp, these clay minerals may also be present in the coal as well, especially near the base of the top of the seam.

CHAPTER 5

Modelling water-rock interactions

5.1 Introduction

Mining companies and regulatory agencies, such as the Department of Water Affairs, have observed a change in water quality in many of the South African collieries over time. In most cases, reasonably pure rainfall, which filters in through fractures and fissures, becomes saline and acidic. In other cases, the waters become saline and sodic. Occasionally, acidic waters may become near-neutral again. The mine water compositions, presented in Chapter 3, and the results of borehole core analyses, presented in Chapter 4, are used here to determine the nature and extent of geochemical reactions that are occurring in the groundwater system of some of the collieries, by identifying the minerals that are reacting and determining the amounts of these minerals that dissolve or precipitate. The processes investigated include the evolution of recharge water to become immature, and then mature mine waters, through precipitation-dissolution reactions involving carbonates, sulphates, oxyhydroxides and sulphides, and cation exchange. This investigation is not intended to represent site specific transport modelling, but rather to provide a more general understanding of the likely mineral dissolution and precipitation reactions that follow oxidative weathering in the mine environment and that could be invoked to explain the composition of resultant mine waters.

5.2 Conceptual model of mine water evolution

It is possible to schematically outline the conversion of reactants to products, via a variety of processes, as a generalized basis for understanding the way in which mine water evolves. Such a scheme is presented in Figure 5.1. The processes involved are familiar to any student of rock weathering but it would be instinctive to briefly discuss the special pertinence of some of these to a description of the mineralochemical events that give the mine water environment its distinctive character.

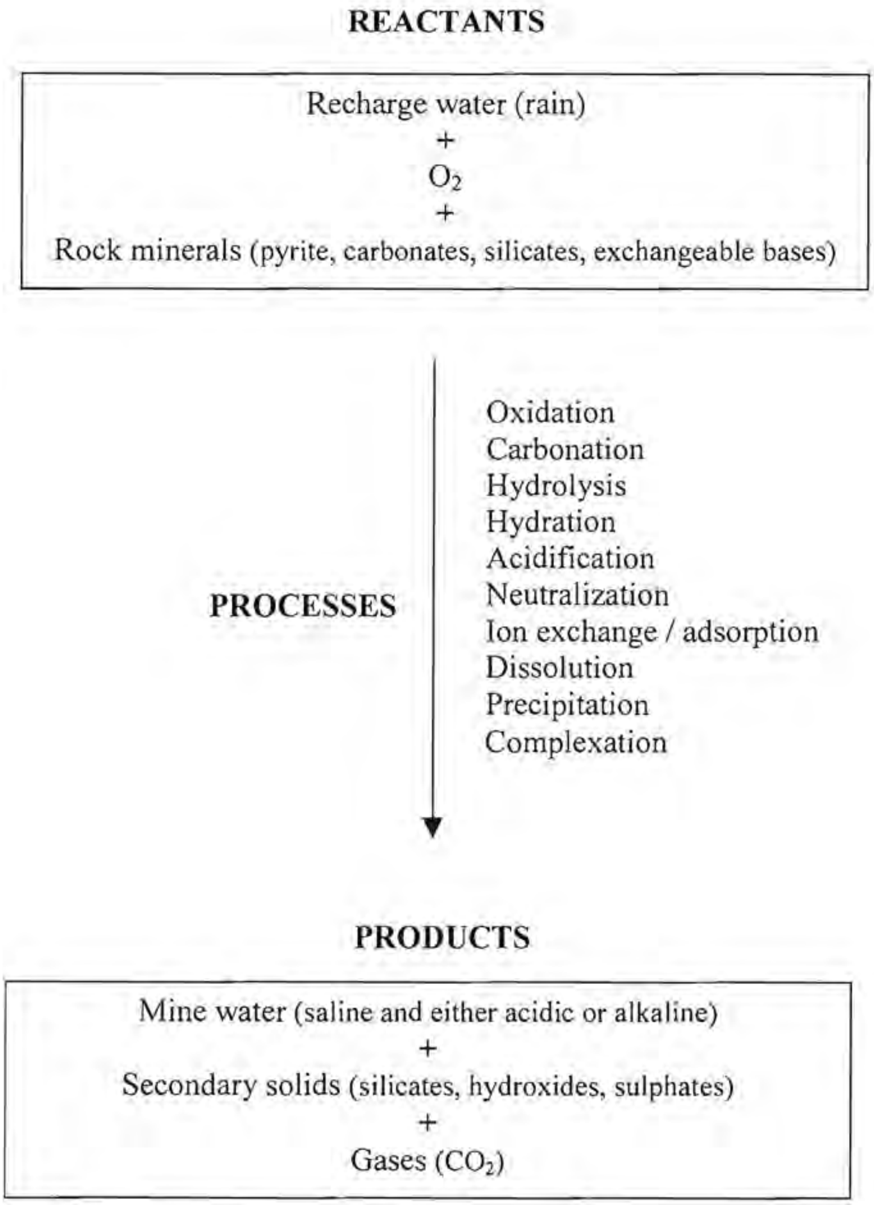


Figure 5.1: *Conceptual model for the geochemical evolution of mine water.*

5.2.1 Sulphide oxidation

According to Rose and Cravotta (1998), pyrite is characteristically oxidized by either Fe(III) or O_2. Perry (2001) reports that in fully flooded Pittsburg seam mines, no detectable levels of dissolved oxygen were found in 12 samples taken. In addition, in about 15 samples speciated for Fe(II) and Fe(III), ferrous iron typically is 99% or more of the dissolved fraction, and Fe(III) is often below detection. He concluded that after initial flooding, dissolved oxygen and Fe(III) are present only in small concentrations and further sulphide oxidation should be inhibited.

Due to unforeseen circumstances, the dissolved oxygen readings taken in this study could not be utilized. The results of iron speciation do, however, indicate that, as with Perry's Appalachian coal mine waters, ferrous iron dominates over ferric iron, which is often below detection limits, especially in the circum-neutral waters. Although no definite statement can be made regarding the inhibition of sulphide oxidation in the South African coalmines, the authors impression is that sulphide oxidation is limited in the older workings, which have filled with water and are no longer pumped or ventilated.

5.2.2 Acid neutralization and alkalinity generation

Collapsed overburden may contain horizons with 5 to > 50% carbonate (Perry, 2001), and the floor-rock is also often calcareous (Donaldson *et al.*, 1979). Brady (1998) reports that calcite, dolomite and siderite have been identified as the dominant carbonate minerals in the Monongahela and overlying Dunkard groups in Pennsylvania. Similarly, in this study all carbonate minerals are undersaturated in the immature mine waters. Many of the mature mine waters, however, are slightly oversaturated with respect to both calcite and dolomite, and highly oversaturated with respect to siderite. Similar trends for carbonate mineral saturation indices were found by Perry (2001).

Carbonate minerals are expected to dissolve, at first, then neutralize the acidity and generate alkalinity in the mine waters, and finally, may precipitate at the end of the flowpath. An exception to this is siderite, which has the potential to oxidize and hydrolyze the Fe. The infiltrating rain water is undersaturated with respect to calcite and dolomite, indicating that both carbonates should dissolve and generate alkalinity. Acid neutralization potential, available from fractured, broken carbonate-containing waste rock, and continuous infiltration of recharge water may exceed the overall acid generating capacity of the acid-forming rock which remains in contact with the water. Given sufficient recharge and reaction time, the acidity present will be neutralized and the system would be expected to turn alkaline eventually. In many of the South African mines, there is insufficient acid neutralization potential to maintain the alkaline system, and so the waters are ultimately expected to turn acid. Studies, funded by the Water Research Commission in South Africa, are underway to determine the extent of this problem (Boer, 2001 and Hodgson *et al.*, 2001).

5.2.3 Silicate mineral dissolution

Aluminosilicate minerals are common components of many mineral deposits or their host rocks. Reactions of acid with aluminosilicate minerals are a well-known part of the rock-weathering process (Stumm and Morgan, 1981). These acid-consuming reactions typically result in the release of some constituents into solution and the transformation of other constituents into more acid-stable and commonly less reactive minerals, such as is shown by the reaction of anorthite to form kaolinite:

$$CaAl_2Si_2O_8 + 2H^+ + H_2O \rightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4\ (s)$$

Variable silicate resistance to weathering is well documented in the literature (Goldich, 1938; Sverdrup, 1990 and Kwong, 1993). Minerals that crystallize from magmas at high temperatures, such as anorthite, tend to be more reactive than minerals that crystallize at lower temperatures, such as albite, muscovite and quartz. Clay minerals such as kaolinite have relatively low reactivity (Table 5.1).

Table 5.1: *Relative reactivities of common rock-forming minerals in coal environments, listed in order of decreasing reactivity. Carbonate minerals are included for comparison (Modified after Plumlee, 1999).*

Mineral Group	Typical minerals in coal environments
Readily dissolving	Calcite, aragonite
Less readily dissolving	Siderite, dolomite, magnesite
Fast weathering	Anorthite
Intermediate weathering	Chlorite, biotite
Slow weathering	Albite, montmorillonite, kaolinite
Very slow weathering	K-feldspar, muscovite
Inert	Quartz, zircon

Note: Dissolving minerals are those whose components are taken completely into solution. Weathering minerals are those whose components are partially removed into solution and partially converted into other minerals.

As demonstrated by the high levels (> 10 000mg/L) of aluminium found in acid mine drainage waters (Nordstrom and Alpers, 1999; Plumlee *et al.*, 1999), aluminosilicate minerals do react with the acid generated by sulphide oxidation. The abundance, however, of the aluminosilicate minerals found in many coal mining environments means that the aluminium in the waters was brought about through relatively limited acid consumption by aluminosilicate weathering reactions.

5.2.4 Ion exchange

Sodium increases substantially in the mature waters from some of the collieries, and evolution from Ca/Mg dominated to Na dominated water may result from exchange of Ca, Mg or Fe (II) for adsorbed sodium (or it may be derived through weathering). Donovan *et al.* (1999) and Perry (2001) report high concentrations of sodium in northern Appalachian and Pittsburgh seam mine waters, respectively. Chloride concentrations generally do not increase stoichiometrically with sodium in the mature mine waters, as would be expected if brine water was entering the underground pools. In a study of hydrochemical facies and groundwater flow, Back (1966) noted a progressive change from Ca/Mg dominated water to Na dominated along a flow path in some Atlantic Coastal Plain aquifers. The differentiation was attributed to ion exchange.

As with the northern Appalachian coals (Perry, 2001), the mineral fraction of the coal itself and associated sedimentary rocks, has been found to contain kaolinite and illite. In addition, the author has reported a cation exchange capacity of up to 32.2 $\mathrm{cmol_c/kg}$ in the weathered surface material and between 10 and 25 $\mathrm{cmol_c/kg}$ in the lithologies overlying the coal seams.

5.2.5 Precipitation of metal hydroxides (Al & Fe)

Iron floc precipitating from acid mine waters commonly contains a mixture of mineral phases ranging from poorly crystalline $Fe(OH)_3$, to ferrihydrite, schwertmannite and goethite (Bigham *et al.*, 1996; Ferris *et al.*, 1989; and Rose and Elliot, 2000). The more soluble oxyhydroxide mineral, amorphous $Fe(OH)_3$, is undersaturated in the mature mine waters, indicating that it is not likely to precipitate. If ferrihydrite is already present in the mine workings prior to flooding, it could dissolve, or convert to more stable oxide minerals, as suggested by Nordstrom's (1982) diagram of pyrite weathering. Goethite is oversaturated by at least 3 orders of magnitude in all the mine waters, indicating that precipitation of this mineral is highly possible, although metastable ferrihydrite is more likely to form first in terms of the GLO step rule (Sposito, 1989).

5.2.6 Formation of sulphate salts

During mining, the workings are dewatered and ventilated. Humidity and aeration provide an ideal atmosphere for the oxidation of pyrite to produce acidity and metal oxy-hydroxide minerals as shown:

$$FeS_2 + 3\tfrac{3}{4}\,O_2 + 3\tfrac{1}{2}\,H_2O \rightarrow 4\,H^+ + 2\,SO_4^{2-} + Fe(OH)_3$$

Frequently, however, sulphate minerals form as intermediate products of sulphide oxidation in the coal and mine waste rock. These are often visible as white and yellow precipitates. Although none of the observed precipitates were analysed in this study, some sulphate minerals that have been identified in Pittsburgh seam mines and Appalachian coal measures include gypsum, melanterite, halotrichite, pickeringite, copiapite, rozenite, and various jarosites (Nuhfer, 1967; Rose and Cravotta, 1998). Many of these salts are moderately soluble and can re-dissolve during mine flooding. Figures 3.52 and 3.61 show that many of the mine waters are undersaturated with respect to gypsum, and some five or more orders of magnitude undersaturated with respect to K-jarosite. Similar trends for sulphate mineral saturation indices exist in about 24 individual mine water analyses compiled, but unpublished, by Perry (c.f. Perry, 2001).

Where present, the above-mentioned sulphate minerals are expected to dissolve during mine flooding, and could account for the observed increase in sulphate concentration from infiltrating rain water to mature mine water. Some complex sulphate salts, like copiapite, lack thermodynamic data, and were not included in the PHREEQC saturation index calculations. Furthermore, except for gypsum, sulphate minerals can be a source of stored metals and acidity, as shown by the net reaction for complete dissolution of copiapite, followed by oxidation and hydrolysis of iron (Perry, 2001):

$$Fe(II)Fe_4(III)(SO_4)_6(OH)_2{\bullet}20\,H_2O + \tfrac{1}{4}\,O_2 \rightarrow 5\,Fe(OH)_3 + 12\,H^+ + 6\,SO_4^{2-} + 7\tfrac{1}{2}\,H_2O$$

If iron hydrolysis is incomplete, the solution will accumulate high concentrations of dissolved iron.

5.3 Materials and methods

5.3.1 Mass-balance modelling

Mass-balance modelling makes use of quantitative geochemical reactions to reproduce the composition of a water and at the same time remain consistent with any constraints applicable to the reactant phases. In this study, geochemical modelling simulations were run using NETPATH. NETPATH is an interactive computer program used to interpret net geochemical mass-balance reactions between initial and final waters along a hydrologic flow path (Plummer *et al.*, 1994). The program uses chemical and isotopic data for waters from a hydrochemical system. The processes of dissolution, precipitation, ion exchange, oxidation/reduction, degradation of organic compounds, incongruent reaction, gas exchange, mixing, evaporation, dilution, isotope fractionation, and isotope exchange can be considered. Geochemical mass-balance reaction models are examined between selected evolutionary waters for every possible combination of the plausible phases that might account for the composition of a selected set of chemical and isotopic constraints in the system (Plummer *et al.*, 1994).

In the present context, a mass-balance model is defined as one that determines the masses (per kilogram H_2O) of a set of plausible minerals and gases that must enter or leave the initial solution in order to define exactly a set of selected elemental, electron transfer, and isotopic constraints observed in a final (evolutionary) water. In hydrochemical systems the number of reacting phases is often larger than the number of constraints necessary to define their composition. NETPATH solves a set of linear equations that account for conservation of mass, and (optionally) conservation of electrons and selected isotopes to find every subset of the selected phases (every model) that satisfies the chosen constraints. Each mass balance problem can be treated as an isotope evolution problem solving isotope mass balance and Rayleigh distillation problems to predict the isotopic composition at the final point on the flow path (Plummer *et al.*, 1994).

The conceptual model presented here was tested with the inverse geochemical model using two solution compositions: one representing the "initial" infiltrating rain water, and the other a "mature" mine water from this study. A rain water sample, taken from Goedehoop colliery, was used as the infiltrating "initial" water for flow-path modelling. It should be noted that the composition of the "initial" water is of no consequence in terms of the modelling process, since it is not possible for such a dilute water to influence the reaction path the mine waters are likely to follow. Twenty samples, thought to be representative of the main water types observed in this study, were selected as the "mature" mine waters. In some cases, these included both an acid and a near-neutral water of the same type. All twenty have a chemical composition representative of a high degree of bedrock weathering (as indicated by the relatively high EC) and most are probably close to equilibrium with secondary minerals. The Eh values used in the calculations were determined from the Nernst equation using the pe values estimated in Section 3.3.2 (Ion speciation). Although not exact, they were deemed to be a more realistic estimate than using the default pe value of 4. Previously, the solutions had been speciated using PHREEQC, and the results examined for mineral saturation indices and the partial pressures of gases. Inverse modelling simulations included only ion exchange, mineral precipitation and dissolution. In order to simplify the system, infiltration and mixing with surface and groundwater were excluded from the modelling exercise.

For the most part, the minerals considered in the flow-path modelling were chosen from those known to occur in the logged boreholes according to the mineralogical investigations conducted and presented in Chapter 4, and that were consistent with computed saturation indices. These included:

- Organic matter: "CH_2O"
- Carbonates: calcite, dolomite and siderite
- Halides: halite
- Silicates: orthoclase, albite, anorthite, kaolinite, illite, SiO_2
- Sulphides: pyrite
- Sulphates: gypsum, jurbanite, schwertmannite, and jarosite-K
- Oxy-hydroxides: amorphous $Fe(OH)_3$

Constraints placed on these phases were consistent with the computed saturation indices for the waters modelled. Generally speaking, however, organic matter, carbonate minerals, halite, most of the silicates and pyrite were constrained to dissolve only. Halite was included as a source of chloride, as fossil salts are believed to be the source of high Na-Cl concentrations in the water in the New Denmark region (pers. comm. Mine Personnel, 1999). In addition, the system was open to O_2 and CO_2. Kaolinite, illite and SiO_2 were allowed to both dissolve and/or precipitate. Although $Al(OH)_3$ is a likely sink for Al in the mature mine waters, it was excluded from the calculations since it cannot co-exist with kaolinite and SiO_2 (c.f. Garrels & Mackenzie, 1971). Furthermore, although amorphous $Fe(OH)_3$, gypsum, jurbanite, schwertmannite and jarosite are potential sources of soluble sulphate and metals, for simplification and because none are likely to be present as initial (host rock) phases, they were constrained to precipitate only. Exchange species included Ca, Na and Mg and the exchange ratio was set at 0.5:2:0.5, this being the most likely of the limited options available in the model.

Although Rose and Elliott (2000) noted substantial desorption of sulphate from ferric precipitates in acid drainage, as the sediments were amended with liming agents, and Perry (2001) included a hydrous ferric oxide surface in his PHREEQC inverse modelling to examine sulphate desorption as mine water pH increased from acid to neutral conditions, no attempt was made in this study to include a desorption pathway.

5.3.2 Calculation limitations

Mass balance calculations, such as those produced by NETPATH, are a useful approach in identifying <u>possible</u> reactions that may explain differences in water chemistry along a flow path. It is important, therefore, to note that if the water analyses have been affected by transient chemical conditions or are not within the same flow system, the technique of mass-balance modelling may produce erroneous results. Thus care must be taken in applying this type of mass-balance modelling to systems with changing flow conditions due to pumping, or with changing chemical composition due to other phenomena, such as mixing, both of which occur on the South African coal mines.

Furthermore, the following limitations, summarized by Appelo and Postma (1996), should be kept in mind:

1. The solution of the mass balance equations is not necessarily unique. Different choices of phases may lead to equally consistent reaction schemes (i.e. A mass balance calculation does not prove that the reactions take place).
2. There are no thermodynamic constraints on mass balance calculations. The mass balance calculation may predict impossible reactions, like precipitation of plagioclase at low temperature, or gibbsite precipitation when kaolinite is the stable phase.

spite of its slower weathering rate. Finally, kaolinite precipitation was favoured, rather than that of illite.

It should be noted that in rare instances, miniscule quantities (< 0.05mmol/kg H_2O) of halite and K-feldspar were found to precipitate, rather than dissolve as expected. Rather than eliminate these otherwise conformable models, they were maintained and the presence of such negligible quantities attributed to analytical error. In general, the anomalous dissolution or precipitation of some minerals was overlooked in the calculated output if the quantities involved were negligible compared with those of the major reacting solids, on the grounds that this result was only produced out of necessity for the model output to balance perfectly in terms of chemical stoichiometry.

5.4 Results and discussion

5.4.1 Anticipated flow paths for particular water types

Two model results are shown in Table 5.3, for each of the waters assessed. Waters are listed in order of type prevalence, with a range in pH for the more dominant types. The left column for each model shows the amount of each reactant and the right column, the amount of each product. If desired, the reaction for GS 4, for example, could be written as:

> Rain water + 58.1 O_2 *(g)* + 8.12 $CaCO_3$ + 7.34 $CaMg(CO_3)_2$ + 2.09 NaCl + 0.44 $Al_4Si_4O_{10}(OH)_8$ + 0.27 Illite + 15.6 FeS_2 + 1.21 Na_2X → Mine water (GS 4) + 23.3 CO_2 (g) + 1.21 CaX/MgX + 1.78 $Fe_8O_8(OH)_6SO_4$ + 1.56 SiO_2

In most cases, one of the chosen models favoured illite dissolution, whilst the other favoured K-feldspar dissolution. The main geochemical transfers included carbonate dissolution, ion exchange of adsorbed Na with Ca and Mg and pyrite oxidation, with SiO_2 precipitation. Albite and anorthite dissolution is generally only invoked in the near-neutral waters, whilst kaolinite dissolution is associated with the acidic waters. Although no obvious trend was evident in the calculated ion exchange process in the acidic waters, Na was noted to replace Ca and Mg in solution in the near-neutral waters. In the near-neutral waters, kaolinite and amorphous $Fe(OH)_3$ were the dominant precipitating minerals, whilst in most of the low pH (acidic) waters assessed, schwertmannite (and occasionally jarosite and jurbanite) were caused to precipitate. Two exceptions to the generalized models presented for all mine waters

Table 5.3: *Mass balance results for representative waters of the major types observed in coal mine environments. Results in mmol/kg substance dissolved (R) or precipitated (P). R-values for* O_2 *and* CO_2 *indicates in-gassing and P-values indicate out-gassing.*

Type	**Ca-Mg-SO_4**												**Mg-Ca-SO4**			
Sample	**GS 4s**				**KK 16**				**GS 13s**				**GH 17s**			
pH	3.10				5.96				8.39				3.23			
EC (mS/cm)	4.13				2.68				4.64				5.79			
	Model 1		*Model 2*		*Model 1*		*Model 2*		*Model 1*		*Model 2*		*Model 1*		*Model 2*	
	R	P	R	P	R	P	R	P	R	P	R	P	R	P	R	P
O_2 (g)	58.1		58.1		43.9		43.9		66.7		66.7		250		261	
CO_2 (g)		23.3		23.4	1.02		1.02		0.41		0.41			33.4		30.4
Calcite	8.12		8.06													
Dolomite	7.34		7.41										16.4		14.9	
Halite	2.09		2.09		0.38		0.38		1.42		1.42		0.19		0.19	
K-feldspar			0.16				0.15				0.36		13.7		15.7	
Kaolinite	0.44		0.67			16.7		16.5		34.4		34.1				
Albite					21.5		21.8		45.5		46.1				5.99	
Anorthite					5.63		5.56		11.0		10.8					
Illite	0.27				0.25				0.59				25.1		25.1	
Exchange	1.21 Na_2X	1.21 CaX / MgX	1.21 Na_2X	1.21 CaX / MgX	10.7 CaX / MgX	10.7 Na_2X	10.8 CaX / MgX	10.8 Na_2X	19.9 CaX / MgX	19.9 Na_2X	20.2 CaX / MgX	20.2 Na_2X	3.00 Na_2X	3.00 CaX / MgX		
Pyrite	15.6		15.6		11.9		11.9		17.9		17.9		94.3		100	
Jurbanite														67.7		75.7
Schwertmannite		1.78		1.78												
Jarosite														28.8		30.8
$Fe(OH)_3$ (a)						9.82		9.82		17.9		17.9				
Gypsum																
SiO_2		1.56		1.56		43.8		43.8		91.7		92.9		129		153

Table 5.3 continued: *Mass balance results for representative waters of the major types observed in coal mine environments. Results in mmol/kg substance dissolved (R) or precipitated (P). R-values for O_2 and CO_2 indicates in-gassing and P-values indicate out-gassing.*

Type	**Mg-Ca-SO_4**				**Ca-SO_4**								**Ca-Na-SO_4-HCO_3**			
Sample	**AC 7s**				**LN 6**				**NLC 6**				**BC 3s**			
pH	7.74				4.16				5.95				7.50			
EC (mS/cm)	5.08				3.15				2.33				1.86			
	Model 1		*Model 2*		*Model 1*		*Model 2*		*Model 1*		*Model 2*		*Model 1*		*Model 2*	
	R	P	R	P	R	P	R	P	R	P	R	P	R	P	R	P
O_2 (g)	81.0		71.9		57.1		57.1		32.6		32.6		15.3		15.3	
CO_2 (g)	3.87		8.74			24.0		24.0	5.68		5.68		7.56		7.56	
Calcite				4.87	15.9		15.9									
Dolomite					3.74		3.77									
Halite	0.65		0.65		0.57		0.57		0.98		0.98		0.31		0.31	
K-feldspar	1.00		1.00		0.06		0.12				0.10				0.09	
Kaolinite		41.2		41.2			0.09			16.7		16.6		12.2		12.1
Albite	81.3		81.3						13.0		13.1		16.4		16.6	
Anorthite									9.99		9.95		3.83		3.79	
Illite					0.10				0.17				0.15			
Exchange	36.4 CaX / MgX	36.4 Na_2X	36.4 CaX / MgX	36.4 Na_2X	0.24 Na_2X	0.24 CaX / MgX	0.24 Na_2X	0.24 CaX / MgX	6.81 CaX / MgX	6.81 Na_2X	6.89 CaX / MgX	6.89 Na_2X	4.75 CaX / MgX	4.75 Na_2X	4.83 CaX / MgX	4.83 Na_2X
Pyrite	21.7		19.2		15.3		15.3		8.73		8.73		4.11		4.11	
Jurbanite																
Schwertmannite						1.80		1.80								
Jarosite																
$Fe(OH)_3$ (a)		21.7		19.2						8.31		8.31		4.11		4.11
Gypsum		4.87														
SiO_2		165		165		0.50		0.50		25.8		26.2		32.8		33.1

Table 5.3 continued: *Mass balance results for representative waters of the major types observed in coal mine environments. Results in mmol/kg substance dissolved (R) or precipitated (P). R-values for O_2 and CO_2 indicates in-gassing and P-values indicate out-gassing.*

Type	**Ca-Mg-Na-SO_4**				**Ca-Mg-SO_4-HCO_3**				**Fe(3)-SO_4**				**Na-SO_4**			
Sample	**NVC 3**				**NVC 6**				**LK 6**				**OC 2**			
pH	7.80				8.08				2.37				3.06			
EC (mS/cm)	2.42				1.50				10.5				10.6			
	Model 1		*Model 2*		*Model 1*		*Model 2*		*Model 1*		*Model 2*		*Model 1*		*Model 2*	
	R	P	R	P	R	P	R	P	R	P	R	P	R	P	R	P
O_2 (g)	27.2		27.2		13.9		13.9		273		273		141		141	
CO_2 (g)	3.47		3.47		3.44		3.44			2.42		2.43		54.5		54.5
Calcite									0.55		0.55		4.33		4.33	
Dolomite									1.28		1.29		24.8		24.8	
Halite	0.30		0.30		0.15		0.15		1.87		1.87		9.33		9.33	
K-feldspar			0.20				0.11				0.01					
Kaolinite		15.5		15.3		8.85		8.74	5.00		5.02				0.01	
Albite	26.3		26.6		15.4		15.5									
Anorthite	1.98		1.90		0.96		0.92									
Illite	0.33				0.19				0.02				0.01			
Exchange	9.42 CaX / MgX	9.42 Na_2X	9.59 CaX / MgX	9.59 Na_2X	6.25 CaX / MgX	6.25 Na_2X	6.34 CaX / MgX	6.34 Na_2X	1.00 CaX / MgX	1.00 Na_2X	1.00 CaX / MgX	1.00 Na_2X	36.8 Na_2X	36.8 CaX / MgX	36.8 Na_2X	36.8 CaX / MgX
Pyrite	7.29		7.29		3.73		3.73		73.4		73.4		37.8		37.8	
Jurbanite													0.01		0.00	
Schwertmannite										3.77		3.77		4.57		4.58
Jarosite													0.81		0.81	
$Fe(OH)_3$ (a)		7.29		7.29		3.73		3.73								
Gypsum																
SiO_2		52.8		53.4		30.8		31.1		9.71		9.71				

Table 5.3 continued: *Mass balance results for representative waters of the major types observed in coal mine environments. Results in mmol/kg substance dissolved (R) or precipitated (P). R-values for O_2 and CO_2 indicates in-gassing and P-values indicate out-gassing.*

Type	**$Na-SO_4-HCO_3$**				**$Ca-Mg-Na-SO_4-HCO_3$**				**$Ca-Na-Mg-SO_4-HCO_3$**				**$Na-Ca-Mg-SO_4$**			
Sample	**ND 6s**				**NVC 15**				**NAC 3**				**NVC 12**			
pH	8.06				7.51				6.77				7.57			
EC (mS/cm)	3.84				1.30				0.88				5.86			
	Model 1		*Model 2*		*Model 1*		*Model 2*		*Model 1*		*Model 2*		*Model 1*		*Model 2*	
	R	P	R	P	R	P	R	P	R	P	R	P	R	P	R	P
O_2 (g)	26.2		26.2		8.69		8.69		5.66		5.66		76.0		76.0	
CO_2 (g)	9.53		9.53		4.02		4.02		3.44		3.44		6.29		6.29	
Calcite																
Dolomite																
Halite	7.04		7.04		0.57		0.57		0.07		0.07		1.03		1.03	
K-feldspar				0.00			0.09				0.11				0.60	
Kaolinite		23.8		23.8		7.18		7.09		4.52		4.41		40.8		40.2
Albite	43.1		43.1		11.5		11.7		6.16		6.35		76.4		77.4	
Anorthite	2.26		2.26		1.26		1.22		1.22		1.18		1.46		1.21	
Illite		0.01			0.15				0.19				1.00			
Exchange	5.1 CaX / MgX	5.1 Na_2X	5.12 CaX / MgX	5.12 Na_2X	4.16 CaX / MgX	4.16 Na_2X	4.23 CaX / MgX	4.23 Na_2X	1.80 CaX / MgX	1.80 Na_2X	1.90 CaX / MgX	1.90 Na_2X	18.0 CaX / MgX	18.0 Na_2X	18.5 CaX / MgX	18.5 Na_2X
Pyrite	7.05		7.05		2.38		2.38		1.51		1.51		20.3		20.3	
Jurbanite																
Schwertmannite																
Jarosite																
$Fe(OH)_3$ (a)		7.05		7.05		2.38		2.38		1.46		1.46		20.3		20.3
Gypsum																
SiO_2		85.9		85.9		22.9		23.2		12.3		12.6		154		156

Table 5.3 continued: *Mass balance results for representative waters of the major types observed in coal mine environments. Results in mmol/kg substance dissolved (R) or precipitated (P). R-values for O_2 and CO_2 indicates in-gassing and P-values indicate out-gassing.*

Type	**Na-Ca-SO_4**				**Ca-Na-Mg-HCO_3-SO_4**				**Fe(2)-SO_4**				**Na-SO_4-Cl**			
Sample	**ND 3s**				**GH 13s**				**LK 7**				**ND 5s**			
pH	7.02				7.28				2.54				7.64			
EC (mS/cm)	6.79				0.61				10.5				5.37			
	Model 1		*Model 2*		*Model 1*		*Model 2*		*Model 1*		*Model 2*		*Model 1*		*Model 2*	
	R	P	R	P	R	P	R	P	R	P	R	P	R	P	R	P
O_2 (g)	77.7		77.7		2.63		2.63		483		483		28.0		28.0	
CO_2 (g)	10.7		10.7		2.92		2.92			14.0		14.0	6.88		6.88	
Calcite									4.21		4.16					
Dolomite									5.15		5.20					
Halite	15.0		15.0			0.05		0.05	2.48		2.48		27.3		27.3	
K-feldspar			0.44				0.11				0.12					0.01
Kaolinite		47.5		47.1		3.79		3.7	3.48		3.65			23.2		23.2
Albite	81.6		82.3		4.28		4.46						43.3		43.2	
Anorthite	5.86		5.68		1.45		1.40						1.63		1.64	
Illite	0.74				0.18				0.20					0.02		
Exchange	16.5 CaX / MgX	16.5 Na_2X	16.9 CaX / MgX	16.9 Na_2X	1.42 CaX / MgX	1.42 Na_2X	1.51 CaX / MgX	1.51 Na_2X	1.26 CaX / MgX	1.26 Na_2X	1.26 CaX / MgX	1.26 Na_2X	6.35 CaX / MgX	6.35 Na_2X	6.34 CaX / MgX	6.34 Na_2X
Pyrite	20.8		20.8		0.70		0.70		130		130		7.50		7.50	
Jurbanite																
Schwertmannite										5.63		5.63				
Jarosite																
$Fe(OH)_3$ (a)		20.8		20.8		0.70		0.70						7.50		7.50
Gypsum																
SiO_2		164		165		8.52		8.88		7.27		7.27		86.3		86.3

involve the Mg-Ca-SO_4 waters (GH 17 and AC 7) and the Na-SO_4 waters (OC 2). These exceptions will be discussed further.

Mg-Ca-SO_4 waters

In the acidic Mg-Ca-SO_4 waters, the bulk of the magnesium is derived from illite dissolution, with only the "usual" amount (< 5mmol/kg H_2O) emanating from the exchange surfaces. Excess quantities of silica (>120mmol/kg H_2O) and jurbanite (~ 70mmol/kg H_2O) precipitate out in order to maintain the stoichiometric balance. The dissolution of dolomite is favoured over that of calcite. In addition, K-feldspar precipitates in both models given for GH 17, as does illite. The higher proportion of K-feldspar dissolution, as compared to the other water types, produces sufficient K for jarosite precipitation to be favoured over that of schwertmannite. The exceptionally high sulphate concentrations observed in the mine water could have evolved through the oxidation of up to 100mmol/kg H_2O of pyrite by 260mmol/kg H_2O of O_2. This represents a considerable amount of pyrite oxidation, which is characteristic of acid mine drainage environments. Although the alternative model presented for the development of GH 17 shows no ion exchange, but dissolution of albite instead, the molar quantities of the other reactant and product phases remains much the same.

The near-neutral, representative, example of a Mg-Ca-SO_4 water presented here (AC 7) also shows K-feldspar dissolution but in much smaller quantities than for its acidic counterpart. In place of illite dissolution, the major cations have evolved through extensive ion exchange and albite dissolution. Similarly large quantities of albite dissolution are invoked in some of the waters from New Denmark and New Vaal collieries. As before, excess quantities of silica (~ 160 mmol/kg H_2O) precipitate out in order to maintain the stoichiometric balance.

Na-SO4

In spite of its acidic nature, the Na-SO_4 water from OC 2 is a unique type in that it may have evolved through the dissolution of a substantial quantity of dolomite (~ 25mmol/kg H_2O). The carbonate produced is largely released as CO_2 (g), and, although Na-dominant, Mg is still very much in evidence in the final water. As with many of the New Denmark waters, the large concentration of Na in OC 2 is calculated to have been supplied by the dissolution of halite (9.33mmol/kg H_2O). In the models presented, extensive cation exchange has also occurred (36.8mmol/kg H_2O) in order to bring more Na into solution. Furthermore, the models produced by NETPATH to explain the evolution of OC 2 ignored the constraints placed on jarosite (based on it's positive saturation index, it was constrained to precipitate only), and as a result it is seen here as a reactant, rather than a product. This would be an additional source of sulphate, iron and potassium for the mine water.

5.4.2 Large-scale evolution of mine waters

As we have seen the same models seem to emerge for a number of the related waters and therefore it could be assumed that one (or a few) general models are applicable to all coal mine waters to explain their evolution. The degree to which the waters have evolved can be ascertained by assessing their overall composition. For example, consider two waters of differing salinity: GH 13 and NVC 12.

GH 13 is a Ca-Na-Mg-HCO_3-SO_4 type water, of pH 7.28 and EC 0.61mS/cm, located underground. NVC 12 is a Na-Ca-Mg-SO_4 type water, of pH 7.57 and EC 5.86mS/cm, and is located on the surface. Therefore, the major differences between these two waters is the disappearance of the co-dominant HCO_3 anion in the NVC 12 water, which has a substantially higher EC than GH 13. A comparison between two of the models produced by NETPATH to explain their development reveals some interesting differences. In the first model, the higher salinity NVC 12 water, which is a surface water body and therefore more likely to experience O_2 in-gassing and CO_2 out-gassing, has undergone substantially more pyrite oxidation (20.3mmol/kg H_2O compared to 0.70mmol/kg H_2O), albite dissolution (76.4mmol/kg H_2O compared to 4.28mmol/kg H_2O) and cation exchange (18.0mmol/kg H_2O compared to 1.42mmol/kg H_2O). This has resulted in the production of excessive quantities of kaolinite (40.8mmol/kg H_2O) and SiO_2 (154mmol/kg H_2O). The magnitude of these differences is very similar in the second model, which predicts orthoclase dissolution, rather than illite dissolution.

Although these waters were sampled at different times, from two completely separate regions, it is intriguing to note their similarity. It could be suggested that reasonably pure rain water (of Na-Ca-SO_4 type in the Witbank coalfield), which infiltrates the mine workings through cracks and fissures, would evolve through the dissolution of carbonate and silicate minerals to a X-HCO_3-SO_4 type water, where X refers to the dominant cation. Ultimately, it could be expected then to mature to a X-SO_4 type water as pyrite oxidation escalates either in well-ventilated or flushed compartments underground or exposed at the surface, and all the alkalinity produced has been neutralized and the buffering capacity exhausted. The nature of the dominant cations expected in a mature water would then be dependent on the degree of weathering of minerals in the host rock through which the water has passed. As illite and anorthite would be the most easily weathered, one would expect Mg and Ca to dominate the relatively immature waters, and Na (from albite dissolution) to dominate the more mature mine waters. The waters from New Denmark colliery would be a minor exception, due to the added influence of the dissolution of fossil salts in the aquifer.

Alternatively, we can consider two acid waters, one substantially more saline than the other: GS 4s, an underground storage dam, and LK 7, which is at surface. GS 4s is a Ca-Mg-SO_4 type water, of pH 3.10 and EC 4.13mS/cm; whilst LK 7 is an Fe(2)-SO_4 type water, of pH 2.37 and EC 10.5mS/cm. Due to their acidic nature, it is not surprising that both waters are dominated by the SO_4 anion. LK 7, however, has more than double the salinity of GS 4s, attributable largely to the presence of considerable quantities of iron in solution.

As before, a comparison between two of the models produced by NETPATH to explain their development reveal some interesting differences. In the first model, the higher salinity LK 7 water, which is a surface water body and therefore more likely to experience O_2 in-gassing and CO_2 out-gassing, has undergone substantially more pyrite oxidation (130 mmol/kg H_2O as compared to 15.6 mmol/kg H_2O). This has resulted in the production of excessive quantities of both iron and sulphate in solution, and the precipitation of marginally more schwertmannite (5.63 mmol/kg H_2O as compared to 5.63 mmol/kg H_2O). For the most part, the degree to which cation exchange and silicate mineral dissolution has occurred, is not significantly different in these two waters. The additional dissolution of kaolinite in LK 7, however, results in the slightly elevated precipitation of SiO_2 from this water. Once again, the magnitude of these differences is very similar in the second model, which predicts K-feldspar dissolution, rather than illite dissolution.

As before, it is important to note that although these waters were sampled at different times, from two completely separate mines, their similarity is intriguing. In the case of acid waters, it could be suggested that reasonably pure rain water (of Na-Ca-SO_4 type in the Witbank coalfield), which infiltrates the mine workings through cracks and fissures, would again evolve through the dissolution of carbonate and silicate minerals to a mature X-SO_4 type. In the same manner, the escalation of pyrite oxidation in well-ventilated or flushed compartments underground or exposed at the surface, would neutralize the alkalinity produced through calcite and dolomite dissolution and the buffering capacity would eventually become exhausted. The nature of the dominant cations expected in this ultra-mature water would again be dependent on the degree of weathering of minerals in the host rock as well as the extent of pyrite oxidation (and in extreme cases, the dissolution of secondary hydroxysulphate minerals formed earlier).

In conclusion, it is believed that once the alkalinity and buffering capacity of a water have been exhausted as it evolves to become acid, there is little chance of that water ever being re-neutralized. In the West Rand gold mining region of South Africa, which is underlain by the Transvaal dolomite sequence, acidic mine drainage has been neutralized over time (pers. comm. Martin Fey, 2001). This is, however, one of only a few known cases in South Africa where this has occurred and is solely a consequence of the surrounding geology.

5.5 Conclusions

The chemical analyses of mine waters at numerous sites in South African collieries have shown a variety of compositions which have allowed the waters to be grouped, based on their dominant ion types. From their compositions it is clear that there is a considerable amount of acid mine drainage production, although highly saline, near-neutral waters are more common than highly saline acid waters. The high concentrations of Na and divalent cations indicate advanced stages of weathering, whilst the high concentrations of iron and sulphate suggest that pyrite oxidation is one of the dominant processes. The high dissolved silica concentrations reflect the ultimate breakdown of primary and secondary aluminosilicate minerals in the acidic environment.

The models that best describe or explain the reactions responsible for mine water composition have been selected on the basis of the greatest probability of satisfying the following criteria: (1) mineralogical data for the host rocks, (2) mineral saturation index data for the mine waters, (3) geochemical reality, especially the expectation that "primary" (i.e. rock-forming) minerals will dissolve and secondary minerals will precipitate, rather than vice versa, as the mine water evolves to its current composition, and (4) that, all other things having been considered, the better model is that which involves the smallest degree of mineral dissolution and precipitation.

Combining saturation index and speciation calculations with mass balance computations has led to a geochemical model that includes (1) dissolution of carbonates (particularly calcite and dolomite), silicate minerals (such as K-feldspar, albite and anorthite) and clays (collectively referred to as illites here), (2) oxidation and dissolution of pyrite, (3) extensive ion exchange, (4) precipitation of kaolinite or an unspecified (possibly amorphous) aluminosilicate of the same composition as kaolinite, SiO_2 and amorphous $Fe(OH)_3$ in near-neutral waters or schwertmannite, occasional jurbanite and/or jarosite and SiO_2 in acid waters, and (5) high partial pressures of CO_2.

In terms of the long-term evolution of mine waters, it is suggested that ultimately coal mine waters can be expected to develop from a reasonably "pure", Ca-Mg-HCO_3-SO_4 type water to a saline Na-SO_4 type, depending on the associated geology, exposure to oxygen and the degree of weathering of the host rock. In extremely acidic cases, waters may proceed to become highly saline and Fe-SO_4 dominated, at which point there is little likelihood of their ever re-neutralizing.

CHAPTER 6

Classification of mine waters

6.1 Introduction

The diversity of uses to which mine water can be put and the range of activities or environments that are affected by its quality, mean that there is a potentially very large array of *ad hoc* classifications of mine water, each designed to match a particular set of water management objectives. In Section 2.4, it was found that current systems for chemically classifying water typically emphasize either geochemical characteristics or engineering or biologically related properties, but not all three. In order to integrate the geochemical and technical criteria required for a general purpose classification, a link was sought between those constituents which characterize a water body as a result of its genesis, and those responsible for limiting its use.

One of the aims of this research has been to identify and explain the relationships between constituents of mine waters and associated, undisturbed groundwaters in South African coal-mining regions. This has involved the systematic characterization of the geochemical nature of mine waters, and has provided a framework for the design of an information system to make water use more effective in the mining industry. The essence of this information system is a geochemically based classification of water bodies on the coal mines, with due recognition being given to technical criteria that are practically relevant to water quality. In this chapter, an improved classsification scheme for systematizing a large body of data on both underground and surface waters on a number of collieries, including a selection of waters believed to be unaffected by mining activities, is developed and tested.

6.2 Water quality assessment

In order to ascertain whether colliery water is suitable for domestic use, mining operations or irrigated agriculture, it is essential to assess quality in terms of health, scaling and corrosion potential, and various factors that may affect crop yield such as salinity, infiltration and specific ion toxicity.

6.2.1 Water for domestic use

The Department of Water Affairs and Forestry (DWAF, 1995) published a series of Draft Water Quality Guidelines for South African waters. The Water Research Commission, in conjunction with DWAF, further updated these guidelines in 1999 (WRC, 1999). A summary of the defined Target Water Quality Ranges for domestic use is presented in Chapter 2 (Table 2.11). The water samples taken from the collieries have been partially assessed in terms of these guidelines. A full assessment would require additional analyses, especially those relating to pathogens. Although the drinking water guideline has not been marked on the relevant box and whisker plots in Figures 3.2 to 3.36 it is important to note that most of the waters are highly unsuitable for drinking and for this reason its domestic use will not be discussed further. The reader is, however, referred to the guidelines (DWAF, 1995a and WRC, 1999) for the effects on health which may result if this water is used for domestic purposes.

6.2.2 Calcium carbonate precipitation potential

The precipitation potential of calcium carbonate (CCPP) in water can be determined using STASOFT4 (Morrison and Loewenthal, 2000). This software has been developed specifically for use in the softening and stabilization of cooling water, mining wastewater and terrestrial water. It is designed for calculating the chemical dosages required for adjusting a water body to a preset calcium (or magnesium) concentration or pH. It can be used to determine the fractions required to blend two waters to a specified pH, or to determine the water condition after blending several waters. It can also be used to determine the condition of a water body after equilibration with air, after a change in temperature has taken place, or following a change in concentration due to evaporation.

The software can be applied to waters with a wide range in salinity. For low salinity (TDS < 1000mg/L) or medium salinity waters (1000mg/L < TDS < 3000mg/L), the following input parameters are required before STASOFT4 can perform any calculations: temperature, pH, calcium and magnesium content, a carbonate system parameter (for example, CO_3 alkalinity or H_2CO_3 acidity, both expressed in mg/L $CaCO_3$) and a salinity parameter (such as EC or TDS). More comprehensive information is required for higher salinity waters (i.e. TDS

> 3000mg/L). This would include the sulphate, sodium and chloride concentrations (Friend and Loewenthal, 1992).

As temperature increases there is an increase in the CCPP towards more positive values. This increase is not constant for each sample but is dependent on both the ionic strength of the solution and pH, as well as the concentration of various constituents such as Ca, Mg and HCO_3. From Figures A6.1 through A6.26 (Appendix 6) it is clear that there is considerable variation in the CCPP both between collieries and within them.

In order for a thin, egg-shell layer of $CaCO_3$ to form as a protective lining in pipes, the ideal precipitation potential is about 4mg/L (pers. comm. Dick Loewenthal, 1998). Because it was recently observed that some dissolved metals, such as zinc, have the capacity to inhibit calcite precipitation (Coetzee *et al.*, 1996; Coetzee *et al.*, 1998), further research may be needed before the 4mg/L value is considered to be universally applicable.

Only five of the 167 sampled water bodies (AC 2s, BC 9s, KC 9s, KK 4 and NVC 7) have close to an ideal CCPP value at 25°C. When heated, the CCPP increases and these waters will become slightly more scaling. Most of the waters have a positive CCPP well in excess of 4mg/L, implying that a thick calcite layer is expected to grow on the surface of pipes and equipment through which the water passes. Those samples with a negative CCPP represent water bodies that are undersaturated with respect to calcite. In the study by Azzie (1999) it was observed that even with a 15°C increase in temperature, calcite is not likely to precipitate out of these solutions, although the Arnot waters were close to calcite precipitation at 40°C.

6.2.3 Scaling and corrosion in equipment

Loewenthal *et al.* (1986) defined tentative guidelines for the prevention of aggression of water to concrete pipes and corrosion of metal surfaces. The aggression prevention guidelines are based on pH, CCPP and sulphate concentration; while the corrosion prevention guidelines are based on $CaCO_3$ SI, alkalinity, and the concentration of calcium, chloride and sulphate. Stabilization treatments involve calculating the chemical dosages to condition the water to meet these guidelines. These guidelines are outlined in Appendix 6.

The guidelines were developed for industrial and mining wastewaters. Therefore, the water bodies at each of the collieries have been interpreted in terms of these guidelines. The figures in Appendix 6 show the aggressive and corrosive tendencies of the colliery waters at 25°C in terms of these guidelines.

6.2.3.1 Aggression

Overall, almost half (~56%) of the waters in this study displayed a negative CCPP, which implies they have non-scaling tendencies and, therefore, may be aggressive. All of the waters at three of the collieries, Landau, New Largo and TNDBC, produced a negative CCPP, as did most of those at Goedehoop. Generally speaking, New Largo is the only one of these likely to be aggressive as a result of its purity rather than its salinity. In terms of the sulphate concentration, over 70% of the waters assessed exceed the 350mg/L threshold value and therefore are considered to be aggressive. Arnot and Kriel are the only collieries in which less than 30% of their waters are aggressive due to excess sulphate concentrations. Furthermore, they are the only collieries the waters of which show an all-inclusive, non-aggressive tendency.

6.2.3.2 Corrosion

Due to their acidity, a calcite saturation index was only determined for 112 of the 167 samples (i.e. about 67%). Of these, 47 samples (about 42%) were found to be undersaturated with respect to calcite and are therefore likely to corrode metal surfaces. The waters at New Denmark and New Vaal were completely supersaturated with respect to calcite. Almost all of the waters sampled in the thirteen collieries are corrosive due to excess sulphate, and a few due to excess chloride as well, particularly at New Denmark. About a third of the waters (37%) are also corrosive due to insufficient alkalinity, and / or calcium in a few cases.

Although New Denmark, on the whole, is highly scaling (due to high calcium and bicarbonate concentrations), its corrosion potential, due to excess chloride and sulphate, will probably over-ride its tendency to scale. Ultimately, it is expected to provide some of the least attractive waters for re-use in industry, along with Landau and TNDBC. In comparison, the Arnot, Kriel, New Vaal and Vierfontein waters are, generally, the least corrosive.

6.2.4 Irrigation

Each of the water samples has been evaluated in terms of the guidelines for irrigation use in the vicinity of the collieries. The results are presented in Appendix 6. Clearly, a variety of problems may arise should many of the waters be used for irrigation purposes without restriction. These problems are described in the ensuing sections (6.2.4.1 through 6.2.4.6).

6.2.4.1 High salinity

Irrigation water salinity (EC) can severely influence crop performance. Some crops can produce acceptable yields at much greater soil salinity than others. This is because some make osmotic adjustments more effectively, enabling them to extract more water from a saline soil (Ayers and Westcot, 1985). It is important to note that salt tolerance varies for different growth stages and is dependent on a multitude of soil, climatic and other factors (Barnard *et al.*, 1998)

The three primary crops currently grown in the vicinity of the collieries are sorghum, maize and sunflower (Mine Personnel, 1993a; 1993b; 1993c; 1993d; 1995; and 1998). A full yield should be obtainable for sorghum, which is a moderately tolerant crop, when using a third of these waters, with an EC ≤ 4mS/cm. The use of many of the Greenside, New Denmark, and Kleinkopje waters, however, will result in a decrease in yield potential. Sunflower and maize are moderately sensitive crops, for which an EC of 1.1mS/cm is the upper limit in order to obtain a maximum yield. Some of the Arnot, Kriel, New Largo and Vryheid Coronation waters, as well as a few others, can be used without a loss in yield. The TNDBC waters, among others, have a zero yield potential if used to irrigate these crops.

Barnard *et al.* (1998) screened a variety of crops and pastures for cultivation on the Highveld under irrigation with high sulphate ($Ca\text{-}SO_4$) and sodic-saline ($Na\text{-}Cl\text{-}SO_4$) waters. Generally germination of most cultivars of both the subtropical and temperate annual crops was not influenced by either the high sulphate or sodic-saline mine water. There were, however, exceptions where germination of the odd cultivar of sorghum and pearl millet was suppressed with the sulphate salinity, while the same was true for lucerne with the sodic-saline water. In addition, there was a relatively wide choice of cultivars that would successfully bridge the sensitive seedling stage by irrigation with the sulphate-saline waters originating from the coal mines. The choice of cultivars to be grown under irrigation with the sodic-saline mine waters was more limited. Furthermore, the vegetative growth of both the subtropical and temperate annuals was mostly not significantly influenced by the sodic-saline mine waters. The vegetative growth of bermuda grass cultivars differed significantly, however, with the sodic-saline water. The vegetative growth of lucerne, tall fescue and cocksfoot was tolerant to the sodic-saline water, but crown vetch and white clover were very sensitive. In summary, sub-tropical and perennial grass species, which are well adapted to local soil and climatic conditions, responded better to irrigation with gypsiferous mine water than sodic-saline water.

6.2.4.2 Infiltration

An infiltration problem related to water quality occurs when the normal infiltration rate for the applied water or rainfall is appreciably reduced and water remains on the soil surface too long, or infiltrates too slowly to supply the crop with sufficient water to maintain acceptable yields.

Low salinity water (< 0.5mS/cm) is not suitable for maintaining soil structure as it is dispersive and tends to leach the surface soils free of soluble minerals and salts, especially calcium, reducing their strong stabilizing influence on soil aggregates and soil structure. Excessive sodium in irrigation water also promotes soil dispersion and structural breakdown but only if sodium exceeds calcium by more than a ratio of 3:1 (Ayers and Westcot, 1985).

Figure 6.1 shows that at a given SAR, infiltration rate decreases as water salinity decreases. Therefore, the high salinity Greenside, Kleinkopje, New Vaal, TNDBC, Vierfontein and Vryheid Coronation waters will improve infiltration, whereas the low salinity waters or those with a high sodium to calcium ratio (as indicated by SAR) will reduce infiltration, as is the case for certain Arnot, Kriel and New Largo waters. In general the colliery waters fall into the safest of the three categories of irrigation suitability in terms of soil stability. It should be noted that this is a generalized diagram in terms of salinity. No data is available to ascertain what the effects of irrigating with a SO_4-dominated water (as compared to a Cl-dominated water) will be. It is thought, however, that a SO_4-dominated water will have more detrimental effect as it increases the negative charge on soil particles through specific adsorption (pers. comm. Martin Fey, 2002).

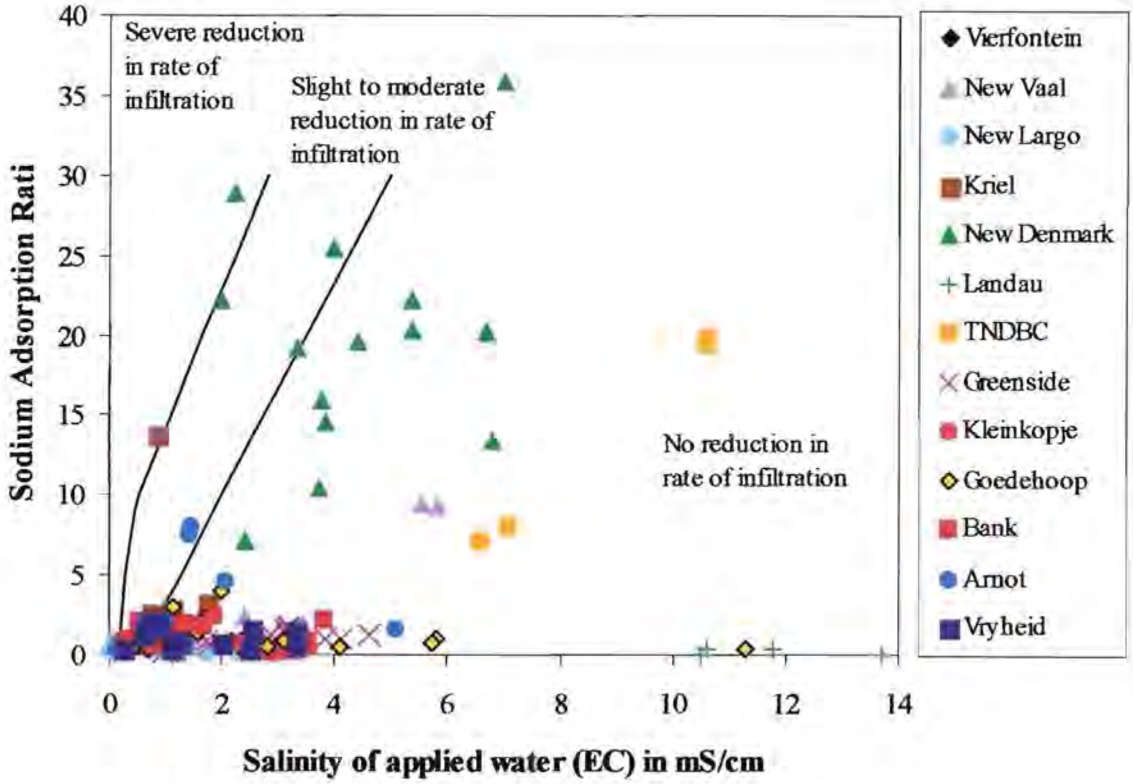


Figure 6.1: *Placement of colliery waters into three categories of suitability for irrigation in terms of the effect on soil physical properties engendered by a particular combination of salinity and sodicity, as defined by Ayers and Westcot (1985).*

6.2.4.3 Specific ion toxicities

Toxicity problems occur if certain constituents in the water are taken up by the plants and accumulate in concentrations high enough to cause crop damage. The degree of damage again depends on crop sensitivity. A toxicity problem differs from a salinity problem in that it occurs within the plant itself and is not related to a water shortage.

The ions of prime concern are sodium, chloride and boron. Not all crops are equally sensitive to these toxic ions. Although toxicity problems may occur even when these ions are in low concentration, toxicity often accompanies and complicates a salinity or water infiltration problem. Damage results when the potentially toxic ions are absorbed in significant amounts with the water taken up by the roots. The absorbed ions are transported to the leaves where they accumulate during transpiration. The ions accumulate to a greater extent in areas where the water loss is greatest, usually the leaf tips and leaf edges. Toxicity can also occur from direct absorption of the toxic ions through leaves wet by sprinklers. Sodium and chloride are the primary ions absorbed through leaves, and toxicity to one or both can be a problem with certain sensitive crops (Ayers and Westcot, 1985). Rotating sprinkler heads present the greatest risk, since between rotations water evaporates and the salts become more concentrated in the shrinking volume of water. As approximately 10 to 20mmol$_c$/L Na^+ or Cl^- will cause foliar injury to maize and sorghum and greater than 20mmol$_c$/L will cause foliar injury to sunflower (Ayers and Westcot, 1985), it is recommended that the New Denmark (as well as many New Vaal and TNDBC) waters should not be utilized to irrigate any of these crops.

Sodium

The importance of the cationic constituents of an irrigation water in relation to the chemical and physical properties of the soil was originally recognized by Scofield and Headley (1921). Today, the alkali hazard involved in the use of a water for irrigation is determined by the absolute and relative concentrations of the cations. If the proportion of sodium is high, the alkali hazard is high; and conversely, if calcium and magnesium predominate, the hazard is low.

Irrigation water that has a high sodium content can bring about a displacement of exchangeable cations Ca^{2+} and Mg^{2+} from the clay minerals of the soil, followed by the replacement of the cations by sodium. Sodium-saturated soils peptize and lose their permeability, so that their fertility and suitability for cultivation decreases. Note that this process can be reversed by the addition of gypsum. The use of the SAR value is empirical and has limited value for geochemical applications (Hem, 1970).

Sodium toxicity results from relatively high sodium concentrations in the water (high Na or SAR). The Ayers and Westcot (1985) toxicity guidelines use SAR as the indicator of potential for a sodium toxicity problem which is expected to develop following surface irrigation with a particular quality of water. Maize is sensitive to exchangeable sodium whereas sorghum and sunflower are semi-tolerant (Ayers and Westcot, 1985). Most of the New Denmark waters, the TNDBC and some New Vaal waters are high SAR waters, and any potential sodium toxicity problems which may develop associated with the use of these waters, may be exacerbated by poor water infiltration. Sodium toxicity relative to that of salinity is dealt with later in Section 6.2.4.6.

Chloride

Since chloride is not adsorbed by soils, it moves readily with the soil water and is taken up by the crop. It then moves in the transpiration stream and accumulates in the leaves. If the chloride concentration in the leaves exceeds the tolerance of the crop, injury symptoms will develop. Such symptoms are likely to occur with the use of at least half the New Denmark waters, and possibly some TNDBC waters, for irrigation purposes. In addition, as already mentioned, a chloride toxicity can occur by direct absorption through leaves during sprinkler irrigation.

Boron

Boron is an essential element for plant growth but is needed in relatively small amounts. If present in amounts appreciably greater than needed, it becomes toxic. Boron toxicity can affect nearly all crops but, as with salinity, there is a wide range of tolerance among crops. Bester (1993) reports that sunflower, maize and sorghum were all semi-tolerant to boron and could tolerate up to 2.0mg/L. These tolerances were based on the first visual signs of toxicity, and did not necessarily indicate reduction in yield.

Ayers and Westcot (1985) noted that sunflowers tend to be sensitive and require between 0.75 and 1.0mg/L boron; maize is moderately tolerant and requires between 2.0 and 4.0mg/L boron; and sorghum is tolerant and requires between 4.0 and 6.0mg/L of boron. In view of this, most crops could be irrigated with the mine waters without developing a boron toxicity. Caution should, however, be exercised when utilizing many of the New Vaal and New Denmark waters on more sensitive crops.

6.2.4.4 Trace elements and their toxicity

Most trace elements accumulate in the soil in a process that tends to be irreversible. Therefore, repeated applications of amounts in excess of plant needs eventually contaminate a soil and render it non-productive or the product unusable. Although plants do take up trace elements, the uptake is normally too small to reduce appreciably the trace element concentration in the soil over a reasonable time period (Ayers and Westcot, 1985). The trace element concentrations in the colliery waters were evaluated in terms of whether they exceeded a recommended maximum concentration defined by Ayers and Westcot (1985).

From Table A6.3 (Appendix 6) it is clear that many of the waters have problematic concentrations of at least one of the listed trace elements. Manganese is the only trace element present in toxic quantities in every one of the collieries studied. Furthermore, iron and fluorine occur in toxic concentrations in most of the collieries. As anticipated, the collieries worst affected are those with large quantities of acidic drainage, including Goedehoop, Landau and TNDBC. Acidic waters at Arnot, Bank, Greenside and Kleinkopje also contain elevated concentrations of various trace elements, such as manganese.

6.2.4.5 Other problems

Excess nitrogen

Nitrogen is a plant nutrient and stimulates crop growth. The usual sources include natural soil nitrogen or added fertilizer. Only fourteen of the colliery waters (AC 6s, AC 9s, GH 2s, KK 1, KK 2, KK 4, LN 1, LN 7, LK 6, LK 7, NLC 11, NVC 2, OC 1 and OC 2) contained nitrogen concentrations in excess of 5mg/L, and irrigation using these waters can affect sensitive crops by causing vegetative growth, lodging, and delayed crop maturity. For example, in grain crops, like wheat, vegetative growth produces weak stalks that cannot support the grain weight, resulting in severe lodging and difficulties for machine harvesting. This problem is exacerbated in areas which experience periodic heavy rains. Most other crops are relatively unaffected until the nitrogen concentration exceeds 30mg/L (Ayers and Westcot, 1985), such as in the case of GH 2s.

Scale deposits

Most of the colliery waters contain high concentrations of slightly soluble salts such as calcium, bicarbonate and sulphate which are likely to form a scale on leaves or fruit exposed to overhead sprinkler irrigation. The most severe waters include KC 1s, ND 2, ND 3, ND 6, ND 7, ND 8, ND 9, ND 15 and ND 17. Although not toxic, these deposits are likely to reduce the marketability of fruit and foliage. In addition, the scaling problems anticipated with the use of the colliery waters in underground machinery can be extended to irrigation equipment and pipes (Ayers and Westcot, 1985).

Abnormal pH

Ayers and Westcot (1985) define the normal pH range for irrigation water as 6.5 to 8.4. Therefore, pH can be used as an indicator of a problematic water. Nearly half of the colliery waters have a pH which falls outside this range, and many of these waters are highly acidic. In these waters, pH itself is not the sole problem, though it is likely to cause other problems through its effect on the water composition. Irrigation water with a pH outside the normal range may induce nutritional imbalances or may contain a variety of toxic ions.

Magnesium problems

Although the role of magnesium in causing infiltration problems is not well documented, soils containing high levels of exchangeable magnesium are thought to be troubled with such problems since magnesium acts on soils in a similar way to calcium, but to a lesser degree. In other words, magnesium is preferentially adsorbed by the soil to a much greater degree than sodium but to a lesser degree than calcium.

Ayers and Westcot (1985) report that the potential effect of sodium may be increased in a magnesium-dominated water. That is, a given SAR value will show slightly more damage if $Ca/Mg < 1$. The lower the ratio the more damaging is the SAR. Research findings show that at a given SAR of the applied water, a higher soil ESP (exchangeable sodium percentage) than normal will result when using water with a Ca/Mg ratio of less than 1 (Rahman and Rowell, 1979). Fortunately, this problem will only affect less than 5% of the waters in this study marginally, as they are only slightly magnesium-dominated.

6.2.4.6 Sodicity-salinity relationships

In terms of the susceptibility of crops to the quality of water used for irrigation it is necessary to consider the salinity and sodicity of the water together. Since high total salt concentrations interfere with osmotic processes in the roots of plants, the electrical conductivity of the water needs to be accounted for. In addition, specific ion effects are important. Owing to its effects on both soil and plants, sodium is one of the governing specific ions. The sodium hazard is often expressed in terms of sodium adsorption ratio (SAR).

The United States Department of Agriculture has adopted an irrigation water classification based on SAR in combination with EC (Richards, 1954). This classification, known as the Wilcox diagram, was suggested by Wilcox (1948) and is presented in Figure 6.2 with data from this study. In this classification it is assumed that the water will be used under average conditions with respect to soil texture, infiltration rate, drainage, quantity of water used, climate, and salt tolerance of the crop. Large deviations from the average for one or more of these variables may make it unsafe to use what, under average conditions, would be a good water; or make it safe to use what, under average conditions, would be a water of doubtful quality.

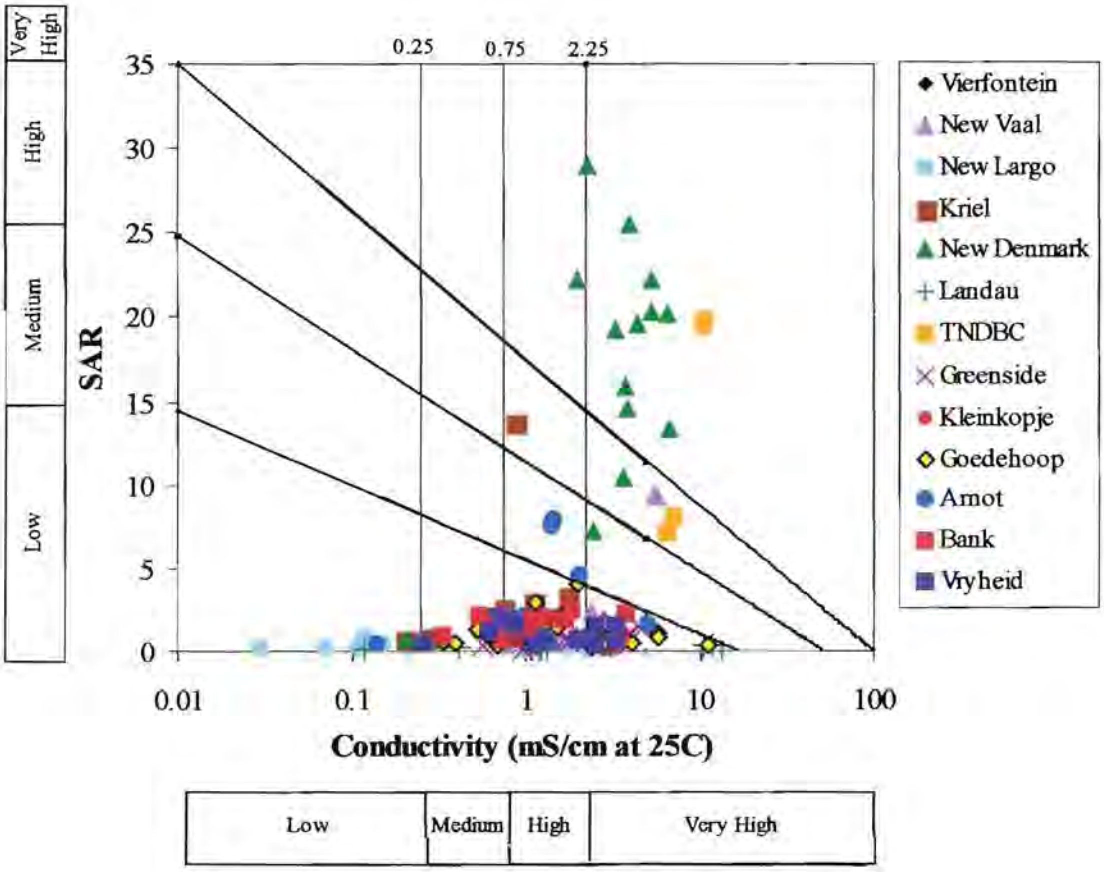


Figure 6.2: Wilcox diagram, showing the relationship between sodicity and salinity, used to classify the mine waters for irrigation.

A wide range in salinity is observed in the waters from the collieries. Those waters having a low EC, such as the bulk of the New Largo waters, can be used for irrigation with most crops, on most soils, with little likelihood that a salinity problem will develop. Some leaching may be required, but this should occur under normal irrigation practices except in soils of extremely low permeability. At the other end of the scale we find the New Denmark and TNDBC waters, which are very high salinity waters. High salinity waters are not suitable for irrigation under ordinary conditions but may be used occasionally under very special circumstances. The soil must be permeable, drainage must be adequate, irrigation water must be applied in excess to provide considerable leaching, and highly salt-tolerant crops should be selected.

Whilst only a few of the New Largo waters have a low salinity (< 0.25mS/cm), some of the colliery waters are of medium salinity (Figure 6.2) and, generally speaking, can be used if a moderate amount of leaching occurs. Plants with a moderate salt tolerance can be grown in most instances without special practices for salinity control. The remaining waters, except New Denmark, Landau, TNDBC and Vryheid, are high salinity waters (Figure 6.2) and cannot be used on soils with restricted drainage. In order to utilize these, special management for salinity control may be required and plants with a good salt tolerance should be selected (c.f. Study by Barnard *et al.* (1998) summarized in Section 6.2.4.1). Very high salinity waters (such as at New Denmark, Landau, TNDBC and Vryheid) are not suitable for irrigation under ordinary conditions, but may be used occasionally under very special circumstances. The soil must be permeable, drainage must be adequate, irrigation water must be applied in excess to provide considerable leaching, and very salt tolerant crops should be selected (Lloyd and Heathcote, 1985).

Most of the colliery waters are low sodium waters and can be used for irrigation on almost all soils with little danger of the development of harmful levels of exchangeable sodium. Sodium sensitive crops, however, may accumulate injurious concentrations of sodium. A few of the New Denmark waters are considered to be medium sodium waters (Figure 6.2) and these present an appreciable hazard in fine textured soils having a high cation exchange capacity, especially under low leaching conditions, unless gypsum is present in the soil. This water can be used on coarse-textured or organic soils with good permeability feasible (Lloyd and Heathcote, 1985). Finally, the remaining New Denmark waters are very high sodium waters

(Figure 6.2) and are geerally unsatisfactory for irrigation purposes. At low and perhaps medium salinity, however, the dissolution of calcium from the soil or the use of gypsum or other additives may make the use of these waters more.

In summary, it is interesting to note that not only do the New Denmark and TNDBC waters have a high salinity, but a high sodicity as well. Furthermore, there are no low salinity, high sodicity waters at the collieries. High, and very high, sodicity waters are likely to produce harmful levels of exchangeable sodium in most soils and usually require special soil management in this respect. It can be seen that most of the colliery waters have a low SAR, which implies they can be used for irrigation on almost all soils with little danger of the development of harmful levels of exchangeable sodium. Sodium-sensitive crops, however, may accumulate injurious concentrations of sodium even at these low levels (Lloyd and Heathcote, 1985).

The high salinity in the New Denmark waters is the result of excessively high concentrations of sodium, chloride and sulphate, whereas in waters from the other collieries it is mainly due to high sulphate concentrations, although sodium does play a role especially at New Vaal, Arnot and Kriel. Datta *et al.* (1995) found that sulphate (SO_4) salinity, in general, was more injurious than chloride (Cl) salinity in four genetically diverse wheat cultivars. Note that wheat has a higher salt tolerance than maize, but lower than sorghum (Ayers and Westcot, 1985). Datta *et al.* (1995) suggested that the salt resistance in the wheat could be ascribed to a marked exclusion of Na and Cl ions; and that sulphate injury might be due to less effective sequestration or mobility of this ion towards some innocuous centres of plant tissues.

Furthermore, a study which considered the interactive effects of sodium chloride, sodium sulphate, calcium sulphate and calcium chloride on snapbean growth, photosynthesis, and ion uptake was conducted by Awada *et al.* (1995). Snapbeans are less tolerant to salt than either maize or sorghum (Ayers and Westcot, 1985). It is well known that excessive sodium accumulations in soil, which can be a problem for production agriculture in semi-arid regions, may be ameliorated by calcium. Awada *et al.* (1995) reported that calcium sulphate treatments ameliorated sodium induced salinity in snapbeans more than did comparable $CaCl_2$ treatments. Therefore waters such as those from Bank, Greenside and Kleinkopje may have potential for improving highly sodic soils.

6.3 Application of existing classification systems

Five major hydrochemical schemes have been employed to classify mine water discharges. These include the Piper and Durov classifications (Piper, 1944; Durov 1948), Glover's scheme (1975), the trace metal classification of Ficklin *et al.* (1992), the US Bureau of Mines' system (Hedin *et al.*, 1994) and Younger's (1995) classification. Some of these consider the major ions that dominate water chemistry in natural environments but they omit metals dominating acidic milieux such as Fe and Al. Others are based primarily on pH (in some cases acidity / alkalinity) and Fe, thereby neglecting the major ions. One, Ficklin *et al.* (1992), is concerned only with trace elements. As was seen in section 2.4.2, all these schemes are hydrogeochemically useful but none adequately addresses the question of quality. Where possible, the data obtained in this study have been classified using the more relevant of these schemes in order to test their applicability and general usefulness, thereby indicating whether there is a need to develop one which is more versatile and informative.

6.3.1 Water type

Chemical facies that determine the water type are calculated by first converting the mmol$_c$/L concentration of the major cations (Na, Ca, Mg, Fe) and anions (Cl, SO_4, HCO_3) to percentages. All ions with concentrations exceeding 10% of the molar concentration in the solution are considered to be major ions. The Water Type expression is formed by listing the major ions in order from highest composition to lowest composition, with cations listed first and anions listed second (Calmbach, 1998). Some 49 different types exist in the 167 colliery waters assessed. Of these 32% were Ca-Mg-SO_4 waters, 6.6% were Mg-Ca-SO_4 waters and 5.4% were Ca-SO_4 waters. Those types amounting to more than 1.5% of the total are listed in Table 6.1.

Table 6.1: *Summary of major water types observed in the colliery waters of this study.*

Water type	Samples of this type	% of total
Ca-Mg-SO_4	53	32
Mg-Ca-SO_4	11	6.6
Ca-SO_4	9	5.4
Ca-Na-SO_4-HCO_3	6	3.6
Ca-Mg-Na-SO_4	5	3.0
Ca-Mg-SO_4-HCO_3	5	3.0
Fe(3)-SO_4	5	3.0
Na-SO_4	5	3.0

Water type	Samples of this type	% of total
Na-SO_4-HCO_3	5	3.0
Ca-Mg-Na-SO_4-HCO_3	4	2.4
Ca-Na-Mg-SO_4-HCO_3	4	2.4
Na-Ca-Mg-SO_4	4	2.4
Na-Ca-SO_4	4	2.4
Ca-Na-Mg-HCO_3-SO_4	3	1.8
Fe(2)-SO_4	3	1.8
Na-SO_4-Cl	3	1.8

6.3.2 Facies diagrams

The use of Piper and Durov diagrams has already been discussed at length in Section 2.4.2 (Classifications used for mine waters). Although the data obtained in this study have been plotted on a Piper diagram in Chapter 3 (Figure 3.40), the plot is repeated here (Figure 6.3) for comparison with the Durov diagram (Figure 6.4). One of the advantages of the Piper diagram is that it can be used to calculate resultant mixing between groundwaters, if they plot on a straight line in each of the three fields. Although some linear tendencies are evident in the two triangles, it is not so easy to define these in the quadrilateral. To demonstrate conclusively that simple mixing is occurring, Piper (1944) recommends that the graphical interpretation is substantiated by calculations. These are not included in this study as the Piper diagram neglects to consider some of the major ions in mine water environments, e.g. iron.

Little further information could be derived from the simple Durov diagram. The expanded Durov, however, provides a better display of hydrochemical types and an indication of some of the processes (including simple dissolution / mixing, ion exchange and reverse ion exchange) likely to be occurring in the waters. No software could be obtained on which to plot the data from this study in order to assess these possibilities.

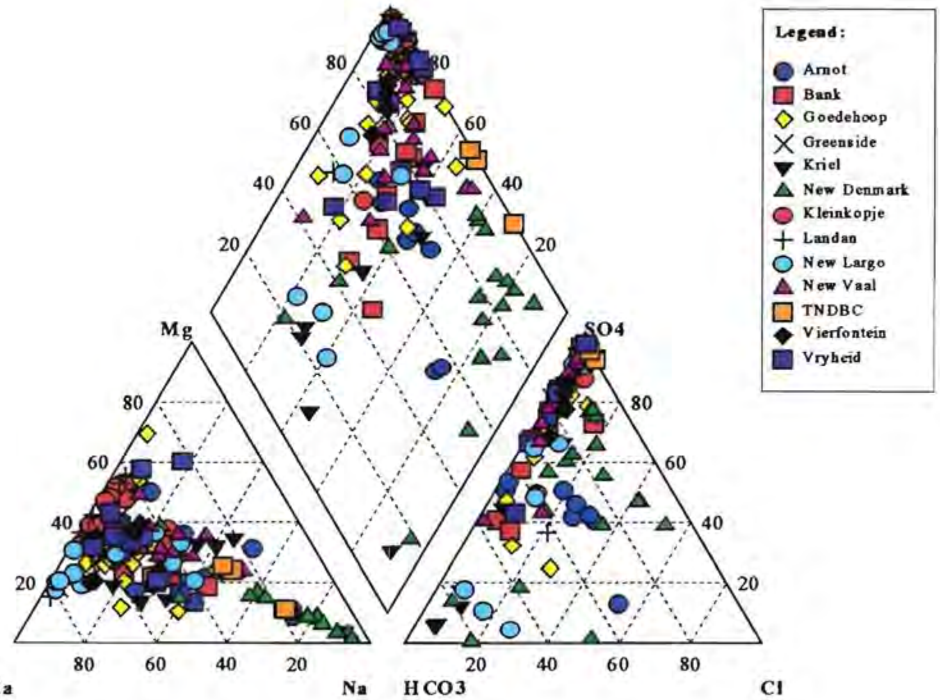


Figure 6.3: Piper (trilinear) diagram of major ions in colliery waters.

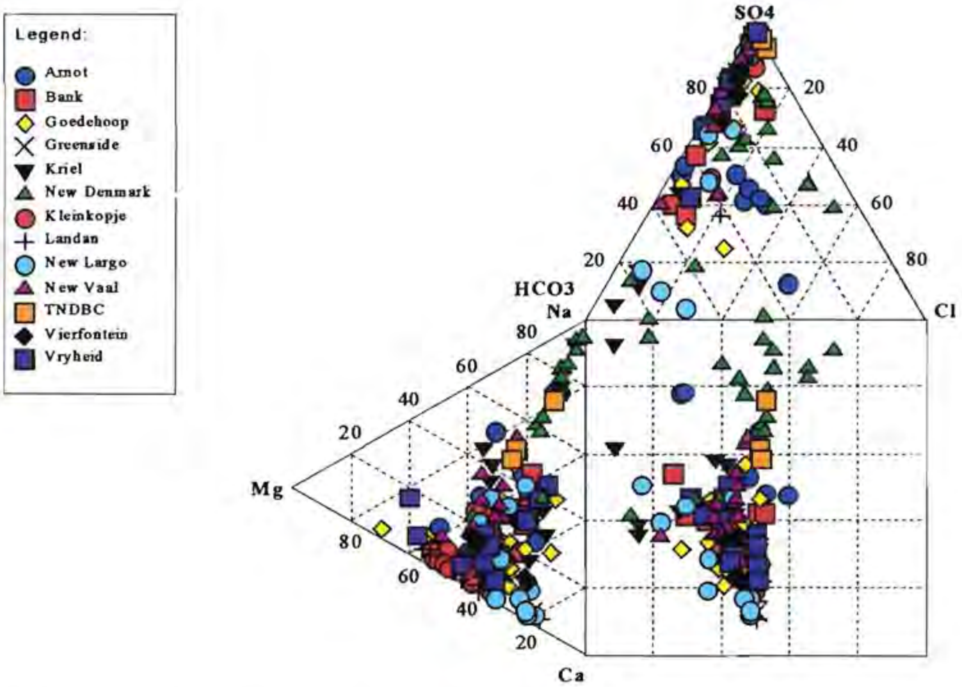


Figure 6.4: Original Durov diagram demonstrating composition of colliery waters.

6.3.3 Ficklin's trace metal classification

The mine drainage classification derived by Ficklin *et al.* (1992) is based on trace metal concentrations. Although all the waters in this study are from only one type of mineral deposit, the classification is useful for summarizing the relationship between pH and metal concentration: metals are generally more soluble in solutions of low pH. An exception to this trend is observed in the Landau and Vryheid waters (Figure 6.5) which, regardless of pH, all contain low concentrations of the heavy metals used in this classification. This may be the result of metal ion adsorption onto iron oxyhydroxides at these collieries.

Furthermore, only two of the waters, GH 24s and LN 2, combined relatively high pH with a large concentration of heavy metals (other than Mn, Al and Fe). No explanation can be given for this except to say that GH 24s is taken from a holding dam into which a mixture of waters are pumped from different parts of the mine and LN 2 was taken from a clean water trench, believed to be unaffected by mining activities.

