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THE EFFECT OF INDUSTRIAL PRACTICES ON STREAM SEDIMENTS, AND THE IMPACT OF THESE SEDIMENTS ON THE GEOCHEMISTRY OF A WETLAND

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PREFACE

The experimental work described in this thesis was carried out in the Department of Geological Sciences, University of Cape Town, from August 1996 to November 1996, under the supervision of Associate Professor James Willis and co-supervision of Dr Martin Fey.

The study represents original work by the author and has not been submitted for degree purposes to another university. Where use has been made of the work of others, it has been duly acknowledged in the text.

Signed by candidate

Ja[redacted]ew Lake.

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ABSTRACT

The objective of this study was to characterise the impact that a major industrial operation, situated at Somerset West and involved in the manufacturing of a diverse range of chemicals, has had on the sediments of the drainage system that drains the site on which these activities occur. Furthermore, the impact of these sediments on the geochemistry of a wetland, *Wagenveldt vlei,* situated downstream of the complex, has been investigated.

Sediment cores and water samples were collected at a number of locations down the length of the drain. The water samples were analysed to determine which constituents were present in solution. The cores were separated into a top and bottom layer which were analysed separately to determine their geochemical composition. In some instances a lack of time resulted in some of the analyses being performed on only a select number of samples. An experiment was performed on the sediments collected from the bottom layer to determine what would happen if the sediments became oxic and the sulphides and organic matter in the sediments were oxidised.

The concentrations of various solutes in the water samples varied at each sample down the length of the drain. Relative to background samples, the majority of samples contained high concentrations of the anions Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, PO_4^{3-} and F^-, with the maximum concentrations being 930, 480, 260, 160, 390 and 10 mg/ℓ, respectively, while the concentrations in the background samples were 25, 9.2, 19.2, 10, 22 and 0.1 mg/ℓ, respectively. Relative to the background samples, the concentrations of the cations Na^+, Ca^{2+}, Mg^{2+}, K^+ and NH_4^+ (maximum concentrations are 410, 120, 100, 250 and 42 mg/ℓ, respectively) were high (concentrations in the background samples were 16, 3.9, 2.8, 2.3 and 0 mg/ℓ, respectively). Other soluble elements that were detected in the water samples were Zn, Ni, Mn and Fe (in concentrations below the ppm level). Aluminium was also present in a number of samples (maximum concentration = 3 mg/ℓ).

The high concentrations of Al, NO_3^-, PO_4^{3-} and F^- in the water samples make the water unsuitable for use as drinking water. Furthermore, if the water was to be piped to a treatment plant the potential exists that if, metal pipes were to be used, they would become corroded. This occurs because there would be no calcite precipitating from solution, thereby creating a protective coat (saturation indices for calcite were < 1). In terms of use in agriculture, the high Electrical Conductivity (EC) values of the waters coupled with the high concentrations of Na^+ and Cl^- would place restrictions on the use of the water for irrigation. However, the high concentrations of Al and NO_3^- in the samples would render the water totally unsuitable for irrigation purposes.

The 1:1 sediment to solution extracts that were prepared from the sediments collected from the drainage system differed, in terms of their constituents, at different locations in the drains. A general trend that was evident was that the extracts from the background samples contained lower concentrations of soluble constituents than the sediments collected on site. The high concentrations of the particular constituents were attributed to possible anthropogenic inputs. None of the constituents detected in the sediment extracts showed evidence of being in higher concentrations in one layer relative to that in the other layer. The constituents detected in the 1:1 sediment to solution extracts were (with the maximum concentration in mg/ℓ reported in parenthesis) Cl^- (1600), SO_4^{2-} (1800), NO_3^- (260), PO_4^{3-} (670), F^- (34), Na^+ (1300), Ca^{2+} (590), Mg^{2+} (480), Zn (4.4), Ni (110), Mn (18), Fe (290), Al (150) and Pb (4.3).

Sediments at specific locations are enriched, relative to the background samples, with the elements (total element concentrations) Ba, Ni, Zn, Cu, Mo, and Pb. This is, however, not conclusive evidence that the sediments are contaminated by these elements because insufficient background samples were collected. It is, however, surmised that the enrichment may have arisen as a result of anthropogenic activity. All sediments are enriched with Cl, P and S, relative to the sediments of the background samples. The sources of these elements have been hypothesised as being marine influence, spills of acids and the phospho-gypsum and sulphur dumps located on site.

A low pH in the wetland was attributed to either the dumping of acids or the oxidation of pyritic minerals. Furthermore, it was found that there was an accumulation of Zn, Cu, Cr, Mo, Nb, Th, U, Pb, Fe, Ti, Ba, Cl, S and P in the sediments within the wetland. These elements are all accumulated, at different degrees, at different locations down the length of the drain. It was, therefore, hypothesised that these elements could have accumulated in the wetland when there was the movement of sediments from further up the drain.

A change in conditions from oxidising to reducing, with a concurrent increase in the oxygen content of the sediments would result in a marked decrease in the pH of the sediments. This change in pH was attributed to the oxidation of pyrite in the drain. It was hypothesised that if this should occur the mobility of Ti, Sr, Ni, Fe, V, P, Zn, Cu and Pb may increase. The possibility exists that these elements could enter a water body. If this occurs on a large enough scale the possibility exists that a contamination problem could arise.

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BACKGROUND TO THE STUDY

1.1. Introduction

As a result of the diversity of operations that normally occur during industrial activity, the potential exists that the surrounding environment can be significantly contaminated. The media that are contaminated include the:

1) Surface and groundwater
2) Soils and sediments
3) Atmosphere

It is not uncommon to find an industrial site where all these media have become contaminated during the course of industrial activity. The mechanisms by which the environment becomes contaminated include release from:

1) routine production,
2) limited process upset,
3) fugitive emissions,
4) accidents and mishandling, and
5) storage facilities.

The release of contaminants during routine production and from storage facilities is relatively easy to control as a result of the fact that there have been developments in the technology for the handling of raw materials and wastes. The other three mechanisms of environmental contamination are less easy to control because they often occur as unplanned incidents or arise as a result of human error. Furthermore, it is often difficult to detect where and when these releases are occurring.

Besides leading to the physical degradation of the environment, environmental contamination may have a significant impact on humans. This occurs when they ingest some of the contaminants that have been released (either via the ingestion of contaminated water or foodstuffs into which the contaminants have been incorporated). Besides human physical health being adversely affected their mental health may also be impaired. This occurs when they are faced with an environment that is "smelly" or badly denuded with the result that humans can not use it for recreational purposes.

1.2. Rationale and aims

The aim of this study is to determine whether the activities of a chemical manufacturing company, situated at Somerset West, have resulted in the contamination of the sediments in the drainage system of their chemical manufacturing complex. The study has been carried out in a such manner that it will be possible to determine whether contamination is localised or if it is spread along the length of the drainage system. From the study it is hoped that it will be possible to identify geochemical processes occurring in the various components of the drainage system that control the behaviour of the contaminants in the system.

This study will form a part of the site evaluation that is being carried out by the site owner during investigation into the suitability of the site for industrial, recreational or other activities not associated with manufacturing operations. It is important to have an understanding of the degree of contamination of the sediments as it allows for an estimate to be made of the potential risk of these sediments to the environment. For example, the possibility exists that contaminants could be leached from the sediment and enter groundwater; or if the contaminated sediments are transported from their current location to a new location, they could have a potential deleterious effect on the environment. This may happen when the sediments are transported by flood conditions during heavy rainfall, when there are other changes in depositional conditions, such as the area being drained, or when the sediments are intentionally moved *eg.* by activities such as grading *etc.* during the redevelopment endeavour that may occur on the site.

1.3. Historical review

Manufacturing activities have been in operation since 1903. However, prior to that, historical records indicate that the site was used for both farming as well as limeburning. Since the commencement of manufacturing activities on site a number of different operations have been performed. Some of these operations were active for a relatively short time while other activities occurred over a much longer time period. In the last decade the majority of the operations on the site have begun to be decommissioned as a result of the owner's wish to develop the land for residential or recreational use. There are, however, a number of activities that until this year (1996) were operational. These activities have now also begun to be decommissioned.

In the following subsections the different operations will be described. These descriptions are based on the activities that have occurred on a particular portion of the site, with the result that it may not be obvious why the activities have been grouped together. The areas that are described are illustrated in the Figure below (see Figure 1.1).

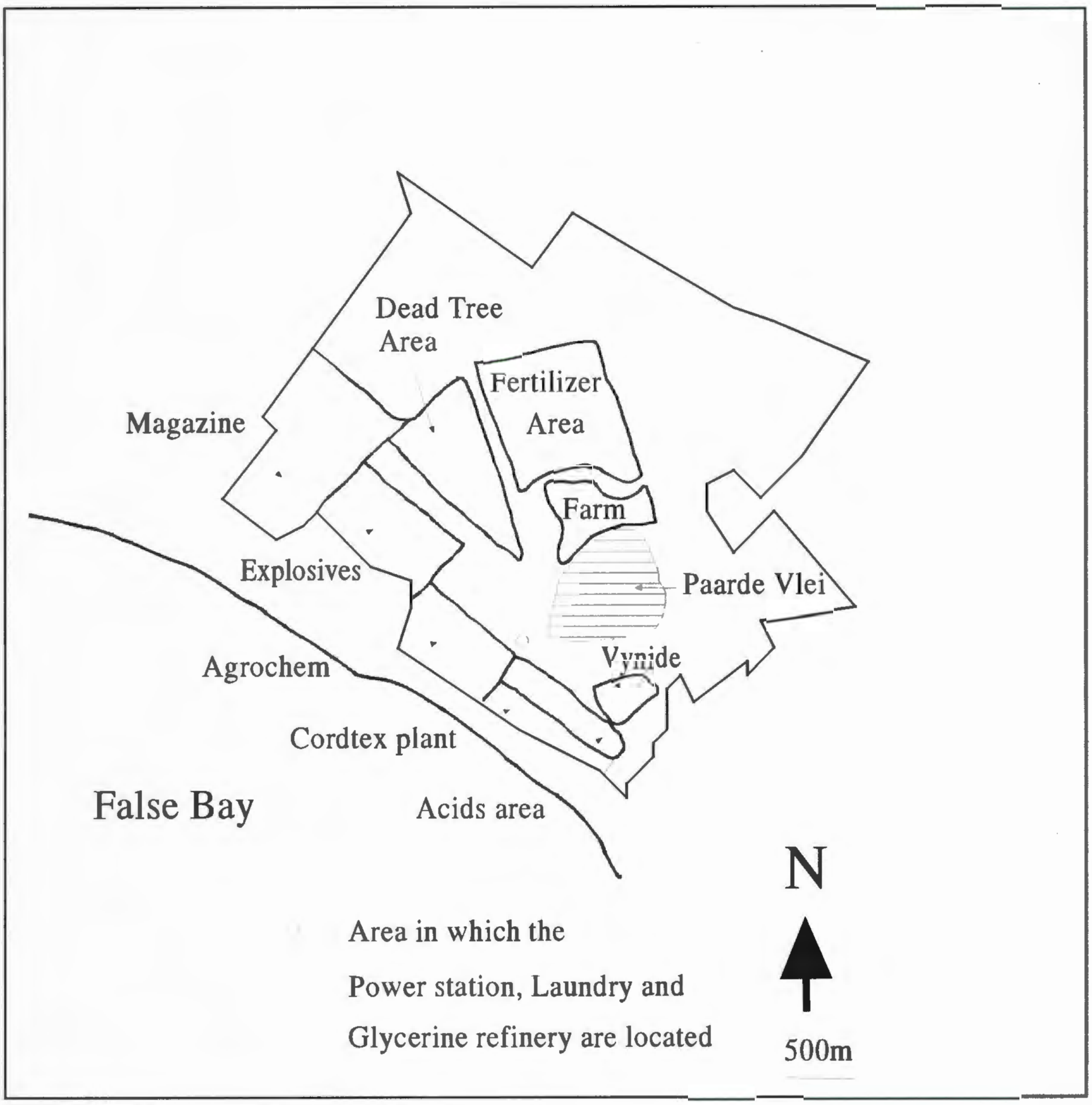

Figure 1.1. Map of the complex illustrating the various operating areas.

1.3.1. Explosives

A large proportion of the activities in this area have been concerned with the manufacture of nitroglycerine-based explosives, as well as peripheral products such as jute, waxed paper shells, nitrocotton, fuses, igniters and detonators. Besides the manufacture of explosives, other operations were involved in the production of insecticidal smoke generators, mercury fulminates and mole and vermin fumigators. The liquid effluent from these different operations was disposed of at a number of different locations.

For example, wastewater from the batch hills went to one of two nitroglycerine soakaways in the dunes, while contaminated acid and soda solution as well as alcoholic potash, went to a soakaway below the acid complex. Effluent from cotton preparation, nitrators and pulper went to a saveall near the nitrocotton plant fence and the supernatant liquid was then pumped to a soakaway. However, water containing nitrocotton often used to spill into Langvlei, as did water from the savealls outside the Stabiliser House and water from the drain at the acid tank area. Other effluent that used to drain into Langvlei came from the ammonia nitrate plant as well as all the effluent from the Central Areas.

1.3.2. Agrochemicals

The activities in this part of the site have been diverse, with a large portion of the manufacturing effort going towards the making, mixing and concentrating of various acids such as nitric, sulphuric and hydrochloric acids. These acids were used in the manufacturing of the different explosives products in other parts of the site. Besides the manufacturing of acids, other products that were manufactured were a variety of chemicals and crop chemicals, most notably those that required or produced parathion, nicotine dust, lead arsenate, lead nitrate, copper sulphate, molybdates, chromic chloride and iron oxide. Prior to 1960 all effluent from these activities went into the Main Drain. However, in 1960 this practice ceased with the development of an acid soakaway in the Coastal Dune Belt. Because there is no meteoric water management in this area, runoff from the various plants still enters the Main Drain.

1.3.3. Fertiliser area

On this part of the site the manufacturing activities were concentrated on the manufacture of single superphosphate, double super phosphate and bonemeal. Because historical records indicate that the raw materials used in these operations were bought cheaply, it has been predicted that they may have contained significant amounts of impurities. The solid wastes generated during these activities contained molybdates and chromic chloride (with traces of mercury) and, before the development of the chemical soakaway, were dumped near the evaporation ponds. Before 1960, when recycling of wastewater was introduced, effluent used to be discharged via the vlei bypass and thence to the sea. When this practice was stopped, the wastewater from scrubbers was sent to evaporation ponds, while the effluent from the double superphosphate manufacturing process, together with gypsum waste, was sent to the gypsum dump. Contaminated water from these areas may still enter the drainage system, particularly in winter, when heavy rains cause the ponds to flood as well as generating leachate from below the different waste areas.

1.3.4. Vynide

The products produced by this operation have changed over the years. Initially the operation concentrated on the manufacturing of paints and leathercloth. However, in later years, paint manufacturing was moved to other sites, while the manufacturing of coated materials superseded the manufacturing of leathercloth. The waste that was generated by this operation was mainly in the form of solvents and pigments which were either dumped next to the acid soak-away or used to light fires at the burning ground. There may, however, have been spills or leaks from tanks that would have gone into the drainage system, eventually ending up in the Main Drain.

1.3.5. Operations services

The activities carried out by this sector are not involved directly in the manufacture of products, rather their operations act as a support to the other operating areas. For example, operating services are involved in power generation at the power station, various workshops and distribution activities, as well as farming and residential operations including sewage treatment and laundry facilities. The bulk of the waste that comes from these activities is in the form of power station ash, which is still dumped at a rate of 100t/month. The power stations liquid effluent used to run into the Main Drain before the present outlet was established. Effluent from the laundry is still discharged into the Main Drain. It is unlikely that there would have been large volumes of effluent generated by the workshops and distribution points. However, spills and leaks may have occurred, thereby contaminating the site.

1.4. Physiography

1.4.1. Locality

The study site is located in the Hottentot Hollands Basin, covering an area of 1230 ha (see Figure 1.2). The site is bordered on both the north and the east by the residential areas of Somerset West and the Strand, respectively. To the west of the site is the Somchem factory, while the southern boundary is the shoreline of False Bay. As has been mentioned, the broad landuse is the manufacturing of a number of different chemicals for use in different sectors of the economy. However, other landuse activities on the site include staff recreational facilities, staff housing and various agricultural practices.

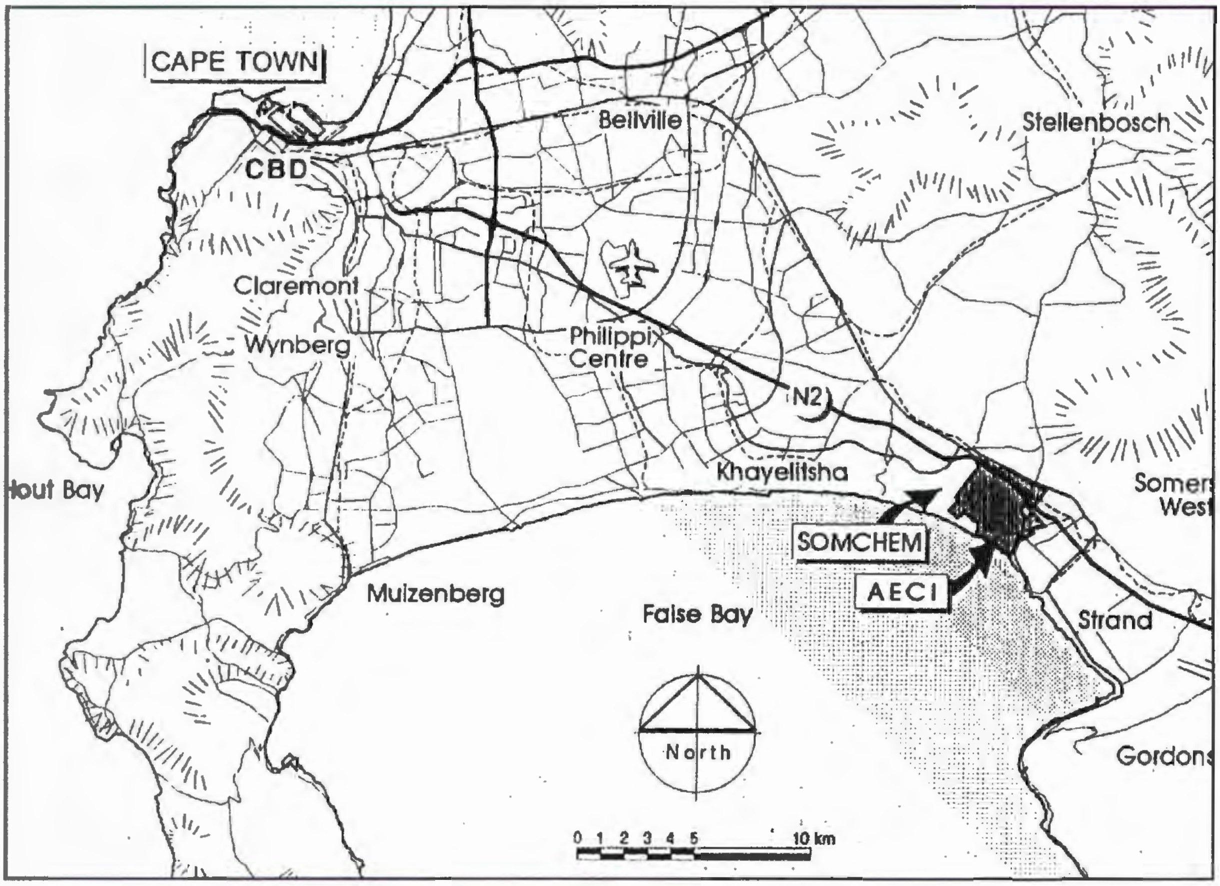

Figure 1.2. Location of the study site. The study site is that marked AECI.

1.4.2. Topography

The majority of the area occupied by the site is flat having an altitude ranging from 3 to 21 m above sea level. The main topographical feature of the site is the sand dunes that are found along the coast on the southern boundary. The dune belt is approximately 500 m wide consisting of a number of longitudinal dune crests paralleling the coast.

1.4.3. Geology and soils

The site can be divided into two distinct zones based on the underlying lithology: the Coastal Plain - which extends from the area north of Langvlei; and the Dune Belt, which extends southwards from Langvlei to *Wagenveldt Vlei* (refer to Figure 1.3).

The Coastal Plain is underlain by the Malmesbury Group shales, hornfels and sandstones, with a peneplained surface 7-15 m below surface that slopes gently to the south. Below the soil in the north east area of the site (the Fertilizer Area) is hard blue grey hornfels which is highly fractured and weathered in places, with vein quartz and iron staining in joints. The soils in this area are comprised mainly of transported material and residual Malmesbury shale that has been completely weathered. The transported material forms a relatively thin cover, 20-100 cm thick, comprising a slightly clayey, fine sand that is probably colluvial in origin.

In the Dune Belt, the Malmesbury group of rocks is overlain by aeolian sands, 4-6 m thick on the margins and 12 m thick in the centre. Throughout the Dune belt the sand profile consists of two distinct horizons, an upper fine-grained sand and a basal pebble and shell horizon. The upper horizon is 2-8 m thick and very uniform in lithology. However, some discontinuities occur in the form of pedocrete formations such as ferricrete and calcrete. The basal horizon is 1-5 m thick and comprises pebbles of Malmesbury rock in a matrix of coarse sand and shell fragments

1.4.4. Hydrogeology

The main water strike is a zone 1-3 m thick above the weathered/fresh rock interface which is at a depth of 7-15 below ground. In the Fertilizer Area the water table lies relatively close to the soil surface, being 1-1.5 m below ground at the end of the summer season (dry period), which is the lower level for the piezometric surface. In the winter months (rainy season) the water level is at ground surface. In the Coastal Dune Belt the piezometric surface is found in the lower soil horizon, *ie.* in the pebble belt. On the land and seaward side of the Dune Belt the water table is relatively shallow at a depth of 1-2 m below ground surface.

The general ground water flow direction is south-westerly with a gradient decreasing from 1:70 in the north east to 1:400 over the rest of the coastal plain. The soils' permeabilities over the site tend to be uniform, averaging 2 x 10^{-4} cm/sec in both the Malmesbury and sand formations. These parameters result in flow velocities that range from 0.9 m/year in the south-west section to 0.2 m/year in the Coastal Plain and 0.5 m/year in the Coastal Dune Belt.

1.4.5. Surface hydrology

The main hydrological feature of the site is a body of water approximately 0.4 km^2 in size called Paardevlei (see Figure 1.3). During the time over which activities have occurred on site, Paardevlei has acted as a source of water for a number of different operations as well as acting as a disposal point for used process water (water normally used for cooling and, therefore, uncontaminated). Besides Paardevlei, other features of hydrological importance are the open drains that traverse most of the site (see Figure 1.3). Most of these drains have been given a name dependant on the area which they drain. All the drains eventually drain into the factory Main Drain which runs in an approximate north-west, south-east direction through the southern portion of the site. About one fifth of the way downstream from the start of the Main Drain (in the south west corner of the site) is a very marshy, wetland type area, known as Langvlei. Downstream of the industrial activity the Main Drain describes a loop to the south around the Coastal Dunes. On the seaward side of the dunes the water from the drain is either discharged into the Lourens river via a small estuary or it enters another wetland known as the *Wagenveldt vlei*. If the water enters the *Wagenveldt vlei* it is eventually discharged into False Bay further down the coast. The main function of these drains is to remove water that has collected on the site. However, over the operational time of the site there have been direct discharges of effluent into the drainage system and even to this day, effluent from the laundry and the sulphur belt (in the Agrochemicals area) is discharged to the drain system.

Another hydrological feature of interest is the Lourens River to which the owners of the industrial site hold riparian rights. This river drains off the Hottentot Holland mountains through the basin formed by these mountains. The river then flows between the residential areas of Somerset West and of the Strand. The mouth of the river is slightly south of the industrial complex.

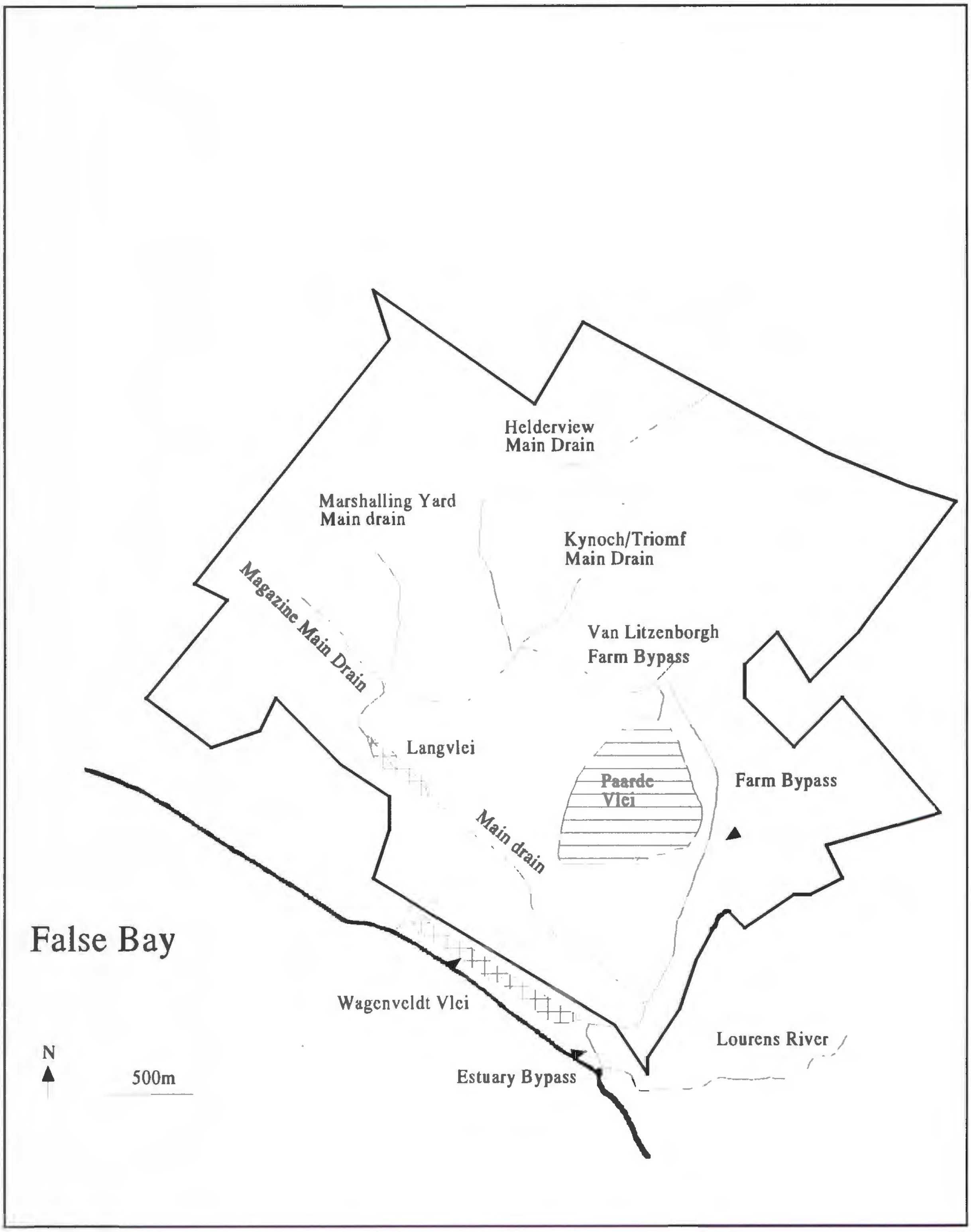

Figure 1.3. Surface hydrology of the industrial complex.

1.4.6. Flora and fauna

Over a large proportion of the site the natural vegetation has been replaced by invasive species such as eucalyptus with a resultant decrease in species diversity. In some patches, isolated populations of spring annuals remain, but these occupy only a small proportion of the site. The few remaining populations of indigenous vegetation are found in the narrow belt of Coastal Dunes, with the populations consisting of various Restionaceae, Protea and Erica species interspersed with various grass species which are indicative of minimal or no disturbance. The species that predominate in *Wagenveldt Vlei* are *Typha capensis* and *Senicio halifolius*.

There is a wide diversity of fauna on the site, ranging from various avian species through amphibians and reptiles to a number of different mammals. The avian population consists of a number of birds of prey as well as aquatic species. Other animals that are found on the site include various frogs and snakes, steenbuck, duiker, mongooses, otters and dune mole rats.

1.5. Key questions

Explicitly, the key questions that will be addressed in this investigation are:

1) What is the quality of the water currently in the drainage system ?

2) Has industrial activity resulted in the contamination of the sediments in the drain that runs through the industrial complex ?

3) If the sediments of the Main Drain are contaminated, what impact does this have on the geochemistry of the wetland situated downstream (*Wagenveldt vlei.*)

4) If the sediments are contaminated, is the contamination localised or is it distributed down the length of the drain ? Are the different layers in the sediments contaminated to the same degree ?

5) If the degree of contamination in the sediment layers is different, what are the factors that could have resulted in these differences ?

6) If conditions should change, for example if stream flow terminated resulting in the drying out of the sediments or if the entire area was inundated by water, what could be the potential effect on the environment ?

CHAPTER 2.

AN INTRODUCTION TO WETLANDS WITH SPECIAL REFERENCE TO PROCESSES OCCURRING IN SATURATED SOILS AND SEDIMENTS.