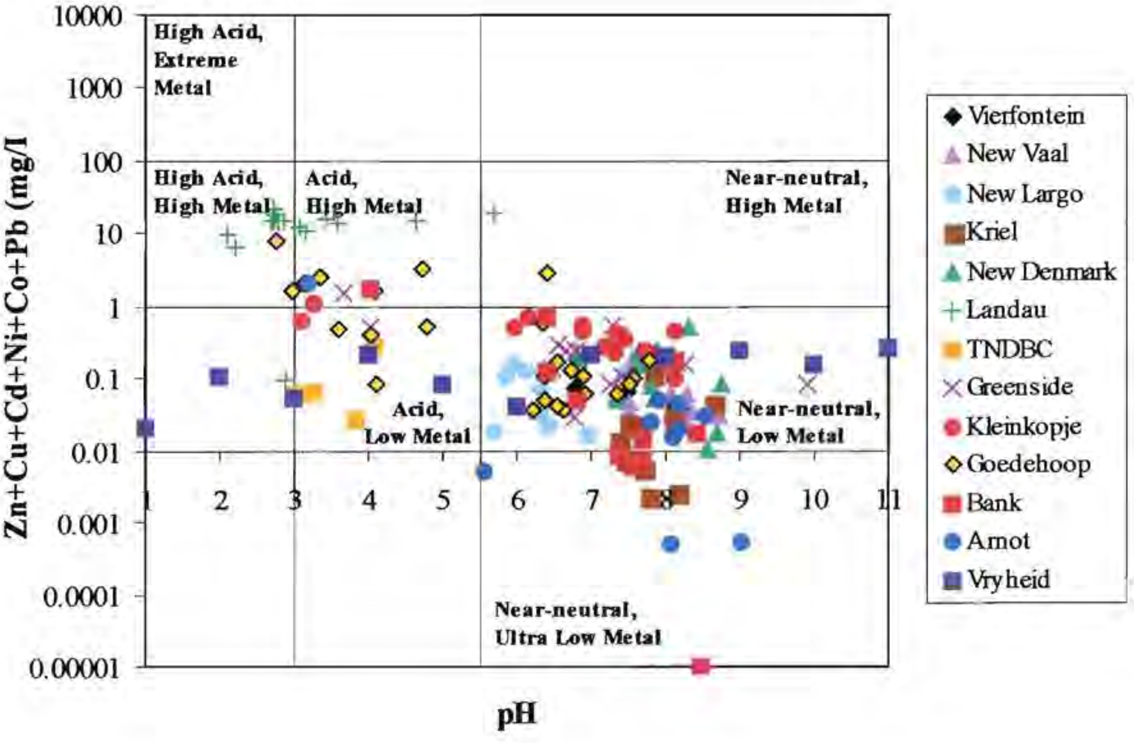


Figure 6.5: *Ficklin plot classifying mine drainage based on trace metal concentrations.*

As seen in the modelling results of Section 5.4 (Modelling water rock interactions: Results and discussion), the most acidic drainage observed here is thought to originate in areas rich in pyrite. Those waters located near well buffered host rocks are expected to have near-neutral pH, but high metal concentrations. The near absence of pyrite in some areas could result in near-neutral, low metal waters. Natural drainage in the mineralised areas, however, is likely to produce waters that are chemically similar to the mine drainage waters.

6.3.4 Younger's classification

The US Bureau of Mines classification (Hedin *et al.*, 1994) was extended by Younger (1995) with the intention of extending its geochemical applicability. The classic polluting acid mine drainages (acidic, high SO_4^{2-}) plot in the lower left field of the graph (Figure 6.6). The vertical displacement observed, towards greater alkalinity without a significant reduction in the sulphate ratio, is consistent with the generation of alkalinity by carbonate dissolution.

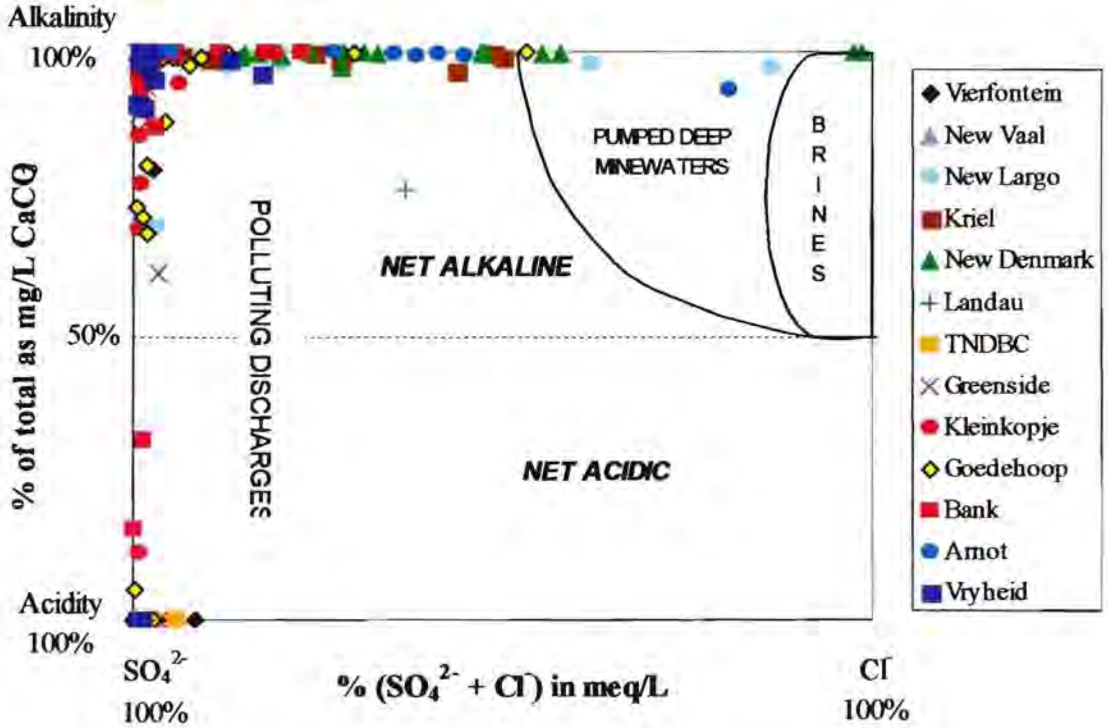


Figure 6.6: *Younger's classification showing origin and affinity of the colliery waters.*

One of the waters (LN 2) shows diagonal displacement towards increased alkalinity and lower sulphate. Younger has interpreted this position as one suggesting microbial sulphate reduction, with the possibility that metals might be fixed as sulphides. This is an interesting explanation in view of the fact that the water in question is one of the purest in this study and was taken from a "clean" trench, where it is supposedly unaffected by mining activities.

6.4 The cardinal properties of water

There are numerous individual criteria by which water can be classified on an *ad hoc* basis either in terms of quality (e.g. hardness, scaling or corrosion potential, irrigation suitability, potability) or geochemical origin (e.g. mineral saturation indices, ionic ratios or products). Some parameters (e.g. sodium adsorption ratio and calcite saturation index) are both geochemically revealing and empirically valuable as indices of quality for specific purposes.

Ideally, criteria for classification should be chosen that not only satisfy both geochemical and quality considerations but also are covariant with as many other properties as possible. There are three cardinal properties of water that could be used to convey a very large amount of information about origin and quality. At this stage only three are contemplated in order to retain the advantages of simple graphical comparison of a number of waters. The properties selected are *alkalinity, salinity and metal ion status.*

6.4.1 Alkalinity /acidity

The *alkalinity* parameter (expressed in mmol/L) represents net alkalinity and includes negative values for waters that are acidic. Pyrite oxidation is responsible for the *acidity* seen in many of the mine waters (Nordström *et al.*, 1979). The oxidation rate is dependent on temperature, pH, oxygen concentration, chemical composition of the pore water and microbial population (Ritchie, 1994). The reactions producing acid in coal mines can be found in Stumm and Morgan (1981) and have been discussed in Section 2.2.1 (Geochemistry of acid mine waters). The subsequent dissolution of the coal seams and surrounding shales and siltstones produces both alkalinity and hardness, which buffers the acidification process (Skousen, 1996; Gray, 1997). The affected mine water often resides in surface containment structures and in storage dams in underground workings. High carbonate content in waters may be problematic if the water is to be used in machinery, especially if it is to be heated. These colliery waters generally contain high concentrations (mean = 230mg/L) of calcium, which could potentially precipitate out as calcite causing scaling of pipes and equipment. On the other hand, metals such as Al, Fe and Mn tend to be more soluble in solutions of low pH and therefore acidic waters are generally toxic (Earle and Callaghan, 1998). Furthermore, these acidic waters contain excess sulphate which renders them corrosive towards metal and aggressive towards concrete.

As already discussed, the CCPP, commonly referred to as scaling potential, of a water is dependent on the calcium concentration and the alkalinity, or lack thereof. As calcium contributes towards the salinity of a solution, a relationship is expected between alkalinity / acidity and salinity (Figure 6.7).

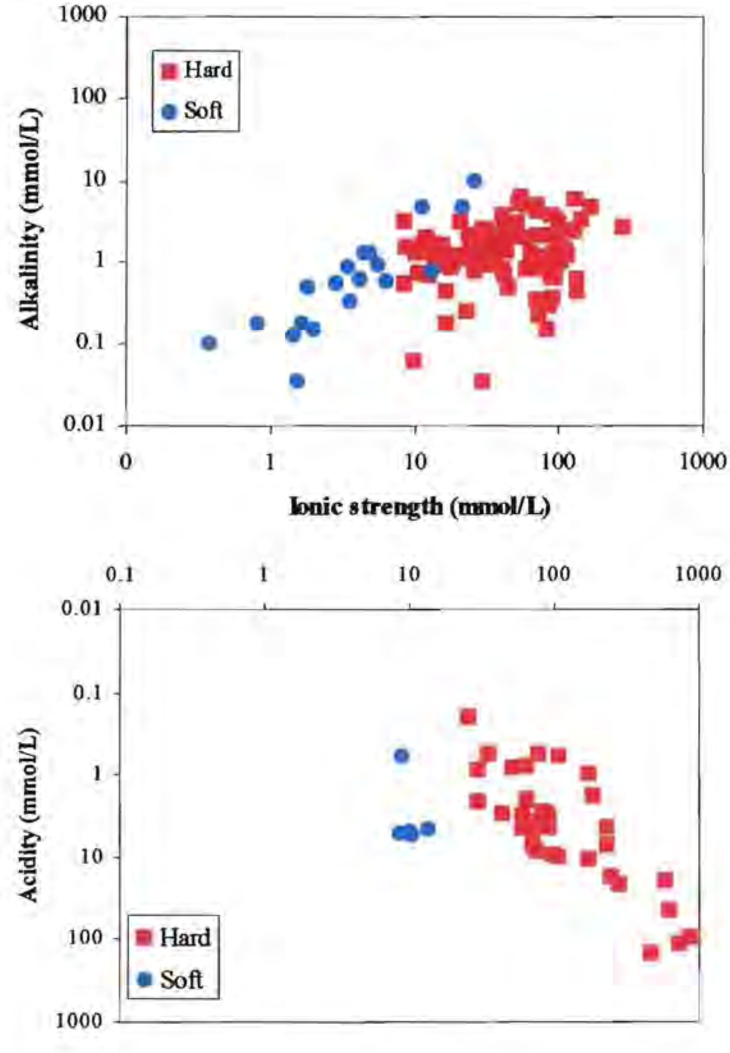


__Figure 6.7:__ Hardness (and scaling potential) of waters in this study as a function of net alkalinity and salinity.

Although there is some overlap, two groups can be clearly differentiated: 1) Soft waters (i.e. total hardness < 150mg/L as $CaCO_3$) with relatively low ionic strength; and 2) Hard waters (i.e. total hardness > 150mg/L as $CaCO_3$) with relatively high ionic strength. If the well-recognized classification of hardness of waters, developed by Kunin (1972), was used, it is expected that six groups could be differentiated, coinciding with his six descriptive classes of hardness. Furthermore, not only is differentiation between the two groups observed in the alkaline waters, but in the acidic waters too. In both cases, ionic strength appears to be a useful basis for anticipating hardness.

In Section 6.2.3, the CCPP was used to determine the aggressiveness and corrosivity of the waters. It is observed that when the CCPP is used as a measure of scaling / corrosion, as opposed to hardness, negative CCPP waters seem to be more constrained than positive CCPP waters (Figure 6.8). This is an indication that, generally speaking, excessive alkalinity would render waters non-corrosive.

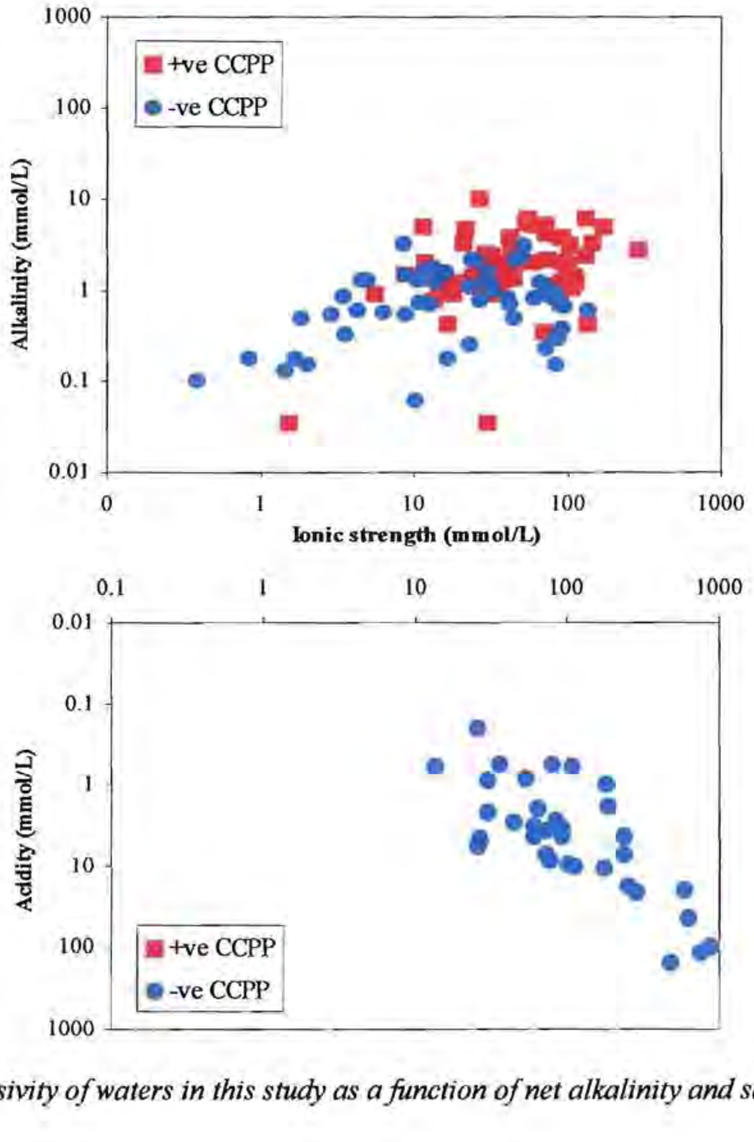


Figure 6.8: *Corrosivity of waters in this study as a function of net alkalinity and salinity.*

6.4.2 Salinity

In the classification, the *salinity* of the waters is represented by the ionic strength (I), rather than by the electrical conductivity (EC) or total dissolved solid (TDS) content. This is given by:

$$I = \frac{1}{2} \Sigma m_i \, z_i^2$$

where m_i is the molar concentration of the ith ion, and
z_i is the charge on the particular ion.

The main reason for this choice is that highly evolved mine waters tend to contain an excess of sulphate relative to other anions and therefore neither EC nor TDS are considered to be representative indicators of salinity. Ionic strength (I) differs from total concentration in that it takes account of the greater electrostatic effectiveness of the polyvalent ions since the contribution from all the ions in solution is summed. Obviously where a full analysis of the water is not available EC would suffice as a rough substitute for I. It should also be noted that EC is a poor indicator of TDS or I at very low pH values on account of the exceptional contribution made by hydrogen ions to electrical conductivity.

The interaction between acid and rock produces highly saline waters, often loaded with toxic elements. Since groundwater is extensively used for the irrigation of crops, plant susceptibility and growth as well as soil physical properties must be considered when assessing the quality of available water. Ayers and Westcot (1985) give a detailed assessment of water quality for irrigation, which was used in this study, and Barnard *et al.* (1998) consider the tolerance of a variety of crops to irrigation with mine affected waters.

Although an ideal CCPP of 4mg/L is required for practical purposes (Loewenthal *et al.*, 1986) waters with a positive CCPP are, by definition, scaling and those with a negative CCPP, corrosive. In addition to metal composition (specifically, calcium), corrosivity is dependent on both the sulphate and the chloride concentration of a water; therefore one would expect a relationship between salinity and the metal ion status. Although Figure 6.9 shows no differentiation between the SAR, salinity and the CCPP, it is interesting to note that only negative CCPP waters plot in the field defined by AAR and salinity. This would imply that all net acidic waters, are corrosive, regardless of the salinity.

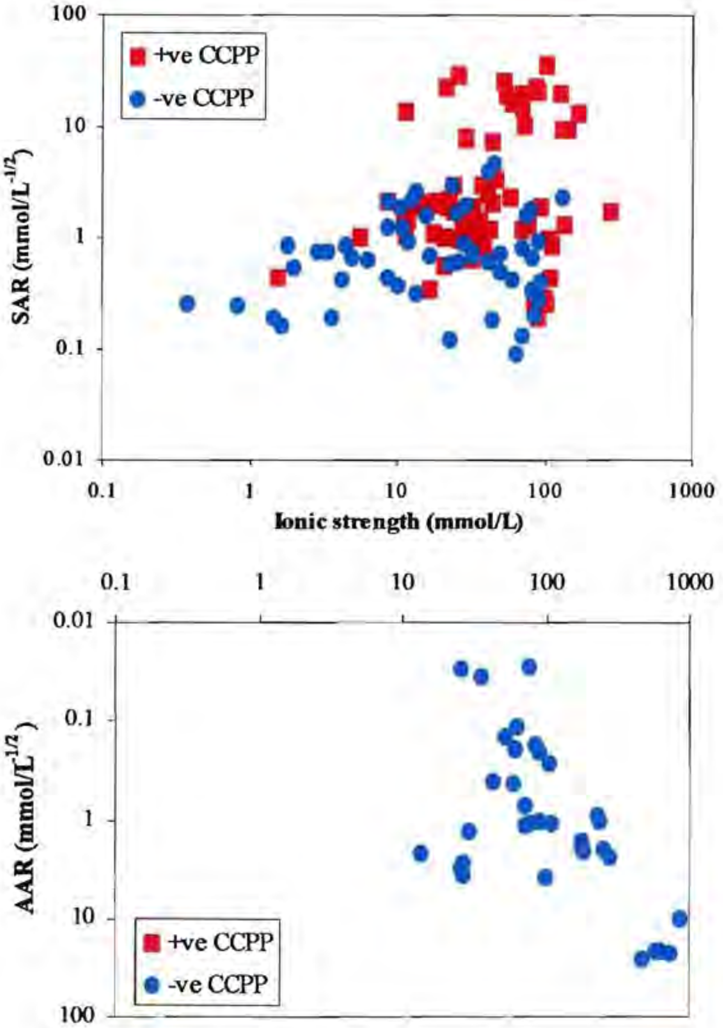


Figure 6.9: *Corrosivity of colliery waters as a function of metal ion status and salinity.*

In considering the relationship between SAR and salinity for soft and hard waters, two groups are clearly delineated, again with marginal overlap (Figure 6.10), as was observed for the alkalinity and salinity relationship. The differentiation here between highly corrosive and less corrosive waters is clearer than when the CCPP was used as an index.

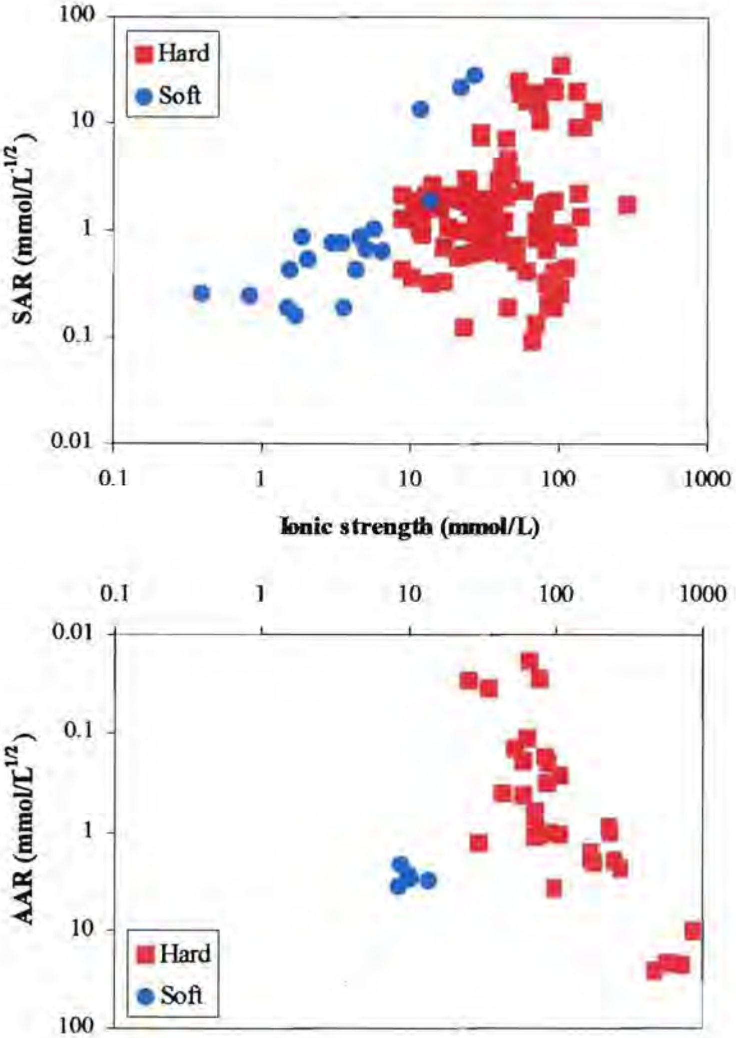


Figure 6.10: Hardness of colliery waters as a function of SAR/AAR and salinity.

6.4.3 Metal ion status

In order to account for the effect that specific ions have on both soil dispersivity and plant growth, a third component has been included in the classification. The positive and negative axes of the alkalinity scale (zero represents a pH of 4.5) effectively divide all waters into those in which the *metal ion status* is either best described in terms of major basic cations (Ca, Mg and Na) or major acidic cations (Al and Fe), respectively. The ion dominance in alkaline waters is often described by the sodium adsorption ratio:

$$SAR = \frac{Na^+}{\sqrt{Ca^{2+} + Mg^{2+}}}$$

in which Na, Ca and Mg concentrations are reported in mmol/L$^{-½}$. This *sodicity* parameter is widely employed as a quality index for irrigation water (since the dispersive effect of high Na levels on soil colloids is widely held to be one of the most important predictors of soil structural response to irrigation) and also has a degree of geochemical significance in that its form derives from the ratio law (valence dilution) of ion exchange (McBride, 1994, p281).

An analogous expression for acidic waters should relate the concentration of dominant acidic cations to those of Ca and Mg in a similar way. Hence the "acid (cation) adsorption ratio" can be defined as:

$$AAR = \frac{Al^{3+} + Fe_{TOTAL}}{\sqrt{Ca^{2+} + Mg^{2+}}}$$

where concentrations are again given in mmol/L$^{-½}$. This expression is necessarily somewhat empirical and less reflective of geochemical reality since its form is no longer related to ion exchange stoichiometry (the unspecified oxidation state of the iron requires this to be so). Since in most acidic waters the Al concentration is likely to exceed that of Fe, we could conveniently term this expression the *aluminicity* (etymologically consistent with sodicity).

Infiltration problems related to water quality have been discussed in Section 2.4.2, where it was noted that low salinity waters tend to have a corrosive effect on soils, effectively reducing the rate of infiltration. The relationship between sodicity and salinity has also been discussed (Section 6.2.4.6) where the Wilcox diagram was utilized to classify irrigation waters on the basis of their composition. Since dispersion is, in effect, a form of corrosion, the relationship between SAR and salinity was considered. The definition used to differentiate between dispersive and flocculating waters is taken from Ayers and Westcot's (1985) determination of the restrictions that would be applied to optimize infiltration of irrigation waters (i.e. flocculating waters constitute no restrictions, whilst dispersive waters imply moderate or severe restrictions), as evaluated using both SAR and EC. As with hard and soft waters, two distinct groups are observed: a low salinity, dispersive group; and a high salinity, flocculating group (Figure 6.11). It is interesting to note that the same two groups can be seen when AAR is considered, as opposed to SAR, even though the group differentiation is based on salinity.

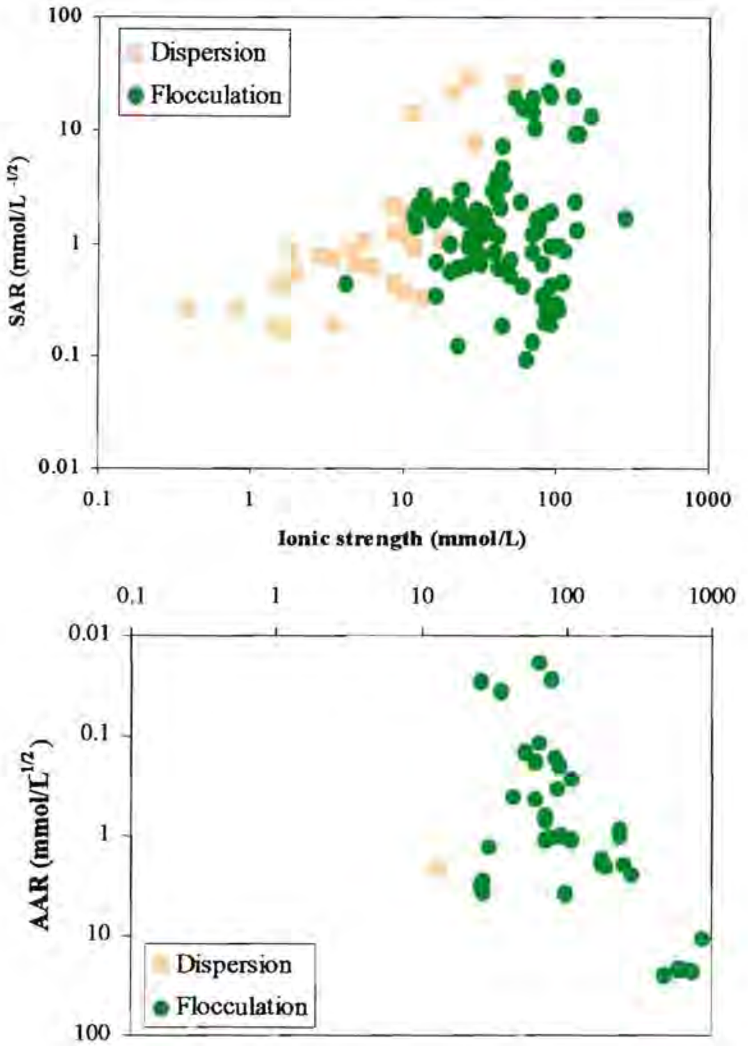


Figure 6.11: Dispersivity of colliery waters as a function of metal ion status and salinity.

It is often assumed that acidic waters automatically have a high metal ion concentration. This is not always the case, as was noted in the Vryheid waters in Figure 6.5. Nevertheless, high metal ion concentrations are almost always found in acidic waters. Figure 6.12 shows that toxic concentrations of zinc (i.e. 2mg/L for plants; cf. Ayers and Westcot, 1985) are only observed in the highly saline and acidic solutions, along with elevated concentrations of aluminium and iron (described by the AAR).

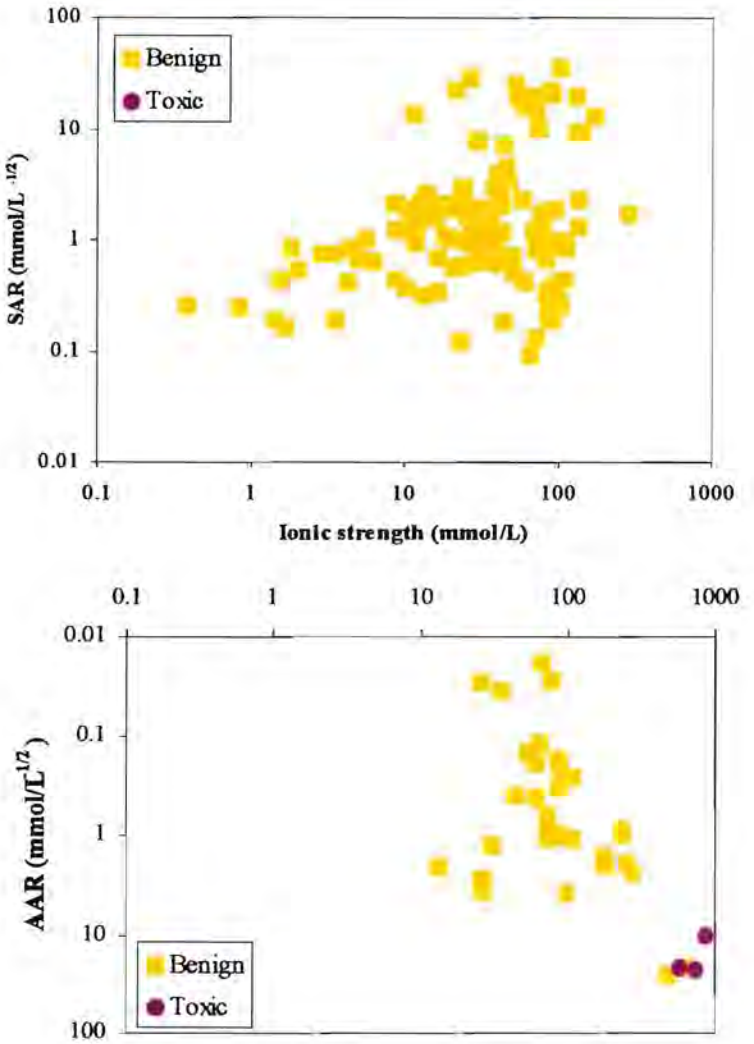


Figure 6.12: *Zinc toxicity status of colliery waters as a function of metal ion status and salinity.*

Boron, on the other hand, tends to be associated with alkaline waters. Its presence in toxic concentrations (i.e. 1.5mg/L for semi-tolerant plants cf. Bester, 1993) is observed in many, but not all, waters having both high sodicity and salinity, in Figure 6.13. These examples are sufficient to suggest that toxic levels of at least some elements can be anticipated on the basis of the magnitude of the three properties selected as classification criteria.

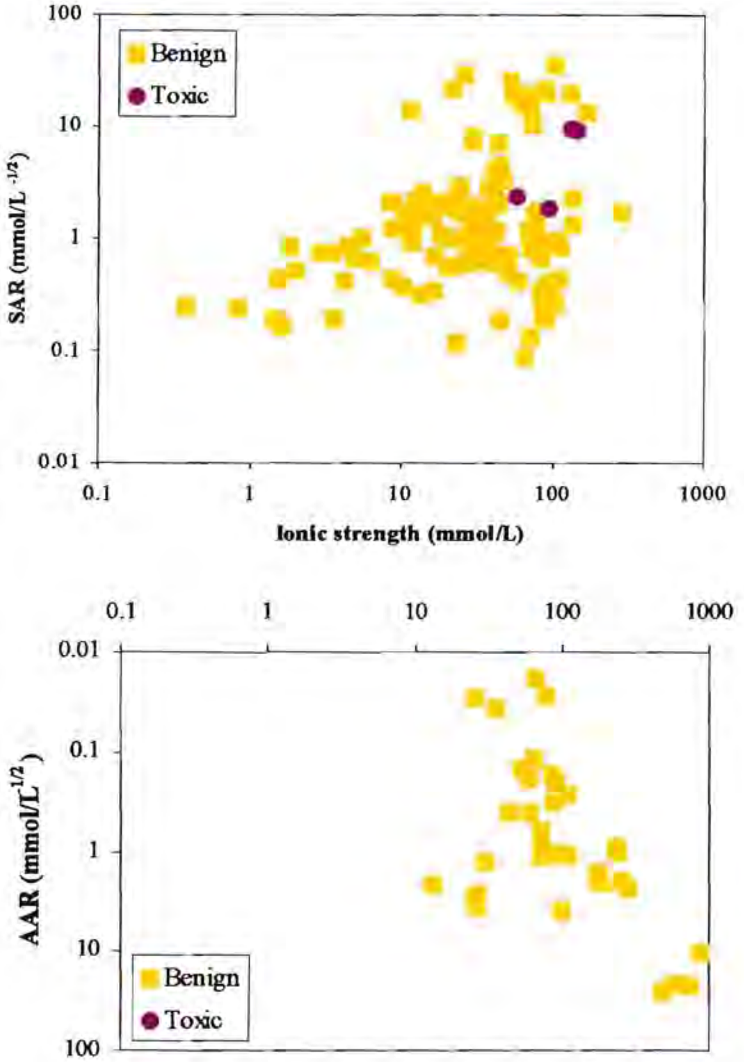


Figure 6.13: *Boron toxicity status of colliery waters as a function of metal ion status and salinity.*

6.5 Development of a general purpose classification scheme

6.5.1 Graphical integration of the three cardinal properties of water

So far in this chapter, mine waters have been examined in terms of traditional schemes for classifying waters, following which three cardinal properties of water (salinity, alkalinity/acidity, and metal ion status (sodicity or aluminicity)) have been proposed and their usefulness as classification criteria has been explored in terms of covariance with other properties more directly related to water quality such as hardness, effects on colloid dispersion/flocculation and toxicity of trace elements. In this section, the possibilities of presenting an integrated description of water quality by considering all three properties simultaneously through a three-dimensional, graphical representation are explored.

In Figure 6.14, three planes subtended by the three axes afford the opportunity of describing a water in terms of its tendency to be either corrosive, scaling, dispersive and/or biologically toxic. Waters are corrosive either because of their purity (dissolving power) or their salinity (complexing power of anions) (C). They will have a maximal tendency to form scale when both alkalinity is high and sodicity is low (B). They will be dispersive at a high sodicity/low salinity combination (A). At high levels of salinity, their toxicity will be greatest when either sodicity or aluminicity is also high (B). At the opposite extreme the water will be highly potable. Furthermore, the fields exhibit gradational tendencies. In other words, the further a water plots from zero within a field, the stronger its characteristics are.

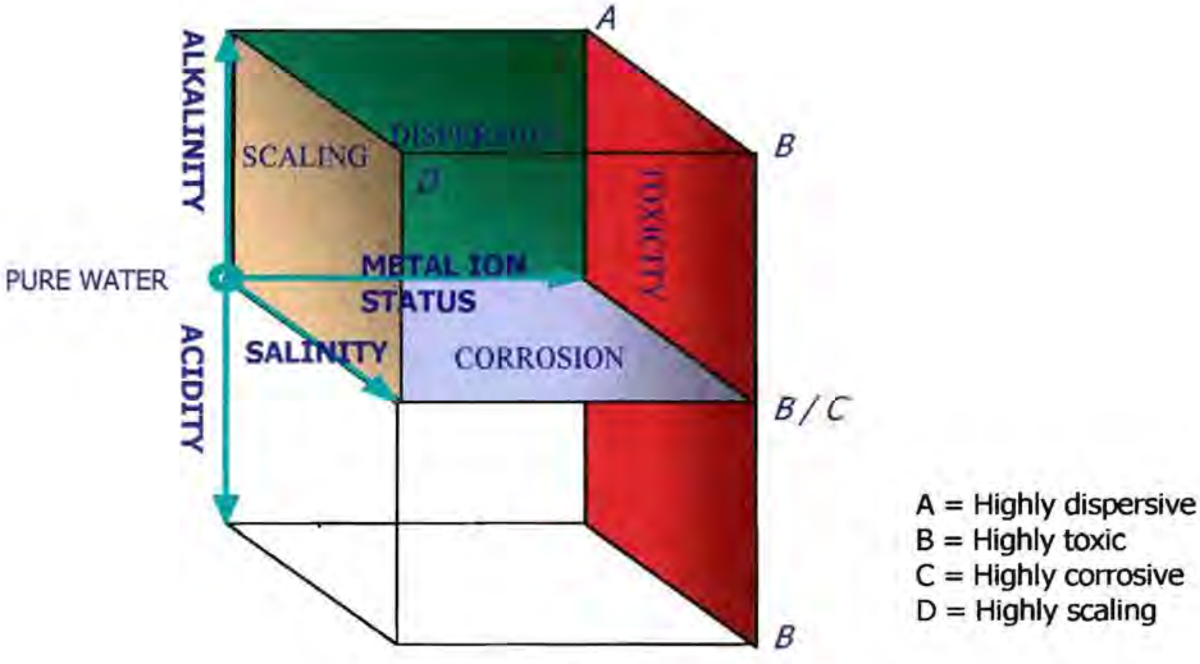


Figure 6.14: Schematic of new classification scheme for mine waters, showing fields describing properties of the water.

6.5.2 Complications

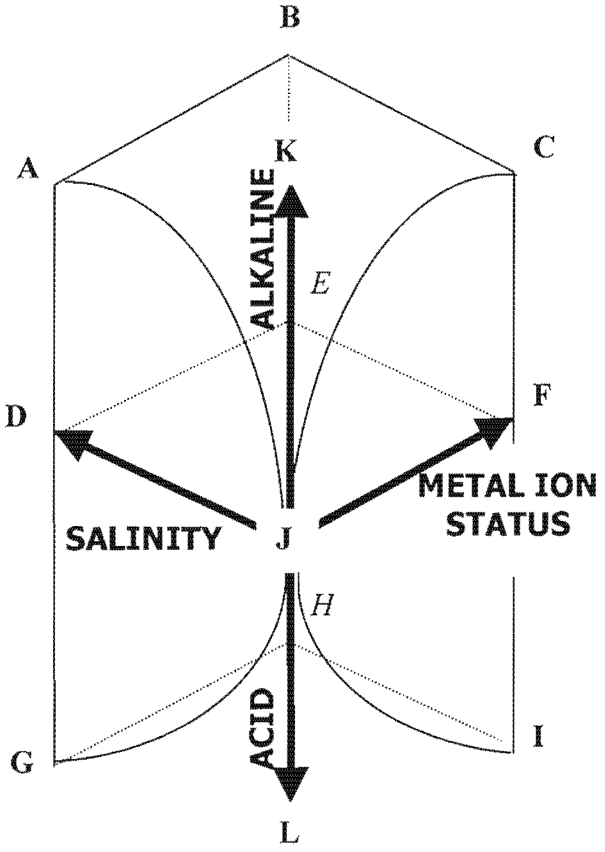
The general purpose classification of mine waters presented here does not differentiate between reduced (low O_2, high CO_2) and oxidized (high O_2, low CO_2) environments. Neither are aerated (i.e. in equilibrium with atmospheric O_2 and CO_2) waters treated differently to non-equilibrium waters. Both redox (pO_2) and carbonate (pCO_2) status are likely to influence the character of a water, and therefore its classification. It should, however, be noted that in any use of the water, handling will probably result in saturation with respect to oxygen and/or carbon dioxide, thereby cancelling that variable. Furthermore, no account has been taken of the dissolved oxygen concentration (DOC) or the chemical oxygen demand (COD) of the waters concerned.

In addition, there are limits to the classification fields beyond which it is not possible for a water to plot. For example, it is not possible for any water with a high alkalinity (or acidity) to have zero ionic strength. Similarly, sodic (or aluminous) waters must have measurable alkalinity (or acidity). The exact location of all the limits is unknown at this stage. An attempt has, however, been made to determine their most likely position (based on the following discussion) and this is presented in Figure 6.15 as a preliminary basis for recognizing their existence.

In the first instance described above, the slope of the boundary line defining the limit will depend on the relationship between alkalinity/acidity and the ionic strength of the solution being considered. The strongest natural base which can be found is NaOH, a 1M solution of which will result in the plotting of a 1:1 line, through the origin, in the alkalinity/ionic strength field. The "excluded zone" will encompass the region above this 1:1 line. Likewise, a 1M H_2SO_4 solution will result in the plotting of a 1:3 line, through the origin, in the acidity / ionic strength field. As before, the "excluded zone" will encompass the region above this line. The boundary lines in each case will be straight on a log-log or linear-linear graph, but curved on a log-linear graph (Figure 6.15 and 6.16).

The second instance referred to above is not as straightforward. SAR is used as a measure of Na toxicity, whereas AAR is used as a measure of (Al + Fe) toxicity. In natural waters, the concentration of Al and Fe depend on the acidity of the solution; Na concentration, however, is not dependent on alkalinity. High concentrations of Na can occur in both acidic or alkaline environments. The limit of the AAR/acidity field, therefore, will be defined by a linear equation which passes through the origin. The slope of this line is, however, uncertain. In defining the limits to the alkalinity/SAR field, one should consider that alkalinity tends to be higher in more sodic waters because Na is a stronger base cation than Ca and Mg and hydrolyzes more easily. So, at zero SAR, alkalinity is not necessarily zero, and vice versa. Therefore, although it is difficult to calculate a y-intercept, it is certain that it will not pass through the origin. Furthermore, there is no proof that the boundary will be defined by a linear equation, even though it is plotted as such here, for consistency.

In spite of these limitations, numerous combinations of the three cardinal properties exist to describe different waters. The extremes be seen in Figure 6.15.



A Alkaline, saline, non-sodic
B Alkaline, saline, sodic
C Alkaline, non-saline, sodic
D Neutral, saline, non-sodic
E Neutral, saline, sodic
F Neutral, non-saline, sodic
G Acidic, saline, non-metallic
H Acidic, saline, metallic
I Acidic, non-saline, metallic
J Neutral, pure water

Excluded combinations:
K Alkaline, non-saline, non-sodic
L Acidic, non-saline, non-metallic

Figure 6.15: *Possible combinations of cardinal properties that will describe a mine water, using the new classification scheme.*

6.5.3 Suitability of new classification to colliery waters

The three parameters (alkalinity/acidity, salinity and sodicity/aluminicity) used in the new classification provide a comprehensive description of water quality relevant to both engineering uses and biological suitability. It was expected that they would also serve as a useful basis for geochemical interpretation. In order to find out, the colliery waters from the South African Highveld, analysed in this study, were classified using the new system. The water analyses are plotted in Figure 6.16. Logarithmic scales have been used to accommodate the wide range of solute concentrations.

The individual graphs in Figure 6.16 can be juxtaposed three dimensionally so as to allow threshold values to be assigned that are appropriate to specific uses. Such a classification could be used to differentiate between waters which are variously corrosive, scaling, dispersive, potable, toxic or otherwise, thereby giving rise to classes of water of varying suitability for transmission through metal or concrete pipes, and for domestic, industrial, mining or agricultural use. The graphs are kept separate here for ease of visual interpretation.

There are areas in some of the graphs, at maximum alkalinity/acidity, in which no data are seen to plot. This confirms the expectations discussed earlier in this chapter (Section 6.5.2) that planes may be used to represent the limit to the size of certain fields. Insufficient data, however, are available to allow the exact delineation of all these boundaries.

Although the points in Figure 6.16, particularly where $pH > 4.5$ (as indicated by the y-axis representing alkalinity), are too numerous to clearly demonstrate it they have revealed a tendency for the waters from some collieries to exhibit clustering, suggesting that the classification could provide some kind of geochemical signature amenable to interpretation in terms of the processes characterizing water-rock interactions in mined environments. Generally, at the lower end of the ionic strength / SAR scale we see the dilute New Largo waters and at the upper end we see the saline and sodic New Denmark waters. Similar clustering is observed in the acidic ($pH < 4.5$) waters, which conform better to a straight line than the alkaline waters. The tight relationship observed here is largely due to the fact that there is an overlap in the constituents used to calculate AAR and those affecting acidity (i.e. $Al + Fe$). Rather than conforming, however, Landau shows eccentric behaviour. This behaviour is thought to be the result of an underestimation in the acidity, which was determined by titration. The Landau waters, being relatively more reduced than the other colliery waters, contain more ferrous iron which interferes with the titration procedure thereby creating a "false" equilibrium. In addition, Landau contains relatively high concentrations of many trace elements barely in evidence in the other acidic mine waters, for example nickel.

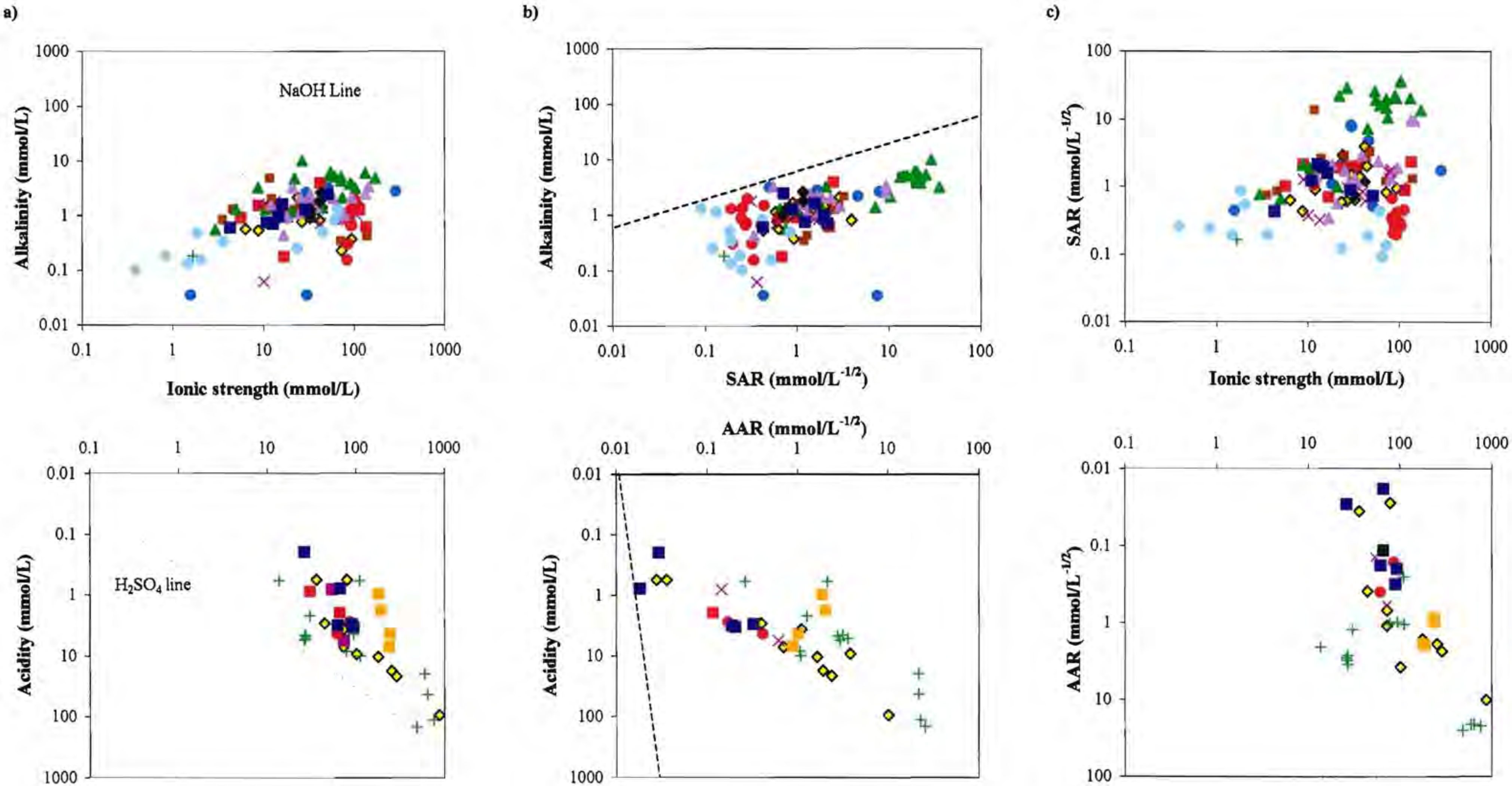


Figure 6.16: (a) Relationship between alkalinity / acidity and ionic strength in colliery waters; (b) Relationship between alkalinity / acidity and SAR / AAR in colliery waters; and (c) Relationship between SAR / AAR and ionic strength in colliery waters. Theoretical limits to water quality in new classification scheme are indicated by grey dashed lines.See Figure 6.6 for legend

The trends from low to high ionic strength and alkalinity or acidity observed in the graphs is thought to be an indication of the possible evolution likely to take place in the colliery waters. These paths are simplified in Figure 6.17. Waters entering the mines are, for all intents and purposes, pure. The waters will then follow one of two paths, becoming either alkaline or acidic depending on the buffering capacity of the lithology with which it is in contact. The longer the water is in contact, the more saline (and sodic or aluminoferric) it is likely to become.

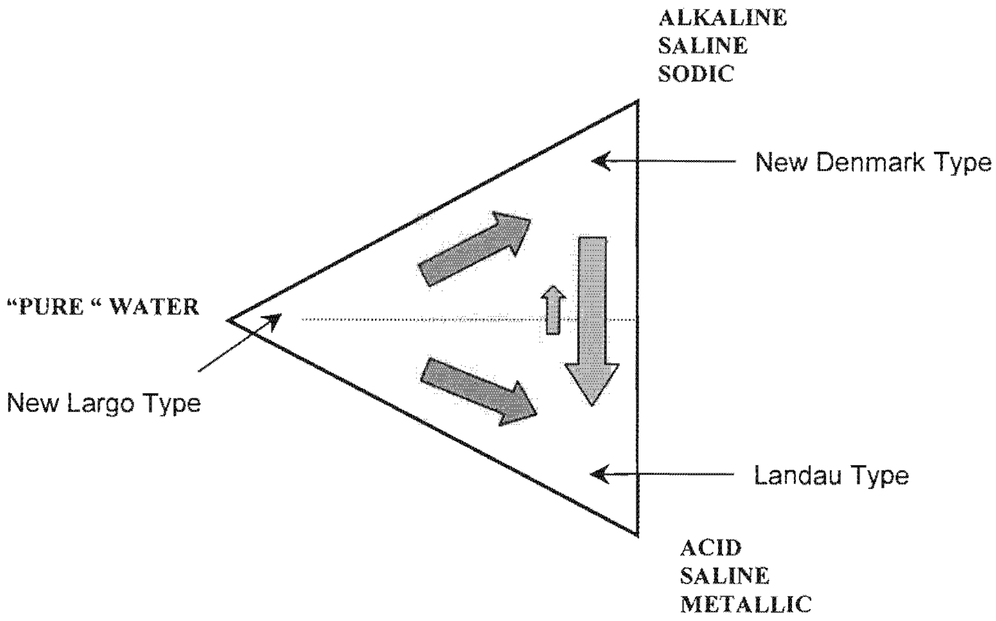


Figure 6.17: *Schematic diagram showing possible evolutionary paths for colliery waters.*

The possibility of waters, once alkaline and even sodic, becoming acid with high metal concentrations should not be ruled out. It is well known that pyrite oxidation and the generation of acidity can turn any potentially usable (even though saline or slightly sodic), source of water nasty, once the buffer capacity of the adjacent lithology is exhausted. No time series data, however, are available to prove that the mine waters do, in fact, evolve in the way the author has hypothesized here.

6.6 Conclusions

A three-fold classification of mine water, which conveniently summarizes the major attributes of the waters, has been developed. This classification can be used to differentiate between waters which are variously corrosive, scaling, dispersive, potable, toxic or otherwise, thereby giving rise to classes of water of varying suitability for transmission through metal or concrete pipes, and for domestic, industrial, mining or agricultural utilization. A simple, yet effective, means of assessing the water quality based on a few analyses, such that potentially usable sources of water could be identified without having to perform a multitude of expensive and time-consuming analyses would then have been developed. Since the undisturbed waters included in this study could be characterized and assessed in the same manner as the mine-affected waters, it is apparent that this classification can be applied to all waters.

CHAPTER 7

General discussion and conclusions

This study has been directed towards the provision and interpretation of quantitative chemical data for the water bodies in numerous collieries on the South African Highveld. Large quantities of water enter the mines through seepage and along fissures. Mining activities are known to contaminate this water through pyrite oxidation and acid neutralization reactions. Since water is extensively used in underground machinery it is imperative to determine whether the affected mine water which resides in the underground impoundments can effectively be used either in this machinery or for agriculture. The present study constitutes a detailed investigation aimed at determining the chemical composition of the waters with a view to assessing their quality and classification.

The approach taken involved: i) geochemically characterizing over 200 water bodies in different collieries; ii) speciation modelling of these water bodies to determine their equilibrium composition; iii) an investigation into the geochemistry of the surrounding Ecca sediments; iv) flow path modelling to ascertain the water-rock interactions likely to be responsible for the evolution of the water; v) further modelling to determine the potential of the waters to either corrode or scale metal pipes and machinery; vi) an assessment of the water for use in irrigated agriculture, assuming they are not suitable for use in mining operations; and vii) the development of a classification system, which integrates both geochemical and technical criteria, for improved water manageability. Standard laboratory techniques were used to chemically characterize the waters. PHREEQC software was employed to model the chemical composition, NETPATH computations were utilized to ascertain the type and extent of water-rock interactions, and STASOFT4 applied to determine the calcite precipitation potential (and thus the tendency to form scale or to corrode). Comparisons were made with published guidelines in order to determine the re-use potential without further treatment. Finally, a classification system for water re-use, was developed and tested using data from this study.

The results of this study confirm that a bimodal distribution occurs in the pH with some collieries being acidic (average pH ~ 3.5) and the others near-neutral (average pH ~ 7.5).

Relatively few samples have pH values between 4 and 6 since the pH will be driven toward one mode or the other depending on the relative abundance and extent of weathering of pyrite (FeS_2; acid-forming), and calcite and/or dolomite ($CaCO_3$ and/or $MgCa(CO_3)_2$; acid-neutralizing). Most of the collieries exhibit an EC below 4mS/cm. Exceptions include New Denmark (up to 7.01mS/cm), TNDBC (ranging between 6.6 and 10.6mS/cm) and Landau (up to 13.7mS/cm). A comparison of the samples taken indicated that there is no dominant cation type in most of the collieries. Exceptions include New Denmark and some of the Arnot waters, which are dominated by Na^+, and New Largo, which is dominated by Ca^{2+}. In terms of the major anions, there is a distinct trend in all the collieries, except New Denmark, Arnot and New Largo, to be SO_4^{2-} dominated. For the most part, the exceptions mentioned do not show any dominant anion (HCO_3^- is a significant anion along with SO_4^{2-}). Furthermore, in the lower pH (acidic) waters, most of the major cations (viz. Ca, Mg, Al and Fe) tend to form complexes with sulphate, whereas at near-neutral pH, hydroxide complexing is more prevalent.

Chemical comparisons with natural groundwater in the area and other coal mining regions clearly indicate that mining has impacted on the groundwater. The oxidation of pyrite introduces acidic conditions in the waters. This acidity interacts with the host rock resulting in high salinity. The acidity is ultimately neutralized by the action of both bicarbonate ions as well as sodium, calcium and magnesium which are produced through rock dissolution and ion exchange. Therefore, in addition to the sulphate concentration, electrical conductivity and the concentration of major ions (such as iron, sodium, calcium and magnesium) are also indicative of the extent to which the waters have been contaminated.

Both electrical conductivity and hardness correlate positively with SO_4 concentration, implying that they are both good indicators of mining impacts. Furthermore, correlations observed between hardness and sulphate in most of the waters suggests that an affinity exists between magnesium and calcium on the one hand, and sulphate on the other. Although no correlation exists between sodium and sulphate, a weak correlation was observed between sodium and bicarbonate concentrations implying that the divalent cations are stripped from exchange surfaces in the clay minerals by H_2SO_4 derived from pyrite oxidation. It is possible then that the monovalent sodium will only dissociate substantially if some other acid, such as H_2CO_3, is available to protonate the exchange sites and in doing so release HCO_3^- into solution. Exceptions to this "coherence theory" exist at one of the collieries, viz. New Denmark, possibly as a consequence of overwhelming sulphate generation, through pyrite oxidation, which may allow for a rather significant degree of sodium dissociation in response to the high sulphate concentration. The correlation between potassium and sulphate in *all* the waters suggests that the potassium concentrations are governed by the high adsorption affinity of potassium for clay mineral surfaces. Similar correlations were found in the baseline study, on coal mine water quality, conducted by Azzie (1999). In addition, some coherence between pH and Fe (III) as well as between EC and Fe (II) was also found here.

The lack of any primary control on the oxidation state (DO or Eh) of the mine waters was a distinct problem. Of the 260 water samples taken, 141 were taken directly from underground, whilst 119 were taken from surface water bodies. Many (but not all) of the underground water bodies exist in areas which are well-ventilated. Furthermore, most of the surface water bodies are filled by pumping from underground when the need arises. Nevertheless, while there may have been some oxidation and exposure to different PCO_2, the waters were still expected to retain someof their sub-surface process character. In addition, some of the conclusions drawn in this study may be affected by the time of exposure of these waters to O_2. Although O_2 can dissolve fairly rapidly in water, the conversion of Fe^{2+} to Fe^{3+} can be slow. Therefore, in some cases equilibrium with atmospheric O_2 had to be assumed even though it may not have been the case at the time of sampling.

For the most part, the near-neutral colliery waters are supersaturated with respect to most carbonate minerals. As dissolved sulphate increases, the colliery waters approach sulphate mineral saturation, with the precipitation of gypsum expected to play an important role in limiting the SO_4 concentration of the waters. Most of the waters having a $pH < 4$ are undersaturated with respect to gibbsite and kaolinite, but close to equilibrium (or slightly supersaturated) with respect to jurbanite and alunite. Furthermore, apparent supersaturation with respect to $Fe(OH)_3$ occurs at $pH > 4$. At lower pH, iron mineral solubility is most likely to be controlled by jarosite or schwertmannite, although it is possible that mixtures of different mineral phases are likely to be precipitating from these waters. Nevertheless, all waters conform to one relationship between the saturation index of key minerals (calcite, gibbsite, jurbanite, ferrihydrite) and pH (more strictly, pH_2SO_4), which suggests a unique relationship between pH and SO_4 activity for all mine waters.

Investigations into the composition of the host rocks revealed that the sediments are largely dominated by carbonate, silicate and sulphide minerals. These include calcite, dolomite, siderite, illite, albite, anorthite, kaolinite, quartz and pyrite. In the coals, some of these are present in forms which indicate concurrent formation with the peat bed, whilst others occur as veins or cleat and fracture fillings, indicating precipitation after compaction. Exchangeable Ca^{2+}, Mg^{2+}, K^+ and Na^+ occur in both the coals and sediments, in varying proportions. In most cases, however, Ca^{2+} occurred in larger quantities than all the other bases combined. Furthermore, the exchangeable Ca^{2+} concentration exceeds the total CEC in some cases, indicating that a substantial amount of free calcium is available in the sediments.

By combining saturation index calculations with mass balance computations, the author has been able to propose a geochemical pathway, to explain the evolution of the mine waters. The model includes (1) dissolution of carbonates, silicate minerals and clays, (2) oxidation and dissolution of pyrite, (3) extensive ion exchange, (4) precipitation of kaolinite, SiO_2 and $Fe(OH)_3$ *(a)* in near-neutral waters or schwertmannite, occasional jurbanite and/or jarosite-K and SiO_2 in acid waters, and (5) high partial pressures of CO_2. In the long-term, this intimates that coal mine waters would develop from a reasonably "pure", Ca-Mg-HCO_3-SO_4 dominant (or "New Largo type") to a saline Na-SO_4 dominant ("New Denmark type"), depending on the associated geology, exposure to oxygen and the degree of weathering of the host rocks. In extremely acidic cases, waters may proceed to become highly saline and Fe-SO_4 dominated (a "Landau type"), at which point there is little likelihood of neutralization and zero potential for re-use.

Although many of the waters in the collieries have a positive calcite precipitation potential, large quantities of chemical constituents are dissolved in most of the waters and therefore they are expected to be highly corrosive. Some of the least corrosive waters can be found at Arnot, Kriel, New Vaal and Vierfontein. In addition, many of the waters appear to be unsuitable for use in irrigation as their composition may affect either crop yield or the physical properties of the soil in which the crops grow. Those envisaged to require only minor treatment and limited restrictions include selected Arnot, Kriel, New Largo and Vryheid Coronation waters. Regardless of whether the water is to be utilized in mining operations or for irrigation purposes, for the most part it is not ideal and would probably require some form of amelioration.

Examination of the mine waters in terms of traditional classification schemes led to the development of a scheme that integrates both geochemical and technical criteria. This scheme is based on three cardinal properties of water: salinity, alkalinity/acidity, and metal ion status (sodicity or aluminicity). Their usefulness as classification criteria was explored in terms of covariance with other properties more directly related to water quality, such as hardness, effects on colloid dispersion/flocculation and trace elements. By considering all three properties simultaneously, a three-dimensional graphical representation can be made which affords the opportunity of describing a water in terms of its tendency to be either corrosive, scaling, dispersive and/or biologically toxic.

The significance of this study lies in the fact that it provides a detailed geochemical assessment of the current state of waters in many of the collieries, across different coalfields. This will assist in the understanding of how the processes acting in these waters will affect their final composition. Until such time as the waters have fully evolved, regular monitoring should be maintained in order to determine whether certain water bodies could still be utilized for use in machinery or for irrigation at a later date. It is anticipated that this would prove to be particularly costly and therefore use should be made of the integrated classification scheme developed here, as a means of assessing the water quality based on a few simple analyses. This, in turn, would facilitate the identification of potentially usable sources of water in the future, and improve their manageability.

In terms of the main aims of this study it is clear that the composition of the water bodies, in the South African coal mines, is affected by its interaction with the host rocks. These interactions, which were modelled using NETPATH, have also been useful for predicting whether acidification or neutralization is likely to be the primary process responsible for the characterization of the water, as well as indicating its potential longevity. The observed coherence between major chemical constituents, such as Ca + Mg and SO_4, have also proved to be useful for predicting future behaviour since they are closely linked to ion exchange reactions which play a major role in the evolutionary sequence. Finally, an important link has been found between those constituents which characterize a water body as a result of its genesis, and those which are responsible for limiting its use, i.e. alkalinity, salinity and metal ion status. The identification of these three cardinal properties has enabled the development of a classification system which has a sound geochemical basis and at the same time is useful for a wide spectrum of applications both within the mining industry, and beyond it.

It is anticipated that the implications of such a classification would be far-reaching, particularly in water-scarce countries like South Africa, where every effort should be made to manage water resources effectively. In addition, the simplicity of the classification system is such that only a few simple analyses are required in order to identify potentially usable sources of water, rendering it both time and cost-effective. Due to the magnitude of the water treatment field, it was, however, not possible to incorporate economic factors relating to water treatment costs to the geochemical and technical criteria which form the basis of the classification system.

In closing, the following suggestions are made for future geochemically-related work that would add to the value of this study. First, and foremost, more consideration should be given to the reaction rates for dissolution and oxidation of the minerals observed in coal mine environments as dissolution kinetics greatly affects metal availability. Secondly, more comprehensive inverse modelling, including the precipitation of siderite and dissolution of secondary minerals such as jarosite, would give a better understanding of the evolution of the mine waters. Thirdly, investigations into the amount and type of bacteria which thrive in these mines, and their effect on the kinetics of geochemical reactions which occur may be useful in placing time-constraints on mine water evolution. Fourthly, crop tolerance to waters dominated by different ions should be examined. Little is known about the effects, on both crops and soils, of irrigating with SO_4-dominated water as opposed to Cl^- or HCO_3^- dominated waters. Finally, in light of the fact that so many of the waters currently have near-neutral pH, despite the fact that there is very little acid neutralization potential in the associated lithology, there is plenty of scope for investigations into the long-term evolution of mine waters. This is particularly important since the waters in many of the abandoned workings are presently acidic and highly saline, although mine records show that they were neutral (though highly saline) at the time that mining was terminated.

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COAL MINE WATERS IN SOUTH AFRICA: THEIR GEOCHEMISTRY, QUALITY AND CLASSIFICATION

VOLUME 2: APPENDICES

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APPENDIX 1

Analytical methods and data reliability

A1.1 Water analysis

A1.1.1 pH measurements

Principle

The pH of a solution is a measure of the hydrogen ion activity (a_H^+) in solution:

$$pH = -\log a_H^+$$

The glass membrane electrode used to measure pH generates an electrical potential in response to the H^+ activity in solution. When combined with a reference electrode of known constant potential, the potential difference between the two electrodes can be measured by a potentiometer (pH meter) to determine the solution pH. Combination electrodes have a glass electrode and reference electrode combined in one probe. pH is measured relative to the known H^+ activity of one or more pH buffer solutions which are used to calibrate the pH meter.

Procedure

Field pH measurements were made using either a Ciba Corning M90 or a Radiometer MeterLab PHM 201 portable pH meter. Laboratory pH was determined using a Metrohm 691 pH meter, which comprises a 3M KCl combined electrode (glass indicator electrode plus reference electrode). All pH meters were calibrated before use with buffer solutions of pH 7.00 and 4.01 and measurements were made on unfiltered samples at room temperature (25°C).

Sources of error

Where the laboratory pH values are much greater than field pH this is because of the exsolution of CO_2. Where the laboratory pH is much less than the field pH this is due to the oxidation and precipitation of Fe. It is important to note that a difference of ±0.5 pH units may be due to the instrument used (Parkhurst and Plummer, 1993).

Standard Methods for the Examination of Water and Wastewater (Eaton *et al.*, 1995) reports the following interferences with pH measurement:

- Reactions with sediment, hydrolysis and oxidation in the sample bottle may alter the laboratory measured pH from that at the time of collection.
- Loss of dissolved gases, absorption of laboratory fumes, and precipitation of calcium carbonate or other salts may also change the pH measurably.
- Significant error can result if the temperature of the buffers and samples differ appreciably (more than 5°C).

Turbidity, colour, organic or colloidal material, oxidizing and reducing substances do not interfere with the accuracy of pH measurement.

Precision

Analysis of a test sample by 34 laboratories resulted in a standard deviation of 0.12 for a sample of mean 8.26 pH units (Eaton *et al.*, 1995).

Replicate measurements were made on all the water samples in the laboratory, approximately 5 days after collection, to test the precision of the pH measurement. Some of the individual measurements as well as mean and standard deviation (SD) values are listed in Table A1.1. The < 5% relative standard deviation (RSD) values indicate fairly good analytical precision. The overall similarity between field and laboratory pH values implies that, for the most part, the laboratory pH values are representative of field conditions and therefore laboratory values were used in geochemical modelling.

Table A1.1: *Results of replicate pH readings for some of the colliery water samples in the short-term (i.e. 5 day interval).*

Sample	Field Reading	Lab Reading 1	Mean	SD	% RSD
AC 3w	8.20	7.90	8.05	0.21	2.64
AC 8w	2.83	3.54	3.19	0.50	15.8
BC 6w	7.78	7.91	7.85	0.09	1.17
BC 13w	5.54	5.73	5.64	0.13	2.38
GH 9w	4.69	4.44	4.57	0.18	3.87
GH 15w	6.81	6.24	6.53	0.40	6.18
GH 22w	8.41	8.27	8.34	0.10	1.19
GS 6w	7.28	7.15	7.22	0.09	1.27
GS 9w	7.37	7.45	7.41	0.06	0.76
KC 5w	8.21	8.24	8.23	0.02	0.26

Sample	Field Reading	Lab Reading 1	Mean	SD	% RSD
KC 8w	8.04	7.96	8.00	0.06	0.71
ND 4w	8.65	8.68	8.67	0.02	0.25
ND 12w	8.06	8.10	8.08	0.03	0.35
ND 13w	9.01	9.08	9.05	0.05	0.55
AC 1s	7.82	7.94	7.88	0.09	1.08
AC 5s	9.03	8.75	8.89	0.20	2.23
BC 3s	7.58	7.50	8.13	0.12	1.48
BC 9s	8.42	8.31	8.37	0.08	0.93
GH 3s	4.04	4.15	4.10	0.08	1.90
GH 20s	3.60	3.98	3.79	0.27	7.09
GH 25s	7.34	8.05	7.70	0.50	6.52
GS 8s	6.82	7.23	7.03	0.29	4.13
GS 14s	9.93	9.91	9.92	0.01	0.14
KC 3s	7.70	7.83	7.77	0.09	1.18
KC 6s	8.16	8.27	8.22	0.08	0.95
ND 4s	8.33	8.41	8.37	0.06	0.68
ND 8s	8.57	8.74	8.66	0.12	1.39
ND 12s	7.35	7.72	7.54	0.26	3.47

pH measurements were repeated on a duplicate set of samples which were stored in sealed plastic containers at 4°C for a week (Reading 2). Each sample was allowed to equilibrate to room temperature and the pH measured immediately on opening the bottle. Some sample bottles were closed immediately after the measurement was taken and stored for another week before repeating the measurement (Reading 3). The relative standard deviation was still found to be below 5% for most samples (Table A1.2). Generally, the samples stored at 4°C display good long-term stability with respect to pH.

Table A1.2: *Long-term (weekly intervals) precision of pH measurements on water samples.*

Sample	Field Reading	Lab Reading 1	Lab Reading 2	Lab Reading 3	Mean	SD	% RSD
AC 3w	8.20	7.90	7.98	8.08	8.03	0.07	0.88
AC 8w	2.83	3.54	3.48	3.09	3.29	0.28	8.40
BC 6w	7.78	7.91	7.79	7.79	7.82	0.06	0.79
BC 13w	5.54	5.73	5.72	4.46	5.36	0.61	11.3
GH 9w	4.69	4.44	2.98	2.62	3.68	1.04	28.1
GH 15w	6.81	6.24	6.72	7.50	6.82	0.52	7.62
GH 22w	8.41	8.27	8.10	7.98	8.19	0.19	2.31
GS 6w	7.28	7.15	7.47	7.61	7.38	0.20	2.75
GS 9w	7.37	7.45	7.31	7.54	7.42	0.10	1.35
KC 5w	8.21	8.24	8.07	8.14	8.17	0.08	0.93
KC 8w	8.04	7.96	7.92	7.91	7.96	0.06	0.74
ND 4w	8.65	8.68	8.45	8.43	8.55	0.13	1.53
ND 12w	8.06	8.10	7.84	7.59	7.90	0.24	2.97

Sample	Field Reading	Lab Reading 1	Lab Reading 2	Lab Reading 3	Mean	SD	% RSD
ND 13w	9.01	9.08	8.84	8.90	8.96	0.11	1.20
AC 1s	7.82	7.94	7.93		7.90	0.07	0.84
AC 5s	9.03	8.75	8.42		8.73	0.31	3.50
BC 3s	7.58	7.50	7.33		7.47	0.13	1.71
BC 9s	8.42	8.31	8.04		8.26	0.20	2.37
GH 3s	4.04	4.15	4.07		4.09	0.06	1.39
GH 20s	3.60	3.98	3.84		3.81	0.19	5.05
GH 25s	7.34	8.05	7.91		7.77	0.38	4.84
GS 8s	6.82	7.23	7.33		7.13	0.27	3.79
GS 14s	9.93	9.91	9.78		9.87	0.08	0.83
KC 3s	7.70	7.83	7.73		7.75	0.07	0.88
KC 6s	8.16	8.27	8.19		8.21	0.06	0.69
ND 4s	8.33	8.41	8.38		8.37	0.04	0.48
ND 8s	8.57	8.74	8.74		8.68	0.10	1.13
ND 12s	7.35	7.72	7.46		7.51	0.19	2.53

A1.1.2 Electrical conductivity (EC)

Principle

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions; on their total concentration, mobility, and valence; and on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all.

Procedure

The electrical conductivity of each water sample was determined using a Crison microCM 2201 conductivity meter on an unfiltered sample. The meter comprises a conductivity cell (cell constant: C = 1.03/cm) and a temperature probe, the latter to provide automatic temperature compensation. Electrical conductivity standards (12.88mS/cm and 1.433mS/cm at 25°C) were measured prior to duplicate sample analysis at room temperature (25°C).

Precision

The precision of commercial EC meters is commonly between 0.1 and 1.0%. Reproducibility of 1 to 2% is expected after an instrument has been calibrated (Eaton *et al.*, 1995).

Replicate measurements were made on all the water samples, approximately 5 days after collection, to test the precision of the EC measurement. Individual measurements as well as mean and sample standard deviation (SD) values, for selected samples, are listed in Table A1.3. Relative standard deviation (RSD) values of < 5% for all replicate analyses, done in the winter ('w'), indicate good precision. The consistently poor precision noted in analyses on most of the samples taken during the summer ('s') are believed to be the result of damage to the EC meter, sustained in the field.

Table A1.3: *Results of duplicate electrical conductivity (EC) readings for some of the colliery water samples, over the short-term (i.e. 5 day interval).*

Sample	Field EC (mS/cm)	Lab Reading 1 (mS/cm)	Mean	SD	% RSD
AC 1w	1.22	1.23	1.23	0.01	0.40
AC 4w	1.34	1.36	1.35	0.01	0.94
AC 5w	2.07	2.11	2.09	0.03	1.35
AC 7w	5.06	5.01	5.04	0.04	0.70
GH 6w	0.79	0.81	0.80	0.01	2.50
GH 12w	2.01	2.04	2.03	0.02	1.05
GS 3w	2.77	2.75	2.76	0.01	0.51
GS 6w	3.66	3.62	3.64	0.03	0.78
AC 2s	0.61	0.68	0.64	0.05	7.58
AC 3s	0.58	0.64	0.61	0.04	6.64
AC 7s	4.71	5.08	4.90	0.26	5.35
AC 8s	1.29	1.37	1.33	0.05	4.09
BC 7s	0.87	1.08	0.98	0.15	15.2
BC 8s	1.41	1.37	1.39	0.03	2.24
BC 10s	0.79	0.74	0.77	0.03	3.79
BC 12s	4.02	3.52	3.77	0.35	9.38
GH 5s	1.47	1.27	1.37	0.14	10.2
GH 9s	5.62	4.10	4.86	1.08	22.1
GH 11s	1.40	1.15	1.27	0.18	13.8
GH 13s	0.71	0.61	0.66	0.07	10.9
GS 10s	2.71	3.21	2.96	0.35	11.9
GS 11s	1.08	1.37	1.22	0.20	16.7
GS 12s	0.47	0.58	0.52	0.08	14.8
GS 13s	3.86	4.64	4.25	0.55	13.0
KC 2s	0.70	0.89	0.80	0.13	16.3
KC 8s	0.76	0.95	0.85	0.14	16.2
KC 9s	0.86	1.04	0.95	0.13	13.4
KC 11s	0.59	0.73	0.66	0.10	15.7
NLC 1	1.72	1.74	1.73	0.01	0.82
NLC 2	0.14	0.15	0.15	0.01	4.07
NLC 5	0.08	0.07	0.07	0.00	5.81
NLC 7	1.06	0.99	1.03	0.05	5.10
VF 1	1.29	1.23	1.26	0.04	3.42
VF 2	1.26	1.24	1.25	0.02	1.30

Sample	Field EC (mS/cm)	Lab Reading 1 (mS/cm)	Mean	SD	% RSD
VF 3	1.18	1.22	1.20	0.03	2.30
VF 5	1.60	1.50	1.55	0.07	4.65

EC measurements were repeated on a duplicate set of summer samples which were stored in sealed plastic containers at 4°C for a week (Lab Reading 1) and again on a third set a week later (Lab Reading 2). Each sample was allowed to equilibrate to room temperature and the EC measured immediately on opening the bottle. The relative standard deviation was still found to be below 5% for most samples (Table A1.4). The samples stored at 4°C display good long-term stability with respect to EC.

Table A1.4: *Long-term (weekly interval) precision of EC measurements on water samples.*

Sample	Field Reading	Lab Reading 1	Lab Reading 2	Mean	SD	% RSD
AC 2s	0.61	0.68	0.57	0.62	0.06	8.84
AC 3s	0.58	0.64	0.52	0.58	0.06	9.85
AC 7s	4.71	5.08	4.21	4.67	0.44	9.36
AC 8s	1.29	1.37	1.16	1.27	0.11	8.52
BC 7s	0.87	1.08	1.06	1.01	0.12	11.5
BC 8s	1.41	1.37	1.35	1.38	0.03	2.32
BC 10s	0.79	0.74	0.75	0.76	0.02	2.92
BC 12s	4.02	3.52	3.49	3.68	0.30	8.10
GH 5s	1.47	1.27	1.29	1.34	0.11	8.18
GH 9s	5.62	4.10	4.15	4.62	0.86	18.7
GH 11s	1.40	1.15	1.13	1.23	0.15	12.2
GH 13s	0.71	0.61	0.61	0.64	0.06	9.35
GS 10s	2.71	3.21	2.72	2.88	0.29	9.93
GS 11s	1.08	1.37	1.17	1.21	0.15	12.2
GS 12s	0.47	0.58	0.59	0.55	0.07	12.7
GS 13s	3.86	4.64	3.85	4.12	0.45	11.0
KC 2s	0.70	0.89	0.75	0.78	0.10	12.3
KC 8s	0.76	0.95	1.65	1.12	0.47	42.0
KC 9s	0.86	1.04	0.88	0.93	0.10	10.6
KC 11s	0.59	0.73	0.61	0.64	0.08	12.1

A1.1.3 Alkalinity measurements

Principle

The alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used. The alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, and is taken as an indication of the concentration of these constituents. The measured values may also include contributions from borates, phosphates, silicates, or other bases if these are present.

Procedure

Alkalinity was measured by potentiometric titration to a pre-selected pH, using a Radiometer DTS 800 multi-titration system, comprising a TTT 85 titrator and an ABU 80 autoburette, to which was attached a PHG201 glass electrode and a REF401 calomel reference electrode. The procedure involved determining the volume of 0.01 *M* HCl required to titrate 10 mL of each sample to an end-point pH of 4.5. De-ionized water was used for a blank titration following the same method. The alkalinity of the de-ionized water blank was substracted from the calculated sample alkalinities.

Alkalinity was initially calculated, in mg $CaCO_3$/L, as described in Eaton *et al.* (1995) using the equation:

$$Alkalinity = \frac{[Volume\ HCl\ added \times Normality\ of\ acid \times 50\,000]}{Volume\ sample}$$

As HCO_3^- is the dominant carbonate species in waters at pH 6.35 to 10.33 (Drever, 1997), all alkalinity readings were recalculated from mg $CaCO_3$/L to mg HCO_3^-/L using the formula:

$$mg\ HCO_3^-/L = mol\ HCO_3^-/L \times 61.0171 \times 1000$$

where

$$mol\ HCO_3^-/L = \frac{mg\ CaCO_3^-/L}{50\,000}$$

Sources of error

- Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes can react with additions of standard acid and contribute excess alkalinity.
- Anions of weak organic and inorganic acids other than the carbonate system also contribute to alkalinity. These introduce error if they are not considered when converting alkalinity measurements to carbonate or bicarbonate concentrations.

- Precipitation in the sample bottles between the time of sample collection and analysis may lead to underestimation of alkalinity.
- Soaps, oily matter, suspended solids or precipitates may coat the glass electrode and cause a sluggish response (Eaton *et al.*, 1995). Since alkalinity titrations involve pH measurement, they are also subject to the potential sources of error in the measurement of pH.

Precision

Eaton *et al.* (1995) reports that no general statement can be made about the precision of alkalinity determinations, because of the great variation in sample characteristics. The precision of the titration is expected to be much greater then the uncertainties involved in sampling and sample handling before analysis.

All of the mine water samples analyzed at UCT, were analyzed in duplicate to test the precision of this method. The second measurement was usually taken approximately one week after the first, on duplicate samples, which had been sealed and stored at 4°C for the interim period. Random samples were selected from the other collieries for duplicate analysis at the ISCW. The duplicates were analyzed at the same time as the original samples but were labelled differently. Individual measurements for each sample as well as mean and sample standard deviation (SD) values are listed in Table A1.5. Relative standard deviation (RSD) values of < 5% for most replicate analyses indicate good precision.

Table A1.5: *Results of duplicate alkalinity measurements (in mg* HCO_3^-*/L) for the colliery water samples.*

Sample	Alkalinity Reading 1	Alkalinity Reading 2	Mean	SD	% RSD
AC 2w	129	128	129	0.17	0.13
AC 6w	6.89	7.38	7.14	0.35	4.84
BC 5w	444	440	442	3.02	0.68
BC 9w	256	250	253	3.88	1.53
GH 8w	151	152	152	0.65	0.47
GH 16w	440	386	413	38.1	9.51
GH 18w	161	159	160	0.91	0.62
GS 3w	52.0	52.5	52.3	0.35	0.66
GS 13w	71.7	71.6	71.7	0.09	0.12
KC 4w	193	197	195	3.15	1.61
KC 7w	414	416	415	1.68	0.41
ND 5w	533	531	532	1.64	0.31

Sample	Alkalinity Reading 1	Alkalinity Reading 2	Mean	SD	% RSD
ND 9w	622	619	621	2.16	0.35
ND 15w	516	517	517	0.17	0.03
AC 4s	108	109	109	0.43	0.40
AC 6s	4.21	4.33	4.27	0.09	2.02
BC 7s	143	142	143	0.99	0.70
BC 8s	190	190	190	0.43	0.23
GH 7s	117	119	118	1.08	1.01
GH 19s	28.0	22.8	25.4	3.67	14.4
GH 27s	188	190	189	1.68	0.99
GS 5s	138	139	138	0.78	0.56
GS 10s	101	101	101	0.30	0.30
KC 5s	263	261	262	1.34	0.51
KC 10s	148	144	146	3.24	2.22
ND 3s	585	587	586	1.42	0.24
ND 11s	515	514	514	0.69	0.13
ND 17s	567	568	567	0.73	0.13
KK 4	91.4	85.4	42.7	4.31	10.1
KK 11	232	219	226	8.62	3.82
KK 17	79.3	67.1	73.2	8.62	11.8
NLC 1	61.0	61.0	61.0	0.00	0.00
NLC 11	15.9	15.9	15.9	0.00	0.00
NAC 2	152	152	152	0.00	0.00
NAC 6	116	116	116	0.00	0.00

A1.1.4 Acidity measurements

Principle

Acidity of a water is its quantitative capacity to react with a strong base to a designated pH. The measured value may vary significantly with the end-point pH used in the determination. Strong mineral acids, weak acids such as carbonic and acetic, and hydrolyzing salts such as iron or aluminium sulphates may contribute to the measured acidity according to the method of determination.

Hydrogen ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard alkali. Acidity thus depends on the end-point pH or indicator used, which is invariably based on practical considerations. For routine control titrations or rapid preliminary estimates of acidity, the colour change of an indicator may be used for the end-point.

Procedure

Acidity was measured by potentiometric titration to a pre-selected pH. The procedure involved determining the volume of 0.01*M* NaOH required to titrate 10 mL of each sample to an end-point pH of 8.3. Samples which were known or suspected to contain hydrolyzable metal ions or reduced forms of polyvalent cations were pre-treated with hot peroxide.

The hot peroxide treatment procedure involves adding 5mL increments of 0.02*N* H_2SO_4 to samples with pH > 4, until the pH is reduced to 4 or less. Then 5 drops of 30% H_2O_2 are added and the solution boiled for 2 – 5 minutes. After cooling, the solution is titrated with standard alkali to pH 8.3 as usual.

Acidity was initially calculated in mg $CaCO_3$/L as described in Eaton *et al.* (1995) using the equation:

$$Acidity = \frac{[Volume\ NaOH\ added \times Normality\ of\ base \times 50000]}{Volume\ sample}$$

All acidity readings were recalculated from mg $CaCO_3$/L to mg H^+/L using the formula:

$$mg\ H^+/L = mol\ H^+/L \times 1.0079 \times 1000$$

where

$$mol\ H^+/L = \frac{mg\ CaCO_3^-/L}{50000}$$

A titration with NaOH to the phenolphthalein endpoint (pH 8.3), as performed in this study, will be a measure of Total acidity. This end point includes H_2CO_3 that may also be present as part of the acidity. Hem (1985) reported that a titration to the methyl-orange endpoint (pH 4.5) is sometimes made, with results representing "free mineral acidity". No record was kept during the titration process in this study, to enable the total acidity to be divided into proton acidity and mineral acidity.

Sources of error

- Reduced forms of polyvalent cations and hydrolyzable metal ions such as iron, aluminium or manganese may contribute to the acidity.

- Dissolved gases contributing to acidity, such as CO_2, hydrogen sulphide or ammonia, may be lost or gained during sampling, storage or titration and their effects should be minimized.
- Precipitation in the sample bottles between the time of sample collection and analysis may lead to underestimation of acidity.
- Oily matter, suspended solids, precipitates or other waste matter may coat the glass electrode and cause a sluggish response. These interferences should *not* be removed as they may contribute to the acidity.
- Since acidity titrations involve pH measurement, they are also subject to the potential sources of error in the measurement of pH.
- The use of indicators with coloured or turbid samples may obscure the colour change when the end-point is reached.

Precision

As with the alkalinity determinations, no general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration, however, is likely to be much greater than the uncertainties involved in sampling and sample handling before analysis (Eaton *et al.*, 1995).

Individual measurements for each sample as well as mean and sample standard deviation (SD) values are listed in Table A1.6. Relative standard deviation (RSD) values of < 5% for most replicate analyses indicate good precision.

Table A1.6: *Results of duplicate acidity measurements (in mg H^+/L) for the colliery water sample.*

Sample	Acidity Reading 1	Acidity Reading 2	Mean	SD	% RSD
AC 8w	2.00	2.07	2.04	0.05	2.46
GH 2w	193	184	188	6.35	0.13
GH 14w	2.87	2.22	2.55	0.46	0.64
GH 20w	2.18	0.81	1.50	0.97	1.76
GH 21w	41.8	39.5	40.7	1.60	0.15
GS 4w	9.68	9.71	9.70	0.02	0.22
AC 8s	2.68	3.78	3.23	0.78	24.1
BC 5s	4.03	1.95	2.99	1.47	49.3
GH 1s	18.8	21.2	20.0	1.71	0.36
GH 9s	21.0	22.4	21.7	1.01	0.19
GH 17s	35.5	35.6	35.5	0.06	0.01

Sample	**Acidity Reading 1**	**Acidity Reading 2**	**Mean**	**SD**	**% RSD**
GH 19s	7.32	7.28	7.30	0.03	0.02
GS 3s	1.66	1.76	1.71	0.07	4.16
GS 4s	11.5	13.0	12.3	1.07	8.73
KK 13	6.05	6.25	6.15	0.14	2.32
KK 15	10.6	10.1	10.3	0.36	3.45
LN 3	11.1	10.3	10.7	0.57	4.34
LN 5	17.6	17.7	17.7	0.07	0.40
LK 2	10.6	11.1	10.8	0.36	3.29
LK 4	5.04	4.43	4.74	0.43	9.03
LK 7	368	367	368	0.43	0.12
OC 1	17.1	16.5	16.8	0.43	2.54
OC 3	36.8	37.3	37.0	0.36	0.96
NAC 5	16.6	16.5	16.6	0.07	0.43
VCC 1	13.6	13.3	13.5	0.21	1.59
VCC 4	10.1	9.68	9.88	0.29	2.89

A1.1.5 Cation and anion concentrations

Cation (K^+, Na^+, NH_4^+, Ca^{2+} and Mg^{2+}) and anion (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) concentrations within the coal mine water samples were determined by ion chromatography (IC). Most of the analyses were performed on a Dionex 300 ion chromatograph within the Department of Geological Sciences at the University of Cape Town. The others were also performed by ion chromatography, but at the Institute of Soil Climate and Water in Pretoria.

Principle

Ion chromatography is a liquid-solid chromatographic method for the separation of ionic analytes, which are detected conductimetrically. Dilute electrolyte solutions are injected into a liquid eluent stream, which is pumped through a column containing a solid stationary phase. The ionic components of the sample progress through the column at different rates and therefore enter the detector at different times (Cavé, 1999).

Procedure

The samples were initially filtered through 0.22μm Millipore filter membranes to remove suspended solids and then diluted with MQ de-ionized water to obtain EC values of between 80 and 100μS/cm. Immediately prior to analysis, the samples were also passed through a Dionex onguard-P cartridge containing a polyvinylpyrrolidone (PVP) polymer designed for removing the phenolic fraction of humic acids, tannic acids, lignins, anthocyanins and azo dyes. Within the ion chromatograph, anions were separated on a Dionex AS14 anion exchange column, preceeded by a Dionex AG4A guard column using an eluent comprising 3.5m*M* Na_2CO_3 and 1.7m*M* $NaHCO_3$. The eluent flow rate was 2mL/min and the sample loop volume 50μL. Detection was by conductivity with chemical eluent suppression. An anion micro-membrane suppressor (AMMS) was fitted. Cations were separated on a Dionex CS12A cation exchange column, preceeded by a Dionex CG12A guard column using a 22m*M* MSA (methanesulfonic acid) eluent. The eluent flow rate was 1mL/min and the sample loop volume 25μL. Detection was by conductivity with chemical eluent suppression. A cation self-regenerating suppressor (CSRS) was fitted.

The instrument was calibrated using a series of calibration standards containing known concentrations of all the analyte ions. The standards were made up by successive dilution of Dionex calibration stock solution. Instrument response (calculated as area under an analyte peak) was plotted against the known concentration of the anion or cation in the standard solution. The r^2 values of the resultant calibration lines are given in Table A1.7. The fit of the calibration lines is considered to be satisfactory for all elements over the specified calibration range.

Table A1.7: *Calibration data for IC determination of major cations and anions.*

Calibration	R-squared	Fit type	Calibration range (mg/L)
Cations			
Lithium	0.999881	Linear	0 – 5
Sodium	0.999832	Linear	0 – 25
Ammonium	0.999466	Quadratic	0 – 5
Potassium	0.995050	Linear	0 – 5
Magnesium	0.998108	Linear	0 – 5
Calcium	0.996499	Linear	0 – 25
Anions			
Fluoride	0.997944	Linear	0 – 10
Chloride	0.998795	Linear	0 – 40
Nitrite	0.998756	Linear	0 – 20
Bromide	0.999820	Linear	0 – 10
Nitrate	0.997855	Linear	0 – 20
Phosphate	0.987997	Linear	0 – 20
Sulphate	0.998123	Linear	0 – 40

Sources of error

Any ionic substance that produces a detector response, and has a retention time coinciding with that of an analyte, or near enough to cause peak overlap, may interfere with the determination. Low molecular weight organic acids, such as formic acid, may interfere with the determination of fluoride and chloride. Furthermore, a high concentration of any one ion may interfere with the resolution, and sometimes the retention, of others (Eaton *et al.*, 1995). Most samples require dilution for determination of major ions by ion chromatography, which can introduce additional error.

Detection limits

Generally, the minimum detectable concentrations for anions by this method are near 0.1mg/L for Br^-, Cl^-, NO_3^-, NO_2^-, PO_4^{3-} and SO_4^{2-}, using a 100μL sample loop and 10μS/cm full scale setting on the conductivity detector. Lower detection limits may be obtained with electronic peak area integration and a larger scale setting (Eaton, *et al.*, 1995).

Accuracy of method

In order to assess accuracy during sample measurement four standards, of known concentrations of ions commonly found in water, were analyzed at the start of the analytical session. The results from the ion chromatographs were then compared with the expected concentrations to assess the accuracy of the major ion determination (Table A1.8). Overall the accuracy of the results is considered satisfactory with an average deviation of less than 10% between expected and measured values for all ions.

Table A1.8: *Comparison of expected and measured conc. to assess the accuracy of the IC method.*

Cations	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**
Solution 1					
Expected (mg/L)	6.25	1.25	1.25	1.25	6.25
Measured (mg/L)	6.44	1.30	1.25	1.24	6.88
Difference (%)	3.04	4.00	0	-0.80	10.1
Solution 2					
Expected (mg/L)	12.5	2.50	2.50	2.50	12.5
Measured (mg/L)	12.9	2.49	2.52	2.49	12.1
Difference (%)	3.20	-0.40	0.80	-0.40	-3.28

Cations	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**
Solution 3					
Expected (mg/L)	25.0	5.00	5.00	5.00	25.0
Measured (mg/L)	25.0	5.00	5.04	5.00	24.5
Difference (%)	-0.12	0	0.80	0	-1.96
Mean difference (%)	1.03	1.05	-0.10	-1.30	-0.21

Anions	**Fluoride**	**Chloride**	**Nitrite**	**Nitrate**	**Sulphate**
Solution 1					
Expected (mg/L)	1.25	5.00	2.50	2.50	5.00
Measured (mg/L)	1.19	4.30	2.17	2.15	4.95
Difference (%)	-4.48	-14.1	-15.4	-14.2	-0.96
Solution 2					
Expected (mg/L)	2.50	10.0	5.00	5.00	10.0
Measured (mg/L)	2.38	8.62	4.57	4.89	9.61
Difference (%)	-4.80	-13.8	-8.64	-2.22	-3.86
Solution 3					
Expected (mg/L)	5.00	20.0	10.0	10.0	20.0
Measured (mg/L)	4.95	18.4	9.38	10.2	19.6
Difference (%)	-0.92	-8.04	-6.16	1.46	-1.95
Solution 4					
Expected (mg/L)	10.0	40.0	20.0	20.0	40.0
Measured (mg/L)	10.1	38.5	20.8	20.3	41.4
Difference (%)	1.17	-3.80	4.13	1.38	3.52
Mean difference (%)	-2.26	-9.94	-6.52	-3.40	-0.81

Precision

In addition, random analyses were repeated in order to test the precision of the ion chromatography method. Table A1.9 presents the results of the repeat analyses of anions and cations for some of the samples. This data shows that the difference between duplicates was generally < 10%. Exceptions usually occur in samples in which large dilutions had to be made for the analytical process.

Table A1.9: Duplicate IC analyses for some of the colliery water samples.

Conc. (mg/L)	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
AC 4w	60.9	0	6.00	57.8	184	2.88	25.4	0	0	539
	61.4	0	6.00	57.3	181	2.81	26.3	0	0	551
Mean	61.1	0	6.00	57.5	182	2.84	25.8	0	0	545
SD	0.32	0	0	0.32	2.12	0.05	0.69	0	0	8.70
%RSD	0.52	0	0	0.55	1.16	1.87	2.67	0	0	1.60
BC 7w	109	0	4.80	55.2	122	1.90	23.2	4.99	0	598
	103	0	5.88	50.2	125	2.11	22.6	3.56	0	586
Mean	106	0	5.34	52.7	123	2.00	22.9	4.28	0	592
SD	3.82	0	0.76	3.56	2.04	0.15	0.38	1.01	0	8.39
%RSD	3.61	0	14.3	6.77	1.65	7.62	1.67	0.00	0	1.42
GH 7w	67.2	0	7.50	282	579	4.89	34.4	0	0	3123
	69.0	0	6.90	312	567	5.40	41.2	0	0	2596
Mean	68.1	0	7.20	297	573	5.15	37.8	0	0	2859
SD	1.27	0	0.42	21.0	8.70	0.36	4.79	0	0	372
%RSD	1.87	0	5.89	7.07	1.52	7.01	12.7	0	0	13.0
GS 1w	200	1.50	6.00	185	465	0	30.8	0	0	2109
	200	1.80	6.00	167	432	5.49	34.7	0	0	2048
Mean	200	1.65	6.00	176	449	2.75	32.7	0	0	2079
SD	0.64	0.21	0	12.1	23.3	3.88	2.78	0	0	43.2
%RSD	0.32	0.00	0	6.87	5.20	141	8.49	0	0	2.08
KC 6w	161	2.70	8.10	70.5	150	2.42	31.5	25.1	0	512
	161	2.55	7.95	57.8	158	2.87	32.0	25.3	0	501
Mean	161	2.63	8.03	64.1	154	2.64	31.8	25.2	0	507
SD	0.11	0.11	0.11	9.02	5.94	0.32	0.33	0.10	0	7.93
%RSD	0.07	4.04	1.32	14.1	3.86	12.1	1.04	0.00	0	1.57
ND 7w	682	0	5.10	19.8	58.2	6.09	448	5.64	0	321
	677	0	4.20	23.4	67.8	6.57	454	12.4	0	328
Mean	679	0	4.65	21.6	63.0	6.33	451	9.00	0	325
SD	3.39	0	0.64	2.55	6.79	0.34	4.12	4.75	0	4.88
%RSD	0.50	0	13.7	11.79	10.8	5.36	0.91	0.00	0	1.50
AC 7s	217	0	40.0	441	534	0	25.1	0	0	3699
	245	0	39.5	421	540	0	24.3	0	0	3623
Mean	231	0	39.8	431	537	0	24.7	0	0	3661
SD	19.80	0	0.35	13.8	3.89	0	0.57	0	0	53.2
%RSD	8.57	0	0.89	3.20	0.72	0	2.29	0	0	1.45
BC 1s	57.9	0	6.00	39.3	155	0.14	17.1	7.04	0	407
	58.5	0	6.00	40.4	147	0.15	17.1	7.84	0	439
Mean	58.2	0	6.00	39.9	151	0.15	17.6	7.44	0	423
SD	0.42	0	0	0.78	5.30	0.01	0.71	0.57	0	22.3
%RSD	0.73	0	0	1.95	3.51	4.88	4.01	7.60	0	5.28

Conc. (mg/L)	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
GH 26s	147	0	5.22	37.3	339	0.86	18.2	5.72	0	929
	137	0	1.26	35.5	312	1.08	18.5	5.49	0	960
Mean	142	0	3.24	36.4	326	0.97	18.4	5.61	0	945
SD	7.07	0	2.80	1.27	19.1	0.16	0.21	0.16	0	21.9
%RSD	4.98	0	86.4	3.45	5.87	16.0	1.16	2.90	0	2.32
GS 11s	54.5	0	4.20	56.7	153	0	2.90	0	0	584
	54.8	0	3.90	56.3	164	0	2.51	0	0	543
Mean	54.6	0	4.05	56.5	158	0	2.70	0	0	563
SD	0.21	0	0.21	0.32	7.53	0	0.28	0	0	28.4
%RSD	0.39	0	5.24	0.56	4.76	0	10.2	0	0	5.05
KC 9s	71.2	0	16.8	33.3	97.0	0.48	38.2	1.43	0	314
	68.8	0	9.40	31.1	93.4	0.41	36.4	1.22	0	304
Mean	70.0	0	13.1	32.2	95.2	0.45	37.3	1.33	0	309
SD	1.70	0	5.23	1.56	2.55	0.05	1.25	0.15	0	6.58
%RSD	2.42	0	39.9	4.83	2.67	11.1	3.35	11.2	0	2.13
ND 13s	398	0	0.75	59.3	134	0	131	0	0	1030
	400	0	0.75	59.5	143	0.18	131	0	0	1029
Mean	399	0	0.75	59.4	138	0.09	131	0	0	1030
SD	1.59	0	0	0.18	6.01	0.12	0.30	0	0	1.31
%RSD	0.40	0	0	0.30	4.35	141	0.23	0	0	0.13
KK 4	28.0		16.7	236	439	0	18.8	31.0	0	2295
	28.5		16.0	238	433	0	23.7	34.7	0	2280
Mean	28.3		16.3	237	436	0	21.2	32.8	0	2287
SD	0.35		0.51	1.34	4.24	0	3.46	2.58	0	11.2
%RSD	1.25		3.12	0.57	0.97	0	16.3	7.86	0	0.49
LN 5	27.6		4.92	133	425	0.79	19.2	8.02	0	2797
	29.3		4.20	143	457	0.42	21.6	8.71	3.90	2705
Mean	28.5		4.56	138	441	0.61	20.4	8.37	1.95	2751
SD	1.20		0.51	6.93	22.6	0.26	1.64	0.49	2.76	65.4
%RSD	4.23		11.2	5.02	5.13	43.2	8.05	5.83	141	2.38
LK 7	4.00		5.62	138	392	7.64	87.4	55.4	0	23711
	4.50		6.55	135	385	7.44	55.2	24.0	0	22375
Mean	4.25		6.09	137	389	7.54	71.3	39.7	0	23043
SD	0.35		0.66	2.19	4.95	0.14	22.8	22.2	0	944
%RSD	8.32		10.8	1.60	1.27	1.88	32.0	56.0	0	4.10
NLC 11	2.60		4.02	2.84	9.20	0.01	2.68	25.7	0	14.5
	2.50		3.40	2.82	9.80	0.02	2.51	25.9	0	14.5
Mean	2.55		3.71	2.83	9.50	0.02	2.60	25.8	0	14.5
SD	0.07		0.44	0.01	0.42	0.01	0.12	0.16	0	0.05
%RSD	2.77		11.8	0.50	4.47	47.1	4.63	0.60	0	0.34

Conc. (mg/L)	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
NAC 2	50.8		4.26	53.0	163	0	5.24	0.29	0	667
	51.4		3.99	52.3	165	0	5.26	0.36	0	663
Mean	51.1		4.13	52.7	164	0	5.25	0.33	0	665
SD	0.42		0.19	0.54	1.41	0	0.01	0.05	0	2.73
%RSD	0.83		4.63	1.03	0.86	0	0.27	15.2	0	0.41
VCC 1	23.7		3.19	104	207	0	6.66	0.62	0	1939
	23.9		2.85	114	225	0.21	9.19	3.25	0	2132
Mean	23.8		3.02	109	216	0.11	7.93	1.94	0	2035
SD	0.14		0.24	7.64	12.7	0.15	1.79	1.86	0	137
%RSD	0.59		7.96	7.01	5.89	141	22.6	96.1	0	6.71

Eaton *et al.* (1995) states that the minimum detectable concentration of an anion is a function of the sample size and conductivity scale used. Generally, minimum detectable concentrations are near 0.1mg/L for Br^-, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-} with a 100µL sample loop and a 10µS/cm full-scale setting on the conductivity detector. In this study the anion analyses were performed using a 50µL sample loop and the background conductivity was 15-20µS/cm; therefore higher values may be expected.

A1.1.6 Measurement of trace metal concentrations

Multi-element analysis of the water samples was carried out using an ELAN 6000 ICP-MS. Elements analyzed for included Li, B, Al, Si, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Cs, Ba, Pb and U.

Principle

A high temperature argon plasma source is used to ionize sample atoms, which are passed through an interface into the source region of a quadrupole mass spectrometer and detected simultaneously by their different charge to mass ratio (Cavé, 1999).

Procedure

All of the water samples were passed through a 0.22 µm Millipore filter and then diluted with 2% HNO_3 to a total aliquot volume of 30 ml. Before the analyses were performed, 100 µL of an internal standard (Rh) solution was added to each sample. The internal standard solution was made up as 3mg/L each of Y, Rh and Re in 2% HNO_3. Its main function is in the calibration of the instrument and to correct for drift.

A blank sample was also prepared from MQ de-ionized water by the addition of 1mL of the same conc. HNO_3 preservative as was added to the filtered water samples in the field. The blank was analyzed along with the other samples to account for any elements, which may be contributed by the acid.

Sources of error

- ICP-MS produces a relatively simple spectrum, with fewer opportunities for interference, compared with the complex optical spectra of atomic absorption or emission techniques.
- Spectral interference arises from ions other than the analyte ions (M^+) which form in the plasma from the plasma gas atoms or atmospheric gases. These complicate the ICP-MS spectrum. Examples of ions causing spectral interference are Ar^+, Ar_2^+, ArO^+, ArH^+, M-Ar, O^+, O_2^+, OH^+, H_2O^+, N_2^+, MO^+, $M\text{-}H^+$, $M\text{-}OH^+$ and doubly charged analyte ions.
- Isobaric effects arise from the overlap of molecular peaks with common analyte peaks e.g. $^{75}As^+$ and $^{50}Ar^{35}Cl^+$. Correction factors are applied to reduce these effects.
- Samples and standards were prepared in the same 2% HNO_3 to minimize matrix effects. Components in the matrix, which ionize easily, can suppress the analyte ionization.

Accuracy of method

In order to assess accuracy during sample measurement, a NIST water standard (CRM 1643d) was analyzed at the start of the analytical session and repeated at regular intervals during the session. The results presented in Table A1.10 give the published values for the NIST standard, the UCT measured concentration, the standard deviation and the percentage error between the two values. Only the values for iron differ by more than 10% from the expected concentrations.

Table A1.10: *ICP-MS analysis of NIST Water CRM: NIST 1643. All data in mg/L and n=17.*

	Published	**+/-**	**UCT**	**RSD**	**% error**
Li	16.5	0.55	16.5	3.8	0.3
B	144.8	5.2	134.4	0.0	7.2
Na	22070	640	21781	4.0	1.3
Mg	7989	35	8018	3.4	0.4
Al	127.6	3.5	127.8	1.3	0.1
Si	2700		2859	5.6	5.9
K	2356	35	2331	3.3	1.1
Ca	31040	500	30517	6.6	1.7
V	35.1	1.4	36.7	0.0	4.4
Cr	18.53	0.20	18.73	1.9	1.1
Mn	37.66	0.83	38.47	1.0	2.2
Fe	91.2	3.9	154	3.0	69.2
Ni	58.1	2.7	58.1	1.4	0.0
Cu	20.5	3.8	20.8	1.7	1.6
Zn	72.48	0.65	76.08	3.3	5.0
As	56.02	0.73	56.74	2.0	1.3
Se	11.43	0.17	12.36	3.6	8.1
Rb	13		12.1	2.2	7.0
Sr	294.8	3.4	297.5	1.4	0.9
Mo	112.9	1.7	114.7	0.8	1.6
Cd	6.47	0.37	6.61	1.5	2.2
Cs			4.8	2.7	
Ba	506.5	8.9	518.9	2.6	2.5
Nd			0.005	16.1	
Tl	7.28	0.25	7.51	1.3	3.2
Pb	18.15	0.64	18.77	4.2	3.4
Th			0.001	0.0	
U			0.022	2.3	

All of the mine water samples were analyzed twice, and the average values are presented in this study.

A1.1.7 Determination of iron

Principle

The principle behind this method is as follows: Iron is brought into solution, reduced to the ferrous state by boiling with acid and hydroxylamine, and treated with 1,10-phenathroline at pH 3.2 to 3.3. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex. The coloured solution obeys Beer's Law; its intensity is independent of pH from 3 to 9. A pH between 2.9 and 3.5 insures rapid colour development in the presence of an excess of phenanthroline.

Procedure

During the summer, iron concentrations were determined using the phenanthroline colorimetric method (Method 3500-Fe, Eaton *et al.*, 1995). Samples were passed through a 0.45μm Millipore filter and then acidified with 2ml/100mL 32% HCl in order to prevent adsorption or deposition on the walls of the sample container. In this way, samples may be stored for up to 6 months without significant changes in the redox distribution because microbial catalysts are removed, the pH is low enough to keep the metals solubilized, and the iron oxidation rate is negligable (To *et al.*, 1999). All glassware was washed and rinsed thoroughly in MQ de-ionized water prior to use in order to minimize iron contamination. A Sequoia-Turner model 340 spectrophotometer with a light path of 1cm was used to measure absorbance at 510nm in each of the samples and standard solutions. The minimum detectable concentration using this method is reported as 50μg/L.

The analytical procedure for total iron involved mixing 2mL conc. HCl(1) and 1mL hydroxylamine solution(2) to a 50mL portion of sample and boiling until the volume was reduced to < 15mL. Once cooled the samples were transferred to a 50mL volumetric flask. Before diluting to the mark with MQ de-ionized water, 10mL ammonium acetate(3) and 4mL phenanthroline solution(4) were added. The sample was mixed thoroughly and allowed to stand for 15 minutes for maximum colour development.

The analytical procedure for ferrous iron involved adding 20mL phenanthroline solution(4) and 10mL ammonium acetate solution(3) to 50mL of sample and shaking vigorously. The sample was then diluted to 100mL with MQ de-ionized water, and the colour intensity measured after approximately 10 minutes. Note that colour development is rapid in the presence of excess phenanthroline due to the kinetics of the complexing process. Ferric iron was calculated by subtracting ferrous from total iron.

The reagents used were prepared as follows:

1. 32% HCl containing 0.00002% iron
2. 10g of $NH_2OH{\bullet}HCl$ was dissolved in 100mL of water
3. 250g of $NH_4C_2H_3O_2$ was dissolved in 150mL of water before adding 700mL of glacial acetic acid
4. 100mg 1,10 phenanthroline monohydrate, $C_{12}H_8N_2{\bullet}H_2O$, was dissolved in 100mL of water by stirring and heating to 80°C

Standard solutions containing Fe concentrations of 0, 5, 15, 25, 50, 150, 200 and 500μg/mL were analyzed in order to derive a calibration curve. The total and ferrous iron content of the colliery water samples could then be calculated from the equation of the standard calibration curve. Iron was not detected in many of the neutral to alkaline colliery water samples but exceptionally high concentrations were noted in the more acidic samples.

Sources of error

Among the interfering substances are strong oxidizing agents, cyanide, nitrite, and phosphates, chromium, zinc in concentrations exceeding 10 times that of iron, cobalt and copper in excess of 5mg/L, and nickel in excess of 2mg/L. Noticeable amounts of colour and organic matter may also affect the analytical results.

Detection limits

Dissolved or total concentrations of iron as low as 10μg/L can be determined with a spectrophotometer using cells with a 5cm or longer light path (Eaton *et al.*, 1995).

Precision

According to Eaton *et al.* (1995), a synthetic sample containing 300μg Fe/L, 500μg Al/L, 50μg Cd/L, 110μg Cr/L, 470μg Cu/L, 70μg Pb/L, 120μg Mn/L, 150μg Ag/L, and 650μg Zn/L in distilled water was analyzed in 44 laboratories by the phenanthroline method, with a relative standard deviation of 25.5% and a relative error of 13.3%.

Replicate total and ferrous iron concentrations for random samples as well as mean and sample standard deviation (SD) values are listed in Table A1.11 and Table A1.12, respectively. Relative standard deviation (RSD) values of < 10% for almost all replicate analyses indicate good precision.

Table A1.11: *Precision data for total iron determinations by the phenanthroline method (Eaton et al., 1995).*

Sample	Fe TOTAL Reading 1	Fe TOTAL Reading 2	Mean	SD	% RSD
AC 3s	0.058	0.058	0.058	0.000	0.000
AC 8s	12.98	13.12	13.05	0.100	0.769
BC 5s	0.482	0.500	0.491	0.013	2.592
BC 11s	161.4	173.5	167.5	8.499	5.076
GH 1s	85.08	86.46	85.77	0.979	1.142
GH 2s	3277	3285	3281	5.439	0.166
GH 4s	12.87	13.30	13.08	0.307	2.346
GH 9s	450.0	451.0	450.5	0.680	0.151
GH 14s	15.19	16.23	15.71	0.735	4.676
GH 17s	435.6	422.1	428.8	9.519	2.220
GH 18s	13.52	13.65	13.59	0.097	0.713
GH 21s	574.0	569.2	571.6	3.399	0.595
GS 2s	5.221	5.100	5.161	0.086	1.658
GS 4s	76.54	76.15	76.35	0.272	0.356
GS 6s	0.733	0.054	0.394	0.480	122.0
KC 4s	0.021	0.023	0.022	0.001	6.428
KC 8s	0.085	0.231	0.158	0.103	65.34
KC 9s	0.000	0.115	0.058	0.081	141.4
ND 15s	0.136	0.000	0.068	0.096	141.4
ND 16s	0.136	0.169	0.153	0.023	15.30
KK 15	54.35	51.65	53.00	1.914	3.612
KK 16	113.3	106.7	110.0	4.644	4.221
LN 7	5865	5862	5864	2.773	0.047
NLC 4	26.58	26.81	26.69	0.167	0.625
NLC 6	23.28	23.32	23.30	0.028	0.121
NVC 5	0.000	0.818	0.409	0.578	141.4
NVC 11	0.000	0.000	0.000	0.000	0.000
OC 3	470.5	441.1	455.8	20.80	4.563
VF 1	0.083	0.000	0.042	0.059	141.4
VF 4	0.000	0.000	0.000	0.000	0.000
NAC 5	40.46	39.99	40.22	0.333	0.828
VCC 1	25.25	22.90	24.07	1.666	6.920
VCC 4	64.65	59.55	62.10	3.605	5.805

***Table A1.12:** Precision data for ferrous iron determinations by the phenanthroline method (Eaton et al., 1995).*

Sample	Fe (II) Reading 1	Fe (II) Reading 2	Mean	SD	% RSD
AC 3s	0.000	0.000	0.000	0.000	0.000
AC 8s	0.330	0.554	0.442	0.158	35.84
BC 5s	0.000	0.000	0.000	0.000	0.000
BC 11s	184.4	178.5	181.4	4.215	2.323
GH 1s	0.000	0.000	0.000	0.000	0.000
GH 2s	2038	2115	2077	54.39	2.619
GH 4s	1.214	1.246	1.230	0.023	1.840
GH 9s	409.6	413.5	411.5	2.720	0.661
GH 14s	12.85	11.54	12.19	0.925	7.586
GH 17s	376.9	375.0	376.0	1.360	0.362
GH 18s	15.96	15.94	15.95	0.015	0.093
GH 21s	509.6	500.0	504.8	6.799	1.347
GS 2s	0.554	0.785	0.670	0.163	24.40
GS 4s	66.46	63.08	64.77	2.394	3.695
GS 6s	0.000	0.000	0.000	0.000	0.000
KC 4s	0.000	0.000	0.000	0.000	0.000
KC 8s	0.000	0.000	0.000	0.000	0.000
KC 9s	0.000	0.000	0.000	0.000	0.000
ND 15s	0.000	0.000	0.000	0.000	0.000
ND 16s	0.000	0.000	0.000	0.000	0.000
KK 15	0.000.	0.000	0.000	0.000	0.000
KK 16	102.9	100.9	101.9	1.368	1.342
LN 7	5621	5637	5629	11.09	0.197
NLC 4	25.15	24.21	24.68	0.665	2.696
NLC 6	22.96	21.94	22.45	0.721	3.213
NVC 5	0.000	0.000	0.000	0.000	0.000
NVC 11	0.000	0.000	0.000	0.000	0.000
OC 3	492.3	454.7	473.5	26.62	5.622
VF 1	0.000	0.000	0.000	0.000	0.000
VF 4	0.000	0.000	0.000	0.000	0.000
NAC 5	31.43	30.41	30.92	0.721	2.331
VCC 1	14.16	13.24	13.70	0.646	4.717
VCC 4	38.31	35.96	37.14	1.664	4.480

A1.1.8 Determination of dissolved organic carbon (DOC)

The method used by the CSIR, in Stellenbosch, for the determination of DOC is a modified version of the Persulphate-Ultraviolet Oxidation Method (pers. comm. Mike Louw, 1998).

Principle

In the persulphate-ultraviolet oxidation method, organic carbon is oxidized to carbon dioxide, CO_2, by persulphate in the presence of ultraviolet light. The CO_2 produced is passed through a semi-permeable membrane into a lightly buffered solution of carbonate / bicarbonate and phenolphthalein. The resulting purple solution is then decolourized in an autoanalyzer flow cell in a colorimeter (Cavé, 1999).

Standards of known organic carbon concentration were used for calibration. The standards are made up using potassium hydrogen phthalate.

Sources of error

Incomplete stripping of inorganic carbon can lead to overestimation of DOC, while incomplete oxidation of organic carbon can cause underestimation (pers. comm. Mike Louw, CSIR, 2000). Large complex organic molecules such as tannins, lignins and humic acid may be oxidized slowly because persulphate oxidation is rate limited. Oxidation is also slowed by the preferential oxidation of chloride. At a chloride concentration of 0.1%, oxidation of organic matter may be completely inhibited (Eaton *et al.*, 1995).

Detection limits

Eaton *et al.* (1995) reports that the minimum detectable concentration for the persulphate-ultraviolet oxidation method is 0.05mg organic carbon/L, provided scrupulous attention is given to minimizing sample contamination and method background. The lower limit of detection for DOC by the modified method is approximately 1mg organic carbon/L (pers. comm. Mike Louw, 2000).

Precision

The duplicate analytical results produced by the CSIR are presented in Table A1.13. Although the precision is poor, it should be noted that most of the results are in close proximity to the detection limit.

Table A1.13: Duplicate DOC results (in mg/L), produced by the CSIR, for colliery water samples.

Sample	DOC Reading 1	DOC Reading 2	Mean	SD	% RSD
AC 1w	3.2	3.2	3.2	0.00	0.00
AC 7w	6.0	4.1	5.05	1.34	26.6
BC 3w	< 1.0	1.1			
BC 12w	2.5	2.2	2.35	0.21	9.03
GH 2w	5.9	5.5	5.7	0.28	4.96
GH 26w	1.0	< 1.0	< 1.0		
GS 4w	1.1	1.4	1.25	0.21	17.0
GS 14w	5.1	5.5	5.3	0.28	5.34
KC 2w	3.2	3.5	3.35	0.21	6.33
KC 10w	1.4	1.6	1.5	0.14	9.43
ND 2w	2.4	3.1	2.75	0.50	18.0
ND 10w	2.3	2.4	2.35	0.07	3.01
AC 7s	3.4	3.0	3.2	0.28	8.84
AC 9s	1.5	< 1.0	< 1.25	-	-
BC 2s	< 1.0	1.1	< 1.05	-	-
BC 12s	2.1	2.0	2.05	0.07	3.45
GH 5s	1.4	1.5	1.45	0.07	4.88
GH 13s	< 1.0	2.0	< 1.50	-	-
GH 23s	1.4	1.5	1.45	0.07	4.88
GS 6s	5.8	6.0	5.9	0.14	2.40
GS 11s	2.7	3.1	2.9	0.28	9.75
KC 2s	4.6	4.8	4.7	0.14	3.01
KC 8s	7.7	8.6	8.15	0.64	7.81
ND 2s	1.7	2.0	1.85	0.21	11.5
ND 10s	1.9	1.8	1.85	0.07	3.82
KK 4	2.3	2.4	2.35	0.07	3.01
KK 11	1.8	2.1	1.95	0.21	10.9
KK 17	2.4	2.6	2.5	0.14	5.66
LN 5	1.2	2.4	1.8	0.85	47.1
LK 1	1.6	2.6	2.1	0.71	33.7
LK 7	15.0	16.0	15.5	0.71	4.56
NLC 1	< 1.0	< 1.0	< 1.0	-	-
NLC 11	< 1.0	< 1.0	< 1.0	-	-
NAC 2	< 1.0	< 1.0	< 1.0	-	-
NAC 6	< 1.0	< 1.0	< 1.0	-	-
VCC 1	< 1.0	< 1.0	< 1.0	-	-

A1.2 Rock analysis

A1.2.1 Sample preparation

Sections of borehole core from 5 different collieries were split with a vice and crushed to < 3mm chip size using a jaw crusher. For each sample, about 70g of crushed rock chips were milled for 2 minutes at a fast speed setting in a Siebtechnik carbon-steel swing mill to produce powdered rock samples of approximately 300# particle size, on which most of the analyses were performed. Approximately 30g of quartz was milled between each sample in the same swing mill vessel to clean the mill and reduce cross-contamination.

Approximately 2g of each powdered sample was weighed out accurately into a metal crucible and oven dried at 110°C for 4 hours. The samples were transferred to a dessicator to cool and the mass loss was measured to determine the original water content of the rock samples. The crucibles were then placed in a furnace and the samples roasted at 950°C for 16 hours. After cooling in a dessicator, the mass loss was again measured, this time to determine the loss on ignition (LOI) of each sample.

Forty gram powder briquettes were prepared for trace element analysis. For each briquette, 32g of powdered rock sample was mixed thoroughly with 8g (20%) Hoechst analytical grade wax in a Turbula mixer mill for 25 minutes. The powder-wax mixture was then pressed at 15 tons pressure, into 40mm diameter cylindrical briquettes, on a steel dye.

A1.2.2 X-ray fluorescence spectrometry (XRFS)

Principle

XRF utilizes the characterization of X-ray spectral information to determine the elemental composition of solid samples. X-ray spectra are created by the interaction of an X-ray source with the electrons of the sample atoms. The excitation source causes ejection of an inner shell electron from a sample atom, creating a vacancy in the electron shell and leaving the atom in an excited state. During de-excitation, an electron transition occurs from an outer electron shell to fill this vacancy. The change in energy associated with the transition takes the form of X-ray radiation, which is detected and analyzed. The electronic configuration for each element is unique and thus the atoms of an element produce a characteristic set of X-ray spectral lines for the elements in the portion of the sample undergoing excitation (Cavé, 1999).

Wavelength dispersive XRF uses the rotation through a measured angle (2θ) of a crystal of known interplanar spacing (*d*) to separate the X-ray energy of different wavelengths (λ) from the sample, in accordance with the Bragg equation:

$$n\lambda = 2d \sin \theta$$

where *n* is an integer denoting the spectral order. A proportional counter detector then measures the intensity of the radiation at each wavelength as the analyzing crystal is rotated. The intensity is plotted against wavelength (or rotation angle) to produce a spectrum of peaks from which the elements in the sample are determined qualitatively, or quantitatively if the instrument is calibrated for each element.

Procedure

Major elements

Eleven major elements, Fe, Mn, Ti, Ca, K, S, P, Si, Al, Mg and Na, were determined using powder briquettes. These were analyzed on a Philips PW 1480 wavelength dispersive XRF spectrometer with a dual target Mo/Sc x-ray tube. All measurements were made with the tube at 50kV and 50mA. Analytical conditions are given in Table A1.14.

Table A1.14: *Analytical conditions for determination of major elements using a Philips PW 1480 WDXRF spectrometer.*

Element / line	**Collimator**	**Crystal**	**Detector**	**PHS**		**Counting time (s)**	**Concentration range ***
				LWL	**UPL**		
FeKα	F	LiF (220)	FL	16	68	100	0 – 17
MnKα	F	LiF (220)	FL	15	66	100	0 – 0.27
TiKα	F	LiF (220)	FL	32	68	100	0 – 3.9
CaKα	F	LiF (220)	FL	30	76	50	0 – 77
KKα	F	LiF (220)	FL	32	74	100	0 – 15.5
SKα	C	GE (111)	FL	32	74	100	0 – 53.5
PKα	C	GE (111)	FL	34	74	100	0 – 3.4
SiKα	C	PE (002)	FL	26	80	100	0 – 100
AlKα	C	PE (002)	FL	26	80	100	0 – 100

Element / line	Collimator	Crystal	Detector	PHS		Counting time (s)	Concentration range *
				LWL	UPL		
MgKα	F	PX – 1	FL	36	68	100	0 – 85
NaKα	F	PX -1	FL	30	78	100	0 – 9.1

* All concentrations expressed as wt% oxide; S as SO_3.

Intensity data was collected using the Philips X40 software. All peaks are corrected for background. Spectral overlap corrections are made for Br on Al, Cr on Mn, Al and Ca on Mg, and Mg and Ca on Na. Matrix corrections were made on all elements using the de Jongh model in the X40 software. Theoretical alpha coefficients, calculated using the Philips on-line ALPHAS programme, are used in the de Jongh model.

Table A1.15 lists the given and calculated concentrations for selected elements in two coal Standard Reference Materials (SRMs), which gives an indication of the accuracy of the major element data.

Table A1.15: *Given and calculated major element data (all values expressed as weight % oxide) for two coal SRMs.*

Element	SARM-19		SARM-20	
	Given	Calculated	Given	Calculated
SiO_2	15.0	13.5	17.7	16.7
TiO_2	0.34	0.29	0.63	0.52
Al_2O_3	8.01	6.64	11.3	9.46
Fe_2O_3	1.75	1.41	1.17	0.97
MnO		0.02		0.01
MgO	0.20	0.18	0.43	0.35
CaO	1.39	1.23	1.87	1.58
Na_2O	0.29	0.28	0.27	0.28
K_2O	0.24	0.18	0.14	0.14
P_2O_5		0.02		0.10
SO_3	2.69	2.31	0.93	0.80

Trace Elements

Trace elements were determined on powder briquettes in a series of analytical runs using a number of different x-ray tubes. Analytical conditions for the elements determined are listed in Tables A1.16 and A1.17.

Table A1.16: *X-ray tubes and tube path settings for the determination of trace elements using a Philips PW1480 WDXRF spectrometer.*

Element / line	**X-ray tube** **Target**	**kV**	**mA**	**X-ray path**
Rh Kα_{Compton}	Rh	80	35	Vacuum
Mo Kα	Rh	80	35	Vacuum
Nb Kα	Rh	80	35	Vacuum
Zr Kα	Rh	80	35	Vacuum
Y Kα	Rh	80	35	Vacuum
Sr Kα	Rh	80	35	Vacuum
U Kα_1	Rh	80	35	Vacuum
Rb Kα	Rh	80	35	Vacuum
Th Lα_1	Rh	80	35	Vacuum
Pb Lβ_1	Rh	80	35	Vacuum
Zn Kα	Au	60	45	Vacuum
Cu Kα	Au	60	45	Vacuum
Ni Kα	Au	60	45	Vacuum
Co Kα	Au	50	55	Vacuum
Mn Kα	Au	50	55	Vacuum
Cr Kα	Au	50	55	Vacuum
V Kα	Au	50	55	Vacuum
Ba Lα_1	Cr	50	55	Vacuum
Sc Kα	Cr	50	55	Vacuum
S Kα	Mo/Sc	40	65	Vacuum

The Rh Kα Compton peak was used to determine the mass absorption coefficients of the specimens at the Rh Kα_{Compton} wavelength, and the Compton peak mass absorption coefficient values are used to correct for absorption effects on the Mo, Nb, Zr, Y, Sr, U, Rb, Th, Pb, Zn, Cu, and Ni analyte wavelengths. Primary and secondary mass absorption coefficients for the Co, Mn, Cr, V, Ba, Sc and S analyte wavelengths were calculated from major element compositions using the tables of Heinrich (1986).

Table A1.17: *Instrumental conditions for determination of trace elements using a Philips PW1480 WDXRF spectrometer.*

Element / line	Colli-mator	Crystal	Detector	PHS		Counting time (s)	Background position(s) relative to peak position	Concentration range *
				LWL	UPL			
Rh K$\alpha_{Compton}$	F	LiF (220)	SC	34	75	200		
Mo Kα	F	LiF (200)	SC	30	74	200	– 1.28 + 0.54	0 – 280
Nb Kα	F	LiF (200)	SC	30	74	200		0 – 268
Zr Kα	F	LiF (200)	SC	30	74	200		0 – 1210
Y Kα	F	LiF (200)	SC	30	74	200	– 0.86 + 0.74	0 – 143
Sr Kα	F	LiF (200)	SC	30	74	200	+ 0.78	0 – 440
U Lα_1	F	LiF (200)	SC	30	74	200		0 – 15
Rb Kα	F	LiF (200)	SC	30	74	200	+ 0.60	0 – 530
Th Lα_1	F	LiF (200)	SC	30	74	200		0 – 51
Pb Lβ_1	F	LiF (200)	SC	30	74	200	+ 1.52	0 – 40
Zn Kα	F	LiF (220)	FS	20	80	200	– 1.08 + 4.24	0 – 235
Cu Kα	F	LiF (220)	FS	20	80	200	+ 4.44	0 – 227
Ni Kα	F	LiF (220)	FS	20	80	200	+ 2.52	0 – 630
Co Kα	F	LiF (220)	FL	15	75	200	+ 1.00	0 – 116
Mn Kα	F	LiF (220)	FL	15	75	200	– 2.30 + 4.70	0 – 1700
Cr Kα	F	LiF (220)	FL	15	75	200	– 4.10 + 2.90	0 – 465
V Kα	F	LiF (200)	FL	13	67	200	+ 3.40	0 – 640
Ba Lα_1	F	LiF (200)	FL	25	75	200	– 5.20	0 – 2680
Sc Kα	F	LiF (200)	FL	25	75	200	– 2.78	0 – 54
S Kα	C	Ge (111)	FL	32	72	100	– 5.00 + 5.00	0 – 54

* All concentrations expressed as parts per million (ppm or mg/kg)

Mass absorption coefficient corrections were made to the net peak intensities, (gross peak intensities corrected for dead time losses, background and spectral overlap), to correct for absorption differences between standards and specimens. No corrections were made for enhancement, which could be small but significant (< ~5% relative) for the elements Cr, V, Ba and Sc in certain specimens, depending on their concentrations of Fe, Mn and Ti.

Measured intensity data were processed through the computer program TRACE to correct gross peak intensities for background and spectral overlap and to make mass absorption coefficient corrections according to the methods outlined in Duncan *et al.* (1984). First order calibration lines with zero intercept were calculated using international rock SRMs. The one standard deviation (1σ) error, due to counting statistics, and the lower limit of detection was calculated for each element in each specimen, using the following equations:

$$1\,\sigma\ error\ (in\ ppm) \quad = \quad conc \times \frac{\sqrt{\dfrac{I_p}{T_p} + \dfrac{I_b}{T_b}}}{I_n}$$

and

$$LLD\ (in\ ppm) \quad = \quad \frac{6}{m}\sqrt{\frac{I_b}{T_{total}}}$$

where

conc = calculated concentration in ppm

m = net peak / concentration

I_p = gross peak count rate in cps

I_b = background count rate under the peak in cps

$I_n = I_p - I_b$ = true net peak count rate in cps

T_p = counting time for peak in seconds

T_b = total counting time for background in seconds

$T_{total} = T_p + T_b$

Note: I_b is the calculated background *plus* any corrections for spectral interference i.e. $I_b = I_p - I_n$.

Table A1.18 lists the given and calculated concentrations for selected elements in a few coal SRMs, which gives an indication of the accuracy of the trace element data.

Table A1.18: *Given and calculated trace element data (all values in ppm) for some coal SRMs.*

Element	**SARM-19**		**SARM-20**		**NBS-1632A**		**NBS-1635**	
	Given	**Calc**	**Given**	**Calc**	**Given**	**Calc**	**Given**	**Calc**
Mo	2	1.24		0.96		1.16		
Nb	10	8.71	16	13.8	3.2	5.35		
Zr	351	337	180	160	43.2	55.2	12.4	9.79
Y	20	20.5	29	28.3	7.6	10.3	1.5	2.13
Sr	126	114	330	294	71	80.1	102	136
U	5	4.50	4	4.46	1.02	< 1.06	0.19	
Rb	9	8.08	10	8.24	24	27.9		
Th	12	12.0	18	16.6	3.6	4.18	0.5	
Pb	20	18.3	26	20.5	9.9	12.1	2.1	
Zn	12	10.6	17	13.7	22.4	21.3	3.8	3.59
Cu	13	7.26	18	11.1	13.2	8.83	2.9	0.93
Ni	16	13.1	25	21.7	15.5	14.3	1.4	1.35
Co	5.6	6.05	8.3	7.94	5.6	2.39	0.6	0.78
Mn	157	141	80	70.4		13.6		17.6
Cr	50	49.7	67	63.9	28	27.9	2	0.98
V	35	30.1	47	41.4	35	11.3	4.2	2.54
Ba	304	260	372	319				
Sc	7.6	7.88	10	11.3				
S	149 000	10 740	51 000	3 720		13 908		2 826

A1.2.3 X-ray diffraction analysis (XRD)

Principle

X-ray diffraction techniques allow the qualitative determination of crystalline solid materials, by measuring the distance between the atomic planes in the crystal lattice. Samples are irradiated with X-rays from a tube source using a monochromator and slits to ensure that radiation of a single known wavelength (λ) is incident on the spectrum. X-ray wavelengths are of the same order of magnitude as the spacing of crystal planes (d) and thus a change in path length of the x-ray beam reflected off successive atomic planes causes constructive or destructive interference of the reflected radiation for a given angle of incidence (θ). The conditions for constructive interference are given by the Bragg Law (Section A1.2.2). Since λ is known, the crystal plane spacing (d) can be calculated for those angles (θ) where the reflection intensity maxima are encountered. A goniometer is used to rotate the sample through a measured angle (2θ) in the path of the incident x-ray beam and the reflected x-ray intensity for each angle is measured by a proportional counter (Cavé, 1999).

X-ray reflection peaks can occur from those crystallographic planes, which lie parallel to the specimen surface. Using a powdered sample, a great number of crystal particles are arranged in random orientation, ensuring that each crystallographic plane will lie parallel to the surface in a fair number of grains (Cavé, 1999).

Plotting the measured intensity against 2θ angle (or corresponding crystal d-spacing) produces a diffractogram from which the minerals in the sample can be characterized. Crystalline compounds are identified by the characteristic spacing of their crystal planes in different orientations. Each compound has a distinctive pattern of XRD spectral lines, which are used to identify the compound from a database of stored XRD spectra (Cavé, 1999).

Procedure

Untreated rock powder samples were pressed into a rectangular 1.5 cm x 2 cm window in a metal sample holder against a alcohol-cleaned glass slide backing to produce a flat analytical surface. The sample holder was then lifted off the glass slide and clipped into the instrument sample holder with no backing that could produce an interference signal.

XRD analyses were carried out, by the author, on all crushed samples on a Philips (PW3710 / 1050) X-ray Diffractometer, housed in the Geological Sciences Department at UCT. Samples were irradiated with Copper K_{α} x-ray radiation of wavelength 0.154056 Å ($K_{\alpha 1}$) and 0.154439 Å ($K_{\alpha 2}$), at a $K_{\alpha 2}/K_{\alpha 1}$ intensity ratio of 0.500. The radiation was generated by a PW2233 Cu NF x-ray tube at a generator current of 25mA with a 40kV applied voltage.

The intensity of diffracted radiation from the sample surface was detected by a PW3011 detector after passing through a Diffracted Beam PW1752 curved graphite monochromator and 0.1 mm receiving slit. An AS fixed 4° diffracted anti-scatter slit was used. An angle range from 4° to 70° 2θ was scanned using a step size of 0.05° and the intensity of the diffracted x-rays counted for 2 seconds at every step. Diffractograms of the x-ray intensity pattern against 2θ angle were used to identify the dominant minerals in the powdered rock samples. Crystal d-spacing data and relative intensities for the major peaks were matched against x-ray diffraction data from JCPDS cards to identify mineral species (JCPDS, 1997).

SIROQUANT™ analysis

The raw diffraction data from XRD traces run at the University of Cape Town were sent to the School of Geology at the University of New South Wales for SIROQUANT analysis. Rietveld-format XRD data (.hkl) files were prepared using SIROQUANT for each mineral present in the samples, drawing on a comprehensive collection of crystal-structure information in the SIROQUANT database. These were produced by SIROQUANT as ASCII files listing (hkl) and F (hkl) values. They also incorporated information on the plane nominated within each mineral to control preferred-orientation effects, and data to allow for anomalous dispersion of the XRD beam by iron and related constituents.

A task (.tsk) file was set up for each individual analysis, with a listing of the minerals expected to be present and the relevant sample XRD pattern. Corrections were made to remove the background, including organic matter in the coals, from the sample XRD trace, after which a calibration function was applied (Matulis and Taylor, 1992) to compensate for the effects of the Bragg-Brentano geometry on the X-ray diffraction pattern.

Operation of SIROQUANT involved interactive adjustment and best-fit matching of the XRD profiles for the individual minerals in the task file to the observed X-ray powder diffraction pattern of the sample under analysis. Overall intensities (scales) of the individual mineral phases, together with unit-cell dimensions, line-widths, and preferred orientation for the minerals, and the zero setting of the diffractometer, were progressively refined under operator instructions to fit the full profile of the sample's XRD pattern. Weight percentages of the different minerals were calculated at each stage of the process, along with errors for each mineral phase and the overall goodness of fit (chi^2 value) between the observed and computed profiles.

Allowance was made in the SIROQUANT analysis for preferred orientation in several minerals, particularly the feldspars and carbonates, where although a match was obtained for the key peak positions the distribution of the peak heights was inconsistent with the standard mineral pattern. The standard patterns for such minerals were refined by SIROQUANT, using computations based on the March Function preferred-orientation correction (Dollase, 1986), and the mineral percentage adjusted accordingly.

The results of the SIROQUANT analysis represent the final output from each task, when the best possible fit had been achieved between the observed and calculated XRD patterns. The error associated with each individual component was evaluated by SIROQUANT from the estimated standard deviation (e.s.d.) of the relevant Rietveld scale factor. An estimate of the overall goodness of fit of each analysis is provided in Appendix 5, expressed as the global chi^2 value derived as indicated by Taylor (1991). This should approach unity for a perfect fit between the measured and interpreted patterns, but in practice is usually greater than 1 (Ward *et al.*, 1999).

The errors derived from the e.s.d. values for each mineral phase are probably an underestimation of the actual error in the respective determinations. Errors given by SIROQUANT for each individual mineral should be multiplied by the square root of the global chi^2 figure for the analysis in question.

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APPENDIX 2

Analytical results

A2.1 Water analysis

A number of procedures for checking the correctness of analyses are applicable to water samples for which relatively complete analyses have been made, such as those in this study. The only check presented here is that of charge balance.

The anion and cation sums, when expressed as millimoles charge per litre, must balance because all potable waters are electrically neutral. As a measure of the quality of the colliery water analytical data, the anion-cation charge balance of each water sample was calculated using the method of Murray and Wade (1996). This data is presented in the ensuing tables. Alkalinity and acidity measurements were also included in the charge balance calculations as HCO_3^- and H^+, respectively; DOC, however, was not included. Results are reported to three significant figures and *n.d.* indicates that the constituent was not determined. Note that H^+ was only determined on samples with pH > 4.5.

Measured ionic concentrations (mg/L) were converted to $mmol_c/L$ prior to calculating the percentage difference:

$$mmol_c / L = \left(\frac{mg / L}{atomic\ or\ molecular\ weight} \right) \times ionic\ charge$$

The percentage difference was calculated as follows:

$$\%\ difference = 100 \times \left[\frac{(\Sigma\ cations - \Sigma\ anions)}{(\Sigma\ cations + \Sigma\ anions)} \right]$$

Although Murray and Wade (1996) state that anion-cation differences of ± 2 to 5% are acceptable for an anion range of 10 to 800 $mmol_c/L$, differences of $\leq 10\%$ are considered acceptable for the purposes of this study. Of the 34 samples (approximately 13%) which reported a cation excess greater than 10%, 7 were particularly dilute (containing less than 10 $mmol_c/L$ total anions) and therefore "minor" experimental errors were significant. Most of the other samples displaying significant charge imbalances contained large quantities of acidity, which was difficult to determine accurately due to the formation of precipitates.

A2.2 Rock analysis

Whole-rock major and trace element compositions from the selected boreholes are presented. Majors are reported in weight % oxide and trace elements in ppm. All Fe is calculated as Fe_2O_3. Analytical conditions are reported in Appendix 1. "<" indicates less than lower limit of detection. As all samples were diluted with 20% wax, the data has been corrected with a factor of x 1.25. Furthermore, the "C" value was obtained by difference and not a specific carbon analysis.

Table A2.1: Analytical results obtained for water samples taken from selected collieries during the winter of 1999.

	AC 1w		AC 2w		AC 3w		AC 4w		AC 5w		AC 6w		AC 7w	
pH	8.09		8.20		8.20		6.71		9.23		5.50		7.66	
EC (mS/cm)	1.23		0.682		0.798		1.36		2.11		0.057		5.01	
SAR	3.87		2.39		1.95		1.00		4.89		0.45		1.53	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	0.120	0.017	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.200	0.029	0.010	0.001	< 0.001	< 0.001
Na^+	157	6.85	72.9	3.17	70.9	3.08	60.9	2.65	269	11.7	3.65	0.159	214	9.29
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	7.20	0.184	5.04	0.129	6.32	0.162	6.00	0.153	31.4	0.803	2.82	0.072	40.5	1.04
Mg^{2+}	32.3	2.66	18.4	1.51	25.9	2.13	57.8	4.75	106	8.74	1.82	0.150	585	48.1
Ca^{2+}	71.9	3.59	40.2	2.00	57.8	2.88	184	9.16	53.6	2.67	2.10	0.105	506	25.2
Cr^{2+}	0.002	< 0.001	0.011	< 0.001	0.006	< 0.001	0.002	< 0.001	0.003	< 0.001	0.001	< 0.001	0.002	< 0.001
Mn^{2+}	0.305	0.011	0.105	0.004	0.003	< 0.001	0.091	0.003	< 0.001	< 0.001	0.002	< 0.001	0.080	0.003
Fe_{TOTAL}	0.180	0.006	0.097	0.003	0.153	0.005	0.614	0.022	0.163	0.006	0.009	< 0.001	1.77	0.063
Co^{2+}	0.009	< 0.001	0.002	< 0.001	< 0.001	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001
Ni^{2+}	0.008	< 0.001	0.003	< 0.001	0.004	< 0.001	0.014	< 0.001	0.002	< 0.001	0.004	< 0.001	0.014	< 0.001
Cu^{2+}	0.018	0.001	0.007	< 0.001	0.082	0.003	0.026	0.001	0.005	< 0.001	< 0.001	< 0.001	0.038	0.001
Zn^{2+}	0.017	0.001	< 0.001	< 0.001	0.049	0.001	3.61	0.111	0.020	0.001	< 0.001	< 0.001	0.169	0.005
As^{3+}	0.001	< 0.001	0.001	0.000	0.001	< 0.001	< 0.001	< 0.001	0.005	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.011	< 0.001	0.010	0.000	0.013	< 0.001	0.013	< 0.001	0.030	< 0.001	0.012	< 0.001	0.045	0.001
Sr^{2+}	2.07	0.047	1.14	0.026	1.70	0.039	2.77	0.063	1.93	0.044	0.033	0.001	1.76	0.040
Ba^{2+}	0.196	0.003	0.126	0.002	0.180	0.003	0.055	0.001	0.142	0.002	0.204	0.003	0.016	< 0.001
Al^{3+}	0.119	0.013	0.023	0.003	0.020	0.002	0.155	0.017	0.041	0.005	0.069	0.008	0.016	0.002
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**13.4**		**6.86**		**8.31**		**16.9**		**24.0**		**0.50**		**83.8**
F^-	2.24	0.118	1.21	0.064	1.34	0.071	2.88	0.152	3.44	0.181	< 0.01	< 0.01	< 0.01	< 0.01
Cl^-	133	3.75	60.8	1.71	107	3.03	25.4	0.715	244	6.88	2.30	0.065	57.7	1.63
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	21.7	0.350	11.4	0.184	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	12.1	0.195	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	196	4.09	109	2.28	101	2.11	539	11.2	397	8.27	1.37	0.029	3694	76.9
HCO_3^-	235	3.85	129	2.11	106	1.74	242	3.96	365	5.98	6.89	0.113	380	6.23
Total anions		**12.0**		**6.28**		**6.88**		**16.0**		**21.3**		**0.40**		**84.8**
Si	6.62		6.50		4.63		5.38		0.117		6.74		1.66	
B	0.190		0.070		0.082		0.251		0.236		< 0.001		0.238	
DOC	3.2		4.1		4.6		4.3		22.0		< 1.0		6.0	
Cation excess (%)		**5.26**		**4.39**		**9.42**		**2.68**		**5.90**		**10.8**		**-0.591**

***Table A2.1 cont.**: Analytical results obtained for water samples taken from selected collieries during the winter of 1999.*

	AC 8w		**AC 9w**		**AC 10w**		**BC 1w**		**BC 2w**		**BC 3w**		**BC 4w**	
pH	2.83		8.51		8.16		7.71		8.22		7.48		7.74	
EC (mS/cm)	1.29		1.29		0.691		2.00		0.393		1.43		1.10	
SAR	0.540		8.80		4.44		1.06		1.39		2.06		1.87	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	< 0.001	< 0.001	*n.d.*	*n.d.*	*n.d.*	*n.d.*	< 0.001	< 0.001	0.000	< 0.001	0.150	0.022	0.120	0.017
Na^+	28.9	1.26	246	10.7	107	4.65	91.4	3.98	38.5	1.68	126	5.50	102	4.46
NH_4^+	1.20	0.067	*n.d.*	*n.d.*	*n.d.*	*n.d.*	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.960	0.053
K^+	7.68	0.196	3.33	0.085	3.88	0.099	8.20	0.210	4.28	0.109	5.85	0.150	5.64	0.144
Mg^{2+}	70.3	5.79	18.6	1.53	11.3	0.930	127	10.4	14.9	1.22	68.3	5.61	54.4	4.47
Ca^{2+}	101	5.04	28.7	1.43	25.3	1.26	355	17.7	34.4	1.72	174	8.71	138	6.86
Cr^{2+}	< 0.001	< 0.001	*n.d.*	*n.d.*	*n.d.*	*n.d.*	< 0.001	< 0.001	0.001	< 0.001	0.010	< 0.001	< 0.001	< 0.001
Mn^{2+}	8.60	0.313	< 0.01	< 0.01	< 0.01	< 0.01	0.004	< 0.001	0.002	< 0.001	0.003	< 0.001	0.217	0.008
Fe_{TOTAL}	16.2	0.581	< 0.01	< 0.01	< 0.01	< 0.01	0.768	0.028	0.133	0.005	0.684	0.024	0.338	0.012
Co^{2+}	0.299	0.010	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Ni^{2+}	0.319	0.011	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.012	< 0.001	0.002	< 0.001	0.008	< 0.001	0.004	< 0.001
Cu^{2+}	0.083	0.003	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.003	< 0.001	< 0.001	< 0.001	0.023	0.001	0.012	< 0.001
Zn^{2+}	0.467	0.014	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.066	0.002	0.047	0.001	0.039	0.001	0.031	< 0.001
As^{3+}	< 0.001	< 0.001	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.004	< 0.001	< 0.001	< 0.001	0.003	< 0.001	0.001	< 0.001
Rb^+	0.025	< 0.001	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.022	< 0.001	0.005	< 0.001	0.013	< 0.001	0.012	< 0.001
Sr^{2+}	0.319	0.007	*n.d.*	*n.d.*	*n.d.*	*n.d.*	2.75	0.063	0.655	0.015	2.27	0.052	1.56	0.036
Ba^{2+}	0.016	< 0.001	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.061	0.001	0.151	0.002	0.041	0.001	0.062	0.001
Al^{3+}	1.39	0.155	< 0.01	< 0.01	0.420	0.047	0.044	0.005	0.219	0.024	0.063	0.007	0.023	0.003
H^+	2.00	1.98	*n.d.*	*n.d.*	0.152	0.15	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**15.4**		**13.7**		**7.14**		**32.5**		**4.77**		**20.1**		**16.1**
F^-	2.04	0.107	1.63	0.086	1.49	0.078	3.56	0.187	0.760	0.040	2.85	0.150	2.15	0.113
Cl^-	13.4	0.379	23.0	0.649	20.0	0.564	35.4	1.00	11.7	0.329	20.2	0.568	17.8	0.502
NO_2^-	< 0.01	< 0.01	*n.d.*	*n.d.*	*n.d.*	*n.d.*	< 0.01	< 0.01	< 0.01	< 0.01	15.6	0.338	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	*n.d.*	*n.d.*	*n.d.*	*n.d.*	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	36.2	0.583	3.05	0.049	< 0.01	< 0.01	3.61	0.058	< 0.01	< 0.01	4.21	0.068
PO_4^{3-}	< 0.01	< 0.01	*n.d.*	*n.d.*	*n.d.*	*n.d.*	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	708	14.7	344	7.16	90.5	1.88	1346	28.0	70.7	1.47	674	14.0	528	11.0
HCO_3^-	< 0.01	< 0.01	344	5.63	276	4.52	177	2.90	159	2.60	321	5.26	260	4.27
Total anions		**15.2**		**14.1**		**7.09**		**32.1**		**4.50**		**20.3**		**15.9**
Si	7.30		*n.d.*		*n.d.*		4.81		12.6		10.9		11.6	
B	< 0.001		*n.d.*		*n.d.*		0.083		0.061		0.096		0.063	
DOC	9.6		*n.d.*		*n.d.*		< 1.0		1.0		< 1.0		< 1.0	
Cation excess (%)		**0.645**		**-1.32**		**0.359**		**0.560**		**2.95**		**-0.672**		**0.383**

Table A2.1 cont.: *Analytical results obtained for water samples taken from selected collieries during the winter of 1999.*

	BC 5w		**BC 6w**		**BC 7w**		**BC 8w**		**BC 9w**		**BC 10w**		**BC 11w**	
pH	6.49		7.78		7.68		7.89		8.57		7.63		5.74	
EC (mS/cm)	2.01		0.866		1.17		1.39		0.477		1.93		3.51	
SAR	2.11		3.37		2.05		4.07		2.71		1.05		2.19	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li$^+$	0.200	0.029	0.090	0.013	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.350	0.050
Na$^+$	152	6.59	139	6.05	108	4.72	193	8.41	71.5	3.11	86.6	3.77	256	11.1
NH$_4^+$	1.40	0.078	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	4.90	0.272
K$^+$	7.00	0.179	5.49	0.140	4.80	0.123	8.54	0.218	4.90	0.125	13.8	0.353	11.6	0.295
Mg^{2+}	82.6	6.80	40.1	3.29	55.2	4.54	51.0	4.19	17.3	1.42	160	13.1	354	29.1
Ca^{2+}	256	12.8	63.3	3.16	122	6.08	87.2	4.35	24.3	1.21	250	12.5	453	22.6
Cr^{2+}	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.012	< 0.001	< 0.001	< 0.001	0.002	< 0.001	< 0.001	< 0.001
Mn^{2+}	0.706	0.026	0.011	< 0.001	0.018	0.001	0.020	0.001	< 0.001	< 0.001	0.244	0.009	6.73	0.245
Fe$_{TOTAL}$	0.837	0.030	0.255	0.009	0.383	0.014	0.519	0.019	0.117	0.004	0.498	0.018	176	6.29
Co^{2+}	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	0.003	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.266	0.009
Ni^{2+}	0.005	< 0.001	0.011	< 0.001	0.010	< 0.001	0.062	0.002	0.002	< 0.001	0.012	< 0.001	0.416	0.014
Cu^{2+}	< 0.001	< 0.001	0.015	< 0.001	0.011	< 0.001	0.110	0.003	< 0.001	< 0.001	0.008	< 0.001	0.008	< 0.001
Zn^{2+}	0.628	0.019	0.057	0.002	0.085	0.003	0.303	0.009	0.006	0.000	0.069	0.002	0.386	0.012
As^{3+}	0.000	< 0.001	0.004	< 0.001	0.002	< 0.001	0.003	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.001	< 0.001
Rb$^+$	0.016	0.000	0.009	< 0.001	0.012	< 0.001	0.014	< 0.001	0.008	< 0.001	0.028	< 0.001	0.052	0.001
Sr^{2+}	2.45	0.056	1.43	0.033	1.43	0.033	1.67	0.038	1.36	0.031	2.44	0.056	6.17	0.141
Ba^{2+}	0.035	0.001	0.143	0.002	0.084	0.001	0.120	0.002	1.13	0.016	0.052	0.001	0.006	< 0.001
Al^{3+}	0.026	0.003	1.87	0.208	0.371	0.041	11.2	1.24	0.077	0.009	0.052	0.006	0.129	0.014
H$^+$	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**26.6**		**12.9**		**15.6**		**18.5**		**5.93**		**29.8**		**70.2**
F$^-$	4.20	0.221	2.28	0.120	1.90	0.100	2.49	0.131	2.61	0.137	3.30	0.174	5.18	0.273
Cl$^-$	24.7	0.698	61.0	1.72	23.2	0.654	22.4	0.631	33.8	0.955	32.4	0.914	29.7	0.837
NO$_2^-$	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br$^-$	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO$_3^-$	< 0.01	< 0.01	3.10	0.050	4.99	0.080	6.71	0.108	6.33	0.102	22.2	0.358	< 0.01	< 0.01
PO$_4^{3-}$	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO$_4^{2-}$	881	18.4	363	7.56	598	12.4	659	13.7	15.1	0.315	1350	28.1	3162	65.8
HCO$_3^-$	444	7.27	168	2.75	186	3.05	228	3.74	256	4.19	137	2.25	56.9	0.932
Total anions		**26.5**		**12.2**		**16.3**		**18.3**		**5.70**		**31.8**		**67.9**
Si	8.81		9.81		7.12		7.17		6.26		0.629		11.9	
B	0.141		0.115		0.059		0.135		0.174		0.025		*n.d.*	
DOC	1.3		1.4		1.1		< 1.0		< 1.0		3.4		1.3	
Cation excess (%)		**0.093**		**2.80**		**-2.42**		**0.455**		**1.93**		**-3.25**		**1.68**

Table A2.1 cont.: Analytical results obtained for water samples taken from selected collieries during the winter of 1999.

	BC 12w		**BC 13w**		**GH 1w**		**GH 2w**		**GH 3w**		**GH 4w**		**GH 5w**	
pH	8.26		5.54		2.51		2.50		6.48		7.51		6.40	
EC (mS/cm)	3.29		1.75		8.46		10.2		1.26		0.360		1.70	
SAR	0.990		2.60		0.430		0.470		3.51		1.45		0.83	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	<0.001	<0.001	0.180	0.026	1.60	0.231	2.00	0.288	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Na^+	122	5.31	143	6.24	82.4	3.58	96.0	4.18	148	6.42	33.3	1.45	60.3	2.62
NH_4^+	<0.01	<0.01	1.26	0.070	18.4	1.02	49.0	2.72	0.840	0.047	<0.01	<0.01	0.720	0.040
K^+	33.6	0.859	7.02	0.180	2.40	0.061	9.00	0.230	12.0	0.307	5.92	0.151	7.56	0.193
Mg^{2+}	405	33.3	74.5	6.13	1411	116	1600	132	33.7	2.77	9.36	0.770	116	9.55
Ca^{2+}	494	24.7	108	5.37	451	22.5	530	26.4	78.6	3.92	24.8	1.24	209	10.4
Cr^{2+}	<0.001	<0.001	<0.001	<0.001	0.024	0.001	0.010	<0.001	<0.001	<0.001	0.012	<0.001	<0.001	<0.001
Mn^{2+}	0.456	0.017	2.24	0.081	34.4	1.25	30.5	1.11	3.00	0.109	0.007	<0.001	8.93	0.325
Fe_{TOTAL}	1.31	0.047	62.6	2.24	116	4.14	496	17.8	0.377	0.014	0.249	0.009	0.772	0.028
Co^{2+}	0.007	<0.001	0.109	0.004	0.573	0.019	0.249	0.008	0.007	<0.001	0.001	<0.001	0.184	0.006
Ni^{2+}	0.018	0.001	0.176	0.006	0.113	0.004	0.072	0.002	0.012	<0.001	0.003	<0.001	0.073	0.002
Cu^{2+}	0.004	<0.001	<0.001	<0.001	0.024	0.001	0.007	<0.001	0.007	<0.001	0.067	0.002	0.009	<0.001
Zn^{2+}	0.127	0.004	0.119	0.004	0.131	0.004	0.200	0.006	0.052	0.002	0.009	<0.001	0.084	0.003
As^{3+}	0.001	<0.001	0.000	<0.001	0.001	<0.001	0.001	<0.001	0.001	<0.001	0.004	<0.001	0.002	<0.001
Rb^+	0.071	0.001	0.013	<0.001	0.002	<0.002	0.026	<0.002	0.019	<0.001	0.011	<0.001	0.017	<0.001
Sr^{2+}	5.50	0.125	1.36	0.031	0.082	0.002	0.254	0.006	0.808	0.018	0.156	0.004	1.83	0.042
Ba^{2+}	0.010	<0.001	0.098	0.001	0.009	<0.001	0.007	<0.001	0.012	<0.001	0.011	<0.001	0.028	<0.001
Al^{3+}	<0.001	<0.001	0.109	0.012	27.5	3.06	17.5	1.95	0.090	0.010	0.094	0.010	0.018	0.002
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	125	124	193	191	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**64.4**		**20.4**		**268**		**356**		**13.6**		**3.63**		**23.3**
F^-	<0.01	<0.01	<0.01	<0.01	15.4	0.808	0.000	0.000	1.08	0.057	0.490	0.026	1.94	0.102
Cl^-	48.1	1.36	16.2	0.456	57.2	1.61	94.6	2.67	50.5	1.43	24.3	0.686	30.8	0.869
NO_2^-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Br^-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
NO_3^-	42.0	0.677	29.9	0.483	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	16.7	0.269	0.360	0.006
PO_4^{3-}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	2.00	0.042	<0.01	<0.01
SO_4^{2-}	3056	63.6	990	20.6	14291	298	17795	370	923	19.2	72.8	1.52	1495	31.1
HCO_3^-	188	3.08	<0.01	<0.01	0.000	0.000	0.000	0.000	41.2	0.675	101	1.66	21.3	0.349
Total anions		**68.7**		**21.5**		**299**		**373**		**21.3**		**4.20**		**32.5**
Si	2.73		13.0		3.35		3.70		1.27		3.64		5.96	
B	0.018		0.032		<0.001		0.080		0.127		0.046		0.044	
DOC	2.5		<1.0		10.0		5.9		4.2		5.1		2.1	
Cation excess (%)		**-3.28**		**-2.74**		**-5.57**		**-2.31**		**-22.0**		**-7.19**		**-16.5**

Table A2.1 cont.: *Analytical results obtained for water samples taken from selected collieries during the winter of 1999.*

	GH 6w		**GH 7w**		**GH 8w**		**GH 9w**		**GH 10w**		**GH 11w**		**GH 12w**	
pH	7.55		7.93		7.69		4.69		8.15		8.48		6.48	
EC (mS/cm)	0.807		3.16		0.880		3.89		1.07		0.580		2.01	
SAR	0.81		0.57		1.15		0.45		0.99		4.33		0.66	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.800	0.115	0.100	0.014	0.120	0.017	0.200	0.029
Na^+	33.2	1.44	67.2	2.92	54.1	2.35	53.20	2.31	56.2	2.44	114	4.96	53.6	2.33
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	0.990	0.055	1.60	0.089	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	5.20	0.13	7.50	0.192	13.1	0.336	14.4	0.368	4.40	0.113	3.72	0.095	9.80	0.251
Mg^{2+}	31.8	2.61	282	23.2	40.5	3.33	344	28.3	57.4	4.72	10.7	0.884	123	10.1
Ca^{2+}	74.6	3.72	579	28.9	101	5.05	468	23.4	151	7.53	35.2	1.75	300	15.0
Cr^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002	< 0.001
Mn^{2+}	0.007	< 0.001	0.076	0.003	0.004	< 0.001	5.63	0.205	0.251	0.009	0.007	0.000	1.712	0.062
Fe_{TOTAL}	0.304	0.011	1.72	0.061	0.338	0.012	133	4.75	0.450	0.016	0.173	0.006	0.952	0.034
Co^{2+}	0.000	< 0.001	0.007	< 0.001	0.000	< 0.001	0.374	0.013	0.004	< 0.001	< 0.001	< 0.001	0.028	0.001
Ni^{2+}	0.004	< 0.001	0.039	0.001	0.004	< 0.001	0.638	0.022	0.010	< 0.001	0.001	< 0.001	0.056	0.002
Cu^{2+}	< 0.001	< 0.001	0.007	< 0.001	0.003	< 0.001	< 0.001	< 0.001	0.050	0.002	< 0.001	< 0.001	< 0.001	< 0.001
Zn^{2+}	0.035	0.001	0.122	0.004	0.021	0.001	0.722	0.022	0.058	0.002	0.027	0.001	0.115	0.004
As^{3+}	0.001	< 0.001	0.002	< 0.001	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	0.004	< 0.001	< 0.001	< 0.001
Rb^+	0.008	< 0.001	0.010	< 0.001	0.011	< 0.001	0.011	< 0.001	0.006	< 0.001	0.003	< 0.001	0.014	< 0.001
Sr^{2+}	1.03	0.024	1.45	0.033	0.624	0.014	2.36	0.054	1.70	0.039	0.555	0.013	4.71	0.108
Ba^{2+}	0.097	0.001	0.037	0.001	0.271	0.004	0.106	0.002	0.025	< 0.001	0.222	0.003	0.123	0.002
Al^{3+}	0.014	0.002	0.045	0.005	0.026	0.003	8.63	0.959	0.117	0.013	0.028	0.003	0.035	0.004
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	13.9	13.8	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**7.95**		**55.3**		**11.2**		**68.2**		**14.9**		**7.74**		**27.9**
F^-	1.45	0.076	4.89	0.257	1.32	0.069	6.32	0.333	1.49	0.215	2.31	0.122	0.000	0.000
Cl^-	14.5	0.409	34.4	0.971	28.8	0.812	32.8	0.926	23.3	1.01	20.7	0.583	22.3	0.629
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	3.10	0.050	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	335	6.96	3123	65.0	382	7.96	3580	74.5	653	13.6	90.7	1.89	1078	22.5
HCO_3^-	90.1	1.48	192	3.15	151	2.48	0.000	0.000	140	2.54	279	4.56	269	4.40
Total anions		**8.93**		**69.4**		**11.3**		**75.8**		**17.4**		**7.21**		**27.5**
Si	1.99		20.6		0.261		8.32		8.67		8.43		11.1	
B	0.058		0.046		0.026		0.008		0.067		0.284		0.032	
DOC	7.3		2.0		14.1		2.9		< 1.0		4.6		1.8	
Cation excess (%)		**-5.79**		**-11.3**		**-0.697**		**-5.29**		**-7.62**		**3.55**		**0.74**

Table A2.1 cont.: Analytical results obtained for water samples taken from selected collieries during the winter of 1999.

	GH 13w		**GH 14w**		**GH 15w**		**GH 16w**		**Gh 17w**		**GH 18w**		**GH 19w**	
pH	7.80		6.03		6.81		8.24		3.31		6.70		6.03	
EC (mS/cm)	0.319		2.56		0.435		0.742		4.06		0.394		2.55	
SAR	0.88		0.59		0.85		1.13		0.97		0.97		0.28	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	< 0.001	< 0.001	0.250	0.036	0.080	0.012	0.080	0.012	0.400	0.058	0.040	0.006	0.250	0.036
Na^+	22.8	0.992	57.0	2.48	34.6	1.50	50.6	2.20	114	4.96	27.4	1.19	24.8	1.08
NH_4^+	0.720	0.040	1.75	0.097	< 0.01	< 0.01	< 0.01	< 0.01	2.40	0.133	< 0.01	< 0.01	4.50	0.249
K^+	4.89	0.125	10.3	0.262	4.72	0.12	2.40	0.061	3.60	0.092	3.76	0.096	17.3	0.441
Mg^{2+}	11.4	0.938	172	14.2	29.4	2.42	42.2	3.47	419	34.5	15.0	1.23	145	11.9
Ca^{2+}	32.1	1.60	429	21.4	76.4	3.81	81.9	4.09	364	18.2	35.1	1.75	376	18.8
Cr^{2+}	0.002	< 0.001	< 0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002	< 0.001	< 0.001	< 0.001
Mn^{2+}	0.076	0.003	3.09	0.112	1.30	0.047	0.142	0.005	9.07	0.330	0.066	0.002	1.881	0.068
Fe_{TOTAL}	0.303	0.011	28.8	1.03	0.258	0.009	0.290	0.010	67.3	2.41	0.116	0.004	158.1	5.66
Co^{2+}	0.002	< 0.001	0.373	0.013	0.022	0.001	0.005	< 0.001	0.166	0.006	< 0.001	< 0.001	0.128	0.004
Ni^{2+}	0.023	0.001	0.473	0.016	0.039	0.001	0.010	< 0.001	0.168	0.006	0.007	< 0.001	0.155	0.005
Cu^{2+}	< 0.001	< 0.001	0.017	0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Zn^{2+}	0.045	0.001	1.031	0.032	0.013	< 0.001	0.011	< 0.001	0.413	0.013	0.020	0.001	0.165	0.005
As^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.010	< 0.001	0.019	< 0.001	0.004	< 0.001	0.003	< 0.001	0.009	< 0.001	0.003	< 0.001	0.020	< 0.001
Sr^{2+}	0.699	0.016	2.96	0.067	0.609	0.014	0.813	0.019	0.992	0.023	0.326	0.007	1.57	0.036
Ba^{2+}	0.463	0.007	0.038	0.001	0.132	0.002	0.296	0.004	0.069	0.001	0.241	0.004	0.058	0.001
Al^{3+}	0.057	0.006	0.114	0.013	< 0.001	< 0.001	0.059	0.007	15.9	1.77	0.007	0.001	1.09	0.121
H^+	*n.d.*	*n.d.*	2.87	2.85	*n.d.*	*n.d.*	*n.d.*	*n.d.*	10.1	10.0	*n.d.*	*n.d.*	9.31	9.24
Total cations		**3.74**		**41.2**		**7.94**		**9.87**		**67.9**		**4.29**		**41.7**
F^-	1.00	0.053	3.05	0.161	1.31	0.069	0.000	0.000	8.28	0.436	0.670	0.035	0.000	0.000
Cl^-	9.52	0.269	13.4	0.378	6.09	0.172	54.9	1.55	30.3	0.854	4.75	0.134	19.4	0.546
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	9.37	0.151	2.66	0.043	< 0.01	< 0.01	5.90	0.095	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.000	0.000	< 0.01	< 0.01
SO_4^{2-}	17.0	0.353	2584	53.8	247	5.14	33.4	0.695	3298	68.7	64.5	1.34	2004	41.7
HCO_3^-	196	3.21	34.4	0.563	169	2.77	440	7.21	< 0.01	< 0.01	161	2.63	< 0.01	< 0.01
Total anions		**3.89**		**54.9**		**8.31**		**9.50**		**70.0**		**4.24**		**42.3**
Si	7.28		9.24		11.5		11.5		8.03		19.0		11.1	
B	0.060		0.037		0.012		0.038		0.049		< 0.001		0.041	
DOC	1.8		1.6		1.0		< 1.0		2.3		< 1.0		3.7	
Cation excess (%)		**-1.92**		**-14.2**		**-2.27**		**1.93**		**-1.52**		**0.640**		**-0.72**

Table A2.1 cont.: *Analytical results obtained for water samples taken from selected collieries during the winter of 1999.*

	GH 20w		**GH 21w**		**GH 22w**		**GH 23w**		**GH 24w**		**GH 25w**		**GH 26w**	
pH	3.96		3.07		8.41		8.05		7.05		8.26		8.01	
EC (mS/cm)	1.92		5.55		0.578		1.67		0.635		0.946		2.24	
SAR	0.70		0.80		1.71		1.57		0.89		1.07		1.70	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	< 0.001	< 0.001	< 0.001	< 0.001	0.060	0.009	0.180	0.026	0.070	0.010	< 0.001	< 0.001	< 0.001	< 0.001
Na^+	61.2	2.66	116	5.04	56.0	2.43	104	4.53	35.6	1.55	55.5	2.41	144	6.27
NH_4^+	< 0.01	< 0.01	6.00	0.333	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	6.20	0.159	3.00	0.077	6.78	0.173	15.5	0.396	13.0	0.331	3.80	0.097	4.25	0.109
Mg^{2+}	73.6	6.06	650	53.5	23.3	1.92	74.9	6.16	28.2	2.32	49.0	4.03	72.8	5.99
Ca^{2+}	459	22.9	529	26.4	42.6	2.13	212	10.6	75.7	3.78	124	6.17	425	21.2
Cr^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.003	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Mn^{2+}	1.83	0.066	7.03	0.256	0.004	< 0.001	0.300	0.011	0.123	0.004	0.980	0.036	0.210	0.008
Fe_{TOTAL}	1.59	0.057	84.4	3.02	0.161	0.006	0.905	0.032	0.243	0.009	0.318	0.011	1.54	0.055
Co^{2+}	0.030	0.001	0.180	0.006	< 0.001	< 0.001	0.003	< 0.001	0.001	< 0.001	0.011	< 0.001	0.002	< 0.001
Ni^{2+}	0.065	0.002	0.121	0.004	0.001	0.000	0.014	< 0.001	0.005	< 0.001	0.018	0.001	0.030	0.001
Cu^{2+}	0.061	0.002	0.006	< 0.001	< 0.001	< 0.001	0.007	< 0.001	0.007	< 0.001	0.005	< 0.001	0.005	< 0.001
Zn^{2+}	0.476	0.015	0.355	0.011	0.010	< 0.001	0.124	0.004	0.077	0.002	0.041	0.001	0.071	0.002
As^{3+}	0.006	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002	< 0.001	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001
Rb^+	0.012	< 0.001	0.007	< 0.001	0.014	< 0.001	0.020	< 0.001	0.011	< 0.001	0.006	< 0.001	0.007	< 0.001
Sr^{2+}	1.50	0.034	0.564	0.013	1.60	0.037	2.53	0.058	0.738	0.017	1.57	0.036	2.24	0.051
Ba^{2+}	0.020	0.000	0.022	< 0.001	0.200	0.003	0.069	0.001	0.049	0.001	0.030	< 0.001	0.054	0.001
Al^{3+}	2.97	0.331	30.1	3.34	0.065	0.007	0.086	0.010	0.038	0.004	0.085	0.009	0.554	0.062
H^+	2.18	2.16	41.8	41.5	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**33.9**		**127**		**6.71**		**21.8**		**8.03**		**12.8**		**33.8**
F^-	3.98	0.209	15.9	0.837	2.02	0.106	3.13	0.165	0.670	0.035	2.21	0.116	4.70	0.247
Cl^-	18.1	0.511	48.7	1.37	42.9	1.21	123	3.46	26.4	0.745	21.7	0.612	31.7	0.893
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	4.53	0.073	6.25	0.101	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	1512	31.5	6273	131	146	3.03	768	16.0	262	5.45	478	9.96	1629	33.9
HCO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	175	2.87	147	2.41	101	1.66	148	2.43	123	2.02
Total anions		**32.2**		**133**		**7.29**		**22.1**		**7.89**		**13.1**		**37.1**
Si	8.29		3.15		5.44		5.82		3.32		8.64		8.18	
B	0.057		0.024		0.160		0.106		0.113		0.073		0.169	
DOC	3.5		1.9		1.1		1.6		6.8		< 1.0		1.0	
Cation excess (%)		**2.60**		**-2.33**		**-4.13**		**-0.789**		**0.870**		**-1.21**		**-4.68**

Table A2.1 ***cont.:*** *Analytical results obtained for water samples taken from selected collieries during the winter of 1999.*

	GH 27w		**GH 28w**		**GS 1w**		**GS 2w**		**GS 3w**		**GS 4w**		**GS 5w**	
pH	8.36		7.80		6.96		6.90		6.73		3.18		7.08	
EC (mS/cm)	0.449		0.613		2.82		2.35		2.77		3.28		2.09	
SAR	2.41		0.46		1.99		0.89		1.25		1.12		0.29	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.350	0.050	< 0.001	< 0.001
Na^+	68.3	2.97	20.8	0.903	200	8.72	84.8	3.69	119	5.17	120	5.21	23.0	1.00
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	1.50	0.083	< 0.01	< 0.01	< 0.01	< 0.01	6.65	0.369	< 0.01	< 0.01
K^+	3.10	0.079	2.46	0.063	6.00	0.153	7.50	0.192	6.90	0.176	7.00	0.179	6.00	0.153
Mg^{2+}	17.5	1.44	45.7	3.76	185	15.2	152	12.5	164	13.5	196	16.1	94.8	7.80
Ca^{2+}	31.9	1.59	77.0	3.84	465	23.2	437	21.8	419	20.9	544	27.2	337	16.8
Cr^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.006	< 0.001
Mn^{2+}	0.097	0.004	0.014	< 0.001	1.75	0.064	2.06	0.075	1.44	0.052	1.90	0.069	1.02	0.037
Fe_{TOTAL}	0.091	0.003	0.156	0.006	1.66	0.059	1.97	0.070	1.22	0.044	6.53	0.234	2.01	0.072
Co^{2+}	0.001	< 0.001	< 0.001	< 0.001	0.016	0.001	0.044	0.001	0.034	0.001	0.078	0.003	0.035	0.001
Ni^{2+}	0.004	< 0.001	0.002	< 0.001	0.063	0.002	0.164	0.006	0.089	0.003	0.103	0.004	0.115	0.004
Cu^{2+}	0.086	0.003	0.009	< 0.001	0.090	0.003	0.048	0.002	0.015	< 0.001	*n.d.*	*n.d.*	0.087	0.003
Zn^{2+}	0.033	0.001	0.010	< 0.001	0.273	0.008	0.364	0.011	0.167	0.005	0.314	0.010	0.250	0.008
As^{3+}	0.003	< 0.001	0.001	< 0.001	0.001	< 0.001	0.003	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002	< 0.001
Rb^+	0.004	< 0.001	0.001	< 0.001	0.017	< 0.001	0.020	< 0.001	0.014	< 0.001	0.010	< 0.001	0.017	< 0.001
Sr^{2+}	0.548	0.013	0.293	0.007	4.03	0.092	2.86	0.065	2.58	0.059	0.795	0.018	1.71	0.039
Ba^{2+}	0.276	0.004	0.057	0.001	0.036	0.001	0.042	0.001	0.032	< 0.001	0.022	0.000	0.014	< 0.001
Al^{3+}	0.169	0.019	0.138	0.015	0.161	0.018	4.38	0.487	0.297	0.033	13.8	1.54	0.017	0.002
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	9.68	9.60	*n.d.*	*n.d.*
Total cations		**6.12**		**8.60**		**47.6**		**38.9**		**39.9**		**58.6**		**25.9**
F^-	1.52	0.080	0.610	0.032	< 0.01	< 0.01	0.000	0.000	4.83	0.254	7.04	0.371	3.46	0.182
Cl^-	17.3	0.487	14.2	0.400	30.8	0.867	28.3	0.798	33.6	0.947	106	2.99	18.1	0.510
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	6.30	0.102	6.10	0.098	< 0.01	< 0.01	4.00	0.065	0.120	0.002	< 0.01	< 0.01	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	45.6	0.950	73.7	1.54	2109	43.9	1885	39.3	1889	39.3	2642	55.0	1264	26.3
HCO_3^-	241	3.95	373	6.11	185	3.04	43.9	0.719	52.0	0.852	< 0.01	< 0.01	106	1.73
Total anions		**5.57**		**8.18**		**47.8**		**40.8**		41.4		**58.4**		**28.7**
Si	7.06		18.8		5.28		6.51		4.77		3.35		5.81	
B	0.080		0.006		0.184		0.111		0.080		0.009		0.052	
DOC	2.2		1.2		< 1.0		< 1.0		1.1		1.1		1.7	
Cation excess (%)		**4.69**		**2.48**		**-0.229**		**-2.42**		-1.79		**0.219**		**-5.16**

Table A2.1 cont.: Analytical results obtained for water samples taken from selected collieries during the winter of 1999.