2.1 Introduction

Larson and Kusler (1979 in Patrick, 1994) point out that "for most of recorded history, wetlands were regarded as wastelands if not bogs of treachery, mires of despair, home of pests, and refuges for outlaw and rebel. A good wetland was considered to be a drained wetland free from this mixture of dubious social factors." In the last decade this view point has changed with wetlands being recognised as an important part of any landscape. This is a result of an appreciation of the biogeochemical and hydrological roles that wetlands provide. For example, they prevent floods, cleanse water, protect shorelines and recharge groundwater aquifers (Mitsch and Cronk, 1992).

The aim of this chapter is to investigate processes that occur in wetlands. Furthermore, because the focus of this study is on geochemical processes occurring in saturated soils and sediments, particular attention will be paid to processes that effect the chemical characteristics of these media.

2.2 Definition

Wetlands are generally transition zones between terrestrial landforms and waterbodies. They have some features of both, resembling uplands because of their ability to support emergent plants, and resembling aquatic systems because of the dominant role of water in the system (Patrick, 1994). It is relatively easy to describe the functions and processes occurring in wetlands. However, difficulty is often encountered in trying to formulate a precise definition. According to Mitsch and Gosselink (1986), there are three main components that any definition must include. These are:

i) Wetlands are distinguished by the presence of water.
ii) Wetlands often have unique soils that differ from adjacent uplands.
iii) Wetlands support vegetation adapted to the wet conditions (*ie.* hydrophytes), and conversely are characterised by an absence of flooding-intolerant vegetation.

Therefore, any definition of a wetland must contain statements about the dominance of water, the presence of saturated soils and the presence of plants growing under these conditions. The definition advanced by the U.S Army Corps of Engineers in regulating wetlands, as called for in the Federal

Clean Water Act, covers all the aspects proposed by Mitsch and Gosselink (1986). This definition is as follows:- *"The term wetland means those areas that are inundated or saturated by surface or groundwater at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions. Wetlands generally included swamps, marshes, bogs and similar areas."*

2.3 Components of a wetland

As is alluded to in the definition presented above, there are a number of components that are common to all wetland systems. These components all impact on the geochemistry of wetlands, therefore it is pertinent to gain an understanding of the different components so that an appreciation of their functions can be gained.

2.3.1 Hydrology

According to Rogers *et al.* (1985), it is the hydrology of a wetland that distinguishes it from aquatic or terrestrial ecosystems. Hydrology is thus one of the primary determinants of all wetland systems. The general hydrological characteristic of wetlands is that water tends to move across the system in sheets rather than as channel flow, resulting in the permanent saturation of the soils and sediments in the system. The hydrology of a specific system is determined by the physical characteristics of the system, which include the system's size, gradient, resistance to flow, infiltration capacity, and the ability of the soil to hold moisture (Phillips, 1989). Often the combination of these factors is unique for a particular system, with the result that only generalisations about hydrology can be made. In a typical wetland there are two routes by which water enters the system and then moves through it, *viz.* overland flow and subsurface flow. According to Phillips (1989), some pollutants, such as heavy metals and pesticides adsorbed to sediment particles, are transported solely or primarily in particulate form in surface runoff. The movement of these particles is thus determined by the energy or transport capacity, with the result that the low energy subsurface flow is unimportant in the movement of these particles. Surface and subsurface flow are, however, important in the transport of pollutants that exist in a dissolved form - or as very small suspended solids - where any significant flow is sufficient for their transport (Phillips, 1989).

The energy of overland flow - and thus the system's ability to move sediments - is a function of the physical factors (mentioned above) that impact on a system's hydrology. Coupled with these physical factors is the proportion of flow which moves overland. The proportion of flow that moves overland can be determined from saturated hydraulic conductivity by making the assumption that infiltration of a slug passing through a wetland is closely approximated by **ponded** infiltration rates

(Phillips, 1989). Saturated hydraulic conductivity represents steady-state infiltration rates under saturated conditions (Skaggs and Khaleel, 1982) and is strongly related to the cumulative infiltration associated with a given event, varying with soil moisture status (Phillips, 1989). According to Phillips (1989), infiltration capacity has a general form consisting of hydraulic conductivity added to or multiplied by a second term related to time-specific conditions such as initial moisture conditions, distance from the surface to the wetting front, and factors such as vegetation.

In a study, performed by Phillips (1989), of the factors determining the effectiveness of water quality buffer zones, it was found that the critical factors determining a system's ability to "buffer" sediment or sediment-associated contaminants - in terms of hydrological factors - are gradient and to a lesser extent soil hydraulic conductivity, with other factors such as system width and soil moisture capacity playing a limited role. The finding that a system's gradient is important can be attributed to the influence that this factor has on the velocity with which water moves. The steeper the gradient, the higher the velocity and by implication energy of overland flow. In the same study, Phillips (1989) found that the width or length of a system is the critical factor in determining the effectiveness of the "buffering" ability in terms of contaminants that are dissolved in the water column. This can be attributed to the fact that the greater the size of the system, the longer will be the time that water - containing the dissolved contaminants - will be in contact with the soil and vegetation in which geochemical transformations occur, thereby allowing for greater contaminant removal.

Wetlands have the "geochemical" potential to transform contaminants into forms or species that are less harmful to the environment. However, if the loading rate - volume of water applied per unit area per time - and the time that water spends in the system - retention time - are not optimised, the wetlands potential to attenuate contaminants is curtailed. Loading rate and retention time are contaminant dependant, but there are some guidelines that can be applied. According to Pesavento, (unpublished data cited in Watson *et al,*. 1989) hydraulic loading rates can be as high as 29 cm/day for acid mine drainage, with 5 cm/day being a conservative estimate (Fennessy and Mitsch, 1989). Fennessy and Mitsch (1989) have suggested that the minimum retention time for acid mine drainage is 1 day with more effective iron removal at much longer periods.

2.3.2 Biotic component

As a result of the abundant water supply, wetlands are amongst the most productive ecosystems in the biosphere (Rogers *et al.*, 1985). This high productivity often creates an ideal habitat for a diverse faunal community, with numerous different functional types present, including species from the functional groups macrophyta and microphyta. It is, however, unusual to find submergent species in wetlands due to a lack of light below the surface as a result of the turbidity of the overlying water column (Mitsch and Cronk, 1992).

As has been mentioned, the water regime, and by implication oxygen supply to roots, is one of the factors limiting (emergent) plant growth in wetlands. However, some plants have adapted to living under these stressful conditions. This has been achieved by the evolution of unique strategies to withstand anaerobic soil conditions (Patrick, 1994). One of the most notable strategies is the development of aerenchymous tissue. This is tissue that consists of cells capable of conducting oxygen from the upper plant body to the roots where oxygen is required for metabolic processes.

The biotic component of a wetland has a number of very important roles to play in the regulation of quality of water in a wetland.

Firstly, the emergent species are responsible for the absorption of a number of different ions in a water column. For example, it was noted by Murdock and Capobianco (1979) that *Glyceria grandis* took up 80 % of available P, and also took up significant quantities of Pb, Zn and Cr. Gallagher and Kibbey (1980) found that other species accumulated Cu, Cr, Fe, Mn, Sr, Pb and Zn.

The second major function that emergent vegetation performs is that it reduces the velocity with which water moves through the system (Rogers *et al.*, 1985). The effect of this is a decrease in the energy of overland flow. This decrease in energy allows sediments to settle out of the water column. The decrease in water velocity also increases the retention time of the water, thereby allowing other biogeochemical transformations to occur.

The last major function that plants have - whether they are macrophytes or microphytes - is that they are a source of organic matter (Rogers *et al.*, 1985). This organic matter influences many of the geochemical processes that occur in these systems - as will be discussed later. According to Rogers *et al.* (1985) there is a wide diversity of different species found in wetland communities. Emergent species include *Cyperus spp, Phragmites spp,* and *Typha latifolia.* Free-floating forms that are found are *Eichhornia crassipes, Salvinia molesta,* and *Pistia straiotes.*

The microbial component - microphyta - of wetlands also have some major implications on the geochemical processes that occur. According to Duncan and Groffman (1994), the functions include the decomposition of organic matter and the degradation of the nutrients contained therein. It has been established by Stumm and Morgan (1981) and by Ponnamperuma (1984) that after anaerobic conditions have been created, there is a sequential reduction of alternate (*ie.* other than O_2) electron acceptors. The sequence of components utilised by facultative anaerobes (microorganisms that only operate under anaerobic conditions) is NO_3^-, Mn^{4+}, and then Fe^{3+}, while the sequence utilised by obligate anaerobes (microorganisms that can operate under either aerobic or anaerobic conditions) is SO_4^{2-} and then CO_2.

2.3.3 Soils and sediments

Soil can be defined as "the unconsolidated mineral matter on the surface of the earth that has been subjected to, and influenced by, genetic and environmental factors of: parent material, climate (including moisture and temperature effects), macro- and micro-organisms, and topography, all acting over a period of time and producing a product - soil - that differs from the material from which it was derived in many physical, chemical, biological, and morphological properties and characteristics" (The Glossary of Soil Science Terms, (Anonymous, 1965 in Ponnamperuma, 1972). According to Ponnamperuma (1972), there are basically two different types of soils that experience saturated conditions for a sufficiently long period, that they be classified as soils of wetland systems. These soils are *Waterlogged (Gley) soils*, and *Marsh soils*.

Waterlogged soils are soils that are saturated annually with water for a sufficiently long time to give the soil the distinctive gley horizon resulting from oxidation-reduction processes (Ponnamperuma, 1972). The characteristics of these soils are that they have a partially oxidised A horizon high in organic matter, a mottled zone in which oxidation and reduction alternate, and a permanently reduced zone which is bluish green (Robinson, 1949 in Ponnamperuma, 1972). As described by Ponnamperuma (1972), waterlogged soils are found in any climatic zone, usually as a result of poorly drained members of drainage catenas.

Marsh soils are soils that are permanently saturated or submerged (Ponnamperuma, 1972). These soils are normally found on the fringes of lakes and on the fringes of streams that feed them. It is also possible to find marsh soils in marine environments, such as those found in estuaries, deltas and tidal flats. A feature of these soils is that there is an accumulation of plant residues in the surface horizon below which is a permanently reduced G horizon (Ponnamperuma, 1972).

Besides the archetypal soils found in wetlands (*ie.* soils formed from classical pedogenic processes), there are also sediments present in wetlands. The term "soils" can be used to describe sediments due to the fact that sediments are formed from soil components during typical soil forming processes such as hydrolysis, oxidation-reduction, precipitation, synthesis and exchange of energy and matter with the surroundings (Ponnamperuma, 1972). According to Ponnamperuma (1972), sediments show physical stratification and they differ in texture, composition, clay mineralogy, organic matter content and oxidation-reduction level, as do soils. The term sediment is usually used to refer to the matter that has settled out of the overlying water column. It has been shown by Feijtel *et al.* (1988) that the rates of accumulation differ in freshwater and saline wetlands. They found that, from the same source, the rate of sediment accretion in freshwater was 0.65 cm/yr, while the rate of accretion in a saline estuary was 1.1 cm/yr.

2.4 Factors that effect the geochemical processes in saturated soils and sediments

The saturated conditions that predominate in these systems often lead to the development of unique chemical conditions. These chemical conditions are potentially very different from those that exist in upland - or unsaturated - soils, with the result that constituents undergo transformations that are distinct from those that occur in upland soils. Gambrell (1994) noted that the idiosyncratic conditions of saturated soils and sediments are related to their oxidation-reduction status (redox potential), pH, organic matter content, salinity and the presence of some organic components such as carbonates and sulphides.

2.4.1 Redox potential and redox conditions

Generally the redox conditions that develop are determined by the presence of oxygen in the soil column. In well aerated soils aerobic or oxidised conditions prevail while in those in which there is a lack of oxygen, anaerobic or reduced conditions predominate.

When a soil is submerged, there is a drastic decrease in the gas exchange between the soil and the atmosphere. Thus, the only pathway by which oxygen and other gases can enter the soil is by molecular diffusion in the interstitial waters. McBride (1994) notes that oxygen has a low solubility in water (8 μg/ml) which results in a great reduction in the rate with which oxygen enters submerged soils and sediments. This fact was demonstrated by Greenwood (1960), who found that the rate of diffusion in water is 10 000 times slower than diffusion in gas filled pores. When the oxygen content falls to trace levels, $\approx 10^{-6}$ M, there is a switch in microbial activity from aerobic to anaerobic respiration (McBride, 1994). During respiratory processes, microbes oxidise a substrate (organic matter) with a concurrent reduction of an oxidant. During aerobic respiration, microbes utilise oxygen as the terminal electron acceptor (oxidant). However, during anaerobic respiration microbes utilise ions other than oxygen as terminal inorganic electron acceptors (Reddy and D'Angelo, 1994). In the absence of oxygen, there is normally a fixed sequence in which species, other than oxygen, are reduced.

According to Ponnamperuma (1972), the reduction sequence proceeds approximately according to the sequence predicted by thermodynamics. The sequence of reduction in submerged soils and sediments as conditions become more reducing is :- O_2 to H_2O; NO_3^- to N_2; MnO_2 to Mn^{2+}; $Fe(OH)_3$ to Fe^{2+}; SO_4^{2-} to H_2S; CO_2 to CH_4; and H_2O to H_2 (McBride 1994). It must, however, be noted that if there is any detectable oxygen in the soil the reduction sequence will not proceed. This is due to the fact that oxygen acts as an inhibitor on NO_3^- reduction (Ponnamperuma, 1972). Similarly, nitrate retards the reduction of the other redox components. However, the influence of MnO_2 on the other reductants is not marked, due to the fact that manganese dioxide is relatively insoluble in water. As the reduction sequence proceeds, there is a nonlinear decrease in the redox potential (millivolts) of the system. Negative redox potentials normally develop after the reduction of $Fe(OH)_3$, but before the reduction of SO_4^{2-} (Ponnamperuma, 1972 and McBride, 1994). There is another mechanism besides the use (by microorganism) of inorganic species as terminal electron acceptors that leads to the development of reducing conditions in wetland soils. Some bacteria exude organic chemicals such as polyphenols which in turn chemically reduce oxides and other easily reducible compounds (McBride, 1994). In this sense, oxides are used as indirect electron acceptors rather than being direct acceptors in enzymatically catalysed reactions within the cell.

According to DeLaune and Pezeshki (1991), the redox conditions that develop in a soil can be described in both intensity and capacity terms. The intensity factor determines the relative ease of the reduction - *ie.* the tendency of the sediment solution to donate electrons or to accept electrons from a chemical species (McBride, 1994) - and is normally represented by the free energy of the reaction. The capacity factor describes the quantity of redox species undergoing reduction and is equal to the total amount of electrons accepted by the soil oxidants in microbial respiratory processes. Both the intensity and capacity factors of the soil are determined by the presence and activity of particular species. Therefore, it is not possible to make quantitative generalisations about these two factors in different soils.

McBride (1994) and Ponnamperuma (1972) use the term "poise" to describe the resistance of a redox system to changes in potential upon the addition of small amounts of oxidants or reductants. Poise increases with the total concentration of oxidant plus reductant, and for a fixed total concentration it is a maximum when the ratio of the oxidant to reductant is 1 (Ponnamperuma, 1972). In electrochemical terms, poise describes the change in Eh with a change in the quantity of reactive electron acceptors in the soil compared with the quantity of electrons generated by biological reactions (McBride, 1994). For example, a large reserve of oxidants, such as Mn^{4+} or Fe^{3+} in the form of oxides, means that the redox potential tends to maintain a nearly constant value as reduction of acceptor continues.

It must be borne in mind that in most wetland systems the reducing conditions do not extend down the whole soil column. Rogers *et al.* (1985) explain that in relatively shallow or well mixed systems it is possible to have a surface layer of soil in which oxygen diffusion is sufficient to maintain oxidised conditions. It is only below this layer that saturation causes a decrease in the oxygen tension, resulting in the generation of reducing conditions.

2.4.2 pH

As for redox potential, the pH of sediments differs from that of soils that are unsaturated. Unsaturated soils can potentially have pH values that cover the spectrum from strongly acid to strongly alkaline soils (Tan, 1994). The range of pH found in uncontaminated saturated soils and sediments is much narrower, ranging from approximately 5 to 7.8, having a mean value of 7 (Ponnamperuma, 1972). It has been found that submergence of either an acidic or alkaline soil causes the pH to tend toward neutrality (McBride, 1994). McBride (1994) attributes this trend to a decrease in the redox potential, coupled with the H_2CO_3-HCO_3^- reaction that occurs in most soils. Without CO_2, the soil pH would increase above 7 due to the fact that reduction normally tends to consume protons as illustrated in equation 1 (McBride, 1994).

$$MnO_2 + 4H^+ + 2e^- \leftrightarrow Mn^{2+} + 2H_2O \qquad \text{(Eq 1)}$$

However, in calcareous soils the reduced species may precipitate as carbonates which leads to a lowering of the pH due to the production of protons, as illustrated by equation 2.

$$Mn^{2+} + H_2CO_3 \leftrightarrow MnCO_3 + 2H^+ \qquad \text{(Eq 2)}$$

Thus, in submerged soils, there is a mechanism responsible for the generation of protons and a separate mechanism for the consumption of protons, leading to wetland soils having a relatively good buffering capacity.

Another potential mechanism that may increase the pH of wetlands soils, is the process of photosynthesis. During this process dissolved carbon dioxide is converted to carbohydrates and hydroxide ions as illustrated in equation 3 (Wildeman *et al.*, 1994).

$$6HCO_3^- (aq) + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 + 6OH^- \qquad \text{(Eq 3)}$$

2.4.3 Organic matter

The productivity of aquatic ecosystems is normally much higher than that of terrestrial ecosystems, which results in the production of large amounts of organic matter. However, under the anaerobic conditions that prevail in the wetland ecosystems, the rates of decomposition and mineralisation are severely reduced (Ponnamperuma, 1972). This leads to an accumulation of organic matter in wetland sediments at rates that range from 0.1 to 0.2 cm per annum (Farnum and Boetler, 1976), with the result that these systems can be considered to be carbon accreting systems.

There are two main functions that organic matter fulfils. Firstly, it is the substrate upon which microorganisms carry out metabolic processes (leading to the redox conditions already discussed). Secondly, organic matter has a high cation exchange capacity, which "buffers" changes in cation concentration via the processes of adsorption onto cation exchange surfaces (Rogers *et al.*, 1985). A lesser function of organic matter is its ability to complex metals with high molecular weight humic materials through the processes of chelation (Gambrells, 1994).

2.5 Geochemical transformations that occur in saturated soils and sediments

2.5.1 Chemical transformations with particular reference to metals

Many of the metals that are found in wetlands - whether they are derived naturally or anthropogenically - are potentially toxic to biological systems and are, therefore, of environmental concern. This problem may be amplified, by the physical and chemical characteristics of the soils that act as potential sinks or sources of these elements. In saturated soils and sediments, there are a number of general chemical forms of metals that differ in mobility (Gambrell, 1994). The different forms include:-

i) Water-soluble metals that are soluble as free ions (*eg.* Zn^{2+}), as inorganic complexes, and organic complexes;
ii) Exchangeable metals;
iii) Metal precipitates as inorganic complexes;
iv) Metals complexed with large molecular-weight humic materials;
v) Metals adsorbed or occluded to precipitated hydrous oxides;
vi) Metals precipitated as insoluble sulphides; and
vii) Metals bound within the crystalline lattice structure of primary minerals.

The factors that determine which of the above forms will be present are: the redox potential of the soil, soil pH, organic matter content, presence of inorganic components such as carbonates and sulphides, and the chemical characteristics of the metal.

As the redox potential of the system tends towards more reducing conditions, there is the reduction of manganese oxide followed by the reduction of iron oxide, to form Mn^{2+} and Fe^{2+}, respectively (McBride, 1994). These two species are relatively soluble and can thus reach appreciable concentrations in aerobic soils. The majority of wetlands contain significant levels of both these elements, with the result that the chemistry of these elements impacts on a number of other processes occurring in these systems. This is discussed by Ponnamperuma (1972), who highlights the fact that the reduction of iron has a number of important chemical consequences.

Firstly, if the system is not well buffered there may be an increase in pH as a result of the consumption of protons during reduction processes. Secondly, there may be a displacement of other cations from their exchange sites. Thirdly, there may be an increase in the solubility of phosphorus and silica; and lastly, there may be the precipitation of new minerals.

In a study by Moore and Reddy (1994) into the controls of the geochemistry of phosphorus in lake sediments, it was found that with a decrease in the redox potential there was an increase in the soluble reactive phosphorus concentration of the water. These researchers attributed this finding to the reduction and dissolution of iron, with a coinciding release of P associated with it. The likely minerals to undergo dissolution would be strengite and vivianite. Moore and Reddy (1994) did, however, find that the phosphorus released upon the reduction of iron, precipitated as calcium phosphate minerals. Precipitation of $Ca(OH)_2$, which is very effective in reducing soluble P levels, through both precipitation and adsorption reactions, was also found to occur. These findings can be summarised as follows: under oxidising conditions, Fe phosphate precipitation controls the behaviour of P solubility, while under reducing conditions, Ca phosphate precipitation governs the solubility of P.

The precipitation of minerals containing iron also influences other elements such as Cu, Cd and to a lesser extent Zn and Ni (Griffin *et al.*, 1989). It was found that these metals precipitate as sulphides and co-precipitate with pyrite thus rendering them non-influential and unavailable to the biota. When co-precipitation occurs, it was found that there was an occlusion of the different metal elements by pyrite. Griffin *et al.* (1989) expected that the behaviour of Pb would be the same as that of Cu, Cd, Zn, and Ni due to the fact that, in the system that they were investigating, the solubility product of Pb in the presence of excess sulphide predicted the rapid formation of PbS. However, it was found that the lead in the system was in a relatively bioavailable form which would indicate that lead was complexed by organic matter. This finding parallels that of Gambrell *et al.* (1980) who found that most of the dissolved mercury in marine sediments was bound as inorganic, non-ionic, or negatively charged complexes or complexed with soluble organics. This finding can be accounted for by the formation of polysulphide complexes, of relatively high solubility, with the Hg that is present in the system.

The results of a study performed by Feijtel *et al.* (1988), indicate that a large proportion of metals occur as precipitates rather than as soluble or exchangeable phases. The results of this study indicate that < 1 % of the total Fe and Mg is present in the pore water (indicating that it is in a soluble form). The inorganic metal precipitates that normally form include metal oxides, hydroxides, carbonates (Gambrell, 1994) and sulphides under highly reduced conditions (Gambrell *et al.* 1980). The main factor controlling the stability of these precipitates is the pH of the system. However, the redox potential also has some influence. At approximately neutral to alkaline conditions, the metals tend to be effectively immobilised. However, as the pH decreases there may be the release of these metals in more soluble forms. Karathanasisa and Thompson (1995) studied the mineralogy of iron precipitates in wetlands constructed to treat acid mine drainage. Although these systems had a relatively low pH, they found that the majority of Fe precipitated as oxihydroxide or oxihydroxysulphates, rather than as sulphate forms. This finding was attributed to the relatively high pE ranges which do not allow for the formation of sulphides.

In a separate study conducted by Griffins *et al.* (1989), it was found that the predominant forms of iron retained in the sediments were oxides as well as some sulphides. This difference in results between the two studies may be due to the fact that they were performed in very different environments. Karathanasisa and Thompsons' (1995) study was performed in an acid environment that had little marine influence, with the result that there was little marine contribution of sulphate. Conversely, the study by Griffins *et al.* (1989) was performed in a marsh soil that had a very definite marine contribution, leading to higher levels of sulphate in the system.

As has been mentioned, there is a thin layer in saturated soils and sediments where conditions are not anaerobic, with the result that relatively oxidising conditions exist. However, it must be borne in mind that this layer is only present so long as the overlying waters are well oxygenated. This layer has an important role to play in the mobility of a number of constituents. According to Ponnamperuma (1972), this layer acts as a sink for phosphate and a number of other constituents, thereby preventing their transmittance from the reduced layers into the water column. As Ponnamperuma (1972) mentions, in the oxic layer any reduced, relatively mobile species, such as Mn^{2+} and Fe^{2+} are quickly oxidised to Mn^{4+} and Fe^{3+} oxide hydrates, that then sink into the sediments carrying with them sorbed phosphates, silicates and sulphates.

2.5.2 Behaviour of organics

The reducing conditions that are prevalent in saturated soils and sediments causes the decomposition of organics to differ from that found in aerated soils. In soils that undergo aerobic respiration, the products of decomposition are carbon dioxide, nitrate, sulphate, and resistant residues, while the products of anaerobic decomposition are carbon dioxide, hydrogen, methane, ammonia, amines, mercaptans, hydrogen sulphide, and partially humified residues (Ponnamperuma, 1972). Most of the organic carbon in wetlands can be divided into two fractions: that which is easily degraded and that which is more refractory to degradation (Rogers *et al.*, 1985). The readily biodegradable fraction will be utilised rapidly as a substrate upon which microbial respiration can occur. The result will be a relatively rapid decomposition of this fraction to produce the products mentioned above. However, the more refractory organics will take more time to decompose, with the result that they may accumulate in the sediments of the system (Rogers *et al.*, 1985). The sedimentation process may, however, be retarded if there is a high concentration of dissolved organic carbon (DOC) in the water column (Pardue *et al.*, 1993). This is due to the ability of DOC to sorb organics, thereby effectively increasing their solubility and preventing their sorption onto settleable particles. Pardue *et al.* (1993) investigated the behaviour of organic contaminants in a wetland to determine the influence of sorption capacity of wetland soils. The results of this study were that sorptive assimilation of organic compounds in wetlands appears to be dependant on the unique hydrological conditions that promote sediment-water exchange and accretion, rather than any enhanced sorptive ability of wetland soils. The implication of this study is that mineral soils are probably more effective than highly organic wetland soils at retaining hydrophobic organics because DOC levels are lower. This finding indicates that wetlands may not be able to degrade waters containing high concentrations of hydrophobic organics.

2.6 Discussion and conclusions

Sediments differ from other soils as result of the water regime that is characteristic of the systems in which they are found. One of the most marked influences of the water regime is a decrease in the amount of oxygen that is found in the submerged soil and sediments. Furthermore, the generally high productivity creates conditions in which large quantities of senescent material are found. This acts as a substrate upon which microbes can perform their metabolic activities. The combination of low oxygen diffusion and high rates of microbial activity lead to the rapid utilisation of whatever oxygen is present. The implication of this is that microbes then shift metabolic pathways with the result that electron acceptors other than oxygen are utilised, leading to the development of reducing conditions in the sediments. This change in oxidation state of the sediments then affects the speciation of the various constituents that are present in the system. Besides speciation being affected by oxidation state, the characteristic pH values that are detected in most saturated soils and sediments also impact on species that are found in these systems.

Generally the chemical conditions that exist in these systems lead to an increase in metal solubility. However, reduced species may be oxidised under oxic conditions, thereby forming insoluble precipitates that are incorporated into the sediments of the system. Iron and manganese appear to be the elements whose mobility is affected the greatest. When these elements are reduced the resulting species are highly mobile. However, if sulphide precipitates form, the solubility is diminished. Besides direct precipitation, mobility of constituents may be affected when they are removed from solution as co-precipitates. For example, when precipitation of Fe occurs there is often the concurrent precipitation or even co-precipitation of other metals. Inorganic precipitation is not the only mechanism whereby metals are rendered insoluble. In sediments with a high organic matter content, the potential exists that metals can complex with organics to form compounds whose solubility is reduced. However, organic complexation does not always lead to the formation of insoluble compounds, because it has been found that there may be an increase in metal solubility when metals complex with organic matter. Furthermore, as has been mentioned, there is often an oxic layer overlying the reduced layer in saturated soils and sediments. The presence of this layer may potentially act as a mechanism to prevent the release, into the water column, of elements that are soluble in their reduced states. That is, there will be a change in oxidation state as the elements move from deeper down to the surface layers. The effect of this change in state may be to reduce the mobility of specific elements. Therefore, the presence of both a reduced as well an oxidised layer in sediments has a marked affect on the solubility of constituents present in these systems.

Thus, in conclusion, the saturated conditions that exist in wetland soils create characteristics unique to these systems. The water regime, biota, and soils of wetlands have unique properties that lead to the creation of conditions that are suitable for the immobilisation of many contaminants found in these systems.

Finally, a large proportion of the work that has been conducted on wetlands has involved investigations of the behaviour of pollutants in these systems. The data base that exists on wetlands that have been unaffected by man is limited. Most of the work has tended to focus particularly on the impact of nitrates and phosphates in these systems. The work that has been performed has also tended to focus on coastal or marine influenced wetlands, rather than on freshwater wetlands. A large body of knowledge exists on the performance of constructed wetlands. However, this work has tended to take the approach of the wetland being a "black box", where only influent and effluent water are examined with little investigation being performed on the actual transformations that are occurring in these systems.

CHAPTER 3.

MATERIALS AND METHODS

3.1. Sampling strategy

The site was sampled in a way that would allow the determination of whether potential contamination was confined to a specific area, or whether contamination was distributed relatively homogenously down the length of the drainage system. In order to achieve this, sample points were located at areas where it was expected that contamination might be present. In areas where the degree of contamination was not expected to be high, samples were taken in order to give a full understanding of the degree of contamination in the system. Locating the sample points in this manner resulted in 17 sites being sampled (see Figure 3.1). Sample points were :-

1 Farm bypass
2 Lourens river
3 Triomf/Kynoch Main Drain (fertiliser area)
4 Magazine Main Drain
5 Marshalling Yard Main Drain
6 Below the confluence of Triomf/Kynoch, Magazine and Marshalling Yard Main Drains
7 Above Langvlei
8 Below Langvlei
9 Laundry discharge
10 Upstream of sulphur belt discharge
11 Downstream of sulphur belt discharge
12 Plants wash water discharge point
13 Explosives discharge
14 Estuary discharge
15 Wetland inlet
16 ± 20 meters into wetland
17 Wetland outlet

At each sample point both water and sediment samples were collected. Prior to the collection of water samples, sample bottles were rinsed thoroughly three times and pre-contaminated with water from the sample site that was then discarded.