	GS 6w		**GS 7w**		**GS 8w**		**GS 9w**		**GS 10w**		**GS 11w**		**GS 12w**	
pH	7.28		7.40		6.53		7.37		6.79		7.86		7.43	
EC (mS/cm)	3.66		1.37		1.48		1.28		2.72		1.38		0.480	
SAR	1.30		0.74		0.72		0.98		1.29		1.21		0.50	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	0.700	0.101	< 0.001	< 0.001	0.150	0.022	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Na^+	152	6.59	49.1	2.13	39.3	1.71	48.5	2.11	105	4.58	60.9	2.65	14.2	0.618
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.200	0.011
K^+	19.6	0.501	4.05	0.104	6.45	0.165	4.50	0.115	7.80	0.199	5.55	0.142	4.15	0.106
Mg^{2+}	310	25.5	89.1	7.33	106	8.75	94.1	7.74	180	14.8	90.2	7.42	23.5	1.93
Ca^{2+}	513	25.6	181	9.02	221	11.0	183	9.11	501	25.0	188	9.39	58.4	2.91
Cr^{2+}	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.006	< 0.001	0.002	< 0.001	< 0.001	< 0.001
Mn^{2+}	0.094	0.003	0.007	< 0.001	1.46	0.053	0.005	< 0.001	1.36	0.050	0.001	< 0.001	0.078	0.003
Fe_{TOTAL}	1.70	0.061	0.657	0.024	0.879	0.031	0.614	0.022	1.61	0.058	0.635	0.023	0.208	0.007
Co^{2+}	0.003	< 0.001	< 0.001	< 0.001	0.035	0.001	< 0.001	< 0.001	0.020	0.001	< 0.001	< 0.001	0.002	< 0.001
Ni^{2+}	0.032	0.001	0.013	< 0.001	0.152	0.005	0.009	< 0.001	0.092	0.003	0.009	< 0.001	0.005	< 0.001
Cu^{2+}	< 0.001	< 0.001	0.035	0.001	0.005	< 0.001	0.040	0.001	0.043	0.001	0.023	0.001	0.008	< 0.001
Zn^{2+}	0.145	0.004	0.043	0.001	0.236	0.007	0.036	0.001	0.204	0.006	0.035	0.001	0.035	0.001
As^{3+}	< 0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.059	0.001	0.011	< 0.001	0.016	< 0.001	0.012	0.000	0.017	0.000	0.010	0.000	0.012	< 0.001
Sr^{2+}	3.78	0.086	1.99	0.045	1.22	0.028	2.05	0.047	3.44	0.078	2.21	0.051	0.302	0.007
Ba^{2+}	0.031	< 0.001	0.016	< 0.001	0.006	< 0.001	0.018	< 0.001	0.038	0.001	0.068	0.001	0.144	0.002
Al^{3+}	0.088	0.010	< 0.001	< 0.001	< 0.001	< 0.001	0.135	0.015	0.060	0.007	0.106	0.012	0.105	0.012
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**58.5**		**18.7**		**21.8**		**19.2**		**44.8**		**19.7**		**5.61**
F^-	5.46	0.287	2.34	0.123	< 0.01	< 0.01	2.39	0.104	< 0.01	< 0.01	1.35	0.071	0.560	0.029
Cl^-	93.5	2.64	19.0	0.536	16.0	0.450	20.9	1.16	36.3	1.02	13.9	0.392	9.79	0.276
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	38.15	0.615	7.92	0.128	0.020	0.000	< 0.01	< 0.01	< 0.01	< 0.01	4.25	0.069	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	2623	54.6	817	17.0	1031	21.5	717	14.9	2247	46.8	754	15.7	237	4.94
HCO_3^-	190	3.12	142	2.32	85.9	1.41	168	3.01	91.8	1.50	187	3.07	36.1	0.592
Total anions		**61.3**		**20.1**		**23.3**		**19.2**		**49.3**		**19.3**		**5.84**
Si	2.75		7.91		8.70		6.00		4.38		3.92		0.645	
B	0.191		0.057		< 0.001		0.030		0.068		0.051		0.008	
DOC	4.4		1.1		< 1.0		2.7		1.0		1.5		3.3	
Cation excess (%)		**-2.33**		**-3.78**		**-3.43**		**-0.123**		**-4.80**		**0.988**		**-2.01**

Table A2.1 cont.: Analytical results obtained for water samples taken from selected collieries during the winter of 1999.

	GS 13w		**GS 14w**		**KC 1w**		**KC 2w**		**KC 3w**		**KC 4w**		**KC 5w**	
pH	7.93		7.84		8.63		7.61		7.61		7.93		8.21	
EC (mS/cm)	4.05		3.71		0.700		0.840		0.580		0.430		1.72	
SAR	1.39		1.83		9.80		2.18		1.67		0.85		3.62	
	Conc (mg/L)	**$mmol_c$/L**	**Conc (mg/L)**	**$mmol_c$/L**	**Conc (mg/L)**	**$mmol_c$/L**	**Conc (mg/L)**	**$mmol_c$/L**	**Conc (mg/L)**	**$mmol_c$/L**	**Conc (mg/L)**	**$mmol_c$/L**	**Conc (mg/L)**	**$mmol_c$/L**
Li^+	< 0.001	< 0.001	0.400	0.058	< 0.001	< 0.001	< 0.001	< 0.001	0.060	0.009	< 0.001	< 0.001	< 0.001	< 0.001
Na^+	140	6.11	164	7.15	178	7.72	91.4	3.97	58.7	2.56	28.0	1.22	218	9.48
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.250	0.014	< 0.01	< 0.01
K^+	17.1	0.437	17.6	0.450	2.66	0.068	6.72	0.172	6.60	0.169	6.30	0.161	9.52	0.24
Mg^{2+}	319	26.2	343	28.2	5.04	0.415	23.0	1.89	15.0	1.23	8.30	0.683	92.1	7.58
Ca^{2+}	768	38.3	600	29.9	16.7	0.835	94.9	4.73	70.0	3.49	69.7	3.48	123	6.15
Cr^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.011	< 0.001	< 0.001	< 0.001
Mn^{2+}	0.001	< 0.001	0.002	< 0.001	0.006	< 0.001	0.011	< 0.001	0.008	< 0.001	0.272	0.010	0.011	< 0.001
Fe_{TOTAL}	2.25	0.081	1.66	0.060	0.053	0.002	0.503	0.018	0.189	0.007	0.226	0.008	0.451	0.016
Co^{2+}	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.003	< 0.001	< 0.001	< 0.001
Ni^{2+}	0.023	0.001	0.017	0.001	0.001	< 0.001	0.016	0.001	0.009	< 0.001	0.004	< 0.001	0.007	< 0.001
Cu^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Zn^{2+}	0.118	0.004	0.117	0.004	0.051	0.002	0.139	0.004	0.063	0.002	0.437	0.013	0.033	0.001
As^{3+}	0.002	< 0.001	0.001	< 0.001	0.003	< 0.001	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001
Rb^+	0.037	< 0.001	0.065	0.001	0.004	< 0.001	0.011	< 0.001	0.009	< 0.001	0.008	< 0.001	0.010	< 0.001
Sr^{2+}	4.79	0.109	4.04	0.092	0.368	0.008	1.67	0.038	0.900	0.021	0.286	0.007	3.26	0.074
Ba^{2+}	0.038	0.001	0.020	< 0.001	0.123	0.002	0.054	0.001	0.083	0.001	0.113	0.002	0.057	0.001
Al^{3+}	0.144	0.016	0.016	0.002	0.192	0.021	0.505	0.056	0.027	0.003	0.037	0.004	0.036	0.004
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**71.3**		**66.0**		**9.07**		**10.9**		**7.49**		**5.59**		**23.6**
F^-	< 0.01	< 0.01	< 0.01	< 0.01	4.07	0.214	1.49	0.078	1.09	0.057	0.890	0.047	3.93	0.207
Cl^-	74.3	2.10	115	3.23	26.2	0.739	25.2	0.712	23.8	0.671	46.6	1.31	29.9	0.843
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	1.95	0.031	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	7.70	0.124
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	3799	79.1	3208	66.8	43.7	0.910	278	5.79	135	2.80	22.3	0.464	804	16.7
HCO_3^-	71.7	1.18	312	5.11	414	6.78	231	3.78	213	3.49	193	3.16	350	5.73
Total anions		**82.4**		**75.1**		**8.46**		**10.3**		**6.97**		**4.99**		**23.7**
Si	0.289		3.84		3.53		8.07		9.94		16.2		1.50	
B	0.037		0.203		0.645		0.313		0.162		0.056		0.350	
DOC	4.5		5.1		2.5		3.2		5.8		6.0		2.1	
Cation excess (%)		**-7.22**		**-6.51**		**3.49**		**2.86**		**3.65**		**5.76**		**-0.216**

Table A2.1 cont: Analytical results obtained for water samples taken from selected collieries during the winter of 1999.

	KC 6w		KC 7w		KC 8w		KC 9w		KC 10w		ND 1w		ND 2w	
pH	7.75		7.98		8.04		8.13		7.34		8.01		6.77	
EC (mS/cm)	1.47		1.52		1.08		0.980		1.09		3.50		6.88	
SAR	2.72		1.31		4.79		1.70		1.09		12.9		14.1	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.300	0.043	0.110	0.016	< 0.001	< 0.001	< 0.001	< 0.001
Na^+	161	7.00	89.9	3.91	188	8.16	79.9	3.48	60.8	2.65	743	32.3	1460	63.5
NH_4^+	2.70	0.150	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	8.10	0.207	7.65	0.196	9.13	0.234	21.9	0.560	4.18	0.107	9.45	0.242	15.4	0.394
Mg^{2+}	70.5	5.80	99.8	8.21	37.5	3.09	43.3	3.56	40.3	3.31	59.2	4.87	197	16.2
Ca^{2+}	150	7.48	192	9.56	54.3	2.71	97.6	4.87	172	8.57	154	7.67	484	24.2
Cr^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	0.002	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Mn^{2+}	0.002	< 0.001	0.002	< 0.001	0.004	< 0.001	0.010	< 0.001	0.077	0.003	0.137	0.005	1.15	0.042
Fe_{TOTAL}	0.361	0.013	0.367	0.013	0.257	0.009	0.500	0.018	0.507	0.018	0.277	0.010	1.43	0.051
Co^{2+}	0.000	< 0.001	0.000	< 0.001	0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.004	< 0.001	0.003	< 0.001
Ni^{2+}	0.006	< 0.001	0.005	< 0.001	0.004	< 0.001	0.006	< 0.001	0.010	< 0.001	0.045	0.002	0.095	0.003
Cu^{2+}	< 0.001	< 0.001	0.003	< 0.001	< 0.001	< 0.001	0.031	0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002	< 0.001
Zn^{2+}	0.021	0.001	0.024	0.001	0.025	0.001	0.063	0.002	0.056	0.002	0.142	0.004	0.281	0.009
As^{3+}	0.001	< 0.001	0.001	< 0.001	0.002	< 0.001	0.002	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.001	< 0.001
Rb^+	0.014	< 0.001	0.014	< 0.001	0.007	< 0.001	0.073	0.001	0.010	< 0.001	0.019	< 0.001	0.046	0.001
Sr^{2+}	3.29	0.075	3.31	0.075	1.32	0.030	1.31	0.030	2.93	0.067	4.04	0.092	9.70	0.221
Ba^{2+}	0.070	0.001	0.068	0.001	0.120	0.002	0.216	0.003	0.122	0.002	0.069	0.001	0.016	< 0.001
Al^{3+}	0.010	0.001	< 0.001	< 0.001	0.097	0.011	0.414	0.046	0.077	0.009	0.041	0.005	0.072	0.008
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**20.7**		**22.0**		**14.2**		**12.6**		**14.7**		**45.2**		**105**
F^-	2.42	0.127	2.37	0.125	2.41	0.127	2.28	0.099	1.87	0.098	3.47	0.183	< 0.01	< 0.01
Cl^-	31.5	0.889	28.9	0.816	36.8	1.04	45.3	2.51	13.1	0.369	298	8.39	581	16.4
NO_2^-	14.8	0.322	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	2.02	0.083	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	25.1	0.405	< 0.01	< 0.01	< 0.01	< 0.01	14.1	0.351	< 0.01	< 0.01	6.13	0.099	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	512	10.7	674	14.0	233	4.86	414	8.62	560	11.7	1434	29.9	3767	78.4
HCO_3^-	470	7.70	414	6.78	433	7.10	116	2.08	195	3.19	380	6.23	652	10.7
Total anions		**20.1**		**21.8**		13.1		13.7		**15.3**		**44.6**		**105**
Si	6.17		5.71		0.580		1.44		8.56		4.23		6.00	
B	0.275		0.300		0.273		0.166		0.306		0.583		0.971	
DOC	2.1		2.2		13.3		22.5		1.4		4.1		2.4	
Cation excess (%)		**1.51**		**0.469**		**4.10**		**-4.28**		**-1.92**		**0.709**		**-0.413**

Table A2.1 cont.: Analytical results obtained for water samples taken from selected collieries during the winter of 1999.

	ND 3w		**ND 4w**		**ND 5w**		**ND 6w**		**ND 7w**		**ND 8w**		**ND 9w**	
pH	7.59		8.65		7.77		7.86		8.51		8.76		8.27	
EC (mS/cm)	5.73		5.26		5.55		3.66		2.79		1.74		2.95	
SAR	12.8		25.8		23.2		15.3		19.7		19.5		15.2	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Na^+	1178	51.2	1247	54.3	1301	56.6	843	36.7	682	29.6	487	21.2	703	30.6
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	2.80	0.155	< 0.01	< 0.01
K^+	12.0	0.307	12.1	0.309	10.5	0.267	7.60	0.194	5.10	0.130	2.40	0.061	5.40	0.138
Mg^{2+}	167	13.7	40.2	3.30	55.0	4.52	50.4	4.15	19.8	1.63	11.0	0.905	35.1	2.89
Ca^{2+}	368	18.4	112	5.57	149	7.44	146	7.29	58.2	2.90	29.0	1.45	103	5.15
Cr^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.003	< 0.001
Mn^{2+}	0.524	0.019	0.009	< 0.001	0.443	0.016	0.015	0.001	0.036	0.001	0.009	0.000	0.368	0.013
Fe_{TOTAL}	1.05	0.038	< 0.001	< 0.001	0.526	0.019	0.323	0.012	0.173	0.006	< 0.001	< 0.001	0.375	0.013
Co^{2+}	0.038	0.001	0.002	< 0.001	0.017	0.001	0.027	0.001	0.020	0.001	0.002	< 0.001	0.055	0.002
Ni^{2+}	0.112	0.004	0.004	< 0.001	0.039	0.001	0.077	0.003	0.033	0.001	0.009	< 0.001	0.072	0.002
Cu^{2+}	0.012	< 0.001	0.011	< 0.001	< 0.001	< 0.001	1.08	0.034	0.302	0.010	0.268	0.008	0.101	0.003
Zn^{2+}	0.174	0.005	0.034	0.001	0.095	0.003	0.626	0.019	0.251	0.008	0.145	0.004	0.186	0.006
As^{3+}	0.001	< 0.001	0.004	< 0.001	0.005	< 0.001	0.002	< 0.001	0.005	< 0.001	0.004	< 0.001	0.003	< 0.001
Rb^+	0.034	0.000	0.017	< 0.001	0.021	< 0.001	0.022	< 0.001	0.011	< 0.001	0.008	< 0.001	0.013	< 0.001
Sr^{2+}	6.94	0.158	1.57	0.036	4.27	0.098	2.37	0.054	0.795	0.018	0.241	0.006	2.03	0.046
Ba^{2+}	0.020	< 0.001	0.051	0.001	0.197	0.003	0.088	0.001	0.117	0.002	0.144	0.002	0.042	0.001
Al^{3+}	0.047	0.005	0.196	0.022	< 0.001	< 0.001	0.206	0.023	0.101	0.011	0.216	0.024	0.040	0.004
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**83.8**		**63.5**		**69.0**		**48.4**		**34.4**		**23.8**		**38.8**
F^-	5.70	0.300	6.00	0.316	6.16	0.324	5.56	0.293	6.09	0.321	16.1	0.845	9.42	0.410
Cl^-	427	12.0	1249	35.2	1388	39.1	436	12.3	448	12.6	115	3.23	131	7.27
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	10.32	0.166	5.64	0.091	< 0.01	< 0.01	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	3197	66.6	788	16.4	793	16.5	1083	22.6	321	6.69	9.90	0.206	1090	22.7
HCO_3^-	275	4.51	525	8.60	533	8.74	539	8.83	736	12.1	1104	18.1	622	11.1
Total anions		**83.1**		**60.5**		**64.7**		**44.1**		**31.8**		**22.4**		41.5
Si	4.98		6.28		3.7		5.24		6.56		4.12		4.06	
B	0.777		0.896		1.024		0.762		0.785		0.838		0.877	
DOC	2.9		2.7		3.2		2.4		2.5		1.8		4.6	
Cation excess (%)		**0.440**		**2.39**		**3.19**		**4.65**		**3.89**		**3.05**		**-3.35**

Table A2.1 cont.: Analytical results obtained for water samples taken from selected collieries during the winter of 1999.

	ND 10w		**ND 11w**		**ND 12w**		**ND 13w**		**ND 14w**		**ND 15w**		**ND 16w**	
pH	7.79		8.51		8.06		9.01		8.70		7.87		8.66	
EC (mS/cm)	5.62		5.83		0.298		4.58		0.219		6.07		0.615	
SAR	18.4		19.8		0.920		15.2		0.690		20.2		0.960	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Na^+	1270	55.2	1381	60.1	22.3	0.970	1015	44.1	15.9	0.693	1347	58.6	41.3	1.80
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.300	0.017
K^+	10.8	0.276	12.0	0.307	5.55	0.142	13.1	0.334	2.85	0.073	11.4	0.292	2.64	0.068
Mg^{2+}	87.0	7.16	110	9.03	6.90	0.568	107	8.77	12.2	1.00	87.0	7.16	57.4	4.72
Ca^{2+}	218	10.9	188	9.40	33.1	1.65	164	8.20	20.4	1.02	195	9.73	47.52	2.37
Cr^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Mn^{2+}	0.535	0.019	0.054	0.002	0.024	0.001	0.005	< 0.001	0.012	0.000	0.575	0.021	0.019	0.001
Fe_{TOTAL}	0.352	0.013	0.331	0.012	0.393	0.014	0.157	0.006	< 0.001	< 0.001	0.342	0.012	0.750	0.027
Co^{2+}	0.015	0.001	0.007	< 0.001	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	0.008	< 0.001	0.004	< 0.001
Ni^{2+}	0.050	0.002	0.065	0.002	0.009	< 0.001	0.046	0.002	0.002	0.000	0.039	0.001	0.034	0.001
Cu^{2+}	0.135	0.004	0.087	0.003	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	1.103	0.035
Zn^{2+}	0.189	0.006	0.142	0.004	0.016	< 0.001	0.072	0.002	0.025	0.001	0.452	0.014	0.486	0.015
As^{3+}	0.003	< 0.001	0.004	< 0.001	0.001	< 0.001	0.002	< 0.001	< 0.001	< 0.001	0.004	< 0.001	0.001	< 0.001
Rb^+	0.025	< 0.001	0.024	< 0.001	0.002	< 0.001	0.013	< 0.001	0.002	< 0.001	0.027	< 0.001	0.009	< 0.001
Sr^{2+}	4.21	0.096	4.30	0.098	0.442	0.010	3.58	0.082	0.098	0.002	4.16	0.095	0.192	0.004
Ba^{2+}	0.103	0.002	0.075	0.001	0.050	0.001	0.015	< 0.001	0.082	0.001	0.098	0.001	0.076	0.001
Al^{3+}	0.086	0.010	0.060	0.007	0.086	0.010	0.081	0.009	0.062	0.007	0.013	0.001	0.189	0.021
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**73.7**		**78.9**		**3.37**		**61.5**		**2.80**		**75.9**		**9.08**
F^-	12.4	0.654	6.36	0.335	0.380	0.020	4.59	0.242	0.310	0.016	6.12	0.322	0.550	0.029
Cl^-	1118	31.5	1015	28.6	15.60	0.440	401	11.3	11.39	0.321	1302	36.7	20.7	0.585
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.720	0.012	< 0.01	< 0.01	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	1368	28.5	1874	39.0	27.4	0.570	2044	42.6	22.5	0.468	1248	26.0	72.7	1.51
HCO_3^-	507	8.30	426	6.98	136	2.23	313	5.13	99.0	1.62	516	8.46	345	5.65
Total anions		**69.0**		**75.0**		**3.26**		**59.2**		**2.44**		71.5		7.77
Si	4.12		0.91		1.79		8.55		3.07		4.59		4.57	
B	0.890		1.052		0.080		0.713		< 0.001		0.963		< 0.001	
DOC	2.3		4.6		11.3		13.4		3.7		1.8		4.9	
Cation excess (%)		**3.31**		**2.58**		**1.64**		**1.90**		**6.88**		**2.99**		7.73

***Table A2.1 cont.**: Analytical results obtained for water samples taken from selected collieries during the winter of 1999.*

	OC 1a		**OC 2a**		**OC 3a**		**LN 7a**		**LK 5a**	
pH	3.67		3.12		3.25		2.54		2.78	
EC (mS/cm)	10.9		9.67		11.0		9.02		4.35	
SAR	24.2		28.4		19.2		0.580		0.120	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	2.40	0.346	1.40	0.202	3.00	0.432	0.900	0.130	0.400	0.058
Na^+	2347	102	2885	126	1940	84.4	85.5	3.72	7.20	0.313
NH_4^+	318	17.6	392	21.7	316	17.5	9.00	0.499	12.0	0.665
K^+	42.0	1.07	28.0	0.716	38.0	0.972	5.40	0.138	4.80	0.123
Mg^{2+}	151	12.4	190	15.7	205	16.9	570	46.9	64.4	5.30
Ca^{2+}	466	23.2	469	23.4	439	21.9	692	34.5	151	7.54
Cr^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001
Mn^{2+}	1.93	0.070	1.96	0.071	1.59	0.058	5.09	0.185	1.05	0.038
Fe_{TOTAL}	31.5	1.13	9.85	0.353	21.8	0.780	102	3.66	66.2	2.37
Co^{2+}	0.071	0.002	0.072	0.002	0.042	0.001	0.184	0.006	0.117	0.004
Ni^{2+}	0.107	0.004	0.107	0.004	0.048	0.002	0.138	0.005	0.167	0.006
Cu^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.003	< 0.001	0.020	0.001
Zn^{2+}	0.360	0.011	0.355	0.011	0.114	0.003	0.341	0.010	0.561	0.017
As^{3+}	0.006	< 0.001	0.000	< 0.001	0.000	< 0.001	0.002	< 0.001	0.002	< 0.001
Rb^+	0.056	0.001	0.047	0.001	0.017	< 0.001	0.001	< 0.001	0.007	< 0.001
Sr^{2+}	0.081	0.002	0.064	0.001	0.024	0.001	0.022	0.001	0.067	0.002
Ba^{2+}	0.013	< 0.001	0.001	< 0.001	0.008	< 0.001	0.009	< 0.001	0.014	< 0.001
Al^{3+}	5.20	0.579	5.95	0.662	7.31	0.813	9.95	1.11	18.8	2.10
H^+	12.1	12.0	12.7	12.6	36.3	36.0	235	233	67.1	66.6
Total cations		**168**		**200**		**178**		**319**		**80.5**
F^-	20.0	1.05	23.7	1.25	20.3	1.07	29.8	1.57	6.96	0.366
Cl^-	300	8.46	366	10.3	245	6.90	84.1	2.37	31.3	0.882
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	8869	185	13726	286	10545	219.56	19727	411	3782	78.7
HCO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Total anions		**194**		**297**		**228**		**415**		**80.0**
Si	6.94		5.87		2.45		1.15		2.74	
B	0.119		0.109		0.009		< 0.001		< 0.001	
DOC	2.7		2.8		4.5		9.5		4.5	
Cation excess (%)		**-7.08**		**-19.7**		**-12.3**		**-13.1**		**0.332**

Table A2.2: *Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.*

	AC 1s		**AC 2s**		**AC 3s**		**AC 4s**		**AC 5s**		**AC 6s**		**AC 7s**	
pH	7.82		8.11		8.19		8.08		9.03		5.56		7.92	
EC (mS/cm)	0.985		0.678		0.636		0.684		2.07		0.141		5.08	
SAR	2.17		2.05		1.90		1.07		4.64		0.432		1.68	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	< 0.001	< 0.001	< 0.001	< 0.001	0.180	0.026	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Na^+	87.1	3.79	64.4	2.80	53.2	2.31	39.1	1.70	235	10.2	5.10	0.222	217	9.44
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	4.50	0.12	3.64	0.093	3.42	0.087	5.39	0.138	26.4	0.675	3.60	0.092	40.0	1.02
Mg^{2+}	23.7	1.95	17.2	1.42	12.0	0.987	14.1	1.16	74.6	6.14	3.28	0.270	441	36.2
Ca^{2+}	83.5	4.17	46.1	2.30	39.9	1.99	77.9	3.89	71.2	3.55	5.18	0.258	534	26.6
Cr^{2+}	0.044	0.002	0.064	0.002	0.177	0.007	0.013	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Mn^{2+}	0.246	0.009	0.044	0.002	0.011	< 0.001	0.067	0.002	0.003	< 0.001	0.041	0.001	0.885	0.032
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.000	< 0.001	< 0.001	< 0.001
Fe^{3+}	0.077	0.004	< 0.001	< 0.001	0.058	0.003	< 0.001	< 0.001	0.437	0.023	0.037	0.002	0.005	< 0.001
Co^{2+}	0.005	< 0.001	0.002	< 0.001	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	0.008	< 0.001	0.002	< 0.001
Ni^{2+}	0.010	< 0.001	0.006	< 0.001	0.010	< 0.001	0.001	< 0.001	< 0.001	< 0.001	0.004	< 0.001	0.018	0.001
Cu^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Zn^{2+}	0.019	0.001	0.019	0.001	0.036	0.001	< 0.001	< 0.001	0.001	< 0.001	0.002	< 0.001	0.130	0.004
As^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.004	< 0.001	0.000	< 0.001	< 0.001	< 0.001
Rb^+	0.010	< 0.001	0.008	< 0.001	0.008	< 0.001	0.010	< 0.001	0.031	< 0.001	0.011	< 0.001	0.042	< 0.001
Sr^{2+}	1.72	0.039	1.043	0.024	0.882	0.020	1.72	0.039	1.99	0.045	0.051	0.001	1.43	0.033
Ba^{2+}	0.147	0.002	0.124	0.002	0.089	0.001	0.061	0.001	0.172	0.003	0.376	0.005	0.035	0.001
Al^{3+}	0.023	0.003	0.112	0.012	0.001	< 0.001	< 0.001	< 0.001	0.022	0.002	< 0.001	< 0.001	0.163	0.018
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.003	0.003	*n.d.*	*n.d.*
Total cations		**10.1**		**6.66**		**5.44**		**6.92**		**20.6**		**0.86**		**73.4**
F^-	0.280	0.015	0.056	0.003	0.144	0.008	0.042	0.002	0.340	0.018	< 0.01	< 0.01	< 0.01	< 0.01
Cl^-	97.8	2.76	51.8	1.46	47.8	1.35	38.5	1.08	196	5.53	3.84	0.108	25.1	0.707
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	1.73	0.028	1.85	0.030	1.89	0.030	2.02	0.033	1.22	0.020	26.1	0.421	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	163	3.38	113	2.35	118	2.47	140	2.92	376	7.83	1.24	0.026	3699	77.0
HCO_3^-	139	2.28	112	1.84	96.8	1.59	108	1.77	311	5.10	4.21	0.069	261	4.28
Total anions		**8.47**		**5.68**		**5.44**		**5.82**		**18.5**		**0.62**		**82.0**
Si	4.15		2.89		2.18		2.71		1.18		3.94		0.763	
B	0.055		0.051		< 0.001		< 0.001		0.233		< 0.001		0.284	
DOC	2.6		2.7		2.1		3.1		17.0		1.3		3.4	
Cation excess (%)		**8.69**		**7.88**		**0.010**		**8.71**		**5.48**		**15.6**		**-5.51**

***Table A2.2 cont.**: Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.*

	AC 8s		**AC 9s**		**AC 10s**		**BC 1s**		**BC 2s**		**BC 3s**		**BC 4s**	
pH	3.20		8.55		8.19		7.70		8.49		7.58		8.21	
EC (mS/cm)	1.37		1.45		1.43		1.03		0.546		1.86		0.617	
SAR	0.502		7.98		7.57		1.08		2.13		2.51		1.52	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	< 0.001	< 0.001	0.045	0.006	< 0.001	< 0.001	2.70	0.389	0.060	0.009	2.20	0.317	< 0.001	< 0.001
Na^+	26.3	1.14	258	11.2	249	10.8	57.9	2.52	64.7	2.82	170	7.41	54.1	2.35
NH_4^+	1.35	0.075	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	6.30	0.161	3.60	0.092	4.50	0.115	6.00	0.153	1.62	0.041	4.60	0.118	3.24	0.083
Mg^{2+}	56.1	4.62	16.2	1.33	19.7	1.62	39.3	3.23	14.2	1.17	59.4	4.89	18.7	1.54
Ca^{2+}	115	5.72	52.4	2.61	49.4	2.46	155	7.73	46.5	2.32	252	12.6	64.6	3.22
Cr^{2+}	0.717	0.028	0.023	0.001	< 0.001	< 0.001	0.056	0.002	0.003	< 0.001	0.041	0.002	0.030	0.001
Mn^{2+}	14.1	0.513	0.002	< 0.001	0.007	< 0.001	0.067	0.002	0.005	< 0.001	0.791	0.029	0.020	0.001
Fe^{2+}	0.330	0.012	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	12.7	0.680	< 0.001	< 0.001	< 0.001	< 0.001	0.058	0.003	0.042	0.002	< 0.001	< 0.001	< 0.001	< 0.001
Co^{2+}	0.472	0.016	0.002	< 0.001	0.027	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Ni^{2+}	0.521	0.018	0.008	< 0.001	0.049	0.002	0.002	< 0.001	< 0.001	< 0.001	0.002	< 0.001	< 0.001	< 0.001
Cu^{2+}	0.022	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Zn^{2+}	0.951	0.029	0.014	< 0.001	0.036	0.001	0.034	0.001	< 0.001	< 0.001	0.027	0.001	0.006	< 0.001
As^{3+}	0.001	< 0.001	0.001	< 0.001	0.003	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.042	< 0.001	0.008	< 0.001	0.008	< 0.001	0.011	< 0.001	0.005	< 0.001	0.011	< 0.001	0.004	< 0.001
Sr^{2+}	0.534	0.012	1.69	0.039	1.68	0.038	1.35	0.031	0.564	0.013	1.79	0.041	0.501	0.011
Ba^{2+}	0.069	0.001	0.072	0.001	0.114	0.002	0.167	0.002	0.108	0.002	0.032	< 0.001	0.069	0.001
Al^{3+}	2.88	0.320	< 0.001	< 0.001	< 0.001	< 0.001	0.020	0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
H^+	0.636	0.631	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**13.97**		**15.3**		**15.0**		**14.1**		**6.37**		**25.4**		**7.21**
F^-	< 0.01	< 0.01	0.645	0.034	0.885	0.047	0.140	0.007	0.270	0.014	1.04	0.055	0.150	0.008
Cl^-	3.59	0.101	9.00	0.254	12.5	0.353	17.1	0.483	10.3	0.291	13.0	0.368	8.61	0.24
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	37.9	0.611	15.3	0.247	7.04	0.114	3.78	0.061	< 0.01	< 0.01	3.31	0.053
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	596	12.4	316	6.58	314	6.54	407	8.48	107	2.22	809	16.8	189	3.94
HCO_3^-	< 0.01	< 0.01	333	5.46	372	6.10	181	2.97	182	2.98	470	7.70	165	2.70
Total anions		**12.52**		**12.9**		**13.3**		**12.1**		**5.56**		**25.0**		**6.95**
Si	10.3		4.77		2.39		7.28		8.10		5.91		8.42	
B	< 0.001		0.351		0.128		0.030		< 0.001		< 0.001		< 0.001	
DOC	< 1.0		1.5		2.7		< 1.0		< 1.0		1.1		< 1.0	
Cation excess (%)		**5.49**		**8.34**		**6.21**		**7.72**		**6.80**		**0.802**		**1.84**

***Table A2.2 cont.**: Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.*

	BC 5s		**BC 6s**		**BC 7s**		**BC 8s**		**BC 9s**		**BC 10s**		**BC 11s**	
pH	4.03		7.71		7.39		6.80		8.42		6.40		6.40	
EC (mS/cm)	2.20		1.69		1.08		1.37		0.340		0.744		3.82	
SAR	0.770		1.85		1.86		1.96		1.00		0.689		2.27	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	3.00	0.432	1.98	0.285	1.32	0.190	3.90	0.562	< 0.001	< 0.001	1.76	0.254	9.20	1.33
Na^+	64.0	2.78	113	4.93	89.4	3.89	114	4.95	26.7	1.16	30.6	1.33	250	10.9
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	4.80	0.266
K^+	5.00	0.128	6.48	0.166	4.92	0.126	5.70	0.146	3.20	0.082	7.92	0.203	12.0	0.307
Mg^{2+}	104	8.54	77.2	6.35	39.6	3.26	46.2	3.80	10.3	0.849	36.7	3.02	225	18.5
Ca^{2+}	353	17.61	159	7.92	110	5.50	180	9.00	36.6	1.83	88.5	4.42	551	27.5
Cr^{2+}	0.243	0.009	0.026	0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.037	0.001	< 0.001	< 0.001	< 0.001	< 0.001
Mn^{2+}	3.10	0.113	0.004	< 0.001	0.153	0.006	0.020	0.001	0.004	< 0.001	1.41	0.051	5.56	0.203
Fe^{2+}	0.015	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	0.485	0.026	< 0.001	< 0.001	< 0.001	< 0.001	0.042	0.002	< 0.001	< 0.001	0.042	0.002	178	9.59
Co^{2+}	0.265	0.009	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	0.008	< 0.001	0.172	0.006
Ni^{2+}	0.420	0.014	0.003	< 0.01	< 0.001	< 0.001	0.014	< 0.001	0.004	< 0.001	0.012	< 0.001	0.263	0.009
Cu^{2+}	0.014	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Zn^{2+}	0.836	0.026	0.028	0.001	0.024	0.001	0.032	0.001	0.002	< 0.001	0.147	0.005	0.294	0.009
As^{3+}	< 0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	0.003	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.021	< 0.001	0.013	< 0.001	0.009	< 0.001	0.009	< 0.001	< 0.001	< 0.001	0.014	< 0.001	0.042	< 0.001
Sr^{2+}	2.38	0.054	2.023	0.046	0.895	0.020	1.40	0.032	0.007	< 0.001	0.625	0.014	5.13	0.117
Ba^{2+}	0.181	0.003	0.051	0.001	0.056	0.001	0.031	< 0.001	0.702	0.010	0.060	0.001	0.014	< 0.001
Al^{3+}	11.1	1.23	< 0.001	< 0.001	0.042	0.005	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
H^+	0.094	0.093	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**31.1**		**19.7**		**13.0**		**18.5**		**3.93**		**9.29**		**68.7**
F^-	1.85	0.097	0.234	0.012	0.252	0.013	0.405	0.021	0.368	0.019	0.080	0.004	< 0.01	< 0.01
Cl^-	8.35	0.236	114	3.23	16.4	0.462	21.3	0.601	13.1	0.369	9.25	0.261	2.88	0.081
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	6.18	0.100	< 0.01	< 0.01	2.83	0.046	< 0.01	< 0.01	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	1633	33.99	708	14.7	493	10.3	631	13.1	59.9	1.25	401	8.34	3324	69.2
HCO_3^-	< 0.01	< 0.01	138	2.26	143	2.35	190	3.12	108	1.78	21.2	0.348	74.6	1.22
Total anions		**34.3**		**20.2**		**13.2**		**16.9**		**3.46**		**8.96**		**70.5**
Si	17.1		5.71		3.62		3.63		9.52		2.11		9.71	
B	< 0.001		< 0.001		< 0.001		< 0.001		< 0.001		< 0.001		< 0.001	
DOC	1.1		< 1.0		2.0		< 1.0		< 1.0		2.9		1.0	
Cation excess (%)		**-4.97**		**-1.34**		**-0.774**		**4.56**		**6.39**		**1.85**		**-1.27**

***Table A2.2 cont.**: Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.*

	BC 12s		**BC 13s**		**GH 1s**		**GH 2s**		**GH 3s**		**GH 4s**		**GH 5s**	
pH	8.13		5.08		3.14		2.76		4.04		2.98		4.12	
EC (mS/cm)	3.52		0.938		2.82		11.3		1.67		2.49		1.27	
SAR	0.857		1.57		0.462		0.360		2.22		0.585		0.806	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	9.10	1.31	*n.d.*	*n.d.*	3.60	0.519	1.50	0.216	0.180	0.026	1.50	0.216	0.720	0.104
Na^+	98.0	4.26	83.3	3.63	35.1	1.53	57.5	2.50	123	5.35	41.5	1.81	51.1	2.22
NH_4^+	6.30	0.349	*n.d.*	*n.d.*	4.80	0.266	46.0	2.55	< 0.01	< 0.01	5.00	0.277	< 0.01	< 0.01
K^+	16.8	0.430	6.75	0.173	4.20	0.107	1.00	0.026	1.08	0.028	6.75	0.173	6.36	0.163
Mg^{2+}	334	27.5	58.7	4.83	158	13.0	838	68.9	60.1	4.95	122	10.0	73.2	6.02
Ca^{2+}	440	22.0	119	5.92	179	8.94	554	27.6	133	6.65	183	9.13	184	9.17
Cr^{2+}	0.063	0.002	*n.d.*	*n.d.*	0.900	0.035	0.715	0.028	0.056	0.002	0.150	0.006	< 0.001	< 0.001
Mn^{2+}	2.81	0.102	1.58	0.058	59.3	2.16	224	8.15	18.2	0.661	41.8	1.52	4.67	0.170
Fe^{2+}	< 0.001	< 0.001	*n.d.*	*n.d.*	< 0.001	< 0.001	2038	73.0	0.069	0.002	1.21	0.043	0.100	0.004
Fe^{3+}	< 0.001	< 0.001	0.010	0.001	85.1	4.57	1238	66.5	0.264	0.014	11.7	0.626	0.264	0.014
Co^{2+}	0.014	< 0.001	*n.d.*	*n.d.*	1.19	0.040	3.94	0.134	0.455	0.015	0.897	0.030	0.096	0.003
Ni^{2+}	0.029	0.001	*n.d.*	*n.d.*	0.303	0.010	1.30	0.044	0.110	0.004	0.227	0.008	< 0.001	< 0.001
Cu^{2+}	< 0.001	< 0.001	*n.d.*	*n.d.*	0.039	0.001	0.278	0.009	< 0.001	< 0.001	0.037	0.001	< 0.001	< 0.001
Zn^{2+}	0.120	0.004	*n.d.*	*n.d.*	0.467	0.014	2.56	0.078	0.095	0.003	0.427	0.013	< 0.001	< 0.001
As^{3+}	0.001	< 0.001	*n.d.*	*n.d.*	0.002	< 0.001	0.010	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.067	0.001	*n.d.*	*n.d.*	0.015	< 0.001	0.106	0.001	0.014	< 0.001	0.019	< 0.001	0.005	< 0.001
Sr^{2+}	4.34	0.099	*n.d.*	*n.d.*	0.432	0.010	0.976	0.022	0.733	0.017	0.497	0.011	0.548	0.013
Ba^{2+}	0.055	0.001	*n.d.*	*n.d.*	0.051	0.001	0.042	0.001	0.065	0.001	0.099	0.001	0.024	< 0.001
Al^{3+}	< 0.001	< 0.001	0.180	0.020	61.4	6.83	341	37.9	25.6	2.85	52.1	5.80	2.49	0.277
H^+	*n.d.*	*n.d.*	0.008	0.008	18.8	18.6	214	213	5.90	5.85	14.3	14.2	1.14	1.13
Total cations		**56.0**		**14.6**		**56.7**		**500**		**26.4**		**43.9**		**19.3**
F^-	< 0.01	< 0.01	*n.d.*	*n.d.*	0.270	0.014	< 0.01	< 0.01	0.864	0.045	0.150	0.008	< 0.01	< 0.01
Cl^-	15.6	0.441	8.00	0.226	11.2	0.315	6.00	0.169	22.2	0.627	10.1	0.283	10.8	0.305
NO_2^-	< 0.01	< 0.01	*n.d.*	*n.d.*	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	*n.d.*	*n.d.*	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	*n.d.*	*n.d.*	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	*n.d.*	*n.d.*	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	2984	62.1	850	17.7	2396	49.9	20795	433	1051	21.9	1643	34.2	887	18.5
HCO_3^-	150	2.46	2.44	0.040	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Total anions		**65.0**		**18.0**		**50.2**		**433**		**22.5**		**34.5**		**18.8**
Si	3.46		*n.d.*		8.29		35.47		0.484		5.67		< 0.001	
B	0.130		*n.d.*		< 0.001		< 0.001		< 0.001		< 0.001		< 0.001	
DOC	2.1		*n.d.*		< 1.0		9.8		2.5		< 1.0		1.4	
Cation excess (%)		**-7.42**		**-10.2**		**6.07**		**7.20**		**7.97**		**12.0**		**1.40**

Table A2.2 cont.: Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.

	GH 6s		**GH 7s**		**GH 8s**		**GH 9s**		**GH 11s**		**GH 13s**		**GH 14s**	
pH	6.72		6.88		6.22		4.74		6.91		6.38		6.34	
EC (mS/cm)	0.392		2.17		0.336		4.10		1.15		0.610		1.15	
SAR	0.431		0.820		0.631		0.455		2.95		0.913		0.613	
	Conc (mg/L)	**mmol/L**	**Conc (mg/L)**	**mmol/L**	**Conc (mg/L)**	**mmol/L**	**Conc (mg/L)**	**mmol/L**	**Conc (mg/L)**	**mmol/L**	**Conc (mg/L)**	**mmol/L**	**Conc (mg/L)**	**mmol/L**
Li^+	0.000	0.000	1.76	0.254	0.160	0.023	0.400	0.058	< 0.001	< 0.001	0.180	0.026	0.480	0.069
Na^+	14.8	0.644	79.0	3.44	17.6	0.766	56.0	2.44	144	6.25	36.5	1.59	35.2	1.53
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	0.440	0.024	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	6.60	0.169	9.46	0.242	6.96	0.178	19.2	0.49	2.52	0.064	5.22	0.13	0.360	0.009
Mg^{2+}	15.7	1.29	158	13.0	11.7	0.964	321	26.4	19.0	1.56	19.2	1.58	48.5	3.99
Ca^{2+}	62.6	3.12	446	22.2	40.5	2.02	622	31.0	149	7.43	90.0	4.49	170	8.47
Cr^{2+}	0.006	< 0.001	0.006	< 0.001	0.014	0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.005	< 0.001	0.020	0.001
Mn^{2+}	0.262	0.010	0.113	0.004	0.271	0.010	13.4	0.488	0.500	0.018	0.200	0.007	1.16	0.042
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	410	14.7	< 0.001	< 0.001	< 0.001	< 0.001	12.8	0.460
Fe^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	0.129	0.007	40.4	2.17	< 0.001	< 0.001	0.340	0.018	2.35	0.126
Co^{2+}	0.002	< 0.001	0.002	< 0.001	0.001	< 0.001	0.891	0.030	0.005	< 0.001	0.001	< 0.001	0.139	0.005
Ni^{2+}	0.007	< 0.001	0.010	< 0.001	0.002	< 0.001	1.40	0.048	0.013	< 0.001	0.007	< 0.001	0.176	0.006
Cu^{2+}	0.006	< 0.001	0.003	< 0.001	0.003	< 0.001	< 0.001	< 0.001	0.005	< 0.001	0.002	< 0.001	0.005	< 0.001
Zn^{2+}	0.102	0.003	0.053	0.002	0.018	0.001	1.40	0.043	0.025	0.001	0.028	0.001	0.253	0.008
As^{3+}	0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.007	< 0.001	0.011	< 0.001	0.007	< 0.001	0.025	< 0.001	0.006	0.000	0.010	< 0.001	0.008	< 0.001
Sr^{2+}	0.433	0.010	2.64	0.060	0.236	0.005	5.49	0.125	0.848	0.019	0.974	0.022	1.16	0.026
Ba^{2+}	0.103	0.001	0.040	0.001	0.091	0.001	0.116	0.002	0.117	0.002	0.316	0.005	0.131	0.002
Al^{3+}	1.25	0.139	0.279	0.031	0.116	0.013	21.8	2.42	0.198	0.022	0.063	0.007	0.048	0.005
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	21.0	20.8	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**5.39**		**39.2**		**4.01**		**101**		**15.4**		**7.88**		**14.8**
F^-	0.124	0.007	< 0.01	< 0.01	0.580	0.031	0.040	0.002	0.888	0.047	0.186	0.010	0.036	0.002
Cl^-	4.92	0.139	11.4	0.321	6.29	0.177	5.88	0.166	19.0	0.537	11.6	0.328	5.75	0.162
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	0.540	0.009	< 0.01	< 0.01	2.004	0.032	< 0.01	< 0.01	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	1.35	0.028	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	150	3.12	1624	33.8	102	2.13	4195	87.3	444	9.24	156	3.24	572	11.9
HCO_3^-	65.4	1.07	117	1.92	69.8	1.14	< 0.01	< 0.01	259	4.24	202	3.31	93.9	1.54
Total anions		**4.34**		**36.1**		**3.52**		**87.5**		**14.1**		**6.89**		**13.6**
Si	2.83		2.92		3.15		13.6		7.31		7.21		10.4	
B	0.042		0.041		< 0.001		< 0.001		0.199		0.011		< 0.001	
DOC	5.9		1.6		5.3		2.4		1.0		< 1.0		< 1.0	
Cation excess (%)		**10.8**		**4.24**		**6.59**		**7.30**		**4.32**		**6.69**		**3.98**

***Table A2.2 cont.**: Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.*

	GH 15s		**GH 17s**		**GH 18s**		**GH 19s**		**GH 20s**		**GH 21s**		**GH 22s**	
pH	6.54		4.08		6.37		4.79		3.60		3.34		7.58	
EC (mS/cm)	1.06		5.79		2.01		2.38		2.34		5.74		1.27	
SAR	0.591		1.06		3.98		0.294		0.931		0.791		1.50	
	Conc (mg/L)	**mmol/L**	**Conc (mg/L)**	**mmol/L**	**Conc (mg/L)**	**mmol/L**	**Conc (mg/L)**	**mmol/L**	**Conc (mg/L)**	**mmol/L**	**Conc (mg/L)**	**mmol/L**	**Conc (mg/L)**	**mmol/L**
Li^+	0.110	0.016	2.40	0.346	< 0.001	< 0.001	0.250	0.036	< 0.001	< 0.001	1.20	0.173	1.40	0.202
Na^+	31.7	1.38	146	6.34	225	9.79	24.0	1.04	93.3	4.06	114	4.96	85.8	3.73
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	2.00	0.111	< 0.01	< 0.01	7.20	0.399	< 0.01	< 0.01
K^+	4.18	0.107	0.600	0.015	1.20	0.031	13.5	0.345	7.75	0.198	2.40	0.061	7.70	0.197
Mg^{2+}	40.0	3.29	512	42.1	64.6	5.31	101	8.29	103	8.43	529	43.5	62.6	5.15
Ca^{2+}	152	7.61	596	29.8	136	6.80	336	16.7	594	29.6	703	35.1	145	7.26
Cr^{2+}	0.007	< 0.001	0.188	0.007	0.006	< 0.001	0.160	0.006	0.233	0.009	0.071	0.003	0.010	< 0.001
Mn^{2+}	2.13	0.078	28.7	1.05	1.20	0.044	2.63	0.096	2.25	0.082	33.1	1.21	0.183	0.007
Fe^{2+}	18.3	0.655	377	13.5	16.0	0.572	212	7.58	0.053	0.002	510	18.3	< 0.001	< 0.001
Fe^{3+}	0.000	< 0.001	58.7	3.15	< 0.001	< 0.001	7.69	0.413	0.993	0.053	64.4	3.46	< 0.001	< 0.001
Co^{2+}	0.047	0.002	0.691	0.023	0.009	< 0.001	0.136	0.005	0.040	0.001	0.847	0.029	0.003	< 0.001
Ni^{2+}	0.067	0.002	0.458	0.016	0.015	0.001	0.234	0.008	0.108	0.004	0.537	0.018	0.011	< 0.001
Cu^{2+}	0.004	< 0.001	0.031	0.001	0.004	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.033	0.001	0.002	< 0.001
Zn^{2+}	0.045	0.001	1.418	0.043	0.060	0.002	0.159	0.005	0.487	0.015	1.40	0.043	0.074	0.002
As^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001
Rb^+	0.007	< 0.001	0.026	< 0.001	0.021	< 0.001	0.033	< 0.001	0.018	< 0.001	0.030	< 0.001	0.017	< 0.001
Sr^{2+}	0.975	0.022	2.42	0.055	2.82	0.064	1.78	0.041	1.71	0.039	1.98	0.045	2.27	0.052
Ba^{2+}	0.106	0.002	0.096	0.001	0.130	0.002	0.088	0.001	0.054	0.001	0.009	< 0.001	0.068	0.001
Al^{3+}	0.058	0.006	101	11.2	0.062	0.007	0.333	0.037	2.78	0.310	126	14.1	0.007	0.001
H^+	*n.d.*	*n.d.*	35.5	35.3	*n.d.*	*n.d.*	7.32	7.26	1.13	1.12	43.4	43.0	*n.d.*	*n.d.*
Total cations		**13.2**		**143**		**22.6**		**42.0**		**44.0**		**164**		**16.6**
F^-	< 0.01	< 0.01	5.10	0.268	< 0.01	< 0.01	< 0.01	< 0.01	1.03	0.054	4.14	0.218	1.44	0.076
Cl^-	7.05	0.199	8.58	0.242	3.82	0.108	4.13	0.116	6.70	0.189	12.7	0.359	32.2	0.908
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	0.682	0.011	< 0.01	< 0.01	11.0	0.178	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	473	9.84	6051	126	1111	23.1	1690	35.2	1824	38.0	6650	138	678	14.1
HCO_3^-	138	2.26	< 0.01	< 0.01	101	1.66	28.0	0.458	< 0.01	< 0.01	< 0.01	< 0.01	129	2.11
Total anions		**12.3**		**126**		**25.1**		**35.8**		**38.2**		**139**		**17.2**
Si	11.2		14.4		16.3		15.7		7.94		12.8		5.86	
B	< 0.001		< 0.001		0.049		0.264		0.113		< 0.001		0.212	
DOC	1.2		1.8		1.0		4.4		3.8		2.2		< 1.0	
Cation excess (%)		**3.39**		**6.08**		**-5.15**		**8.05**		**6.98**		**8.34**		**-1.80**

Table A2.2 **cont.**: *Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.*

	GH 23s		**GH 24s**		**GH 25s**		**GH 26s**		**GH 27s**		**GH 28s**		**GS 1s**	
pH	7.79		6.41		7.34		7.51		6.63		6.54		6.56	
EC (mS/cm)	1.55		3.09		1.26		1.66		0.530		0.683		3.12	
SAR	1.41		0.932		0.640		2.02		1.25		0.319		1.57	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	1.20	0.173	0.300	0.043	0.560	0.081	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Na^+	93.6	4.07	98.1	4.27	41.3	1.80	147	6.38	41.8	1.82	15.1	0.655	149	6.49
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	11.7	0.299	1.80	0.046	5.88	0.150	5.22	0.134	1.86	0.05	2.94	0.075	5.40	0.138
Mg^{2+}	72.2	5.94	219	18.0	56.7	4.66	37.3	3.07	20.6	1.69	29.2	2.40	134	11.0
Ca^{2+}	213	10.6	481	24.0	224	11.2	339	16.9	51.2	2.55	121	6.04	459	22.9
Cr^{2+}	0.008	< 0.001	0.005	< 0.001	0.020	0.001	0.019	0.001	0.015	0.001	0.026	0.001	0.051	0.002
Mn^{2+}	0.115	0.004	9.46	0.344	0.450	0.016	0.436	0.016	0.006	< 0.001	0.015	0.001	1.25	0.046
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Co^{2+}	0.002	< 0.001	0.292	0.010	0.005	< 0.001	0.004	< 0.001	0.001	< 0.001	< 0.001	< 0.001	0.030	0.001
Ni^{2+}	0.016	0.001	0.516	0.018	0.011	< 0.001	0.014	< 0.001	0.001	< 0.001	0.003	< 0.001	0.087	0.003
Cu^{2+}	0.011	< 0.001	0.007	< 0.001	0.001	< 0.001	0.003	< 0.001	0.004	< 0.001	0.003	< 0.001	0.003	< 0.001
Zn^{2+}	0.132	0.004	1.97	0.060	0.041	0.001	0.059	0.002	0.026	< 0.001	0.030	0.001	0.166	0.005
As^{3+}	0.001	< 0.001	0.001	< 0.001	0.000	< 0.001	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.015	< 0.001	0.020	< 0.001	0.007	< 0.001	0.008	< 0.001	0.003	< 0.001	0.001	< 0.001	0.017	< 0.001
Sr^{2+}	2.23	0.051	2.78	0.063	1.47	0.034	1.48	0.034	0.500	0.011	0.286	0.007	3.89	0.089
Ba^{2+}	0.067	0.001	0.096	0.001	0.037	0.001	0.100	0.001	0.133	0.002	0.096	0.001	0.030	< 0.001
Al^{3+}	0.033	0.004	0.058	0.006	< 0.001	< 0.001	0.001	< 0.001	0.070	0.008	< 0.001	< 0.001	0.057	0.006
H^+	*n.d.*	*n.d.*	*n.d*	*n.d*	*n.d*	*n.d*	*n.d.*	*n.d.*	*n.d*	*n.d*	*n.d.*	*n.d.*	*n.d*	*n.d*
Total cations		**21.2**		**46.8**		**17.9**		**26.5**		**6.14**		**9.18**		**40.7**
F^-	0.810	0.043	0.270	0.014	0.224	0.012	0.864	0.045	0.312	0.016	1.81	0.095	< 0.01	< 0.01
Cl^-	82.4	2.32	32.3	0.911	22.3	0.628	18.2	0.514	27.6	0.780	74.03	2.09	9.66	0.272
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	1.17	0.019	< 0.01	< 0.01	< 0.01	< 0.01	5.72	0.092	0.564	0.009	2.65	0.043	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	764	15.9	2328	48.5	706	14.7	929	19.3	87.4	1.82	88.0	1.83	1867	38.9
HCO_3^-	118	1.93	45.7	0.749	112	1.83	171	2.80	188	3.07	212	3.47	103	1.69
Total anions		**20.2**		**50.1**		**17.2**		**22.8**		**5.70**		**7.53**		**40.8**
Si	5.89		5.97		9.31		6.96		6.83		11.4		6.32	
B	0.183		0.274		0.096		0.279		0.117		0.041		0.212	
DOC	1.4		1.2		< 1.0		1.2		1.8		2.3		1.4	
Cation excess (%)		**2.30**		**-3.39**		**2.13**		**7.57**		**3.68**		**9.90**		**-0.128**

Table A2.2 cont.: Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.

	GS 2s		GS 3s		GS 4s		GS 5s		GS 6s		GS 7s		GS 8s	
pH	6.49		4.02		3.67		7.43		7.29		7.28		6.82	
EC (mS/cm)	3.21		0.974		4.13		3.16		3.84		1.74		1.79	
SAR	1.63		0.150		1.01		1.30		0.956		0.825		0.603	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	0.000	0.000	0.100	0.014	0.400	0.058	< 0.001	< 0.001	< 0.001	< 0.001	0.180	0.026	0.360	0.052
Na^+	156	6.79	7.40	0.322	108	4.70	121	5.25	106	4.61	58.0	2.52	43.9	1.91
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	5.20	0.288	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	5.10	0.130	1.90	0.049	7.20	0.184	7.50	0.192	8.40	0.215	4.68	0.120	3.60	0.092
Mg^{2+}	137	11.2	21.0	1.73	166	13.6	157	12.9	263	21.7	79.9	6.58	83.3	6.86
Ca^{2+}	466	23.2	150	7.49	597	29.8	398	19.9	500	24.9	243	12.1	265	13.2
Cr^{2+}	0.038	0.001	0.142	0.005	0.314	0.012	0.057	0.002	0.075	0.003	0.063	0.002	0.040	0.002
Mn^{2+}	0.955	0.035	0.788	0.029	7.45	0.271	2.39	0.087	2.74	0.100	0.093	0.003	0.300	0.011
Fe^{2+}	0.554	0.020	< 0.001	< 0.001	66.5	2.38	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	4.67	0.251	0.141	0.008	10.1	0.541	< 0.001	< 0.001	0.733	0.039	< 0.001	< 0.001	< 0.001	< 0.001
Co^{2+}	0.013	< 0.001	0.094	0.003	0.263	0.009	0.002	< 0.001	0.032	0.001	0.004	< 0.001	0.016	0.001
Ni^{2+}	0.038	0.001	0.148	0.005	0.338	0.012	0.020	0.001	0.210	0.007	0.022	0.001	0.085	0.003
Cu^{2+}	< 0.001	< 0.001	0.013	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.045	0.001	< 0.001	< 0.001	0.006	< 0.001
Zn^{2+}	0.095	0.003	0.268	0.008	0.988	0.030	0.094	0.003	0.283	0.009	0.064	0.002	0.138	0.004
As^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.015	< 0.001	0.015	< 0.001	0.032	0.000	0.035	< 0.001	0.033	< 0.001	0.012	< 0.001	0.016	< 0.001
Sr^{2+}	3.67	0.084	0.459	0.010	3.13	0.071	3.16	0.072	3.16	0.072	2.21	0.050	1.13	0.026
Ba^{2+}	0.037	0.001	0.090	0.001	0.039	0.001	0.033	< 0.001	0.036	0.001	0.030	< 0.001	0.025	< 0.001
Al^{3+}	< 0.001	< 0.001	8.34	0.927	40.3	4.48	< 0.001	< 0.001	< 0.001	< 0.001	0.023	0.003	0.048	0.005
H^+	*n.d.*	*n.d.*	1.66	1.65	11.5	11.4	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d*	*n.d.*	*n.d*	*n.d.*
Total cations		**41.8**		**12.2**		**67.8**		**38.4**		**51.7**		**21.4**		**22.2**
F^-	< 0.01	< 0.01	< 0.01	< 0.01	1.56	0.082	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.110	0.006
Cl^-	10.29	0.290	3.84	0.108	75.9	2.14	43.6	1.23	37.1	1.05	13.4	0.379	16.2	0.456
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	1.37	0.022	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	3.92	0.063	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	1960	40.8	531	11.1	2842	59.2	1958	40.8	2680	55.8	872	18.1	1000	20.8
HCO_3^-	118	1.94	< 0.01	< 0.01	< 0.01	< 0.01	137	2.25	127	2.08	161	2.64	84.8	1.39
Total anions		**43.0**		**11.2**		**61.4**		**44.24**		**58.9**		**21.2**		**22.7**
Si	4.75		8.14		7.33		4.89		4.53		6.62		8.80	
B	0.087		< 0.001		< 0.001		0.178		0.249		0.111		0.043	
DOC	1.7		1.3		2.9		4.9		5.8		1.7		1.7	
Cation excess (%)		**-1.47**		**4.50**		**4.99**		**-7.09**		**-6.58**		**0.427**		**-1.07**

***Table A2.2 cont.**: Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.*

	GS 10s		**GS 11s**		**GS 12s**		**GS 13s**		**GS 14s**		**KC 1s**		**KC 2s**	
pH	6.68		8.12		6.79		8.27		9.93		8.65		7.51	
EC (mS/cm)	3.21		1.37		0.575		4.64		2.88		0.864		0.704	
SAR	1.76		0.955		0.367		1.31		1.20		13.8		1.73	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	7.80	1.12	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.120	0.017	< 0.001	< 0.001
Na^+	170	7.40	54.5	2.37	13.0	0.566	167	7.28	110	4.78	218	9.50	62.2	2.71
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	0.540	0.030	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	6.00	0.153	4.20	0.107	3.90	0.100	14.9	0.380	6.30	0.161	2.52	0.064	7.29	0.186
Mg^{2+}	137	11.3	56.7	4.66	19.5	1.60	245	20.2	150	12.3	4.92	0.405	13.2	1.09
Ca^{2+}	479	23.9	153	7.63	63.1	3.15	839	41.9	393	19.6	10.9	0.545	75.7	3.78
Cr^{2+}	0.042	0.002	< 0.001	< 0.001	0.014	0.001	0.031	0.001	0.029	0.001	< 0.001	< 0.001	< 0.001	< 0.001
Mn^{2+}	0.676	0.025	0.007	< 0.001	2.12	0.077	0.118	0.004	0.005	< 0.001	0.004	< 0.001	0.028	0.001
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Co^{2+}	0.028	0.001	0.001	< 0.001	0.009	< 0.001	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Ni^{2+}	0.065	0.002	0.003	< 0.001	0.011	< 0.001	0.026	0.001	0.011	< 0.001	0.001	< 0.001	0.001	< 0.001
Cu^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.028	0.001	0.005	< 0.001
Zn^{2+}	0.159	0.005	0.011	< 0.001	0.006	< 0.001	0.128	0.004	0.069	0.002	0.042	0.001	0.019	0.001
As^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	0.000	< 0.001	0.005	< 0.001	0.001	< 0.001
Rb^+	0.015	< 0.001	0.008	< 0.001	0.015	< 0.001	0.031	< 0.001	0.030	< 0.001	0.004	< 0.001	0.011	< 0.001
Sr^{2+}	3.88	0.089	1.62	0.037	0.265	0.006	5.43	0.124	2.85	0.065	0.210	0.005	1.38	0.032
Ba^{2+}	0.053	0.001	0.075	0.001	0.115	0.002	0.024	< 0.001	0.015	< 0.001	0.085	0.001	0.080	0.001
Al^{3+}	0.060	0.007	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.932	0.104	0.531	0.059
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**44.0**		**14.8**		**5.54**		**69.8**		**36.9**		**10.6**		**7.85**
F^-	< 0.01	< 0.01	< 0.01	< 0.01	0.048	0.003	< 0.01	< 0.01	< 0.01	< 0.01	2.18	0.115	0.261	0.014
Cl^-	11.1	0.314	2.90	0.082	6.41	0.181	52.2	1.47	37.6	1.06	21.3	0.601	14.6	0.413
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.440	0.007
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	2055	42.8	584	12.1	233	4.85	3440	71.6	1712	35.7	28.9	0.601	170	3.54
HCO_3^-	101	1.66	167	2.74	7.38	0.121	52.1	0.853	42.0	0.688	585	9.59	244	4.00
Total anions		**44.8**		**15.0**		**5.15**		**74.0**		**37.4**		**10.8**		**7.96**
Si	5.63		2.36		1.13		0.589		3.11		2.90		6.61	
B	0.192		< 0.001		n.d.		0.087		0.196		0.412		0.236	
DOC	< 1.0		2.7		2.8		4.4		3.9		2.1		4.6	
Cation excess (%)		**-0.828**		**-0.515**		**3.58**		**-2.87**		**-0.608**		**-0.714**		**-0.681**

***Table A2.2 cont.**: Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.*

	KC 3s		KC 4s		KC 5s		KC 6s		KC 8s		KC 9s		KC 10s	
pH	7.70		7.83		8.11		8.16		7.45		7.64		7.79	
EC (mS/cm)	0.205		0.269		1.76		1.12		0.755		0.860		0.829	
SAR	0.746		0.862		3.29		2.92		2.63		1.92		0.983	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	0.930	0.134	0.040	0.006	6.25	0.901	< 0.001	< 0.001	< 0.001	< 0.001	0.200	0.029	< 0.001	< 0.001
Na^+	15.8	0.686	20.2	0.879	227	9.86	141	6.14	90.5	3.94	71.2	3.10	49.7	2.16
NH_4^+	0.780	0.043	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	5.70	0.146	4.96	0.127	9.75	0.249	4.95	0.127	6.40	0.164	16.8	0.430	6.20	0.159
Mg^{2+}	3.93	0.323	6.72	0.553	110	9.07	57.9	4.76	23.7	1.95	33.3	2.74	27.6	2.27
Ca^{2+}	27.4	1.37	30.6	1.52	178	8.88	81.9	4.09	51.0	2.54	97.0	4.84	148	7.40
Cr^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Mn^{2+}	0.010	< 0.001	0.109	0.004	0.022	0.001	0.001	< 0.001	0.341	0.012	0.014	0.001	0.166	0.006
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	< 0.001	< 0.001	0.021	0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.085	0.005	< 0.001	< 0.001	< 0.001	< 0.001
Co^{2+}	0.001	< 0.001	0.010	< 0.001	< 0.001	< 0.001	0.000	< 0.001	0.002	< 0.001	< 0.001	< 0.001	0.001	0.000
Ni^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002	< 0.001	< 0.001	< 0.001
Cu^{2+}	0.005	< 0.001	0.012	< 0.001	0.006	< 0.001	0.002	< 0.001	0.004	< 0.001	0.013	< 0.001	0.001	< 0.001
Zn^{2+}	< 0.001	< 0.001	0.124	0.004	0.035	0.001	0.006	< 0.001	< 0.001	< 0.001	0.021	0.001	< 0.001	< 0.001
As^{3+}	< 0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.002	< 0.001	< 0.001	< 0.001
Rb^+	0.007	< 0.001	0.006	< 0.001	0.007	< 0.001	0.003	< 0.001	0.004	< 0.001	0.044	0.001	0.010	< 0.001
Sr^{2+}	0.316	0.007	0.200	0.005	3.31	0.076	0.988	0.023	0.759	0.017	0.873	0.020	1.90	0.043
Ba^{2+}	0.139	0.002	0.099	0.001	0.084	0.001	0.053	0.001	0.046	0.001	0.161	0.002	0.035	0.001
Al^{3+}	0.267	0.030	0.769	0.085	0.448	0.050	0.056	0.006	0.030	0.003	0.038	0.004	0.013	0.001
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**2.74**		**3.19**		**29.1**		**15.1**		**8.63**		**11.2**		**12.0**
F^-	0.213	0.011	0.244	0.013	0.050	0.003	0.045	0.002	0.350	0.018	0.480	0.025	0.050	0.003
Cl^-	5.34	0.151	10.9	0.307	17.1	0.482	16.2	0.458	14.3	0.403	38.2	1.08	8.64	0.244
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	3.34	0.073
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	1.75	0.028	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.43	0.023	1.69	0.027
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	18.7	0.390	19.0	0.396	1053	21.9	535	11.1	283	5.88	314	6.53	416	8.66
HCO_3^-	103	1.68	155	2.55	263	4.31	177	2.90	150	2.45	138	2.26	148	2.43
Total anions		**2.25**		**3.26**		**26.7**		**14.5**		**8.76**		**9.91**		**11.4**
Si	8.93		9.48		0.806		0.528		1.35		1.98		4.80	
B	< 0.001		0.005		0.346		0.086		0.114		0.089		0.061	
DOC	2.8		4.9		2.1		2.2		7.7		22.0		4.3	
Cation excess (%)		**9.85**		**-1.12**		**4.24**		**2.16**		**-0.716**		**5.94**		**2.59**

Table A2.2 cont.: Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.

	KC 11s		**ND 1s**		**ND 2s**		**ND 3s**		**ND 4s**		**ND 5s**		**ND 6s**	
pH	7.37		7.82		6.84		6.81		8.33		7.64		7.89	
EC (mS/cm)	0.586		3.73		6.70		6.79		7.01		5.37		3.84	
SAR	2.09		10.4		20.2		13.4		35.8		20.3		14.6	
	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L
Li^+	0.080	0.012	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Na^+	62.7	2.73	723	31.4	1611	70.1	1457	63.4	1755	76.3	1328	57.8	918	39.9
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	5.12	0.131	1.20	0.031	8.40	0.215	18.2	0.465	9.10	0.233	0.550	0.014	0.800	0.020
Mg^{2+}	25.8	2.13	89.6	7.37	102	8.35	204	16.8	34.3	2.82	77.6	6.38	62.8	5.17
Ca^{2+}	25.5	1.27	218	10.9	317	15.8	565	28.2	126	6.29	195	9.74	196	9.78
Cr^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.006	< 0.001	0.010	< 0.001	0.015	0.001	0.027	0.001
Mn^{2+}	0.432	0.016	0.140	0.005	0.469	0.017	1.09	0.040	0.026	0.001	0.316	0.011	0.094	0.003
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	< 0.001	< 0.001	0.003	< 0.001	0.011	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Co^{2+}	< 0.001	< 0.001	0.008	< 0.001	0.003	< 0.001	0.004	< 0.001	0.002	< 0.001	0.012	< 0.001	0.030	0.001
Ni^{2+}	< 0.001	< 0.001	0.032	0.001	0.078	0.003	0.081	0.003	0.037	0.001	0.036	0.001	0.059	0.002
Cu^{2+}	0.003	< 0.001	0.007	< 0.001	0.012	< 0.001	0.013	< 0.001	0.058	0.002	0.011	< 0.001	0.011	< 0.001
Zn^{2+}	< 0.001	< 0.001	0.066	0.002	0.110	0.003	0.128	0.004	0.419	0.013	0.102	0.003	0.146	0.004
As^{3+}	< 0.001	< 0.001	0.001	< 0.001	0.002	< 0.001	0.002	< 0.001	0.005	< 0.001	0.003	< 0.001	0.002	< 0.001
Rb^+	0.009	< 0.001	0.020	< 0.001	0.038	< 0.001	0.051	0.001	0.025	< 0.001	0.021	< 0.001	0.014	< 0.001
Sr^{2+}	0.844	0.019	3.63	0.083	6.96	0.159	9.29	0.212	2.88	0.066	4.40	0.100	2.60	0.059
Ba^{2+}	0.018	< 0.001	0.048	0.001	0.018	< 0.001	0.042	0.001	0.050	0.001	0.055	0.001	0.037	0.001
Al^{3+}	0.027	0.003	0.048	0.005	0.002	< 0.001	0.015	0.002	0.094	0.010	0.038	0.004	0.043	0.005
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**6.31**		**49.8**		**94.7**		**109**		**85.8**		**74.0**		**55.0**
F^-	< 0.01	< 0.01	0.280	0.015	0.350	0.018	< 0.01	< 0.01	0.840	0.044	2.09	0.110	3.52	0.185
Cl^-	14.6	0.412	257	7.26	643	18.1	531	15.0	1538	43.4	964	27.2	251	7.08
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	1.80	0.029	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	20.9	0.435	1680	35.0	2787	58.0	3991	83.1	1513	31.5	1455	30.3	1370	28.5
HCO_3^-	393	6.44	257	4.22	733	12.0	585	9.59	382	6.25	456	7.47	616	10.1
Total anions		**7.29**		**46.5**		**88.2**		**108**		**81.2**		**65.1**		**45.9**
Si	0.639		5.75		5.40		6.56		6.89		4.11		5.40	
B	0.046		0.368		1.110		0.901		0.948		0.891		0.803	
DOC	< 1.0		6.4		1.7		4.2		2.4		1.7		3.1	
Cation excess (%)		**-7.23**		**3.47**		**3.55**		**0.657**		**2.76**		**6.43**		**9.03**

Table A2.2 cont.: Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.

	ND 7s		**ND 8s**		**ND 9s**		**ND 10s**		**ND 11s**		**ND 12s**		**ND 13s**	
pH	8.16		8.57		7.90		7.72		8.12		7.35		8.75	
EC (mS/cm)	3.99		2.26		3.35		5.39		4.41		0.690		2.44	
SAR	25.5		28.9		19.2		22.2		19.6		1.88		7.19	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	1.650	0.238	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Na^+	923	40.2	583	25.4	825	35.9	1271	55.3	1035	45.0	63.5	2.76	398	17.3
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	2.80	0.072	2.00	0.051	0.700	0.018	0.550	0.014	0.450	0.012	7.49	0.192	0.750	0.019
Mg^{2+}	18.4	1.51	3.50	0.288	32.2	2.65	66.6	5.48	57.6	4.74	12.7	1.04	59.3	4.87
Ca^{2+}	69.2	3.45	25.0	1.25	87.2	4.35	138	6.89	116	5.79	65.59	3.27	134	6.69
Cr^{2+}	0.014	0.001	0.010	< 0.001	0.012	< 0.001	0.006	< 0.001	0.004	< 0.001	< 0.001	< 0.001	0.002	0.002
Mn^{2+}	0.197	0.007	0.002	< 0.001	0.412	0.015	0.246	0.009	0.011	< 0.001	0.114	0.004	0.042	0.002
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	< 0.001	< 0.001	0.019	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.011	0.001	0.003	< 0.001
Co^{2+}	0.018	0.001	< 0.001	< 0.001	0.036	0.001	0.012	< 0.001	0.021	0.001	0.013	< 0.001	0.001	< 0.001
Ni^{2+}	0.028	0.001	< 0.001	< 0.001	0.057	0.002	0.036	0.001	0.051	0.002	0.021	0.001	0.015	0.001
Cu^{2+}	0.010	< 0.001	0.005	< 0.001	0.008	0.000	0.016	0.001	0.011	< 0.001	0.006	< 0.001	0.011	< 0.001
Zn^{2+}	0.101	0.003	0.003	< 0.001	0.074	0.002	0.121	0.004	0.124	0.004	0.015	< 0.001	0.047	0.001
As^{3+}	0.002	< 0.001	0.009	< 0.001	0.002	< 0.001	0.003	< 0.001	0.002	< 0.001	0.001	< 0.001	0.002	< 0.001
Rb^+	0.010	< 0.001	0.007	< 0.001	0.012	< 0.001	0.022	< 0.001	0.016	< 0.001	0.007	< 0.001	0.004	< 0.001
Sr^{2+}	1.37	0.031	0.306	0.007	1.89	0.043	4.67	0.107	2.97	0.068	1.83	0.042	2.13	0.049
Ba^{2+}	0.070	0.001	0.159	0.002	0.041	0.001	0.053	0.001	0.053	0.001	0.092	0.001	0.091	0.001
Al^{3+}	0.033	0.004	0.017	0.002	0.017	0.002	0.024	0.003	0.006	0.001	0.022	0.002	0.663	0.074
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**45.2**		**27.0**		**43.0**		**68.0**		**55.6**		**7.32**		**29.0**
F^-	4.24	0.223	12.3	0.649	5.50	0.289	1.60	0.084	2.21	0.116	0.077	0.004	< 0.01	< 0.01
Cl^-	528	14.9	158	4.46	158	4.45	1013	28.6	490	13.8	39.9	1.12	130	3.68
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	781	16.3	3.15	0.07	1048	21.8	1537	32.0	1340	27.9	138	2.87	1030	21.5
HCO_3^-	647	10.6	1214	19.9	742	12.2	455	7.45	515	8.44	156	2.56	166	2.71
Total anions		**42.0**		**25.1**		**38.7**		**68.1**		**50.3**		**6.55**		**27.8**
Si	3.59		4.10		4.17		3.86		3.87		5.67		5.99	
B	0.882		0.922		0.814		0.887		0.856		0.093		0.484	
DOC	1.6		< 1.0		5.0		1.9		2.7		9.6		9.1	
Cation excess (%)		**3.73**		**3.62**		**5.21**		**-0.085**		**5.02**		**5.52**		**2.02**

Table A2.2 cont.: Analytical results obtained for water samples taken from selected underground collieries, during the summer of 2000.

	ND 14s		**ND 15s**		**ND 16s**		**ND 17s**	
pH	7.86		7.66		7.34		8.71	
EC (mS/cm)	0.209		3.79		0.318		1.98	
SAR	0.761		15.9		0.655		22.2	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Na^+	14.9	0.649	834	36.3	17.7	0.771	472	20.5
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	0.800	0.020	0.400	0.010	0.750	0.019	0.400	0.010
Mg^{2+}	7.78	0.640	50.4	4.15	16.6	1.36	8.60	0.708
Ca^{2+}	16.4	0.818	124	6.19	28.1	1.40	20.0	0.998
Cr^{2+}	< 0.001	< 0.001	0.008	< 0.001	0.015	0.001	0.008	< 0.001
Mn^{2+}	0.001	< 0.001	0.003	< 0.001	0.003	< 0.001	0.004	< 0.001
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	< 0.001	< 0.001	0.136	0.007	0.136	0.007	< 0.001	< 0.001
Co^{2+}	< 0.001	< 0.001	0.029	0.001	< 0.001	< 0.001	< 0.001	< 0.001
Ni^{2+}	0.002	< 0.001	0.052	0.002	0.009	< 0.001	< 0.001	< 0.001
Cu^{2+}	0.005	< 0.001	0.008	< 0.001	0.009	< 0.001	0.004	< 0.001
Zn^{2+}	0.028	0.001	0.134	0.004	0.022	0.001	0.007	< 0.001
As^{3+}	< 0.001	< 0.001	0.002	< 0.001	0.001	< 0.001	0.001	< 0.001
Rb^+	0.002	< 0.001	0.014	< 0.001	0.003	< 0.001	0.006	< 0.001
Sr^{2+}	0.054	0.001	2.31	0.053	0.116	0.003	0.298	0.007
Ba^{2+}	0.056	0.001	0.041	0.001	0.071	0.001	0.121	0.002
Al^{3+}	0.120	0.013	0.117	0.013	0.065	0.007	0.016	0.002
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**2.14**		**46.7**		**3.58**		**22.2**
F^-	0.038	0.002	5.80	0.305	0.072	0.004	3.46	0.182
Cl^-	15.3	0.432	220	6.20	7.09	0.200	360	10.2
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	0.324	0.005	4.76	0.077	< 0.01	< 0.01	< 0.01	< 0.01
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	16.7	0.347	1191	24.8	21.1	0.440	11.7	0.243
HCO_3^-	67.3	1.10	622	10.2	157	2.57	567	9.29
Total anions		**1.89**		**41.6**		**3.21**		**19.9**
Si	2.90		4.74		7.79		6.84	
B	< 0.001		0.707		0.014		0.480	
DOC	3.9		3.4		9.0		< 1.0	
Cation excess (%)		**6.32**		**5.79**		**5.42**		**5.63**

Table A2.3: Analytical results obtained for water samples taken from selected opencast and closed collieries, during the winter of 2000.

	KK 1		KK 2		KK 3		KK 4		KK 5		KK 6		KK 7	
pH	6.79		6.70		7.89		7.49		7.18		7.32		7.31	
EC (mS/cm)	2.95		2.96		0.63		3.04		3.14		2.77		2.70	
SAR	0.283		0.275		1.03		0.268		0.257		0.247		0.322	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	0.088	0.013	0.044	0.006	0.011	0.002	0.048	0.007	0.138	0.020	0.043	0.006	0.086	0.012
Na^+	28.5	1.24	28.3	1.23	38.4	1.67	28.0	1.22	27.4	1.19	25.1	1.09	31.4	1.37
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	17.5	0.448	16.3	0.416	6.07	0.155	16.7	0.43	17.0	0.434	13.8	0.353	11.5	0.293
Mg^{2+}	233	19.2	239	19.62	31.8	2.61	236	19.4	276	22.7	236	19.4	177	14.5
Ca^{2+}	386	19.3	410	20.46	52.7	2.63	439	21.9	404	20.2	392	19.6	429	21.4
Cr^{2+}	0.001	< 0.001	0.002	< 0.001	0.003	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.002	< 0.001	< 0.001	< 0.001
Mn^{2+}	3.59	0.131	1.89	0.069	0.046	0.002	1.65	0.060	4.37	0.159	1.04	0.038	4.09	0.149
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.516	0.028
Co^{2+}	0.025	0.001	0.018	0.001	0.001	< 0.001	0.012	< 0.001	0.079	0.003	0.012	< 0.001	0.049	0.002
Ni^{2+}	0.056	0.002	0.039	0.001	0.005	< 0.001	0.029	0.001	0.105	0.004	0.056	0.002	0.190	0.006
Cu^{2+}	0.003	< 0.001	0.002	< 0.001	0.004	< 0.001	0.002	< 0.001	0.003	< 0.001	0.002	< 0.001	0.002	< 0.001
Zn^{2+}	0.316	0.010	0.174	0.005	0.089	0.003	0.171	0.005	0.229	0.007	0.171	0.005	0.302	0.009
As^{3+}	0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.092	0.001	0.045	0.001	0.005	< 0.001	0.036	0.000	0.040	< 0.001	0.026	< 0.001	0.029	< 0.001
Sr^{2+}	3.48	0.080	1.75	0.040	0.385	0.009	2.11	0.048	1.93	0.044	1.69	0.039	1.98	0.045
Ba^{2+}	0.125	0.002	0.063	0.001	0.076	0.001	0.043	0.001	0.035	0.001	0.030	< 0.001	0.031	< 0.001
Al^{3+}	0.077	0.009	0.037	0.004	0.057	0.006	0.052	0.006	0.023	0.003	0.023	0.003	0.029	0.003
H^+	*n.d.*	*n.d*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d*	*n.d.*	*n.d*	*n.d.*	*n.d.*
Total cations		**40.4**		**41.9**		**7.09**		**43.1**		**44.7**		**40.5**		**37.9**
F^-	0.270	0.014	2.92	0.154	0.670	0.035	< 0.01	< 0.01	< 0.01	< 0.01	0.430	0.023	3.71	0.195
Cl^-	25.7	0.724	15.6	0.440	31.3	0.883	18.8	0.530	20.9	0.588	14.9	0.419	16.1	0.455
NO_2^-	2.35	0.051	1.79	0.039	< 0.01	< 0.01	2.37	0.052	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	41.6	0.670	36.8	0.593	0.650	0.010	31.0	0.500	11.1	0.179	10.6	0.170	16.6	0.267
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	2417	50.3	2426	50.5	176	3.67	2295	47.8	2408	50.1	2267	47.2	2228	46.4
HCO_3^-	85.4	1.40	79.3	1.30	174	2.85	92	1.50	159	2.60	104	1.70	36.6	0.600
Total anions		**53.2**		**52.9**		**7.4**		**50.4**		**53.5**		**49.5**		**47.9**
Si	4.24		2.35		0.953		1.83		4.06		3.09		3.56	
B	0.136		0.067		0.016		0.067		0.123		0.055		0.038	
DOC	2.1		1.8		6.9		2.3		3.7		2.8		2.5	
Cation excess (%)		**-13.7**		**-11.6**		**-2.21**		**-7.80**		**-8.92**		**-10.1**		**-11.7**

Table A2.3 cont.: Analytical results obtained for water samples taken from selected opencast and closed collieries, during the winter of 2000.

	KK 8		KK 9		KK 10		KK 11		KK 12		KK 13		KK 14	
pH	7.41		7.26		7.47		7.02		7.90		3.10		6.72	
EC (mS/cm)	2.69		3.03		3.39		3.33		3.58		2.91		2.78	
SAR	0.338		0.192		0.255		0.291		0.443		0.135		0.653	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	0.079	0.011	0.058	0.008	0.247	0.036	0.152	0.022	0.067	0.010	0.026	0.004	0.018	0.003
Na^+	32.9	1.43	20.1	0.874	28.4	1.24	31.9	1.39	51.6	2.24	12.6	0.548	62.9	2.74
NH_4^+	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
K^+	15.1	0.387	13.9	0.354	20.2	0.518	19.5	0.498	16.6	0.425	9.19	0.235	21.9	0.559
Mg^{2+}	177	14.5	241	19.9	305	25.1	273	22.4	345	28.4	158	13.0	219	18.0
Ca^{2+}	426	21.3	430	21.5	441	22.0	464	23.2	460	23.0	399	19.9	343	17.1
Cr^{2+}	<0.001	<0.001	0.002	<0.001	0.001	<0.001	0.003	<0.001	0.002	<0.001	<0.001	<0.001	0.002	0.000
Mn^{2+}	3.61	0.131	1.92	0.070	4.71	0.171	6.23	0.227	2.00	0.073	3.26	0.119	0.062	0.002
Fe^{2+}	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Fe^{3+}	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	30.4	1.63	<0.001	<0.001
Co^{2+}	0.040	0.001	0.080	0.003	0.072	0.002	0.052	0.002	0.074	0.002	0.151	0.005	0.002	<0.001
Ni^{2+}	0.167	0.006	0.142	0.005	0.103	0.004	0.073	0.002	0.182	0.006	0.269	0.009	0.021	0.001
Cu^{2+}	0.001	<0.001	0.001	<0.001	0.001	<0.001	0.001	<0.001	0.001	<0.001	0.024	0.001	0.002	<0.001
Zn^{2+}	0.249	0.008	0.220	0.007	0.191	0.006	0.154	0.005	0.219	0.007	0.642	0.020	0.141	0.004
As^{3+}	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	0.001	<0.001	0.001	<0.001	<0.001	<0.001	0.001	0.000
Rb^+	0.028	<0.001	0.025	<0.001	0.048	0.001	0.044	0.001	0.030	<0.001	0.012	<0.001	0.034	<0.001
Sr^{2+}	1.93	0.044	2.04	0.047	2.17	0.050	1.96	0.045	1.79	0.041	0.609	0.014	1.87	0.043
Ba^{2+}	0.030	<0.001	0.040	0.001	0.040	0.001	0.030	<0.001	0.037	0.001	0.017	<0.001	0.041	0.001
Al^{3+}	0.031	0.003	0.018	0.002	0.022	0.002	0.017	0.002	0.022	0.002	3.85	0.428	0.037	0.004
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	6.05	6.00	*n.d.*	*n.d.*
Total cations		**37.8**		**42.7**		**49.1**		**47.8**		**54.1**		**41.9**		**38.5**
F^-	3.23	0.170	5.58	0.294	5.16	0.272	0.490	0.026	0.360	0.019	3.30	0.174	3.55	0.187
Cl^-	12.6	0.354	18.6	0.525	19.5	0.551	124	3.49	17.0	0.480	11.1	0.314	38.3	1.08
NO_2^-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Br^-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
NO_3^-	14.8	0.239	8.20	0.132	7.05	0.114	6.09	0.098	4.87	0.079	2.23	0.036	2.76	0.045
PO_4^{3-}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
SO_4^{2-}	2227	46.4	2375	49.4	2632	54.8	2460	51.2	2794	58.2	2364	49.2	2168	45.1
HCO_3^-	18.3	0.300	153	2.50	153	2.50	232	3.80	177	2.90	<0.01	<0.01	110	1.80
Total anions		**47.4**		**52.9**		**58.2**		**58.6**		**61.7**		**49.7**		**48.3**
Si	3.46		3.77		4.15		4.47		3.83		2.68		0.268	
B	0.046		0.054		0.186		0.166		0.080		<0.001		0.020	
DOC	2.1		2.5		6.0		1.8		2.4		1.0		6.2	
Cation excess (%)		**-11.3**		**-10.7**		**-8.49**		**-10.2**		**-6.51**		**-8.51**		**-11.2**

***Table A2.3 cont.**: Analytical results obtained for water samples taken from selected opencast and closed collieries, during the winter of 2000.*

	KK 15		**KK 16**		**KK 17**		**LN 1**		**LN 2**		**LN 3**		**LN 4**	
pH	2.90		5.95		5.82		3.16		5.70		3.42		2.79	
EC (mS/cm)	2.38		2.68		2.87		10.6		0.120		2.94		2.72	
SAR	0.639		0.200		0.408		0.315		0.162		0.456		0.356	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	0.069	0.010	0.079	0.011	0.105	0.015	0.115	0.017	0.002	0.000	0.175	0.025	0.052	0.007
Na^+	46.8	2.04	18.6	0.809	43.3	1.88	34.7	1.51	2.40	0.104	41.4	1.80	26.1	1.14
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	10.6	0.272	6.82	0.174	13.7	0.350	18.1	0.464	1.27	0.032	7.59	0.194	5.44	0.139
Mg^{2+}	96.6	7.95	131	10.8	208	17.1	304	25.0	4.18	0.344	142	11.7	91.4	7.52
Ca^{2+}	247	12.3	441	22.0	509	25.4	417	20.8	9.80	0.489	390	19.5	256	12.8
Cr^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001
Mn^{2+}	1.45	0.053	3.39	0.124	5.88	0.214	32.4	1.18	0.172	0.006	9.04	0.329	15.7	0.570
Fe^{2+}	< 0.001	< 0.001	103	3.68	0.001	< 0.001	5541	198	0.001	< 0.001	166	5.95	< 0.001	< 0.001
Fe^{3+}	54.4	2.92	10.4	0.561	0.001	< 0.001	42.1	2.26	0.001	< 0.001	27.5	1.48	126	6.76
Co^{2+}	0.089	0.003	0.067	0.002	0.134	0.005	1.02	0.035	0.008	0.000	0.227	0.008	0.422	0.014
Ni^{2+}	0.116	0.004	0.117	0.004	0.223	0.008	5.94	0.202	18.7	0.637	14.6	0.496	13.8	0.472
Cu^{2+}	0.006	< 0.001	< 0.001	< 0.001	0.004	< 0.001	0.030	0.001	0.051	0.002	0.047	0.001	0.049	0.002
Zn^{2+}	0.425	0.013	0.341	0.010	0.371	0.011	3.63	0.111	0.120	0.004	0.842	0.026	0.835	0.026
As^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.017	0.001	0.007	< 0.001	0.005	< 0.001	0.007	< 0.001
Rb^+	0.011	< 0.001	0.014	< 0.001	0.027	< 0.001	0.071	0.001	0.002	< 0.001	0.028	< 0.001	0.036	< 0.001
Sr^{2+}	0.325	0.007	1.26	0.029	1.64	0.037	0.539	0.012	0.045	0.001	2.01	0.046	0.835	0.019
Ba^{2+}	0.027	< 0.001	0.033	< 0.001	0.030	< 0.001	0.024	< 0.001	0.088	0.001	0.020	< 0.001	0.020	< 0.001
Al^{3+}	9.38	1.04	0.320	0.036	0.107	0.012	112	12.4	0.958	0.106	13.3	1.48	30.3	3.37
H^+	10.6	10.5	*n.d.*	*n.d.*	*n.d.*	*n.d.*	256	254	*n.d.*	*n.d.*	11.1	11.0	15.1	15.0
Total cations		**37.1**		**38.3**		**45.1**		**516**		**1.73**		**54.0**		**47.8**
F^-	6.57	0.346	4.21	0.222	0.550	0.029	15.2	0.801	0.180	0.009	1.38	0.073	3.29	0.173
Cl^-	30.8	0.869	15.3	0.432	13.2	0.371	41.5	1.17	6.34	0.179	15.4	0.433	15.2	0.430
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	1.49	0.024	3.21	0.052	1.47	0.024	24.2	0.390	4.03	0.065	1.97	0.032	2.26	0.036
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	94.1	1.98	< 0.01	< 0.01	< 0.01	< 0.01	2.48	0.052
SO_4^{2-}	1612	33.6	2292	47.7	2429	50.6	15405	321	14.6	0.305	2412	50.2	1949	40.6
HCO_3^-	< 0.01	< 0.01	36.6	0.600	79.3	1.30	< 0.01	< 0.01	21.4	0.350	< 0.01	< 0.01	< 0.01	< 0.01
Total anions		**34.8**		**49.0**		**52.3**		**324**		**0.90**		**50.7**		**41.3**
Si	3.28		2.77		4.40		9.82		2.95		7.30		7.90	
B	< 0.001		< 0.001		0.038		< 0.001		0.072		0.005		< 0.001	
DOC	5.3		1.4		2.4		4.2		1.8		1.5		2.3	
Cation excess (%)		**3.23**		**-12.3**		**-7.40**		**22.8**		**31.6**		**3.15**		**7.33**

Table A2.3 cont.: Analytical results obtained for water samples taken from selected opencast and closed collieries, during the winter of 2000.

	LN 5		LN 6		LN 7b		LK 1		LK 2		LK 3		LK 4	
pH	2.86		4.66		2.90		2.76		2.73		3.07		3.60	
EC (mS/cm)	3.31		3.15		11.8		1.13		1.34		1.07		0.42	
SAR	0.299		0.260		0.348		0.306		0.144		0.140		0.207	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	0.084	0.012	0.159	0.023	0.001	< 0.001	0.034	0.005	0.053	0.008	0.036	0.005	0.010	0.001
Na^+	27.6	1.20	28.8	1.25	38.8	1.69	5.60	0.244	2.80	0.122	4.70	0.204	3.20	0.139
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	4.92	0.126	5.76	0.147	10.3	0.264	1.35	0.035	2.53	0.065	1.88	0.048	1.13	0.029
Mg^{2+}	133	11.0	89.2	7.34	330	27.1	5.92	0.487	6.90	0.568	12.2	1.01	4.97	0.409
Ca^{2+}	425	21.2	783	39.1	400	20.0	15.7	0.783	17.2	0.858	65.8	3.28	10.0	0.499
Cr^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.017	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Mn^{2+}	21.5	0.782	4.82	0.176	0.475	0.017	0.250	0.009	0.983	0.036	2.16	0.079	3.26	0.119
Fe^{2+}	5.38	0.192	41.6	1.49	5621	201	18.3	0.655	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	172	9.22	12.1	0.650	244	13.1	58.8	3.16	42.3	2.27	5.40	0.290	< 0.001	< 0.001
Co^{2+}	0.579	0.020	0.151	0.005	0.012	< 0.001	0.146	0.005	0.161	0.005	0.230	0.008	0.173	0.006
Ni^{2+}	13.7	0.466	13.9	0.472	0.011	< 0.001	16.6	0.567	13.7	0.468	11.3	0.384	13.6	0.463
Cu^{2+}	0.058	0.002	0.077	0.002	0.000	< 0.001	0.040	0.001	0.054	0.002	0.066	0.002	0.040	0.001
Zn^{2+}	0.983	0.030	0.511	0.016	0.031	0.001	0.803	0.025	0.721	0.022	0.728	0.022	0.456	0.014
As^{3+}	0.008	< 0.001	0.005	< 0.001	< 0.001	< 0.001	0.008	< 0.001	0.005	< 0.001	0.005	< 0.001	0.006	< 0.001
Rb^+	0.035	< 0.001	0.045	0.001	0.001	< 0.001	0.010	< 0.001	0.016	< 0.001	0.009	< 0.001	0.008	< 0.001
Sr^{2+}	1.12	0.026	1.50	0.034	0.007	< 0.001	0.083	0.002	0.112	0.003	0.151	0.003	0.073	0.002
Ba^{2+}	0.011	< 0.001	0.066	0.001	0.016	< 0.001	0.034	< 0.001	0.031	< 0.001	0.016	< 0.001	0.078	0.001
Al^{3+}	31.0	3.44	8.08	0.899	1.08	0.120	40.4	4.49	42.6	4.73	47.4	5.27	38.8	4.31
H^+	17.6	17.5	5.04	5.00	286	284	10.6	10.5	10.6	10.5	10.6	10.5	4.43	4.40
Total cations		**65.2**		**56.6**		**547**		**21.0**		**19.7**		**21.1**		**10.4**
F^-	0.790	0.042	< 0.01	< 0.01	3.37	0.177	0.060	0.003	0.320	0.017	3.40	0.179	0.650	0.034
Cl^-	19.2	0.542	22.2	0.625	119	3.36	3.97	0.112	2.92	0.082	6.19	0.175	4.47	0.126
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	8.02	0.129	10.1	0.162	37.1	0.599	0.690	0.011	0.960	0.015	2.86	0.046	0.730	0.012
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.990	0.021	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	2797	58.2	2785	58.0	17679	368	646	13.5	720	15.0	832	17.3	286	5.96
HCO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Total anions		**59.0**		**58.8**		**372**		**13.6**		**15.1**		**17.7**		**6.13**
Si	5.66		1.30		0.068		10.7		11.2		14.1		6.01	
B	< 0.001		< 0.001		< 0.001		0.026		< 0.001		< 0.001		< 0.001	
DOC	1.2		1.9		5.6		1.6		1.3		3.3		2.5	
Cation excess (%)		**5.02**		**-1.90**		**19.0**		**21.4**		**13.0**		**8.68**		**25.8**

Table A2.3 cont.: Analytical results obtained for water samples taken from selected opencast and closed collieries, during the winter of 2000.

	LK 5b		LK 6		LK 7		LK 8		NLC 1		NLC 2		NLC 3	
pH	2.69		2.10		2.21		2.73		5.73		6.34		7.15	
EC (mS/cm)	1.20		10.5		13.7		1.25		1.74		0.15		2.55	
SAR	0.120		0.040		0.044		0.112		0.186		0.528		0.420	
	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L
Li^+	0.043	0.006	0.151	0.022	0.350	0.050	0.041	0.006	0.035	0.005	0.002	0.000	0.036	0.005
Na^+	2.20	0.096	1.90	0.083	4.00	0.174	2.00	0.087	13.9	0.605	7.30	0.318	36.2	1.57
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	2.17	0.055	1.53	0.039	5.62	0.144	1.59	0.041	5.96	0.152	5.83	0.149	12.7	0.324
Mg^{2+}	4.89	0.402	43.6	3.59	138	11.4	5.06	0.416	46.4	3.81	4.11	0.338	81.4	6.70
Ca^{2+}	17.5	0.873	95.5	4.77	392	19.6	16.0	0.798	348	17.4	7.70	0.384	428	21.4
Cr^{2+}	< 0.001	< 0.001	0.057	0.002	< 0.001	< 0.001	0.008	< 0.001	< 0.001	< 0.001	0.002	< 0.001	0.002	< 0.001
Mn^{2+}	0.736	0.027	1.29	0.047	8.05	0.293	0.655	0.024	1.04	0.038	0.094	0.003	0.014	0.001
Fe^{2+}	< 0.001	< 0.001	966	34.6	3891	139	< 0.001	< 0.001	8.72	0.312	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	34.4	1.85	1406	75.6	705	37.8	35.0	1.88	0.351	0.019	0.066	0.004	< 0.001	< 0.001
Co^{2+}	0.179	0.006	0.461	0.016	0.554	0.019	0.154	0.005	0.012	< 0.001	0.001	< 0.001	0.001	< 0.001
Ni^{2+}	14.4	0.490	6.25	0.213	3.12	0.106	20.2	0.689	0.036	0.001	0.005	< 0.001	0.013	< 0.001
Cu^{2+}	0.045	0.001	0.745	0.023	0.360	0.011	0.071	0.002	< 0.001	< 0.001	0.001	< 0.001	0.001	< 0.001
Zn^{2+}	0.666	0.020	1.77	0.054	2.14	0.065	0.838	0.026	0.058	0.002	0.027	0.001	0.099	0.003
As^{3+}	0.015	0.001	0.034	0.001	0.019	0.001	0.010	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001
Rb^+	0.011	< 0.001	0.024	< 0.001	0.018	< 0.001	0.011	< 0.001	0.008	< 0.001	0.016	< 0.001	0.026	< 0.001
Sr^{2+}	0.121	0.003	0.294	0.007	0.266	0.006	0.111	0.003	0.927	0.021	0.049	0.001	2.49	0.057
Ba^{2+}	0.039	0.001	0.033	< 0.001	0.100	0.001	0.044	0.001	0.024	< 0.001	0.127	0.002	0.025	< 0.001
Al^{3+}	51.4	5.72	267	29.7	195	21.6	45.2	5.03	0.251	0.028	0.008	0.001	0.008	0.001
H^+	10.3	10.2	230	229	368	365	11.1	11.0	*n.d.*	*n.d*	*n.d.*	*n.d*	*n.d.*	*n.d.*
Total cations		**19.7**		**377**		**596**		**20.0**		**22.4**		**1.20**		**30.0**
F^-	0.160	0.008	< 0.01	< 0.01	7.64	0.402	0.160	0.008	0.260	0.014	< 0.01	< 0.01	0.150	0.008
Cl^-	2.94	0.083	67.2	1.90	87.4	2.47	3.12	0.088	7.17	0.202	4.42	0.125	17.4	0.490
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	2.25	0.036	107	1.73	55.4	0.894	1.82	0.029	0.430	0.007	3.74	0.060	6.69	0.108
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	663	13.8	13526	282	23711	494	690	14.4	1108	23.1	39.8	0.829	1492	31.07
HCO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	61.0	1.00	18.3	0.300	97.6	1.60
Total anions		**13.9**		**285**		**497**		**14.5**		**24.3**		**1.31**		**33.3**
Si	14.1		10.2		11.1		11.9		3.47		4.91		1.81	
B	< 0.001		< 0.001		< 0.001		< 0.001		0.037		0.000		0.012	
DOC	2.0		17.0		15.0		1.8		< 1.0		< 1.0		4.0	
Cation excess (%)		**17.3**		**13.9**		**8.98**		**16.0**		**-4.11**		**-4.48**		**-5.14**

***Table A2.3 cont.**: Analytical results obtained for water samples taken from selected opencast and closed collieries, during the winter of 2000.*

	NLC 4		NLC 5		NLC 6		NLC 7		NLC 8		NLC 9		NLC 10	
pH	6.31		6.33		5.98		6.37		5.33		6.88		6.24	
EC (mS/cm)	2.28		0.07		2.33		0.99		0.03		0.12		0.21	
SAR	0.090		0.240		0.133		0.120		0.250		0.850		0.190	
	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L	Conc (mg/L)	mmol/L
Li^+	0.041	0.006	0.002	0.000	0.038	0.006	0.022	0.003	0.002	0.000	0.001	0.000	0.006	0.001
Na^+	8.10	0.352	2.40	0.104	12.6	0.548	6.50	0.283	1.60	0.070	12.1	0.526	4.10	0.178
NH_4^+	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
K^+	5.27	0.135	1.63	0.042	5.01	0.128	3.80	0.097	1.08	0.028	3.88	0.099	3.91	0.100
Mg^{2+}	116	9.52	2.11	0.174	84.4	6.94	28.1	2.31	0.720	0.059	3.24	0.267	4.40	0.362
Ca^{2+}	426	21.3	4.10	0.205	539	26.9	175	8.73	1.90	0.095	10.2	0.509	27.3	1.36
Cr^{2+}	0.009	<0.001	0.001	<0.001	0.005	<0.001	0.001	<0.001	0.004	<0.001	0.001	<0.001	0.002	<0.001
Mn^{2+}	3.67	0.133	0.055	0.002	3.50	0.127	0.758	0.028	0.048	0.002	0.191	0.007	0.104	0.004
Fe^{2+}	25.2	0.901	<0.001	<0.001	23.0	0.822	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Fe^{3+}	1.42	0.076	<0.001	<0.001	0.325	0.017	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Co^{2+}	0.012	<0.001	0.002	<0.001	0.025	0.001	0.008	<0.001	0.001	<0.001	<0.001	<0.001	0.004	<0.001
Ni^{2+}	0.047	0.002	0.001	<0.001	0.078	0.003	0.023	0.001	0.002	<0.001	0.001	<0.001	0.005	<0.001
Cu^{2+}	0.001	<0.001	0.001	<0.001	<0.001	<0.001	0.001	<0.001	0.001	<0.001	0.001	<0.001	<0.001	<0.001
Zn^{2+}	0.066	0.002	0.014	<0.001	0.052	0.002	0.036	0.001	0.014	<0.001	0.013	<0.001	0.022	0.001
As^{3+}	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Rb^+	0.016	<0.001	0.003	<0.001	0.009	<0.001	0.009	<0.001	0.003	<0.001	0.010	<0.001	0.010	<0.001
Sr^{2+}	3.63	0.083	0.025	0.001	2.89	0.066	0.990	0.023	0.010	<0.001	0.060	0.001	0.162	0.004
Ba^{2+}	0.114	0.002	0.076	0.001	0.029	<0.001	0.149	0.002	0.035	0.001	0.067	0.001	0.107	0.002
Al^{3+}	0.004	<0.001	0.052	0.006	0.100	0.011	0.022	0.002	0.017	0.002	0.006	0.001	0.017	0.002
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**32.5**		**0.53**		**35.6**		**11.5**		**0.26**		**1.41**		**2.01**
F^-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.020	0.001	0.010	0.001
Cl^-	5.56	0.157	2.84	0.080	36.8	1.04	5.04	0.142	2.80	0.079	3.49	0.098	2.54	0.072
NO_2^-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Br^-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
NO_3^-	1.42	0.023	14.1	0.227	2.16	0.035	3.73	0.060	3.51	0.057	0.060	0.001	9.52	0.154
PO_4^{3-}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
SO_4^{2-}	1551	32.3	2.35	0.049	1693	35.26	570	11.9	0.590	0.012	10.5	0.219	63.0	1.31
HCO_3^-	153	2.50	21.4	0.350	134	2.20	30.5	0.500	12.2	0.200	58.0	0.950	39.7	0.650
Total anions		**35.0**		**0.71**		**38.53**		**12.57**		**0.35**		**1.27**		**2.19**
Si	6.70		3.82		9.09		5.31		3.34		2.00		5.53	
B	0.108		0.002		0.040		0.028		<0.001		0.016		0.012	
DOC	<1.0		1.1		<1.0		1.4		<1.0		1.4		<1.0	
Cation excess (%)		**-3.71**		**-13.8**		**-3.99**		**-4.50**		**-15.3**		**5.28**		**-4.10**

Table A2.3 cont.: Analytical results obtained for water samples taken from selected opencast and closed collieries, during the winter of 2000.

	NLC 11		**NVC 1**		**NVC 2**		**NVC 3**		**NVC 4**		**NVC 5**		**NVC 6**	
pH	6.51		7.49		8.12		8.01		7.97		8.26		7.72	
EC (mS/cm)	0.11		3.44		1.16		2.42		2.71		1.26		1.50	
SAR	0.190		1.87		0.552		2.11		1.30		1.14		1.18	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	0.006	0.001	0.659	0.095	0.012	0.002	0.133	0.019	0.284	0.041	0.042	0.006	0.119	0.017
Na^+	2.60	0.113	194	8.44	30.6	1.33	183	7.96	122	5.31	64.6	2.81	73.8	3.21
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	4.02	0.103	13.2	0.337	5.88	0.150	8.79	0.225	8.35	0.214	4.37	0.112	5.37	0.137
Mg^{2+}	2.84	0.234	201	16.5	77.5	6.38	117	9.63	158	13.0	69.9	5.75	77.8	6.40
Ca^{2+}	9.20	0.459	481	24.0	105	5.25	271	13.5	407	20.3	128	6.39	167	8.33
Cr^{2+}	0.004	< 0.001	0.007	< 0.001	0.008	< 0.001	0.002	< 0.001	0.002	< 0.001	0.002	< 0.001	0.009	< 0.001
Mn^{2+}	0.095	0.003	1.34	0.049	0.220	0.008	0.454	0.017	0.292	0.011	0.012	< 0.001	0.221	0.008
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Co^{2+}	0.002	< 0.001	0.019	0.001	0.001	< 0.001	0.003	< 0.001	0.005	< 0.001	0.001	< 0.001	0.004	< 0.001
Ni^{2+}	0.003	< 0.001	0.039	0.001	0.006	< 0.001	0.010	< 0.001	0.026	0.001	0.006	< 0.001	0.010	< 0.001
Cu^{2+}	0.003	< 0.001	0.002	< 0.001	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	0.002	< 0.001
Zn^{2+}	0.025	0.001	0.145	0.004	0.022	0.001	0.087	0.003	0.135	0.004	0.051	0.002	0.047	0.001
As^{3+}	< 0.001	< 0.001	0.004	< 0.001	0.015	0.001	0.003	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.004	< 0.001
Rb^+	0.011	< 0.001	0.034	< 0.001	0.014	< 0.001	0.023	< 0.001	0.014	< 0.001	0.008	< 0.001	0.016	< 0.001
Sr^{2+}	0.062	0.001	8.87	0.203	2.90	0.066	7.84	0.179	5.45	0.124	3.59	0.082	5.27	0.120
Ba^{2+}	0.218	0.003	0.060	0.001	0.223	0.003	0.065	0.001	0.048	0.001	0.064	0.001	0.046	0.001
Al^{3+}	0.016	0.002	0.015	0.002	0.010	0.001	0.011	0.001	0.013	0.001	0.009	0.001	0.015	0.002
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**0.92**		**49.7**		**13.2**		**31.6**		**39.0**		**15.2**		**18.2**
F^-	0.010	0.001	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cl^-	2.68	0.076	17.7	0.500	7.38	0.208	12.7	0.357	11.6	0.328	11.2	0.316	7.23	0.204
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	25.7	0.415	7.39	0.119	105	1.70	4.94	0.080	5.32	0.086	1.03	0.017	2.07	0.033
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	0.640	0.013	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	14.5	0.301	2274	47.3	212	4.42	1419	29.5	2021	42.1	614	12.8	737	15.3
HCO_3^-	15.3	0.250	256	4.20	390	6.40	244	4.00	122	2.00	189	3.10	250	4.10
Total anions		**1.04**		**52.2**		**12.7**		**34.0**		**44.5**		**16.2**		**19.7**
Si	3.71		8.40		6.86		6.82		1.40		0.804		4.88	
B	0.006		2.66		0.280		1.58		1.14		0.754		1.06	
DOC	< 1.0		1.6		5.9		2.0		1.6		2.3		1.6	
Cation excess (%)		**-6.21**		**-2.44**		**1.76**		**-3.68**		**-6.60**		**-3.38**		**-3.82**

Table A2.3 cont.: Analytical results obtained for water samples taken from selected opencast and closed collieries, during the winter of 2000.

	NVC 7		**NVC 8**		**NVC 9**		**NVC 10**		**NVC 11**		**NVC 12**		**NVC 13**	
pH	8.42		8.20		8.92		8.20		7.83		7.29		8.08	
EC (mS/cm)	0.780		1.19		0.960		1.70		0.720		5.86		5.57	
SAR	0.337		1.73		2.09		2.91		1.40		9.31		9.45	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	0.004	0.001	0.011	0.002	0.003	0.000	0.043	0.006	0.004	0.001	0.338	0.049	0.271	0.039
Na^+	15.5	0.674	88.2	3.84	89.2	3.88	174	7.57	53.5	2.33	951	41.4	920	40.0
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	5.05	0.129	4.50	0.115	3.28	0.084	5.18	0.132	6.49	0.166	24.4	0.624	21.2	0.541
Mg^{2+}	41.5	3.42	59.2	4.87	46.5	3.82	73.0	6.01	28.2	2.32	225	18.5	216	17.8
Ca^{2+}	91.6	4.57	98.9	4.94	61.2	3.05	151	7.53	64.1	3.20	421	21.0	362	18.06
Cr^{2+}	0.002	< 0.001	0.001	< 0.001	0.001	< 0.001	0.002	< 0.001	0.002	< 0.001	0.009	< 0.001	0.005	< 0.001
Mn^{2+}	0.000	< 0.001	0.006	< 0.001	0.003	< 0.001	0.212	0.008	0.133	0.005	2.070	0.075	0.395	0.014
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fe^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Co^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	0.013	< 0.001	0.003	< 0.001
Ni^{2+}	0.004	< 0.001	0.003	< 0.001	0.002	< 0.001	0.005	< 0.001	0.005	< 0.001	0.030	0.001	0.017	0.001
Cu^{2+}	< 0.001	< 0.001	0.001	< 0.001	0.002	< 0.001	0.002	< 0.001	0.001	< 0.001	0.006	< 0.001	0.006	< 0.001
Zn^{2+}	0.027	0.001	0.030	< 0.001	0.026	0.001	0.042	0.001	0.017	0.001	0.139	0.004	0.129	0.004
As^{3+}	< 0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	0.003	< 0.001	0.002	< 0.001
Rb^+	0.002	< 0.001	0.003	< 0.001	0.002	< 0.001	0.007	< 0.001	0.003	< 0.001	0.043	0.001	0.036	< 0.001
Sr^{2+}	0.900	0.021	1.81	0.041	1.04	0.024	3.44	0.078	0.220	0.005	7.37	0.168	7.16	0.163
Ba^{2+}	0.047	0.001	0.082	0.001	0.080	0.001	0.067	0.001	0.130	0.002	0.042	0.001	0.031	< 0.001
Al^{3+}	0.011	0.001	0.007	0.001	0.014	0.002	0.007	0.001	0.012	0.001	0.005	0.001	0.007	0.001
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**8.81**		**13.8**		**10.9**		**21.3**		**8.02**		**81.8**		**76.6**
F^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cl^-	2.14	0.060	12.7	0.357	17.7	0.499	13.4	0.377	45.2	1.28	38.4	1.08	37.5	1.06
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	3.75	0.060	0.230	0.004	4.51	0.073	7.98	0.129
PO_4^{3-}	< 0.01	< 0.01	0.330	0.007	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	381	7.94	582	12.1	408	8.49	947	19.7	158	3.29	3901	81.2	3592	74.8
HCO_3^-	51.9	0.850	128	2.10	110	1.80	171	2.80	186	3.05	403	6.60	299	4.90
Total anions		**8.85**		**14.6**		**10.8**		**23.0**		7.6		**89.0**		**80.9**
Si	0.204		2.06		0.056		3.47		4.30		8.41		7.39	
B	0.111		0.529		0.436		1.14		0.051		3.99		4.20	
DOC	1.6		2.2		4.8		2.7		5.6		2.4		2.3	
Cation excess (%)		**-0.215**		**-2.72**		**0.383**		**-3.66**		**2.61**		**-4.21**		**-2.68**

Table A2.3 cont.: Analytical results obtained for water samples taken from selected opencast and closed collieries, during the winter of 2000.

	NVC 14		**NVC 15**		**OC 1b**		**OC 2b**		**OC 3b**		**OC 4**		**VF 1**	
pH	7.00		6.94		3.32		3.23		3.78		4.01		5.94	
EC (mS/cm)	1.50		1.30		10.6		10.6		7.07		6.63		1.23	
SAR	1.36		1.68		19.4		19.8		8.08		7.10		0.698	
	Conc (mg/L)	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**	**Conc (mg/L)**	**mmol$_c$/L**
Li^+	0.038	0.005	0.022	0.003	0.024	0.004	0.025	0.004	0.033	0.005	0.274	0.039	0.034	0.005
Na^+	84.4	3.67	91.1	3.96	1850	80.5	1890	82.2	774	33.7	687	29.9	43.4	1.89
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	5.07	0.130	4.45	0.114	28.0	0.717	32.4	0.827	26.9	0.688	27.0	0.691	2.22	0.057
Mg^{2+}	67.9	5.59	52.2	4.30	156	12.9	156	12.8	198	16.3	201	16.5	39.8	3.27
Ca^{2+}	178	8.88	137	6.84	428	21.4	431	21.5	368	18.4	377	18.8	228	11.4
Cr^{2+}	0.011	< 0.001	0.011	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.009	< 0.001
Mn^{2+}	0.810	0.029	0.686	0.025	0.209	0.008	0.209	0.008	0.315	0.011	2.534	0.092	2.00	0.073
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	226	8.09	118	4.21	470	16.8	425	15.2	< 0.001	< 0.001
Fe^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	7.91	0.425	86.0	4.62	< 0.001	< 0.001	< 0.001	< 0.001	0.083	0.004
Co^{2+}	0.003	< 0.001	0.002	< 0.001	0.008	< 0.001	0.008	< 0.001	0.007	< 0.001	0.077	0.003	0.009	< 0.001
Ni^{2+}	0.009	< 0.001	0.007	< 0.001	0.013	< 0.001	0.013	< 0.00	0.008	< 0.001	0.082	0.003	0.016	0.001
Cu^{2+}	0.001	< 0.001	0.002	< 0.001	0.000	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001
Zn^{2+}	0.035	0.001	0.026	0.001	0.036	0.001	0.035	0.001	0.010	< 0.001	0.112	0.003	0.045	0.001
As^{3+}	0.002	< 0.001	0.002	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.015	< 0.001	0.010	< 0.001	0.005	< 0.001	0.005	< 0.001	0.003	< 0.001	0.030	< 0.001	0.003	< 0.001
Sr^{2+}	4.28	0.098	3.06	0.070	0.009	< 0.001	0.009	< 0.001	0.003	< 0.001	0.035	0.001	1.26	0.029
Ba^{2+}	0.177	0.003	0.116	0.002	0.013	< 0.001	0.011	< 0.001	0.033	< 0.001	0.044	0.001	0.054	0.001
Al^{3+}	0.014	0.002	0.006	0.001	0.563	0.063	0.565	0.063	1.33	0.148	8.16	0.907	0.014	0.002
H^+	*n.d.*	*n.d*	*n.d.*	*n.d.*	17.1	17.0	16.1	16.0	36.8	36.5	34.8	34.5	*n.d.*	*n.d.*
Total cations		**18.4**		**15.3**		**141**		**142**		**123**		**117**		**16.7**
F^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	26.4	1.39	43.4	2.28	< 0.01	< 0.01
Cl^-	10.7	0.302	22.2	0.627	333	9.38	329	9.29	115	3.26	114	3.23	14.7	0.415
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	3.41	0.055	2.61	0.042	44.9	0.725	37.6	0.607	< 0.01	< 0.01	< 0.01	< 0.01	4.23	0.068
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	658	13.7	478	9.96	7308	152	6937	144	5711	119	5291	110	745	15.5
HCO_3^-	293	4.80	262	4.30	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	122	2.00
Total anions		**18.9**		**14.9**		**162**		**154**		**122**		**116**		**18.0**
Si	9.19		8.01		0.527		0.523		0.469		3.16		14.2	
B	0.861		0.806		0.004		0.004		< 0.001		0.011		0.245	
DOC	2.3		2.9		2.3		2.5		106		176		< 1.0	
Cation excess (%)		**-1.21**		**1.28**		**-7.01**		**-4.06**		**0.144**		**0.421**		**-3.71**

Table A2.3 cont.: *Analytical results obtained for water samples taken from selected opencast and closed collieries, during the winter of 2000.*

	VF 2		**VF 3**		**VF 4**		**VF 5**		**NAC 1**		**NAC 2**		**NAC 3**	
pH	6.81		7.78		7.95		7.67		7.35		6.86		6.39	
EC (mS/cm)	1.24		1.22		1.41		1.50		0.260		1.26		0.880	
SAR	0.737		0.777		1.18		1.19		0.426		0.884		1.59	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	0.039	0.006	0.035	0.005	0.015	0.002	0.018	0.003	0.003	0.000	0.083	0.012	0.052	0.007
Na^+	46.0	2.00	48.8	2.12	85.1	3.70	86.7	3.77	10.3	0.448	50.8	2.21	65.2	2.84
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	2.36	0.060	3.31	0.085	5.35	0.137	5.89	0.151	2.14	0.055	4.26	0.109	5.33	0.136
Mg^{2+}	41.4	3.41	43.0	3.53	104	8.52	114	9.40	19.5	1.61	53.0	4.36	23.8	1.96
Ca^{2+}	227	11.3	228	11.4	227	11.3	215	10.7	12.2	0.609	163	8.13	88.6	4.42
Cr^{2+}	0.003	< 0.001	0.004	< 0.001	0.008	0.000	0.006	< 0.001	0.002	< 0.001	0.004	< 0.001	0.006	< 0.001
Mn^{2+}	1.10	0.040	0.038	0.001	0.013	0.000	0.011	< 0.001	0.106	0.004	2.36	0.086	1.03	0.038
Fe^{2+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.431	0.015	2.48	0.089	2.36	0.084
Fe^{3+}	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	1.66	0.089	0.560	0.030
Co^{2+}	0.002	< 0.001	< 0.001	< 0.001	0.000	0.000	< 0.001	< 0.001	0.001	< 0.001	0.020	0.001	0.004	< 0.001
Ni^{2+}	0.015	0.001	0.005	< 0.001	0.006	0.000	0.006	< 0.001	0.003	< 0.001	0.043	0.001	0.013	< 0.001
Cu^{2+}	0.001	< 0.001	0.002	< 0.001	0.002	0.000	0.001	< 0.001	0.001	< 0.001	0.001	< 0.001	0.000	< 0.001
Zn^{2+}	0.049	0.001	0.044	0.001	0.029	0.001	0.036	0.001	0.015	< 0.001	0.046	0.001	0.035	0.001
As^{3+}	< 0.001	< 0.001	0.004	< 0.001	0.003	0.000	0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.003	< 0.001	0.003	< 0.001	0.003	0.000	0.002	< 0.001	0.001	< 0.001	0.006	< 0.001	0.006	< 0.001
Sr^{2+}	0.919	0.021	1.09	0.025	0.847	0.019	0.946	0.022	0.146	0.003	6.34	0.145	4.79	0.109
Ba^{2+}	0.046	0.001	0.069	0.001	0.064	0.001	0.069	0.001	0.043	0.001	0.026	< 0.001	0.031	< 0.001
Al^{3+}	0.015	0.002	0.015	0.002	0.016	0.002	0.016	0.002	0.036	0.004	0.029	0.003	0.041	0.005
H^+	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
Total cations		**16.9**		**17.2**		**23.7**		**24.1**		**2.75**		**15.2**		**9.63**
F^-	< 0.01	< 0.01	< 0.01	< 0.01	0.290	0.015	0.240	0.013	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cl^-	14.8	0.417	18.0	0.507	45.5	1.28	47.8	1.35	8.07	0.228	5.24	0.148	4.62	0.130
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	2.48	0.040	0.560	0.009	0.300	0.005	0.200	0.003	1.15	0.019	0.290	0.005	0.400	0.006
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	84.6	1.782	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	741	15.4	735	15.3	682	14.2	838	17.4	51.6	1.07	667	13.9	311	6.48
HCO_3^-	134	2.20	159	2.60	317	5.20	220	3.60	73.2	1.20	153	2.50	192	3.15
Total anions		**18.1**		**18.4**		**22.5**		**22.4**		**2.52**		**16.5**		**9.76**
Si	9.35		10.3		4.49		3.26		9.92		7.86		8.19	
B	0.214		0.212		0.151		0.198		0.011		0.012		0.014	
DOC	< 1.0		1.4		6.9		5.6		1.1		< 1.0		< 1.0	
Cation excess (%)		**-3.49**		**-3.53**		**2.64**		**3.58**		**4.28**		**-4.10**		**-0.686**

Table A2.3 cont.: Analytical results obtained for water samples taken from selected opencast and closed collieries, during the winter of 2000.

	NAC 4		**NAC 5**		**NAC 6**		**NAC 7**		**NAC 8**		**VCC 1**		**VCC 2**	
pH	6.47		3.20		8.17		4.00		6.90		2.85		6.38	
EC (mS/cm)	0.730		3.32		0.810		1.12		0.620		2.51		2.00	
SAR	2.16		0.574		1.96		0.321		1.22		0.336		0.717	
	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L	Conc (mg/L)	mmol$_c$/L
Li^+	0.062	0.009	0.001	0.000	0.053	0.008	0.023	0.003	0.056	0.008	0.007	0.001	0.061	0.009
Na^+	69.4	3.02	52.3	2.27	70.9	3.08	17.6	0.766	40.7	1.77	23.7	1.03	54.4	2.37
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K^+	3.41	0.087	9.52	0.243	2.79	0.071	3.64	0.093	3.61	0.092	3.19	0.082	5.16	0.132
Mg^{2+}	11.1	0.915	235	19.3	16.2	1.33	46.4	3.82	15.0	1.24	104	8.52	103	8.50
Ca^{2+}	59.6	2.97	242	12.1	72.7	3.63	151	7.53	59.0	2.94	207	10.3	266	13.3
Cr^{2+}	0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.003	< 0.001	< 0.001	< 0.001	0.003	0.000
Mn^{2+}	1.80	0.066	0.548	0.020	0.669	0.024	2.65	0.097	0.500	0.018	0.841	0.031	5.85	0.213
Fe^{2+}	0.654	0.023	31.4	1.13	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	14.2	0.507	26.8	0.960
Fe^{3+}	0.873	0.047	9.03	0.485	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	11.1	0.596	1.23	0.066
Co^{2+}	0.025	0.001	0.014	< 0.001	0.004	< 0.001	0.037	0.001	0.035	0.001	0.025	0.001	0.039	0.001
Ni^{2+}	0.056	0.002	0.023	0.001	0.009	< 0.001	0.081	0.003	0.073	0.003	0.049	0.002	0.056	0.002
Cu^{2+}	0.001	< 0.001	0.002	< 0.001	0.001	< 0.001	0.003	< 0.001	0.001	< 0.001	0.004	< 0.001	0.001	< 0.001
Zn^{2+}	0.131	0.004	0.035	0.001	0.026	0.001	0.096	0.003	0.097	0.003	0.151	0.005	0.059	0.002
As^{3+}	0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001
Rb^+	0.005	< 0.001	0.001	< 0.001	0.003	< 0.001	0.002	< 0.001	0.004	< 0.001	0.001	< 0.001	0.006	< 0.001
Sr^{2+}	3.50	0.080	0.064	0.001	3.61	0.082	2.84	0.065	2.73	0.062	0.193	0.004	6.40	0.146
Ba^{2+}	0.025	< 0.001	0.011	< 0.001	0.019	< 0.001	0.060	0.001	0.063	0.001	0.013	< 0.001	0.041	0.001
Al^{3+}	0.031	0.003	2.209	0.246	0.050	0.006	1.88	0.209	0.028	0.003	3.21	0.356	0.055	0.006
H^+	*n.d.*	*n.d.*	16.6	16.5	*n.d.*	*n.d.*	1.21	1.20	*n.d.*	*n.d.*	13.6	13.5	*n.d.*	*n.d.*
Total cations		**7.23**		**52.32**		**8.23**		**13.8**		**6.14**		**35.0**		**25.7**
F^-	< 0.01	< 0.01	4.77	0.251	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cl^-	3.94	0.111	14.5	0.408	5.12	0.144	7.02	0.198	4.73	0.133	6.66	0.188	8.89	0.251
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	0.590	0.010	1.51	0.024	0.770	0.012	0.480	0.008	0.780	0.013	0.62	0.010	1.27	0.020
PO_4^{3-}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4^{2-}	303	6.30	2772	57.7	337	7.02	664	13.83	235	4.89	1939	40.4	1172	24.4
HCO_3^-	85.4	1.40	< 0.01	< 0.01	116	1.90	< 0.01	< 0.01	91.5	1.50	< 0.01	< 0.01	293	4.80
Total anions		**7.82**		**58.39**		**9.07**		**14.0**		**6.54**		**40.6**		**29.5**
Si	7.47		0.180		7.73		12.0		9.40		1.40		9.86	
B	0.032		< 0.001		0.029		0.001		0.013		< 0.001		0.020	
DOC	< 1.0		3.8		< 1.0		< 1.0		< 1.0		1.1		< 1.0	
Cation excess (%)		**-3.94**		**-5.49**		**-4.86**		**-0.851**		**-3.13**		**-7.41**		**-6.88**

Table A2.3 cont.: *Analytical results obtained for water samples taken from selected opencast and closed collieries, during the winter of 2000.*

	VCC 3		VCC 4	
pH	3.52		3.11	
EC (mS/cm)	2.54		3.33	
SAR	1.60		1.50	
	Conc (mg/L)	$mmol_c/L$	Conc (mg/L)	$mmol_c/L$
Li^+	0.028	0.004	0.026	0.004
Na^+	129	5.61	135	5.87
NH_4^+	< 0.01	< 0.01	< 0.01	< 0.01
K^+	5.95	0.152	5.54	0.142
Mg^{2+}	127	10.4	146	12.0
Ca^{2+}	282	14.1	371	18.5
Cr^{2+}	< 0.001	< 0.001	0.001	< 0.001
Mn^{2+}	3.25	0.118	1.27	0.046
Fe^{2+}	< 0.001	< 0.001	38.3	1.37
Fe^{3+}	2.30	0.123	26.3	1.41
Co^{2+}	0.076	0.003	0.039	0.001
Ni^{2+}	0.085	0.003	0.073	0.002
Cu^{2+}	0.001	< 0.001	0.003	< 0.001
Zn^{2+}	0.087	0.003	0.118	0.004
As^{3+}	< 0.001	< 0.001	< 0.001	< 0.001
Rb^+	0.002	< 0.001	0.001	< 0.001
Sr^{2+}	1.78	0.041	0.650	0.015
Ba^{2+}	0.016	< 0.001	0.012	< 0.001
Al^{3+}	0.611	0.068	2.95	0.329
H^+	1.81	1.796	10.1	10.0
Total cations		**32.4**		**49.8**
F^-	< 0.01	< 0.01	< 0.01	< 0.01
Cl^-	10.5	0.296	7.62	0.215
NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01
Br^-	< 0.01	< 0.01	< 0.01	< 0.01
NO_3^-	0.540	0.009	2.63	0.042
PO_4^{3-}	0.000	0.000	< 0.01	< 0.01
SO_4^{2-}	1835	38.2	2490	51.8
HCO_3^-	< 0.01	< 0.01	< 0.01	< 0.01
Total anions		**38.5**		**52.1**
Si	3.44		2.25	
B	0.003		< 0.001	
DOC	< 1.0		< 1.0	
Cation excess (%)		**-8.58**		**-2.30**

Table A2.4: Analytical results obtained for XRF analyses of selected core samples from the Vryheid Formation.

	NVC-1	NVC-2	NVC-3	NVC-4	NVC-5	NVC-6	NVC-7$_A$	NVC-7$_B$	NVC-8	NVC-9$_A$	NVC-9$_B$	NVC-10	NVC-11
	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %
SiO_2	41.4	50.4	51.8	46.1	50.3	27.6	45.3	44.6	59.6	13.2	27.8	46.3	51.8
TiO_2	0.47	0.57	0.72	0.43	0.58	0.44	0.46	0.25	0.76	0.18	0.63	0.89	0.77
Al_2O_3	10.7	13.6	16.1	10.3	13.6	9.91	15.2	5.27	15.2	6.81	8.81	23.1	17.0
Fe_2O_3	8.81	7.33	3.88	21.48	6.01	2.30	12.6	16.5	2.75	4.08	0.46	5.82	2.69
MnO	0.04	0.07	0.01	0.31	0.06	0.01	0.04	0.03	0.02	<0.01	<0.01	0.03	0.01
MgO	1.35	1.98	1.47	3.00	1.28	0.63	1.51	2.42	0.75	0.21	0.21	1.81	1.00
CaO	0.88	0.87	0.61	3.13	3.30	0.30	2.90	2.95	0.27	5.28	0.52	0.30	0.32
Na_2O	0.10	0.26	0.33	0.26	0.62	0.25	0.08	0.01	0.24	<0.01	0.07	0.57	0.80
K_2O	1.42	2.16	2.00	1.72	2.07	1.08	2.18	4.50	2.05	0.09	0.11	2.00	1.51
P_2O_5	0.08	0.07	0.05	0.13	0.05	0.03	0.45	0.04	0.02	0.02	0.02	0.06	0.04
SO_3	0.06	0.93	0.25	0.90	4.63	1.16	1.95	2.91	0.19	5.47	0.34	0.62	0.39
Cl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01
H_2O	2.25	2.38	1.88	1.25	2.25	1.38	1.38	1.38	1.25	2.13	2.38	1.75	1.25
C	32.5	18.8	20.0	10.0	15.0	55.0	15.0	18.8	16.3	62.5	57.5	16.3	22.5
Total	**100**	**99.4**	**99.1**	**99.0**	**99.8**	**100**	**99.0**	**99.5**	**99.3**	**100**	**98.8**	**99.5**	**100**
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
S	286	4214	1164	4075	21085	5353	8936	13381	881	25908	1548	2852	1824
Ba	396	369	472	287	403	260	171	137	364	137	145	500	494
Sc	12.9	12.8	16.6	14.8	14.4	10.9	23.0	25.3	12.1	11.5	8.64	17.5	19.2
V	18.5	13.8	81.8	17.7	14.5	62.2	21.6	56.8	12.2	161	6.08	52.7	34.86
Cr	105	104	98.3	194	158	63.7	139	223	147	97.7	35.2	148	144
Mn	229	360	127	1505	290	104	266	215	115	39.6	19.8	143	94.0
Co	<1.94	<1.97	13.73	<3.3	<1.94	10.2	<2.56	<2.92	<1.44	11.6	<0.69	12.5	33.1
Ni	33.5	37.0	34.7	27.8	32.6	20.7	45.1	32.2	19.5	65.2	2.83	56.5	70.6
Cu	12.6	10.0	25.3	4.41	7.64	20.0	13.1	9.40	7.30	6.83	10.1	10.2	19.3
Zn	66.7	58.7	92.4	50.7	49.7	65.3	40.3	37.7	26.2	28.2	1.63	301	129
Rb	111	146	116	93.8	102	79.6	140	265	93.2	5.95	10.9	178	96.7
Sr	100	104	99.2	71.4	117	75.4	73.7	70.8	61.2	231	126	74.5	118
Y	29.2	15.3	32.9	13.3	15.9	34.4	21.2	3.28	11.2	12.1	22.0	11.9	42.0
Zr	151	181	164	118	193	172	142	217	248	97.7	159.31	92.8	256
Nb	15.1	14.6	18.5	9.33	13.6	13.9	9.99	6.13	14.3	7.99	18.3	22.8	19.6
Mo	1.94	<0.83	1.35	<1.04	<0.85	1.04	<0.95	<1.01	<0.76	4.09	<0.57	2.60	2.20
Pb	15.2	21.8	26.1	6.31	15.9	22.5	26.6	5.40	16.5	324	7.50	46.9	20.8
Th	13.4	13.1	26.0	6.14	10.0	16.5	18.2	5.23	9.41	4.26	17.7	7.75	14.3
U	3.33	<1.84	3.50	<2.38	2.59	6.38	4.91	<2.31	2.56	2.45	3.05	<1.78	4.40

Table A2.4 cont.: Analytical results obtained for XRF analyses of selected core samples from the Vryheid Formation.

	NVC-12	NVC-13	NVC-14$_A$	NVC-14$_B$	NVC-15	KRL-L	KRL-K	KRL-J$_A$	KRL-J$_B$	KRL-I	KRL-H	KRL-G	KRL-F
	wt %	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**
SiO_2	56.6	6.1	34.5	53.0	13.3	50.8	58.4	50.7	45.0	78.9	50.6	45.1	67.9
TiO_2	0.79	0.22	0.95	0.78	0.36	0.70	0.92	0.75	0.85	0.41	0.79	0.75	0.49
Al_2O_3	17.6	4.51	20.1	18.4	8.69	14.2	22.4	15.6	17.0	10.9	16.7	18.6	13.2
Fe_2O_3	3.61	0.13	0.43	0.40	0.17	4.10	3.38	10.9	4.05	2.04	4.92	2.70	2.95
MnO	0.01	0.00	0.00	<0.001	0.01	0.02	0.02	0.25	0.05	0.01	0.06	0.01	0.06
MgO	0.96	0.18	0.09	0.09	0.14	1.21	1.26	1.73	1.12	0.34	1.27	0.90	0.88
CaO	0.26	0.87	0.12	0.07	0.59	0.46	1.25	0.64	0.36	0.23	0.39	0.21	4.11
Na_2O	0.74	0.31	0.18	0.16	0.21	0.65	0.28	1.00	0.53	1.33	0.83	0.51	1.47
K_2O	2.06	0.03	0.17	0.23	0.18	2.47	2.53	2.68	2.39	3.84	2.59	2.21	3.81
P_2O_5	0.04	0.08	0.03	0.02	0.02	0.06	0.07	0.08	0.05	0.05	0.07	0.03	0.04
SO_3	0.87	0.35	0.31	0.09	0.66	0.01	0.13	0.07	0.46	0.01	0.11	0.66	0.21
Cl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
H_2O	1.63	2.38	1.25	1.75	1.75	1.75	1.25	2.00	2.13	2.16	2.38	2.13	1.38
C	15.0	85.0	42.5	25.0	75.0	22.5	7.50	12.5	25.0	0.00	18.8	25.0	3.75
Total	**100**	**100**	**101**	**100**	**101**	**98.9**	**99.4**	**99.0**	**99.0**	**100**	**99.4**	**98.8**	**100**
	ppm	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
S	3957	1692	1440	395	3137	41	610	342	2099	56	524	3021	1001
Ba	499	409	157	111	151	543	795	643	573	935	616	592	886
Sc	21.6	5.96	30.1	20.8	11.8	12.8	24.0	14.9	14.3	7.38	16.2	18.8	10.7
V	45.3	<0.65	97.6	27.7	39.7	16.7	163	20.4	30.5	9.35	22.8	31.9	9.11
Cr	130	28.3	343	160	45.9	65.3	126	73.0	99.2	45.3	85.4	89.9	45.6
Mn	49.8	14.4	8.98	16.4	72.5	126	191	1223	256	111	283	76.1	298
Co	27.6	1.94	11.3	16.9	7.61	3.68	12.6	<2.39	11.6	3.39	<1.68	4.36	<1.73
Ni	50.3	14.2	130	59.5	22.8	24.7	63.0	22.2	44.1	13.7	26.8	29.2	12.7
Cu	31.8	3.71	66.7	25.7	16.8	13.1	59.3	5.70	25.98	2.10	15.9	34.3	<0.86
Zn	131	2.43	121	64.7	23.9	69.3	121	101	147	52.6	105	99.1	54.9
Rb	129	1.39	12.7	11.4	16.0	139	126	123	144	119	132	136	129
Sr	120	460	50.9	23.6	113	103	135	114	113	117	112	154	235
Y	38.0	23.0	21.6	10.5	43.3	26.6	48.8	25.0	26.5	14.1	36.3	44.5	16.5
Zr	223	98.4	238	109	132	350	167	265	309	148	340	246	159
Nb	19.1	5.08	11.9	8.75	8.69	19.9	20.7	16.1	20.1	9.63	18.9	20.2	11.5
Mo	2.08	<0.46	2.93	2.16	<0.49	<0.81	1.20	<0.92	2.24	1.73	1.46	1.58	1.46
Pb	28.3	5.84	25.3	11.7	15.5	20.2	39.3	24.2	38.3	28.5	28.3	36.7	28.6
Th	19.4	10.9	10.3	6.48	14.9	14.7	28.8	12.2	23.8	5.88	18.1	31.3	7.11
U	5.85	3.20	2.53	3.40	2.79	4.23	11.4	2.63	5.24	<1.71	5.86	9.43	2.68

Table A2.4 cont.: Analytical results obtained for XRF analyses of selected core samples from the Vryheid Formation.

	KRL-E	**KRL-D**	**KRL-C**	**KRL-B**	**KRL-A**	**KRL-2**	**KRL-3$_A$**	**KRL-3$_B$**	**KRL-4**	**KRL-5**	**GH-A**	**GH-B**	**GH-C**
	wt %	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**	**wt %**
SiO_2	49.7	46.8	84.9	42.3	37.8	43.3	11.7	30.3	8.59	3.06	49.6	30.5	42.4
TiO_2	0.77	0.76	0.41	0.70	0.68	0.44	0.17	0.47	0.20	0.12	0.87	0.75	0.69
Al_2O_3	17.9	18.2	7.94	16.6	16.4	15.2	5.60	10.4	3.89	2.45	20.3	9.94	23.8
Fe_2O_3	5.08	5.19	1.13	10.3	10.9	2.57	3.77	0.87	0.85	0.04	2.07	0.36	0.91
MnO	0.06	0.06	0.02	0.08	0.11	< 0.001	< 0.001	0.00	0.01	0.01	0.01	0.01	0.01
MgO	1.45	1.35	0.20	1.70	1.45	0.47	0.24	0.42	0.41	0.56	0.76	0.15	0.17
CaO	0.40	0.37	0.18	1.67	0.77	0.15	1.06	0.84	1.98	4.28	0.21	0.25	0.09
Na_2O	0.90	0.78	0.98	0.60	0.44	0.26	0.09	0.17	0.07	0.10	0.13	0.02	0.08
K_2O	2.72	2.54	3.04	2.11	1.76	1.84	0.18	0.36	0.11	0.07	2.23	0.18	1.29
P_2O_5	0.07	0.07	0.02	0.04	0.07	0.02	0.09	0.02	0.10	0.64	0.20	0.02	0.02
SO_3	0.28	0.22	0.03	0.56	0.40	2.52	5.83	1.01	1.41	0.69	0.16	0.28	0.20
Cl	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
H_2O	1.38	2.38	1.21	2.25	1.88	1.38	1.75	2.13	1.63	1.38	0.50	2.25	1.00
C	18.8	21.3	0.00	21.3	27.5	32.5	68.8	53.8	81.3	87.5	21.8	54.6	29.4
Total	**99.5**	**100**	**100**	**100**	**100**	**101**	**99.3**	**101**	**100**	**101**	**98.9**	**99.3**	**100**
	ppm	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
S	1276	1019	172	2543	1815	11409	27141	4657	6755	3438	754	1268	963
Ba	683	648	768	513	445	374	249	196	265	970	719	163	402
Sc	16.0	17.0	4.93	14.8	15.4	7.73	7.05	12.1	5.44	3.51	17.8	17.6	6.80
V	21.1	24.1	3.29	23.6	19.9	4.79	6.88	11.5	1.73	< 0.7	26.3	6.75	5.45
Cr	70.8	82.1	33.2	104	101	56.6	33.0	71.3	20.4	12.2	93.0	70.1	60.3
Mn	293	310	99.5	465	588	25.3	12.8	17.0	32.3	54.2	62.5	30.9	36.5
Co	3.23	4.10	< 1.55	< 2.26	< 2.18	4.33	< 1.02	3.44	< 0.59	2.19	11.9	< 0.67	6.41
Ni	23.2	30.1	4.48	24.5	31.0	23.1	15.2	17.8	4.03	10.8	45.7	13.0	47.5
Cu	16.5	19.6	< 0.86	6.85	7.78	6.10	4.08	7.63	3.16	3.55	25.0	14.4	3.29
Zn	93.1	104	20.0	91.9	89.1	43.8	26.5	18.8	2.14	1.51	109	6.73	63.2
Rb	150	148	84.2	136	128	123	12.1	29.8	3.06	3.40	136	12.8	69.7
Sr	161	162	94.5	171	132	121	286	199	433	1925	355	57.8	43.2
Y	39.4	42.4	9.59	23.2	29.9	26.6	20.2	30.3	19.2	16.6	51.9	47.91	4.55
Zr	379	318	296	243	203	288	88.1	251	80.1	44.7	347	283	83.4
Nb	18.0	17.6	8.65	18.8	18.3	15.5	7.65	14.7	6.00	4.31	23.7	21.6	18.2
Mo	< 0.82	< 0.82	1.51	< 0.92	< 0.9	1.55	4.95	< 0.62	1.61	< 0.53	1.19	1.49	1.66
Pb	29.7	32.7	19.4	21.6	22.6	16.9	5.76	17.2	7.04	< 1.61	49.9	23.0	24.0
Th	20.1	19.9	6.96	11.0	13.7	11.1	4.35	17.4	7.01	< 1.28	26.1	29.9	6.11
U	5.63	7.44	< 1.65	< 2.06	< 2.05	3.11	2.60	5.69	3.84	4.03	11.4	5.46	1.94

Table A2.4 cont.: Analytical results obtained for XRF analyses of selected core samples from the Vryheid Formation.

	GH-D	GH-E	GH-F	GH-G	GH-H	GH-I	GH-K_1	GH-K_2	ND-A	ND-B_1	ND-B_2	ND-C	ND-D_1
	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %
SiO_2	86.5	77.6	45.2	46.1	44.4	4.91	60.3	50.3	48.8	60.2	71.8	50.7	79.3
TiO_2	1.34	0.33	0.77	0.81	0.83	0.15	1.03	0.91	0.77	0.35	0.56	0.83	0.25
Al_2O_3	9.18	13.5	18.4	20.1	19.9	3.94	15.4	19.1	15.6	8.72	13.1	16.2	9.27
Fe_2O_3	0.66	0.62	5.72	3.26	3.62	0.28	0.74	0.58	6.44	1.24	2.41	7.08	0.98
MnO	0.01	0.01	0.06	0.05	0.16	0.02	<0.01	0.01	0.07	0.02	0.03	0.08	0.03
MgO	0.11	0.08	0.94	0.76	0.70	0.28	0.11	0.12	1.62	0.29	0.63	1.88	0.19
CaO	0.04	0.04	0.30	0.17	0.37	1.14	0.07	0.07	0.51	10.5	3.63	0.42	2.61
Na_2O	0.13	0.18	0.13	0.11	0.11	<0.01	0.07	0.08	1.16	1.27	1.52	1.13	1.78
K_2O	2.70	3.99	2.19	1.75	1.63	0.16	0.51	0.54	2.92	2.77	3.47	3.05	3.61
P_2O_5	0.02	0.02	0.09	0.06	0.08	0.26	0.03	0.03	0.09	0.03	0.04	0.06	0.02
SO_3	0.05	0.02	0.35	0.21	0.21	1.03	0.59	0.34	0.13	0.01	0.03	0.06	0.03
Cl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
H_2O	0.00	0.38	0.88	0.63	1.00	2.00	0.00	<0.01	1.88	1.38	1.63	1.25	1.74
C	0.38	3.63	24.4	25.0	26.5	85.0	21.5	28.8	18.8	12.5	<0.01	16.3	<0.01
Total	**101**	**100**	**99.4**	**99.0**	**99.5**	**99.2**	**100**	**101**	**98.8**	**99.3**	**98.9**	**99.0**	**99.8**
	ppm	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
S	239	124	1601	981	978	4877	2715	1564	605	86.9	149	294	219
Ba	588	840	669	488	502	628	117	124	663	652	790	711	893
Sc	4.68	3.43	19.5	19.1	20.5	3.96	4.08	3.78	15.4	7.35	9.00	15.9	5.19
V	<2.5	2.63	30.7	32.1	31.4	3.18	4.20	4.26	22.4	4.34	11.5	22.7	3.68
Cr	119	26.6	85.0	115	121	15.4	82.4	59.2	77.8	23.8	53.4	84.1	22.5
Mn	50.6	44.0	323	218	734	70.9	27.5	18.8	338	111	159	377	193
Co	1.88	<1.24	<1.71	24.2	19.9	5.64	<1.06	<0.97	<1.86	1.85	5.99	<1.97	<1.48
Ni	10.6	5.75	34.3	61.4	62.4	11.9	13.4	15.6	32.8	7.00	21.9	30.4	5.61
Cu	1.56	<0.74	29.5	36.1	28.2	4.01	3.46	4.16	18.9	<0.83	5.34	11.6	<0.84
Zn	19.9	32.4	129	122	133	4.18	23.7	28.6	107	18.8	48.1	109	19.6
Rb	60.9	115	120	112	102	6.58	25.5	31.4	160	88.0	115	168	105
Sr	50.0	86.6	120	130	211	1508	24.7	26.6	186	186	153	131	200
Y	18.5	5.18	51.5	51.0	59.6	16.4	23.6	22.0	32.4	13.2	16.8	30.5	9.98
Zr	391	140	223	274	217	63.7	650	530	299	214	261	330	136
Nb	25.8	8.73	18.0	23.0	23.4	5.99	28.2	27.7	19.0	7.46	12.6	20.5	5.45
Mo	1.35	1.74	2.11	2.61	2.09	1.25	1.48	0.93	1.49	1.39	2.66	2.43	0.96
Pb	21.3	30.1	35.5	30.2	30.9	5.58	13.5	15.9	28.2	25.2	30.7	29.6	25.2
Th	9.20	5.24	25.3	24.4	30.9	<1.16	11.6	12.4	16.5	8.75	12.3	15.6	5.59
U	<1.63	<1.64	9.10	5.98	11.8	2.93	2.19	<1.54	5.74	<1.8	<1.77	5.30	<1.69

Table A2.4 cont.: *Analytical results obtained for XRF analyses of selected core samples from the Vryheid Formation.*

	$ND\text{-}D_2$	ND-E	ND-F	ND-G	ND-1	ND-2	ND-3	ND-4	ND-5	ND-6
	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %
SiO_2	74.6	43.1	77.1	7.05	54.1	47.6	40.6	82.8	33.1	82.9
TiO_2	0.54	0.74	1.06	0.22	0.81	0.97	0.85	0.14	0.84	0.17
Al_2O_3	13.6	16.3	11.7	3.05	14.9	17.5	12.1	8.00	14.8	7.86
Fe_2O_3	2.42	6.85	1.98	0.90	9.93	8.73	10.2	1.51	9.15	1.69
MnO	0.02	0.04	0.04	0.01	0.15	0.07	0.16	0.02	0.08	0.01
MgO	0.74	1.39	0.31	0.28	5.98	2.49	3.27	0.39	1.91	0.49
CaO	0.34	0.32	0.37	0.83	8.47	0.41	8.00	0.47	0.30	0.12
Na_2O	1.28	0.88	1.39	0.10	3.05	1.02	2.72	1.52	0.70	1.31
K_2O	4.12	2.34	3.83	0.05	0.78	3.10	0.52	3.25	2.13	3.78
P_2O_5	0.05	0.09	0.05	<0.01	0.12	0.04	0.12	0.02	0.05	0.01
SO_3	0.25	2.57	0.37	1.21	0.05	0.07	0.28	0.02	0.39	0.24
Cl	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.01	<0.01
H_2O	1.88	1.75	1.74	1.75	1.54	2.00	1.75	1.50	2.38	1.14
C	0.00	22.5	0.00	83.8	0.00	15.0	18.8	0.00	33.8	0.00
Total	**99.8**	**98.9**	**99.9**	**99.2**	**99.9**	**98.9**	**99.3**	**99.6**	**99.6**	**99.7**
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
S	1151	11675	1848	5690	299	327	1300	163	1787	1255
Ba	953	607	1025	111	244	701	276	881	490	861
Sc	11.1	17.2	10.7	6.36	27.3	16.9	31.2	6.20	26.2	5.99
V	19.6	22.8	6.34	2.88	67.5	30.2	74.6	6.33	51.7	9.50
Cr	66.8	75.4	43.7	21.8	456	113	120	26.0	131	44.4
Mn	105	253	223	50.7	772	384	776	133	450	47.0
Co	< 1.59	2.49	< 1.66	2.39	17.8	<2.15	7.21	< 1.67	< 1.95	< 1.62
Ni	15.7	34.6	9.16	5.65	127	45.5	46.3	9.41	46.6	5.89
Cu	4.21	18.9	<0.86	7.89	78.0	9.63	83.2	<0.89	25.6	1.69
Zn	70.6	103	41.2	20.7	79.2	158	78.3	22.1	142	19.2
Rb	140	140	113	2.71	17.0	191	14.8	95.9	165	135
Sr	135	201	133	143	155	126	346	107	118	114
Y	22.8	45.6	25.3	16.7	22.3	19.5	27.5	6.69	45.9	4.35
Zr	153	298	526	72.4	93.0	213	109	87.3	244	126
Nb	11.5	17.1	22.0	5.76	4.03	22.4	6.01	3.86	19.2	4.61
Mo	<0.78	2.83	3.15	<0.49	<0.97	1.48	< 1.0	1.66	1.13	1.55
Pb	32.7	39.2	28.5	28.4	<3.02	28.2	6.19	25.0	30.2	21.2
Th	10.2	21.3	20.2	6.75	<2.34	10.1	3.56	3.06	19.3	5.23
U	< 1.73	7.44	3.93	3.80	<2.22	2.98	<2.28	< 1.67	4.55	< 1.68

APPENDIX 3

Ion speciation

Ure and Davidson (1995) define speciation as either "the process of identifying and quantifying the different, and defined species, forms or phases present in a material"; or "the description of the amounts and kinds of these species, forms or phases present". Ionic speciation was determined in this study in order to characterize the most important forms of the elements present in the water bodies. This information could then be used to understand the transformations between forms that can occur, and to infer from this the likely environmental consequences.

The analytical data for all water samples was modelled using the computer program PHREEQC. This is a geochemical speciation model for dilute aqueous systems. PHREEQC is based on equilibrium thermodynamics which calculates the equilibrium composition of dilute aqueous systems among soluble, solid, adsorbed and gas phases. It can also be used to calculate the mass distribution between the dissolved, adsorbed, and multiple solid phases under a variety of environmental conditions, such as pH, ionic strength, temperature and redox conditions. The program also contains three extensive databases which includes thermodynamic data for soluble complexes, mineral solubilities, gas solubilities and redox couples (Parkhurst, 1995).

Input to the model required the total analytically measured concentrations of constituents in the colliery water samples in mg/L. The pH and temperature of the samples, at which analyses were conducted, were also entered into the model. The Davies equation was used to compute the activity coefficients. This equation is an extension of the Debye-Huckel equation and was preferred because only the ionic strength of the medium and the charge on the species are required to calculate the activity coefficients (Lumsdon and Evans, 1995). The relative distributions of dissolved and adsorbed ionic species, within each of the water samples, are presented here.

Figure A3.1: *Speciation of selected ions in waters from Vierfontein colliery.*

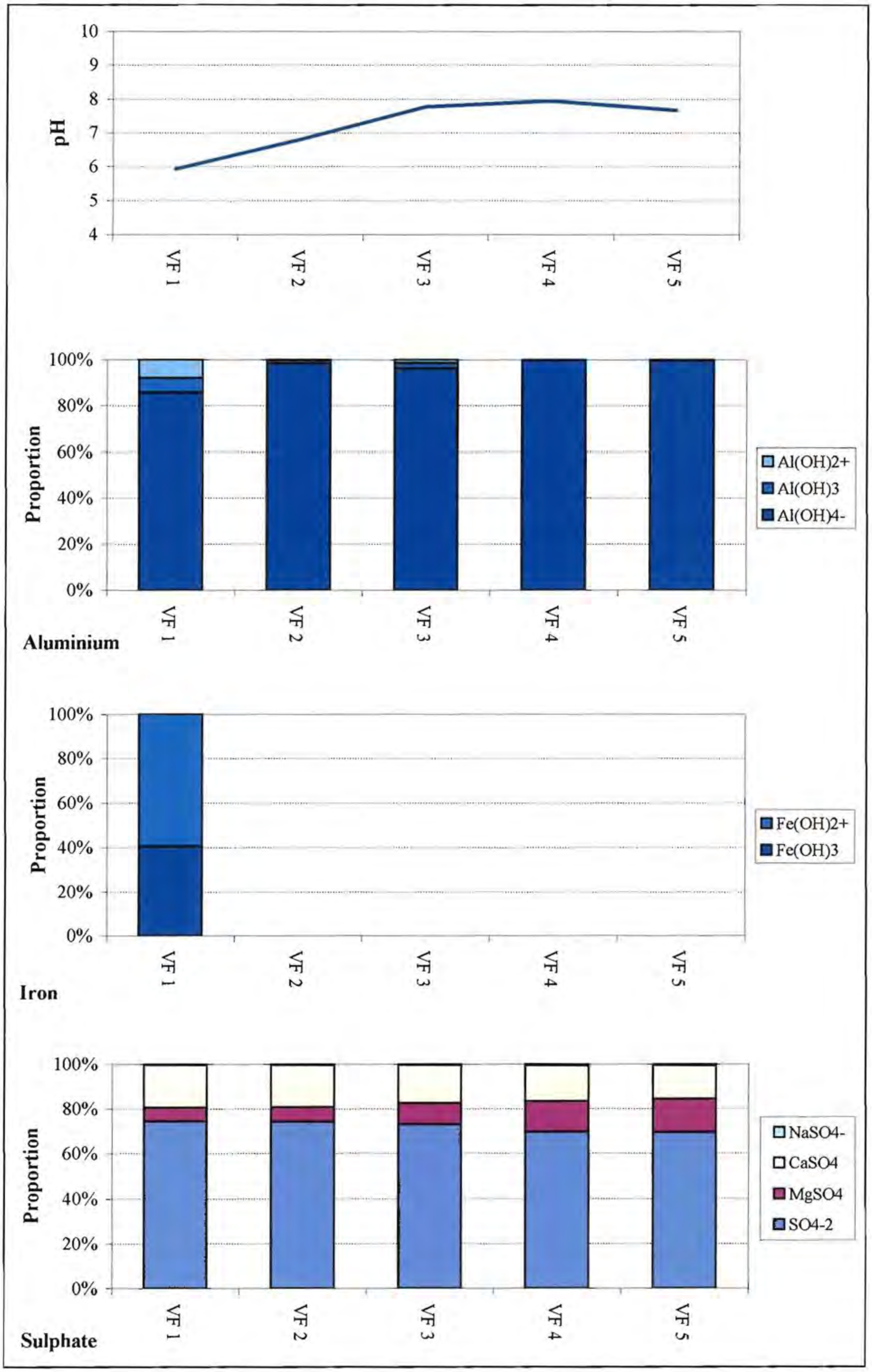
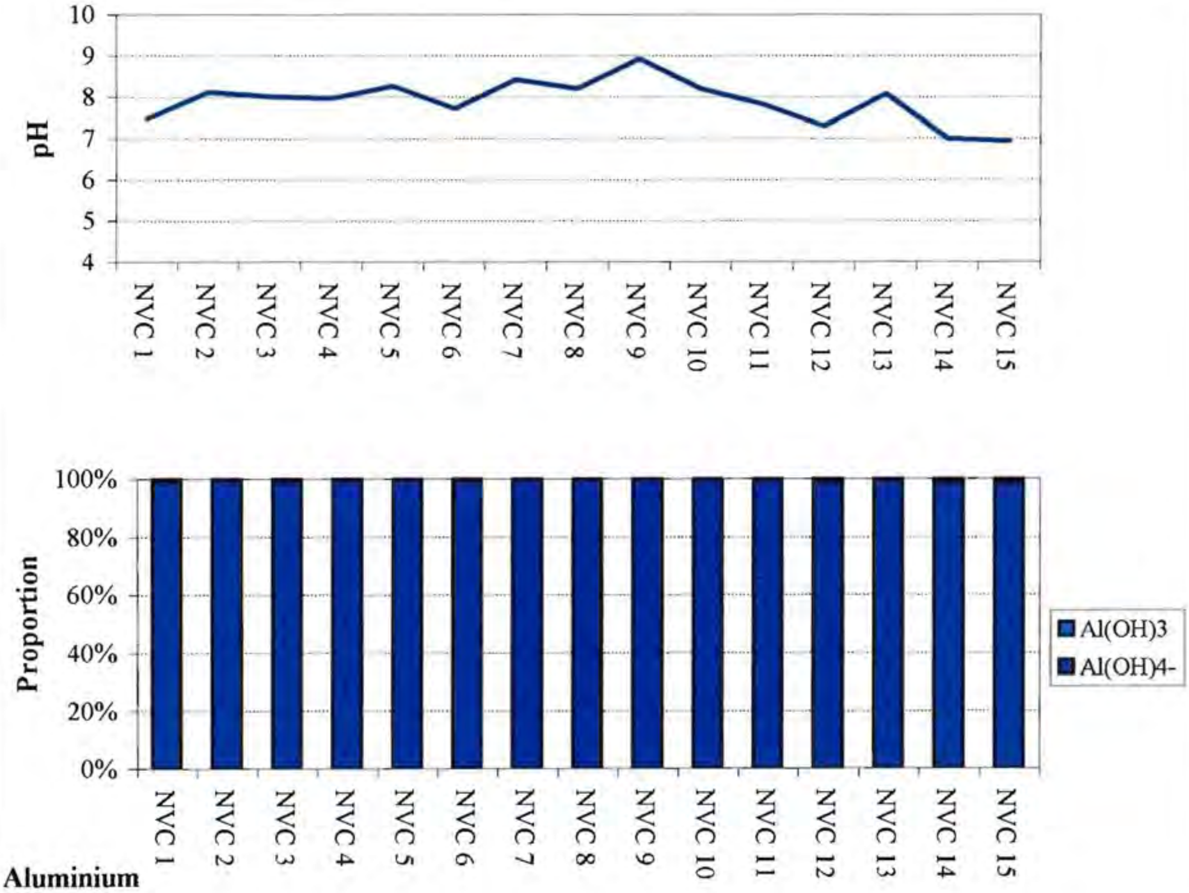
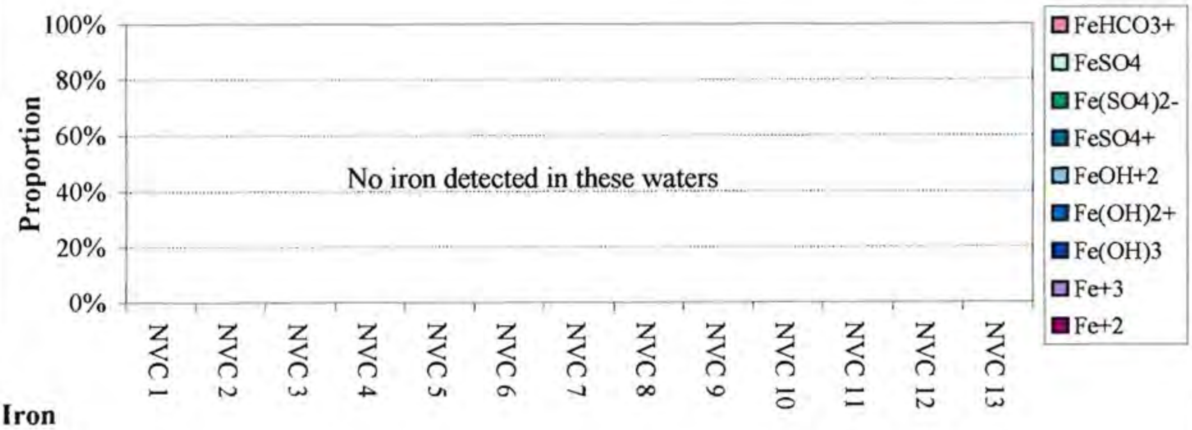


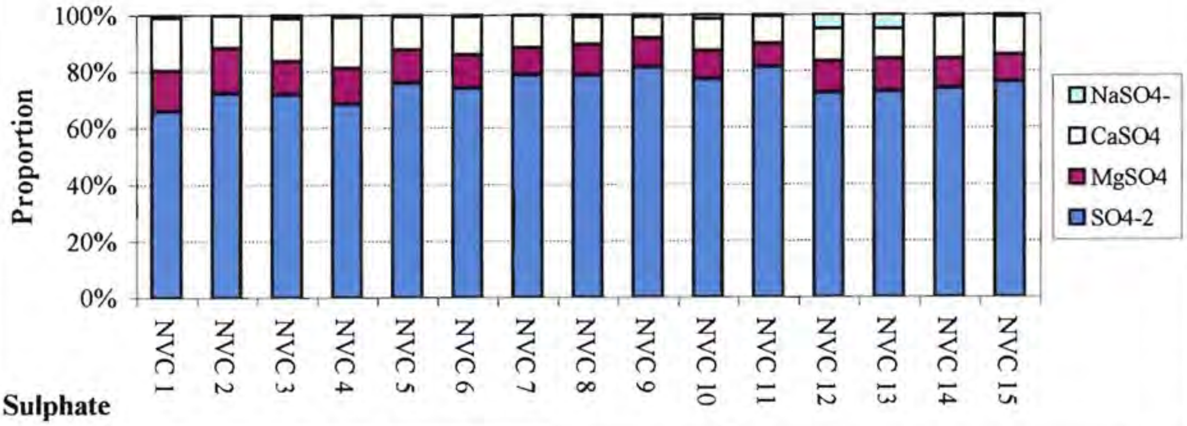
Figure A3.2: Speciation of selected ions in waters from New Vaal colliery.