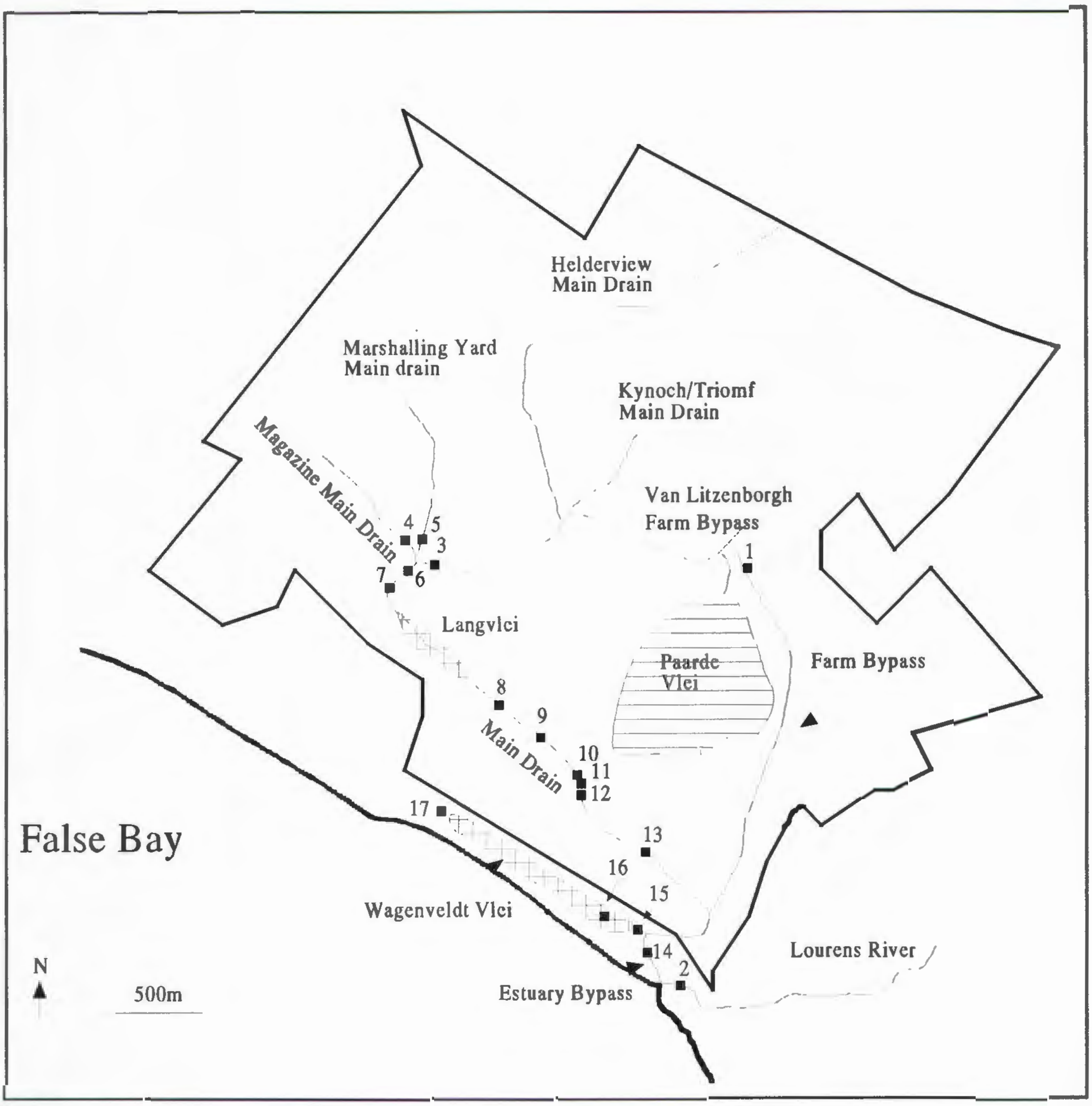

Figure 3.1. Location of the position where samples were collected. The numbers on the map refer to the sample number. It must be born in mind that both water and sediment samples were collected at each point (with the sediments being separated into a top and bottom layer).

Sediments were collected using a hand coring device. This consisted of a 40 cm length of PVC tube that was forced into the sediments. Once the corer had been pushed into the sediment, its top was sealed in order to create a vacuum as the device was pulled from the sediment. In some instances the corer had to be dug out from the drain bed. Once the core had been collected, it was sealed by means of caps at the top and bottom ends of the PVC tube. In transporting the cores back to the every effort was made to keep the cores in a vertical position, in the orientation in which they were collected.

Once the cores had been brought back to the laboratory, they were immediately placed in a freezer at minus 20 °C. The cores were allowed to freeze for 10 days before they were cut. Cutting was achieved by means of a power saw equipped with a tungsten carbide blade. During the cutting procedure, only the PVC "case" of the core was cut in an attempt to minimise contamination of the samples. Once the cores had been cut they were photographed (see Figure 3.2) and then separated into a top and bottom horizon by means of a hydraulically operated sample splitter. The separation was made based on obvious visual physical differences in the cores. The physical differences included both colour and texture of the different layers. The cores collected at sample points 10, 14 and 16 had no structure and were therefore not separated into different layers. It was not known whether the physical differences in the cores resulted from different redox conditions in the different layers, differences in organic carbon contents, or differences in sedimentation conditions; therefore the two layers were simply labelled top and bottom. For each sample the top layer was given the label T, while the bottom layer was labelled B.

Figure 3.2. Illustration of cores after removing them from coring device, but prior to splitting.

3.2. Water analyses

Where possible, the methods that have been used are those that are prescribed in the Standard Methods for Examination of Water and Wastewater (Franson, 1985). Details of materials and methods are presented in Appendix 2.

3.2.1. Treatment of samples

Prior to analyses water samples were kept in a cool dark place.

Before the concentrations of major ions were determined by High Pressure Ion Chromatography (HPIC) and before total elemental concentrations were determined by Inductively Coupled Plasma-Optical Emission Spectrophotometry (ICP-OES), the water samples were filtered through a 0.45 μm filter using Millipore apparatus.

3.2.2. Electrical conductivity and pH

Electrical conductivity (EC) was measured by a Crison Micro electrical conductivity meter, while pH was measured using a Crison Micro 2001 pH meter. The measurement of pH and EC was done twice on each sample in order to determine the precision of the measurements and ensure accuracy.

3.2.3. Alkalinity

Alkalinity was determined by means of an end-point titration using an automatic titration assembly (Radiometer TTT 85 Titrator with a Radiometer ABU 80 auto-burette). This involved titrating a 10 ml aliquot subsample against 0.01 M HCl to an end-point of 4.5 pH units. The result is given as the number of millimoles of carbonate per millilitre of ℓ sample.

3.2.4. Major ions

The concentrations of the major cations and anions in the water samples were determined using HPIC. Prior to analysis, samples were diluted with < 18 MΩ Milli-Q water in order to achieve an electrical conductivity of < 100 μS/cm. The sample was then passed through an On-Guard P filter to remove organics and particulates. Analysis was carried out using a Dionex DX 300 series suppressed IC system. Chromatograms were analysed with AI-450 chromatography software. Duplicates were run every 5 samples to determine the precision of the technique and to ensure accuracy.

3.2.4.1. Anions

The concentration of F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-} was determined using a Dionex HPIC-AG4A guard column with a Dionex HPIC-AS4A-SC column as the separator column. The eluent was a mixed sodium carbonate/sodium bicarbonate solution that was delivered at a flow rate of 2.0 ml/min. Sample loop volume was 50 $\mu\ell$. Run time per sample was 8 min.

3.2.4.2. Cations

The concentration of Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} was determined using a Dionex HPIC-CG12A-guard column with an Dionex HPIC-CS12A column as the separator column. The eluent used was 22 mM methanesulphonic acid (MSA) that was delivered at a flow rate of 1.0 ml/min. Sample loop volume was 50 $\mu\ell$. Run time was 14 min per sample.

3.2.5. Total elemental concentrations

The total elemental concentration of Zn, Pb, Ni, Si, Mn, Fe, Al, Cu, Ca, Na and K was determined by Inductively Coupled Plasma-Optical Emission, Spectrometry using a JOBIN-YVON 70C (JY70C) combined simultaneous/sequential ICP spectrometer coupled with J-Yess version 4.0 software. See Appendix 2 for details of instrumental settings.

3.2.6. Phosphate

The necessity of diluting water samples to an EC > 100 μS/cm for HPIC analysis resulted in the PO_4^{3-} concentration of the samples being at or very near the instrument's detection limits, with the result that the PO_4^{3-} concentrations that were calculated may be erroneous. Therefore, phosphate concentration was also determined colorimetrically using the method of Murphy and Riley (1962). This method is specific for the orthophosphate form of phosphorus, and entails the conversion of orthophosphate to phosphomolybdate by acidified ammonium molybdate reagent. Once the conversion is complete, absorbance was measured on a Turner 340 spectrophotometer at a wavelength of 880 nm.

3.2.7. Fluoride

Fluoride analyses by HPIC were similar to those of phosphate in that dilution resulted in concentrations at or near the detection limits of the HPIC. Therefore, fluoride concentration was determined using an ion selective electrode.

A Corning ion analyser 255, coupled with a fluoride ion selective electrode and a Calomel reference electrode was used for the analysis. Prior to measuring the F^- concentration in the sample, any complexed F^- was converted to the uncomplexed form through the use of a decomplexation agent. The decomplexing agent that was used was a TISAB buffer consisting of 1,2 cyclohexylenediaminetetraacetic acid (CDTA).

3.2.8. Prediction of chemical speciation and saturation indices

The geochemical equilibrium speciation model for dilute aqueous systems, *MINTEQA2* (Allison *et al.,* 1991) was used to calculated the saturation indices (S.I.) of minerals likely to occur under the prevailing conditions.

The *MINTEQA2* model is based on the assumption of thermodynamic equilibrium between phases, with the thermodynamic equilibrium constant defined as follows:

$$aA + bB \rightleftharpoons A_aB_b$$

$$K^0 = \frac{A_aB_b}{A^aB^b}$$

where A and B are chemical entities that react to form the reaction product A_aB_b, having a thermodynamic equilibrium constant K^0. The various chemical reactions that are modelled are quantified by the Davies equation which is used to calculate thermodynamic constants at the relevant ionic strength of the test solution.

3.3. Sediment analyses

Where possible the methods that have been used are those that are prescribed in the Methods of Soil Analysis (Part 1, Klute, 1986; Part 2, Page *et al.,* 1982). Details of materials and methods are given in Appendix 2.

3.3.1. Treatment of samples

Prior to analysis, samples were air dried for a week at room temperature. They were then gently crushed to break up soil aggregates. Samples were sieved through nylon bolting cloth with a pore diameter of 2 mm. Bolting cloth was used instead of a conventional metal sieve to prevent possible contamination from metals[1]. Samples were stored in plastic bags until they were needed for analysis.

3.3.2. Total elemental concentrations

Major and trace elements in the sediments were analysed using a Philips PW X'Unique II X-ray spectrometer. Due to time restrictions, both major and trace elements were analysed on powder briquettes, rather than majors being analysed on fusion disks which would have eliminated mineral and particle size effects, thus increasing the accuracy of the results. The accuracy of the major element analysis was nevertheless sufficient for this study in that they give an adequate indication of differences in major element composition.

Powder briquettes were prepared by crushing air-dried samples in a carbon-steel vessel using a Siebtechnik swing mill to 300 # (≈ μm) grain size. Six grams of milled sample were mixed with 1 drop of Mowiol per gram of sample and then pressed in a 30 mm diameter tool steel die under 10 tons of pressure. See Appendix 1 for details of instrumental conditions.

3.3.3. Organic carbon

The organic carbon content of the sediments was determined by the method of Walkley-Black (Walkley, 1935). This method involves the rapid oxidation of organic matter by potassium dichromate. Excess dichromate is then titrated against ferrous ammonium sulphate. The titration is based on the assumption that the reduced dichromate is equivalent to the organic carbon present in the sample, assuming that the soil organic matter has an average valence of zero.

3.3.4. Carbonate

Calcium carbonate content was determined using a "Karbonat-bombe" as described by Birch (1981). This method involves the reaction between the $CaCO_3$ in a crushed 1g subsample of sediment and concentrated HCl, resulting in the evolution of carbon dioxide. The volume of CO_2 evolved is

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[1] Willis (1996 pers. comm.)

proportional to $CaCO_3$ content and is measured by means of a pressure gauge on the apparatus. When $CaCO_3$ content was lower than 20% samples were re-analysed using a sample weight of 4g.

3.3.5. Soil extracts

Due to the fact that the amount of sample collected was not large, it was not possible to make saturated paste extracts for the different sediment samples. Therefore, extracts were made using a 1:1 soil to water ratio, followed by centrifugation to obtain the extract. According to Rhoades (1982) this ratio does not relate well to field soil water contents and errors may arise as a result of peptization, hydrolysis, cation exchange and mineral dissolution. However, these extracts are suitable for determining relative differences rather than absolute solute concentrations, and they are treated as such in this work.

The extracts were filtered through a 0.45 μm Millipore filter and then EC, pH, anions, cations and total elemental concentrations were determined as for the water samples.

3.3.6. Clay content

As a result of budgetary and time constraints the clay content was determined in only a few samples. The samples that were analysed were those from the top horizon at sample positions 5, 6, 12, 13, 15 and 16. These were selected partly as a result of there being insufficient sample remaining from other sample locations, but also because these samples were located along the length of the drain, thereby giving an overall picture of clay content of the sediments.

The pipette method as described in the Handbook of Standard Soil Testing methods for Advisory Purposes (The Non-Affiliated Soil Analysis Work Committee, 1990) was used. This technique is based on the principle that spherical particles settle at a velocity that can be calculated from Stockes' Law. The technique involves dispersing the sample in 5% Calgon solution. The sample is then transferred to a 1 L cylinder whereafter aliquots are removed at appropriate time and depth intervals using a Lowry pipette (See Appendix 2 for details).

3.3.7. Clay mineralogy

As a result of time limitations, only a selected number of samples were used for the determination of clay mineralogy. The samples on which clay mineralogy was determined were selected to give an indication of the clay mineralogy along the length of the drain. Thus, the samples on which clay mineralogy was determined were a composite of samples 2 T and B, a composite of 3 T and B, a composite of 4 T and B, a composite of 9 T and B, sample 16 (not split into layers) and a composite of sample 17 T and B.

Prior to separation, organic matter in the samples was removed by means of a hydrogen peroxide digestion step. This involved reacting the sample with an initial volume of 25 ml of 100 % H_2O_2. Once the initial effervescence had subsided the samples were heated in a water bath to 75 °C until the samples had stopped effervescing.

Clay separation was then achieved by dispersing the samples in a dilute Na_2CO_3 solution and repeatedly collecting the supernatant after the settling of the > 63 µm fraction. The clay that was collected in this way was flocculated through the addition of sodium chloride. Once flocculation had occurred, the clay fraction was concentrated by centrifugation and then dialysed with tap water for 48 hours and distilled water for another 48 hours. Slides of a subsample of clay were prepared by placing a 2 ml aliquot of the clay-water mix on a glass slide.

Clay mineralogy was determined by scanning the slides using a Philips PW 1390 X-ray diffractometer fitted with a variable slit assembly, monochromator, scintillation detector and pulse height selector. A copper tube operating at 40 kV and 25 mA was used for the analysis, and the samples were scanned through a range of 4.00-70.00° 2Θ with a step size of 0.1° 2Θ and a counting time of 1 sec/step.

3.3.8. Extractable acidity

Extractable acidity was determined by making a 1:2.5 sediment: solution in 0.01 M KCl solution, shaking for 30 min, allowing to settle for 10 min and then filtering through Whatman's N°. 1 filter paper. Acidity was determined by means of an endpoint titration using an automatic titration assembly (Radiometer TTT 85 Titrator with a Radiometer ABU 80 auto-burette). This involved titrating a 10 ml aliquot subsample of the extract against 0.01 M NaOH to a end-point of 8.3 pH units.

3.3.9. Electrical conductivity and pH (H_2O and $CaCl_2$)

Electrical conductivity was determined on a 1:2.5 soil to water solution that had been made up with 10 grams of sediment and 25 ml of distilled water. EC was measured with a Crisons Micro electrical conductivity meter. pH was determined on the same 1:2.5 soil to water solution using a Crisons 2001 pH meter.

The pH of a 1:2.5 sediment to 0.1 M $CaCl_2$ solution was determined in order to obtain an understanding of the sediments' cation exchange capacity.

3.3.10. Oxidation experiment

This experiment was performed to determine the change in pH that may potentially occur if reduced sediments in the drain were to become oxidised as a result of the sediments becoming less saturated. This experiment was only performed on sediments from the bottom layer because it was expected that these sediments would be reduced. There was insufficient sample for 1B, 2B and 7B and there was no bottom layer for samples 10 and 14. Therefore, the experiment was not performed on those samples. Even though there was no bottom layer from sample 16, the experiment was still performed on the entire sample. It was not possible to perform the experiment on the whole samples of 10 and 14 as a result of there being insufficient sample.

In this experiment, sediments that had remained in an air tight container for 6 weeks at their initial water content, were used. The water content of the samples was determined by oven drying a subsample at 105°C and determining the mass loss. This enabled the calculation of the amount of wet sediment needed to obtain a theoretical 10 g dry mass of sediment. This mass was made up to 35 g with distilled water on the assumption that there would be a 1:2.5 sediment to solution ratio for the sample.

The samples were shaken on a flatbed shaker for an hour, whereafter they were left to stand for an hour. Samples were centrifuged at 6000 revs/min for 5 minutes and pH of the supernatant solution in the centrifuge tube was determined using a Crisons 2001 pH meter to determine the pre-oxidation pH.

The sediments were then resuspended in the solution and transferred to 250 ml Erlenmeyer flasks. Twenty-five ml of 30 % hydrogen peroxide was added to each sample. Once the initial effervescence had subsided a further 25 ml of H_2O_2 was added. The samples were then heated in a water bath at 80 °C until all visible effervescence had ceased. The samples were removed from the water bath and allowed to stand until all audible effervescence had ceased. Samples were then transferred to centrifuge tubes, centrifuged at 6000 revs/min and the post-oxidation pH determined.

3.3.11. Acid extractable elements

The concentration of the elements As, Se, Mo, Ag, Ti, Sr, Mg, Al, Ni, Hg, Mn, Fe, Cr, V, Na, Be, B, Ca, P, Zn, Cd, Cu, Sb, Pb, Bi, Li, Co, Sn and K in an acid extract made from a select number of sediment samples was analysed. The samples that were analysed were a composite (1:1) made from the top and bottom layers of samples 1, 4, 6, 9, 12 and 16.

The method involved shaking a 10-g subsample of sediment in a 100 ml of a 0.1 M nitric acid solution for 15 minutes on a flatbed shaker. The sediment solution was then filtered and anlaysed by ICP-OES. The results of this technique are semi-quantitative as a result of instrumental set-up conditions that are required for a multi-element analysis

3.3.12. Statistical analysis

The computer package *STATISTICA* for Windows was utilised for the calculation of the descriptive statistics reported in this study. This package was also used for to calculate the correlation coefficients that are reported.

CHAPTER 4.

WATER CHEMISTRY

4.1. Introduction

The aim of this chapter is to evaluate the quality of water in the Main Drain. However, it must be borne in mind that the various water parameters that have been determined are dynamic, with the result that the analyses that were obtained on the various samples apply only to the condition of the water on the day on which they were sampled. This means that a "snapshot" of potential conditions was determined.

4.2. Results and discussion of water analyses

The pH, alkalinity and electrical conductivities of the different samples are given in Table 4.1. Figure 4.1 illustrates the differences in analyte concentrations at the various sample locations graphically. Detailed results of the constituents in the different water samples are presented in Table 4.2. The sample numbers in these figures and tables refer to the sample locations as described in Chapter 3 (Figure 3.1). An analytical appraisal of results is presented in Appendix 1 and includes information on detection limits, precision and accuracy of the various analyses.

4.2.1. pH

It is well known from thermodynamic principles that pH is one of the more important factors controlling reactions that occur in a water column. Solution pH affects the concentration of a large number of chemical constituents by affecting dissolution and precipitation rates as well as controlling the chemical species that are present in a water body. According to Dallas and Day (1993), by controlling speciation of constituents, pH has an important effect on the availability and toxicity of a number of elements.

Table 4.1. The pH, alkalinity and electrical conductivity of the water samples collected at the various sample locations in the drainage system.

	pH	Alkalinity (mg HCO_3^-/ℓ)	EC (mS/m)
1	7.10	19.2	14
2	7.45	36.0	24
3	3.92	bdl	260
4	7.73	258	171
5	7.46	122	339
6	5.92	74.1	217
7	6.13	7.65	296
8	6.32	5.11	233
9	6.26	2.87	190
10	6.17	4.24	243
11	6.29	13.4	190
12	7.19	29.9	27
13	6.21	2.23	113
14	6.57	7.31	80
15	6.52	11.3	78
16	6.54	6.24	77
17	6.53	66.4	123

Fifteen of the seventeen samples have a pH that is approximately neutral ranging between 6.3 and 7.7. This range falls within that described by Dallas and Day (1993) as being common for most natural waters in Southern Africa. This would tend to indicate that processes occurring on site are not leading to a significant decrease in pH (acidification) of the water in the drains. However, it must be noted that there is a slight decrease in pH of the water in the drainage system compared to that of the waters of the background samples (samples 1 and 2) (mean pH of water in the drainage system = 6.56; excluding sample 3, mean pH of background water = 7.28), indicating that processes are occurring that lead to a small decrease in pH. This may, however, be a result of water at neutral pH mixing with water that is draining from the Fertiliser area - sample 3 - (as discussed below), rather than processes occurring at each sample location. The evidence for this statement is the fact that samples 7 through 11 and samples 13 and 14 have relatively similar pH, indicating that there are no major geochemical factors resulting in a change in pH. The slightly higher pH of sample 12 could be a result of the fact that this sample was collected right at the discharge point (where plant washing water was being discharged) rather than in the Main Drain, which would mean that, at the time of collection, the sample had not had time to come into equilibrium with the water into which it was being discharged. The similarity in samples only applies to pH, as can be seen by the disparity in ionic concentrations at the different sample locations.

The sample from the Kynoch/Triomf Main Drain draining the Fertiliser area (sample 3) does not conform to this generalisation. The pH of this sample is in the range that would lead to it being classified as acidic (Drever, 1988). It is expected that the low pH is a result of acid leaks that used to occur frequently in this area. Even if the acid had not been spilled directly into the drainage system, but had spilled onto the soil, it is possible that there could be leaching of the acid from this area as groundwater moves through the subsurface and into the drain. The high sulphate and phosphate concentrations in the water sample may indicate that the acid that was spilled was either sulphuric or phosphoric acid.

The pH values of the water samples that were collected at the wetland inlet, in the middle of the wetland and at the wetland outlet (samples 15-17) are all relatively similar, having a median value of 6.5 pH units. This would confirm that wetland processes - such as oxidation and reduction - are occurring which result in the pH of the overlying water being relatively well buffered at an approximately neutral pH.

4.2.2. Alkalinity

Besides the oxidation and reduction reactions that may be occurring in the sediments resulting in the buffering of pH, the carbonate system may also have an important effect on pH. In fact, Drever (1988) states that the pH of most natural waters is controlled by reactions involving the carbonate system. Implicit in this statement is the fact that the carbonate system, of which alkalinity is a measure, acts as a mechanism for buffering pH changes that could potentially occur in water bodies. Alkalinity refers to the equilibrium that results between a water body and the atmosphere or the water body and $CaCO_3$, when CO_2 becomes solubilised. Its determination is usually an estimation of the carbonate and bicarbonate ions in solution. Since the concentration of other ions is relatively high in some samples, the determination of alkalinity may not be a true reflection of HCO_3^- activity, because some of the other ions may react with the H^+ in the titre resulting in a potentially spurious result. However, according to Dallas and Day (1993) other ions usually only contribute a small amount to alkalinity.

In essence, the carbonate system buffers pH via a change in the activities of carbonate-bicarbonate species as the activity of hydrogen ions changes, resulting in the evolution of CO_2. When all the bicarbonate has been utilised any change in hydrogen ion activity will result in a rapid change in pH (Drever, 1988).

The water samples collected from the different locations on site exhibit a wide range of alkalinities from 258 mg/ℓ in the Magazine drain to below detection limits in the Kynoch/Triomf drain (sample 3 with a pH to low for HCO_3^- to be in solution). The low alkalinities that were detected in some samples indicate that these samples are at the limit of their buffering capacity, and any significant change in hydrogen ion activity that may occur at these locations could lead to a marked change in pH. Conversely, the samples that have high alkalinity will be able to resist changes in pH which could potentially occur with changes in the hydrogen ion activity.

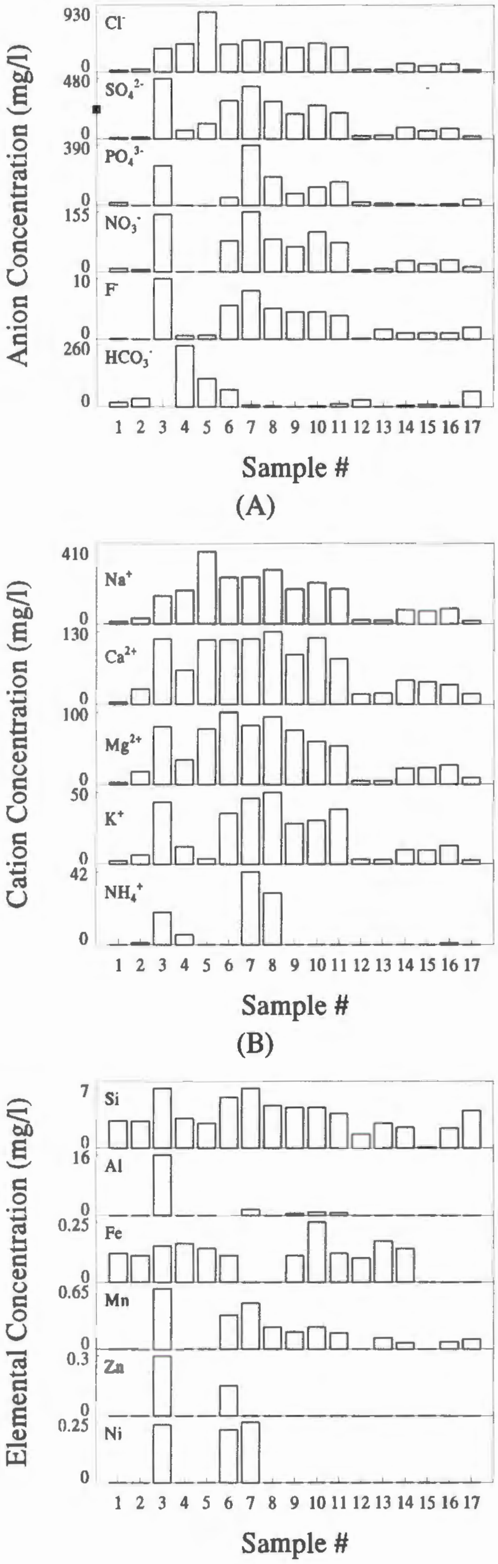
The large variation in alkalinities may be attributed to the fact that at the different locations there may be different concentrations of H^+ entering the system. As has been discussed, this eventuality is not reflected in the pH of the samples, but this lack of variation in pH can be attributed to the protons forming different complexes at the different sample locations.

4.2.3. Ions in solution

4.2.3.1. Electrical conductivity (EC)

Electrical conductivity is a function of the number of charged particles in solution. Therefore, its magnitude can be used as a measure of the amount of dissolved material in solution.

The EC values of the different water samples exhibit a wide range (325 $mS.m^{-1}$) indicating that the water from the different sample locations contains widely differing concentrations of dissolved constituents. The EC values of the background samples (samples 1 and 2) are low relative to those of the samples collected at the other sample sites. This indicates that activities within the industrial complex have resulted in an increase in ionic concentrations in the water. The ionic and elemental concentrations that were determined in the various samples are illustrated in Figure 4.1. with exact concentrations presented in Table 4.2.



(A)

(B)

(C)

Figure 4.1. Chemical characteristics of the water samples collected at the various sample locations in the Main Drain: (A) anion concentrations; (B) cation concentrations; (C) elemental concentrations.