Aluminium



Iron



Sulphate

Figure A3.3: *Speciation of selected ions in waters from New Largo colliery.*

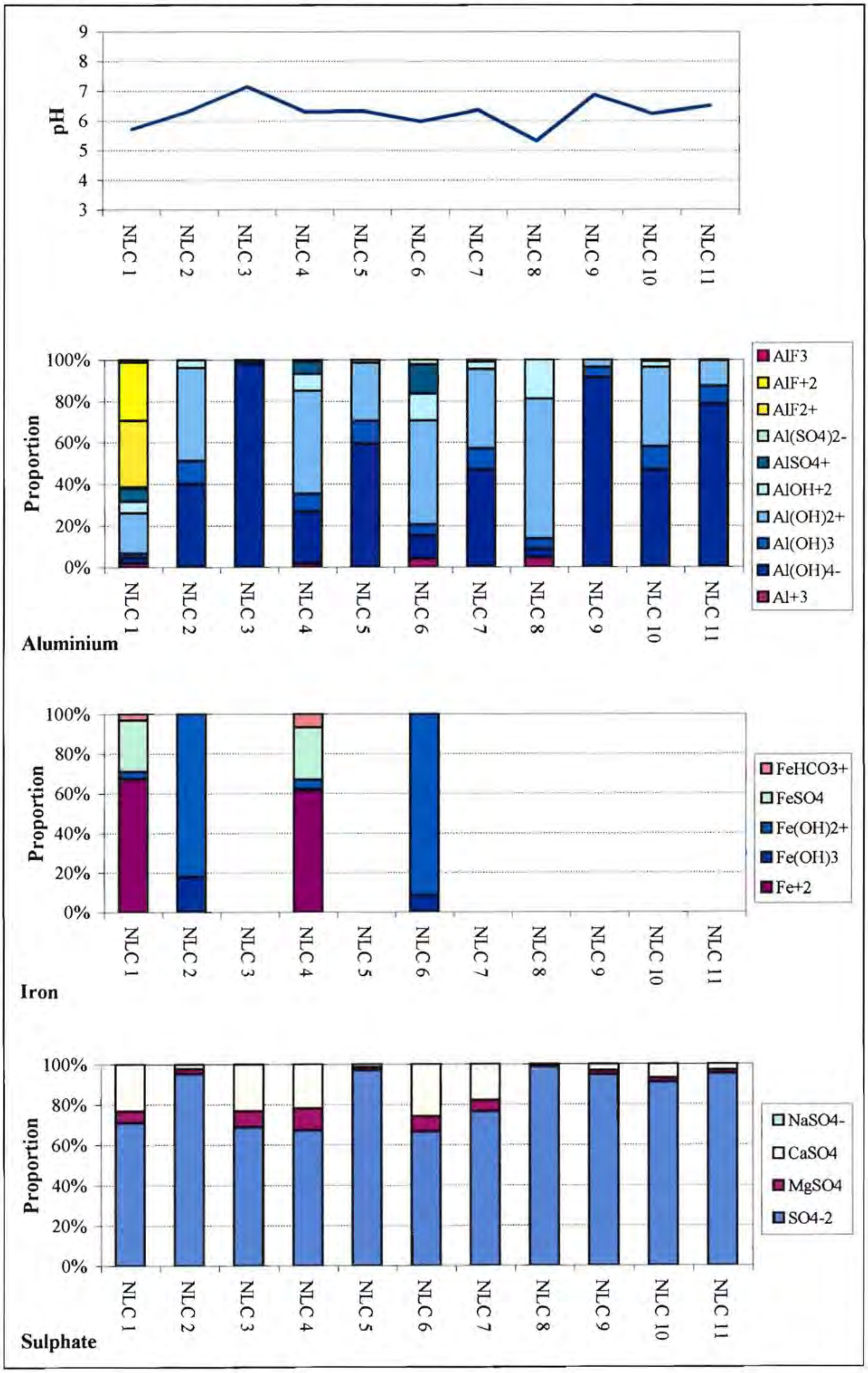


Figure A3.4: *Speciation of selected ions in waters from Kriel colliery.*

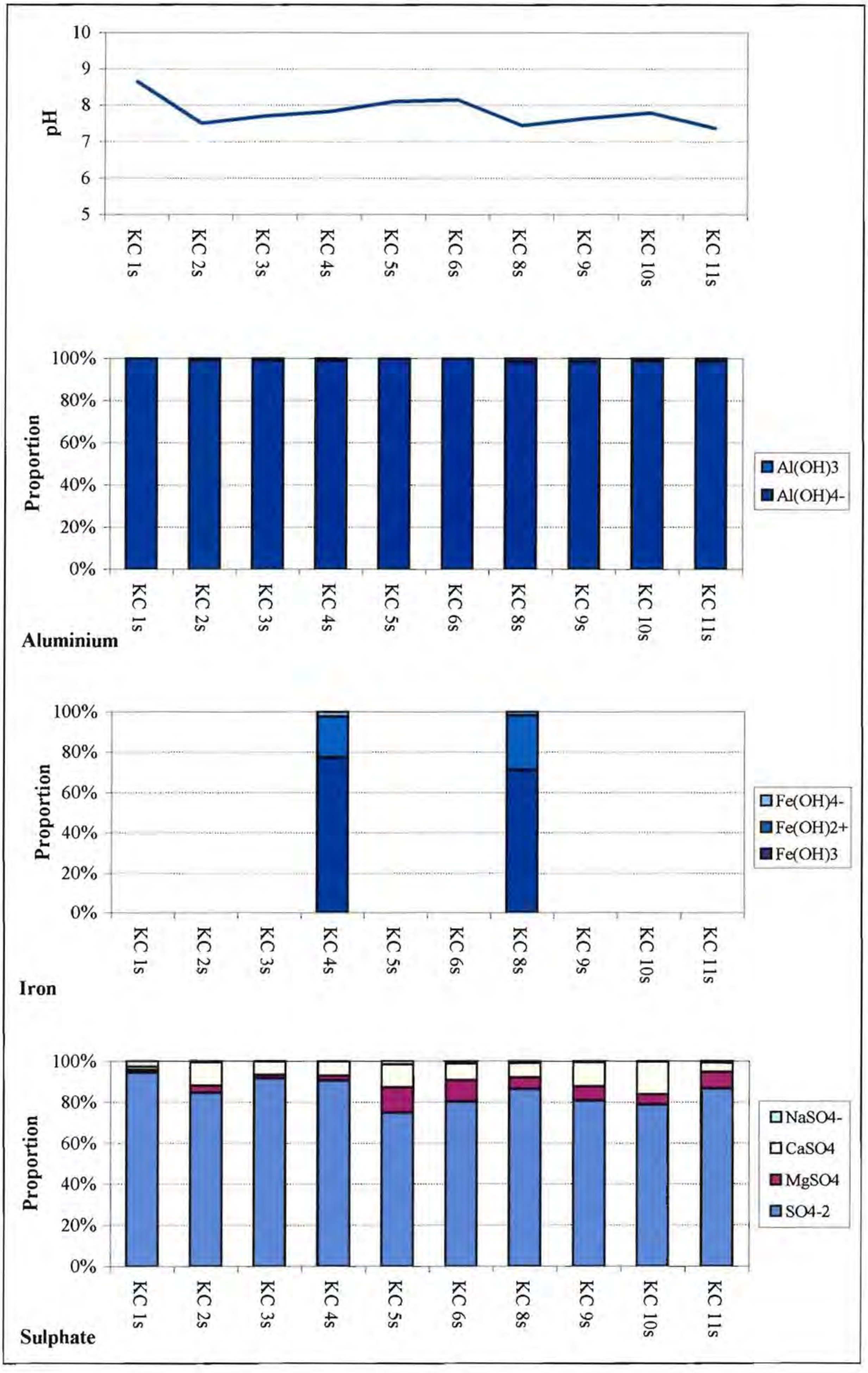


Figure A3.5: Speciation of selected ions in waters from New Denmark colliery.

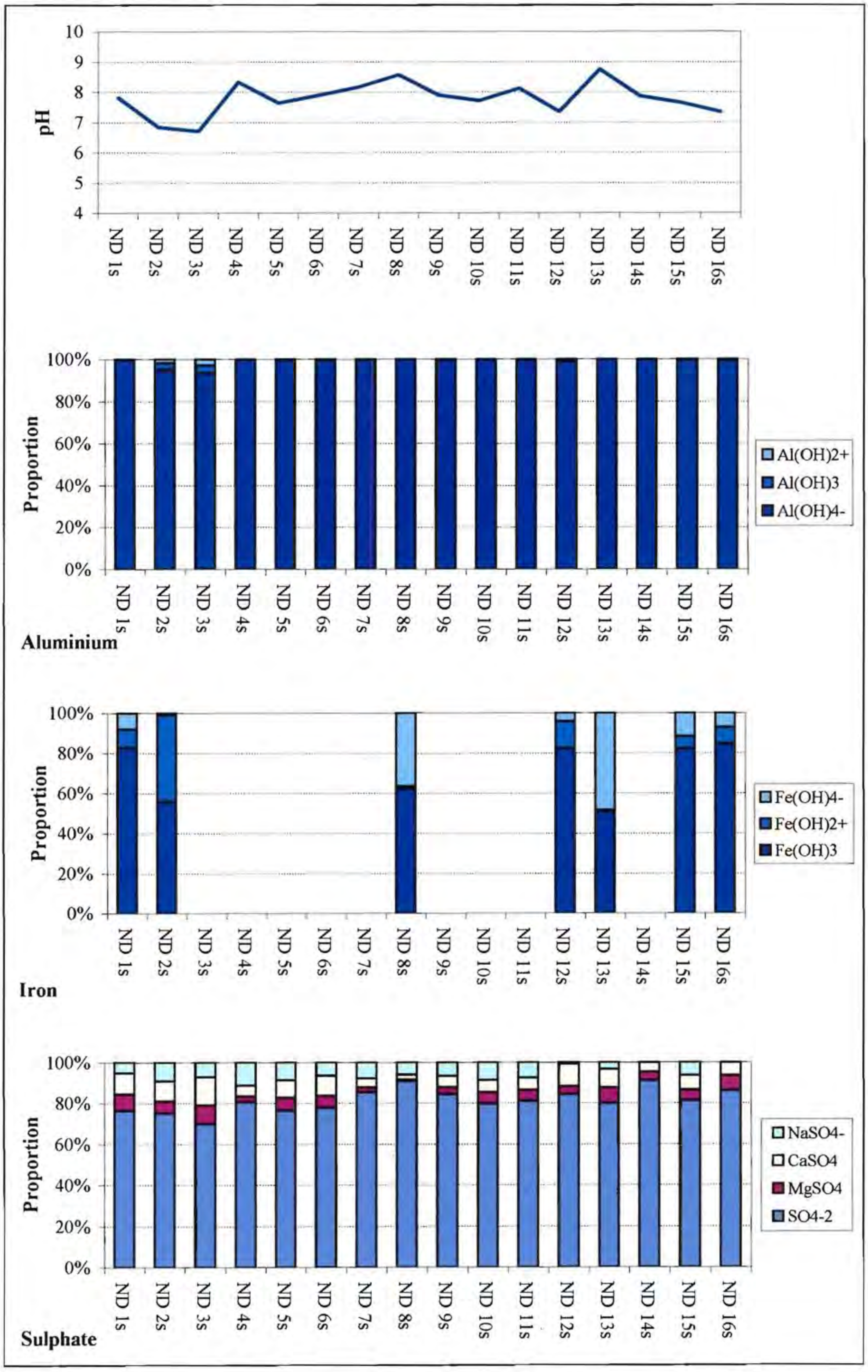
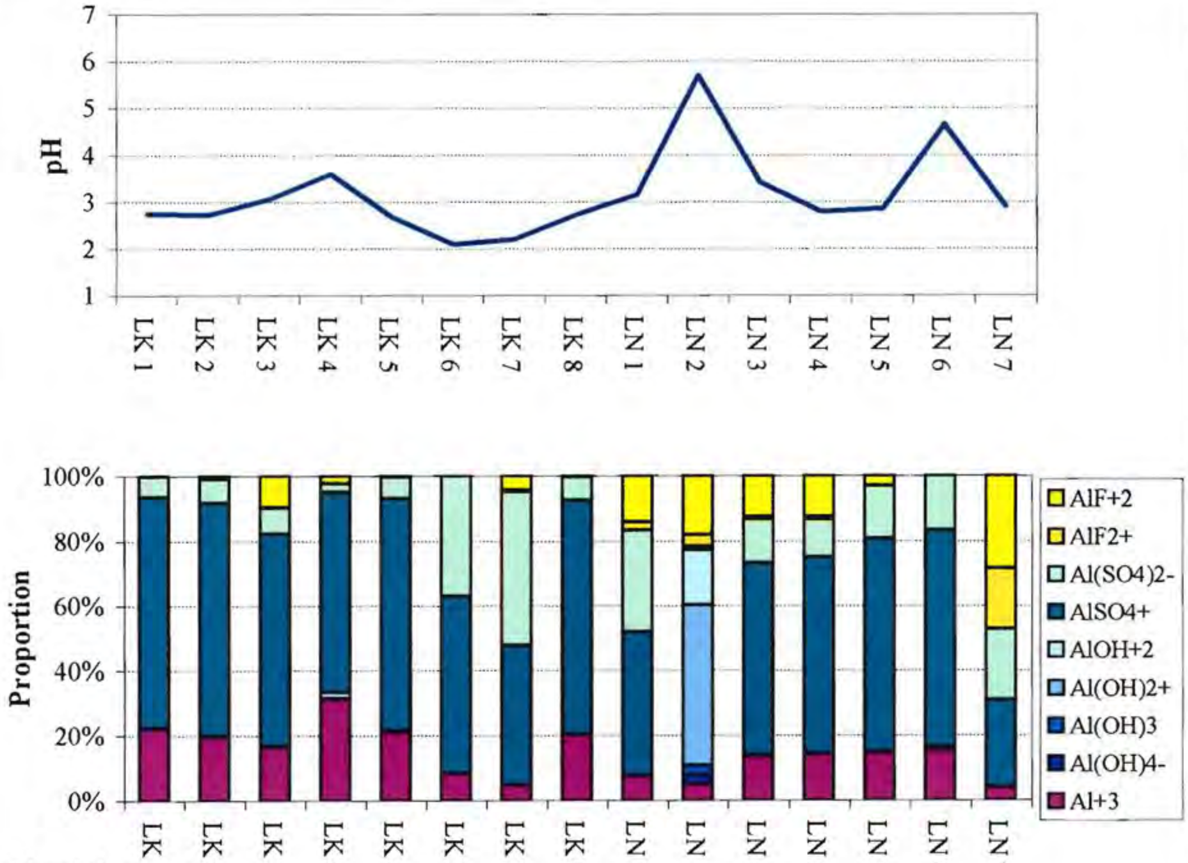
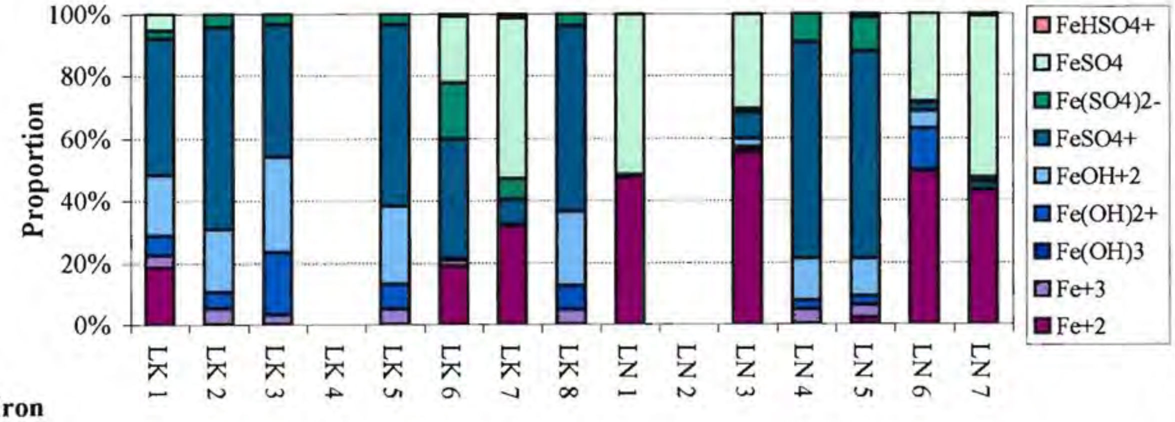


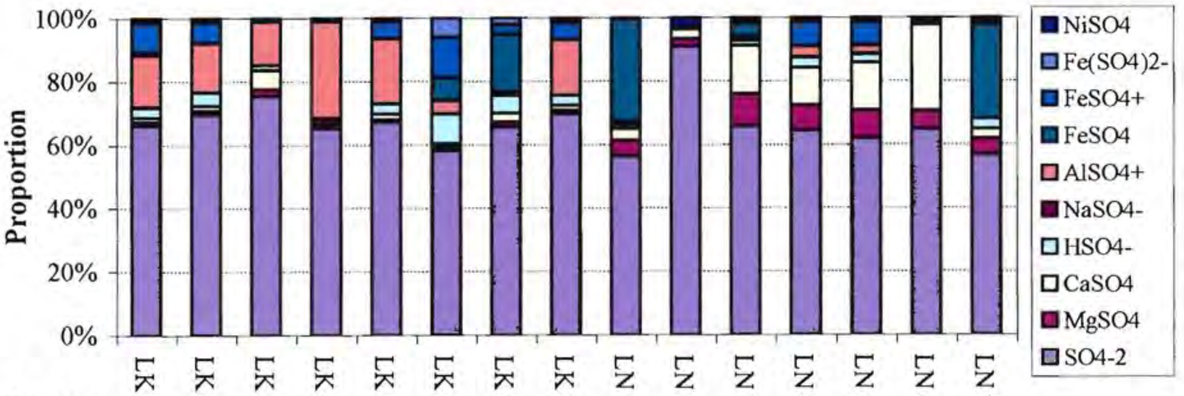
Figure A3.6: Speciation of selected ions in waters from Landau colliery.



Aluminium



Iron



Sulphate

Figure A3.7: *Speciation of selected ions in waters from TNDBC.*

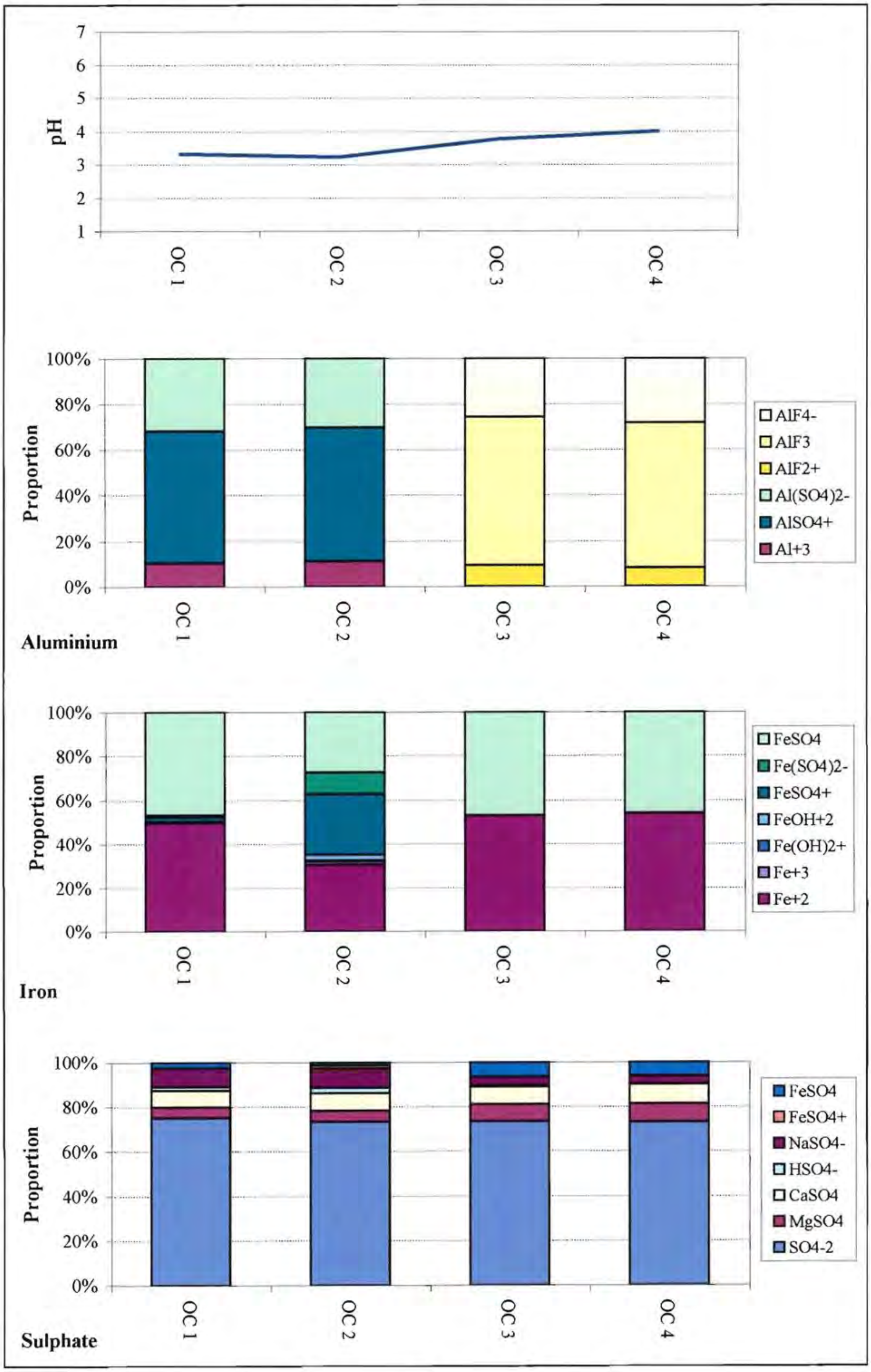
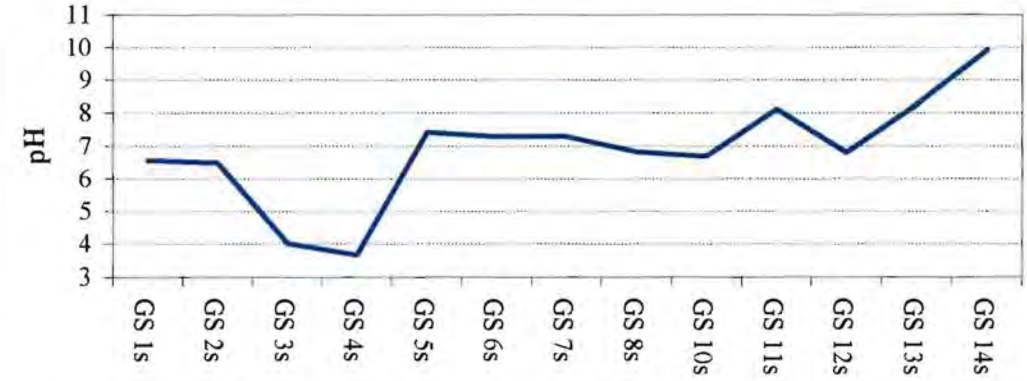
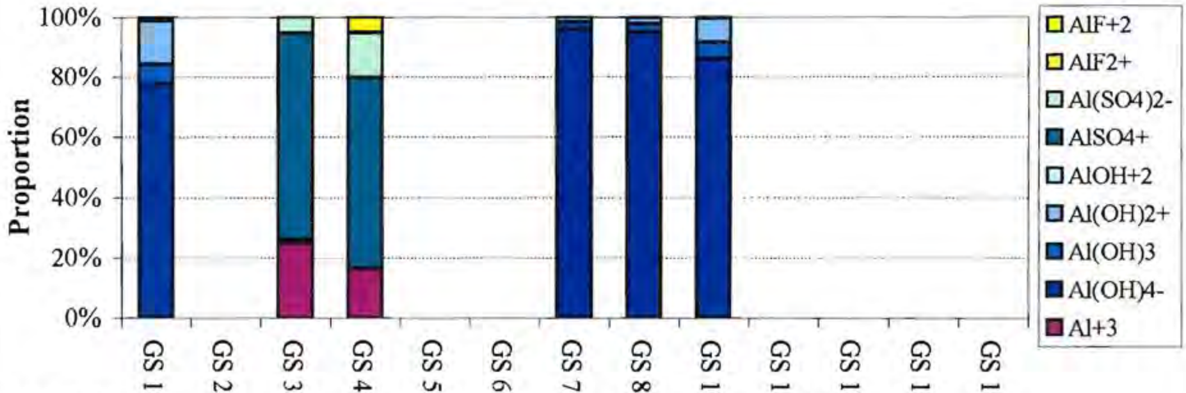
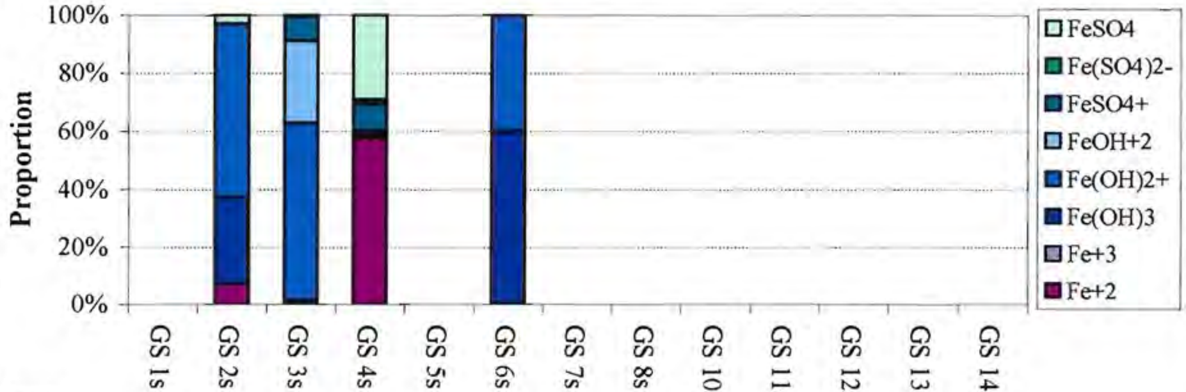


Figure A3.8: *Speciation of selected ions in waters from Greenside colliery.*

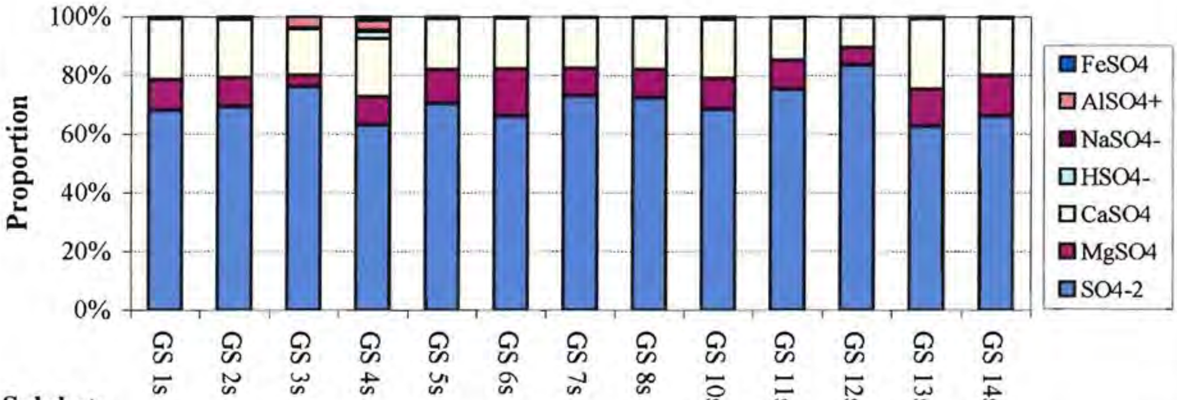




Aluminium



Iron



Sulphate

Figure A3.9: Speciation of selected ions in waters from Kleinkopje colliery.

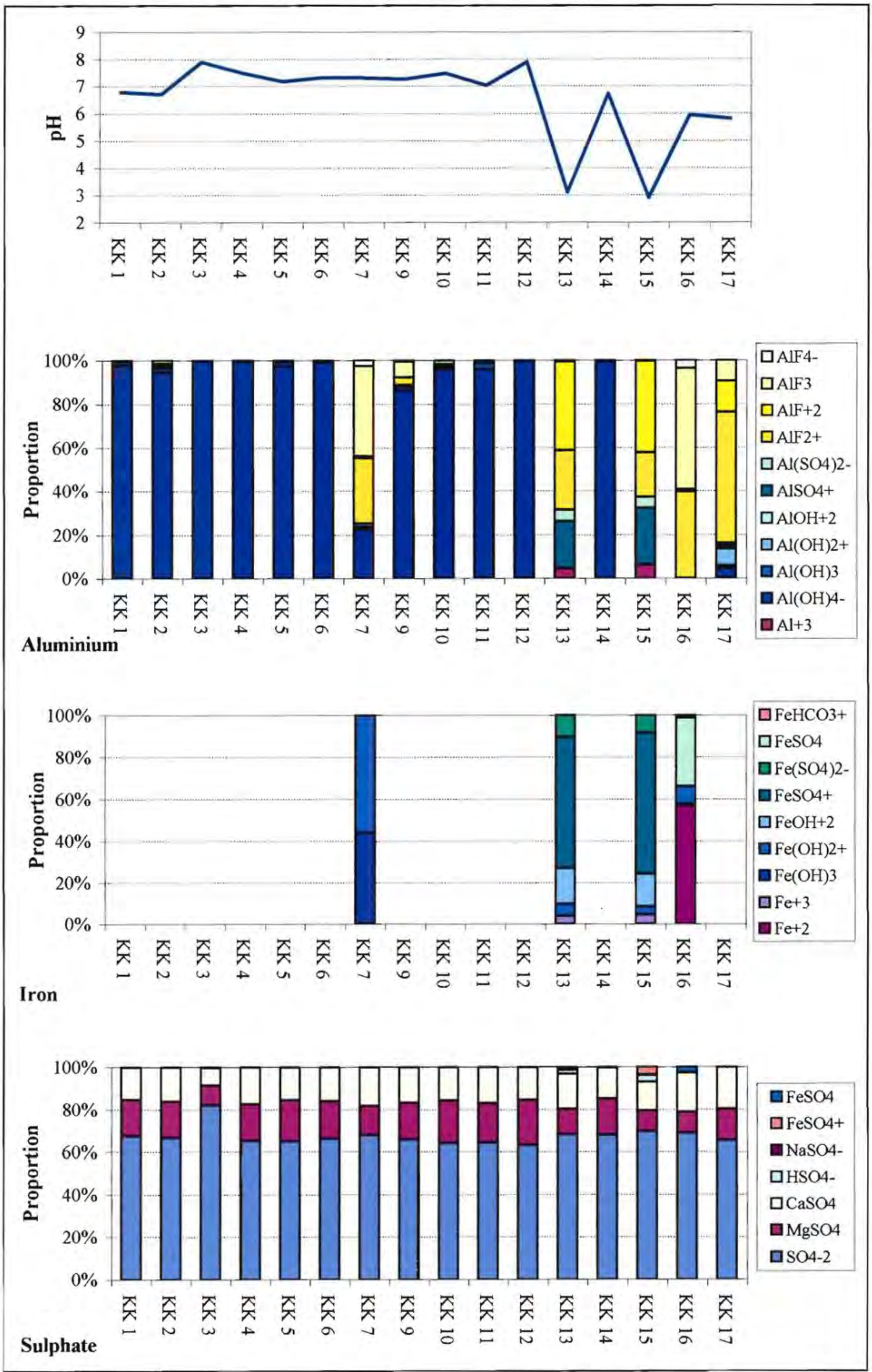


Figure A3.10: Speciation of selected ions in waters from Goedehoop colliery.

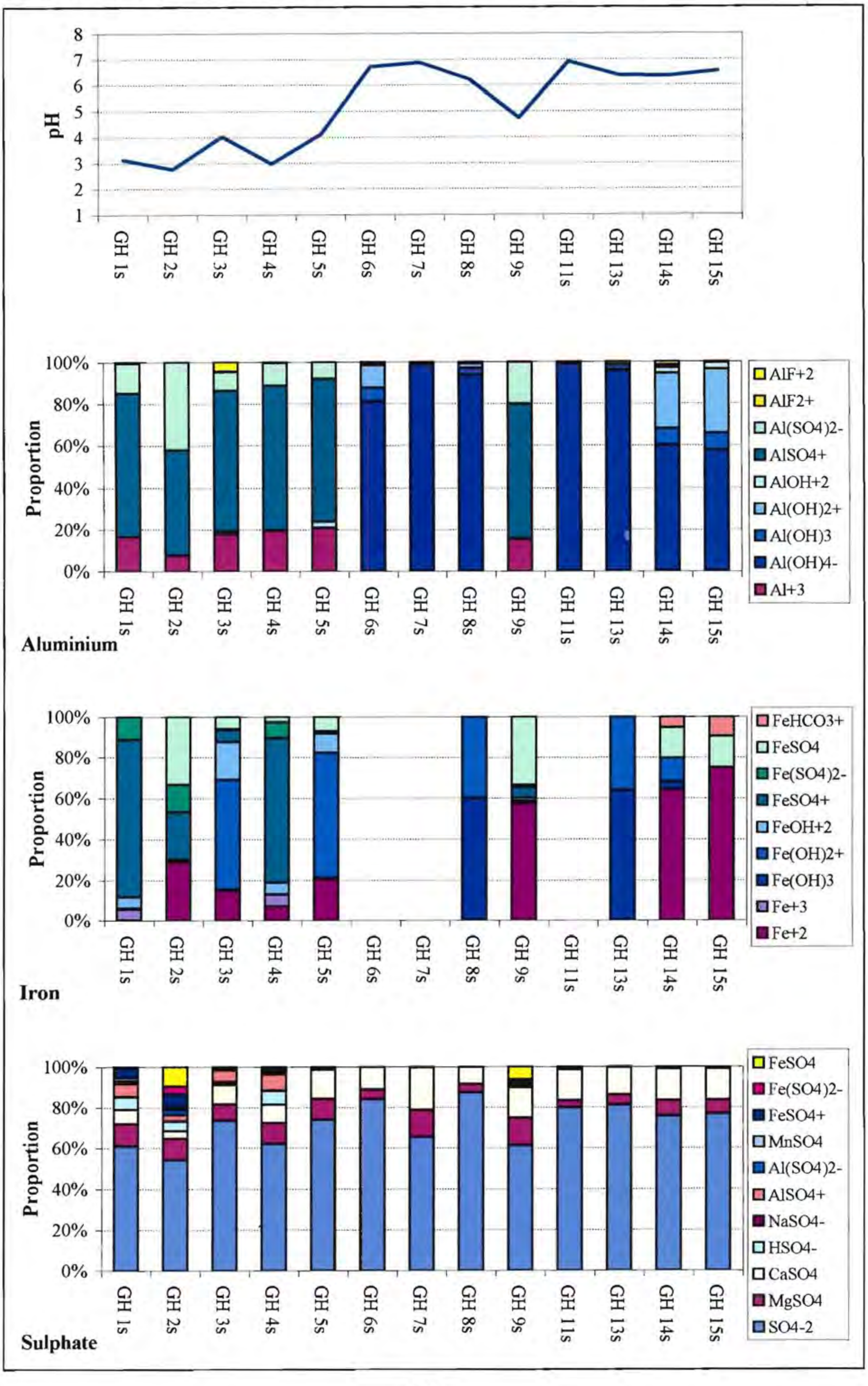


Figure A3.10 cont.: *Speciation of selected ions in waters from Goedehoop colliery.*

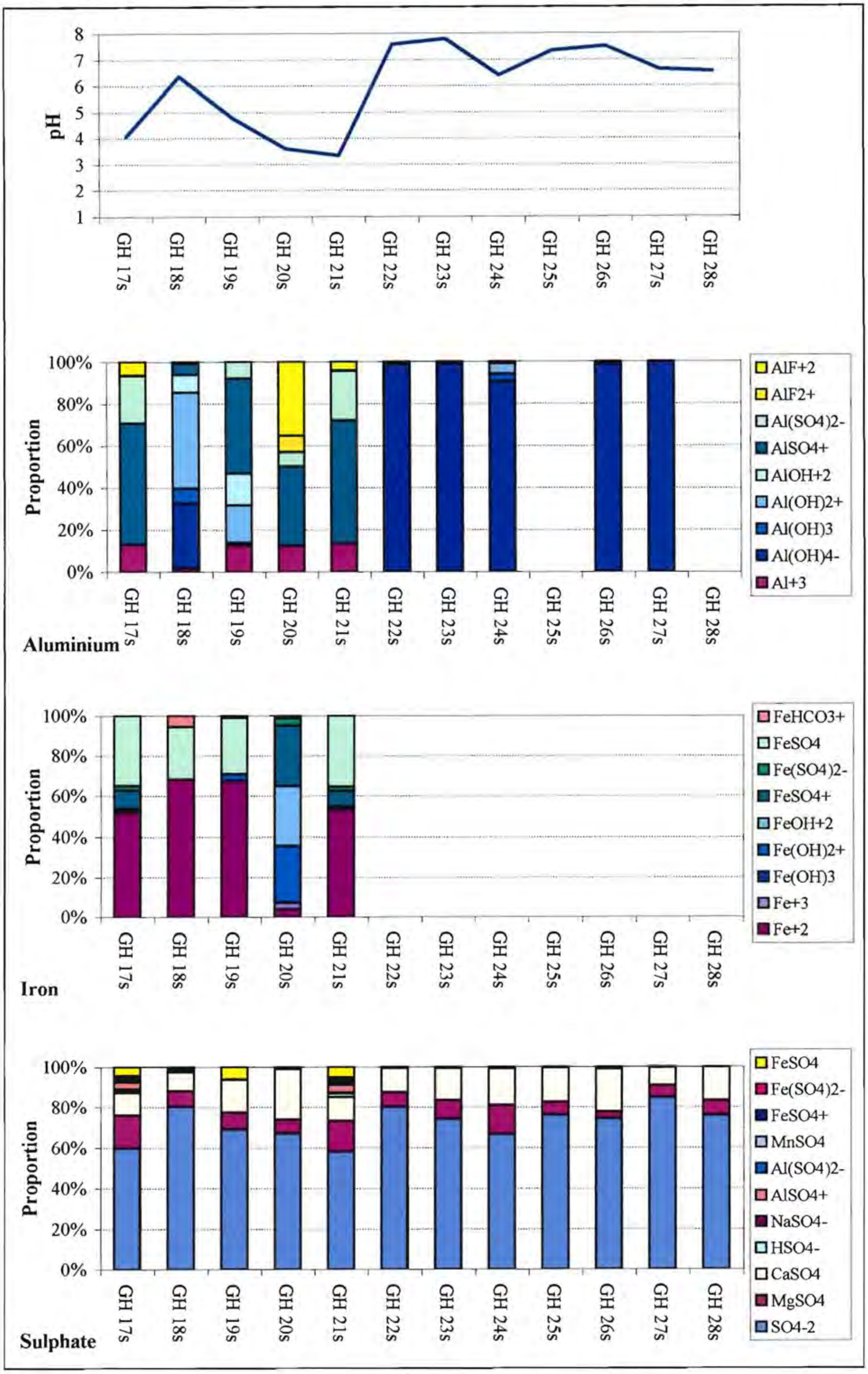


Figure A3.11: Speciation of selected ions in waters from Bank colliery.

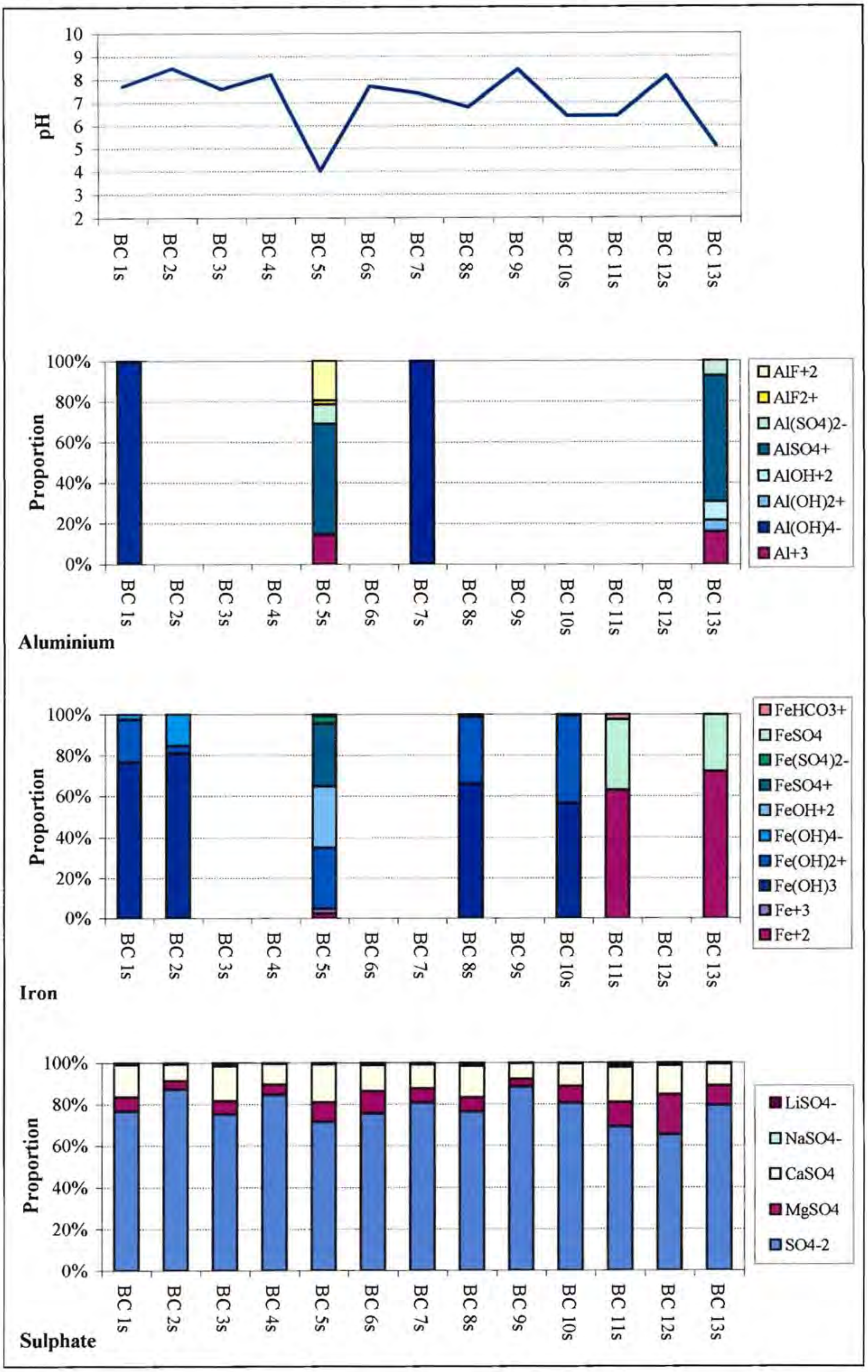


Figure A3.12: *Speciation of selection ions in waters from Arnot colliery.*

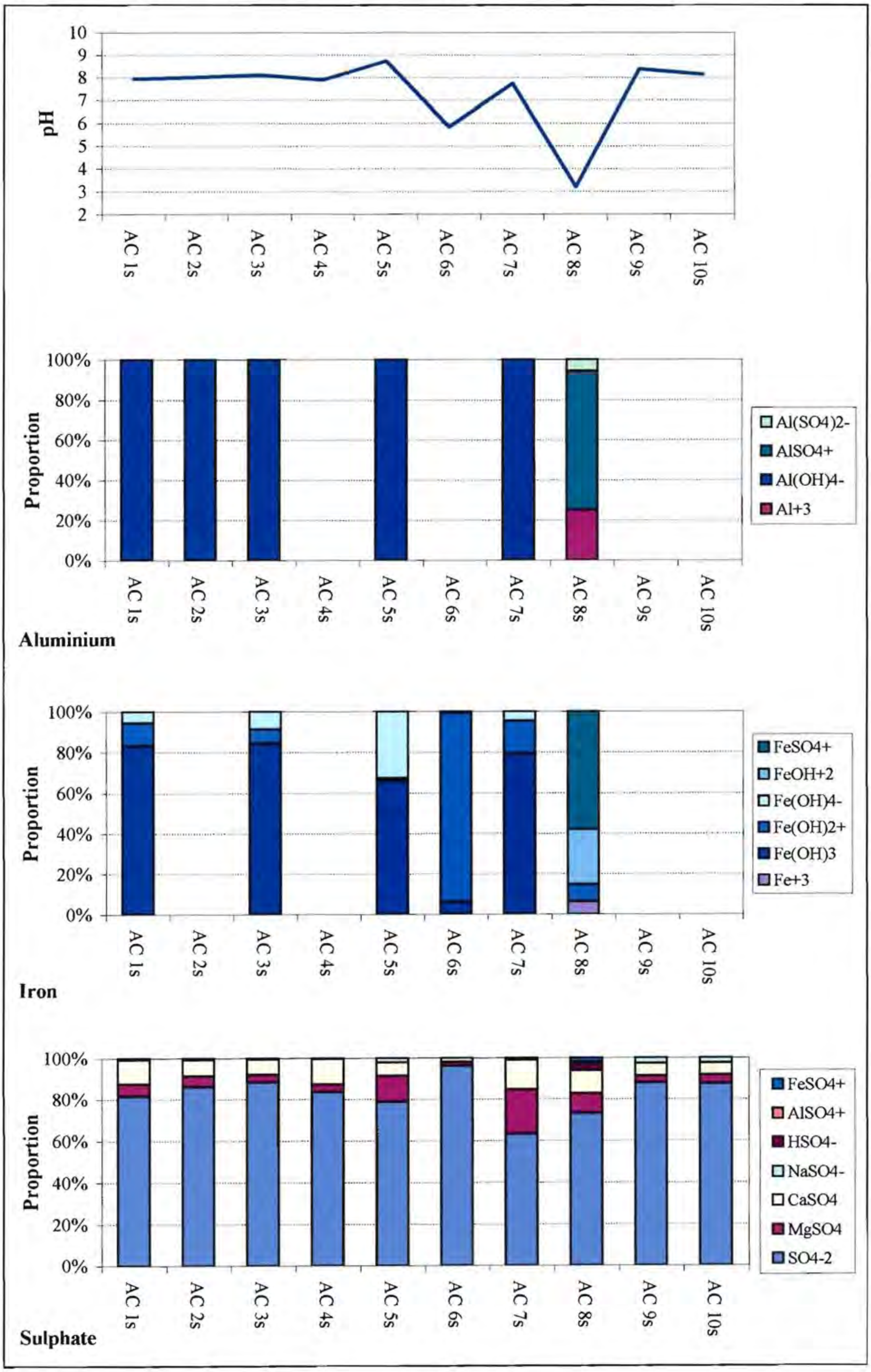
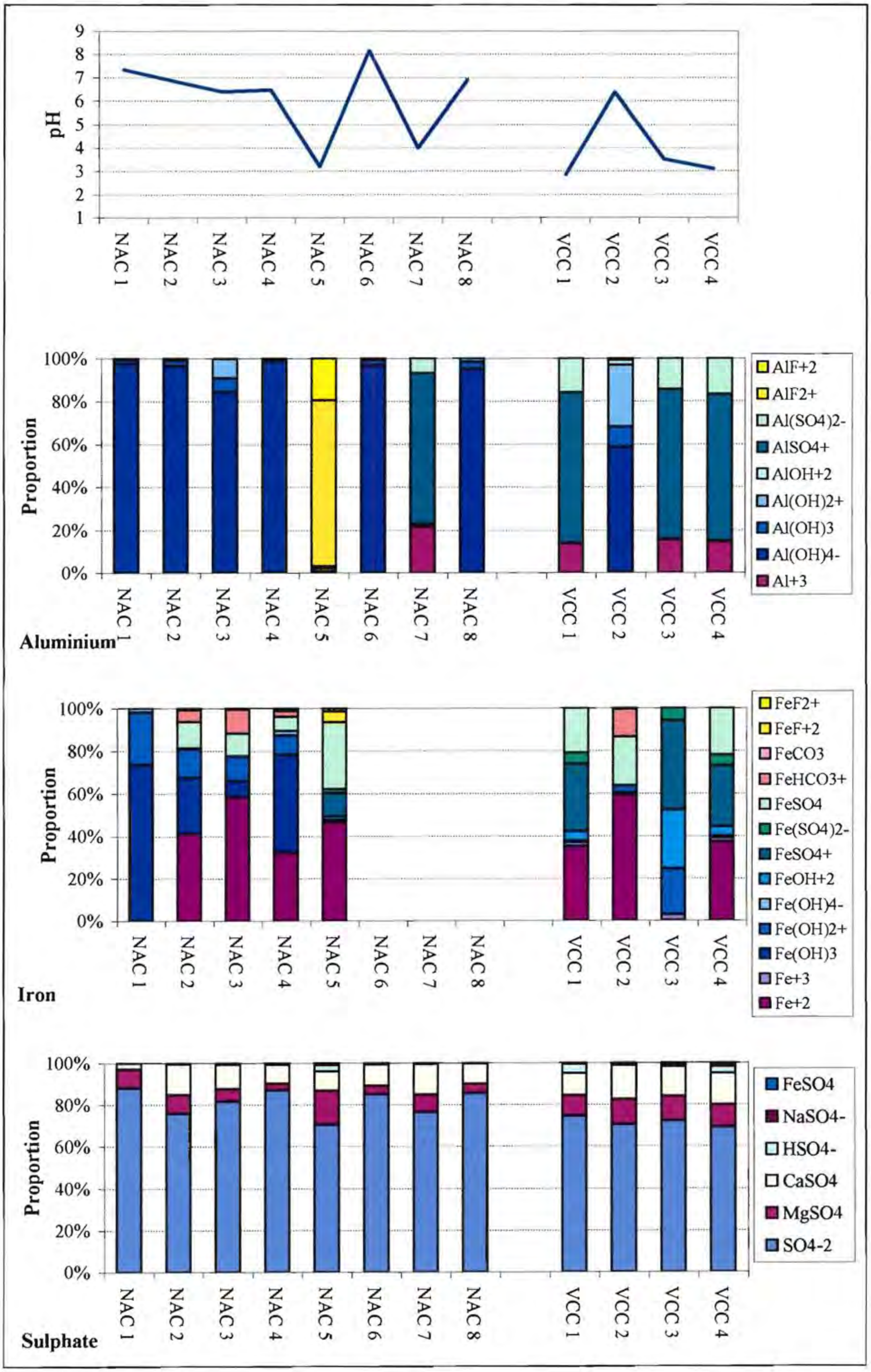


Figure A3.13: *Speciation of selected ions in waters from NAC and VCC.*



APPENDIX 4

Borehole logs

COLLIERY: KRIEL (KRL)
LOCATION: –
BOREHOLE NUMBER: KRL 3710
CO-ORDINATES: X: -15 603 Y: 2 908 891
SURFACE ELEVATION: 1592.39m

SAMPLE	DEPTH (m)	INTERVAL (m)	LITHOLOGY
	0.00		
	5.10	5.10	No recovery
L	10.57	5.47	Medium-grained, brownish-white sandstone. Highly weathered
K	11.90	1.33	Black shale
	12.56	0.66	Interlaminated sandstone and shale. Medium weathered
J	13.65	1.09	Interlaminated / interbedded sandstone / shale
I	19.87	6.22	Medium to coarse-grained sandstone with occasional shale laminae, oxidized.
	20.00	0.13	Interlaminated shale / sandstone
	20.18	0.18	Medium-grained, grey sandstone
	20.97	0.79	Interbedded shale / sandstone
H	21.39	0.42	Grey sandstone with silty laminae
	24.17	2.23	Coal: 5 seam
	24.20	0.03	Black shale
	24.25	0.05	Coal
	24.28	0.03	Black shale
	24.34	0.06	Coal
G	25.69	1.35	Shale with sandy laminae and beds
F	32.82	7.13	Medium-grained, grey sandstone
E	39.43	6.61	Interlaminated / interbedded shale / sandstone
D	40.43	1.00	Fine-grained, grey, silty sandstone
C	44.41	3.98	Medium-grained, grey sandstone
	44.57	0.16	50% coal, 25% sandstone and 25% grit
	44.68	0.11	Grey, silty sandstone
	44.82	0.14	Black shale. Coaly at the top
B	46.10	1.28	Interlaminated, gritty sandstone / shale
	46.53	0.34	Dark-grey shale with sandy laminae
	46.59	0.04	White grit
A	48.03	1.44	Interlaminated sandstone / shale
	48.39	0.36	Black shale. Sandy and gritty
	48.71	0.32	Interlaminated shale / sandstone
	48.82	0.11	Coarse-grained glauconitic sandstone with coaly bands
	55.13	6.31	Coal: 4 seam
	55.48	0.35	Medium-grained, grey sandstone. Silty at top

COLLIERY: KRIEL (KRL)
LOCATION: 4 seam coal
BOREHOLE NUMBER: BH 3449
CO-ORDINATES: X: – Y: –

SAMPLE	DEPTH (m)	INTERVAL (m)	LITHOLOGY
1	77.84 – 78.99	1.15	Roof siltstone / sandstone
2	78.99 – 79.20		S4R: Coaly shale with occasional glauconitic sandstone lenses
3_A	79.20 –		S4R: Bright coal
3_B	79.52		S4R: Black coaly to carbonaceous shale
4	80.11 – 80.46	5.63	S4T: Massive lustrous to dull coal
5	83.62 – 83.78		S4M: Thickly banded bright and lustrous coal. Abundant siderite nodules in bright zones. Pyrite nodules. Calcite on cleats.

COLLIERY: GOEDEHOOP (GHC)
LOCATION: Hope 200 Area
BOREHOLE NUMBER: GHC 0859 (Temporary. No. I-12)
CO-ORDINATES: X: -45 082 Y: 2 892 852
SURFACE ELEVATION: 1590,48m

SAMPLE	DEPTH (m)	INTERVAL (m)	LITHOLOGY
	0.00		
	1.00	1.00	Orange-brown soil
	7.80	6.80	No recovery
A	8.81	1.01	Dark grey shale. Slips 30° closely spaced between 8.40 and 8.81m.
	10.00	1.19	Coal: 4 seam
B	10.16	0.16	Coaly shale
	11.91	1.73	Coal: 4 seam. Calcite on cleats. Pyrite nodules
	12.02	0.11	Grey, highly micaceous siltstone
C	12.54	0.52	Grey, fine-grained sandstone with irregular basal contact
D	13.14	0.60	White, fine-grained sandstone with irregular basal contact
E	32.41	19.27	Medium-grained, gritty sandstone with occasional silty laminae. Shale bed from 32.21 – 32.40m
F	37.67	5.26	Black shale. Slip 45° at 35.51m
G	39.78	2.11	Sandy, streaky, bioturbated shale
H	41.08	1.30	Black shale
I	46.89	5.81	Coal: 2 seam
	46.95	0.06	Grit
J	47.46	0.51	Black shale. 4cm grit to 47.03m
K	50.50	3.04	Interbedded shale / grit (40% / 60%)

COLLIERY: NEW DENMARK (ND)
LOCATION: -
BOREHOLE NUMBER: BH 3218
CO-ORDINATES: X: -39 135.0 Y: 2 955 386.0
SURFACE ELEVATION: 1635.22m

SAMPLE	DEPTH (m)	INTERVAL (m)	LITHOLOGY
	0.00		
	3.70	3.70	No recovery
	16.40	12.70	Yellowish-cream, micaceous siltstone. Muddy, friable and highly weathered.
	21.15	4.75	Yellowish-grey, micaceous siltstone. Muddy, friable and moderately weathered.
	30.60	9.45	Dark blackish-grey, micaceous siltstone. Carbonaceous and fissile.
	33.60	3.00	Whitish-green, medium-grained sandstone. Indurated.
	83.76	50.16	Greenish-grey, medium crystalline, non-porphyritic dolerite. Clayey on joints. Horizontal contact at top. Jointed.
	83.83	0.07	Coarse to medium-grained sandstone. Indurated.
	122.32	38.49	Dark greenish-grey, finely crystalline, non-porphyritic dolerite. Clayey on joints. Sandy fragments at bottom. Irregular contact at bottom. Few joints.
	125.42	3.10	Greenish brown, coarse to medium-grained sandstone. Thinly laminated, micaceous and indurated.
	131.69	6.27	60% Dark grey, coarse to medium-grained sandstone. Interlaminated, micaceous and interbedded. 40% Black siltstone. Interlaminated, carbonaceous and micaceous.
	133.54	1.85	Brownish-grey, coarse-grained sandstone. Micaceous with few carbonaceous lenses.
	144.52	10.98	Dark grey siltstone / sandstone. Bioturbated, micaceous, thinly laminated.
	144.71	0.19	Light grey, coarse to medium-grained sandstone. Bioturbated and micaceous.
A	152.92	8.21	Black siltstone with sandy laminae. Carbonaceous, micaceous and bioturbated.
B	157.71	4.79	Greyish-white coarse to medium-grained sandstone. Few carbonaceous lenses. Pebbly zone (156.78 – 156.96m).
C	165.35	7.64	Black and grey banded, medium to fine-grained sandstone with silty lenses. Interbedded, micaceous and interlaminated.
	175.02	9.67	Greyish-white, coarse to medium-grained sandstone. Micaceous with few carbonaceous lenses.
	180.72	5.70	Greyish-white, coarse-grained sandstone. Massive.
	181.58	0.86	Greyish-white, coarse-grained sandstone with wavy carbonaceous lenses. Gritty.
	189.75	8.17	Black and grey banded, coarse to medium-grained sandstone. Micaceous. Silty and bioturbated at the bottom.

SAMPLE	DEPTH (m)	INTERVAL (m)	LITHOLOGY
D	203.93	14.18	Greyish-white, coarse to medium-grained sandstone. Massive.
	209.16	5.23	Light grey, medium-grained interlaminated sandstone. Thinly laminated, micaceous and silty.
	230.52	21.36	Greyish-white, coarse to medium-grained sandstone. Thinly laminated in places.
E	240.20	9.68	Dark blackish-grey, thinly laminated siltstone / sandstone. Micaceous. Carbonaceous.
	242.40	2.20	Dark grey sandstone / siltstone. Micaceous. Bioturbated.
	242.60	0.20	Brownish-grey, fine-grained sandstone. Micaceous. Glauconitic.
	242.75	0.15	Green, coarse to medium-grained sandstone. Micaceous. Glauconitic.
	247.30	4.55	Light grey, medium-grained sandstone. Massive. Micaceous.
	247.46	0.16	Interlaminated siltstone / sandstone. Micaceous and thinly laminated.
	247.62	0.16	Greyish-white, coarse-grained sandstone. Few carbonaceous lenses.
	247.68	0.06	Coal
	249.65	1.97	Light grey,medium-grained silty sandstone. Thinly laminated and micaceous.
F	269.60	19.95	Greyish-white, coarse-grained sandstone. Massive. Pebbly and gritty zones in places.
	269.93	0.33	Brownish-grey, coarse to medium-grained sandstone. Highly micaceous. Slickensided at bottom.
G	271.39	1.46	Coal: 4 Seam. Mixed dull with few bright streaks. Silty.
	271.43	0.04	Coal: 4 Seam. Lustrous, laminated with bright streaks. Calcite on cleats.
	271.57	0.14	Brown siltstone. Highly micaceous.
	271.98	0.41	Light brown, fine-grained sandstone. Highly micaceous. Silty.
	275.79	3.81	Whitish-grey, fine-grained sandstone. Bioturbated. Micaceous.
	276.13	0.34	Coal: 3 Seam. Bright, laminated with bright streaks. Calcite on cleats.
	276.31	0.18	Dark blackish-grey, fine-grained sandstone. Silty. Micaceous.
	277.33	1.02	Light brownish-white, medium-grained sandstone. Micaceous.

COLLIERY: NEW DENMARK (ND)
LOCATION: -
BOREHOLE NUMBER: Surface Directional No. 10
CO-ORDINATES: X: Unknown Y: Unknown
SURFACE ELEVATION: Unknown

SAMPLE	DEPTH (m)	INTERVAL (m)	LITHOLOGY
	0.00		
1	162.18	162.18	Greenish-grey dolerite. Medium crystalline.
	166.26	4.08	Coarse-grained sandstone.
	173.50	7.24	Medium-grained siltstone / sandstone. Bioturbated, silty and micaceous.
	177.05	3.55	Coarse-grained sandstone.
	190.50	13.45	Dark grey siltstone. Bioturbated and sandy.
	209.90	19.40	Siltstone
	219.00	9.10	Sandstone
	225.50	6.50	White coarse-grained sandstone.
	228.10	2.60	Sandstone
	249.50	21.40	Coarse to medium-grained sandstone. Thinly laminated and micaceous.
	251.60	2.10	60% Sandstone / 40% Siltstone. Interbedded. Thinly laminated.
	254.30	2.70	Greyish-white sandstone
	255.10	0.80	Siltstone / sandstone ?
2	285.50	30.40	Interlaminated siltstone / sandstone. Micaceous.
	299.38	13.88	Sandstone. Bioturbated.
	303.78	4.40	White sandstone
	312.35	8.57	Interlaminated siltstone / sandstone. Micaceous.
	314.60	2.25	Light grey, thinly laminated sandstone / siltstone. Micaceous.
	321.45	6.85	Interlaminated siltstone / sandstone
	341.30	19.85	Speckled greenish-white, coarse-grained sandstone. Glauconitic.
	349.95	8.65	White coarse-grained sandstone
	627.60	277.65	Greyish-white, coarse to medium-grained sandstone. Laminated. Micaceous.
	630.55	2.95	Black, carbonaceous siltstone. Laminated. Micaceous.
	632.65	2.10	Whitish-cream, fine-grained sandstone. Micaceous.
	634.05	1.40	Brownish-black, fine-grained sandstone. Micaceous.
	648.90	14.85	Whitish-grey, medium-grained sandstone. Micaceous.
	664.10	15.20	Whitish-grey coarse to medium-grained sandstone. Micaceous. Silty bands in places
3	665.90	1.80	Light greenish-grey dolerite. Finely crystalline. Calcite spotted. Inclined contacts.
	670.20	4.30	Whitish-grey, coarse to medium-grained sandstone. Micaceous.
	680.00	9.80	Whitish-red, coarse to medium-grained sandstone. Micaceous. Oxidized.
	732.10	52.10	Greyish-white, coarse to medium-grained sandstone. Massive. Gritty in places with few silty bands
	732.75	0.65	Coal

SAMPLE	DEPTH (m)	INTERVAL (m)	LITHOLOGY
	772.10	39.35	Greyish-white, coarse to medium-grained sandstone. Micaceous.
	799.55	26.80	Coarse-grained sandstone. Gritty, Pebbles. Micaceous.
4	1036.90	237.35	Greyish-white, coarse to medium-grained sandstone. Micaceous. Gritty. Silty lenses and bands in places.
	1045.55	8.10	Interbedded black and grey sandstone / siltstone. Interlaminated. Micaceous.
	1060.25	15.25	Greyish-white, medium-grained sandstone. Silty. Micaceous.
	1124.10	45.51	Light grey, medium-grained sandstone. Interlaminated. Micaceous.
	1147.80	23.70	Black and grey interlaminated sandstone / siltstone. Thinly laminated. Micaceous
5	1179.95	55.85	Black, carbonaceous siltstone. Micaceous. Sandy lenses and bands in places.
	1181.95	2.00	Whitish-cream, fine-grained sandstone. Interlaminated. Micaceous. Silty.
	1187.70	5.75	Whitish-grey, coarse-grained sandstone. Micaceous. Few silty lenses.
	1210.10	22.40	Brownish-grey sandstone / siltstone. Interlaminated. Micaceous.
	1210.75	0.65	Sandstone
	1248.20	37.45	70% Medium to fine-grained sandstone. Thinly laminated. Micaceous. Bioturbated. 30% Black siltstone. Carbonaceous. Bioturbated. Micaceous.
6	1250.65	2.45	Greenish-cream, medium to fine-grained sandstone. Glauconitic. Micaceous.
	1279.50	28.85	Greyish-white, coarse to medium-grained sandstone. Massive. Micaceous.
	1281.30	11.80	Light grey interbedded sandstone / siltstone. Interlaminated. Micaceous.
	1293.90	12.60	Dark grey siltstone / sandstone. Interlaminated. Micaceous.
	1301.20	7.30	Interbedded sandstone / siltstone. Interlaminated. Micaceous.
	1302.10	0.90	Black, carbonaceous siltstone. Micaceous.
	1308.25	6.15	Greyish-white, coarse-grained sandstone. Gritty. Silty bands in places.
	1334.70	26.45	Greyish-white, coarse to medium-grained Sandstone. Gritty. Few silty lenses
	1353.90	19.20	Brownish-grey, medium to fine-grained sandstone. Micaceous. Silty. Interlaminated.
	1424.45	70.55	Light brownish-white, coarse-grained sandstone. Gritty. Micaceous. Pebbles.
	1425.55	1.10	Brownish-grey, coarse-grained. Sandstone. Highly micaceous.
	1428.80	3.25	Coal: 4 Seam

COLLIERY: NEW VAAL (NVC)
LOCATION: Ramp 0
BOREHOLE NUMBER: 79 464
CO-ORDINATES: X: -95 573 Y: 2 956 662
SURFACE ELEVATION: 1432.0m

SAMPLE	DEPTH (m)	INTERVAL (m)	LITHOLOGY
	0.00		
1	7.65	7.65	Weathered sandstone
2	8.21	0.56	Medium to fine-grained, greyish-black micaceous shale. Moderately sorted. Dipping 65° to core axis at base.
	8.70	0.49	Medium to fine-grained, greyish-brown dolerite. Moderately sorted, strong rock. Dipping 88° at base.
3	12.23	3.63	Fine-grained, greyish-black carbonaceous shale / siltstone. Moderately sorted. Muscovite. Biotite.
4	13.15	0.92	Medium to fine-grained, greenish-green sandstone. Moderately sorted. Glauconitic band.
5	14.89	1.74	Medium to fine-grained, greyish-green sandstone interbedded with shale. Moderately sorted, Cross-bedded.
6	22.50	7.61	Fine-grained, greyish-black shale. Moderately sorted. Muscovite. Biotite. Pyritic.
	22.79	0.29	Medium to fine-grained, greyish-brown sandstone. Moderately sorted with mudstone bands.
7_B	23.04	0.25	Medium-grained, greenish-green sandstone. Moderately sorted. Glauconite layer.
7_A	23.97	0.93	Leader seam (Dull coal)
	24.12	0.15	Fine-grained, greyish sandstone. Moderately sorted with mudstone bands.
	24.35	0.23	Dull coal. Minor seam.
	24.48	0.13	Medium to fine-grained, brownish-brown mudstone. Shaly. Moderately sorted.
8	24.85	0.37	Fine-grained, greyish mud / sandstone. Moderately sorted.
9_A	29.80	4.95	Top Seam (T_1). Dull coal alternating with thick shaly / mudstone bands. Calcite lenses.
9_B	33.80	4.00	Top Seam (T_2). Dull coal alternating with very thin shaly / mudstone bands. Thin carbonate (siderite & calcite) layers. Calcite lenses and on cleats.
10	34.44	0.64	Medium to fine-grained, greyish siltstone. Moderately sorted. Muscovite.
11	41.60	7.16	Fine-grained, greyish-grey siltstone. Moderately sorted. Biotite. Bioturbated.
12	45.57	3.97	Medium to fine-grained, greyish-black carbonaceous shale. Moderately sorted.
	47.40	2.23	Middle seam. Dull, lustrous coal. Bright in places (<1%). Occasional pyrite lenses. Shaly bands.
	48.05	0.25	Brownish-brown mudstone. Shaly.
13	55.00	6.95	Middle seam. Dull, lustrous coal. Bright in places (<1%). Scattered pyrite lenses.
14	56.03	1.03	Coarse-grained greyish-white sandstone. Poorly sorted. Fining up with shale bands. Parting seam.

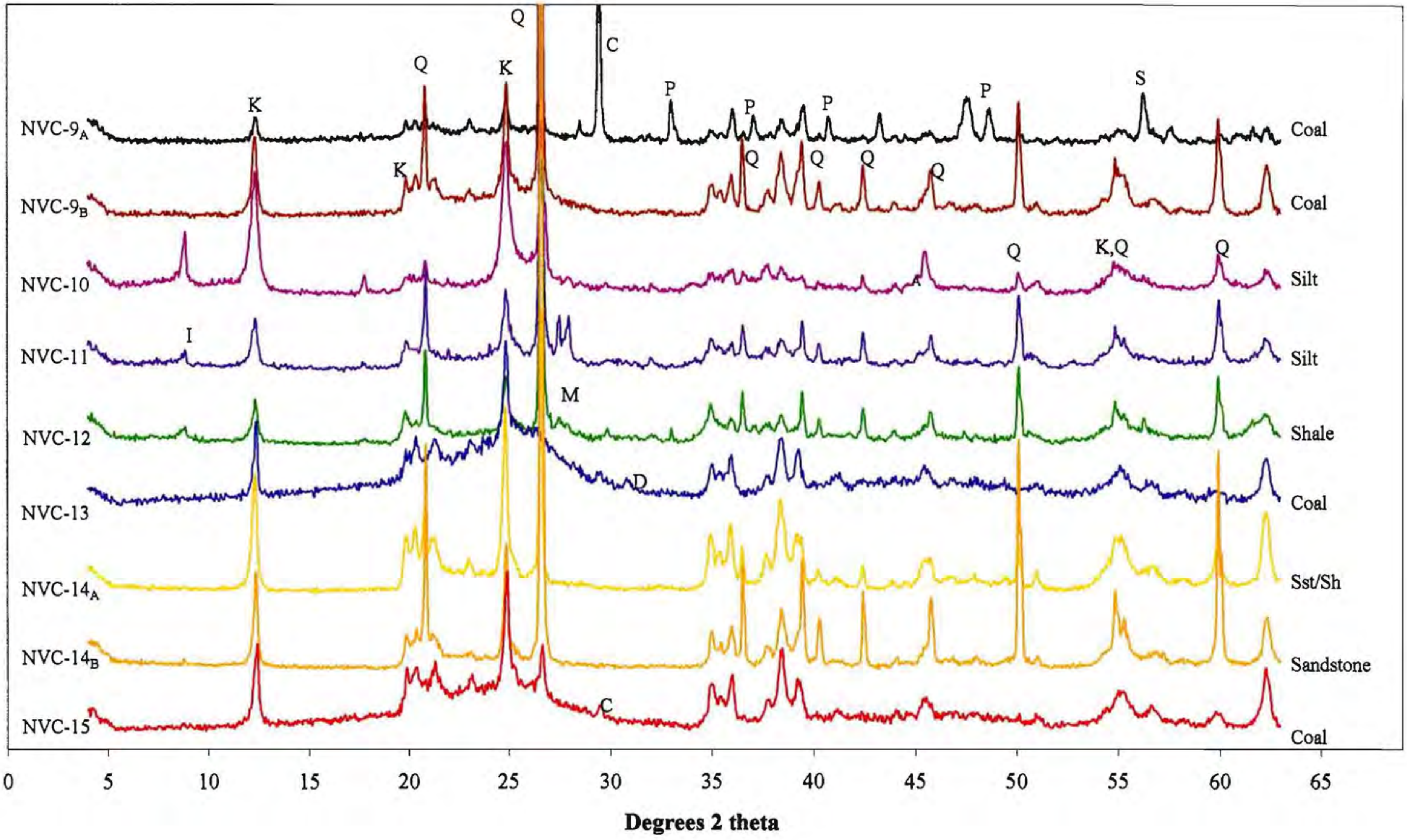
SAMPLE	DEPTH (m)	INTERVAL (m)	LITHOLOGY
15	59.75	3.72	Bottom seam. Dull, lustrous coal. < 10% bright. With minor shaly bands.
	60.87	1.12	Coarse-grained brownish-grey Dwyka Tillite. Poorly sorted with scattered pebbles.

APPENDIX 5

Mineralogical data

Mineralogical data was obtained through XRD analyses of selected lithological units in borehole cores taken from four of the collieries, viz. New Vaal, Kriel, New Denmark and Goedehoop. The analytical methods used are outlined in Section 4.3, and details can be found in Appendix 1. Figures A5.1 through A5.4 show the original stacked XRD traces from unashed samples. All the traces are ordered with increasing depth from the surface and the intensity scales are the same thoughout. At New Denmark, two cores were sampled and these are presented as separate figures (i.e. Figure A5.3a and 5.3b).

The results of normative calculations using SEDNORM (Cohen and Ward, 1991) are presented in Table A5.1; whilst mineral proportions determined by SIROQUANT analysis on the unashed samples can be found in Table A5.2. More information on these techniques can be found in Section 4.3 and Appendix 1.


Q
C
Q
K
K
P
P
P
P
S
NVC-9$_{A}$
Coal
K
Q
Q
Q
Q
NVC-9$_{B}$
Coal
Q
K,Q
Q
NVC-10
A
Silt
I
NVC-11
Silt
M
NVC-12
Shale
D
NVC-13
Coal
NVC-14$_{A}$
Sst/Sh
NVC-14$_{B}$
Sandstone
C
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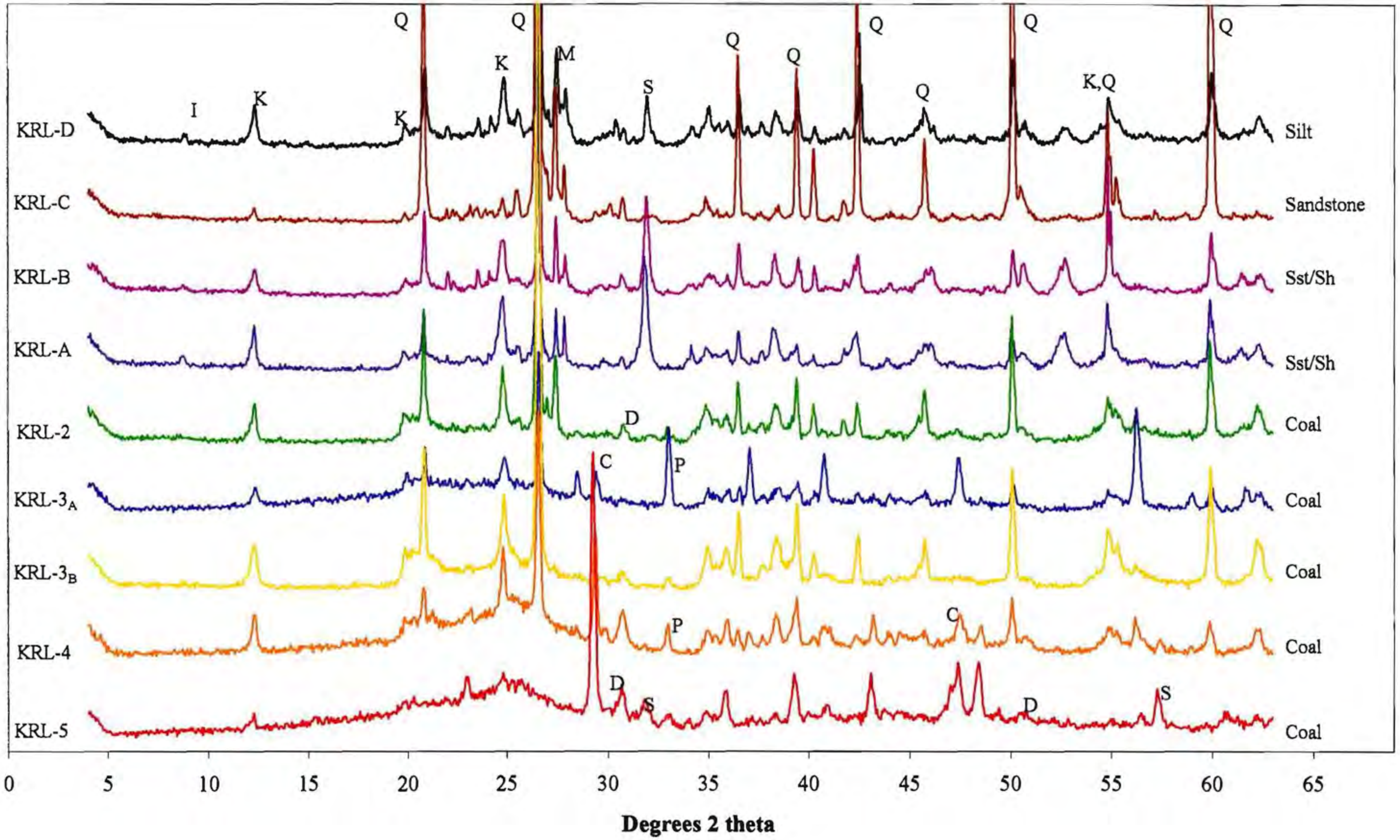
Q
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K,Q
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S
S
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D
D
C
C
P
P
KRL-D
KRL-C
KRL-B
KRL-A
KRL-2
KRL-3A
KRL-3B
KRL-4
KRL-5
Silt
Sandstone
Sst/Sh
Sst/Sh
Coal
Coal
Coal
Coal
Coal
0
5
10
15
20
25
30
35
40
45
50
55
60
65
Degrees 2 theta

Figure A5.3b: *Stacked XRD patterns of selected New Denmark lithologies. Symbols: K=kaolinite, Q=quartz, I=illite, S=siderite, C=calcite, A=ankerite, D=dolomite, P=pyrite and M=microcline.*

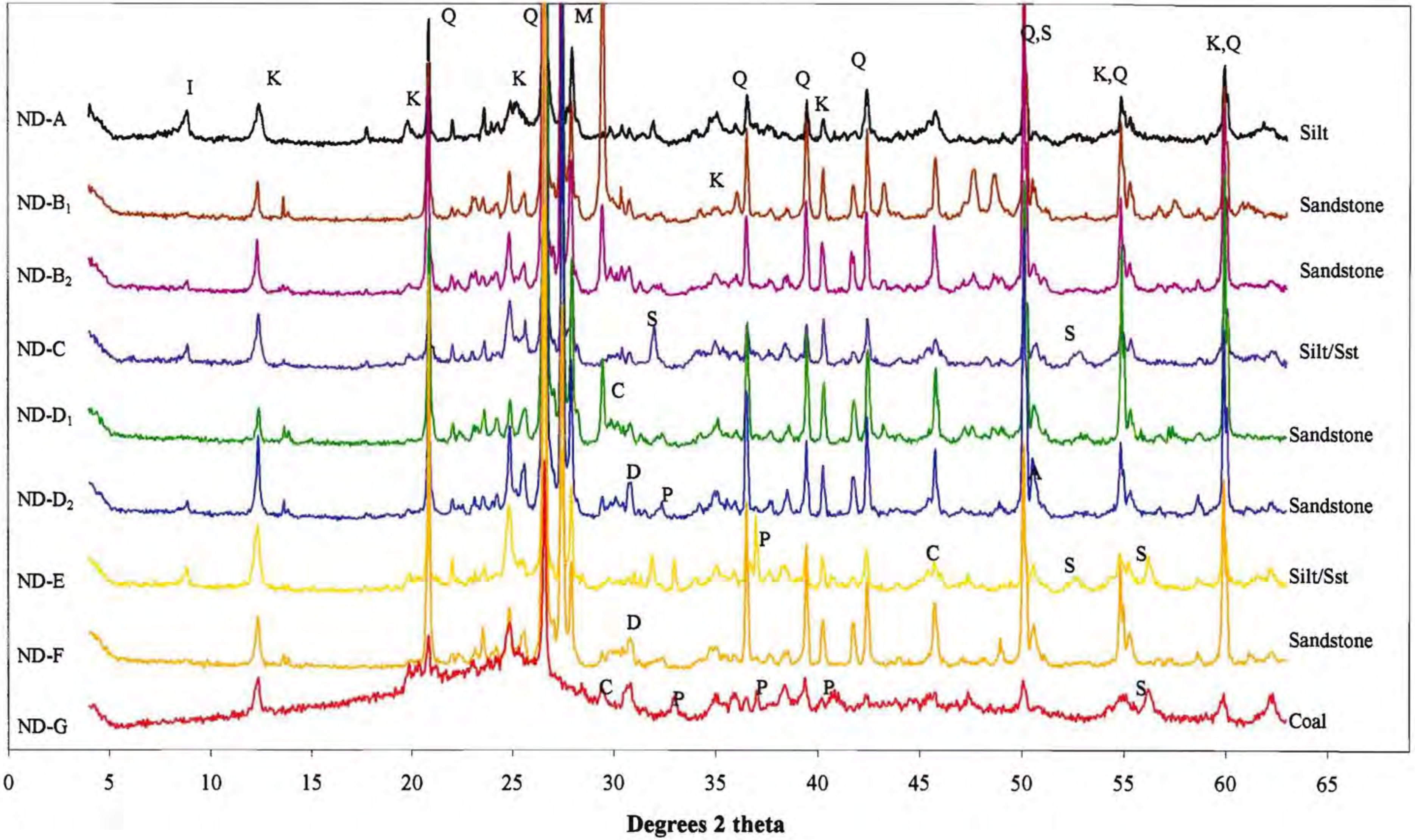


Figure A5.4: *Stacked XRD patterns of selected Goedehoop lithologies. Symbols: K=kaolinite, Q=quartz, I-illite, S=siderite, C=calcite, A=ankerite, D=dolomite, P=pyrite and M=microcline.*

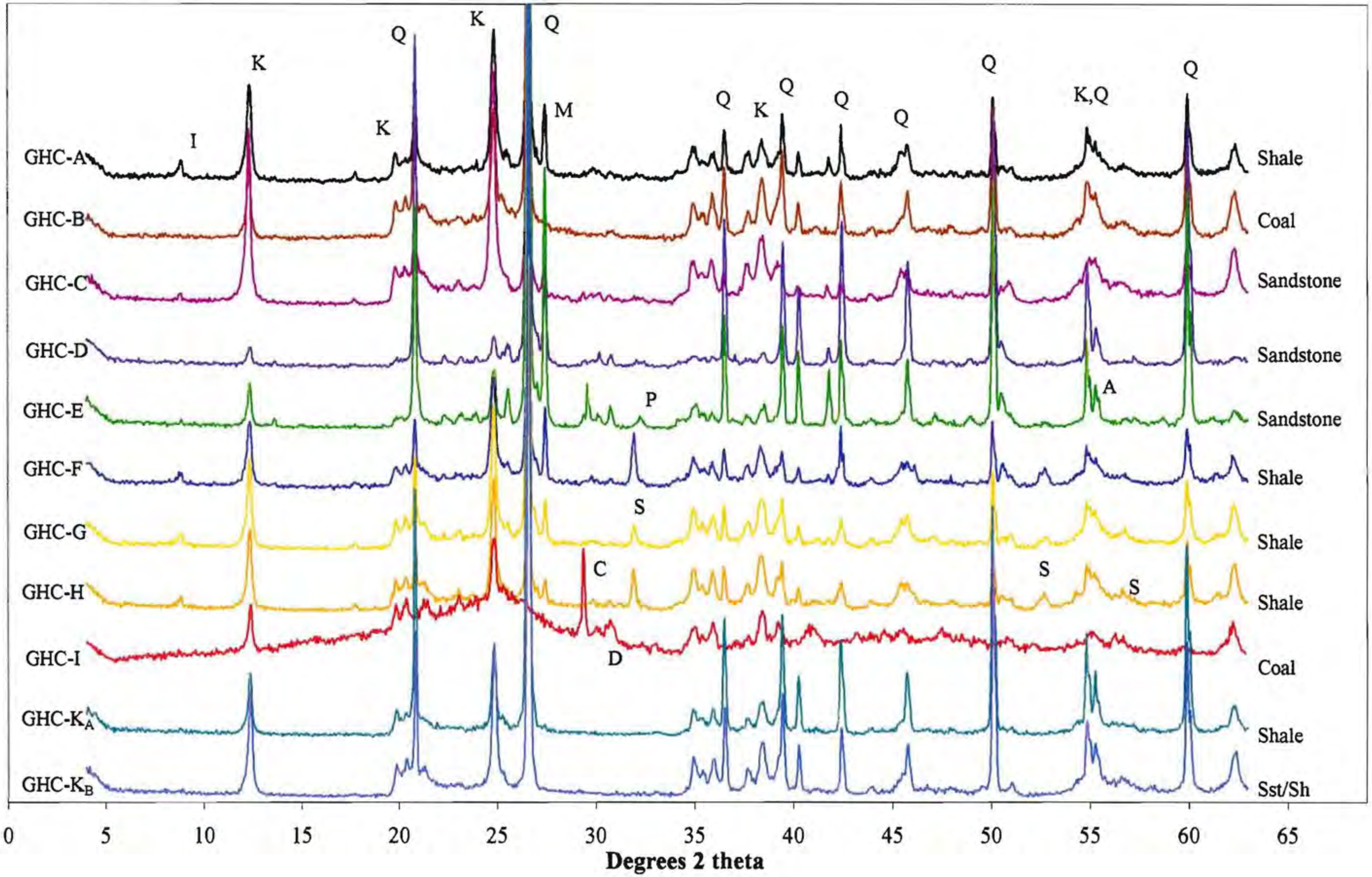


Table A5.1: Detailed mineral composition of cores as determined by normative calculation.