Table 4.2. Chemical characteristics of the water samples collected from the Main Drain. (bdl indicates that the concentration of the analyte is below detection limit). Sample numbers refer to sample locations as described in Chapter 3 (Figure 3.1).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Anions (mg/ℓ)																	
F^-	0.1	bdl	10	0.6	0.6	5.6	8.1	5.1	4.5	4.5	3.9	0.2	1.68	1.0	1.0	1.0	2.0
Cl^-	25	46	370	440	930	430	500	480	380	450	390	40	41	140	100	120	39
NO_3^-	10	6.0	150	bdl	bdl	80	160	84	66	100	77	5.6	8.0	30	21	32	14
PO_4^{3-}	22	1.6	260	0.69	1.3	54	390	190	77	120	150	bdl	15	13	5.8	12	bdl
SO_4^{2-}	9.2	11	480	67	120	310	420	300	200	270	210	24	28	90	66	83	39
Cations (mg/ℓ)																	
NH_4^+	bdl	1.4	19	6.0	bdl	bdl	42	30	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1.2	bdl
Na^+	16	34	160	190	410	260	270	310	200	240	200	24	20	81	77	90	20
Ca^{2+}	3.9	27	120	61	120	120	120	130	89	120	82	18	20	43	40	35	18
Mg^{2+}	2.8	18	80	34	77	97	82	94	75	59	53	5.6	5.5	22	23	27	9.4
K^+	2.3	6.3	43	12	3.7	36	46	50	29	30	38	3.3	3.0	10	9.7	13	2.7
Elements (mg/ℓ)																	
Zn	bdl	bdl	0.31	bdl	bdl	0.15	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Ni	bdl	bdl	0.24	bdl	bdl	0.22	0.25	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Si	3.2	3.2	7.3	3.5	2.9	5.9	7.3	5.0	4.7	4.8	4.0	1.7	2.9	2.4	0.13	2.3	4.4
Mn	bdl	bdl	0.65	bdl	bdl	0.37	0.50	0.24	0.19	0.24	0.18	bdl	0.12	0.07	bdl	0.08	0.11
Fe	0.12	0.11	0.15	0.16	0.14	0.11	bdl	bdl	0.11	0.25	0.12	0.10	0.17	0.14	bdl	bdl	bdl
Al	bdl	bdl	16	bdl	bdl	3.0	1.5	bdl	0.60	0.86	0.73	bdl	bdl	bdl	bdl	bdl	bdl
Na	15	23	180	220	430	230	250	230	190	230	190	24	93	63	61	61	98
Ca	5.7	7.0	96	66	67	83	100	86	71	87	70	12	45	32	32	32	73
Mg	3.1	4.1	37	26	56	36	41	37	31	35	30	5.0	17	12	12	12	17
K	bdl	bdl	77	12	9.6	49	79	57	40	54	39		19	12	11	11	18

4.2.3.2. Anions

There is a wide variation in anion concentration in the various samples (Table 4.2 and Figure 4.1), as was reflected in the differing EC values that were recorded at the different sample locations. The dominant ions in most samples are Cl^- and SO_4^{2-}. However, in a number of samples there are also high concentrations of PO_4^{3-} and NO_3^-. Even though the concentration of F^- is not high enough that it would be classified as a dominant anion, the ion is present in concentrations that could result in human health being endangered as discussed in section 4.2.7.6.

According to Wetzel (1996) and Cole (1979) the relationship that exists between anions, in the average stream waters of the world, is usually $HCO_3^- > SO_4^{2-} > Cl^-$. Chloride is, however, the dominant anion in 16 out of the 17 samples. It is possible that the general dominance of Cl^- ions is a result of the proximity of the site to the coast, with the result that there has been wind deposition of NaCl. This finding is supported by the ratio of Na^+ to Cl^- which is relatively constant throughout the site (ranging from 0.44-0.75) and not largely different from the ratio of 0.56 for Na^+ to Cl^- in seawater reported by Drever (1988) (see Table A3.1 for the ratios at each sample location). However, it must be noted that the concentrations of Cl^- and Na^+ are very different at different sample locations, indicating that there are sources other than marine deposition which account for the high sodium chloride levels. This is illustrated by the differences in Cl^- content between the background samples (concentration of $Cl^- = 25$ and 46 mg/ℓ in samples 1 and 2, respectively) and the samples collected on site (maximum concentration of 930 mg/ℓ detected in sample 5).

The lack of dominance of the anions HCO_3^- in the water samples can be attributed to there having been inputs of protons into the water, during industrial activity, which has resulted in a shift in the equilibrium that exists between atmospheric CO_2 and that dissolved in water.

4.2.3.3. Cations

As with anions, the concentrations of cations in the different samples differ widely at the various sample locations (Table 4.2 and Figure 4.1). The dominant ions in solution are Na^+, Ca^{2+}, Mg^{2+} and K^+, with NH_4^+ only being found in low concentrations in some samples (except sample 7 and 8 where the concentrations of NH_4^+ are high relative to those at other sample locations). The relationship between these ions differs from that which has been found to be the average concentration in river waters from around the world (Wetzel, 1996). That is, in the Main Drain the concentration of $Na^+ > Ca^{2+} > Mg^{2+} > K^+$, whereas the relationship described by Wetzel (1996) is $Ca^{2+} > Mg^{2+} \geq Na^+ > K^+$. As alluded to in section 4.2.3.2 the dominance by Na^+ could be as a result of a marine influence. As with anions, the concentration of cations in the background samples is low relative to the concentrations recorded in the samples collected on site, indicating that besides the marine influence, there are other factors leading to the contamination of water in the drainage system.

4.2.3.4. Hydrochemical facies

A technique that is useful for determining the hydrochemical facies of water samples is to plot the major ion data on a Piper Trilinear diagram (Freeze and Cherry, 1979). From these diagrams it is possible to identify distinct zones that have cation and anion concentrations describable within defined composition categories (as illustrated in Figure 4.2A). Thus, by plotting the data for a number of samples on the Piper plot, it is possible to determine whether a group of samples have similar chemical characteristics. It must, however, be borne in mind that even if samples contain very different total ion concentrations, they will still be grouped on the plot if particular ions occur in the same proportion of the total ion content.

The Piper Trilinear plot that was generated from the results of the various ion analyses for the different samples (Figure 4.2B) confirms the finding that the samples are dominated by Na^+ and Cl^- and SO_4^{2-}. The diagram also illustrates that samples 1, 2, 4, 12 and 17 have similar compositions, while samples 3, 6 through 11 and 13 through 16 all have similar compositions.

4.2.4. Elements in solution

The total elemental analysis (Table 4.2 and Figure 4.1) indicates that the dominant elements in solution are similar to the dominant ions in solution *ie.* Na, Ca, Mg and K, with the minor elements being Si, Al, (both in concentrations above 1 ppm) and Zn, Ni, Mn and Fe (in concentrations below 1 ppm). The elements Pb, Cu, Cd, Cr and Co were analysed for, however, these elements were either not present in the samples or they were present in concentrations below the detection limits of the ICP-OES.

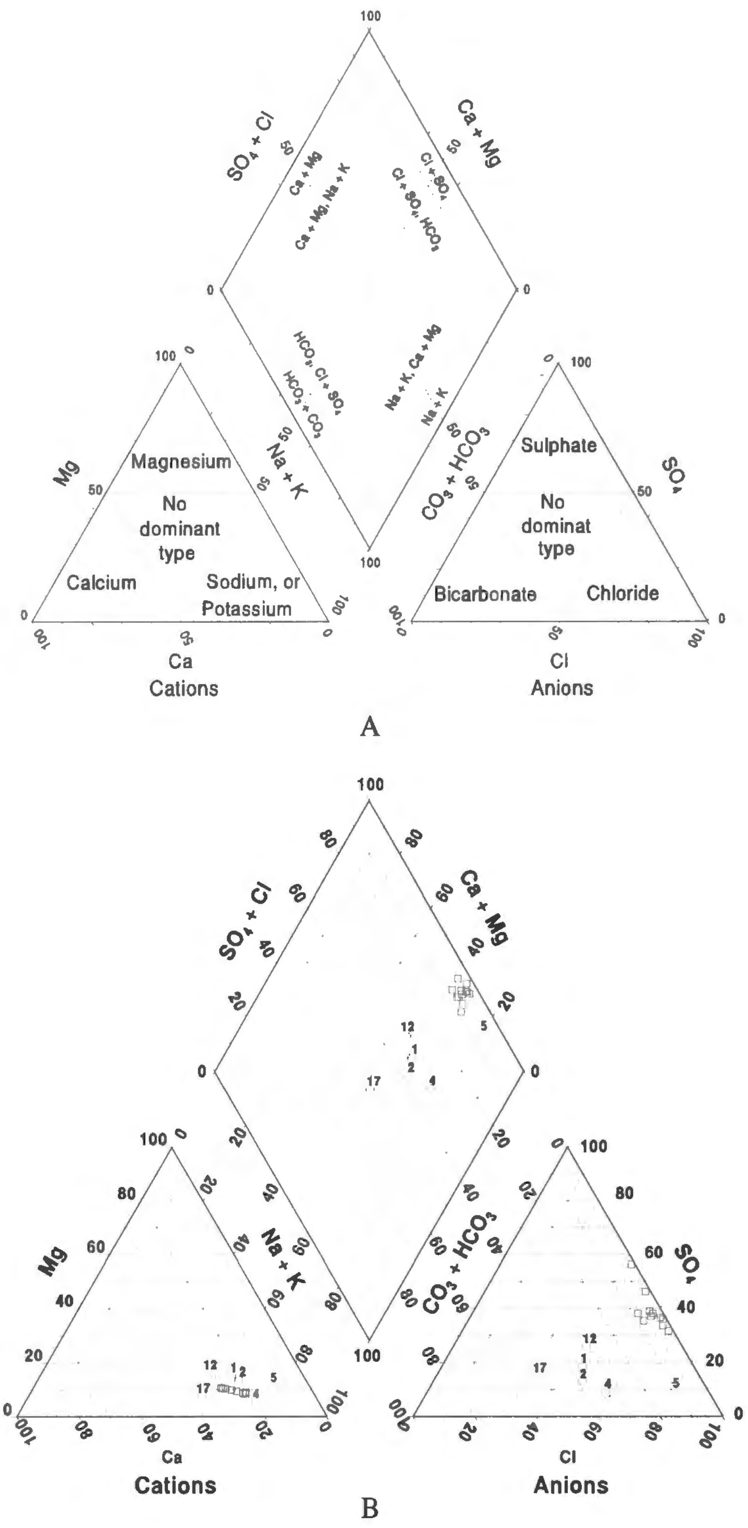


Figure 4.2. (A) Classification diagram for anion and cation facies in terms of major-ion percentages (Freeze and Cherry, 1979). (B) Piper plot generated from the major ion data recorded at the different sample locations.

4.2.5. Contaminants in the samples

As Figure 4.1 illustrates, the chemical composition of the waters is very inhomogeneous down the length of the drain. Generally, the concentrations in the samples collected on site, were higher than those detected in the background samples (samples 1 and 2). The concentrations of the different ions in the majority of samples are higher than the concentrations which have been found to be average in river water (Table 4.3) (it is assumed that the average water is still in its natural state and not contaminated by human activities). It is interesting to note that the concentrations in the background samples are also higher than the average concentrations detected in river water. This results from the fact that the background samples may themselves be contaminated because they run through areas where they are likely to have been impacted by anthropogenic activity. Therefore in determining whether a particular sample is contaminated by activities occurring on site, the concentration of a particular analyte will be compared to the concentrations in the background samples. A general trend that is evident is that the concentrations of the various analytes is higher at sample locations 3-17 than the concentrations detected in the background samples (samples 1 and 2).

Table 4.3. Average concentration of ions in river water (from Henderson, 1982)

Analyte	Concentration in the average river water (mg/ℓ)
Na^+	6.3
K^+	2.3
Ca^{2+}	15
Mg^{2+}	4.1
Cl^-	7.8
F^-	<1.0
NO_3^-	1.0
SO_4^{2-}	11.2

The sample collected from the Fertiliser area (sample 3) contained the highest concentrations of SO_4^{2-}, NO_3^-, F^-, Al, Mn, Zn and Ni. This sample also contained high concentrations of PO_4^{3-}, Ca^{2+}, Mg^{2+} and K^{2+}, relative to the concentrations in other samples (particularly compared to the background samples). The sample collected above Langvlei (sample 7) also contained high concentrations of SO_4^{2-}, PO_4^{3-}, NO_3^- and F^-. The chemical characteristics of samples 6 and 8 to 11 are similar in that they all contain similar concentrations of Cl^-, SO_4^{2-}, NO_3^-, F^-, Na^+, Ca^{2+} and Mg^{2+}. Besides the elements already mentioned, sample 6 contains Zn while samples 6 and 7 contain Ni. Relative to the other samples collected on site, samples 12 to 16 contain low concentrations of the various analytes, with sample 12 containing some of the lowest concentrations detected **on site**. Sample 16 contained an anomalous concentration of Fe, with the concentration of this element being higher than that detected at any of the other sample locations. Relative to the samples collected from the estuary (sample 14) and those collected from the wetland (samples 15 and 16), sample 17 contained high concentrations of PO_4^{3-}, F^-, Na^+, Ca^{2+} and Mg^{2+}. However, the concentrations of Cl^-, SO_4^{2-}, NO_3^- and K^+ in sample 17 were lower than those detected in samples 14 to 16.

The high concentrations of ions and elements in sample 3 are believed to be a result of effluent discharge from the fertiliser manufacturing operations that are still occurring on site. Furthermore, runoff from the phospho-gypsum dump in this area could be collected in the drain. The chemical composition of the waters is consistent with this hypothesis in that it is known that SO_4^{2-}, PO_4^{3-} and NO_3^- are often associated with fertiliser manufacturing operations. It is also known that F^-, PO_4^{3-}, SO_4^{2-} and Ca^{2+} are associated with phospho-gypsum, all analytes that were detected in relatively high concentration in the water collected from the drain draining this area.

The water in the drains from the Magazine area (sample 4) and from the Marshalling Yard (sample 5) appear to contain high concentrations of constituents. That is, both these samples had high concentrations of Cl^- and Fe, while sample 5 had high concentrations of Mg and Na.

The decrease in concentration of most analytes in sample 6 (the confluence of the three drains) is attributed to the mixing of waters that contain very different concentrations of the various analytes. As a result of the fact that the waters which are mixing at this point (those from the Fertiliser area, the Magazine drain and the Marshalling Yard drain) contain very different concentrations of the various analytes (with high concentrations of some analytes in some samples and low concentrations in other samples), it is expected that a dilution effect will occur.

The concentrations of SO_4^{2-}, PO_4^{3-}, NO_3^-, F^- detected in sample 7 may indicate that discharge of contaminants is occurring at or near this sample position. Discharge of contaminants could be occurring directly into the drain via the disposal of industrial effluent, or it may occur via the discharge of contaminated groundwater into the drain. The latter hypothesis is the most likely one to be occurring because it is known that the majority of industrial activity has ceased on site. Furthermore, extensive groundwater sampling on site has indicated that the groundwater is contaminated with a number of contaminants (see Appendix 3 for a select number of groundwater analyses). As has been mentioned the flow of groundwater is in a south-easterly direction. Therefore, it is likely that the Main Drain will be in the flow path of any groundwater that is moving through the site.

The general decrease in analyte concentrations at sample 8, relative to those detected in sample 7, could arise via a dilution effect and/or via processes that occur within the wetland. It is hypothesised that the most likely processes resulting in the decrease in concentrations are those that occur in the wetland. This hypothesis is based on the finding that there is a slight increase in pH of the water exiting Langvlei (sample 8) relative to that entering Langvlei (sample 7). As pH increases, precipitation of a number of hydroxides may occur (McBride, 1994). Associated with the precipitation of the hydroxides are co-precipitation and adsorption reactions between the hydroxides and a number of constituents in solution (Fietjel *et al.,* 1994). The effect of these reactions would thus be the removal of a number of constituents from solution.

The low solute concentrations detected in sample 12 may arise as a result of the fact that this sample was not collected within the drain, but was collected at the discharge point where wash water from the acid area is discharged into the drain. This water appears to be uncontaminated with the result that when it enters the Main Drain it will tend to dilute the constituents that are present. This appears to be the case because it can be seen that the concentrations detected in the samples collected below sample 12 are generally lower than those collected above this sample point.

The higher concentrations of constituents in the water samples collected from the wetland outlet (sample 17), relative to the concentrations that are present in the water sample collected from the inlet and from within the wetland (samples 15 and 16 respectively), may be a result of decomposition of organic matter within the wetland resulting in an increase in the concentration of a number of constituents. However, a more likely mechanism is evaporative concentration. This would occur within the wetland where the water would have a high retention time and thus, more time in which evaporation could occur, leading to an increase in the concentrations of constituents in the samples.

4.2.6. Hydrogeochemical modelling

In order to determine whether any minerals have the potential to precipitate from solution, saturation indices were calculated by making use of the geochemical model *MINTEQA2* (Allison *et al.*, 1985). In order to make the best utilisation of the modelling process, a number of assumptions had to be made. Firstly, it was assumed that the elements that were detected as being present in the samples, were present in the ionic form. This assumption was made based on the grounds that the samples had been filtered prior to analysis by ICP, with the result that solids (colloidal matter) had been removed. Furthermore, *STATISTICA* calculated that significant correlations ($p < 0.05$) exist between the concentrations of the ions Na^+, Ca^{2+} and Mg^{2+} and the "elements" Na, Ca and Mg in the different samples (Appendix 1, Figure A1.1). However, during the modelling exercise, the concentration of the ion K^+ was used (HPIC data) because it is suspected that the elemental concentrations of K^+ (detected by IPC-OES) may be spurious as a result of machine calibration conditions[1]. The second assumption that was made was that the ions were present in their most common oxidation state. If more than one common oxidation state exists, it was assumed that the ions were in the most oxidised state, *eg*. Fe^{3+} was used in the modelling process as opposed to Fe^{2+}. This assumption was made based on the fact that the water columns were exposed to the atmosphere and thus in equilibrium with atmospheric oxygen. Furthermore, the water samples were collected near the atmosphere-water interface and are, therefore, unlikely to be influenced by microbes consuming oxygen in the sediments. The anion concentrations used as input during the modelling process, were those determined by the HPIC analysis *viz*. Cl^-, SO_4^{2-} and NO_3^-; PO_4^{3-} by the Murphy Riley method; F^- using the ion selective electrode and HCO_3^- by HCl titrations using the automatic titration assembly.

The above assumptions were made because a larger suite of constituents was determined during the analysis of total elemental concentrations (ICP-OES) than in the ion determination (HPIC). Thus, if the elemental data was used as input to the model, a wider range of constituents could be modelled which would give a wider range of minerals that have the potential to precipitate from solution (*ie.* SI values would be calculated for a wider range of minerals). The results of the calculations are presented in Appendix A3, Table A3.3).

As a result of the fact that the concentrations of the elements Mn, Fe, Al, Zn and Ni were those determined by ICP-OES it is possible that even after filtration these elements may still exist in the colloidal form. The effect of this would be an overestimation of the concentration of these elements in solution. This overestimation of the concentration of elements in solution would then effect the model's calculations of saturation indices. Furthermore, because the elements were detected by ICP-OES, nothing is known about the oxidation state in which these elements exist in solution. Thus, the assumption above that the element exists in its most common oxidation state may be erroneous because it is possible that more that one oxidation state will be present in solution.

Due to the fact that there are a number of unknowns that cannot be controlled or corrected for the results of the SI will not be discussed in detail. The results do, however, indicate that there is very little uniformity as to which minerals have the potential to precipitate from solution. That is, at each sample location, different combinations of minerals are calculated to have a SI > 1, indicating that at the various sample locations, different minerals have the potential to precipitate from solution.

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[1] D.Handforth (pers. comm. 1997).

4.2.7. Water quality

In order to evaluate the environmental quality of the waters in the drainage system, the concentrations of the various analytes has to be related to a guideline. The guidelines that were used in this study are those that have been set by the South African Department of Water Affairs and Forestry (1996) as limits to the concentrations of a number of constituents in drinking water (Table 4.4). The other set of guidelines used are those for water quality for agriculture (Ayers and Westcot, 1985) (Table 4.4). These guidelines have been used because the owners of the site propose that in the future the site may be occupied by humans. Even though it is unlikely that humans will consume water directly from the drain, water may accidentally be ingested during recreational activity. The guidelines for agriculture have been used because the possibility exists that water from the drain may be used to irrigate parks, gardens and/or playing fields.

Table 4.4. Guidelines for the concentrations of a number of constituents in water for use in different sectors of the economy. Values that are in italics are the concentrations reported by Ayers and Westcot (1985) as the usual range in irrigation water.

	Target quality range for drinking water	Concentration at which there is severe restriction on use of water in agriculture
pH	6.0-9.0	8.4
EC (mS/m)	0-70	300
Ions (mg/ℓ)		
Na^+	0-100	> 210
Ca^{2+}	0-32	*0-1600*
Mg^{2+}	0-30	*0-240*
K^+	0-50	
NH_4^+		
Cl^-	0-100	> 360
SO_4^{2-}	0-200	*0-3860*
NO_3^-	0-6	> 30
PO_4^{3-}	0.3*	0-2
F^-	0-1	
Soluble elements (mg/ℓ)		
Fe	0-0.1	5.0
Al	0-0.15	5.0
Mn	0-0.05	0.2
Zn	0-3	2.0
Ni		0.2

* = standard set by the World Health organisation for the maximum **phosphorus** concentration in drinking water

4.2.7.1. pH

The pH of the majority of the samples falls within the range acceptable to both human consumption and irrigation purposes. The anomalous pH of sample 3 (3.9) may cause health problems if accidentally ingested. However, because the pH of this sample is increased when it mixes with water from other areas of the site, the low pH is unlikely to be of serious environmental concern.

4.2.7.2. Electrical conductivity

Electrical conductivity is a measure of the amount of salts that are present in a solution. Thus, a high conductivity indicates a high concentration of salts, whereas a low conductivity indicates a low concentration of salts. A relatively high concentration of salts may not impact on health because not all salts are harmful (even at relatively high concentrations). For example, if a high conductivity is determined for a particular solution, one has to look at the nature of the ions that are contributing to the high conductivity. That is, if the ions are Na^+ and Cl^-, there will be little impact on human health, while if the salt is magnesium sulphate, a laxative effect may occur.

The EC of the majority of the water samples is higher than the limit set by the Department of Water Affairs and Forestry (1996), which would indicate that if this water is ingested, human health may be detrimentally effected. On the other hand, the EC of the majority of the samples is below the limit at which the use of the water would be severely restricted for irrigation purposes. The EC is, however, above that at which there may be slight to moderate restrictions on the use for irrigation (70-300 ms/cm) (Ayers and Westcot, 1985). It is therefore, concluded that if the water is to be used for irrigation purposes, only salt tolerant species will survive the waters being applied.

4.2.7.3. Sodium, magnesium and potassium

Even though the a number of samples contain concentrations of Na that are above the limit that has been set by the Department of Water Affairs and Forestry (1996), human health is not affected by Na below concentrations of > 600-1000 mg/ℓ (Department of Water Affairs and Forestry, 1996). It is therefore, concluded that this ion will not affect human health.

The use of waters containing high concentrations of Na can have two potential impacts on agriculture. Firstly, toxicity symptoms may develop in vegetation (Ayers and Westcot, 1985). A number of samples contain concentrations of Na higher than the limit identified by Ayers and Westcot, (1985). However, if the irrigation water is extracted from a part of the drain in which a dilution effect is occurring (*ie.* where the Na concentration is below 210 mg/ℓ) it is unlikely that the high Na content in some samples will affect vegetation. The second consequence of high Na concentrations is a reduction in the soils infiltration capacity (Ayers and Westcot, 1985 and McBride, 1995). Infiltration capacity is reduced when sodium in irrigation water causes clay particles to become dispersed, thereby blocking soil pores so that water can not percolate through the soil profile. When soil pores are blocked as a result of Na causing the dispersion of clay, the soil is referred to as sodic (McBride, 1995). It must, however, be noted that sodic soils can develop when the irrigation water has a low concentration of Na in conjunction with even lower concentrations of the divalent cations Mg and Ca (*ie.* the water has a low EC) (McBride, 1995). In order to determine whether sodic soils are likely to develop, a ratio known as the Sodium Adsorption Ratio (SAR) is usually calculated (McBride, 1994). This ratio is the ratio of Na to Ca and Mg in solution. To determine whether a soil's infiltration capacity can potentially be reduced, SAR was plotted against EC (Figure 4.3) and then compared to ratios at which it is know that infiltration is reduced (Ayers and Westcot, 1985).

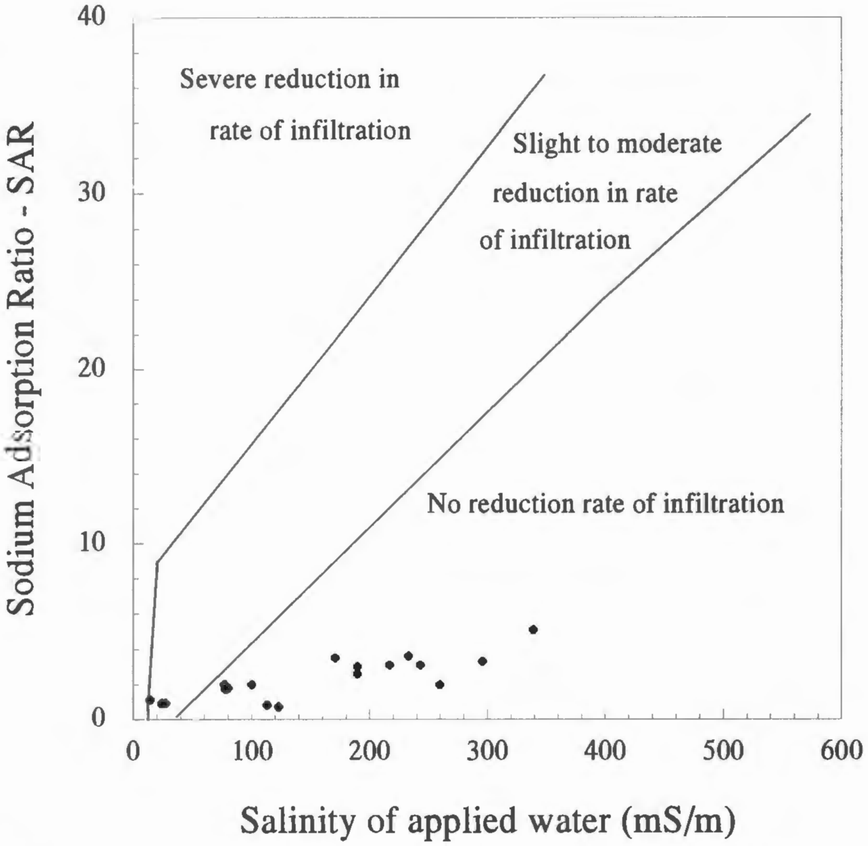


Figure 4.3. Relative rate of water infiltration as affected by salinity and sodium adsorption ratios (From Ayers and westcot, 1985).

Figure 4.3 illustrates that even though there are a small number of samples which have SAR values and EC values that would classify water as causing slight to moderate reduction in rate of infiltration, the majority of the water will not effect soil infiltration. Based on Na concentrations it is, therefore, concluded that the water from the Main Drain can be used to irrigate salt tolerant species, without soil structure being significantly altered.

As with Na, a number of samples contain concentrations of Mg that are above the limit set by the Department of Water Affairs and Forestry (1996). However, according to the Department of Water Affairs and Forestry (1996) if ingested, this ion is readily excreted from the body, with the result that it will not effect human health. The effect that Mg can potentially have on irrigation waters is that it may be present in such low concentrations that the water would have a relatively high SAR. However, as can be seen from Figure 4.3. it is unlikely that the SAR of the water will result in reduced infiltration. Furthermore, the concentration of Mg is below the concentration that is usual in irrigation water, which implies that Mg will not affect the quality of the irrigation water. It can therefore, be concluded that the concentration of Mg in the Main Drain is unlikely to cause significant environmental concern.

The concentration of K is below the limit at which human health is affected. Therefore, it is unlikely to cause significant environmental concern.

4.2.7.4. Calcium

Calcium is a desirable element to humans due to the fact that it may prevent cardiovascular disease as well as mitigating the toxic effects of certain heavy metals (Department of Water Affairs and Forestry 1996). Therefore, the limit that has been set by the Department of Water Affairs and Forestry (1996) is based on aesthetic effects rather than on human health effects. Calcium may, however, cause a problem known as scaling if it is present in water that is being piped (by metal pipe) from one location to another. Scaling occurs when the solution in the pipes is super-saturated with respect to $CaCO_3$ with the result that $CaCO_3$ precipitates from solution. If this occurs a "scale" accumulates in the pipes which, in extreme cases, can eventually lead to the pipes becoming blocked (Snoeyink and Jenkins, 1980). On the other hand, if the solution in the pipes is undersaturated with respect to $CaCO_3$ pipes can be corroded because there is no thin protecting layer of calcite precipitate (Snoeyink and Jenkins, 1980). In order to determine whether pipes can potentially become blocked by $CaCO_3$, or if they are likely to be corroded, an index known as the Langlier index can be calculated (Snoeyink and Jenkins, 1980). The Langlier index is essentially the same as the saturation index for calcite (Snoeyink and Jenkins, 1980). A positive Langlier index or a positive SI indicates that the waters are saturated with $CaCO_3$, while a negative Langlier or SI indicates that the water is undersaturated with $CaCO_3$. The SI for calcite was calculated by *MINTEQA2* for the various water samples collected in the Main Drain (Table 4.5).

Table 4.5. Saturation indices (SI) for calcite calculated for the various water samples collected from the Main Drain.

Sample number	SI for calcite
1	-4.5
2	-1.5
3	*
4	0.4
5	-0.3
6	-2.4
7	-3.1
8	-2.9
9	-3.3
10	-3.3
11	-2.7
12	-1.7
13	-1.7
14	-2.7
15	-2.6
16	-2.8
17	-1.5

* No HCO_3^- present in solution, therefore, it is not possible to calculate a SI for calcite for this sample.

The negative SI values indicate that the water from the Main Drain is potentially corrosive. This can be attributed to the low concentrations of HCO_3^- in solution as well as the lack of dominance by the Ca^{2+} ion. The problem of corrosivity can, however, be overcome by treating the water via the addition of $CaCO_3$ so that a slightly negative or zero SI is maintained (Snoeyink and Jenkins, 1985).

4.2.7.5. Chloride and sulphate

Even though the concentration of Cl, in a number of samples, exceeds the target quality range that has been set by the Department of Water Affairs and Forestry (1996), it is unlikely that human health will be affected because health effects normally occur at concentration > 600 mg/ℓ (Department of Water Affairs and Forestry, 1996). The high concentrations of Cl may, however, produce toxicity symptoms in plants (Ayers and Westcot, 1985). Therefore, if the water in the Main Drain is to be used as irrigation water, the water must be abstracted from parts of the drain where the concentration of Cl is below 360 mg/ℓ.

As with Cl, the concentration of SO_4^{2-} exceeds the target quality range that has been set by the Department of Water Affairs and Forestry (1996). However, the majority of samples contain concentrations below 600 mg/ℓ, which is the concentration at which SO_4^{2-} begins to effect human health. The concentration of SO_4^{2-} is below that usual in irrigation water, with the result that this compound will not affect irrigation water quality. Sulphate may, however, contribute to the relatively high EC values that were recorded, which makes some of the water in the Main Drain unsuitable for use as irrigation water.

4.2.7.6. Nitrate

As with the other ions mentioned, NO_3^-, can upset the osmotic balance of aquatic organisms if it is present in solution at high concentrations. A more serious effect of high NO_3^- concentrations in water is the development of eutrophic conditions. When NO_3^- is present in concentrations < 300 mg/ℓ there is usually an increase in the floral biomass in an aquatic system. When this vegetation has senesced and starts to decompose, the decomposition processes can deplete the oxygen concentrations of the water to levels at which aquatic fauna can no longer survive.

In the majority of samples the concentration of NO_3^- exceeds the limit of 0-6 mg/ℓ which is the target water quality range set by the Department of Water Affairs and Forestry (1996) for the concentration of NO_3^- in water. Furthermore, the concentration in a large proportion of the samples exceeds the concentration at which deleterious health affects may occur (6-10 mg/ℓ, Department of Water Affairs and Forestry, 1996).

The high concentrations of NO_3^- that were detected in a number of samples would also preclude the use of the water for irrigation. It is thus concluded that the concentrations of NO_3^- in the water samples may be such that it can cause significant environmental impact.

4.2.7.7. Phosphate

No standard has been set by the Department of Water Affairs and Forestry (1996), for the maximum allowable concentration of PO_4^{3-} in water. Therefore, the standard that has been used is that which has been set by the World Health Organisation (1993). As with NO_3^-, PO_4^{3-} can lead to the eutrophication of aquatic ecosystems. The range of **phosphorus** in the samples analysed in this study (0.75-186 mgP/ℓ) exceeds the limit at which health effects can occur (0.6-100 mg/ℓ). Furthermore, the concentrations exceeds the limit of 0.3 mg/ℓ set by the World Health Organisation (1993). Thus, it is concluded that the concentration of PO_4^{3-} in the samples could lead to the development of significant environmental problems.

4.2.7.8. Fluoride

The concentration of fluoride in the majority of water samples collected from the Main Drain exceeds the limit that has been set by the Department of Water Affairs and Forestry (1996). Furthermore, the concentration of F exceeds the level of 6 mg/ℓ which is the concentration that has been identified by the Department of Water Affairs and Forestry (1996) as being the concentration at which human health is effected. It is therefore, concluded that the concentration of F in the waters of the Main Drain will cause significant environmental concern.

4.2.7.9. Trace elements

The concentrations of the trace elements Fe, Al and Mn are above the target quality range that has been set by the Department of Water Affairs and Forestry (1996). However, the concentrations of Fe and Mn are below the concentrations at which human health will be affected (10 and 14 mg/ℓ, respectively, Department of Water Affairs and Forestry, 1996). The concentrations of these elements are also below the value at which their concentrations would render the water unsuitable for use in agriculture.

The concentration of Al is above the concentration at which neurotoxic diseases may develop (0.05 mg/□ Department of Water Affairs and Forestry, 1996). The concentration of Al is also above that at which water is no longer suitable for use as irrigation water. It is, therefore, concluded that Al present could effect human health as well as render the water from the Main Drain unsuitable for irrigation.

4.3. Conclusions

The distribution of constituents in the water of the drainage system is not homogenous. This could indicate that there are point sources of constituents entering the water. These could either be direct disposal of effluent into the water, or it could be more diffuse when groundwater containing the constituents discharges to the drain.

The sample collected on site contain high concentrations of Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, F^- Na^+, Ca^{2+}, Mg^{2+}, K^+, NH_4^+, Al, Fe, Mn, Zn and Ni relative to the concentrations that were detected in the background samples. This indicates that the waters in the drain may have been contaminated with these constituents at a number of locations down the length of the drainage system.

The concentrations of Al, NO_3^-, PO_4^{3-} and F^- are above the concentrations at which human health is adversely affected, should the water be ingested. Furthermore, the concentrations of NO_3^- and PO_4^{3-} are such that the could lead to eutrophic conditions developing in the waters of the Main Drain. It is therefore, concluded that every attempt should be made to prevent humans ingesting this water, whether ingestion occurs directly through the drinking of the water or indirectly as may occur during recreational activities.

The waters in the drain are unsuitable for use as irrigation water. This is partly as a result of the relatively high EC values and the relatively high concentrations of Na^+, Cl^- but more importantly the high concentrations of Al and NO_3^- are above those at which the use of the water in agriculture is severely restricted .

The high potential corrosivity of the waters, as indicated by the low saturation indices for calcite, would mean that if the water was to be piped in metal pipes, the potential exists that these pipes would become corroded. It is therefore, concluded that if the water is to be piped, it will have to be treated in order to raise the saturation index of calcite to a less negative or zero value.

CHAPTER 5.

GEOCHEMISTRY OF SEDIMENTS AND THE IMPACT OF THESE SEDIMENTS ON THE WETLAND, *WAGENVELDT VLEI*

5.1. Introduction

The chemical characteristics of sediments depend on a number of factors. These include pH, redox conditions, mineralogy, organic matter content and the chemical characteristics of the water with the which the sediments are in contact (both groundwater and surfacewater). The characteristics of the waters with which the sediments are in contact are important in the context of this study. This is because it is expected that effluent containing a number of different chemicals has been discharged to the drain, (Chapter 1) which could potentially impact on the chemical characteristics of the sediments. This is illustrated by Zullig, (1956 in Förstner 1995) who found that sediments reflect the biological, chemical and physical conditions in a water body.

The aim of this chapter is to determine the characteristics of the sediments, with particular reference to the nature of possible contaminants. Furthermore, the potential impact of the chemical characteristics of the sediments in the Main Drain on the wetland *Wagenveldt vlei* will be investigated.

5.2. Results and Discussion of Chemical Analyses

5.2.1. pH

Generally, whether sediments are acidic, neutral, or alkaline has an effect on the solubilities of various compounds, the bonding of ions to exchange sites as well as the activities of various microorganisms.

As can be seen from Table 5.1, the pH of the sediments varies widely, ranging from very acidic (particularly in the wetland {sample 16}) through neutral to alkaline. Down the length of the drainage system there is no consistent trend to the pH values. Furthermore, the pH of the top layer is neither consistently higher nor lower than that of the bottom layer. The latter finding is surprising because it is anticipated that under oxidising conditions (which may exist in the top layer) pH values would be slightly less than those found in the bottom layer (which is expected to be more reducing). This arises through release of protons during oxidation of sulphidic minerals (McBride, 1994).

However, because the cores were separated into top and bottom layers based on visual appearance, rather than on redox conditions, it cannot be said with any certainty whether conditions were oxidising or reducing in the various layers.

Table 5.1. pH (in water and calcium chloride) and extractable acidity measured in a 1:2.5 sediment to water solution. Included are the results of pH measured on the 1:1 sediment extract as well as the bicarbonate content of the extract.

	Bulk sample						1:1 Sediment extract			
	Top layer			Bottom layer			Top layer		Bottom layer	
	pH H_2O	pH $CaCl_2$	Extractable Acidity (mmol$_c$/ℓ)	pH H_2O	pH $CaCl_2$	Extractable Acidity (mmol$_c$/ℓ)	pH	Alkalinity mgHCO_3^-/ℓ	pH	Alkalinity mgHCO_3^-/ℓ
1	8.01	7.39	n.d.	8.55	7.59	n.d.	7.92	185	8.07	125
2	8.83	7.94	n.d.	8.00	7.86	n.d.	8.32	352	7.82	148
3	4.73	4.41	18.1	5.19	4.49	2.22	5.46	bdl	5.27	14.3
4	8.25	7.39	n.d.	8.36	7.60	n.d.	7.90	146	7.77	156
5	6.14	5.89	0.55	5.43	5.15	0.63	6.20	104	5.55	193
6	5.10	3.64	5.32	4.41	3.80	8.14	4.51	bdl	4.30	bdl
7	5.15	5.91	n.d.	6.01	5.84	n.d.	5.91	bdl	6.13	19.8
8	6.30	6.06	n.d.	5.96	5.66	1.3	6.23	22.7	6.85	13.9
9	7.81	7.14	n.d.	8.09	7.72	n.d.	7.58	15.9	8.02	81.4
10	7.14	7.07	n.d.	No bottom layer			7.17	168	No bottom layer	
11	7.02	7.01	n.d.	4.75	4.87	2.68	7.29	120	4.68	bdl
12	4.27	4.24	28.7	6.42	6.36	n.d.	3.17	bdl	6.62	99.2
13	7.43	7.24	n.d.	7.63	7.53	n.d.	7.70	114	7.85	81.7
14	8.00	7.45	n.d.	No bottom layer			7.91	100	No bottom layer	
15	5.49	2.97	3.05	4.49	4.36	10.6	4.00	bdl	4.61	bdl
16	3.49	2.41	14.3	No bottom layer			3.90	bdl	No bottom layer	
17	8.60	7.73	n.d.	7.78	7.20	n.d.	8.12	107	8.57	95.3

The pH(H_2O) values can be divided into three broad groups: those greater than 8 and, therefore, considered to be alkaline, those that range between 6 and 8 and considered to be neutral and those less than 5.5 and considered to be acidic. The sediments in which the pH values were relatively high are those from the background samples (samples 1 and 2), that from the Magazine Main Drain (sample 4) and that from the estuary discharge and the wetland outlet (samples 14 and 17, respectively). The acidic pH values (*ie.* pH < 5.5) were detected in the sediments of the Fertiliser area drain (sample 3), at the confluence of the drains from the Fertiliser area, the Marshalling Yard and the Magazine Yard (sample 6), above Langvlei (sample 7), above the plant waste water discharge (sample 12), at the inlet to *Wagenveldt Vlei* (sample 15) and the sample taken within *Wagenveldt Vlei* (sample 16). A sample in which the pH of the top layer falls in the neutral range while that of the bottom layer is in the acidic range is sample 11 (the difference in pH between the top layer and the bottom is ≈ 2.3 pH units). In samples 3, 7, 9 and 12 the pH of the bottom layer is higher than that of the top layer.

According to Thomas (1967), pH values > 4.5 are usually indicative of the presence of free acids that arise during the oxidation of sulphidic minerals. In the systems investigated in this study it is also possible that the low pH values are a result of spills of acids, either directly into the drain or onto the adjacent soils, as it is known that over the time in which operations have been occurring on site, acids have been spilled (Chapter 1). If the spill is onto the adjacent soil the possibility exists that the contaminants could migrate into the drain in groundwater. Furthermore, Thomas' (1967) discussion focuses more on unsaturated systems where it is expected that conditions are more oxidising than those that exist in the sediments. Thus, under the more reducing conditions of the sediments, it is unlikely that there would be extensive oxidation of pyritic minerals leading to the formation of free acids.

At the other end of the pH scale, *ie.* the alkaline range where pH > 8, Thomas (1967) hypothesises that high pH values are indicative of the presence of $CaCO_3$. This is a trend that was detected in samples from both the top and bottom layers of the sediments. That is, no $CaCO_3$ was detected in the samples from either the top or the bottom layer where the pH was less than ≈ 7 (Figure 5.1.).

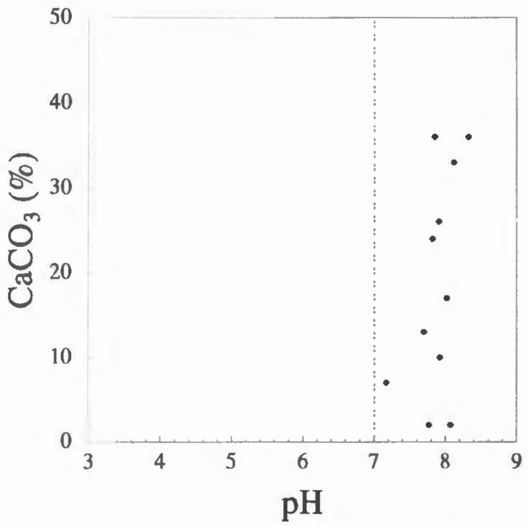


Figure 5.1. Relationship between the calcium carbonate content of the sediments and pH of the 1:2.5 sediment solution extract. Dashed line marks pH below which no $CaCO_3$ was detected.

The pH of the samples from the wetland inlet and that collected from within the wetland (samples 15 and 16 respectively) is generally lower than that detected at other sample positions along the length of the drain (with the exception of samples 3 and 12). On the other hand, the pH of the sample collected at the discharge point of the wetland (sample 17) is approximately 4 pH units higher than that of the samples collected at the inlet and within the wetland, indicating that there has been a marked decrease in proton activity in the sediments at sample position 17. It is expected that cation exchange capacity of the sediments could account for a proportion of the H^+ that is removed. More importantly, it is predicted that a large proportion of protons is removed during the dissolution of metal oxides, particularly those of iron. This hypothesis is supported by the finding that there were high concentrations of metals (especially Fe) in the sediment solution in the wetland. Because sample 17 was collected close to the coastline, it is also possible that pH may be increased by neutralisation reactions with shell fragments containing $CaCO_3$.

The pH detected using $CaCl_2$ was consistently lower than that detected using H_2O in all samples except in the top layer of sample 7 and the bottom layer of sample 11. The pH decrease using $CaCl_2$ occurs because H^+ ions are displaced by cations in the electrolyte-rich replacing solution. Besides protons being displaced, Al ions are also exchanged, which upon hydrolysis, increases the concentration of H^+ in solution (McLean, 1982). From the difference in pH determined in water and that determined in $CaCl_2$, it is possible to get an indication of the cation exchange capacity (CEC) of the sediments, which is a function of clay mineralogy (see section 5.2.6) and organic matter content. From these results it is concluded that the sediments of the wetlands have a higher CEC than the samples collected at other positions in the drainage system.

5.2.2. Alkalinity

As with pH, the concentration of bicarbonate ions in the top layer was not consistently higher or lower than that in the bottom layer, nor was there any consistent increase or decrease in bicarbonate concentration down the length of the drain (Table 5.1). This occurs because the concentration of HCO_3^-, in solution, is effected by pH (Drever, 1988), which varies in the sediments.

The bicarbonate content of the samples collected from both the top and bottom layers at the wetland inlet, and within the wetland (samples 15T and B and sample 16) were low relative to the concentrations that were detected at other positions throughout the drain. This implies that the input of acidic constituents to the wetland has been relatively high, resulting in the conversion of HCO_3^- to H_2CO_3 or dissolved CO_2.

5.2.3. Extractable acidity

Extractable acidity was only measured on samples that had a pH < 5.5. This acidity can therefore be attributed to exchangeable H^+ and hydrolysis of exchangeable Al (Thomas, 1982). At sample positions where this variable was detected in both layers, extractable acidity was not consistently higher nor consistently lower than that found in the bottom layer (Table 5.1). Therefore, no generalisation can be made as to which layer contains greater extractable acidity. However, there appears to be an association between the concentration of Al present in solution and the amount of extractable acidity that was detected, with samples containing high concentrations of soluble Al (Table 5.2) containing high extractable acidities. This is in accord with Thomas' (1982) statement that at the pH values that were detected in these sediments, the hydrolysis of Al would be the most important contributor to extractable acidity.

5.2.4. Ions in sediment extracts

5.2.4.1. Electrical conductivity.

The concentration of salt in the sediment varies widely. This is reflected in the very different EC values (Table 5.2). Except for sample locations 2, 6 and 17, the EC in the top layer was higher than that in the bottom layer. In the samples in which the EC of the bottom layer was higher than that of the top layer, the percent difference between the two layers was ≈ 100 % or even greater (*eg.* 300 % for sample 2). This may indicate that there have been some unusual sources of contamination such as soluble solids that may have been dumped at these locations (particularly at samples 2 and 6). This hypothesis is made because it is expected that if contaminants were entering the sediments in the form of effluents that were discharged directly to the drain, they would first come into contact with the top layer where exchange or sorption processes would result in their being incorporated into the sediments which would result in high EC values being recorded in the top layer. It is possible, however, that the high EC values (of sample 2) could be a result of marine influence. This statement is based on the result that the dominant ions in the 1:1 sediment extracts are those commonly found in seawater *ie.* Cl^-, SO_4^{2-}, Na^+, Ca^{2+} and Mg^+ (Drever, 1988). Even though the ratio of sodium to chloride (0.8) is greater than the ratio of Na to Cl in sea water (0.56 {Drever, 1988}), there could be a contribution of sodium from the weathering of the Malmesbury shales of the area. Furthermore, high EC values of sample 6 could have arisen as a result of there having been the deposition of salt rich sediments in this area, which have then been covered by relatively uncontaminated sediments.

Table 5.2a. Chemical parameters of the 1:1 sediment to solution extracts that were prepared from the sediments collected from the top layer. Insufficient extract was obtained from sample T7 and T15 to run trace element analysis by ICP-OES.

	1T	2T	3T	4T	5T	6T	7T	8T	9T	10T	11T	12T	13T	14T	15T	16T	17T
EC (mS/m)	58.4	189	229	158	716	264	234	248	112	325	274	396	288	78.8	131	354	46.4
Anions (mg/ℓ)																	
F^-	0.25	bdl	34	0.08	9.9	15	2.8	14	1.3	0.50	0.17	45	0.76	0.85	1.8	11	1.9
Cl^-	38	420	380	300	1800	530	530	390	160	220	140	210	140	110	100	180	51
NO_3^-	bdl	bdl	12	14	bdl	34	60	bdl	68	bdl	bdl	bdl	42	20	59	28	3.8
PO_4^{3-}	bdl	bdl	340	71	3.8	0.8	44	140	43	bdl	69	bdl	31	54	400	3.8	7.1
SO_4^{2-}	120	110	480	150	860	330	180	720	270	1800	1700	2500	1500	93	460	2100	62
Cations (mg/ℓ)																	
NH_4^+	bdl	bdl	20	bdl	bdl	41	20	23	29	12	7.9	26	bdl	bdl	12	140	bdl
Na^+	44	280	190	230	820	250	220	240	140	180	99	130	140	75	82	160	40
Ca^{2+}	51	59	170	73	300	200	120	200	72	590	590	430	480	63	210	430	48
Mg^{2+}	11	42	68	28	480	110	81	120	21	95	47	84	56	20	60	100	11
K^+	10	18	59	14	100	57	49	60	27	31	15	56	20	14	21	26	7.8
Elements (mg/ℓ)																	
Zn	bdl	bdl	0.48	bdl	0.23	0.82		0.10	bdl	bdl	bdl	36	bdl	bdl		2.9	bdl
Ni	bdl	bdl	bdl	bdl	bdl	bdl		bdl	bdl	bdl	bdl	bdl	bdl	bdl		0.35	bdl
Si	2.6	1.0	12	2.9	5.5	12		13	15	3.4	7.4	9.7	4.8	2.2		7.7	0.75
Mn	bdl	bdl	0.80	bdl	1.8	1.7		0.39	bdl	0.30	0.06	4.9	1.4	bdl		1.4	bdl
Fe	bdl	bdl	8.9	bdl	bdl	10		0.50	0.37	bdl	bdl	290	bdl	bdl		220	bdl
Al	bdl	bdl	12	bdl	7.1	20		3.0	0.74	bdl	bdl	150	bdl	bdl		24	bdl
Pb	bdl	bdl	bdl	bdl	bdl	bdl		bdl	bdl	bdl	bdl	4.3	bdl	bdl		bdl	bdl
Co	bdl	bdl	bdl	bdl	bdl	bdl		bdl	bdl	bdl	bdl	0.30	bdl	bdl		bdl	bdl
Cu	bdl	bdl	bdl	bdl	bdl	bdl		bdl	bdl	bdl	bdl	4.2	bdl	bdl		bdl	bdl

* bdl indicates that analyte concentration is below detection limits

Table 5.2b. Chemical parameters of the 1:1 sediment to solution extracts that were prepared from the sediments collected from the bottom. No samples B10, B14 or B16 were collected, hence the lack of results in the table.

	1B	2B	3B	4B	5B	6B	7B	8B	9B	11B	12B	13B	15B	17B
EC (mS/m)	34	760	200	88	480	560	81	190	110	280	170	280	120	84
Anions (mg/ℓ)														
F^-	0.36	0.13	2.2	0.68	2.7	2.0	0.98	6.5	0.64	0.70	0.24	0.99	1.5	0.97
Cl^-	23	1600	330	170	1800	1200	140	190	43	180	48	150	170	67
NO_3^-	bdl	bdl	15	11	bdl	bdl	29	bdl	260	14	4.6	27	2.6	4.6
PO_4^{3-}	10	bdl	180	36	210	670	360	550	71	100	10	88	88	5.4
SO_4^{2-}	23	1500	420	53	860	1300	85	670	230	1700	800	1600	380	150
Cations (mg/ℓ)														
NH_4^+	bdl	bdl	5.9	bdl	30	bdl	52	bdl	17	35	4.4	bdl	19	bdl
Na^+	29	1300	200	130	760	530	850	130	66	96	31	170	120	68
Ca^{2+}	34	290	130	42	300	530	440	160	420	560	310	540	96	86
Mg^{2+}	9.2	320	79	13	480	200	200	86	23	54	30	52	26	15
K^+	9.6	70	72	12	75	95	290	56	23	21	10	14	25	25
Elements (mg/ℓ)														
Zn	bdl	bdl	bdl	bdl	0.60	0.51	bdl	0.17	bdl	4.39	0.50	bdl	0.47	bdl
Ni	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.38	110	bdl	bdl	bdl
Si	3.4	2.3	39	8.8	9.4	8.6	38	16	2.6	7.9	6.7	7.1	7.2	1.4
Mn	bdl	bdl	0.07	bdl	1.6	0.45	0.04	0.33	bdl	1.88	18	bdl	0.23	bdl
Fe	0.22	bdl	0.33	2.0	bdl	0.24	0.15	bdl	bdl	12	bdl	bdl	0.38	0.03
Al	bdl	bdl	4.0	4.7	6.9	5.4	1.2	12	bdl	3.7	bdl	bdl	5.9	bdl
Pb	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2.8	bdl	bdl	bdl	bdl
Co	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.13	0.15	bdl	bdl	bdl
Cu	1.6	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl

*bdl indicates that analyte concentration is below detection limits

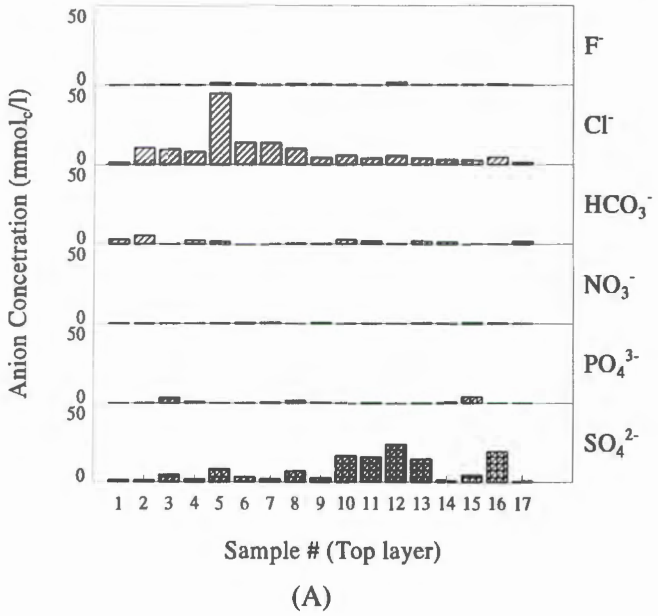
As a result of the anomalously high EC of sample 2 (one of the background samples), relative to other samples, it is not possible to state with conviction that the sediments within the drainage system have been contaminated, by salts, during industrial operations. However, if a comparison is made between the sample collected at sample location 1 (also a background sample) and the samples collected within the drainage system, it can be seen that the EC values of the sediment extract prepared from samples collected within the drainage system (sample 3-17) are higher than that of the sample 1. Furthermore, the EC values detected in the top layer of both background samples are generally lower than those detected in the samples collected on site. This would tend to indicate that at least in the top layers of the sediments there has been the incorporation of salts that entered the system during industrial activity.

5.2.4.2. Anions

Generally, the dominant anions in the sediment extracts are Cl^- and SO_4^{2-} (Figure 5.2.). However, neither of these anions was dominant in the extract obtained from all the samples. That is, in the top layer Cl^- was dominant in samples 2 to 9 and 14 with SO_4^{2-} being dominant in samples 10 to 13 and 15 and 16. Bicarbonate is the dominant anion in samples 1 and 17. In the bottom layer Cl^- was the dominant anion in samples 2 to 7 and sample 15, with SO_4^{2-} being dominant in samples 11 to 13 (bearing in mind that there were no samples 10B, 14B and 16B). The dominant anion in sample 9B was NO_3^-.

Besides sulphate and chloride, other ions that were present in the majority of samples are phosphate, nitrate (both in relatively large concentrations) and to a lesser extent fluoride (Table 5.2 and Figure 5.2.). The anions SO_4^{2-} and Cl^- are the ones commonly found in seawater. However, because the ratio of sodium to chloride in the extracts is very different to that detected in seawater, it is hypothesised that marine deposition does not account for a large proportion of the ions that are found in solution. Furthermore, the ions NO_3^-, PO_4^{3-} and F^- are not normally present in high concentrations in seawater, nor are these ions normally present, in sediment solutions, in the concentrations that were detected in the 1:1 sediment solutions prepared from the sediments of the Main Drain. This is illustrated by Knesl (1995) who found that the concentration of PO_4^{3-} in the sediments of Barbers Pan (a pan that he considered to be contaminated by P) was 0.9mg/ℓ which is up to two orders of magnitude less than that found in the sediments of the Main Drain. Furthermore, the concentration of NO_3^- detected in the sediments of Verlorenvlei ranged between 0.25 and 0.36 mg/ℓ (Harck, 1995) which is also up to 2 orders of magnitude less than those detected in the sediments of the Main Drain. This leads to the hypothesis that there has been the incorporation of ions into the sediments during industrial activity that has occurred on site.

It is interesting to note that the only samples in which HCO_3^- is the dominant ion are the samples collected from the wetland outlet and that collected from the Lourens river. It is surmised that these samples are relatively uninfluenced by acid contamination that would have resulted in the conversion of HCO_3^- to CO_2 as the pH of the sediments decreased. The HCO_3 content of the 1:1 sediment:solution extracts would allow the sediments to tolerate inputs of acidity without the pH of the solution changing to a large extent, *ie.* these samples are relatively well buffered.



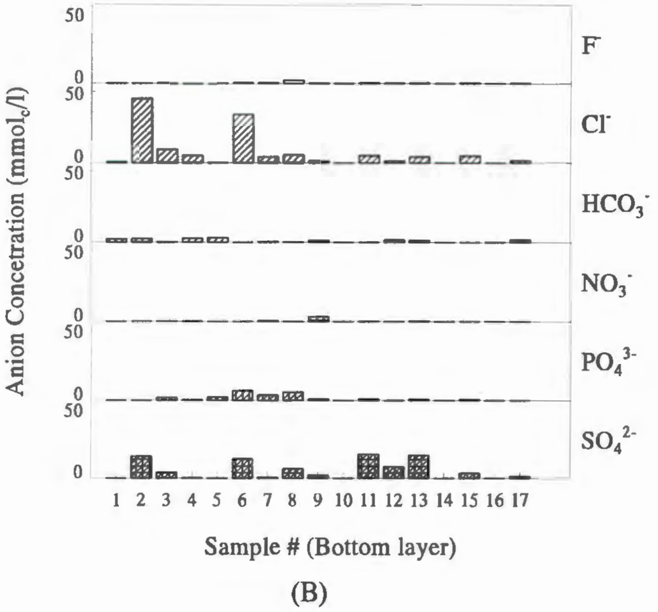


Figure 5.2. Relative dominance of anions detected in the 1:1 sediment solution prepared from the sediments collected from the Main Drain. (A) Dominance in the top layer, (B) Dominance in the bottom layer.

5.2.4.2.1. Chloride

The concentration of Cl^- was neither consistently higher nor lower than that in the bottom layer at the different sample positions. The Cl^- concentrations are, however, generally higher in the sample 3-17 than in the background samples (samples 1 and 2). It is hypothesised that the concentration of Cl^- would be higher in the top layer than that in the bottom layer, merely as a result of the fact that the top layer is closer to the source of Cl^-, assuming that the anion is diffusing from the overlying waters into the sediment solution. Therefore, it is expected that Cl^- would enter solution in the top layer, before it would enter solution in the bottom layer. The lack of this trend (Figure 5.2) could be attributed to the fact that over the time in which operations were occurring on site there may have been periods when the sediments were unsaturated (*eg.* during times of drought). The implication of this is that there would have been the evaporative concentration of Cl^- (it is known that Cl^- is a conservative ion (Drever, 1988)) in the sediments. When conditions change and the sediments are re-saturated the possibility exists that fresh sediments could be deposited which may cover those in which Cl^- had become concentrated resulting in high concentrations of Cl^- in the bottom layer. However, evaporative concentration would be season-dependent, only occurring during the dry season (summer). The concentration of Cl^- in sample 5T is higher than that found at other locations throughout the site. It is hypothesised that the source of this ion is from the Dead Tree area located slightly north-east of where this sample was collected. This is an area that is not well drained with the result that there is likely to be a build up of Cl^- ions by evaporative concentration during the dry months. Chloride can then leach from this area into the Marshalling Yard drain, thereby resulting in an increase in Cl^- concentration in the sediments of this drain.