		Quartz	Feldspar	Illite	Kaolinite	Calcite	Magnesite	Siderite	Apatite	Hematite	Gibbsite	Pyrite	Anatase	Halite	Gypsum	**TOTAL**
NVC-1	Sandstone	33.8	6.40	9.40	25.0	1.80	3.80	18.8	0.20			0.10	0.60			**99.9**
NVC-2	Shale	32.9	9.30	12.2	24.2	1.60	4.70	12.9	0.20	0.00		1.40	0.60			**100**
NVC-3	Shale	32.2	9.80	11.7	33.0	1.10	3.60	7.20	0.10			0.40	0.80			**99.9**
NVC-4	Sandstone	27.2	6.40	7.90	14.1	4.90	5.80	31.5	0.30	0.30	0.00	1.10	0.40			**99.9**
NVC-5	Sst/Sh	30.0	11.9	11.2	22.2	6.30	2.90	8.20	0.10	0.00		6.50	0.60			**99.9**
NVC-6	Shale	26.4	10.6	11.2	37.4	1.00	2.70	6.60	0.10			3.10	0.90			**100**
NVC-7$_A$	Sandstone	23.4	6.90	11.2	26.7	4.30	3.30	20.0	1.10			2.60	0.50			**100**
NVC-7$_B$	Sandstone	39.1		17.8		5.60	5.50	27.5	0.10			4.10	0.30			**100**
NVC-8	Silt/Sst	41.6	8.80	11.6	29.5	0.50	1.80	4.90				0.30	0.90			**99.9**
NVC-9$_A$	Coal	11.7		1.00	38.5	21.6	1.00	9.40				16.2	0.40			**99.8**
NVC-9$_B$	Coal	40.4		1.30	50.8	2.10	1.00	1.40				1.00	1.50	0.40		**99.9**
NVC-10	Silt	13.8	11.1	10.7	48.1	0.40	4.10	9.80	0.20			0.90	1.00			**100**
NVC-11	Silt	30.6	13.1	9.00	37.5	0.60	2.50	5.00	0.10			0.60	0.90			**99.9**
NVC-12	Shale	31.6	13.2	11.3	33.1	0.40	2.20	6.00	0.10			1.20	0.90			**100**
NVC-13	Coal		18.0	1.00	59.3	9.10	2.50		1.30		4.10	3.00	1.50			**99.8**
NVC-14$_A$	Sst/Sh	15.2	3.10	1.30	76.6	0.20	0.30	0.90	0.10		0.10	0.60	1.50			**99.9**
NVC-14$_B$	Sandstone	38.1	2.50	1.40	55.6	0.00	0.20	0.80				0.10	1.00			**99.7**
NVC-15	Coal	7.00	8.30	3.30	72.1	3.70	1.10				0.30	2.80	1.30			**99.9**
KRL-L	Sandstone	32.6	15.1	15.1	24.0	0.80	3.10	8.10	0.20				0.90			**99.9**
KRL-K	Shale	25.7	9.30	12.6	41.0	2.10	2.60	5.40	0.20		0.10	0.20	0.90			**100**
KRL-J$_1$	Sst/Sh	23.9	16.5	13.9	21.4	1.00	3.80	18.3	0.20	0.30		0.00	0.80			**100**
KRL-J$_2$	Sst/Sh	22.8	14.0	15.0	34.5	0.70	3.00	7.90	0.10	0.00	0.10	0.70	1.10			**99.9**
KRL-I	Sandstone	53.0	21.9	19.2	1.10	0.30	0.70	3.30	0.10				0.40			**100**
KRL-H	Silt/Sst	26.1	16.5	15.0	28.3	0.60	3.10	9.10	0.20	0.00		0.20	0.90			**100**
KRL-G	Shale	21.2	13.3	14.0	41.5	0.40	2.40	5.10	0.00			1.10	1.00			**100**
KRL-F	Sandstone	38.2	22.5	18.6	6.30	7.10	1.80	4.60	0.00	0.00		0.30	0.50			**99.9**
KRL-E	Sst/Sh	22.3	17.2	15.5	30.2	0.60	3.50	9.20	0.20	0.00		0.40	0.90			**100**
KRL-D	Silt	20.2	16.0	14.9	33.7	0.60	3.30	9.70	0.20	0.00		0.30	0.90			**99.8**
KRL-C	Sandstone	66.2	15.6	15.2		0.30	0.40	1.70		0.00			0.40			**99.8**

Table A5.1cont.: Detailed mineral composition of cores as determined by normative calculation.

		Quartz	Feldspar	Illite	Kaolinite	Calcite	Magnesite	Siderite	Apatite	Hematite	Gibbsite	Pyrite	Anatase	Halite	Gypsum	**TOTAL**
KRL-B	Sst/Sh	18.0	12.2	11.7	31.0	3.20	4.00	18.1	0.10	0.00		0.80	0.80			**99.9**
KRL-A	Sst/Sh	15.9	10.3	10.5	35.6	1.40	3.60	20.8	0.20	0.10	0.10	0.60	0.80			**99.9**
KRL-2	Coal	28.5	10.1	12.7	37.7	0.30	1.40	4.10				4.50	0.60			**99.9**
KRL-3$_A$	Coal	15.2		2.70	40.5	5.10	1.50	10.3	0.60			22.8	0.50	0.70		**99.9**
KRL-3$_B$	Coal	33.7	4.90	3.60	47.4	2.90	1.80	1.90				2.60	1.00			**99.8**
KRL-4	Coal	18.9		2.60	43.4	15.6	4.10	3.40	1.10		0.50	8.60	0.90	0.80		**99.9**
KRL-5	Coal	0.70		2.20	36.2	33.6	7.30		9.30			1.10	0.70	1.60	7.30	**100**
GHC-A	Shale	24.6	8.70	13.3	45.9		1.90	3.90	0.60			0.20	1.00			**100**
GHC-B	Coal	40.3		2.00	52.6	0.90	0.70	1.00				0.80	1.60			**99.9**
GHC-C	Sandstone	14.7	5.50	8.30	67.8	0.10	0.50	1.80				0.30	0.90			**99.9**
GHC-D	Sandstone	68.0	8.40	13.2	7.70		0.20	0.90				0.00	1.30			**99.7**
GHC-E	Sandstone	53.7	12.8	20.2	11.6		0.20	1.00			0.00		0.30			**99.8**
GHC-F	Shale	22.3	8.60	13.1	40.6	0.40	2.40	10.9	0.30	0.00		0.50	0.90			**100**
GHC-G	Shale	22.6	7.10	10.7	49.5	0.20	2.00	6.30	0.20	0.00		0.30	1.00			**99.9**
GHC-H	Shale	21.5	6.80	10.1	50.1	0.60	1.80	7.10	0.20	0.20	0.20	0.30	1.00			**99.9**
GHC-I	Coal	1.30		5.60	64.2	10.0	4.10		4.30			8.80	1.10			**99.4**
GHC-K$_1$	Shale	48.6	2.40	3.00	42.3		0.30	1.10	0.00			0.90	1.20			**99.8**
GHC-K$_2$	Sst/Sh	33.6	2.80	3.40	57.0		0.30	1.00	0.00			0.60	1.20			**99.9**
ND-1	Dolerite	19.2	23.2	3.20	17.1	12.3	10.5	13.3	0.20	0.10	0.00	0.00	0.70			**99.8**
ND-2	Silt/Sst	17.9	18.4	16.6	24.5	0.70	5.60	15.00	0.10	0.00		0.00	1.00			**99.8**
ND-3	Dolerite	15.2	25.1	2.7	16.9	14.4	7.10	16.9	0.30	0.20		0.40	0.90			**100**
ND-4	Sandstone	65.0	14.3	16.4		0.80	0.80	2.40					0.10			**99.8**
ND-5	Silt	11.6	15.9	14.3	30.6	0.60	5.40	19.6	0.20	0.10		0.70	1.10			**100**
ND-6	Sandstone	67.4	9.10	19.1		0.20	1.00	2.60				0.30	0.20			**99.9**
ND-A	Silt	23.0	20.6	16.8	21.5	0.80	3.90	11.9	0.20	0.00		0.20	0.90			**99.8**
ND-B$_1$	Sandstone	41.5	19.3	14.6	1.60	19.7	0.60	2.10	0.00		0.10		0.40			**99.9**
ND-B$_2$	Sandstone	42.0	21.7	16.8	7.60	6.20	1.30	3.70	0.00				0.50			**99.8**
ND-C	Silt/Sst	23.1	19.8	16.8	21.6	0.70	4.30	12.5	0.20	0.00		0.00	0.90			**99.9**

Table A5.1cont.: Detailed mineral composition of cores as determined by normative calculation.

		Quartz	Feldspar	Illite	Kaolinite	Calcite	Magnesite	Siderite	Apatite	Hematite	Gibbsite	Pyrite	Anatase	Halite	Gypsum	**TOTAL**
ND-D$_1$	Sandstone	57.4	17.7	18.0		4.60	0.40	1.50		0.00			0.20			**99.8**
ND-D$_2$	Sandstone	44.6	21.9	20.3	6.50	0.50	1.50	3.70	0.10			0.30	0.50			**99.9**
ND-E	Silt/Sst	18.8	16.7	14.0	29.7	0.40	3.50	11.8	0.30			4.00	0.90			**100**
ND-F	Sandstone	49.9	22.3	19.0	2.90	0.50	0.60	2.90	0.10	0.00		0.50	1.10			**99.8**
ND-G	Coal	21.2		1.6	46.3	9.2	3.7	5.6				9.6	1.4	1.6		**100**

Table A5.2: Detailed mineral composition of cores as determined by SIROQUANT analysis.

		Quartz	Microcline	Albite	Anorthite	Mica	Mixed layer illite-smectite	Illite	Kaolinite	Calcite	Dolomite	Ankerite	Siderite	Apatite	Pyrite	Anatase	**TOTAL**	Global Chi^2
NVC-1	Sandstone	31.0	7.00	6.10			13.5	14.5	22.8	0.10	0.50		1.50		3.10		**100**	5.47
NVC-2	Shale	23.5	6.60	7.40			15.4	21.7	17.8	0.00	0.00		6.70		0.90		**100**	4.34
NVC-3	Shale	27.0	10.4	8.30			9.1	16.6	27.2	0.00	0.00		0.70		0.90		**100**	4.71
NVC-4	Sandstone	19.3	3.80	6.20				11.2	4.50	1.50	0.20		52.10		1.00		**99.8**	3.64
NVC-5	Sst/Sh	39.4	12.6	10.9				12.1	13.0	3.70	0.60		5.60		2.10		**100**	4.64
NVC-6	Shale	28.9	14.2	9.70				15.1	27.6	0.00	0.00		1.70		2.90		**100**	5.37
NVC-7$_A$	Sandstone	21.3	0.50	2.20				20.0	27.0	2.70	0.30		22.8		3.10		**99.9**	3.96
NVC-7$_B$	Sandstone	19.8	2.60	3.30				43.4	3.8	7.00	0.60		10.3		9.20		**100**	5.08
NVC-8	Silt/Sst	58.4	6.50	6.20				7.10	17.6	0.10	0.70		2.80		0.80		**100**	4.62
NVC-9$_A$	Coal	9.20							33.9	30.9	0.6		2.60		22.8		**100**	3.81
NVC-9$_B$	Coal	45.2							53.6						1.20		**100**	4.88
NVC-10	Silt	13.7				25.0			59.1				2.20				**100**	5.21
NVC-11	Silt	31.1	9.20	10.3				19.2	26.9	0.00	0.00		2.40		0.90		**100**	4.59
NVC-12	Shale	34.9	4.40	4.30				22.4	29.4	0.00	0.20		1.80		2.50		**99.9**	5.14
NVC-13	Coal	1.00							87.2	2.80	3.30				2.40	3.50	**100**	5.05
NVC-14$_A$	Sst/Sh	17.7							82.3								**100**	4.28
NVC-14$_B$	Sandstone	51.2						5.30	43.5								**100**	4.35
NVC-15	Coal	5.80							90.2	2.40						1.60	**100**	4.78
KRL-L	Sandstone																	
KRL-K	Shale	24.6	8.50	5.20	7.70			15.6	36.3	0.00	0.30		1.00		0.7		**99.9**	5.33
KRL-J$_1$	Sst/Sh																	
KRL-J$_2$	Sst/Sh																	
KRL-I	Sandstone																	
KRL-H	Silt/Sst																	
KRL-G	Shale																	
KRL-F	Sandstone	62.7	13.4	7.70	5.30				5.70	2.50	0.80		1.80		0.00		**99.9**	5.48
KRL-E	Sst/Sh																	
KRL-D	Silt	38.7	11.7	12.1				10.9	17.7	0.00	0.10		8.50		0.30		**100**	6.11
KRL-C	Sandstone																	
KRL-B	Sst/Sh																	
KRL-A	Sst/Sh																	
KRL-2	Coal	41.8							36.9	0.00	0.80		1.50	16.0	3.10		**100**	4.36

Table A5.2 cont.: Detailed mineral composition of cores as determined by SIROQUANT analysis.

		Quartz	Microcline	Albite	Anorthite	Mica	Mixed layer illite-smectite	Illite	Kaolinite	Calcite	Dolomite	Ankerite	Siderite	Apatite	Pyrite	Anatase	**TOTAL**	Global Chi^2
KRL-3$_A$	Coal	22.1	1.10						26.5	6.00	1.10		1.40		41.7		**99.9**	5.18
KRL-3$_B$	Coal	51.2							41.5	1.50	2.50				3.30		**100**	5.32
KRL-4	Coal	21.9							36.1	17.5	8.80				14.6	1.10	**100**	5.51
KRL-5	Coal	0.20							18.0	57.1	8.30		2.30	10.3	2.20	1.60	**100**	
GHC-A	Shale																	
GHC-B	Coal	43.2							52.6		1.60					2.70	**100**	5.69
GHC-C	Sandstone																	
GHC-D	Sandstone	76.7	12.1						9.30	0.00	0.50		1.10	0.00	0.30		**100**	4.45
GHC-E	Sandstone																	
GHC-F	Shale	28.9	9.70					14.2	31.4	0.00	0.10		14.9	0.00	0.70		**99.9**	4.47
GHC-G	Shale																	
GHC-H	Shale																	
GHC-I	Coal	0.10							64.5	18.1	8.80				7.10	1.50	**100**	5.42
GHC-K$_1$	Shale																	
GHC-K$_2$	Sst/Sh																	
ND-1	Dolerite	4.00	2.60	9.90	75.3				0.20	1.60	5.60		0.80		0.00		**100**	6.62
ND-2	Silt/Sst																	
ND-3	Dolerite																	
ND-4	Sandstone																	
ND-5	Silt	13.9	13.5	4.80	6.60			30.5	16.2		0.70		14.0				**100**	6.73
ND-6	Sandstone	72.5	15.5	8.60					1.90		0.70		0.20		0.40		**99.8**	4.89
ND-A	Silt																	
ND-B$_1$	Sandstone																	
ND-B$_2$	Sandstone																	
ND-C	Silt/Sst																	
ND-D$_1$	Sandstone	67.0	12.6	10.1					5.50	3.40	0.40		0.70		0.20		**99.9**	5.32
ND-D$_2$	Sandstone	68.3	13.8	7.10				5.40	4.10		0.70		0.50				**99.9**	5.99
ND-E	Silt/Sst																	
ND-F	Sandstone																	
ND-G	Coal	26.3							49.6	3.20	6.70		1.00		11.8	1.50	**100**	4.84

Table A5.2 cont.: *Detailed mineral composition of cores as determined by SIROQUANT analysis.*

	Quartz	Microcline	Albite	Anorthite	Mica	Mixed layer illite-smectite	Illite	Kaolinite	Calcite	Dolomite	Ankerite	Siderite	Apatite	Pyrite	Anatase	**TOTAL**	Global Chi^2

APPENDIX 6

Water quality

A6.1 Scaling and corrosion

Loewenthal *et al.* (1986) defined tentative guidelines for the prevention of aggression of water to concrete pipes and corrosion to metal surfaces.

For the prevention of aggression:

1. The water should be adjusted to a slight state of supersaturation with respect to calcium carbonate. A precipitation potential of about 4mg/L $CaCO_3$ is recommended;
2. The sulphate concentration should be less than 350mg/L. For waters with a SO_4^{2-} content exceeding this value, the cement material used in the manufacture of asbestos cement and concrete should have a tricalcium aluminate content of < 5.5%.

For corrosion passivation:

1. The bulk water should be saturated, or slightly supersaturated, with respect to $CaCO_3$;
2. Both the alkalinity and calcium concentrations each to exceed about 50mg/L as $CaCO_3$;
3. The ratio (Cl^- + SO_4^{2-}) / Alkalinity should be < ~0.2 (where species concentrations are expressed on the equivalent scale); and/or the concentrations of each of Cl^- and SO_4^{2-} must not exceed 50mg/L. This guideline has relatively little value in South Africa because so many of the inland waters exceed it. Therefore, it is suggested that waters be regarded as potentially corrosive when either the chloride or sulphate concentration exceeds 50mg/L;
4. The dissolved oxygen concentration should be greater than about 4mg/L (as O_2).

All these guidelines can be satisfied by appropriate chemical addition and aeration. Satisfaction of corrosion guideline (3), however, may not be practical if either of both of the SO_4^{2-} and Cl^- concentrations are high, because either the chemical dosing costs are too high, or the water will be too hard after stabilization. In that event, because this guideline is relevant to the termination of corrosion of mild steel and cast iron conduits, it might be necessary to use concrete, asbestos cement and/or plastic pipes, or to line the metal pipes with inert plastic, resins or cement (Loewenthal *et al.*, 1986).

Loewenthal's guidelines were developed for industrial and mining wastewaters. Therefore, the water bodies sampled at each of the collieries have been interpreted in terms of these guidelines. Figures A6.1 through A6.24 show the aggressive and corrosive tendencies of the colliery waters at 25°C in terms of the guidelines.

A6.2 Irrigation

Guidelines for the evaluation of the water samples, in terms of their use in irrigation, have been defined by Ayers and Westcot (1985). The guidelines, which are given in Section 2.3.2, are repeated again for ease of reference in Table A6.1.

Trace elements occur in almost in all water supplies but at very low concentrations, usually less than a few mg/L, with most less than 100µg/L. Not all trace elements are toxic, and, in small quantities, many are essential for plant growth (Fe, Mn, Mo, Zn). Suggested maximum concentrations of some trace elements in irrigation water are shown in Section 2.3.2, and again in Table A6.2. Further information can be found in Ayers and Westcot (1985). The maximum concentration is based on a water application rate which is consistent with good irrigation practice (i.e. 1000 mm/yr).

Each of the water samples in this study, excluding those taken in the winter of 1999, has been evaluated in terms of these guidelines for irrigation use in the area of the collieries. The results are presented in Table A6.3. The degree to which restrictions would need to be imposed, should the waters be used for irrigation, are indicated as "None", "Moderate" or "Severe". In the case of trace elements and pH, "Problematic" indicates that the value exceeds the recommended amount. Clearly, a variety of problems may arise should many of the sampled waters be used for irrigation purposes if restrictions are not placed on its use. These problems are described in Section 6.2.4.

Table A6.1: *Guidelines for evaluating water quality for irrigation purposes (from Ayers and Westcot, 1985).*

Potential irrigation problem	Units	Degree of Restriction on Use		
		None	**Slight to moderate**	**Severe**
Salinity *(affects crop water availability)*				
EC	mS/cm	< 0.7	0.7 – 3.0	> 3.0
TDS	mg/L	< 450	450 – 2000	> 2000
Infiltration *(affects infiltration rate of water into the soil. Evaluate using EC and SAR together)*				
SAR = 0 – 3 and EC =		> 0.7	0.7 – 0.2	< 0.2
SAR = 3 – 6 and EC =		> 1.2	1.2 – 0.3	< 0.3
SAR = 6 – 12 and EC =		> 1.9	1.9 – 0.5	< 0.5
SAR = 12 – 20 and EC =		> 2.9	2.9 – 1.3	< 1.3
SAR = 20 – 40 and EC =		> 5.0	5.0 – 2.9	< 2.9
Specific Ion Toxicity *(affects sensitive crops)*				
Sodium (Na)				
Surface irrigation	SAR	< 3	3 - 9	> 9
Sprinkler irrigation	mmol$_c$/L	< 3	> 3	
Chloride (Cl)				
Surface irrigation	mmol$_c$/L	< 4	4 - 10	> 10
Sprinkler irrigation	mmol$_c$/L	< 3	> 3	
Boron (B)	mg/L	< 0.7	0.7 – 3.0	> 3.0
Trace Elements (See Table A6.2)				
Miscellaneous Effects *(affects susceptible crops)*				
Nitrogen (NO_3 – N)	mg/L	< 5	5 - 30	> 30
Bicarbonate (HCO_3) *(overhead sprinkling only)*	mmol$_c$/L	< 1.5	1.5 – 8.5	> 8.5
pH		Normal range 6.5 – 8.4		

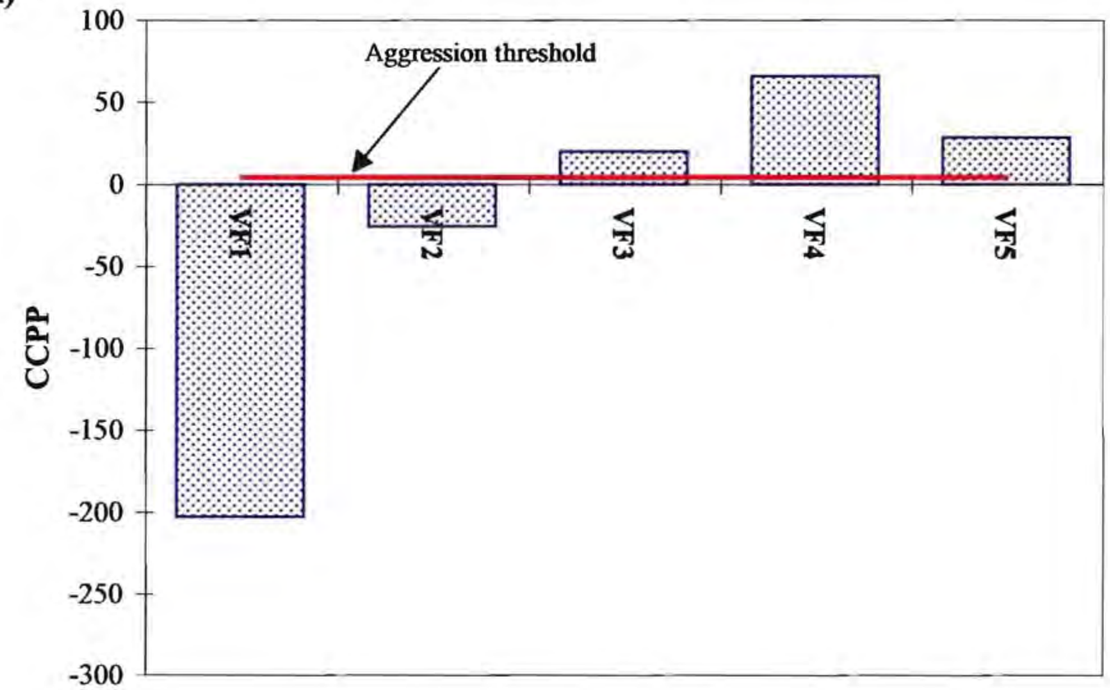
The guidelines are based on the following assumptions:

1. EC is the electrical conductivity (measure of the water salinity) reported in mS/cm at 25°C. TDS is the Total Dissolved Solids, reported in mg/L.
2. SAR is the Sodium Adsorption Ratio. Concentrations are in mmol$_c$/L.
3. $SAR = Na / \sqrt{[(Ca+Mg)/2]}$
4. At a given SAR, infiltration rate decreases as water salinity decreases.
5. For surface irrigation, the guideline values are acceptable for most tree crops and woody plants which are sensitive to sodium and chloride. Most annual crops are not sensitive, however, and Ayers and Westcot (1985) should be consulted for the relevant salinity tolerance figures.
6. NO_3 – N is the nitrate nitrogen reported in terms of elemental nitrogen. NH_4 – N and Organic – N should be included when wastewater is being tested.

Table A6.2: *Recommended maximum concentrations of selected trace elements in irrigation water* *(from Ayers and Westcot, 1985).*

Element	Recommended max conc. (mg/L)	Remarks
Al	5.0	Can cause non-productivity in acid soils (pH < 5.5), but more alkaline soils at pH > 7.0 will precipitate the ion and eliminate any toxicity.
Cr	0.10	Not generally recognized as an essential growth element. Conservative limits recommended due to a lack of knowledge on its toxicity to plants.
Cu	0.20	Toxic to a number of plants at 0.1 to 1.0 mg/L in nutrient solutions.
F	1.0	Inactivated by neutral and alkaline soils.
Fe	5.0	Not toxic to plants in aerated soils, but can contribute to soil acidification and loss of availability of essential phosphorus and molybdenum. Overhead sprinkling may result in unsightly deposits on plants, equipment and buildings.
Li	2.5	Tolerated by most crops up to 5 mg/L; mobile in soil. Toxic to citrus at low concentrations (< 0.075 mg/L).
Mn	0.20	Toxic to a number of crops at a few tenths to a few mg/L, but usually only in acid soils.
Ni	0.20	Toxic to a number of plants at 0.5 mg/L to 1.0 mg/L; reduced toxicity at neutral or alkaline pH.
Zn	2.0	Toxic to many plants at varying concentrations; reduced toxicity at pH > 6.0 and in fine textured or organic soils.

a)



b)

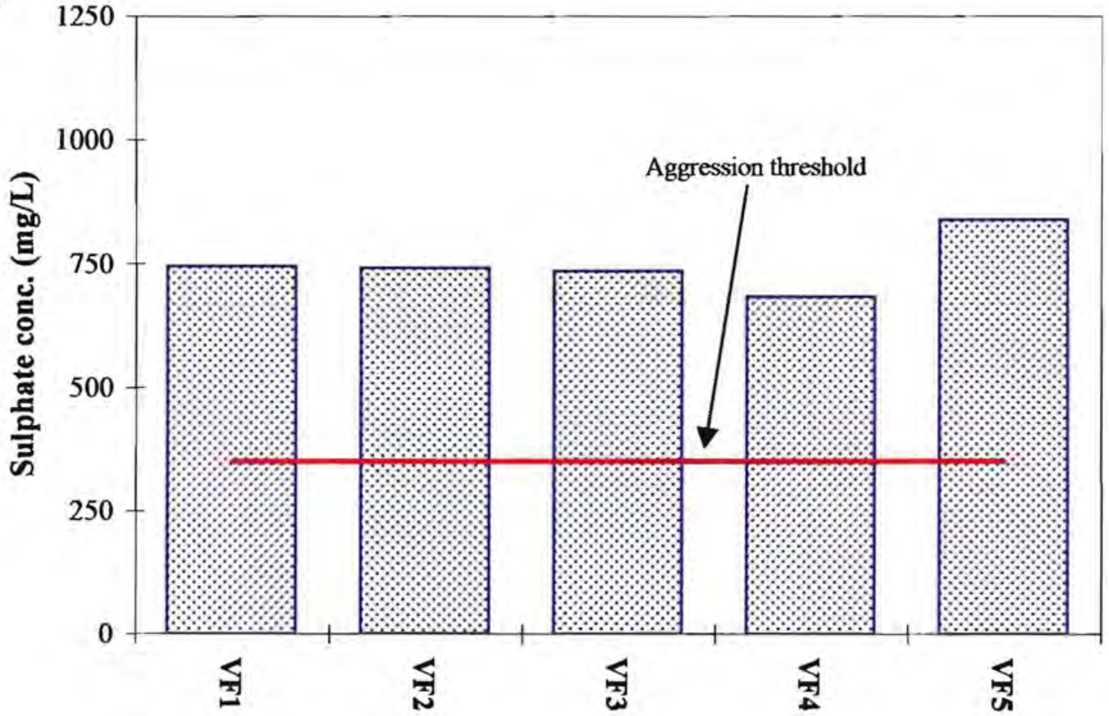


Figure A6.1:(a) *CCPP of Vierfontein waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. A CCPP of 4mg/L is recommended.* ***(b)*** *Sulphate concentration of Vierfontein waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. The concentration should not exceed 350mg/L.*

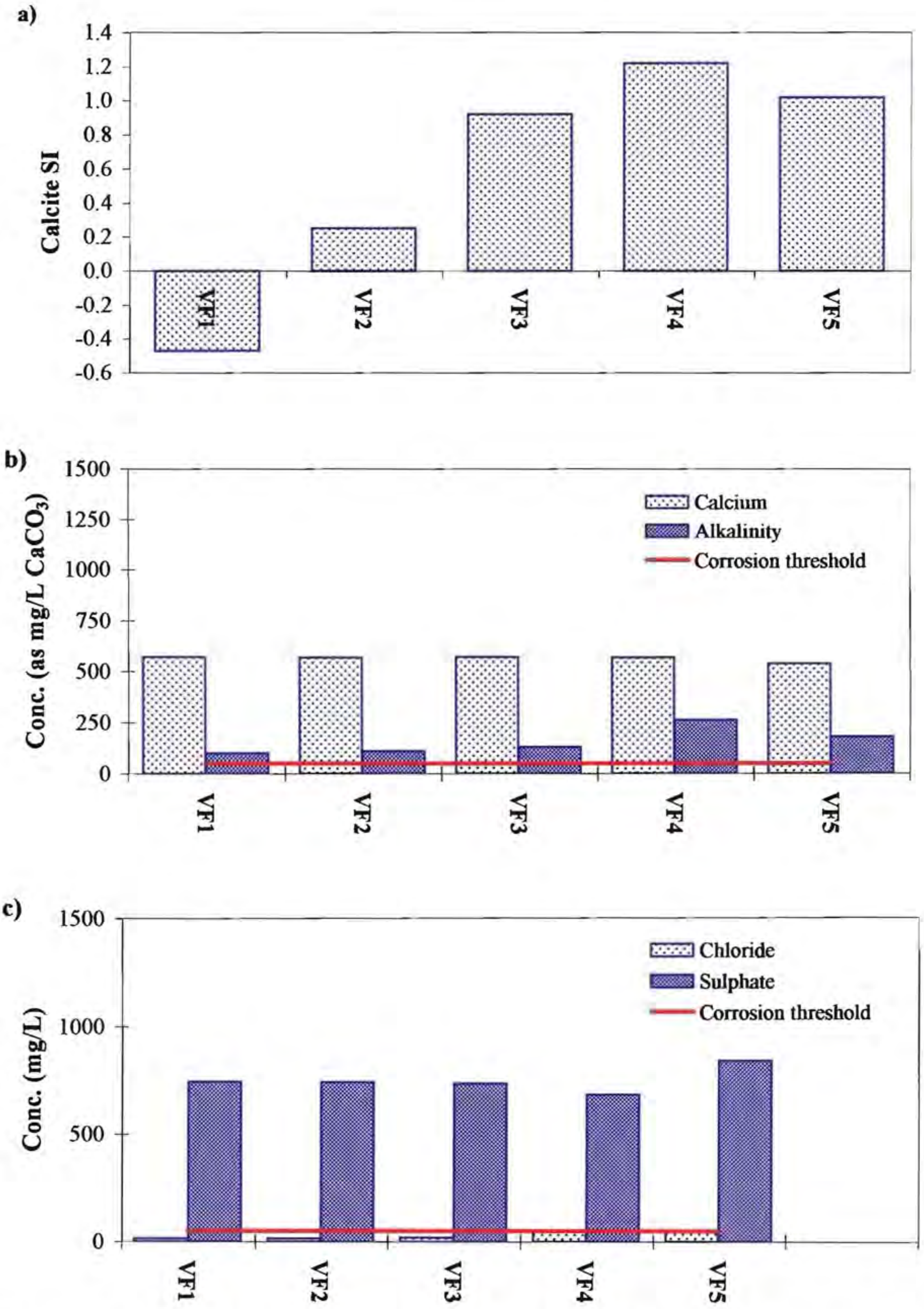


Figure A6.2: ***(a)*** *Calcite saturation index of Vierfontein waters. For corrosion prevention, SI > 0 (Loewenthal, 1986).* ***(b)*** *Calcium and alkalinity con-centrations of Vierfontein waters. Both calcium and alkalinity concentrations should exceed 50mg/L ($CaCO_3$ equivalent) for the prevention of corrosion (Loewenthal, 1986).* ***(c)*** *Chloride and sulphate concentration of Vierfonetin waters. If chloride or sulphate concentration exceeds 50mg/L the waters will corrode metal surfaces (Loewenthal, 1986).*

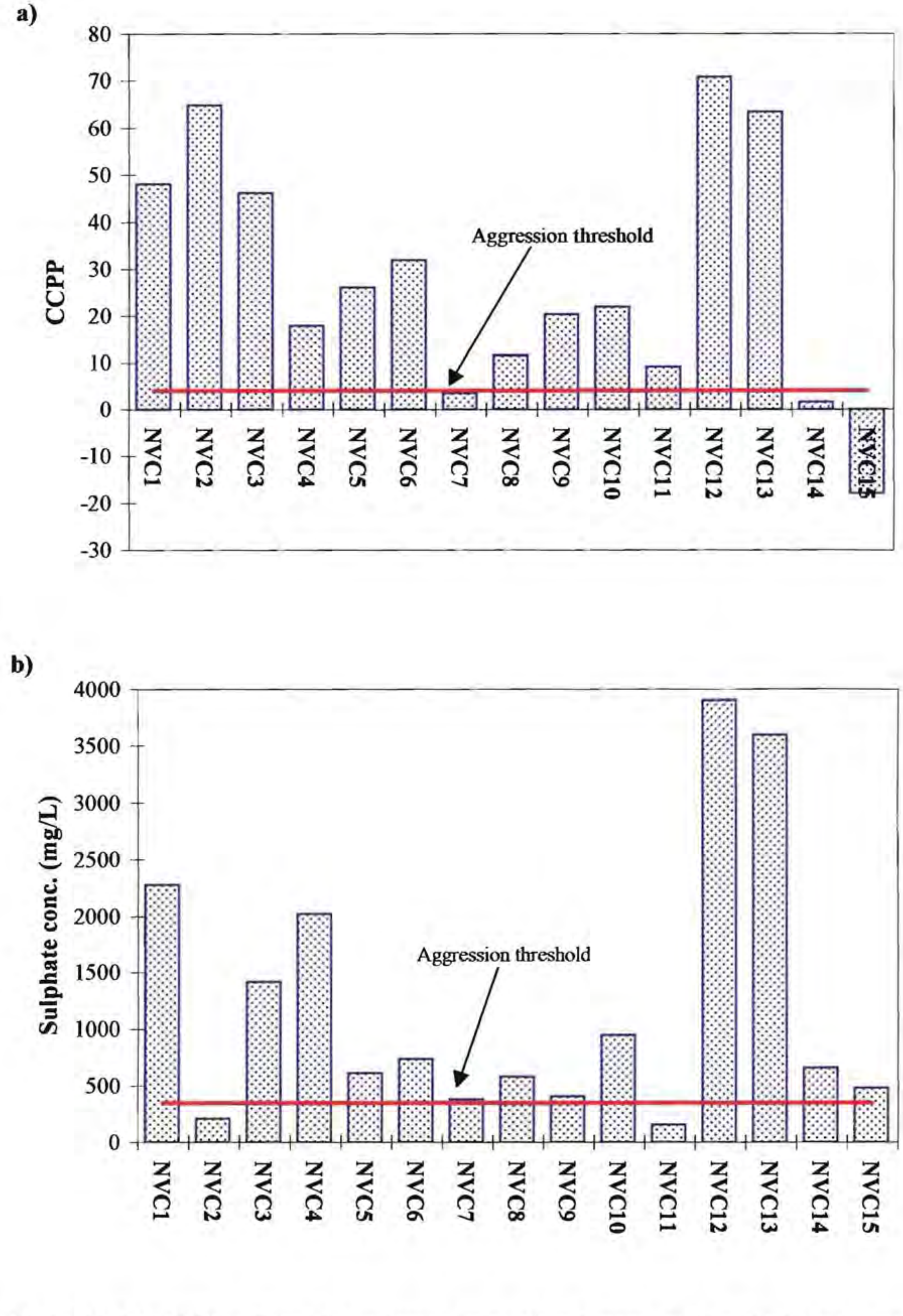


Figure A6.3:(a) *CCPP of New Vaal waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. A CCPP of 4mg/L is recommended.* ***(b)*** *Sulphate concentration of New Vaal waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. The concentration should not exceed 350mg/L.*

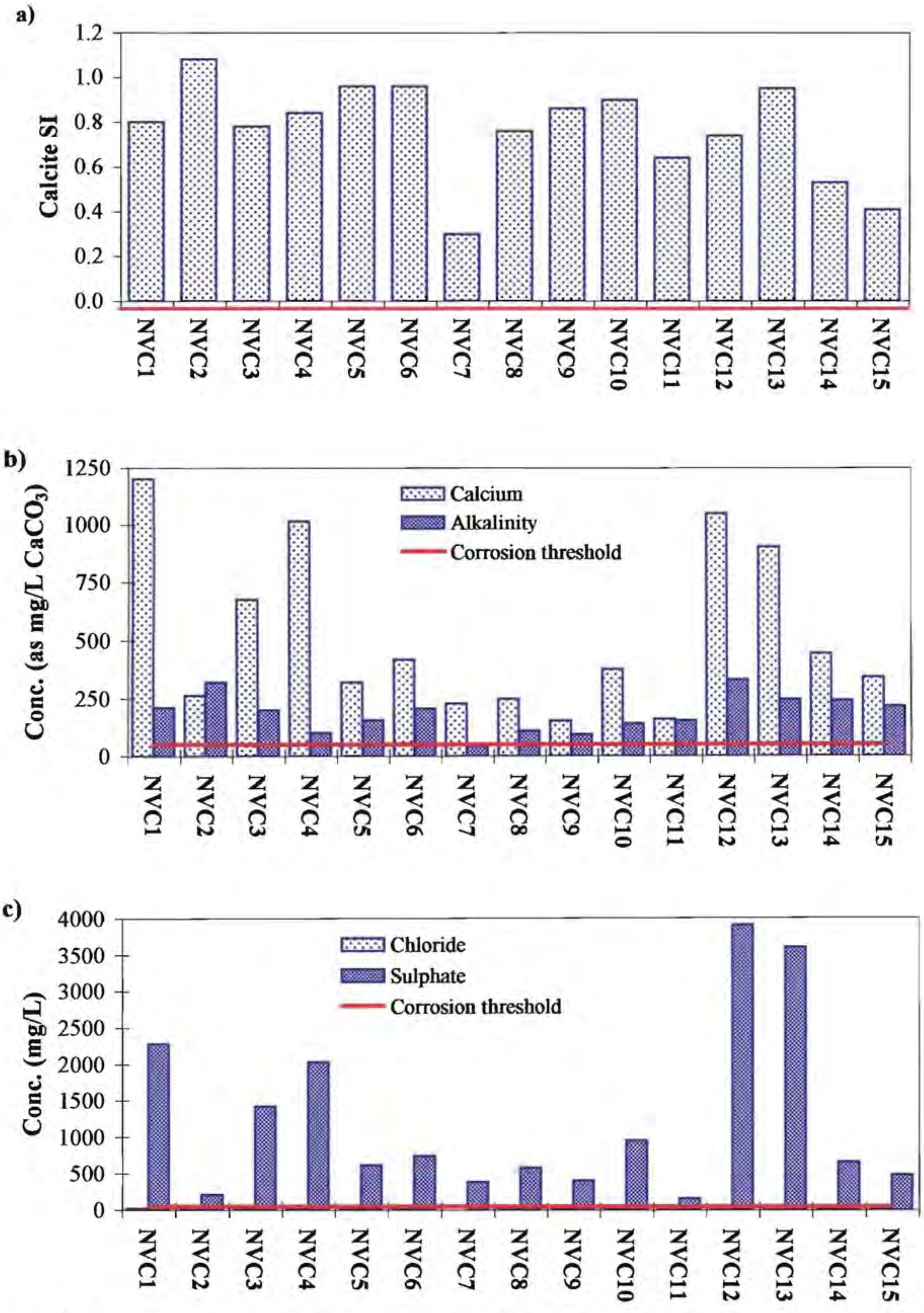


Figure A6.4: ***(a)*** *Calcite saturation index of New Vaal waters. For corrosion prevention, SI > 0 (Loewenthal, 1986).* ***(b)*** *Calcium and alkalinity concentrations of New Vaal waters. Both calcium and alkalinity concentrations should exceed 50mg/L ($CaCO_3$ equivalent) for the prevention of corrosion (Loewenthal, 1986).* ***(c)*** *Chloride and sulphate concentration of New Vaal waters. If chloride or sulphate concentration exceeds 50mg/L the waters will corrode metal surfaces (Loewenthal, 1986).*

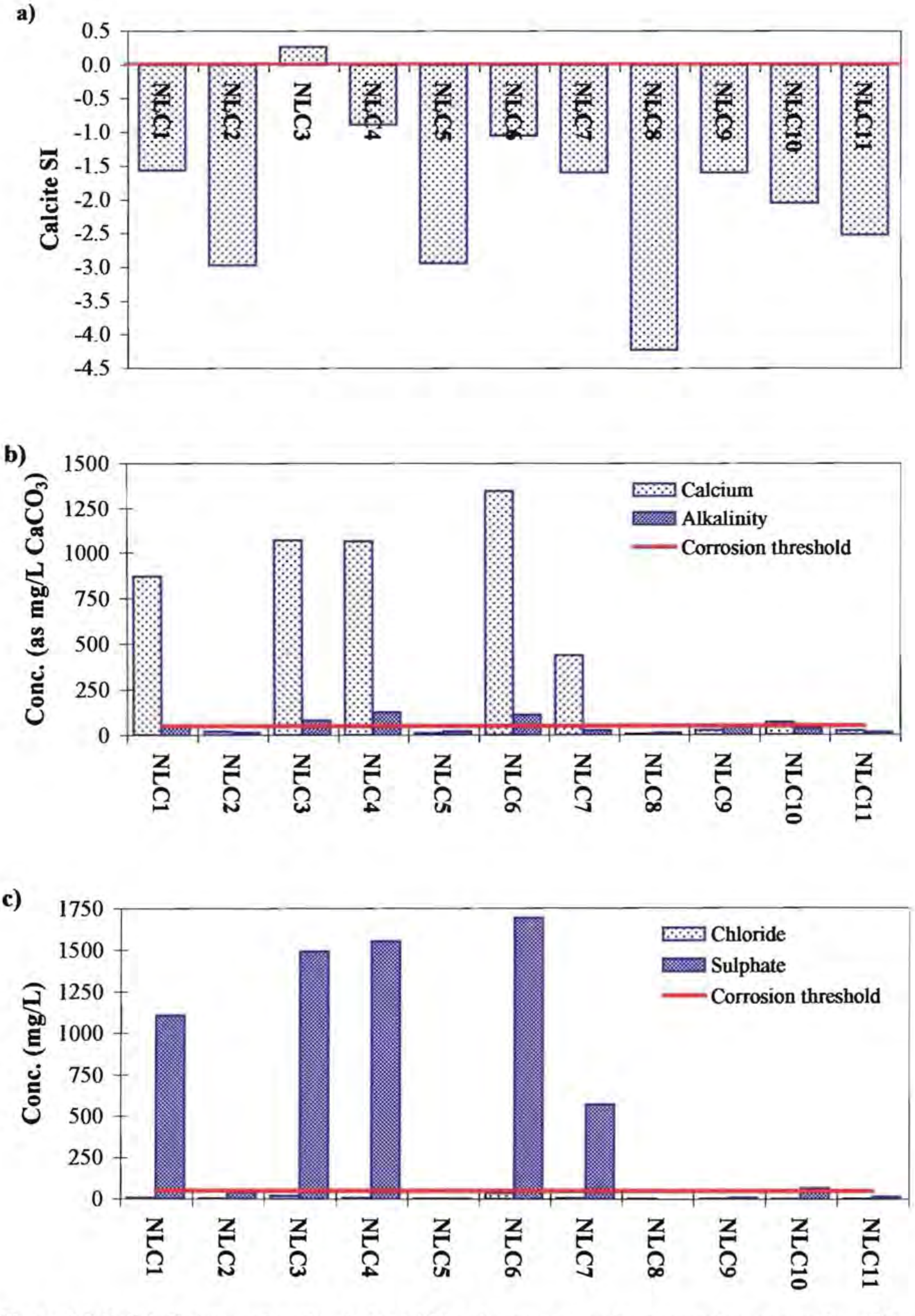


Figure A6.6: ***(a)*** *Calcite saturation index of New Largo waters. For corrosion prevention, SI > 0 (Loewenthal, 1986).* ***(b)*** *Calcium and alkalinity concentrations of New Largo waters. Both calcium and alkalinity concentrations should exceed 50mg/L ($CaCO_3$ equivalent) for the prevention of corrosion (Loewenthal, 1986).* ***(c)*** *Chloride and sulphate concentration of New Largo waters. If chloride or sulphate concentration exceeds 50mg/L the waters will corrode metal surfaces (Loewenthal, 1986).*

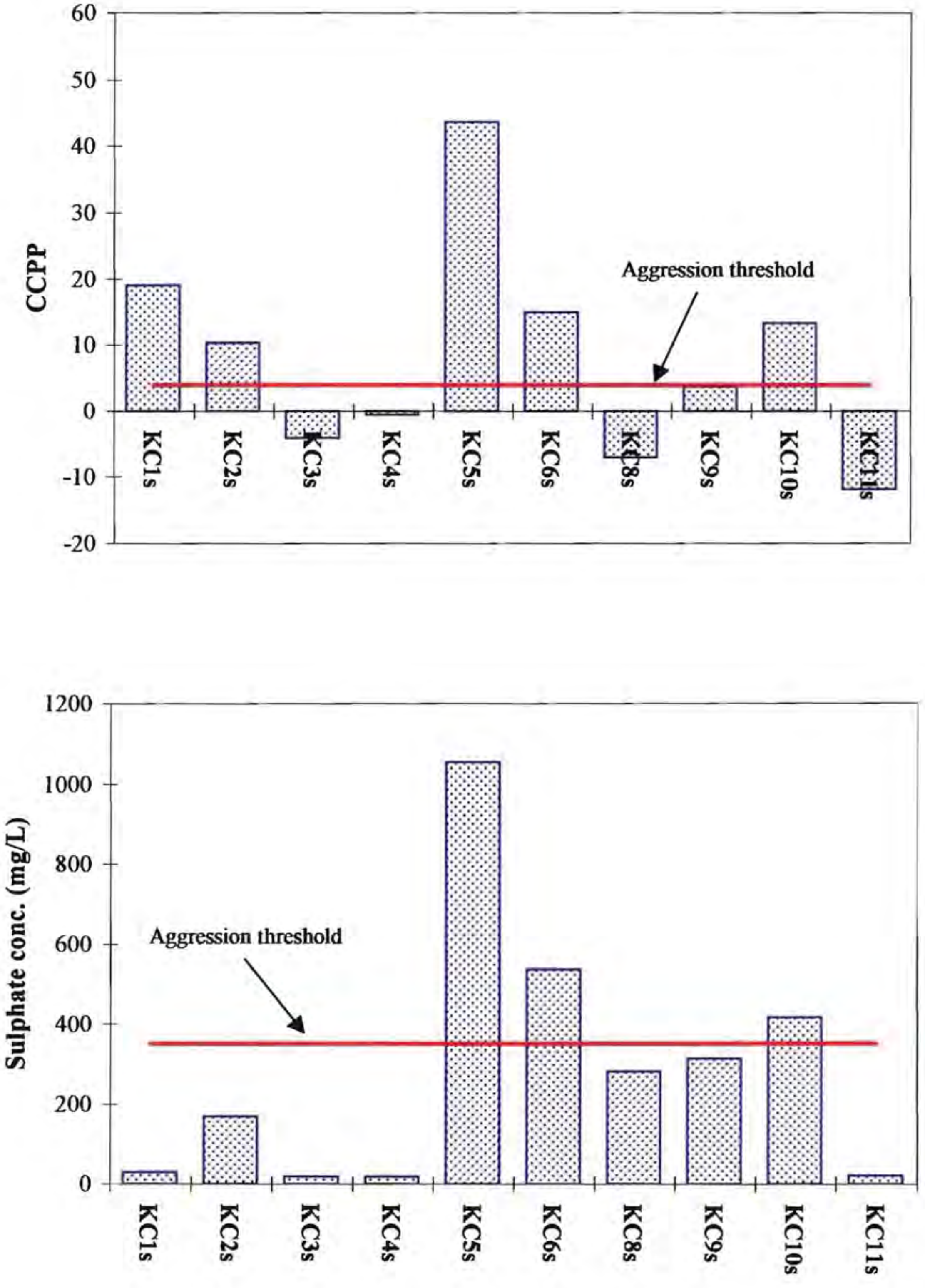


Figure A6.7:(a) *CCPP of Kriel waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. A CCPP of 4mg/L is recommended.* ***(b)*** *Sulphate con-centration of Kriel waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. The concentration should not exceed 350mg/L.*

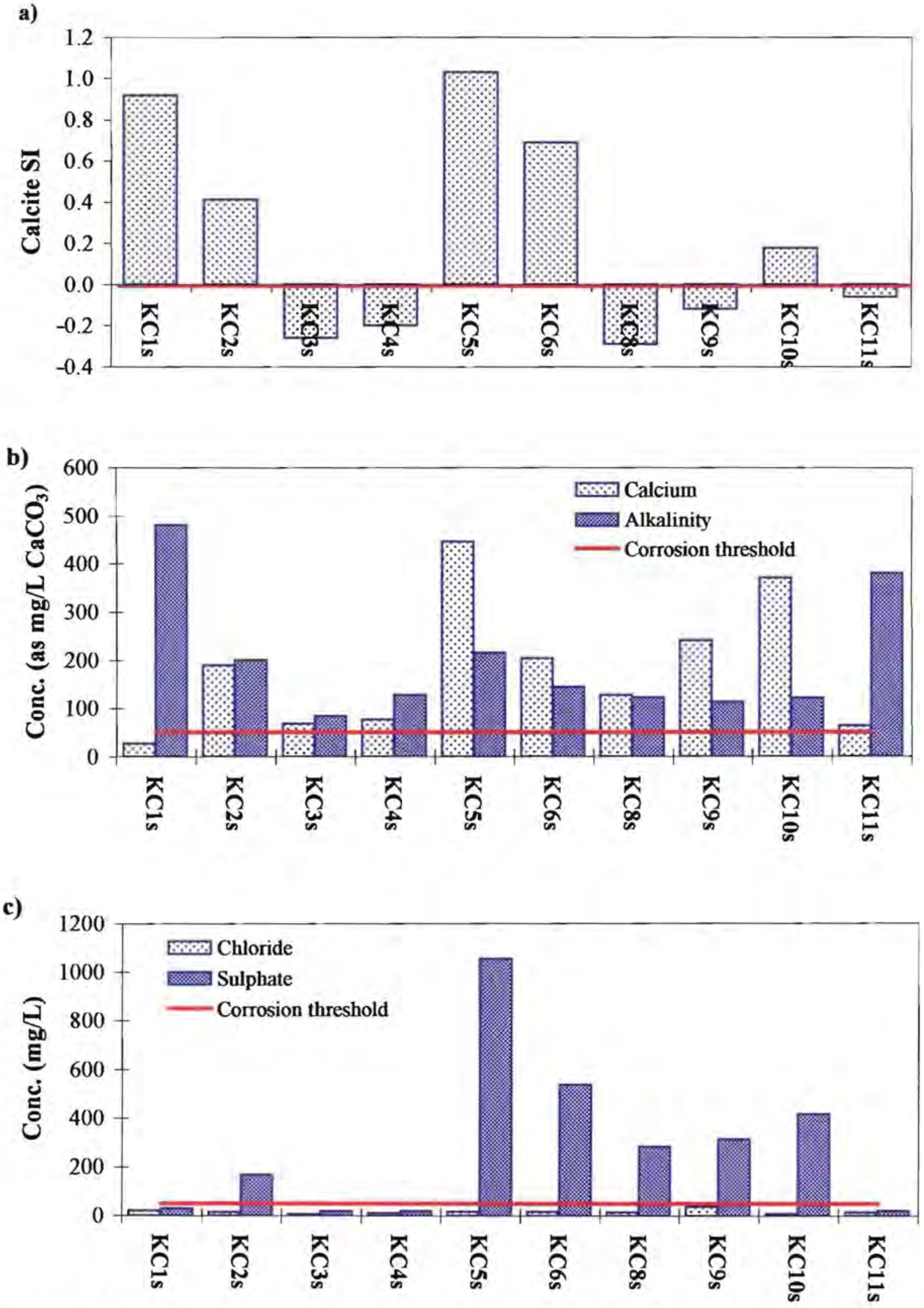
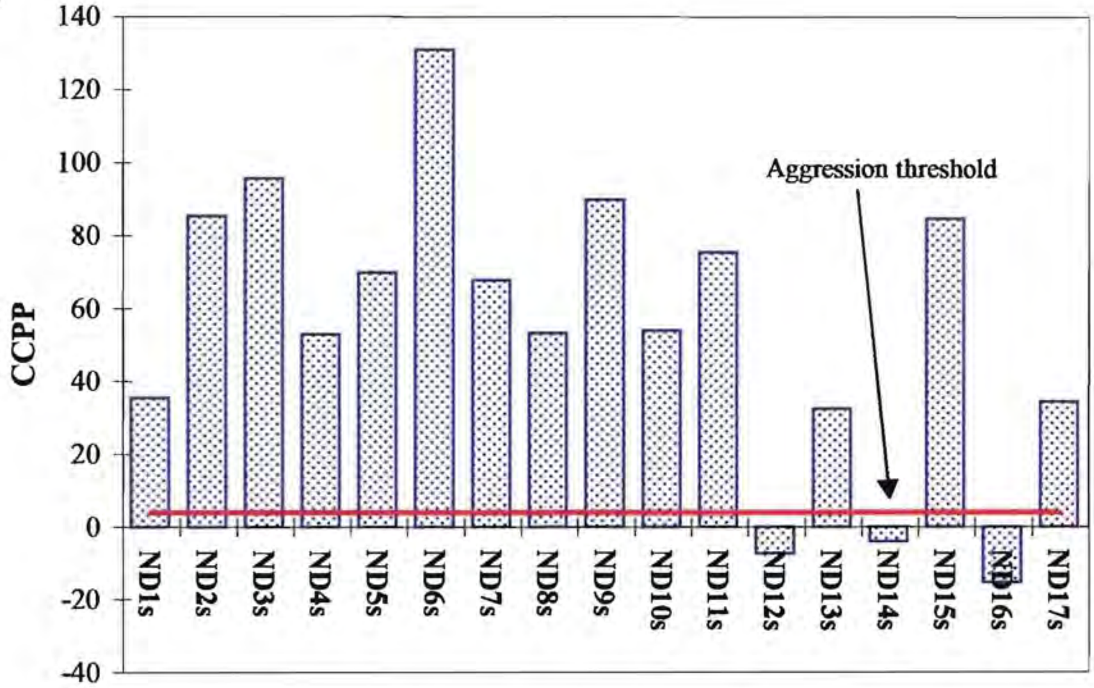


Figure A6.8: ***(a)*** *Calcite saturation index of Kriel waters. For corrosion prevention, SI > 0 (Loewenthal, 1986).* ***(b)*** *Calcium and alkalinity concentrations of Kriel waters. Both calcium and alkalinity concentrations should exceed 50mg/L ($CaCO_3$ equivalent) for the prevention of corrosion (Loewenthal, 1986).* ***(c)*** *Chloride and sulphate concentration of Kriel waters. If chloride or sulphate concentration exceeds 50mg/L the waters will corrode metal surfaces (Loewenthal, 1986).*

a)



b)

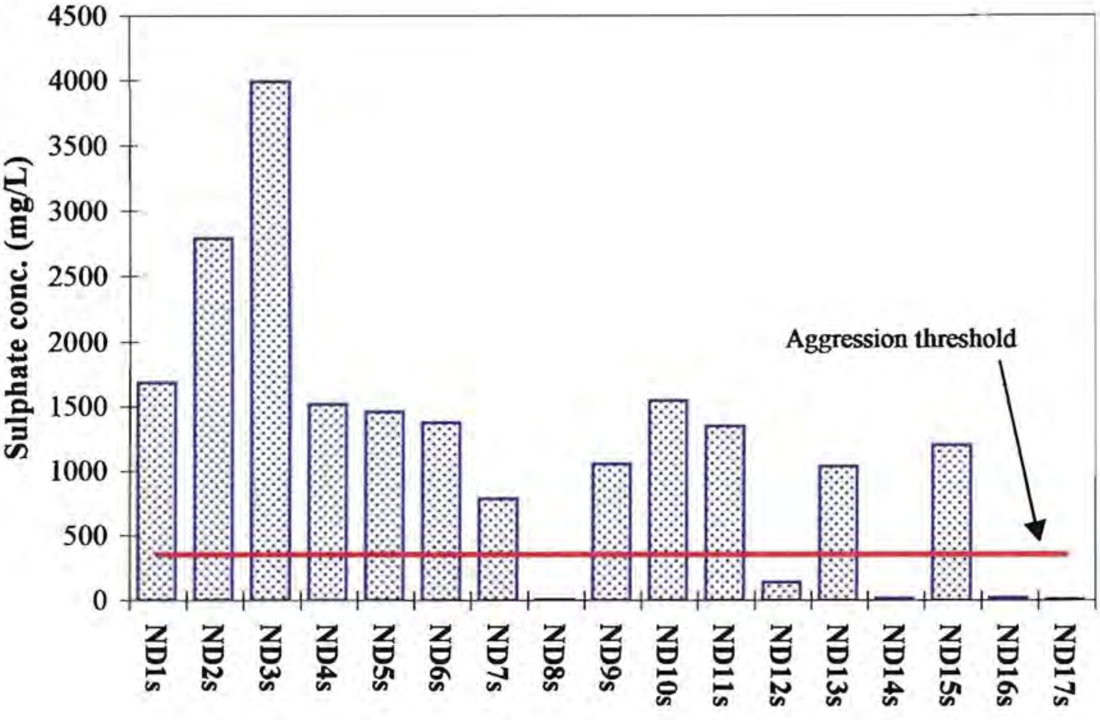
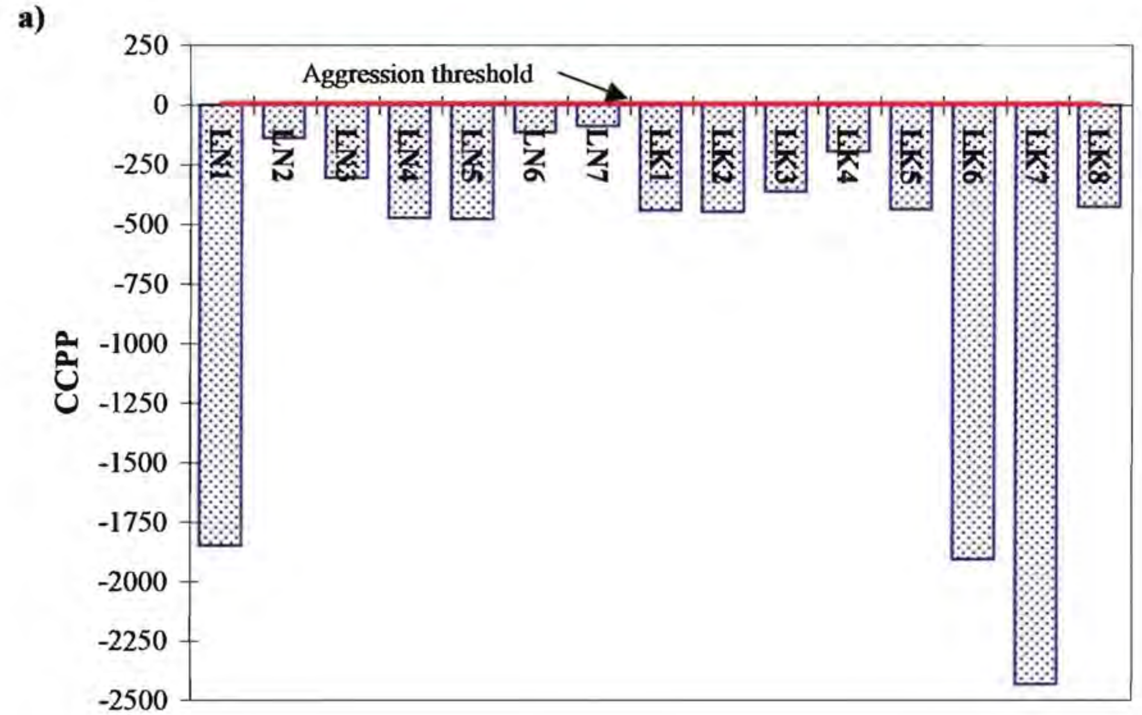


Figure A6.9:(a) *CCPP of New Denmark waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. A CCPP of 4mg/L is recommended.* ***(b)*** *Sulphate concentration of New Denmark waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. The concentration should not exceed 350mg/L.*



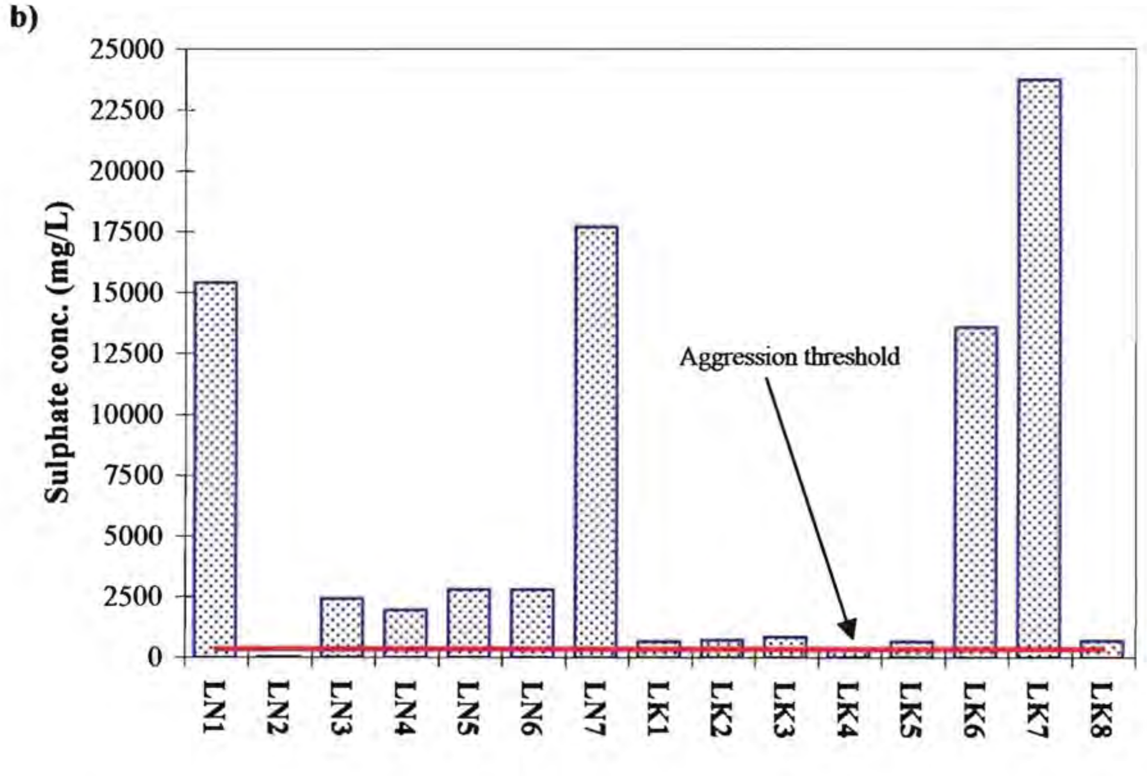


Figure A6.11:(a) *CCPP of Landau waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. A CCPP of 4mg/L is recommended.* ***(b)*** *Sulphate concentration of Landau waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. The concentration should not exceed 350mg/L.*

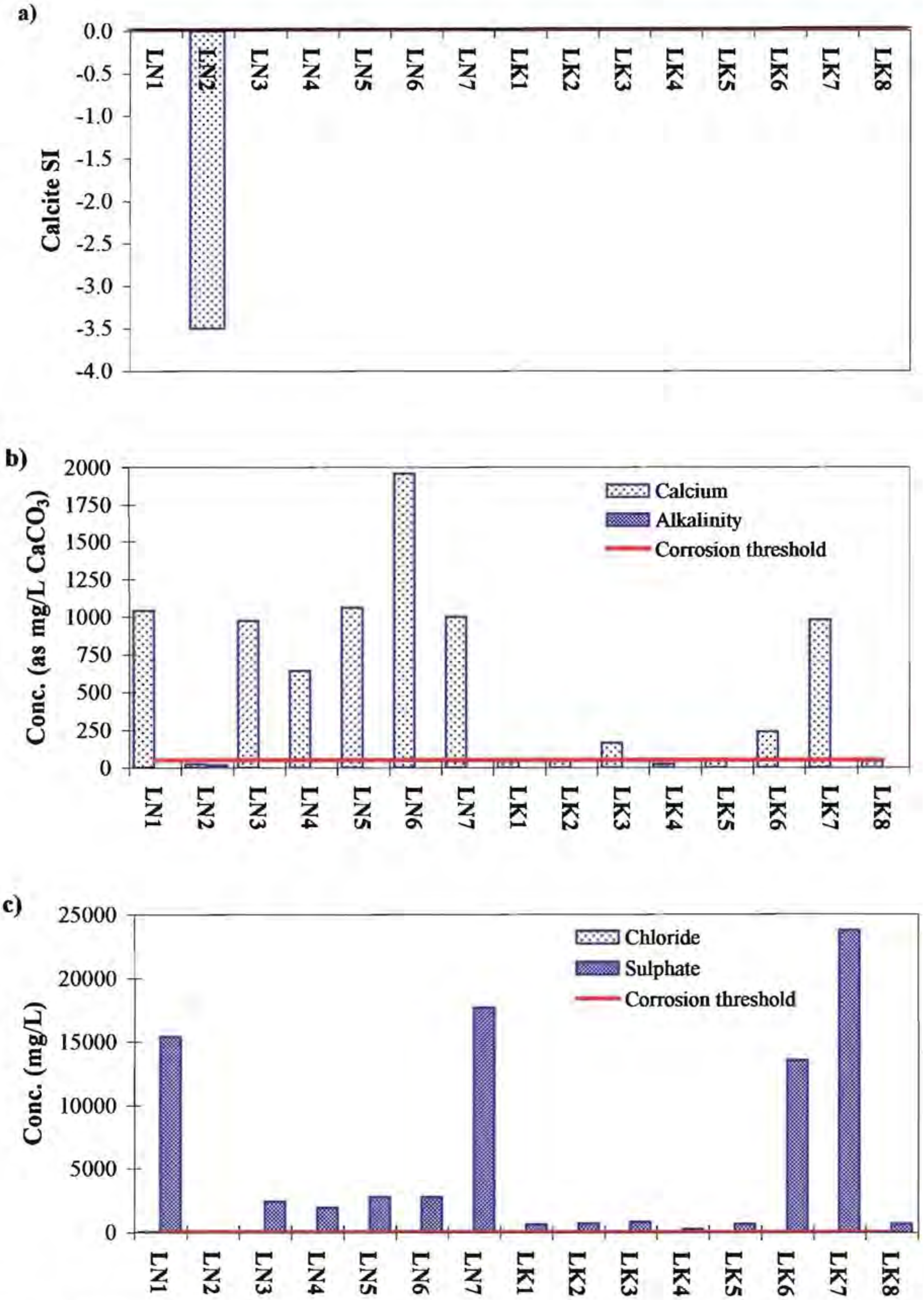


Figure A6.12: ***(a)*** *Calcite saturation index of Landau waters. For corrosion prevention, SI > 0 (Loewenthal, 1986).* ***(b)*** *Calcium and alkalinity concentrations of Landau waters. Both calcium and alkalinity concentrations should exceed 50mg/L ($CaCO_3$ equivalent) for the prevention of corrosion (Loewenthal, 1986).* ***(c)*** *Chloride and sulphate concentration of Landau waters. If chloride or sulphate concentration exceeds 50mg/L the waters will corrode metal surfaces (Loewenthal, 1986).*

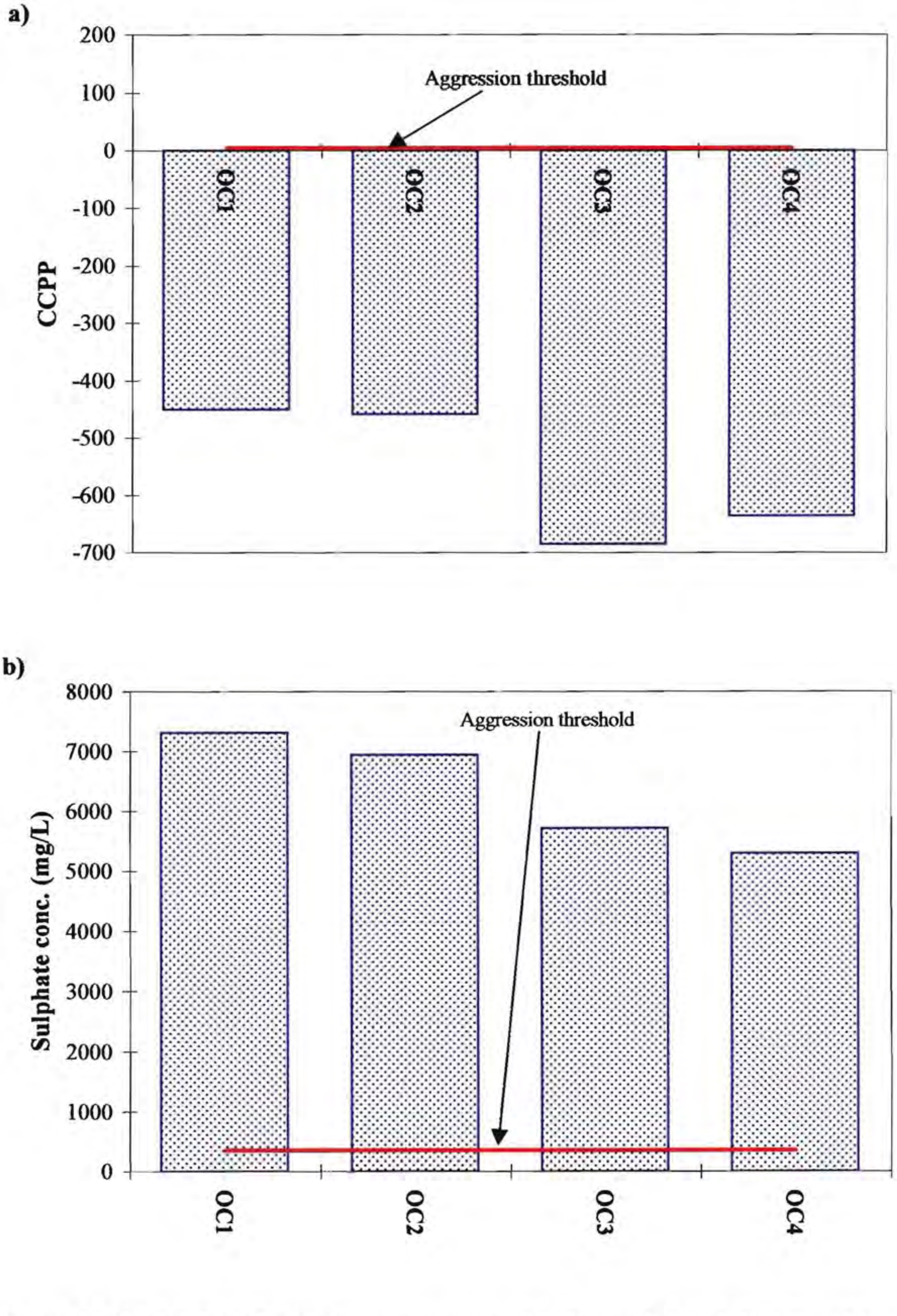


Figure A6.13:(a) *CCPP of TNDBC waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. A CCPP of 4mg/L is recommended.* ***(b)*** *Sulphate concentration of TNDBC waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. The concentration should not exceed 350mg/L.*

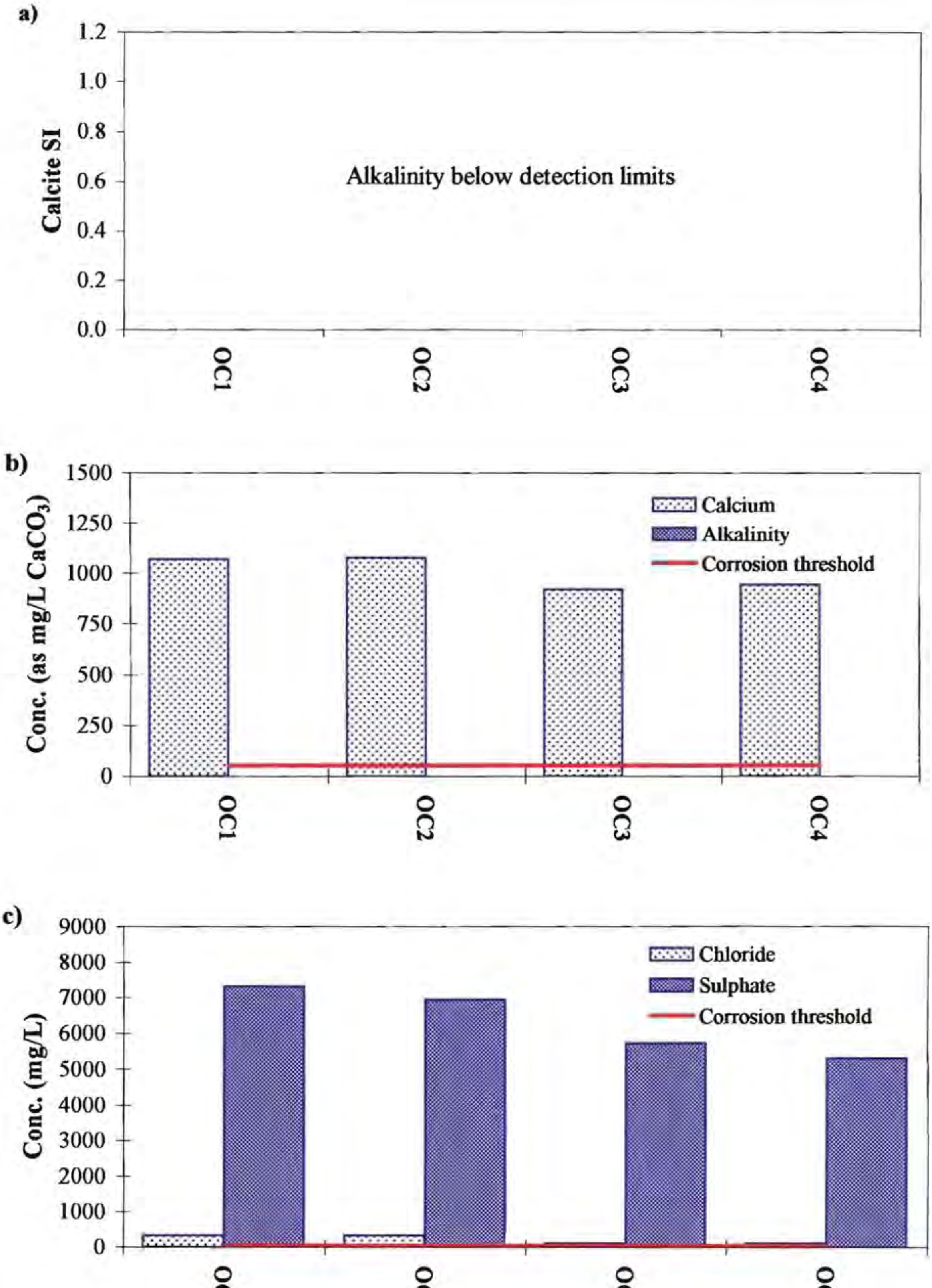


Figure A6.14: ***(a)*** *Calcite saturation index of TNDBC waters. For corrosion prevention, SI > 0 (Loewenthal, 1986).* ***(b)*** *Calcium and alkalinity con-centrations of TNDBC waters. Both calcium and alkalinity concentrations should exceed 50mg/L ($CaCO_3$ equivalent) for the prevention of corrosion (Loewenthal, 1986).* ***(c)*** *Chloride and sulphate concentration of TNDBC waters. If chloride or sulphate concentration exceeds 50mg/L the waters will corrode metal surfaces (Loewenthal, 1986).*

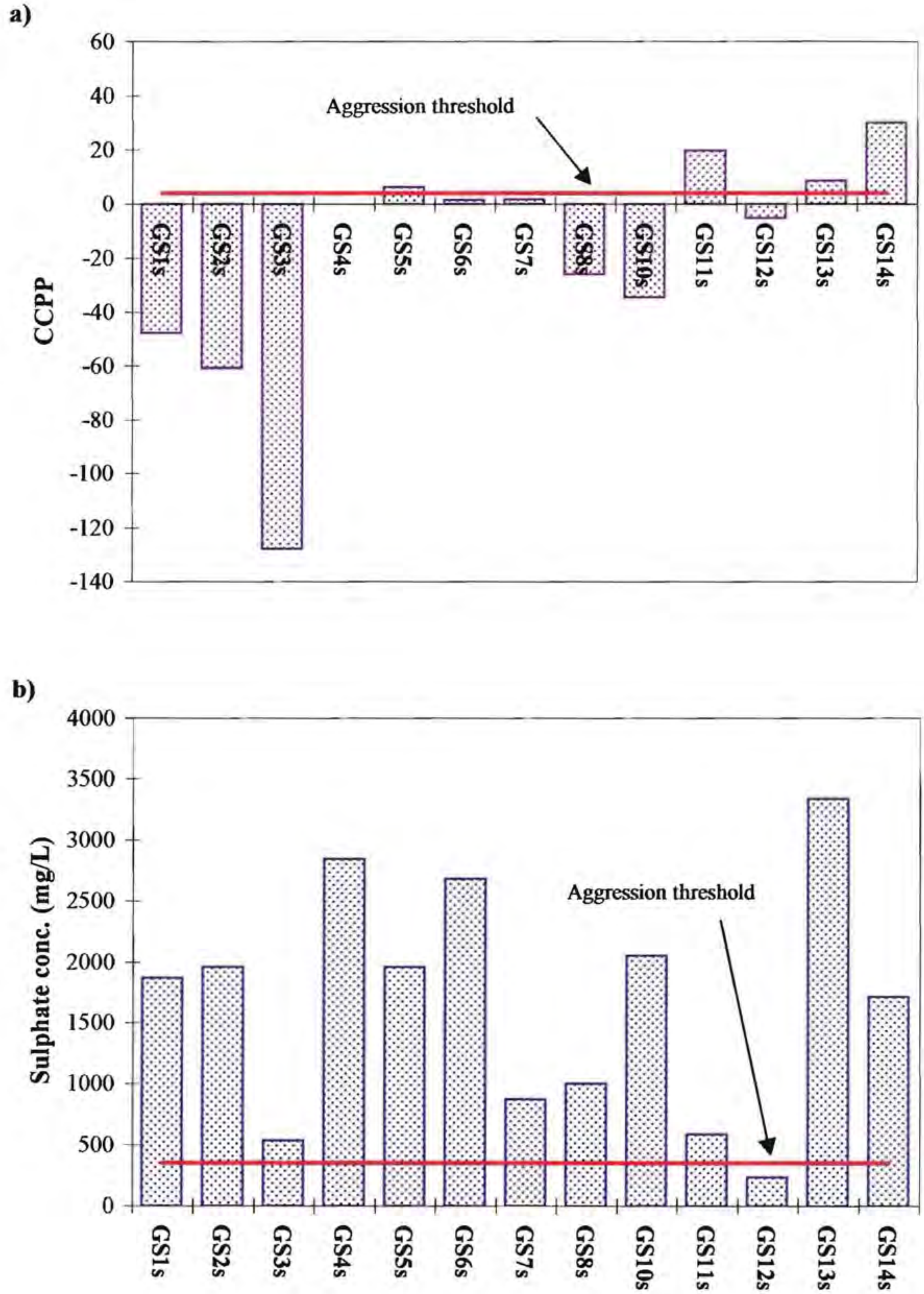


Figure A6.15:(a) *CCPP of Greenside waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. A CCPP of 4mg/L is recommended.* ***(b)*** *Sulphate concentration of Greenside waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. The concentration should not exceed 350mg/L.*