5.2.4.2.2. Sulphate

As a result of the expectation that SO_4^{2-} would be converted to H_2S under reducing conditions (McBride, 1994), it is expected that the concentration of sulphate would be lower in the bottom layer relative to that of the top layer (assuming that conditions are more reducing in the bottom layer relative to those in the top layer). Generally, this was the case, however in samples 2, 6 and 17 the concentration of SO_4^{2-} was higher in the bottom layer relative to that in the top layer (Table 5.2 and Figure 5.2.). Another general trend that was evident was that the concentrations in the background samples were higher than those in samples collected on site.

It has been found by D'Angelo and Reddy (1994a) that the concentrations of soluble SO_4^{2-} in lake sediments receiving hypereutrophic water ranged from 0-11 mg/ℓ. The concentration of soluble sulphate in the sediments in the Main Drain ranged from 5-2500 mg/ℓ, which is three orders of magnitude higher than that detected by D'Angelo and Reddy (1994a). The high concentrations of sulphate in both layers of samples 10, 11, 12 and 13 as well as the dominance of the SO_4^{2-} anion in these samples, would indicate that in this area of the drainage system there have been processes occurring that have resulted in SO_4^{2-} being concentrated in the sediments. The likely cause of this is discharge from the cast sulphur belt which is located midway between samples 10 and 11. The cast sulphur belt is used for washing sulphur during the manufacturing of sulphuric acid. Thus, it is expected that there would be high concentrations of sulphur in the waste water. The sulphur in the waste water would then be oxidised to SO_4^{2-}. Even though sample 10 was taken upstream of the belt, the sample was only collected approximately 1.5 m upstream of the discharge point. Therefore, it is possible that during periods of low flow, discharge water could mix with the water in the drain with the result that there may have been relatively high concentrations of sulphur in the water that came into contact with the sediments at sample 10.

The high concentration of sulphate within the wetland, relative to that of the wetland inlet and outlet, would indicate that there is some mechanism responsible for the build up of sulphate in solution. It is hypothesised that this may occur as a result of the fact that within the wetland there is likely to be a reduction in water velocity (Phillips, 1989). The implication of this is that there will be a longer retention time within the wetland, which may allow for the evaporative concentration of SO_4^{2-}.

5.2.4.2.3. Phosphate

It has been found that the sediments of a lake receiving hypereutrophic water may contain soluble P concentrations between 0-31 mg/ℓ (D'Angelo and Reddy, 1994a). Moore and Reddy (1994) found that the concentrations of water soluble P from lake Okeechobee ranged between 0.1 and 1.1 mg/ℓ. The concentrations of soluble P in the sediments collected in the Main Drain were in some cases two to three orders of magnitude higher than those found by D'Angelo and Reddy (1994a) and Moore and Reddy (1994), ranging up to 670 mg/ℓ. Furthermore, the concentration of PO_4^{3-} in the background samples (samples 1 and 2) was generally lower than that detected in the other samples.

The concentration of phosphate was generally higher in the bottom layer relative to that detected in the top layer (Table 5.2 and Figure 5.2.). This finding does not, however, apply to samples 3 and 4, and samples 15 and 17 (bearing in mind that there were no samples 10B, 14B and 16B). It is hypothesised that the high concentration of PO_4^{3-} in the bottom layer arises as a result of the fact that as conditions become more reducing (an occurrence likely to occur in the bottom layer) there is a reduction of Mn oxides followed by a reduction of Fe oxides (McBride, 1994), with a concurrent release of soluble phosphate that was sorbed to these oxides (Reddy and D'Angelo, 1994). Furthermore, because the bottom layer contains relatively high concentrations of SO_4^{2-}, it is hypothesised that the manganese and iron that have been mobilised may form sulphides which are known to inhibit the sorption of P (Caraco *et al.,* 1991).

The area of the site in which there are high concentrations of phosphate is between samples 6 to 8. The likely source of PO_4^{3-} in sample 6 is from PO_4^{2-} deposition from the Kynoch/Triomf Main Drain (sample 3). This is an area of the site that was involved in the manufacturing of superphosphate and double superphosphate (Chapter 1) It is, therefore, likely that there would have been spills of phosphate in this area. The relatively high concentrations of phosphate in sample 7 is surprising, because in this area no manufacturing activity occurred. Therefore, it is hypothesised that PO_4^{3-} is present due to the deposition of this nutrient from the waters and sediments of the Kynoch/Triomf drain or it could be present in groundwater that is discharging at or near this sample. Sample 8, which was collected below the wetland, contains a higher concentration of PO_4^{3-} than in sample 7. This could indicate that at this position activities are occurring that are resulting in PO_4^{3-} concentrating in the sediments or it could indicate that processes within the wetland are mobilising PO_4^{3-} which is then concentrated in the sediments of sample 8.

Saturation indices for the various samples were calculated using the geochemical model *MINTEQA2* (Allison *et al.*, 1991). This program predicted that a number of samples are supersaturated with respect to a number of phosphorus containing minerals (Table 5.3).

Table 5.3a. Saturation indices (SI) calculated by *MINTEQA2* for the 1:1 sediment solution extracts obtained from the top layer. *MINTEQA2* calculated that there would be no minerals in samples 1, 2, 15 and 16 that have saturations indices > 1. Minerals for which SI < 1 at a specific sample location have not been included in the table.

	3T	4T	5T	6T	7T	8T	11T	12T	13T	14T	17T
$Pb_3(PO_4)_2$		4.5						5.1	6.7		2.6
$PbHPO_4$						1.2					
$MnPO_4$	12.4	18.2	15.5	4.5		20		19.6		18.2	14.6
Hydroxyapatite		12.2	1.6		2.1	6.6	12.9		13.6	12.8	10.4
Carbonate-fluorapatite		25.8	10.4			20.9	28		30.5		24.9

Table 5.3b. Saturation indices calculated using *MINTEQA2* for the 1:1 sediment solution extracts obtained from the bottom layer. In sample 2, no minerals had saturation indices > 1. Minerals for which SI < 1 at a specific sample location have not been included in the table.

	1B	3B	4B	5B	6B	7B	8B	9B	11B	12B	13B	15B	17B
$Pb_3(PO_4)_2$	5	2.2	4.1	1.3		6.3	8.3	5.1	1.1	4.6	5.7		1.9
$PbHPO_4$						1.8	2.1						
$MnHPO_4$						3.1							
$MnPO_4$	17.9	15.8	17.6	15	11.7	21.6		18.4	14	18.5	20.7	11.9	13.6
Vivianite			4.8										
Hydroxyapatite	12.5		10.2			3.7	11.7	14.3		7.9	15.7		12.9
Carbonate-fluorapatite	26	3	23.8	5.5		14.2	26.4	30.4		20.2	33.9		28.7

Because a number of these minerals contain either Fe, Mn or Pb (all elements present in relatively low concentrations), it is unlikely that significant amounts of these minerals would precipitate because of the limiting influence of Fe, Mn and Pb. However, the concentration of Ca in the majority of samples is relatively high (Table 5.2). Therefore, precipitation of Ca minerals could remove PO_4^{3-} from solution *viz* hydroxyapatite and carbonate-fluorapatite. This is a finding that has been reported by numerous authors (Syers *et al.,* 1973; Khalid *et al.,* 1977; Berkheiser *et al.,* 1980; White, 1981; Bostrom *et al.,* 1982; Logan, 1982; Sonzogni *et al.,* 1982 and Froelich, 1988) cited by Reddy and D'Angelo (1994).

Another factor that may be controlling the mobility of P in the sediments is the high concentration of phosphate in the sediment solution relative to that which is found in the overlying water column. The implication of this is that there would be a net diffusion of P from the sediment solution into the water column, thereby affecting the retention of P by the sediments. This is a finding that has been reported by Reddy and D'Angelo (1994), who state that retention of phosphorus in sediments is limited by diffusion. Thus, if the gradient in phosphorus concentration is from the sediments to the water column (*ie.* high concentration in the sediments relative to the water column), P will diffuse from the sediments into the water column, rather than being retained in the sediments. This finding may also account for the lower concentration of P in the top layer relative to that in the bottom layer. That is, phosphate in the top layer may be diffusing from this layer into the water column, with a resultant loss from the top layer. This finding must, however, be treated with caution because the concentration of PO_4^{3-} may be higher in the 1:1 extracts solutions than an interstitial solution that is likely to exist in the sediments. Concentration has occurred because of the way in which the sediment solution had to be prepared (using a 1:1 sediment to water ration, rather than a saturated paste extract where the sediment to solution ratio is > 1) as a result of the limited amount of sediment sample that was present.

In *Wagenveldt Vlei*, the sediments at the inlet contain high concentrations of phosphate relative to that which is detected within the system and that detected in the sediments at the outlet of the wetland (samples 16 and 17). This indicates that there is some mechanism responsible for the removal of soluble phosphorus in the wetland. It has been found by Murdock and Capobianco (1979) that vegetation of a wetland is capable of removing P from solution. It is possible that this process is occurring in *Wagenveldt vlei*. This transfer is, however, not permanent because once the vegetation dies, decomposition processes can result in the release of P back into solution (Rogers *et al.*, 1985). It is interesting to note that *MINTEQA2* calculations showed that the SI of the various phosphate containing minerals, in the wetland, is less than 1, indicating that mineral precipitation is not controlling the solubility of phosphate.

5.2.4.2.4. Nitrate

Generally, the concentration of nitrate is highest in the top layer relative to that which is found in the bottom layer (in all samples in which NO_3^- was detected, except sample 9) and the concentration in the background samples was generally lower than that in the other samples (Table 5.2 and Figure 5.2.). As with the ions already mentioned, there is a lack of uniformity in the distribution of NO_3^- down the length of the drain. In the top layer, the concentration of NO_3^- is highest at the wetland inlet (59 mg/ℓ in sample 15). It drops dramatically to 28 mg/ℓ in the extract from the sediment within the wetland (sample 16) and is lowest in the extract at the wetland outlet (3.8 mg/ℓ in sample 17). This trend is consistent with the well known tendency for nitrate disappearance in wetlands as a result of denitrification and, to some extent, uptake by vegetation (D'Angelo and Reddy, 1994 a and b).

The highest concentration of NO_3^- was detected in the sample collected below the laundry (sample 9). This indicates that discharge of nitrate rich waters from the laundry has occurred over the time in which this facility has been active. In the other samples in which NO_3^- was detected, its concentration was higher than the concentration of NO_3^- in the sediments of lake water receiving hypereutrophic water (where no NO_3^- was detected D'Angelo and Reddy, 1994a).

5.2.4.2.5. Fluoride

Generally, higher concentrations of soluble fluoride were detected in the upper layer relative to that in the bottom layer (Table 5.2 and Figure 5.2). Furthermore, higher concentrations were detected in samples 3-17 than were detected in the background samples. This can be attributed to fluoride coming into contact with these sediments as it diffuses from the overlying water column into the sediments. As with Cl^-, F^- is not involved in any redox reactions resulting in the conversion of one oxidation state to another. Therefore, F^- will not be affected by redox potential.

As was mentioned in Chapter 4, it was speculated that the major source of F^- on site would be the phospho-gypsum dump located in the Fertiliser area. This speculation is supported by the evidence that there is a high concentration of F^- in the sediments of the drain traversing this area (sample 3), while only low concentrations of F^- were detected in the background samples (samples 1 and 2). The high concentration of F^- in sample 6 can be attributed to the accumulation of F^--rich sediments coming from the fertiliser area.

5.2.4.3. Cations

5.2.4.3.1. Sodium, calcium, magnesium and potassium

The concentrations of these cations in the 1:1 sediment to solution extract are expected to be affected by ion exchange reactions as well as mineral precipitation and dissolution reactions. As has been mentioned, precipitation and dissolution reactions are affected by redox potential and pH of the sedimentary environment. Generally, at low pH the solubility of minerals is increased (McBride, 1994), which could result in an increase in the concentration of these cations in the sediment solution. The cations can then be involved in ion exchange or precipitation reactions which may remove them from solution.

The concentrations of the above cations were not consistently higher or lower in either the top or the bottom layers of the samples. However, a general trend that is evident is that the concentrations of the various cations are lower in the background samples than they are in the other samples (Table 5.2 and Figure 5.3). Furthermore, there was a lack of uniformity in the distribution of these cations down the length of the drain. In the top layer the concentrations ranged from approximately 44-820 mg/ℓ for Na^+, 50-595 mg/ℓ for Ca^{2+}, 11-480 mg/ℓ for Mg^{2+} and 10-60 mg/ℓ for K^+, while in the bottom layer the concentrations ranged from approximately 30-1300 mg/ℓ for Na^+, 35-550 mg/ℓ for Ca^{2+}, 10-200 mg/ℓ for Mg^{2+} and 10-300 mg/ℓ for K^+ (Table 5.2 and Figure 5.3). This variation could merely be a result of variations in the concentrations of these elements in the sediments which have arisen as a result of differential rates of weathering and diagenesis that may have occurred at the different sample locations. The variation could also indicate that there have been inputs of different constituents (containing these cations) at the different sample locations. These inputs may be direct, such as would occur during the discharge of effluent or dumping of wastes to the drain or discharge of contaminated groundwater. The elevated concentrations could also arise indirectly after contaminants that reduce pH or redox potential have entered the drain, leading to an increase in the mobility of the cations. The different concentrations may have arisen as a result of there being different rates of evaporation at the different sample locations. This may have lead to the build-up of cations, at the different sample locations, via evaporative concentration.

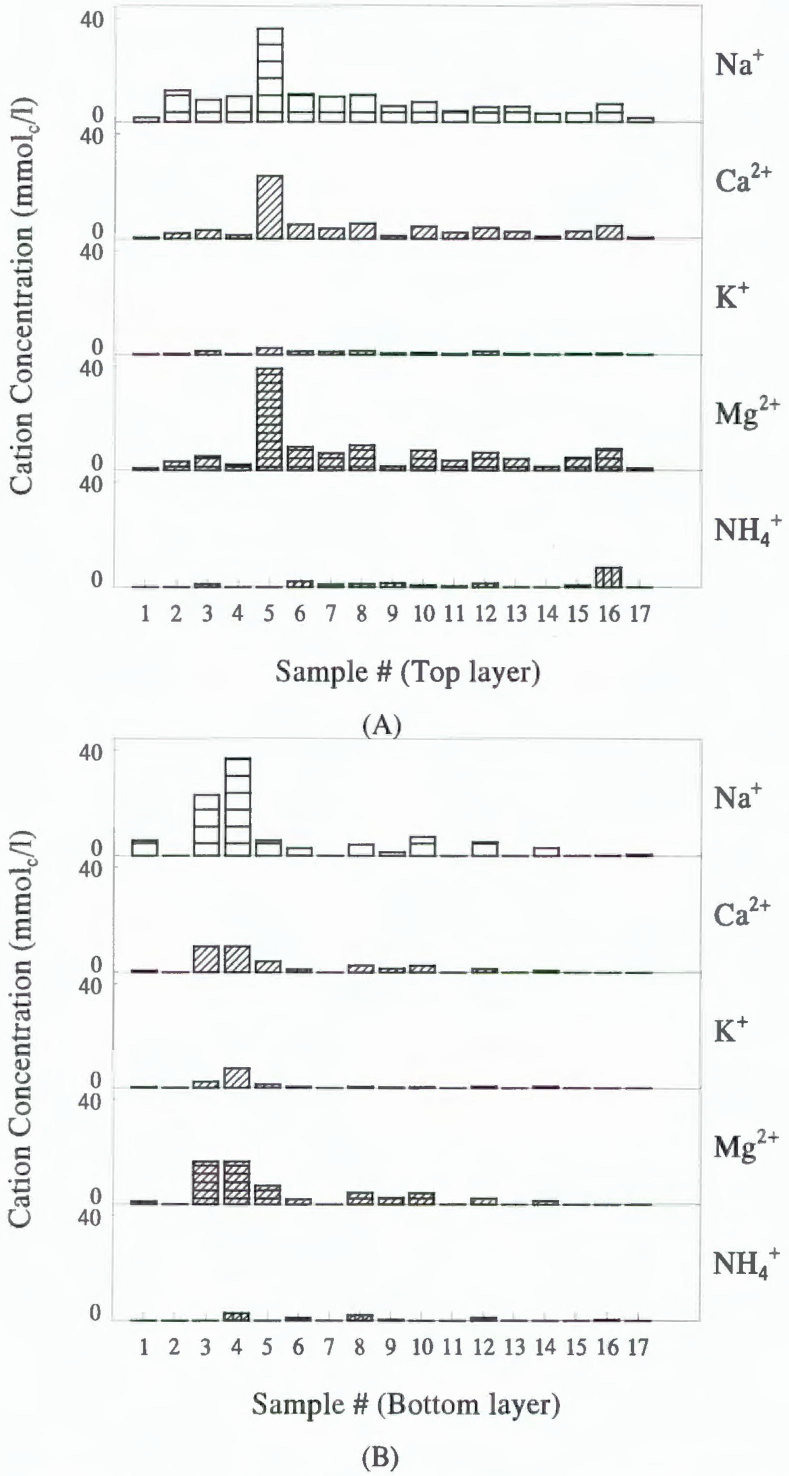


Figure 5.3 Dominance of the cations in the 1:1 sediment to solution extracts prepared from sediments collected from the Main Drain. (A) dominance in the top layer, (B) dominance in the bottom layer.

The high concentrations of the ions Na^+, Ca^{2+} and Mg^{2+} in the sediments collected from the drain traversing the Marshalling Yard (sample 5) can be attributed to evaporative concentration that is occurring in the Dead Tree area. The low concentration of the ions Na^+, Ca^{2+} and Mg^{2+} in sample 6 (the sample where the three drains converge) is surprising because it is expected that these ions could move from sample position 3 (where high concentrations of the cations were detected) to sample position 6, either in water or via the transport of sediments. However, because the concentration of these ions is relatively low in samples 4 and 5, a dilution effect may be occurring at sample 6.

For all the cations mentioned, there is an increase in their concentration within the wetland relative to the concentrations detected at the inlet and outlet (samples positions 15 and 17, respectively). A possible explanation for the high concentrations is that the pH of the sediments within the wetland is low (pH of extract = 3.90), leading to an increase in cation mobility. It is also possible that the high retention times that are likely to exist in the wetland, could result in an accumulation of ions via evaporative concentrations processes. A further possible explanation for the relatively high concentrations in the wetland is that the vegetation of the system could be trapping windblown, marine, particles which then enter the sediment.

5.2.4.3.2. Ammonium

In the samples in which ammonium was detected, no generalisation can be made as to which layer has the highest concentration of NH_4^+ (Table 5.2 and Figure 5.3). The only generalisation that can be made is that the concentration of NH_4^+ in the background samples (samples 1 and 2) is lower than that detected in the other samples. It is expected that the top layer would have lower concentration than the bottom layer as a result of nitrification processes which occur under oxidising conditions (D'Angelo and Reddy, 1994a). However, because ammonium is affected by ion exchange processes to a larger degree than is nitrate (Rogers *et al.,* 1985), it is possible that the two layers may contain different amounts of NH_4^+ because there have been variable rates of NH_4^+ sorption (depending on the cation exchange capacity of the sediments). Therefore, the different concentrations in the different layers may be a function of exchange processes rather than nitrification or denitrification.

The concentration of NH_4^+ was similar in the majority of samples. There were however, a number of anomalous concentrations, particularly in the wetland (sample 16) and the sample collected above Langvlei (sample7). These anomalous concentrations are much higher than those detected in sediments by D'Angelo and Reddy (1994a) in which they found concentrations that ranged between 0-18 mg/ℓ. The similarity in NH_4^+ concentrations in the majority of samples could indicate that there has been minimal disposal of wastes containing this compound. The anomalous concentrations may arise as a result of the conversion of NO_3^- to NH_4^+ under reducing conditions (Ponnamperuma, 1972) rather than the disposal of this compound.

5.2.5. Trace elements

The trace elements Zn, Ni, Fe, Al, Pb, Co and Cu were detected in the 1:1 sediment solution extracts (Figure 5.4 and Table 5.1). These elements were not, however, present in all samples. In some cases these elements were present in the top layer but not in the bottom layer and vice versa. Generally these trace elements were absent in the 1:1 sediment solution extracts of the background samples.

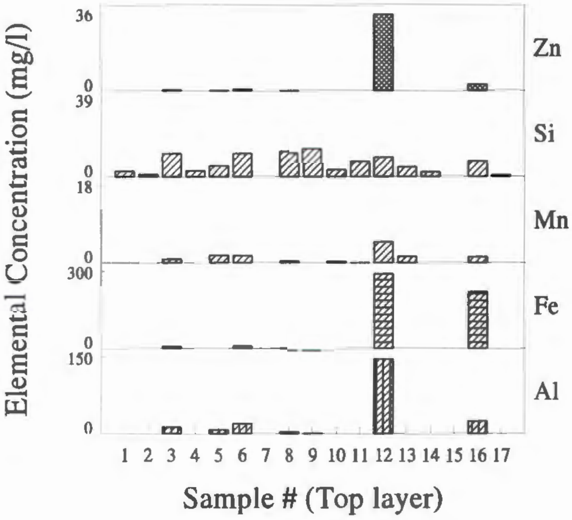
Anomalously high concentrations of Zn, Fe and Al were detected in sample 12T (opposite plant washwater discharge point in Agrochemicals). The concentrations of these elements at this sample location were higher than those at the other sample locations. More interestingly, they were higher than the concentrations detected by Feijtel *et al.* (1988) in the sediments of a relatively uncontaminated lake basin in Louisiana.

The concentration of Mn in sample 12T was higher than that detected in the other samples from the top layer. The concentration of Mn in sample 12B was higher than that detected at any other sample location. Other anomalous concentrations detected were those of Fe and Al in the sediments from *Wagenveldt vlei* (samples 14-16). The concentration of Al in sample 6 was also anomolusly high.

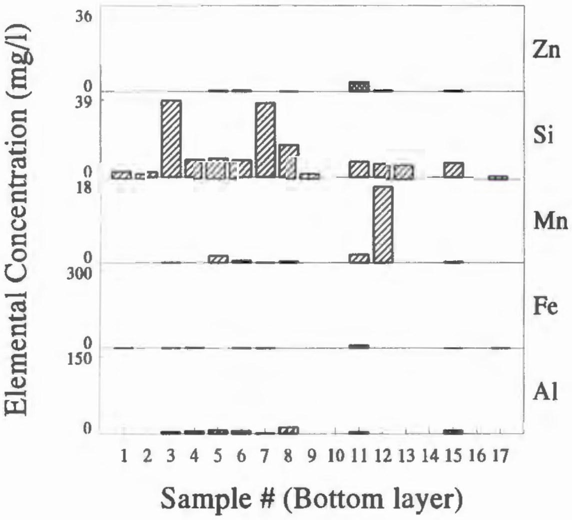
Because it is known that pH controls the mobility of a number of metals (McBride, 1995), the logs of the concentrations of Mn, Fe and Al were plotted against pH to determine if there were any relationships (Figure 5.5). The general trend was, that with an increase in pH there is a decrease in the concentration of the particular element in solution. The finding that the log of the concentration of the element and pH did not correlate well (as indicated by the scatter of points), would indicate that there is some variable other than pH controlling the solubility of Fe, Al and Mn.

It is possible, that in the case of Fe and Mn, redox conditions may be influencing solubility (McBride, 1995). However, because redox conditions were not measured, this hypothesis can not be tested. This potential hypothesis does not hold for Al, due to the fact that Al is not a transitional element and is, therefore, not affected by redox conditions. Another mechanism that may be controlling the solubility of Mn, Fe and Al is their interaction with other constituents. For example, Tisdale *et al.* (1985) reports that nitrogen sources can influence manganese availability (and, by implication, solubility). Furthermore, Kabata-Pendias and Pendias (1985) state that the interaction of Al and P is related to the formation of sparingly soluble Al-phosphates.

The scatter of points evident in Figure 5.5 could be as a result of anthropogenic inputs of these elements. If there have been anthropogenic inputs, it is surprising that there are such high concentrations of soluble Fe and Al in the sediments of the wetland (sample 16), which is at a relatively large distance from industrial activity. However, the high concentrations in this sample are as a result of the low sediment pH, which has caused the dissolution of minerals containing Fe and Al. Furthermore, it is possible that there may have been an accumulation of Fe and Al rich sediments in *Wagenveldt vlei*, when sediments have been transported down the drain during floods. It is hypothesised that a major source of Fe and Al to the wetland is from the sediments below the point where plant wash water is entering the drain (sample 12). This hypothesis is supported by the finding that the sediments of sample 12 also contain high concentrations of soluble Fe and Al.



(A)



(B)

Figure 5.4. Elemental concentrations in the 1:1 sediment to solution extracts prepared from sediments collected from the Main Drain. (A) concentrations in the top layer, (B) concentrations in the bottom layer.

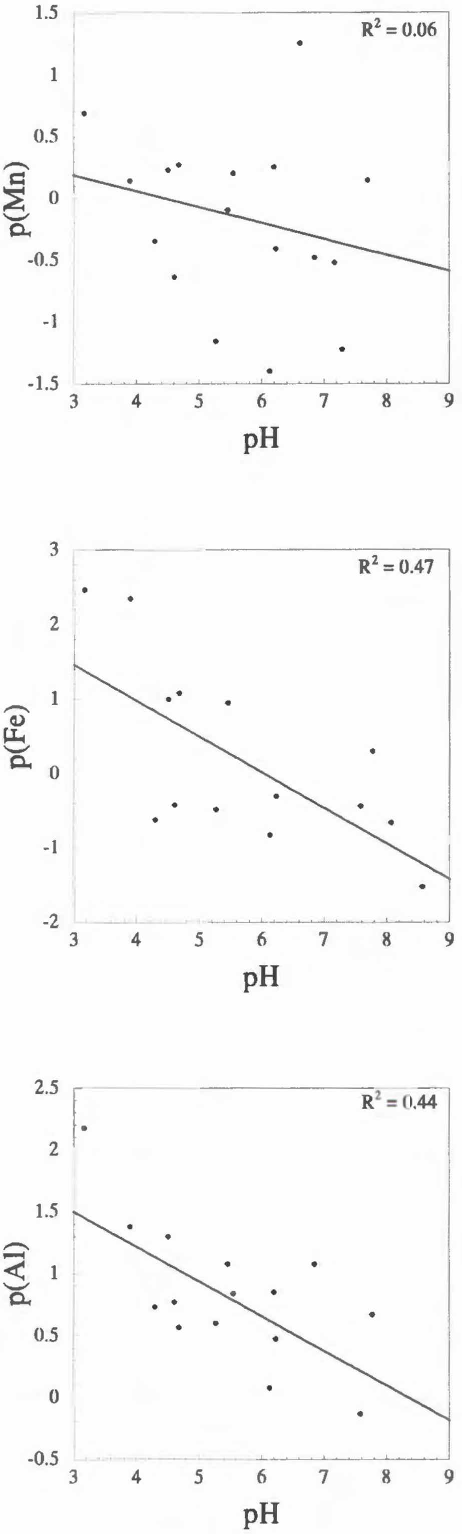


Figure 5.5. Correlations between pH and the log of Mn, Fe and Al in a 1:1 sediment to solution extract prepared from sediments collected from the Main Drain. The straight line represents the line of best fit.

5.2.6. Clay mineralogy

Difficulty was experienced in getting slides prepared from the clay fraction of samples 15 and 16, to dry without peeling at the edges or cracking in the centre. A number of attempts were made to try and overcome this problem. The techniques that were attempted included diluting the clay with distilled water to obtain a very dilute suspension with which to prepare the slides or concentrating the clay by centrifugation and then smearing the concentrate onto the slide. Different types of slides were also used in an attempt to get the clay to dry adequately, namely smooth glass slides as well as slides that had been scarified. None of these attempts was successful, and therefore, there is no data on the mineralogy for samples 15 and 16. Furthermore, insufficient clay was extracted from sample 17 to prepare a slide for XRD analysis.

The diffractograms that were obtained are presented in Figure 5.6. The minerals that were detected in the samples were mica (d spacing = 10 and 5 Å), kaolinite (d spacing = 7.1 and 3.59 Å) and quartz (d spacing = 3.35 and 4.27 Å). The broad peaks that were detected between 4 and 10 ° 2Θ are likely to be undifferentiated 2:1 layer silicate material. The minerals that were dominant in all samples were kaolinite and quartz.