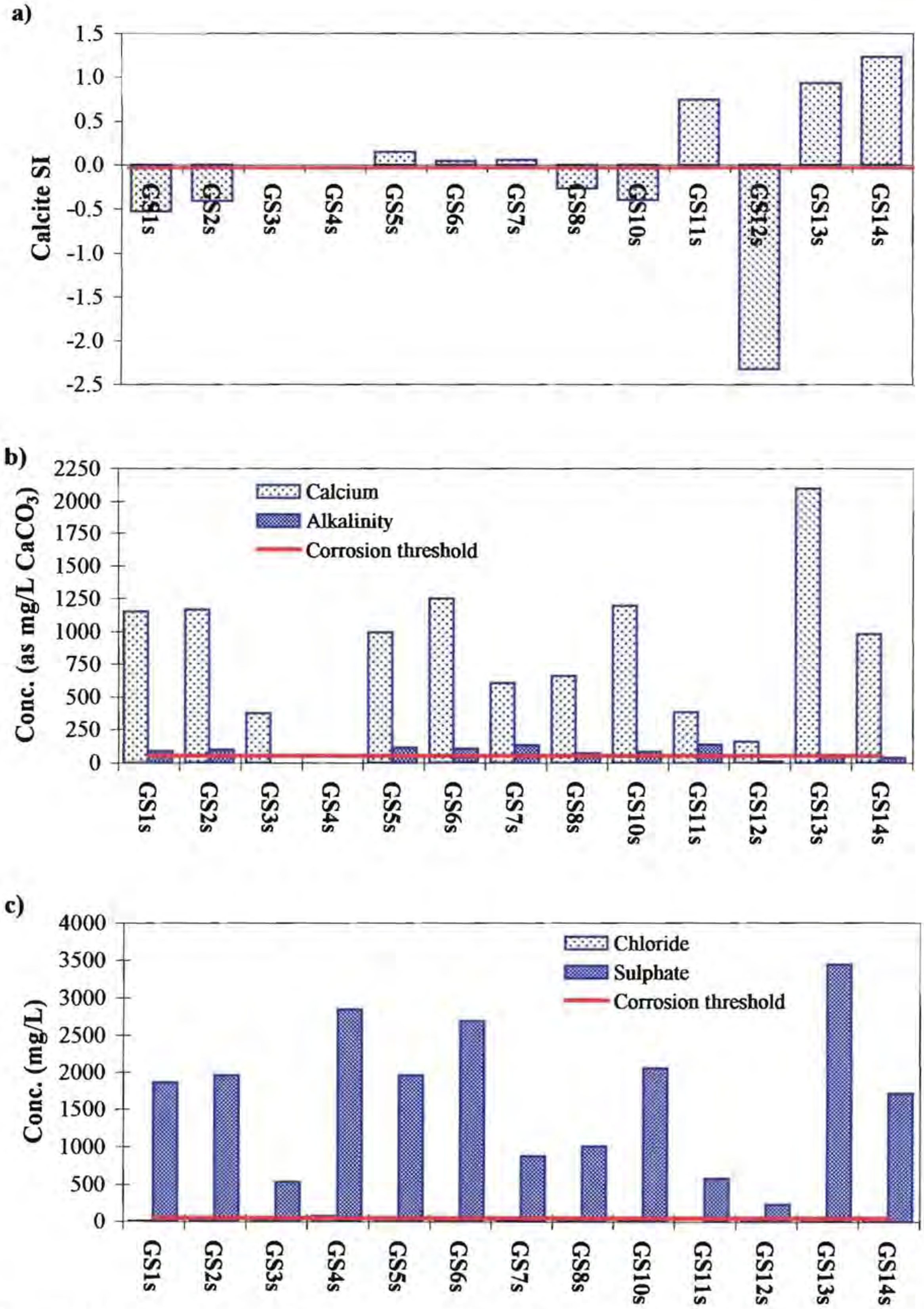
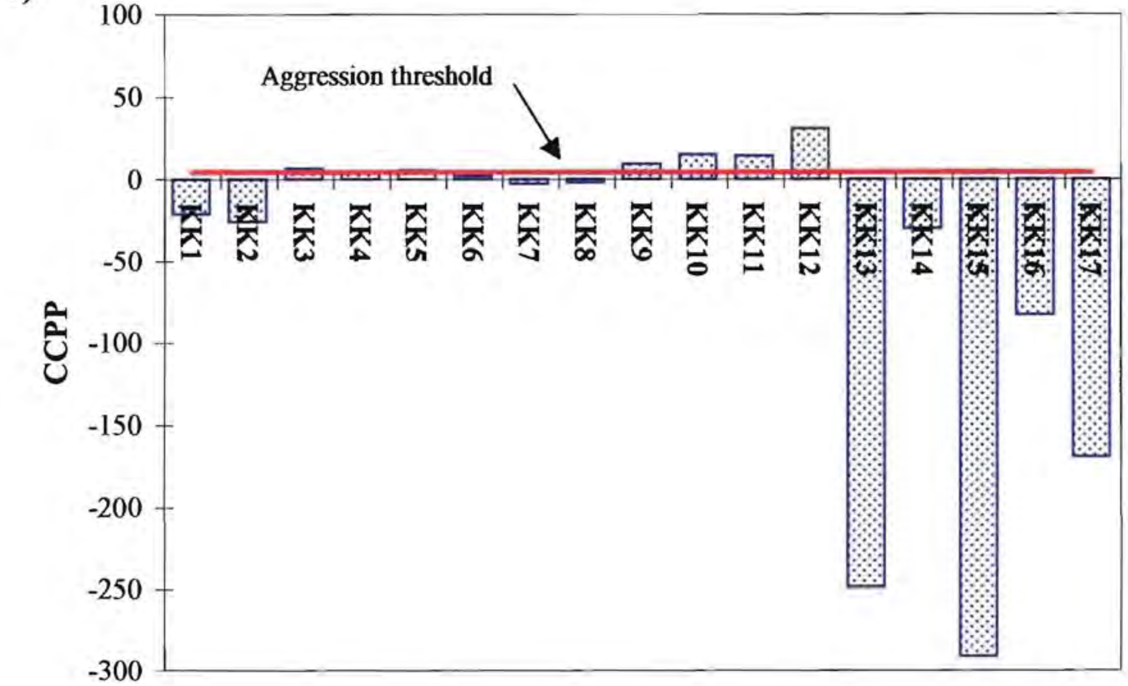


Figure A6.16:* *(a) *Calcite saturation index of Greenside waters. For corrosion prevention, SI > 0 (Loewenthal, 1986).* ***(b)*** *Calcium and alkalinity concentrations of Greenside waters. Both calcium and alkalinity concentrations should exceed 50mg/L ($CaCO_3$ equivalent) for the prevention of corrosion (Loewenthal, 1986).* ***(c)*** *Chloride and sulphate concentration of Greenside waters. If chloride or sulphate concentration exceeds 50mg/L the waters will corrode metal surfaces (Loewenthal, 1986).*

a)



b)

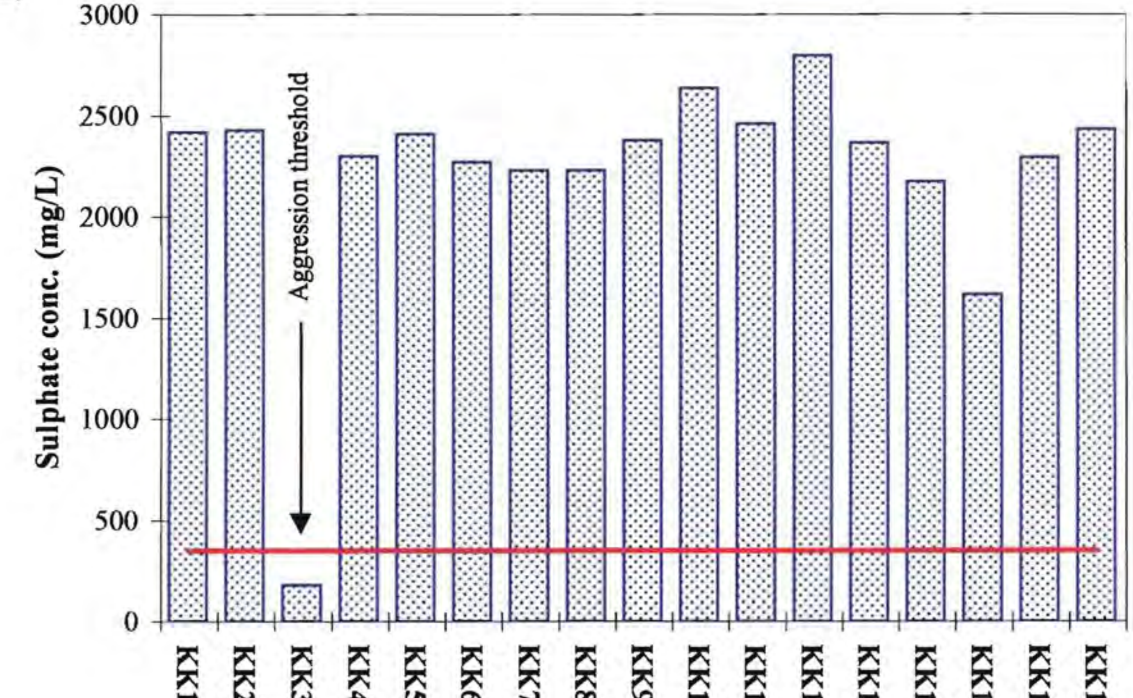


Figure A6.17:(a) *CCPP of Kleinkopje waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. A CCPP of 4mg/L is recommended.* ***(b)*** *Sulphate concentration of Kleinkopje waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. The concentration should not exceed 350mg/L.*

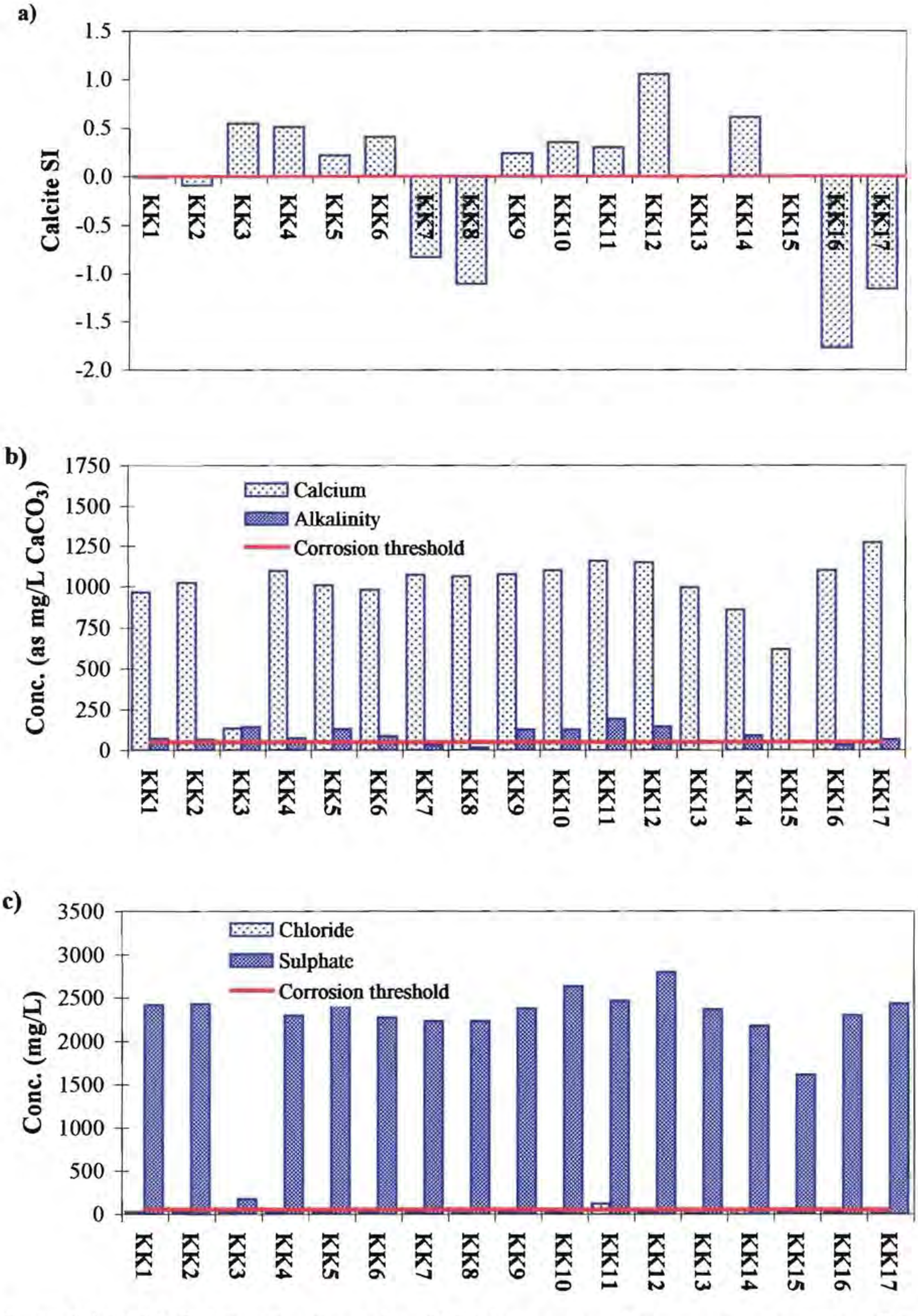
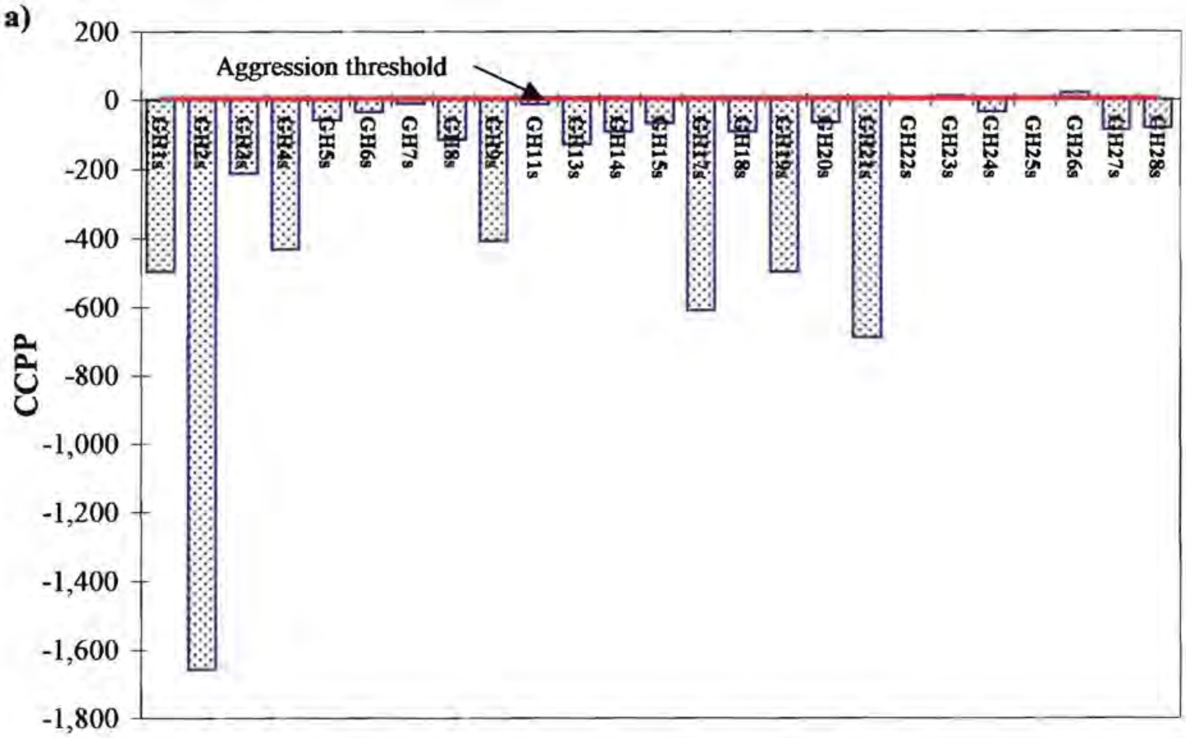


Figure A6.18: ***(a)*** *Calcite saturation index of Kleinkopje waters. For corrosion prevention, SI > 0 (Loewenthal, 1986).* ***(b)*** *Calcium and alkalinity concentrations of Kleinkopje waters. Both calcium and alkalinity concentrations should exceed 50mg/L ($CaCO_3$ equivalent) for the prevention of corrosion (Loewenthal, 1986).* ***(c)*** *Chloride and sulphate concentration of Kleinkopje waters. If chloride or sulphate concentration exceeds 50mg/L the waters will corrode metal surfaces (Loewenthal, 1986).*



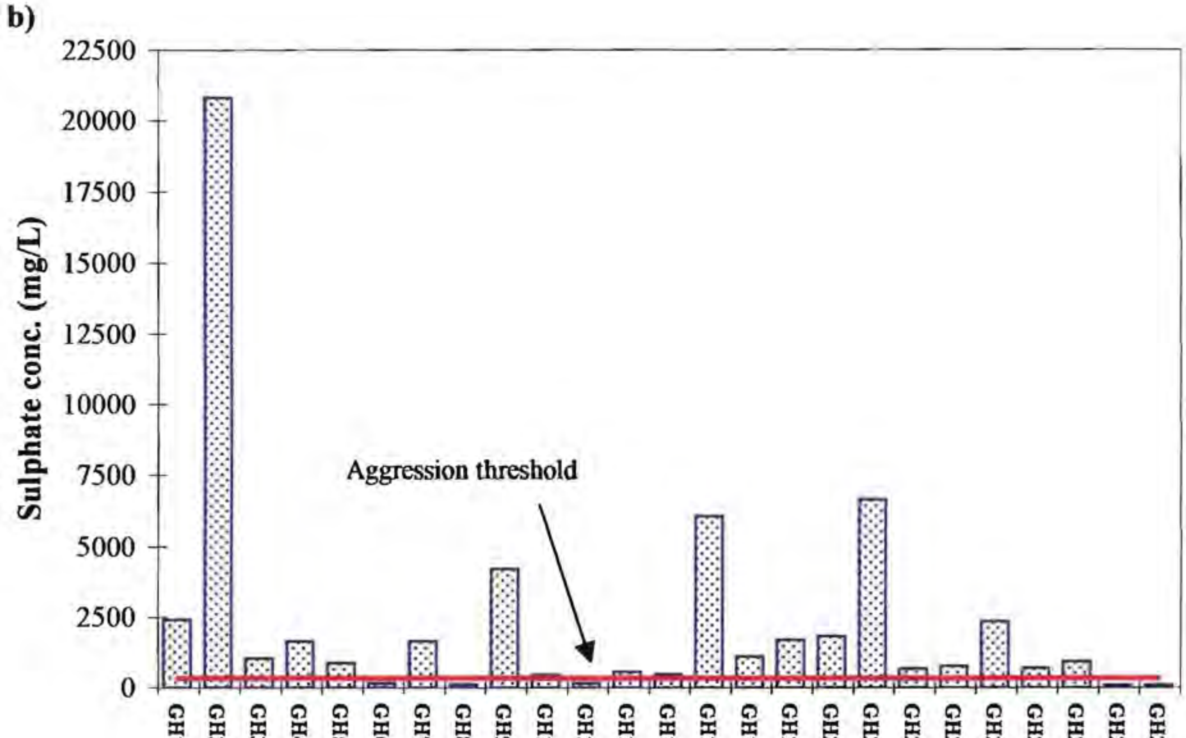


Figure A6.19(a) *CCPP of Goedehoop waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. A CCPP of 4mg/L is recommended.* ***(b)*** *Sulphate concentration of Goedehoop waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. The concentration should not exceed 350mg/L.*

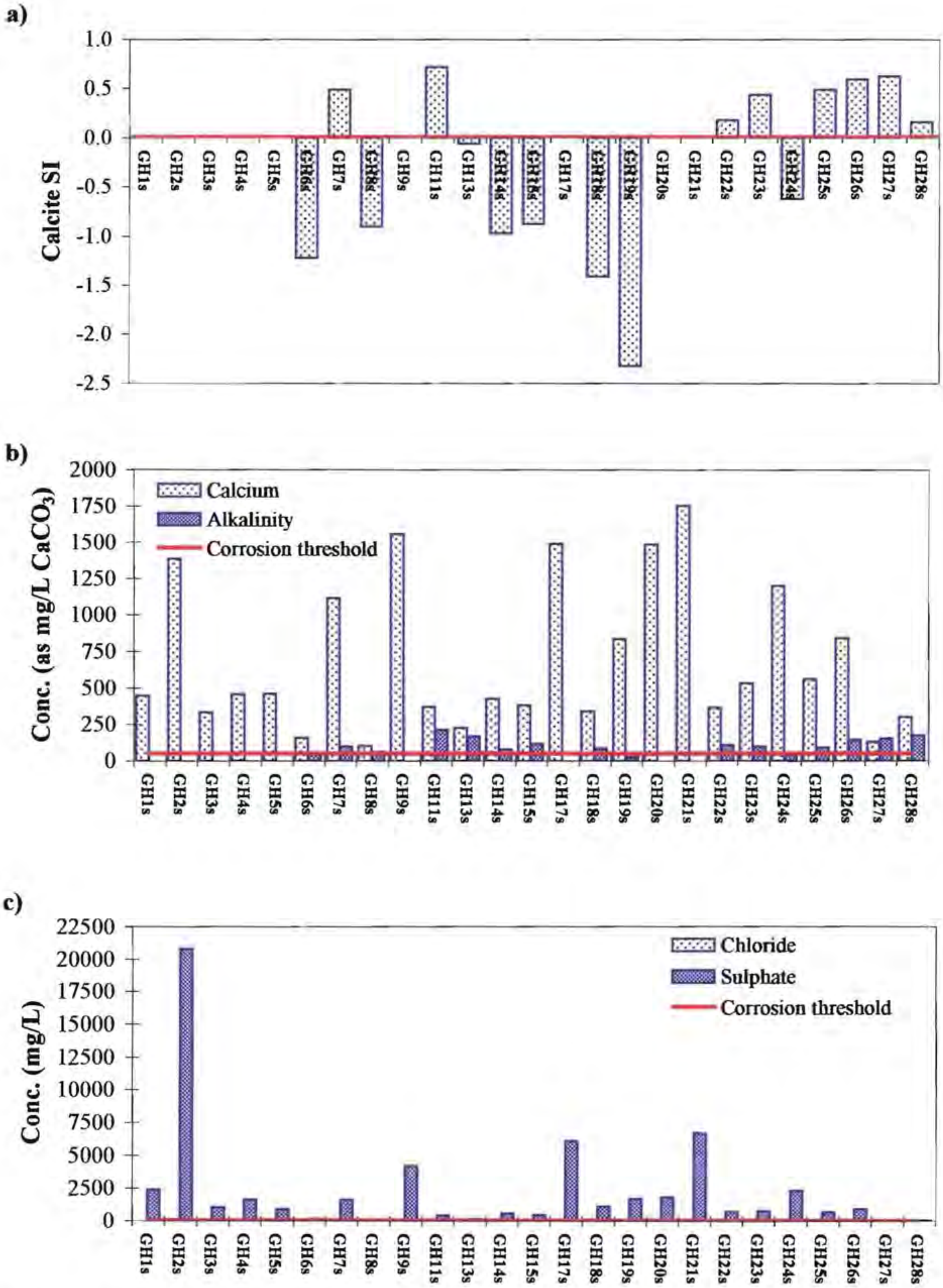
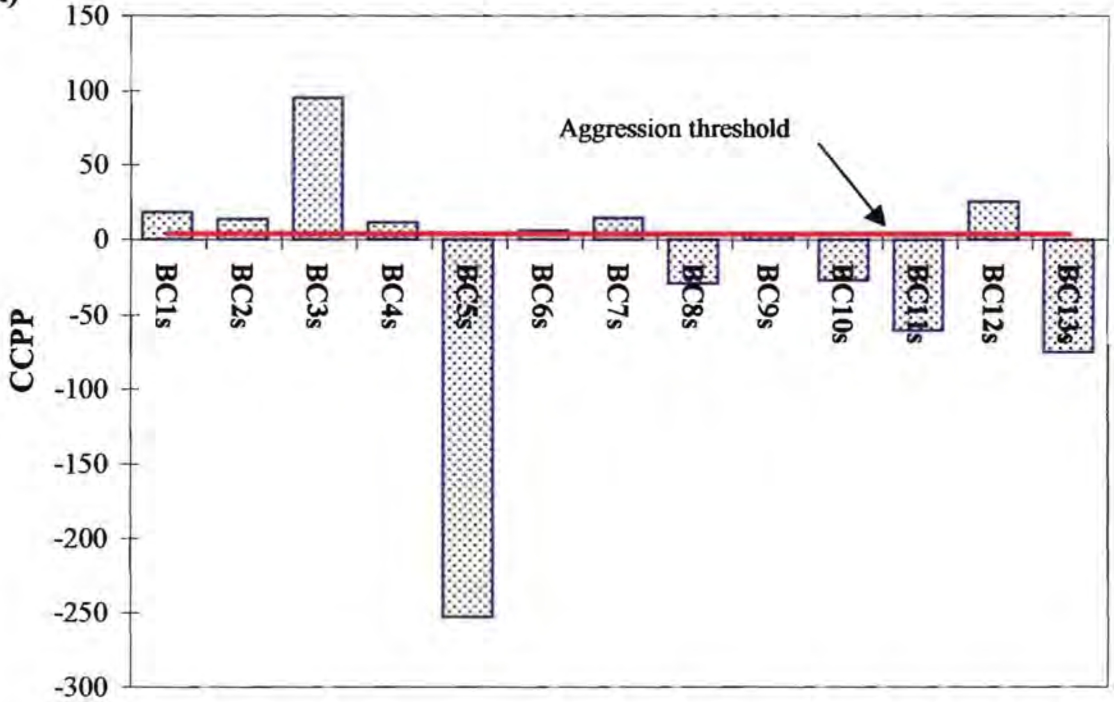


Figure A6.20: ***(a)*** *Calcite saturation index of Goedehoop waters. For corrosion preven-tion, SI > 0 (Loewenthal, 1986).* ***(b)*** *Calcium and alkalinity concentrations of Goedehoop waters. Both calcium and alkalinity concentrations should exceed 50mg/L ($CaCO_3$ equivalent) for the prevention of corrosion (Loewenthal, 1986).* ***(c)*** *Chloride and sulphate concentration of Goedehoop waters. If chloride or sulphate concentration exceeds 50mg/L the waters will corrode metal surfaces (Loewenthal, 1986).*

a)



b)

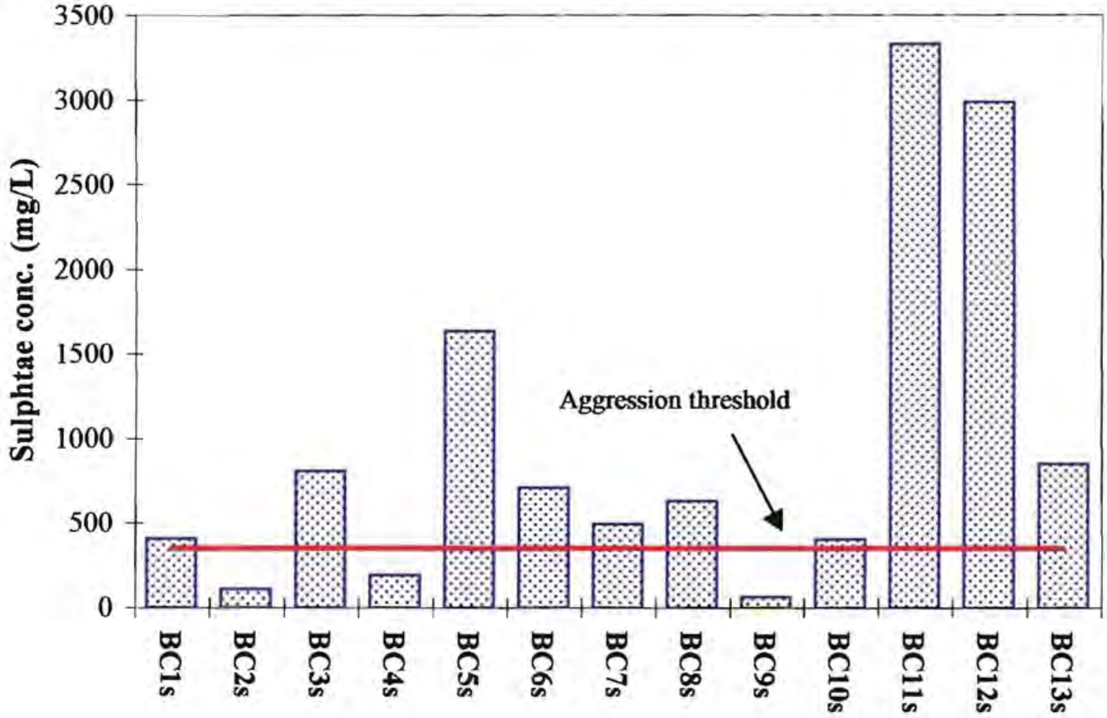


Figure A6.21(a) *CCPP of Bank waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. A CCPP of 4mg/L is recommended.* ***(b)*** *Sulphate concen-tration of Bank waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. The concentration should not exceed 350mg/L.*

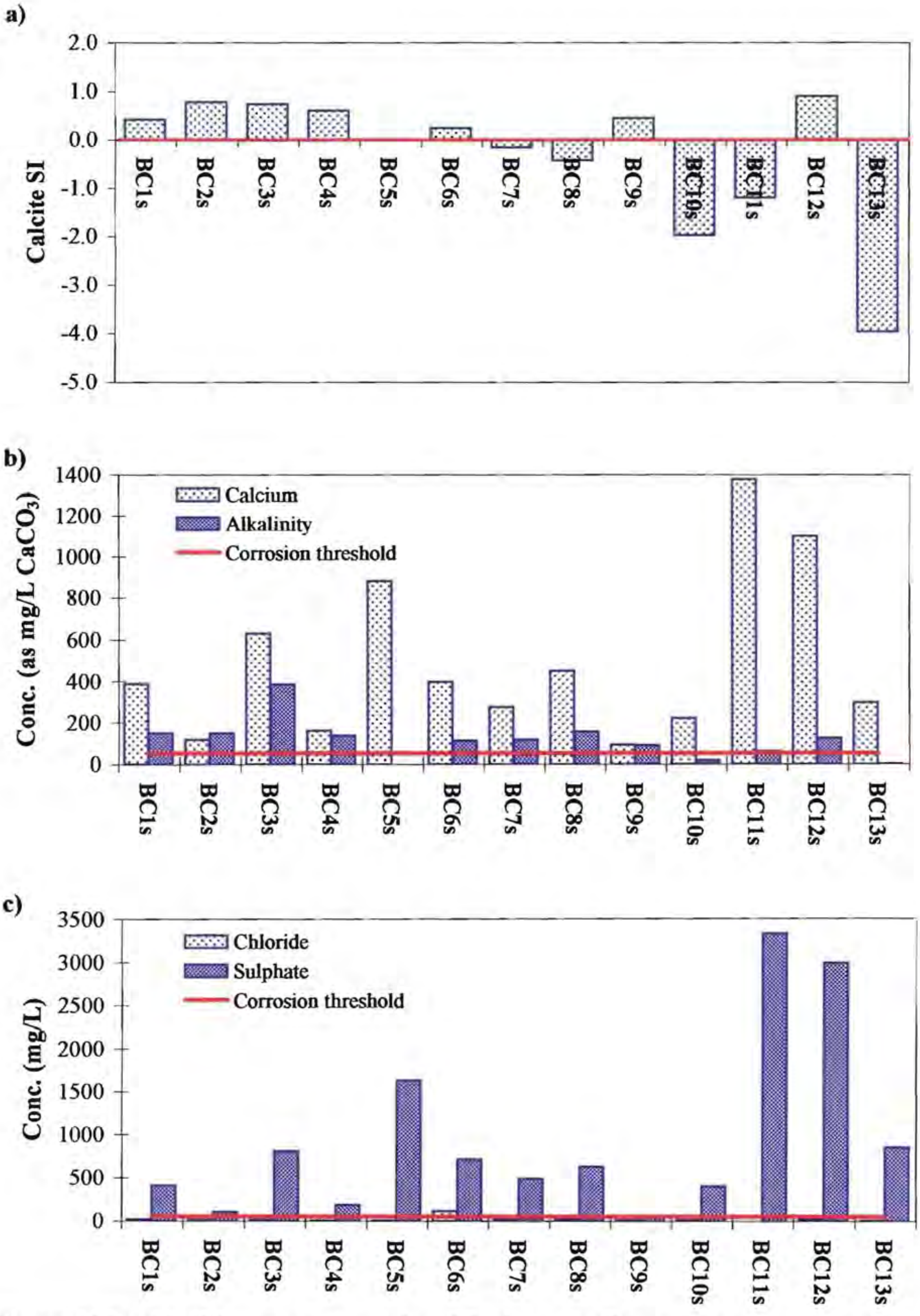
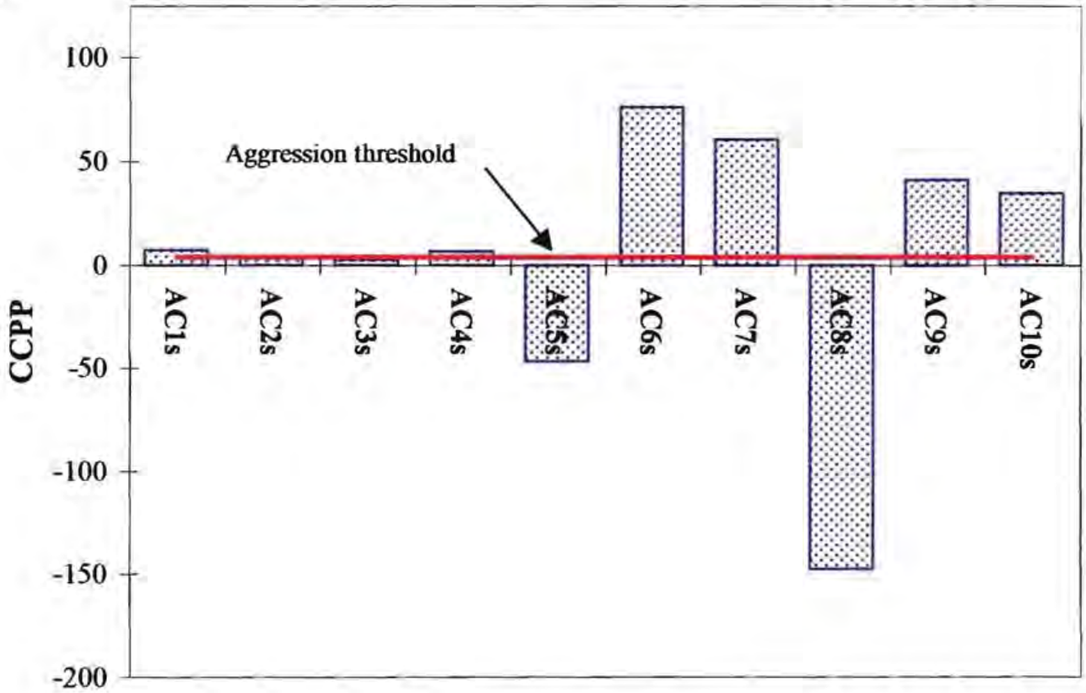


Figure A6.22: ***(a)*** *Calcite saturation index of Bank waters. For corrosion prevention, SI > 0 (Loewenthal, 1986).* ***(b)*** *Calcium and alkalinity concentrations of Bank waters. Both calcium and alkalinity concentrations should exceed 50mg/L ($CaCO_3$ equivalent) for the prevention of corrosion (Loewenthal, 1986).* ***(c)*** *Chloride and sulphate concentration of Bank waters. If chloride or sulphate concentration exceeds 50mg/L the waters will corrode metal surfaces (Loewenthal, 1986).*

a)



b)

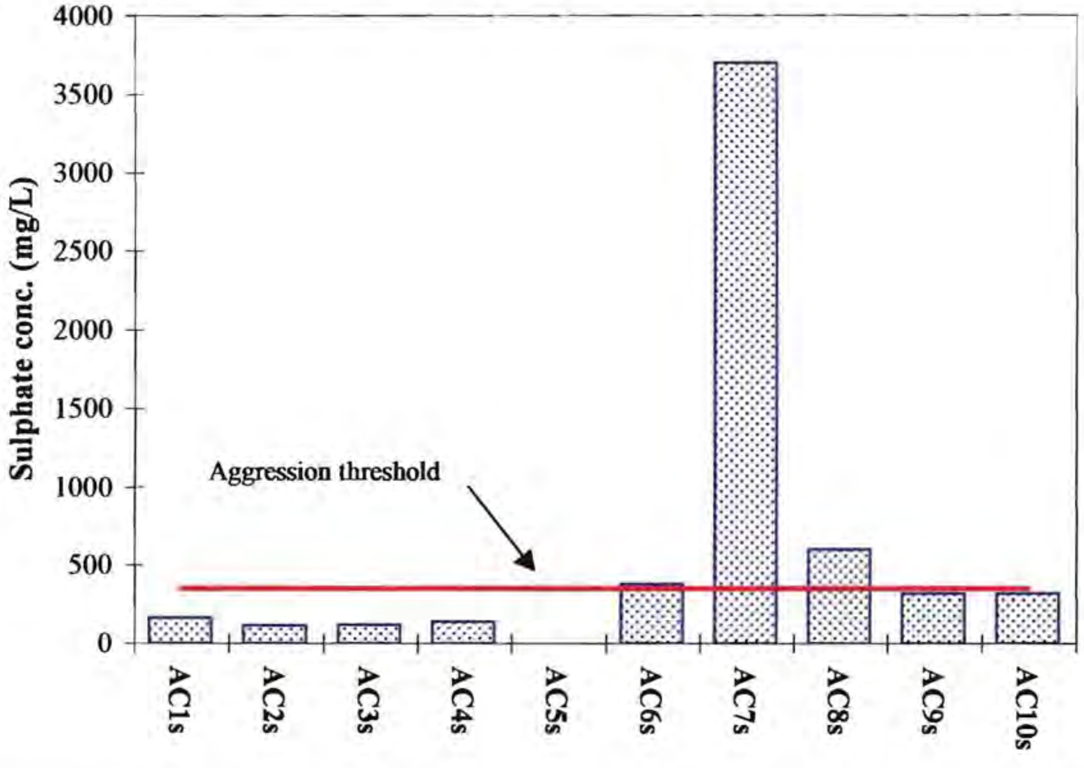


Figure A6.23:(a) *Calcium carbonate precipitation potential (CCPP) of Arnot waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. A CCPP of 4mg/L is recommended.* ***(b)*** *Sulphate concentration of Arnot waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. The concentration should not exceed 350mg/L.*

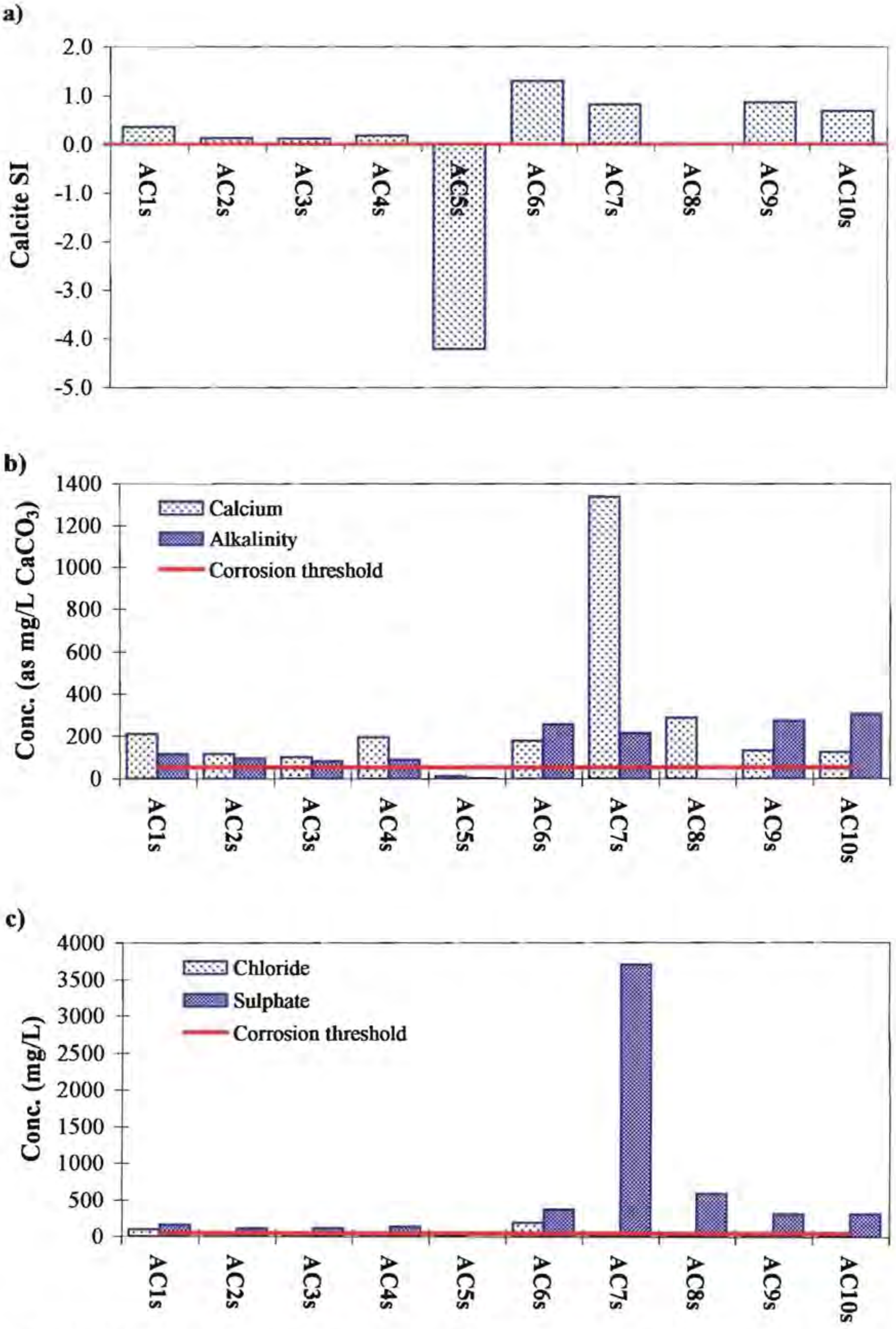
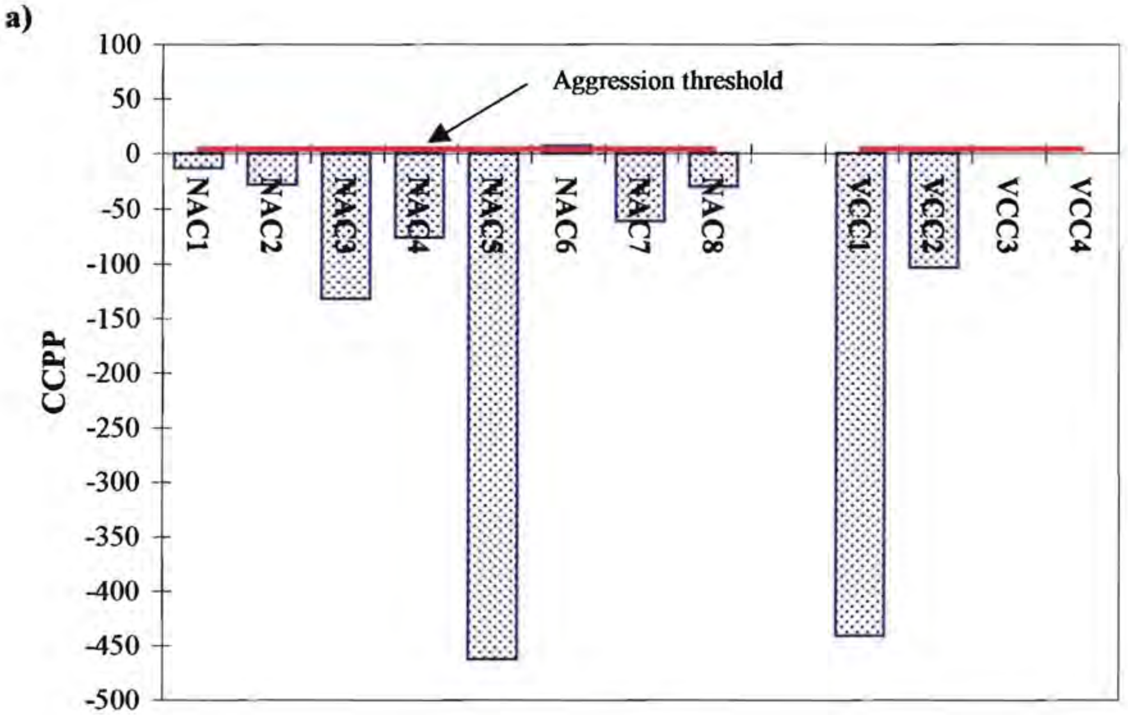


Figure A6.24: ***(a)*** *Calcite saturation index of Arnot waters. For corrosion prevention, SI > 0 (Loewenthal, 1986).* ***(b)*** *Calcium and alkalinity concentrations of Arnot waters. Both calcium and alkalinity concentrations should exceed 50mg/L ($CaCO_3$ equivalent) for the prevention of corrosion (Loewenthal, 1986).* ***(c)*** *Chloride and sulphate concentration of Arnot waters. If chloride or sulphate concentration exceeds 50mg/L the waters will corrode metal surfaces (Loewenthal, 1986).*



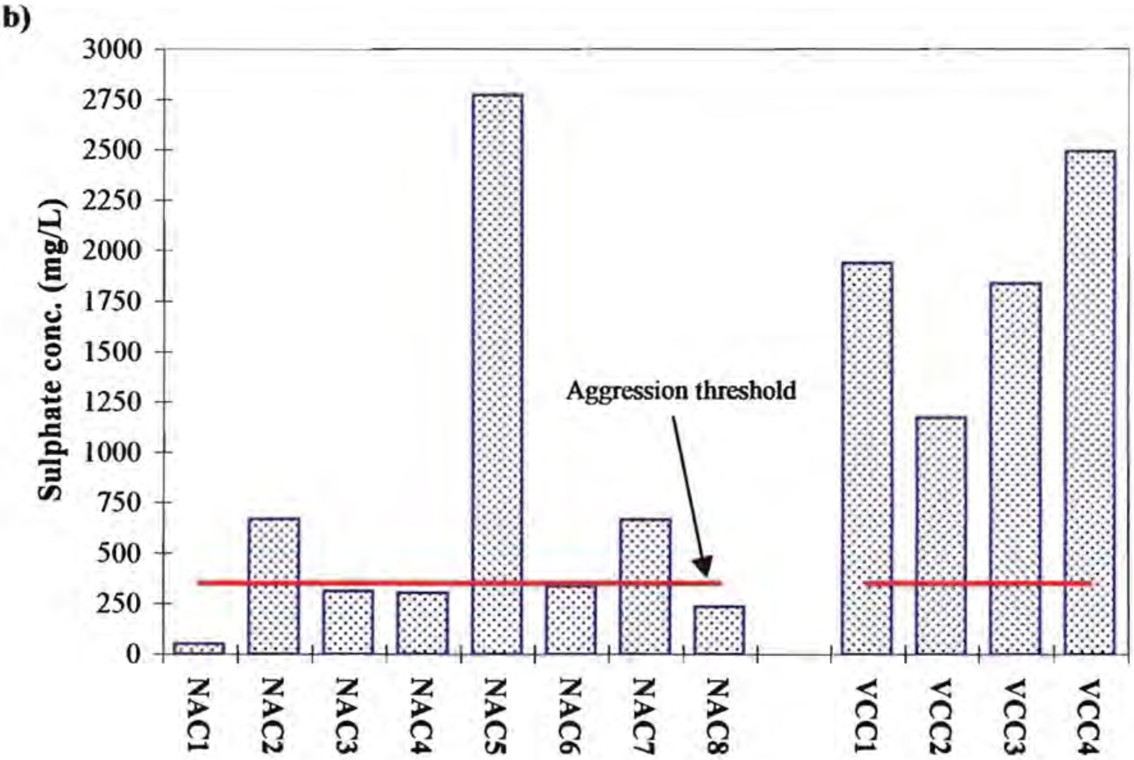


Figure A6.25:(a) *CCPP of Vryheid waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. A CCPP of 4mg/L is recommended.* ***(b)*** *Sulphate concentration of Vryheid waters in terms of the Loewenthal et al. (1986) guidelines for the prevention of aggression. The concentration should not exceed 350mg/L.*

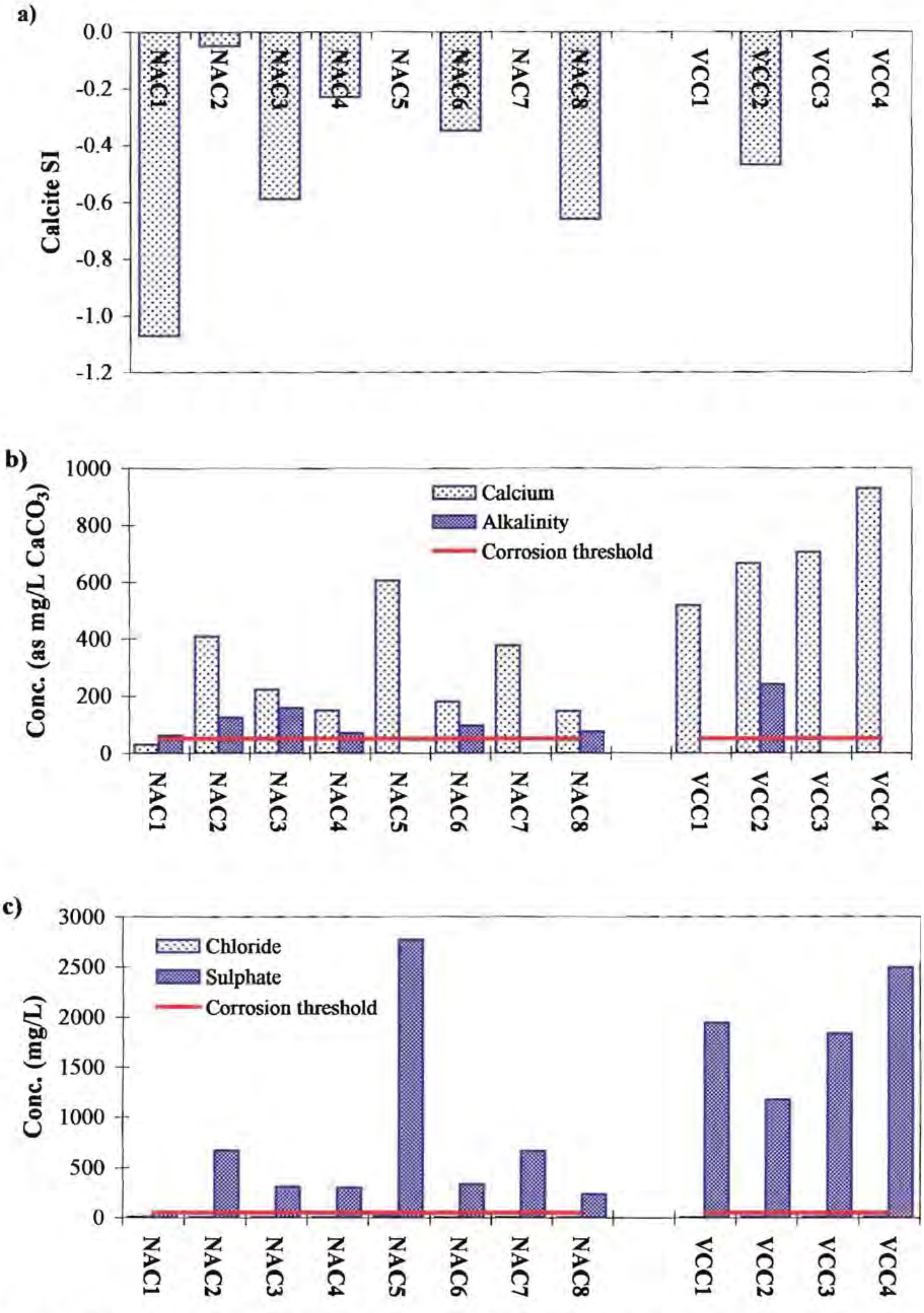


Figure A6.26: ***(a)*** *Calcite saturation index of Vryheid waters. For corrosion prevention, SI > 0 (Loewenthal, 1986).* ***(b)*** *Calcium and alkalinity concentrations of Vryheid waters. Both calcium and alkalinity concentrations should exceed 50mg/L ($CaCO_3$ equivalent) for the prevention of corrosion (Loewenthal, 1986).* ***(c)*** *Chloride and sulphate concentration of Vryheid waters. If chloride or sulphate concentration exceeds 50mg/L the waters will corrode metal surfaces (Loewenthal, 1986).*

Table A6.3: Evaluation of colliery water for irrigation purposes. Degree of restriction on use indicated by "None", "Moderate" and "Severe". "Problematic" trace element conc. are marked.

Potential irrigation	Units	VF1	VF2	VF3	VF4	VF5	NVC1	NVC2	NVC3	NVC4	NVC5
Salinity											
EC	mS/cm	Moderate	Moderate	Moderate	Moderate	Moderate	Severe	Moderate	Moderate	Moderate	Moderate
TDS	mg/L	Moderate	Moderate	Moderate	Moderate	Moderate	Severe	Moderate	Severe	Severe	Moderate
Infiltration											
SAR (in conjunction with EC)		None	None	None	None	None	None	None	None	None	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	Moderate	Moderate	Moderate	None	Moderate	Moderate	None
Chloride:											
Surface	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Boron	mg/L	None	None	None	None	None	Moderate	None	Moderate	Moderate	Moderate
Trace Elements											
Aluminium	mg/L	None	None	None	None	None	None	None	None	None	None
Chromium	mg/L	None	None	None	None	None	None	None	None	None	None
Copper	mg/L	None	None	None	None	None	None	None	None	None	None
Fluoride	mg/L	None	None	None	None	None	None	None	None	None	None
Iron	mg/L	None	None	None	None	None	None	None	None	None	None
Lithium	mg/L	None	None	None	None	None	None	None	None	None	None
Manganese	mg/L	Problematic	Problematic	None	None	None	Problematic	Problematic	Problematic	Problematic	None
Nickel	mg/L	None	None	None	None	None	None	None	None	None	None
Zinc	mg/L	None	None	None	None	None	None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	None	None	None	None	None	None	Moderate	None	None	None
Bicarbonate (HCO_3)	mmol$_c$/L	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate
pH		Problematic	None	None	None	None	None	None	None	None	None

Table A6.3 cont.: *Evaluation of colliery water for irrigation purposes. Degree of restriction on use indicated by "None", "Moderate" and "Severe". "Problematic" trace element conc. are marked.*

Potential irrigation	Units	NVC6	NVC7	NVC8	NVC9	NVC10	NVC11	NVC12	NVC13	NVC14	NVC15
Salinity											
EC	mS/cm	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Severe	Severe	Moderate	Moderate
TDS	mg/L	Moderate	Moderate	Moderate	Moderate	Moderate	None	Severe	Severe	Moderate	Moderate
Infiltration											
SAR (in conjunction with EC)		None	None	None	None	None	None	None	None	None	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	None	None	None	None	None	Severe	Severe	None	None
Sprinkler	mmol$_c$/L	Moderate	None	Moderate	Moderate	Moderate	None	Moderate	Moderate	Moderate	Moderate
Chloride:											
Surface	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Boron	mg/L	Moderate	None	None	None	Moderate	None	Severe	Severe	Moderate	Moderate
Trace Elements											
Aluminium	mg/L	None	None	None	None	None	None	None	None	None	None
Chromium	mg/L	None	None	None	None	None	None	None	None	None	None
Copper	mg/L	None	None	None	None	None	None	None	None	None	None
Fluoride	mg/L	None	None	None	None	None	None	None	None	None	None
Iron	mg/L	None	None	None	None	None	None	None	None	None	None
Lithium	mg/L	None	None	None	None	None	None	None	None	None	None
Manganese	mg/L	Problematic	None	None	None	Problematic	None	Problematic	Problematic	Problematic	Problematic
Nickel	mg/L	None	None	None	None	None	None	None	None	None	None
Zinc	mg/L	None	None	None	None	None	None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	None	None	None	None	None	None	None	None	None	None
Bicarbonate (HCO_3)	mmol$_c$/L	Moderate	None	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate
pH		None	Problematic	None	Problematic	None	None	None	None	None	None

Table A6.3 cont.: Evaluation of colliery water for irrigation purposes. Degree of restriction on use indicated by "None", "Moderate" and "Severe". "Problematic" trace element conc. are marked.

Potential irrigation	Units	NLC1	NLC2	NLC3	NLC4	NLC5	NLC6	NLC7	NLC8	NLC9	NLC10
Salinity											
EC	mS/cm	Moderate	None	Moderate	Moderate	None	Moderate	Moderate	None	None	None
TDS	mg/L	Moderate	None	Severe	Severe	None	Severe	Moderate	None	None	None
Infiltration											
SAR (in conjunction with EC)		None	Severe	None	None	Severe	None	None	Severe	Severe	Moderate
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Chloride:											
Surface	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Boron	mg/L	None	None	None	None	None	None	None	None	None	None
Trace Elements											
Aluminium	mg/L	None	None	None	None	None	None	None	None	None	None
Chromium	mg/L	None	None	None	None	None	None	None	None	None	None
Copper	mg/L	None	None	None	None	None	None	None	None	None	None
Fluoride	mg/L	None	None	None	None	None	None	None	None	None	None
Iron	mg/L	Problematic	None	None	Problematic	None	Problematic	None	None	None	None
Lithium	mg/L	None	None	None	None	None	None	None	None	None	None
Manganese	mg/L	Problematic	None	None	Problematic	None	Problematic	Problematic	None	None	None
Nickel	mg/L	None	None	None	None	None	None	None	None	None	None
Zinc	mg/L	None	None	None	None	None	None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	None	None	None	None	None	None	None	None	None	None
Bicarbonate (HCO_3)	mmol$_c$/L	None	None	Moderate	Moderate	None	Moderate	None	None	None	None
pH		Problematic	Problematic	None	Problematic	Problematic	Problematic	Problematic	Problematic	None	Problematic

Table A6.3 cont.: Evaluation of colliery water for irrigation purposes. Degree of restriction on use indicated by "None", "Moderate" and "Severe". "Problematic" trace element conc. are marked.

Potential irrigation	Units	NLC11	KC1s	KC2s	KC3s	KC4s	KC5s	KC6s	KC8s	KC9s	KC10s
Salinity											
EC	mS/cm	None	Moderate	Moderate	None	None	Moderate	Moderate	Moderate	Moderate	Moderate
TDS	mg/L	None	None	None	None	None	Moderate	Moderate	Moderate	Moderate	Moderate
Infiltration											
SAR (in conjunction with EC)		Severe	Severe	None	Moderate	Moderate	None	None	None	None	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	Severe	None	None	None	Moderate	None	None	None	None
Sprinkler	mmol$_c$/L	None	Moderate	None	None	None	Moderate	Moderate	Moderate	Moderate	None
Chloride:											
Surface	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Boron	mg/L	None	None	None	None	None	None	None	None	None	None
Trace Elements											
Aluminium	mg/L	None	None	None	None	None	None	None	None	None	None
Chromium	mg/L	None	None	None	None	None	None	None	None	None	None
Copper	mg/L	None	None	None	None	None	None	None	None	None	None
Fluoride	mg/L	None	Problematic	None	None	None	None	None	None	None	None
Iron	mg/L	None	None	None	None	None	None	None	None	None	None
Lithium	mg/L	None	None	None	None	None	Problematic	None	None	None	None
Manganese	mg/L	None	None	None	None	None	None	None	Problematic	None	None
Nickel	mg/L	None	None	None	None	None	None	None	None	None	None
Zinc	mg/L	None	None	None	None	None	None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	Moderate	None	None	None	None	None	None	None	None	None
Bicarbonate (HCO_3)	mmol$_c$/L	None	Severe	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate
pH		None	Problematic	None	None	None	None	None	None	None	None

Table A6.3 cont.: Evaluation of colliery water for irrigation purposes. Degree of restriction on use indicated by "None", "Moderate" and "Severe". "Problematic" trace element conc. are marked.

Potential irrigation	Units	KC11s	ND1s	ND2s	ND3s	ND4s	ND5s	ND6s	ND7s	ND8s	ND9s
Salinity											
EC	mS/cm	None	Severe	Severe	Severe	Severe	Severe	Severe	Severe	Moderate	Severe
TDS	mg/L	None	Severe	Severe	Severe	Severe	Severe	Severe	Severe	Moderate	Severe
Infiltration											
SAR (in conjunction with EC)		Moderate	None	None	None	None	None	None	Moderate	Severe	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	Severe	Severe	Severe	Severe	Severe	Severe	Severe	Severe	Severe
Sprinkler	mmol$_c$/L	None	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate
Chloride:											
Surface	mmol$_c$/L	None	Moderate	Severe	Severe	Severe	Severe	Moderate	Severe	Moderate	Moderate
Sprinkler	mmol$_c$/L	None	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate
Boron	mg/L	None	None	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate
Trace Elements											
Aluminium	mg/L	None	None	None	None	None	None	None	None	None	None
Chromium	mg/L	None	None	None	None	None	None	None	None	None	None
Copper	mg/L	None	None	None	None	None	None	None	None	None	None
Fluoride	mg/L	None	None	None	None	None	Problematic	Problematic	Problematic	None	None
Iron	mg/L	None	None	None	None	None	None	None	None	None	None
Lithium	mg/L	None	None	None	None	None	None	None	None	None	None
Manganese	mg/L	Problematic	None	Problematic	Problematic	None	Problematic	None	None	None	Problematic
Nickel	mg/L	None	None	None	None	None	None	None	None	None	None
Zinc	mg/L	None	None	None	None	None	None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO$_3$ - N)	mg/L	None	None	None	None	None	None	None	None	None	None
Bicarbonate (HCO$_3$)	mmol$_c$/L	Moderate	Moderate	Severe	Severe	Moderate	Moderate	Severe	Severe	Severe	Severe
pH		None	None	None	None	None	None	None	None	Problematic	None

Table A6.3 cont.: Evaluation of colliery water for irrigation purposes. Degree of restriction on use indicated by "None", "Moderate" and "Severe". "Problematic" trace element conc. are marked.

Potential irrigation	Units	ND10s	ND11s	ND12s	ND13s	ND14s	ND15s	ND16s	ND17s	LN1	LN2
Salinity											
EC	mS/cm	Severe	Severe	None	Moderate	None	Severe	None	Moderate	Severe	None
TDS	mg/L	Severe	Severe	None	Moderate	None	Severe	None	Moderate	Severe	None
Infiltration											
SAR (in conjunction with EC)		None	None	Moderate	None	Moderate	None	Moderate	Severe	None	Severe
Specific Ion Toxicity											
Sodium:											
Surface	SAR	Severe	Severe	None	Moderate	None	Severe	None	Severe	None	None
Sprinkler	mmol$_c$/L	Moderate	Moderate	None	Moderate	None	Moderate	None	Moderate	None	None
Chloride:											
Surface	mmol$_c$/L	Severe	Severe	None	None	None	Moderate	None	Severe	None	None
Sprinkler	mmol$_c$/L	Moderate	Moderate	None	Moderate	None	Moderate	None	Moderate	None	None
Boron	mg/L	Moderate	Moderate	None	None	None	Moderate	None	None	None	None
Trace Elements											
Aluminium	mg/L	None	None	None	None	None	None	None	None	Problematic	None
Chromium	mg/L	None	None	None	None	None	None	None	None	None	None
Copper	mg/L	None	None	None	None	None	None	None	None	None	None
Fluoride	mg/L	None	None	None	None	None	None	None	None	Problematic	None
Iron	mg/L	None	None	None	None	None	None	None	None	Problematic	None
Lithium	mg/L	None	None	None	None	None	None	None	None	None	None
Manganese	mg/L	Problematic	None	None	None	None	None	None	None	Problematic	None
Nickel	mg/L	None	None	None	None	None	None	None	None	Problematic	Problematic
Zinc	mg/L	None	None	None	None	None	None	None	None	Problematic	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	None	None	None	None	None	None	None	None	Moderate	None
Bicarbonate (HCO_3)	mmol$_c$/L	Moderate	Moderate	Moderate	Moderate	None	Severe	Moderate	Severe	None	None
pH		None	None	None	Problematic	None	None	None	Problematic	Problematic	Problematic

Table A6.3 cont.: *Evaluation of colliery water for irrigation purposes. Degree of restriction on use indicated by "None", "Moderate" and "Severe". "Problematic" trace element conc. are marked.*

Potential irrigation	Units	LN3	LN4	LN5	LN6	LN7	LK1	LK2	LK3	LK4	LK5
Salinity											
EC	mS/cm	Moderate	Moderate	Severe	Severe	Severe	Moderate	Moderate	Moderate	None	Moderate
TDS	mg/L	Severe	Severe	Severe	Severe	Severe	Moderate	Moderate	Moderate	None	Moderate
Infiltration											
SAR (in conjunction with EC)		None	None	None	None	None	None	None	None	Moderate	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Chloride:											
Surface	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	Moderate	None	None	None	None	None
Boron	mg/L	None	None	None	None	None	None	None	None	None	None
Trace Elements											
Aluminium	mg/L	Problematic	Problematic	Problematic	Problematic	None	Problematic	Problematic	Problematic	Problematic	Problematic
Chromium	mg/L	None	None	None	None	None	None	None	None	None	None
Copper	mg/L	None	None	None	None	None	None	None	None	None	None
Fluoride	mg/L	Problematic	Problematic	None	None	Problematic	Problematic	Problematic	Problematic	None	Problematic
Iron	mg/L	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	None	Problematic
Lithium	mg/L	None	None	None	None	None	None	None	None	None	None
Manganese	mg/L	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic
Nickel	mg/L	Problematic	Problematic	Problematic	Problematic	None	Problematic	Problematic	Problematic	Problematic	Problematic
Zinc	mg/L	None	None	None	None	None	None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	None	None	None	None	Moderate	None	None	None	None	None
Bicarbonate (HCO_3)	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
pH		Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic

Table A6.3 cont.: *Evaluation of colliery water for irrigation purposes. Degree of restriction on use indicated by "None", "Moderate" and "Severe". "Problematic" trace element conc. are marked.*

Potential irrigation	**Units**	**LK6**	**LK7**	**LK8**	**OC1**	**OC2**	**OC3**	**OC4**	**GS1s**	**GS2s**	**GS3s**
Salinity											
EC	mS/cm	Severe	Severe	Moderate	Severe	Severe	Severe	Severe	Severe	Severe	Moderate
TDS	mg/L	Severe	Severe	Moderate	Severe	Severe	Severe	Severe	Severe	Severe	Moderate
Infiltration											
SAR (in conjunction with EC)		None	None	None	None	None	None	None	None	None	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	None	None	Severe	Severe	Moderate	Moderate	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	None
Chloride:											
Surface	mmol$_c$/L	None	None	None	Moderate	Moderate	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	Moderate	Moderate	Moderate	Moderate	None	None	None
Boron	mg/L	None	None	None	None	None	None	None	None	None	None
Trace Elements											
Aluminium	mg/L	Problematic	Problematic	Problematic	None	None	None	Problematic	None	None	Problematic
Chromium	mg/L	None	None	None	None	None	None	None	None	None	Problematic
Copper	mg/L	Problematic	Problematic	None	None	None	None	None	None	None	None
Fluoride	mg/L	Problematic	Problematic	Problematic	None	None	Problematic	Problematic	None	None	None
Iron	mg/L	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	None	Problematic	None
Lithium	mg/L	None	None	None	None	None	None	None	None	None	None
Manganese	mg/L	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic
Nickel	mg/L	Problematic	Problematic	Problematic	None	None	None	None	None	None	None
Zinc	mg/L	None	Problematic	None	None	None	None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	Moderate	Moderate	None	Moderate	Moderate	None	None	None	None	None
Bicarbonate (HCO_3)	mmol$_c$/L	None	None	None	None	None	None	None	Moderate	Moderate	None
pH		Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	None	Problematic	Problematic

Table A6.3 cont.: *Evaluation of colliery waters for irrigation purposes. Degree of restriction on use are indicated by "None", "Moderate" and "Severe". "Problematic" trace elements are marked.*

Potential irrigation	**Units**	**KK1**	**KK2**	**KK3**	**KK4**	**KK5**	**KK6**	**KK7**	**KK8**	**KK9**	**KK10**
Salinity											
EC	mS/cm	Moderate	Moderate	None	Severe	Severe	Moderate	Moderate	Moderate	Severe	Severe
TDS	mg/L	Severe	Severe	None	Severe	Severe	Severe	Severe	Severe	Severe	Severe
Infiltration											
SAR (in conjunction with EC)		None	None	Moderate	None	None	None	None	None	None	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Chloride:											
Surface	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Boron	mg/L	None	None	None	None	None	None	None	None	None	None
Trace Elements											
Aluminium	mg/L	None	None	None	None	None	None	None	None	None	None
Chromium	mg/L	None	None	None	None	None	None	None	None	None	None
Copper	mg/L	None	None	None	None	None	None	None	None	None	None
Fluoride	mg/L	None	Problematic	None	None	None	None	Problematic	None	None	None
Iron	mg/L	None	None	None	None	None	None	None	None	None	None
Lithium	mg/L	None	None	None	None	None	None	None	None	None	None
Manganese	mg/L	Problematic	Problematic	None	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic
Nickel	mg/L	None	None	None	None	None	None	None	None	None	None
Zinc	mg/L	None	None	None	None	None	None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	Moderate	Moderate	None	Moderate	None	None	None	None	None	None
Bicarbonate (HCO_3)	mmol$_c$/L	None	None	Moderate	None	Moderate	Moderate	None	None	Moderate	Moderate
pH		None	None	None	None	None	None	None	None	None	None

Table A6.3 cont.: *Evaluation of colliery waters for irrigation purposes. Degree of restriction on use are indicated by "None", "Moderate" and "Severe". "Problematic" trace elements are marked.*

Potential irrigation	**Units**	**KK11**	**KK12**	**KK13**	**KK14**	**KK15**	**KK16**	**KK17**	**GH1s**	**GH2s**	**GH3s**
Salinity											
EC	mS/cm	Severe	Severe	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Severe	Moderate
TDS	mg/L	Severe	Severe	Severe	Severe	Severe	Severe	Severe	Severe	Severe	Moderate
Infiltration											
SAR (in conjunction with EC)		None	None	None	None	None	None	None	None	None	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	None	None	Moderate
Chloride:											
Surface	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	Moderate	None	None	None	None	None	None	None	None	None
Boron	mg/L	None	None	None	None	None	None	None	None	None	None
Trace Elements											
Aluminium	mg/L	None	None	None	None	Problematic	None	None	Problematic	Problematic	Problematic
Chromium	mg/L	None	None	None	None	None	None	None	Problematic	Problematic	None
Copper	mg/L	None	None	None	None	None	None	None	None	Problematic	None
Fluoride	mg/L	None	None	Problematic	None	Problematic	Problematic	None	None	None	None
Iron	mg/L	None	None	Problematic	None	Problematic	Problematic	None	Problematic	Problematic	None
Lithium	mg/L	None	None	None	None	None	None	None	Problematic	None	None
Manganese	mg/L	Problematic	Problematic	Problematic	None	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic
Nickel	mg/L	None	None	Problematic	None	None	None	Problematic	Problematic	Problematic	None
Zinc	mg/L	None	None	None	None	None	None	None	None	Problematic	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	None	None	None	None	None	None	None	None	Severe	None
Bicarbonate (HCO_3)	mmol$_c$/L	Moderate	Moderate	None	Moderate	None	None	None	None	None	None
pH		None	None	Problematic	None	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic

Table A6.3 cont.: *Evaluation of colliery waters for irrigation purposes. Degree of restriction on use are indicated by "None", "Moderate" and "Severe". "Problematic" trace elements are marked.*

Potential irrigation	**Units**	**GH4s**	**GH5s**	**GH6s**	**GH7s**	**GH8s**	**GH9s**	**GH11s**	**GH13s**	**GH14s**	**GH15s**
Salinity											
EC	mS/cm	Moderate	Moderate	None	Moderate	None	Severe	Moderate	None	Moderate	Moderate
TDS	mg/L	Severe	Moderate	None	Severe	None	Severe	Moderate	None	Moderate	Moderate
Infiltration											
SAR (in conjunction with EC)		None	None	Moderate	None	Moderate	None	None	Moderate	None	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	Moderate	None	None	Moderate	None	None	None
Chloride:											
Surface	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Boron	mg/L	None	None	None	None	None	None	None	None	None	None
Trace Elements											
Aluminium	mg/L	Problematic	None	None	None	None	Problematic	None	None	None	None
Chromium	mg/L	Problematic	None	None	None	None	None	None	None	None	None
Copper	mg/L	None	None	None	None	None	None	None	None	None	None
Fluoride	mg/L	None	None	None	None	None	Problematic	None	None	Problematic	Problematic
Iron	mg/L	Problematic	None	None	None	None	Problematic	None	None	Problematic	Problematic
Lithium	mg/L	None	None	None	None	None	None	None	None	None	None
Manganese	mg/L	Problematic	Problematic	Problematic	None	Problematic	Problematic	Problematic	None	Problematic	Problematic
Nickel	mg/L	Problematic	None	None	None	None	Problematic	None	None	None	None
Zinc	mg/L	None	None	None	None	None	None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	None	None	None	None	None	None	None	None	None	None
Bicarbonate (HCO_3)	mmol$_c$/L	None	None	None	Moderate	None	None	Moderate	Moderate	Moderate	Moderate
pH		Problematic	Problematic	None	None	Problematic	Problematic	None	Problematic	Problematic	None

Table A6.3 cont.: Evaluation of colliery waters for irrigation purposes. Degree of restriction on use are indicated by "None", "Moderate" and "Severe". "Problematic" trace elements are marked.

Potential irrigation	Units	GH17s	GH18s	GH19s	GH20s	GH21s	GH22s	GH23s	GH24s	GH25s	GH26s
Salinity											
EC	mS/cm	Severe	Moderate	Moderate	Moderate	Severe	Moderate	Moderate	Severe	Moderate	Moderate
TDS	mg/L	Severe	Moderate	Severe	Severe	Severe	Moderate	Moderate	Severe	Moderate	Moderate
Infiltration											
SAR (in conjunction with EC)		None	None	None	None	None	None	None	None	None	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	Moderate	None	None	None	None	None	None	None	None
Sprinkler	mmol_c/L	Moderate	Moderate	None	Moderate	Moderate	Moderate	Moderate	Moderate	None	Moderate
Chloride:											
Surface	mmol_c/L	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol_c/L	None	None	None	None	None	None	None	None	None	None
Boron	mg/L	None	None	None	None	None	None	None	None	None	None
Trace Elements											
Aluminium	mg/L	Problematic	None	None	None	Problematic	None	None	None	None	None
Chromium	mg/L	Problematic	None	Problematic	Problematic	None	None	None	None	None	None
Copper	mg/L	None	None	None	None	None	None	None	None	None	None
Fluoride	mg/L	Problematic	Problematic	Problematic	Problematic	Problematic	None	None	None	None	None
Iron	mg/L	Problematic	Problematic	Problematic	None	Problematic	None	None	None	None	None
Lithium	mg/L	None	None	None	None	None	None	None	None	None	None
Manganese	mg/L	Problematic	Problematic	Problematic	Problematic	Problematic	None	None	Problematic	Problematic	Problematic
Nickel	mg/L	Problematic	None	Problematic	None	Problematic	None	None	Problematic	None	None
Zinc	mg/L	None	None	None	None	None	None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	None	None	None	None	None	None	None	None	None	None
Bicarbonate (HCO_3)	mmol_c/L	None	Moderate	None	None	None	Moderate	Moderate	None	Moderate	Moderate
pH		Problematic	Problematic	Problematic	Problematic	Problematic	None	None	Problematic	None	None

Table A6.3 cont.: *Evaluation of colliery waters for irrigation purposes. Degree of restriction on use are indicated by "None", "Moderate" and "Severe". "Problematic" trace elements are marked.*

Potential irrigation	**Units**	**GH27s**	**GH28s**	**BC1s**	**BC2s**	**BC3s**	**BC4s**	**BC5s**	**BC6s**	**BC7s**	**BC8s**
Salinity											
EC	mS/cm	None	None	Moderate	None	Moderate	None	Moderate	Moderate	Moderate	Moderate
TDS	mg/L	None	Moderate	Moderate	None	Moderate	None	Severe	Moderate	Moderate	Moderate
Infiltration											
SAR (in conjunction with EC)		Moderate	Moderate	None	Moderate	None	Moderate	None	None	None	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	Moderate	None	None	Moderate	Moderate	Moderate
Chloride:											
Surface	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	Moderate	None	None
Boron	mg/L	None	None	None	None	None	None	None	None	None	None
Trace Elements											
Aluminium	mg/L	None	None	None	None	None	None	Problematic	None	None	None
Chromium	mg/L	None	None	None	None	None	None	Problematic	None	None	None
Copper	mg/L	None	None	None	None	None	None	None	None	None	None
Fluoride	mg/L	None	None	None	None	Problematic	None	Problematic	None	None	None
Iron	mg/L	None	None	None	None	None	None	Problematic	None	None	None
Lithium	mg/L	None	None	Problematic	None	None	None	Problematic	None	None	Problematic
Manganese	mg/L	None	None	None	None	Problematic	None	Problematic	None	None	None
Nickel	mg/L	None	None	None	None	None	None	Problematic	None	None	None
Zinc	mg/L	None	None	None	None	None	None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	None	None	None	None	None	None	None	None	None	None
Bicarbonate (HCO_3)	mmol$_c$/L	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	None	Moderate	Moderate	Moderate
pH		None	None	None	Problematic	None	None	Problematic	None	None	None

Table A6.3 cont.: *Evaluation of colliery waters for irrigation purposes. Degree of restriction on use are indicated by "None", "Moderate" and "Severe". "Problematic" trace elements are marked.*

Potential irrigation	Units	BC9s	BC10s	BC11s	BC12s	BC13s	AC1s	AC2s	AC3s	AC4s	AC5s
Salinity											
EC	mS/cm	None	Moderate	Severe	Severe	Moderate	Moderate	None	None	None	Moderate
TDS	mg/L	None	Moderate	Severe	Severe	Moderate	Moderate	None	None	None	Moderate
Infiltration											
SAR (in conjunction with EC)		Moderate	None	None	None	None	None	Moderate	Moderate	Moderate	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	None	None	None	None	None	None	None	None	Moderate
Sprinkler	mmol$_c$/L	None	None	Moderate	Moderate	Moderate	Moderate	None	None	None	Moderate
Chloride:											
Surface	mmol$_c$/L	None	None	None	None	None	None	None	None	None	Moderate
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	None	None	Moderate
Boron	mg/L	None	None	None	None		None	None	None	None	None
Trace Elements											
Aluminium	mg/L	None	None	None	None	None	None	None	None	None	None
Chromium	mg/L	None	None	None	None		None	None	Problematic	None	None
Copper	mg/L	None	None	None	None		None	None	None	None	None
Fluoride	mg/L	None	None	Problematic	None		None	None	None	None	None
Iron	mg/L	None	None	Problematic	None	None	None	None	None	None	None
Lithium	mg/L	None	None	Problematic	Problematic		None	None	None	None	None
Manganese	mg/L	None	Problematic	Problematic	Problematic	Problematic	Problematic	None	None	None	None
Nickel	mg/L	None	None	Problematic	None		None	None	None	None	None
Zinc	mg/L	None	None	None	None		None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	None	None	None	None		None	None	None	None	None
Bicarbonate (HCO_3)	mmol$_c$/L	Moderate	None	None	Moderate	None	Moderate	Moderate	Moderate	Moderate	Moderate
pH		Problematic	Problematic	Problematic	None	Problematic	None	None	None	None	Problematic

***Table A6.3 cont.:** Evaluation of colliery waters for irrigation purposes. Degree of restriction on use are indicated by "None", "Moderate" and "Severe". "Problematic" trace elements are marked.*

Potential irrigation	Units	AC6s	AC7s	AC8s	AC9s	AC10s	NAC1	NAC2	NAC3	NAC4	NAC5
Salinity											
EC	mS/cm	None	Severe	Moderate	Moderate	Moderate	None	Moderate	Moderate	Moderate	Severe
TDS	mg/L	None	Severe	Moderate	Moderate	Moderate	None	Moderate	Moderate	Moderate	Severe
Infiltration											
SAR (in conjunction with EC)		Severe	None	None	Moderate	Moderate	Moderate	None	None	None	None
Specific Ion Toxicity											
Sodium:											
Surface	SAR	None	None	None	Moderate	Moderate	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	Moderate	None	Moderate	Moderate	None	None	None	Moderate	None
Chloride:											
Surface	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None	None	None	None
Boron	mg/L	None	None	None	None	None	None	None	None	None	None
Trace Elements											
Aluminium	mg/L	None	None	None	None	None	None	None	None	None	None
Chromium	mg/L	None	None	Problematic	None	None	None	None	None	None	None
Copper	mg/L	None	None	None	None	None	None	None	None	None	None
Fluoride	mg/L	None	None	Problematic	None	None	None	None	None	None	Problematic
Iron	mg/L	None	None	Problematic	None	None	None	None	None	None	Problematic
Lithium	mg/L	None	None	None	None	None	None	None	None	None	None
Manganese	mg/L	None	Problematic	Problematic	None	None	None	Problematic	Problematic	Problematic	Problematic
Nickel	mg/L	None	None	Problematic	None	None	None	None	None	None	None
Zinc	mg/L	None	None	None	None	None	None	None	None	None	None
Miscellaneous Effects											
Nitrogen (NO_3 - N)	mg/L	Moderate	None	None	Moderate	None	None	None	None	None	None
Bicarbonate (HCO_3)	mmol$_c$/L	None	Moderate	None	Moderate	Moderate	None	Moderate	Moderate	None	None
pH		Problematic	None	Problematic	Problematic	None	None	None	Problematic	Problematic	Problematic

Table A6.3 cont.: *Evaluation of colliery waters for irrigation purposes. Degree of restriction on use are indicated by "None", "Moderate" and "Severe". "Problematic" trace elements are marked.*

Potential irrigation	Units	NAC6	NAC7	NAC8	VCC1	VCC2	VCC3	VCC4
Salinity								
EC	mS/cm	Moderate	Moderate	None	Moderate	Moderate	Moderate	Severe
TDS	mg/L	Moderate	Moderate	None	None	None	None	None
Infiltration								
SAR (in conjunction with EC)		None	None	Moderate	None	None	None	None
Specific Ion Toxicity								
Sodium:								
Surface	SAR	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	Moderate	None	None	None	None	Moderate	Moderate
Chloride:								
Surface	mmol$_c$/L	None	None	None	None	None	None	None
Sprinkler	mmol$_c$/L	None	None	None	None	None	None	None
Boron	mg/L	None	None	None	None	None	None	None
Trace Elements								
Aluminium	mg/L	None	None	None	None	None	None	None
Chromium	mg/L	None	None	None	None	None	None	None
Copper	mg/L	None	None	None	None	None	None	None
Fluoride	mg/L	None	None	None	Problematic	Problematic	Problematic	Problematic
Iron	mg/L	None	None	None	Problematic	Problematic	None	Problematic
Lithium	mg/L	None	None	None	None	None	None	None
Manganese	mg/L	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic	Problematic
Nickel	mg/L	None	None	None	None	None	None	None
Zinc	mg/L	None	None	None	None	None	None	None
Miscellaneous Effects								
Nitrogen (NO_3 - N)	mg/L	None	None	None	None	None	None	None
Bicarbonate (HCO_3)	mmol$_c$/L	Moderate	None	None	None	Moderate	None	None
pH		None	Problematic	None	Problematic	Problematic	Problematic	Problematic

Figure 3.1: *Regional locality map of collieries investigated (Adapted from Barker, 1999).*