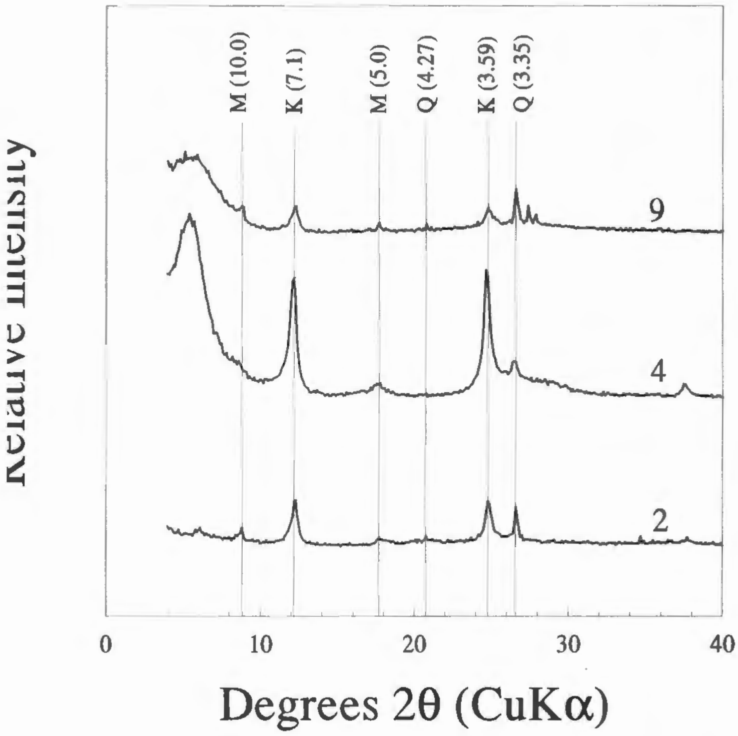


Figure 5.6. Clay mineralogy of a select number of sediments from the Main Drain. M = mica; K = kaolinite and Q = quartz.

As a result of the fact that the dominant minerals in the samples analysed were similar, it is hypothesised that the mineralogy of the other samples (not analysed) is the same, *ie.* the dominant minerals are kaolinite and quartz.

Relative to other clay minerals, kaolinite has a low cation exchange capacity (Degens, 1965). Kaolinite may, however, be more involved in anion exchange reactions as a result of the fact that 1:1 layer clays show preference for anion sorption (Degens, 1965). Therefore, it is hypothesised that a large proportion of the cation exchange capacity of the sediments would arise from the presence of negatively charged organic matter in the sediments (Table 5.4). Furthermore, the finding that there is a wide range in both organic carbon content (range = 0.1-17%) and clay content (range = 0.8-47%), indicates that the CEC will vary at the different sample locations. This is indicated by the different ΔpH values, between pH(H_2O) and pH($CaCl_2$), calculated for the various sample locations (Table 5.4). The implication of the potentially low CEC that may arise as a result of the fact that kaolinite and quartz are the dominant minerals is that the potential exists that mobile ions may readily diffuse through the sediment column, thereby entering groundwater. However, because the majority of samples contain significant concentrations of organic matter (Table 5.4), the organic matter may act to retard the movement of potential contaminants. Furthermore, even though the CEC of the clay minerals may be low, the finding that the sediments contain significant concentrations (up to ≈ 40 %) of clay could imply that the sediments have a relatively high **effective** CEC, thereby also retarding contaminant leaching.

Table 5.4 Concentration of organic carbon and clay of the various sediment samples collected from the Main Drain. Included in the table is ΔpH, the difference between pH(H_2O) and pH($CaCl_2$). N.M. indicates that clay content not measured.

	Organic Matter (%)		Clay Content (%)	ΔpH	
	Top layer	Bottom layer	Top layer	Top layer	Bottom layer
1	1.7	1.4	N.M.	0.6	1.0
2	0.1	2.5	N.M.	0.9	0.1
3	4.6	4.2	N.M.	0.3	0.7
4	2.4	2.5	41.9	0.9	0.8
5	1.2	1.7	8.0	0.3	0.3
6	7.6	6.2	47.3	1.5	0.6
7	2.8	1.2	N.M.	-0.8	0.2
8	3.2	3.1	N.M.	0.2	0.3
9	0.7	0.4	N.M.	0.7	0.4
10	11	No bottom layer	N.M.	0.1	
11	6.9	17	N.M.	0.01	-0.1
12	11	15	11.9	0.03	0.1
13	6.4	2.8	15.3	0.2	0.1
14	1.8	No bottom layer	N.M.	0.5	
15	15	11	18.4	2.5	0.1
16	14	No bottom layer	N.M.	1.1	
17	0.5	bdl	0.8	0.9	0.6

5.2.7. Elemental composition

Analysis, by XRF, on a bulk subsample of the sediments indicated that the trace elements Zn, Cu, Ni, Mn, Cr, Mo, Y, Rb, Nb, Sr, Th, Zr and Pb were present in all samples from both layers (Figure 5.7). The trace element Co was present in all samples except T2, T15, T17, B7, B9 and B17, V was present in all samples except T2 and B13 and U was present in all samples except B2. The major elements Fe, Ti, Ba, Ca, K, Cl, S, P, Si, Al, Mg and Na were present in all the samples collected from both layers (Figure 5.8).

As with the other analytes mentioned, the concentrations of the various trace and major elements are site and depth specific.

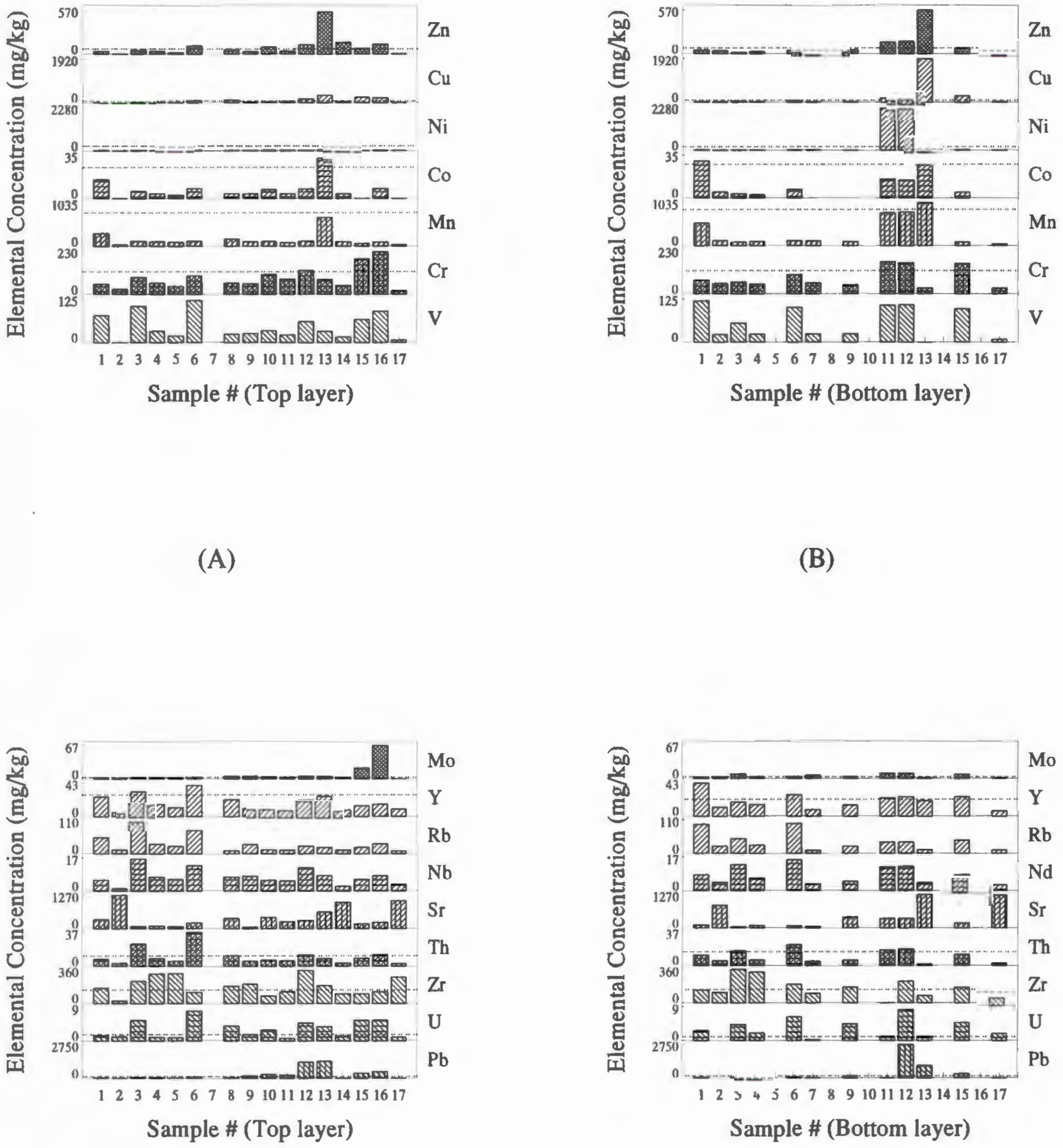
In order to determine which sediment samples have been contaminated by the different analytes, the concentrations detected in the sediments were compared to concentrations reported in the literature for material that has not been contaminated (Table 5.5). The literature values are not necessarily always those for sediments, but in some cases no literature could be found on the concentrations in sediments, therefore concentrations for soils and highly weathered rocks have been used. No average concentrations could be found for the elements Nb, Sr, and S. Therefore, it is not possible to determine the extent to which the various sediment samples are contaminated with these elements. These average concentrations are plotted on Figure 5.7 and 5.8 to allow a comparison to be made between concentrations in the sediments from the drain and concentrations in uncontaminated sediments.

A large majority of the samples contained concentrations of Zn, Cu, Mo, U, Fe, Ti, Na, Ca, Mg and K (Figure 5.7 and 5.8) above the averages reported in the literature (Table 5.5).

Even though not all samples have concentrations of Ni, Co, Mn, Cr, Y, Rb, Th and Zr, that are above those reported in the literature, there are still some samples in which the concentrations of these elements exceed the concentrations in uncontaminated material. The only analytes that were not present in the sediments in concentrations greater than the average concentrations were the analytes V, Rb and Al.

Table 5.5 Average concentrations of different constituents that have been detected as being present in a particular material type. Values reported as ppm unless otherwise indicated.

Constituent	Average Composition	Material	Reference
Zn	80	shale	Krauskopf (1969)
Cu	57	shale	Baker and Senft (1995)
Ni	20-250	shales/clay	Krauskopf (1969)
Co	20	shale	Krauskopf (1969)
Mn	850	shale	Krauskopf (1969)
Cr	100	shale	Krauskopf (1969)
V	130	shales	Krauskopf (1969)
Mo	2	sedimentary rock	Lepp *et al.* (1995)
Y	26	shales	Krauskopf (1969)
Rb	140	shales	Krauskopf (1969)
Th	12	shales	Krauskopf (1969)
Zr	160	shales	Krauskopf (1969)
U	3.2	shales	Krauskopf (1969)
Pb	23	mudstone/shale	Davies (1995)
Fe_2O_3	3.72 %	weathered material	Krauskopf (1969)
Al_3O_2	26.1 %	weathered material	Krauskopf (1969)
BaO	0.07 %	shales	Krauskopf (1969)
TiO_2	0.76 %	weathered material	Krauskopf (1969)
Na_2O	0.05 %	weathered material	Krauskopf (1969)
CaO	0.16 %	weathered material	Krauskopf (1969)
MgO	0.33 %	weathered material	Krauskopf (1969)
K_2O	0.14 %	weathered material	Krauskopf (1969)
Cl	180	shales	Krauskopf (1969)
P	700	shales	Krauskopf (1969)
SiO_2	55.1 %	weathered material	Krauskopf (1969)



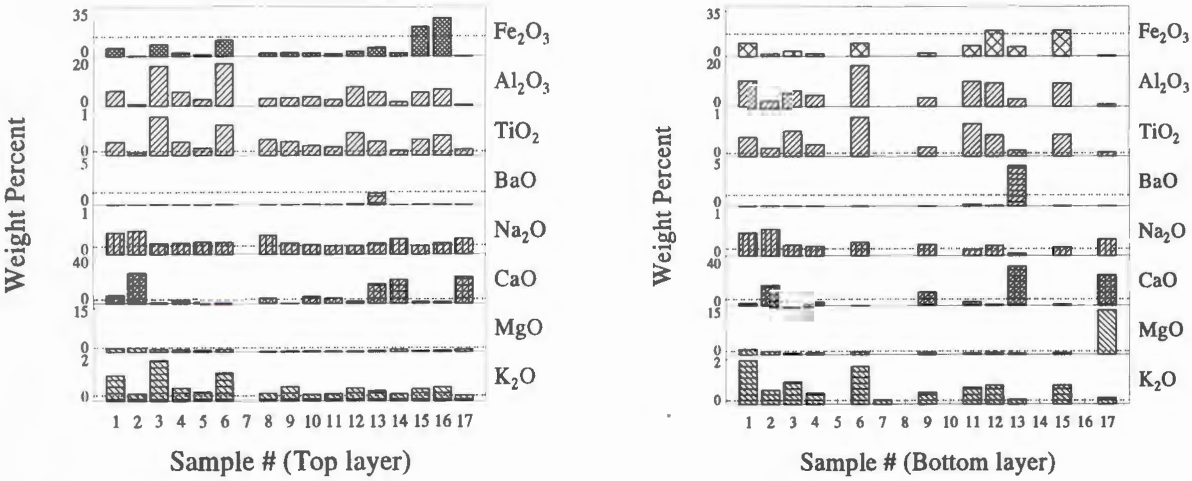
(A)

(B)

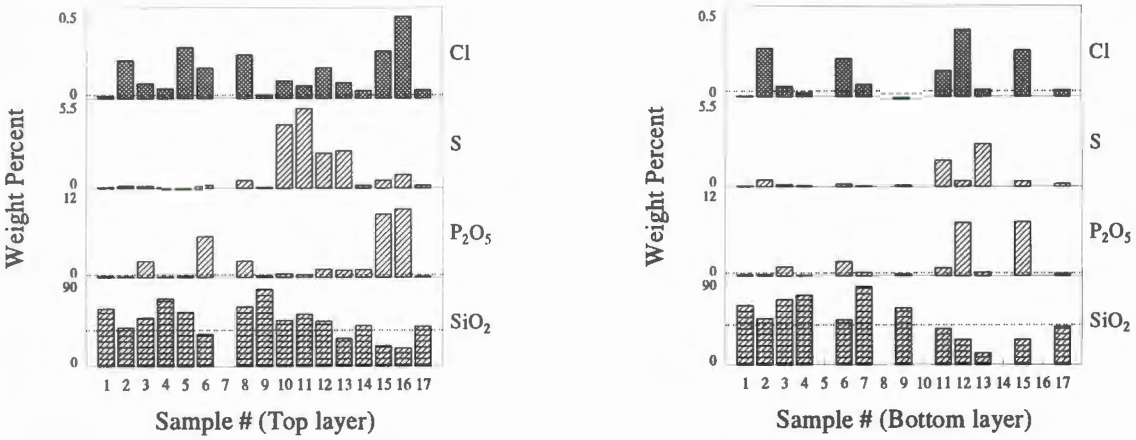
(A)

(B)

Figure 5.7 Trace elements detected in the bulk samples of the two layers of the sediments collected from the Main Drain. (A) concentration in the top layer, (B) concentration in the bottom layer. The dotted lines superimposed on the graph represent the average values taken from Table 5.5. Data from which these figures were derived are presented in Appendix 4.



(A) (B)



(A) (B)

Figure 5.8. Major elements detected in the bulk samples of the two layers of the sediments collected from the Main Drain. (A) concentration in the top layer, (B) concentrations in the bottom layer. Dotted lines represent average concentrations in uncontaminated material. Data from which these figures were derived are presented in Appendix 4.

A more useful technique used to determine the degree of contamination, is to compare the concentrations in the sediments from the industrial site to concentrations in samples that are suspected to be unaffected by industrial activity, or as Shimp *et al.* (1971) states "when attempting to determine the extent of pollution in a river or a lake by means of the heavy metal load in sediments, it is of primary importance to establish the natural level of these substances". In order to do this the mean concentration of a particular analyte in the top and bottom layer of sample 1 was determined. A ratio was then calculated between the analyte in a particular sample (*ie.* samples 3-17) and the mean value in the background sample. This ratio was then converted to a percent in order to determine an enrichment factor. The enrichment factors are reported in Table 5.6. It was decided not to use concentrations detected in sample 2 because this sample may not be a "true" background sample as it was collected off-site in a river that may be influenced by activities (other than those that may be occurring on the industrial site) which occur upstream. The results of this exercise must, however, be treated with caution because, according to Förstner and Wittmann (1971), in order to generate a basis for comparison, a number of criteria must be fulfilled so as to achieve representative analyte concentrations. The conditions that must be met are that there must be:

1) a large sample size,
2) correspondence between grain size,
3) correspondence between material composition (between background samples and "contaminated" samples),
4) correspondence between conditions of origin, and
5) no anthropogenic contamination in the background samples.

It was not possible to meet all of the above conditions in this study. Therefore, the enrichment results must be considered as preliminary and tentative. However, the comparison is still a useful ***provisional indicator*** as to whether industrial practices have resulted in the contamination of the sediments.

The results of the comparison indicate that the degree of enrichment is dependent on the analyte of interest, as well as the location from which the sample was obtained. The elements that are enriched in the majority of the samples collected from both the top and bottom layer are Cu, Mo, Cl, S and P (Figure 5.9 and Table 5.6). However, at a number of sample locations one or more element is enriched by a factor greater than a 100 %. This enrichment at a particular sample location may indicate that at or near the location, there is a source of the analyte that is resulting in analyte deposition in the sediments. Other elements that are enriched, but not in a large proportion of the samples, are Ni, Co, Mn, V, Y, Rb, Fe, K, Al, Mg and Na (Figure 5.9 and Tables 5.6a and b).

Table 5.6.a Enrichment factors for each element from the top layer of the different samples. Enrichment factors reported as percentages. Negative results indicate that the concentration of a particular analyte is higher in the background sample than in the sample taken on site. No XRF analysis were performed on 7T

	3T	4T	5T	6T	8T	9T	10T	11T	12T	13T	14T	15T	16T	17T
Zn	10	-18	-55	150	40	-27	110	-8.2	170	1100	250	78	190	-89
Cu	364	97	-7.4	620	830	120	330	250	1300	2600	280	1900	1700	-62
Ni	-18	-35	-48	-1.5	-50	-30	-9.3	-22	20	81	-27	-44	-20	-84
Co	-74	-83	-87	-65	-83	-83	-67	-82	-65	45	-83	*	-65	*
Mn	-72	-74	-78	-72	-58	-74	-72	-79	-70	62	-75	-85	-75	-92
Cr	41	-6.8	-33	56	-4.3	-10	66	27	100	26	-26	200	260	-68
V	7.2	-67	-81	24	-75	-73	-66	-78	-39	-67	-84	-33	-8.3	-93
Mo	23	20	6.0	35	110	120	60	49	130	80	8.2	760	2500	-94
Y	-5.9	-54	-66	19	-36	-69	-70	-73	-38	-23	-76	-59	-53	-72
Rb	44	-57	-66	3.2	-86	-58	-83	-84	-67	-73	-84	-71	-56	-88
Nb	140	5.6	-12	90	4.6	12	-20	-26	74	15	-65	-12	14	-49
Sr	-70	-59	-70	-5	67	-76	85	15	35	180	340	-22	3	360
Th	160	-15	-46	290	18	-45	-31	-38	28	-15	-63	-12	32	-71
Zr	55	110	110	-22	20	36	-47	-18	130	23	-33	-32	-19	84
U	180	-53	-57	300	96	-15	46	-66	140	91	-39	170	180	-55
Pb	93	16	-66	144	6.1	430	930	730	4100	4400	-50	1200	1600	-81
Fe	10	-68	-84	50	-69	-68	-69	-77	-53	-16	-69	180	260	-95
Ti	140	-17	-56	91	-0.7	-14	-40	-47	42	-12	-69	0.4	25	-63
Ba	20	-65	-60	20	-47	-63	20	-33	190	3300	-73	65	65	-83
Ca	-91	-35	-85	-73	0.6	-92	35	10	-58	280	360	-70	-73	420
K	19	-62	-74	-18	-77	-58	-80	-78	-62	-69	-79	-64	-59	-82
Cl	970	620	3600	2100	300	140	1200	790	2100	990	450	3300	5900	490
S	110	3.5	39	220	810	11	7500	9400	4100	4300	200	820	1500	190
P	1500	-37	41	3900	1500	36	210	130	670	590	630	5900	6500	-18
Si	-18	15	-7.1	-45	2.5	32	-22	-11	-23	-53	-30	-65	-69	-32
Al	100	-31	-67	113	-61	-59	-53	-68	-7	-32	-80	-33	-18	-93
Mg	-34	-47	-56	-37	-77	-74	-74	-87	-78	-67	-37	-68	-57	-43
Na	-50	-48	-45	-47	-14	-49	-55	-62	-62	-49	-30	-61	-48	-29

* Co was below detection limit in these two samples, therefore, no enrichment factor could be calculated.

Table 5.6.b Enrichment factors for each elements at the different sample locations in the bottom layer. Enrichment factors reported as percentages. Negative results indicate that the concentration of a particular analyte is higher in the background sample, than in the sample taken on site. No XRF analysis were performed on samples 5B and 8B. At sample location 10, 14 and 16, there was no bottom layer.

	3B	4B	6B	7B	9B	11B	12B	13B	15B	17B
Zn	-60	-38	-2.4	-71	25	150	160	1200	78	-66
Cu	300	59	490	69	100	1400	1500	16000	2200	34
Ni	-51	-42	-0.7	-26	-46	9400	9600	85	-28	-73
Co	-85	-88	-69	0.0	0.0	-32	-37	28	-80	*
Mn	-80	-76	-71	-72	-76	85	89	140	-80	-89
Cr	-0.9	-18	59	-7.4	-22	170	160	-49	150	-52
V	-44	-77	2.8	-76	-76	9.2	10	0.0	-2.1	-93
Mo	260	43	77	160	28	300	330	-22	220	-17
Y	-46	-55	-18	-76	-58	-31	-27	-42	-28	-81
Rb	-34	-63	32	-87	-67	-52	-50	-83	-42	-86
Nb	92	-5.3	131	-50	-30	78	82	-42	18	-59
Sr	-80	-58	-66	-72	86	58	62	460	-22	450
Th	70	-35	140	-50	-35	80	91	-80	29	-73
Zr	140	120	31	-33	12	-99	52	-49	9.2	-49
U	110	-3	220	-89	120	-45	310	-48	140	-8.5
Pb	58	-13	130	-43	400	-92	8600	3100	990	-29
Fe	-52	-75	19	-78	-70	-3.0	140	-14	140	-91
Ti	56	-29	140	-60	-44	99	32	-64	34	-74
Ba	0.0	-65	18	-27	-75	470	77	11000	93	-78
Ca	-93	-27	-99	-95	150	-29	-82	650	-84	490
K	-35	-68	8.2	-88	-66	-52	-46	-86	-45	-82
Cl	650	180	2600	760	5.9	1700	4700	400	3200	360
S	98	-14	210	-32	42	3000	590	5000	540	240
P	780	-49	1300	220	73	660	5000	240	5100	90
Si	12	19	-23	34	-2.7	-38	-57	-80	-57	-35
Al	-23	-45	103	-85	-58	22	14	-65	15	-89
Mg	-68	-59	-37	-92	-47	-69	-57	-73	-58	9900
Na	-52	-56	-38	-81	-48	-71	-53	-89	-59	-25

* Co was not present in the sample, therefore an enrichment factor could not be calculated.

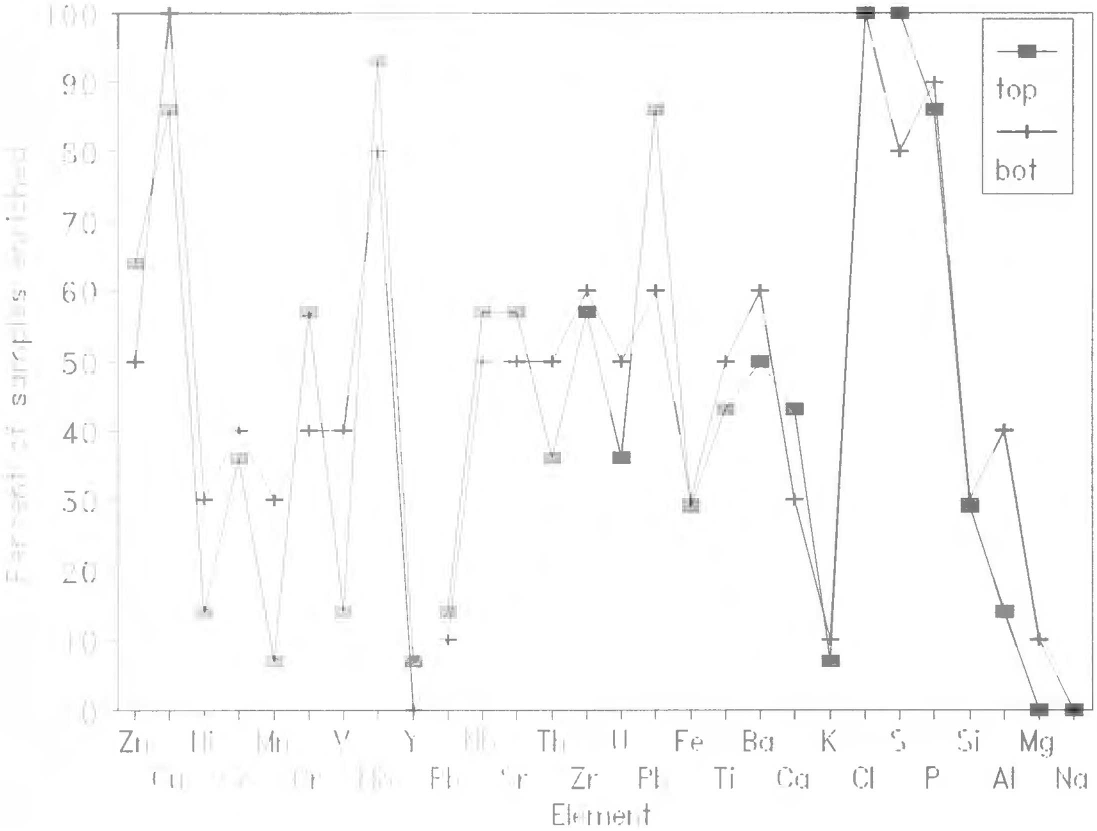


Figure 5.9. Proportion of samples in the different layers which are enriched with a particular element.

In the following discussion only elements that are markedly enriched at a particular sample location will be discussed. The high enrichment factors calculated for Cu in samples 11-13 and 15 (particularly in the bottom layer) compared to other samples may indicate that anthropogenic activity may be responsible for the accumulation of Cu in the sediments in this area. It is speculated that the source of the Cu was the disposal of $CuSO_4$ into the Main Drain, prior to 1960 (Chapter 1). The high concentration of Cu in the sediment extract prepared from sample T12 (concentration approximately 7000 times that found in uncontaminated soil solutions (Tisdale *et al.* 1985)) would support this hypothesis because it is known that $CuSO_4$ is relatively soluble in solution. However, it is also possible that the high concentration at this sample can be attributed to the low pH of the sediments because, as Tisdale *et al.* (1985) reports, there is a 100 fold increase in the solubility of Cu for every decrease of 1 pH unit. At sample locations 11 and 13, Cu was not detected in the sediment extracts, even though there were high concentrations of Cu in the bulk sample. A possible explanation for this is that at the relatively high pH values of these samples, $CuSO_4$ has dissolved and then precipitated or become sorbed with the result that it exists in an insoluble form in the sediments. The greater enrichment in the bottom layers can be attributed to the fact that the deposition of Cu happened over 35 years ago. Thus, since deposition has ceased, fresh uncontaminated sediments have covered those in which Cu became concentrated.

It is speculated that a major source of Zn in the sediments results from the incorporation of this element into the sediments after Zn has entered the system in runoff from the galvanised metal roofs that abound on site. This speculation holds particularly well for sample 13 (both layers are greatly enriched with Zn) where there are a number of buildings, (approximately 5 meters to the south) which have galvanised roofing material. At this sample location no Zn was detected in the sediment extract. The explanation for this could be that the Zn that entered the sediments in a soluble form in runoff may have precipitated from solution to form an insoluble phase that exists at the relatively high pH values detected in the sediments. Furthermore, storm water management may result in no further inputs of Zn occurring, with the result that there is no further input of soluble Zn. The high concentration of Zn in the sediment extract from sample 12 (the normal concentration in an uncontaminated soils extract range between 2 and 75 µg/ℓ, Tisdale *et al.* (1985)) relative to those in the other sample extracts, can be attributed to continual input of Zn to the sediments which is not precipitating or being sorbed from solution. This lack of sorption or precipitation occurs because of the relatively low pH values of the sediments, but it can also occur because it is expected that there will be continual input of Zn from runoff as a result of the lack of stormwater management in the Agrochemicals area (Chapter 1). The finding that there are high concentrations of Zn in the bottom layer relative to the top layer of the sediments at sample positions 11-13 can be attributed to the deposition of Zn from rain water early in the history of the site.

Both layers of sample 13 are markedly enriched with Ba. Barium is often associated with phosphate fertilisers, being present in concentrations of up to 200 mg/kg (Kabata-Pendias and Pendias, 1985). However, sample 13 was located in the explosives area, an area in which it is unlikely that there have been Ba containing fertiliser spills. The very high concentrations detected at this sample location would indicate that there has been a spill of a Ba containing compound. It is thought that this spill has occurred over a relatively small area, as a result of the fact that high degrees of enrichment by Ba are not detected anywhere else on site. According to Fairbridge (1972), of particular importance to the geochemistry of Ba is the highly insoluble compound $BaSO_4$. If this compound is the one in which Ba exists in the sediments, it is unlikely that Ba will pose a health hazard in terms of soluble Ba entering the water body.

The high enrichment of Mo within the wetland is surprising because this sample was collected at a relatively large distance from any industrial activity. The only other sediments in which Mo is highly enriched are those from the bottom layer of sample 11 and 12. This is expected as it is known that molybdates were deposited into the sediments prior to 1960 during activities that occurred in the Agrochemicals area (Chapter 1). A possible explanation for the high concentrations that are found in the wetland is that Mo has moved down the length of the drain and then accumulated in the wetland as Mo rich sediments have been deposited, or Mo has been sorbed by the wetland sediments as water velocity has decreased (and by implication retention time increased). Molybdate would be mobilised in samples where the pH is relatively high (*ie.* samples upstream of the wetland) because it is known that because Mo exists as an anion, its solubility increases with an increase in pH (Lepp *et al.,* 1995). Furthermore, the low pH of the sediments in the wetland would result in a decrease in the solubility of Mo in these sediments with the result that this element would be incorporated into the sediment column as Mo precipitates from solution. Therefore, it is possible that Mo has moved from the Agrochemical area (particularly from sample 11 where the pH is relatively high). This hypothesis can not be tested because Mo was not analysed for in the 1:1 sediment to solution extract. Therefore, it is not known whether this element exists in a soluble form in the sediments. A further explanation for the high Mo content in the wetland is that Mo is sorbed strongly by Fe and Al oxides (Tisdale *et al.* 1985). Thus, because there is a high concentration of Fe in this sample, it is possible that Mo is associated with Fe. This explanation may, however, be tenuous in that in the other samples that contained high concentrations of iron there were not high concentrations of Mo.

As a result of the fact that Ni is often associated with phosphate containing fertilisers (McGrath, 1995),
it is expected that high concentrations of Ni would be present in the sediments in the drain coming from the fertiliser area (sample 3). This was not a finding that was evident in the current study, rather high concentrations of Ni were detected in the bottom layer of samples 11 and 12. Nickel was in high concentrations in the bulk samples but was only present in high concentrations in the sediment extract of sample 12. It is hypothesised that the low concentrations of Ni occur as a result of Ni being immobilised by the high concentrations of phosphate in sample 11. This hypothesis is based on the fact that phosphate immobilises divalent cations (Kabata-Pendias and Pendias, 1985). Therefore, if both high concentrations of Ni and P are present it is likely that there would be the precipitation of zinc phosphates. Thus, at sample 11 the high phosphate in solution could potentially have removed Ni from the sediment extract. Even though relatively high concentrations of soluble Ni were detected in sample 12B, Ni has not become concentrated in any of the other samples downstream to the degree in which it has occurred at samples 11 and 12, indicating that Ni is not a mobile anion in the sediments.

A high degree of Pb enrichment has occurred in the sediments of samples 12 and 13 as well as in samples 15 and 16. It is speculated that the source of the Pb was the dumping of lead arsenates and lead nitrates from the Agrochemical operations (Chapter 1). The accumulation of Pb in the sediments of samples 15 and 16 could have arisen when Pb rich sediments moved down the length of the drain which were then deposited in the wetland. It is unlikely that Pb would have moved in solution because Pb minerals are relatively insoluble (Kabata-Pendias and Pendias, 1985; and Davies, 1995). Therefore, in order for Pb to concentrate in the sediments of the wetland, Pb contaminated sediments would have to have been transported down the drain. If this has occurred, it is expected that there would be an accumulation of Pb in the sediments of the estuary bypass (sample 14). This has not occurred, but a possible explanation for this finding is that during the time at which Pb rich sediments were moving down the drain, streamwater was not being discharged via this bypass, rather it was being diverted into the wetland.

The enrichment of Cl in all sediments can be attributed to the deposition of sea salts in these areas as well as the evaporative processes that are expected to occur in the area, particularly in the Dead Tree area. The salts of Cl then enter the drain resulting in the incorporation of Cl into the sediments. The low concentration of Cl in the background sample is attributed to the fact that this sample is at a relatively large distance from the coastline compared to the other samples, with the result that this sample will not be greatly influenced by marine deposition.

The enrichment of all sediment samples with the element P can be attributed to a number of sources. Firstly, it is known that phosphoric acid has been manufactured in the Agrochemical areas. Therefore, if any of this acid has been spilled, it is expected that the sediments of this area would contain high concentrations of P. It was only the bottom layer of sample 12 (sample collected in the Agrochemicals area) that had a high concentration of P, however, the pH of this sample was not very low which would indicate that an acid spill is unlikely to be the source of P. Other sources of P have been the manufacturing of single and double superphosphates (Chapter 1) in the fertiliser area as well as the phospho-gypsum dump located in this area. Sample 3T (collected in the drain from the fertiliser area) is enriched by 1500% by P, which would indicate that the fertiliser area is a major source of P. The enrichment of P down the rest of the length of the drain could also be attributed to deposition of P that is sourced from the Fertiliser area. The high enrichment factor of P in the sediments of the wetland (sample 16) indicates that these sediments are accumulating P. This is a finding that has been reported by Rogers *et al.* (1985).

The S enrichment of the sediments can be attributed to processes that are occurring in the Agrochemical area, particularly the disposal of waste water from the sulphur washing belt. Evidence for this is the high enrichment (generally greater than 3000 %) in the sediments of samples 10-13.

Other sources of S may be spills during the manufacturing of sulphuric acid or during any of the other manufacturing processes that utilised sulphuric acid. Other possible sources of sulphur are the sulphur and phospho-gypsum dumps that are located in the Fertiliser area. It is possible that there has been the deposition of wind blown sulphur particles (either as elemental S or as S incorporated in the phospho-gypsum) over the time in which these two dumps have been on site.

No generalisation can be made as to which layer contains the most samples that are enriched by the different elements (Figure 5.9). This is in conflict with the findings of Johnson (1977), who found that the surface layers from the Kingston Basin, Upper St Lawrence river were enriched with Cd, Co, Cu, Ni, Pb, Zn, Hg and As. It is speculated that this conflict arises as a result of the nature of the systems that are being compared. In Johnson's (1977) study, a basin was investigated whereas in the present study a stream was investigated. The implication of this is that there is far greater movement of water in a stream compared to that in a basin, with the result that sediments will be transported and mixed far more in a stream than would occur in a basin. However, numerous studies reported by Förstner and Wittmann (1979), have shown that industrial activity has lead to the accumulation of contaminants in the sediments of a system, whether that system is a stream, lake or wetland. These findings therefore support the findings of this study that industrial activity leads to the accumulation of elements in sediments.

The sediments of *Wagenveldt vlei* are enriched by Cu, Cr, Mo, Nb, Sr, Th, U, Pb, Fe, Ti, Ba, Cl, S and P. A number of these elements are enriched at other sample locations, especially Cu, Mo, Pb, Ba, Cl, S and P. The enrichment in the wetland could arise when sediments that are already enriched with these elements are transported down the length of the drainage system where the sediments are deposited in the wetland as there is a reduction in water velocity (Phillips, 1989). The enrichment of Nb, Sr, Th, U and Ti may merely be as a result of the natural variation that exists in the concentration of these elements in sediments. The implication of the enrichment by Cu, Mo, Pb, Ba, Cl, S and P is that sediments from upstream have an influence on the characteristics of the wetland sediments.

5.2.8. Effect of changes in oxidation potential in the sediments

It is well known that, when the redox potential of a system changes there is a resultant change in the mobility and bioavalibility of heavy metals that are incorporated in the sediments (McBride, 1994). If the redox potential becomes more reducing, *ie.* there is a decrease in the Eh of the system, there can be a change in speciation of a number of metals. For example iron changes from the ferric form to the ferrous form. The effect of this change in speciation is an increase in the mobility (and by implication an increase in the concentration in solution) of these metals as a result of the fact that

they are more soluble under reducing conditions. Furthermore, a decrease in redox potential may indirectly affect the mobility of metals that occur in only one valence state (*eg.* zinc and cadmium). These metals may increase in mobility if they are present as impurities or sorbed to oxides that become reduced.
Conversely, if sulphur is present, insoluble sulphides may form, resulting in a decrease in the mobility of the metal ions (Stigliani, 1992).

If the opposite situation occurs, and redox conditions become more oxidising, the reactions that have been described above reverse. That is, oxides may form while sulphides are dissolved (Stigliani, 1992). Associated with the dissolution of the sulphides is a release of protons into solution. This decrease in pH may further affect the mobility of a number of metals as the protons begin to dissolve the minerals that are present in the sediments, particularly those that contain Mn, Fe and Al.

A decrease in redox conditions may occur when unsaturated soils become saturated, resulting in a decrease in the amount of oxygen that is available to the microbial community. The microbes will then start to utilise other oxidants, such as metal ions, as a source of terminal electrons. On the other hand, oxidising conditions may develop if saturated soils dry out, resulting in an increase in the concentration of oxygen in the soil. This may occur if sediments are dried out or if they are removed, from the drain, and dumped.

The aim of the oxidising experiment performed in this study was to simulate the drying out of the sediments to determine whether, with drying, there is a decrease in pH as any sulphides that are potentially in the sediments become oxidised.

According to Konsten and Klepper (1992), the preferred method of simulating the drying out of sediments is to take a fresh sample that still contains moisture and then leave them to air dry, measuring pH before drying and then measuring the pH once the samples are completely dry. However, according to these authors, it may take more than a year for all the pyrite to be fully oxidised. An alternative method proposed by Konsten *et al.* (1988), is to oxidise the samples with hydrogen peroxide. The method of Konsten *et al.* (1988) was used in this study due to time limitations. The pH prior to oxidising and the pH after oxidising are presented in Figure 5.10.

The results indicate that for all samples, except samples 9 and 10, the oxidation of the sediments results in a marked decrease in pH. The post-oxidation pH of samples 11 and 12 was below pH 2. Sample 8 and sample 12 exhibited the most marked decrease in pH, with a decrease larger than 2 pH units. Similar results have been noted by Gambrell *et al.* (1991), who continuously stirred a suspension of sediments collected from a New Jersey marsh in order to simulate oxidation of the sediments. These authors noted that there was decrease in pH from 7.0 to 3.0 over the 8 day period. Furthermore, Prasana (1994) found that a sediment suspension stirred under an atmosphere of argon showed no change in pH while a suspension that was stirred under ambient atmospheric conditions showed a decrease in pH of 3.8 pH units.

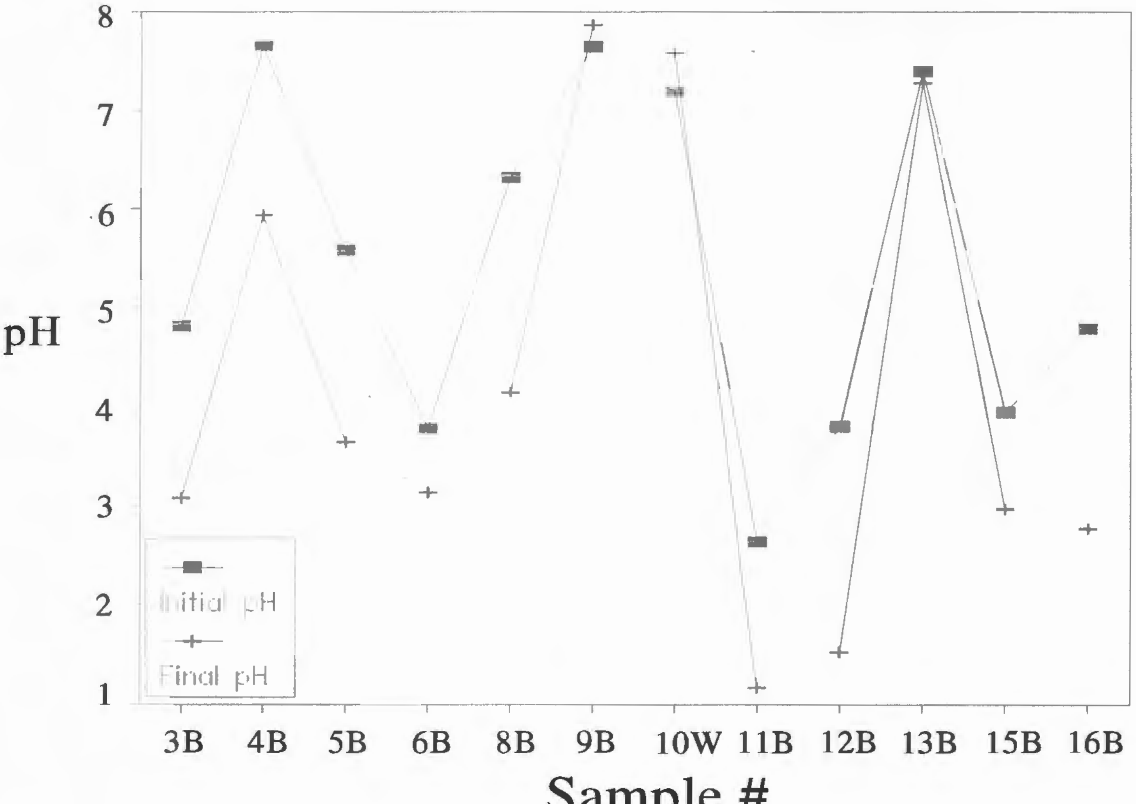


Figure 5.10. Sediment pH prior to oxidation and after oxidation. The pH was determined in a 1:2.5 sediment to water solution. B refers to samples collected from the bottom layer while W refers to whole sample (*ie.* both the top and bottom layer).

A decrease in pH after oxidation has been attributed to oxidation of pyrite by Konsten and Klepper (1992). In this study there was no significant correlation between S and Fe, which was interpreted as meaning that there is not a high pyrite concentration in the sediments. However, the results of the oxidation experiment would indicate that there is still sufficient pyrite in the sediments to result in a decrease in pH as protons are released as pyrite is oxidised.

The pH of samples 9 and 10 increased slightly, while the pH of sample 13 only decreased by 0.11 pH units. This indicates that these samples are relatively well buffered. This buffering is attributed to the $CaCO_3$ that was detected in these samples (Table 5.7).

Table 5.7. Concentration of $CaCO_3$ in sediment samples on which the oxidation experiment was performed. Included in the table is the change in pH that occurs when the samples were oxidised. B refers to the bottom layer, W refers to samples that were not split into two layers.

Sample No	$CaCO_3$ content (%)	Change in pH
3B	0	1.7
4B	2	1.7
5B	0	1.9
6B	0	0.7
8B	0	2.2
9B	17	-0.2
10W	7	-0.4
11B	0	1.5
12B	0	2.3
13B	36	0.1
15B	0	1
16B	0	2

As mentioned, a decrease in pH may result in the mobilisation of a number of constituents that are incorporated into the mineral fraction of the sediments. The acid leach test that was performed on a select number of sediment samples gave an indication of the degree to which metals could become mobilised. However, it must be borne in mind that this test was performed with a relatively concentrated acid solution (0.1 M HNO_3), with the result that the pH of the leaching solution is expected to be lower than that which would be generated in the samples if oxidation was to occur. This leaching test, therefore, gives an indication of the maximum leaching likely. Furthermore, as a result of the fact that this was a multi-element analysis with all elements being analysed for concurrently, this analysis is only semi-quantitative. Therefore, the results of this test only serve as an approximate estimation of the constituents that may be found in solution after oxidation. The results of this acid leach test are presented in Table 5.8.

Table 5.8. Concentrations of a variety of constituents in an acid extract after sediments have been leached with a 0.1 M HNO_3 solution. All values reported as mg/l. Included in this table are the target quality guidelines set by the Department of Water Affairs and Forestry (1996) for drinking water. Excessively high concentrations have been embolded.

	1	4	6	9	12	15	16	Target value (mg/ℓ)
Ti	0.2	0.3	4	0.1	**190**	68	**8**	N.V.
Sr	110	62	64	**120**	73	49	52	N.V.
Mg	590	790	820	820	210	390	600	0-30
Al	130	310	5400	330	930	1400	1200	0.-0.015
Ni	1	0.8	2	0.9	**500**	3	2	N.V.
Mn	87	13	15	13	150	10	12	0-0.05
Fe	150	140	**1990**	120	**1600**	**4500**	**9000**	0-0.1
Cr	0.2	0.4	3	0.7	4	6	7	N.V.
V	1	3	**11**	2	**10**	6	**14**	N.V.
Na	230	430	931	260	170	450	790	0-100
Be	0.1	0.2	0.7	0.1	0.1	0.2	0.1	N.V.
B	1	3	1	2	1	0.8	1	N.V.
Ca	15000	13000	3500	22000	8200	2700	2700	0-32
P	13	74	**2900**	15	**640**	**1200**	**1800**	0-0.3
Zn	4	13	**25**	15	**46**	20	**33**	0-0.15
Cd	bdl*	0.4	0.3	0	0.2	0.4	1	N.V.
Cu	1	6	21	5	**38**	**88**	**50**	N.V.
Pb	4	12	3	**42**	**390**	12	22	N.V.
Li	bdl	0.4	0.1	0.8	0.1	0	0.2	N.V.
Co	3	0.4	0.8	0.1	1	0.3	0.5	N.V.
Sn	bdl	bdl	bdl	bdl	bdl	20	46	N.V.
K	85	170	760	120	79	320	320	0-50

N.V. = No value given by Department of Water Affairs and Forestry (1996).
* bdl = below detection limit.

The results indicate that under acid conditions the potential exists that there could be relatively large amounts of constituents released into solution, particularly the concentrations of the elements Mg, Al, Ni, Mn, Fe, Ca, P and K. The concentrations of all elements is markedly higher than the target water quality range that has been set by the Department of Water Affairs and Forestry (1996) which would indicate that if the sediments do become oxidising the potential exists that the constituents that are mobilised could exist in solution in concentrations that could be harmful if ingested. The implication of this is that if the sediments do become oxidising, with a resultant increase in metal mobility, the metals could enter the groundwater, thereby causing a contamination problem. The concentrations of the elements that are likely to exist in solution after oxidation are such that the water would be unsuitable for human use in any activity. This scenario is however, the worst case scenario as it is unlikely that pH would reach the levels of the HNO_3 solution (as mentioned). Furthermore exchange and sorption reactions in the sediments would effectively retard the movement of the contaminants through the sediment column, with the effect that, a proportion of the contaminants would be removed before they entered the groundwater.

6. Conclusions

Concentrations of various analytes in the 1:1 sediment to solution vary considerably both down the length of the drain and in the different layers. Relative to concentrations in the background samples, the concentrations of the major ions Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, F^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ and the elements Fe, Al, Cu, Ni and Zn in the 1:1 sediment extract are high. The increased concentration of the above analytes can be attributed to either natural processes such as marine influence, or the increased concentrations can be attributed to wastes entering the drain at specific sample locations. Important sources of soluble constituents are spills of a variety of acids, dumping of solid wastes that are then solubilised and the phospho-gypsum and sulphur dumps situated in the fertiliser area.

The total elemental composition of the sediments was also site and depth specific with marked variation evident down the length of the drain. The concentrations of Zn, Cu, Mo, Pb, Cl and P in the majority of samples were above the average concentrations for sediments or sedimentary rocks. At specific sample locations the concentrations of one or more of the elements Ni, Co, Cr, Y, Th, Zr, U, Ba, Na, Ca, Mg and K were present in the sediments in concentrations greater than the average concentrations reported for sediments or sedimentary rocks. This is, however, not necessarily an indication that the sediments have been contaminated because there is normally great variation in the concentrations of particular elements in sediments. Therefore, the high concentrations, relative to average concentrations, could merely be a result of natural variation.

A better **indication** of whether the sediments have been contaminated is the calculation of enrichment factors relative to background samples. From these results it is not, however, possible to conclude with conviction that the sediments have been contaminated. This is because insufficient background samples were collected and the background samples that were collected did not necessarily match the physical conditions of the samples collected on site. However, the enrichment results indicate that the majority of samples are enriched with Cl, P and S. This enrichment could possibly be as a result of marine influence as well as spills of acids, the dumping of wastes and chemicals coming from the phospho-gypsum and sulphur dumps, located in the fertiliser area. A number of specific samples were also enriched with Zn, Pb, Ni, Cu and Ba. This is attributed to the wastes, containing these elements, coming into contact with the sediments.

The chemical composition of the sediments of the wetland *Wagenveldt vlei* is similar to those of the sediments from further upstream in the drainage system. That is the sediments of the wetland contain similar constituents to those found further upstream. The elements that are enriched in the wetland are similar to those which are enriched at other sample locations. The implication of this is that the wetland is acting as a trap for sediments that are moving down the system.

Kaolinite and the quartz, the dominant clay minerals, have low cation exchange capacities relative to a number of other clay minerals. The implication of this is that the potential exists that elements may not be strongly sorbed to the sediments. However, because the clay and organic matter content of the sediments is large, the CEC of the sediments is potentially increased. The implication of this is that any mobile cations can potentially be sorbed to the sediments with the result that the cations may be removed from solution and therefore they do not enter groundwater or the overlying water column.

It is concluded that if conditions change in the sediments and the sediments are oxidised, the potential exists for a reduction in the pH of the sediments. The reduced pH could result in an increase in the mobility of a number of constituents. The acid leach test indicates that under low pH conditions, there is an increase in the mobility of elements such as Ti, Sr, Ni, V, Zn, Cu and Pb. The pH of this acid leach is probably much lower than that which would develop if the sediments were to become oxidised. Therefore, this test is only an indication of which elements are likely to experience a marked increase in mobility.

CHAPTER 6.

CONCLUSIONS AND RECOMMENDATIONS

6.1 General conclusions

A number of key questions were posed in the introduction to this study. In this chapter an attempt will be made to answer these questions implicitly.

The EC value and the concentrations of the analytes Al, NO_3^-, F^- and PO_4^{3-} in water samples collected from the Main Drain are such that they could potentially impact detrimentally on human health if the water in the drain was to be ingested. Furthermore, the concentrations of NO_3^- and PO_4^{3-} detected in a number of samples could lead to the eutrophication of the water in the Main Drain. From these findings it is concluded that the water currently in the Main Drain is unsuitable as either drinking water or water that could be used in recreational activity where the possibility exists that water could be accidentally ingested.

The EC values of a number of water samples are such that there might be slight to moderate restrictions on the use of the water for agricultural purposes. The concentrations in which Al, NO_3^-, Na^+ and Cl^- are present in the water samples may result in the development of toxicity symptoms if applied to vegetation. It is therefore, concluded that the water in the Main Drain should not be used for irrigation purposes without the water being treated prior to its application to vegetation. Furthermore, if the water is to be piped, the potential exists that pipes could be corroded due to the fact that there would be no protective calcite precipitate in the pipes. This occurs because the waters of the Main Drain are undersaturated with respect to calcite (saturation index less than 1).

Therefore, it is concluded that, at present, the water in the Main Drain is unsuitable for both human consumption and use as irrigation water.

The results of this study indicate that industrial activity has resulted in there being elevated concentrations of a number of constituents in the sediments of the Main Drain. The 1:1 sediment to solution extract of a number of samples contained elevated concentrations, relative to the concentrations found in the background samples, of the major ions Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, F-, Na^+, Ca^{2+}, K^+, Mg^{2+} and NH_4^+. The elements Al, Fe, Pb and Cu in the 1:1 extract were present in higher concentrations in the samples collected on site, relative to the concentrations in the background samples.

In terms of element concentrations in bulk sediment samples, Zn, Cu, Ni, Cr, Mo, Th, Zr, Pb, Fe, Al, Ti, Ba, Na, Ca, Mg, K, Cl and P are above the concentrations that have been determined as being the average concentrations in sediments or sedimentary rocks of the world.

Relative to the background sediments, the sediments of the Main Drain have been enriched with the elements Cl, P and S. Sources of these elements are marine influence, spills of phosphoric and sulphuric acid as well as the phospho-gypsum and sulphur dumps. Individual samples are enriched with Zn, Cu, Mo, Pb, Ni and Ba. Enrichment was attributed to wastes, containing these elements, coming into contact with the sediments.

It is thus concluded that industrial activity could have resulted in elevated concentrations of a number of analytes in the sediments.

The concentrations of SO_4^{2-}, Al, Zn and Fe in the 1:1 sediment to solution extract and the concentrations of Mo, Fe, Cl and P in the bulk sediments of the wetland are generally higher than the concentrations that were detected upstream of the wetland. Relative to the background sample, the wetland sediments are enriched with the elements Zn, Cu, Cr, Mo, Nb, Th, U, Pb, Fe, Ti, Ba, Cl, S and P. These elevated concentrations and/or enrichment may arise when there has been the deposition of sediments that are enriched with these analytes. This finding could indicate that the wetland is acting as a sediment trap, where sediments in the overlying water column are deposited after there is a reduction in water velocity as water enters the wetland. This finding would lead to the conclusion that the chemical composition of the sediments in the Main Drain are reflected in the sediments of the wetland.

Insufficient background samples were collected. Furthermore, these samples may not truly be reflective of uncontaminated sediments because, even though they were collected upstream of industrial activity (sample 1) and off site (sample 2), they may still be influenced by activities occurring on site or activities occurring upstream. The physical characteristics of the background sample (grain size and sedimentary environment) may be different to that of the samples collected on site. As a result of the above, a comparison of chemical characteristics of samples collected on site with those of the background samples does not allow the conclusion that sediments that show elevated concentrations or high enrichment factors, to be made with conviction.

Due to the fact that it cannot be stated with conviction that the sediments are contaminated by industrial activity it is not possible to explicitly answer the key question "*if the sediments of the Main Drain are contaminated, is the contamination localised or is it distributed down the length of the drain ? Are the different layers of the sediments contaminated to the same degree ?* However, the results indicate that the distribution of analytes down the length of the drainage system is not homogenous, both in terms of sample location as well as in terms of which layer is contaminated. This, however, needs to be qualified because it was found that the elements Cl, S and P were enriched in both layers of all samples.

The nature of the background samples also means that the key question "*if the degree of contamination in the sediments is different, what are the factors that could have resulted in the difference ?*" cannot be explicitly answered because it cannot be stated with conviction that contamination has occurred. However, the large inhomogeneity that exists in the distribution of analytes, as well as elemental enrichment at a number of sample locations, could lead to the conclusion that anthropogenic activity is a primary factor responsible for the chemical differences, both at different sample locations and depths. Natural differences in pH and redox conditions may also account for the inhomogeneity of constituents in the 1:1 sediment to solution extracts.

The results of the oxidation experiment indicate that if the conditions change, with the result that the sediments are oxidised, the potential exists that there would be a marked decrease in sediment pH. Associated with the decrease in pH could be an increase in the mobility of Ti, Sr, Ni, Fe, V, P, Zn, Cu and Pb. As a result of the increase in mobility, these elements could potentially leach through the sediments into the groundwater or they could move from the sediments into the overlying water. Because the concentrations of these elements are above the limits set by the Department of Water Affairs and Forestry (1996), it is concluded that if the elements should enter the groundwater or the overlying water column, it could lead to the water becoming unsuitable for human consumption. This conclusion does need to be qualified. Even though the concentrations of Ti, Sr, Ni, Fe, V, P, Zn, Cu and Pb are high in the acid extract, this extract is only indicative of the maximum increase in mobility that may occur. Furthermore, the quantity of sediments that may be oxidised is not known, nor can the extent of oxidation be predicted. Thus, even if redox conditions change so that conditions become extremely oxidising, oxidation may only be very localised with the result that it is unlikely that the increase in mobility would result in significant increases in concentrations of the elements in the groundwater or in the overlying water column.

6.2 **Recommendations**

In order to better quantify the extent and nature of contaminants in the sediments, it is recommended that a more detailed investigation be implemented. This study should be designed so that a larger number of representative background samples be collected. Figure 6.1 indicates likely background sample positions that could be used. It must, however, be stated that these sample positions have merely been located on the basis of their distance from industrial activity, rather than on whether the sediments physical characteristics are similar to those of the Main Drain. If this study is performed it should be possible to determine with conviction whether the sediments have been contaminated. It is also recommended that during this follow-up study, a number of samples should be collected in areas where the present study has indicated that there is a high degree of enrichment. These supplementary samples should be collected at 0.5 meter intervals over approximately 10 m, upstream and downstream of the locations where there is a high degree of enrichment. By doing this it should be possible to get an indication of the area in the drain that contains contaminated sediments. This information may help with the design of a remediation project. It is recommended that a remediation project be implemented to try and remove the sediments that have been found to have high concentrations of analytes. It must, however, be stated that it is seriously recommended that remediation does not involve the removal of the sediment and then dumping at a new location where the potential exists that they may be oxidised.

It is recommended that an attempt be made to preserve *Wagenveldt vlei.* This recommendation is based on the finding that the wetland is acting as a sediment trap for sediments that may be enriched by a variety of elements. The sediment trapping function of the wetland is useful because it prevents the sediments being washed out into the ocean, where they could be deposited over marine life, leading to potential siltation problems. In order to facilitate the sediments trapping role that the wetland fulfils, it is recommended that some of the dead biomass that is choking the system, be removed. This biomass is causing water that is entering the wetland to move in channels rather than in a sheet through the system. By implementing sheet flow, water retention time may be increased which would increase the efficiency with which sediments are trapped.

To further increase the efficiency of the wetland it is recommend that the pH of the sediments be artificially increased by liming. This would result in a decrease in the mobility of a number of constituents, particularly heavy metals. This decrease in mobility would result in the metals being retained in the wetland, rather than potentially moving through the system where they could enter the marine environment. It is not possible to determine to what degree this recommendation is necessary because it is not known whether the metals that are moving through the system are resulting in a detrimental effect on the marine environment. Furthermore, the pH of the sediments at the wetland outlet is markedly higher than that found within the wetland. This may indicate that further into the system than the position at which sample 16 was collected, there may be natural processes resulting in an increase in pH.

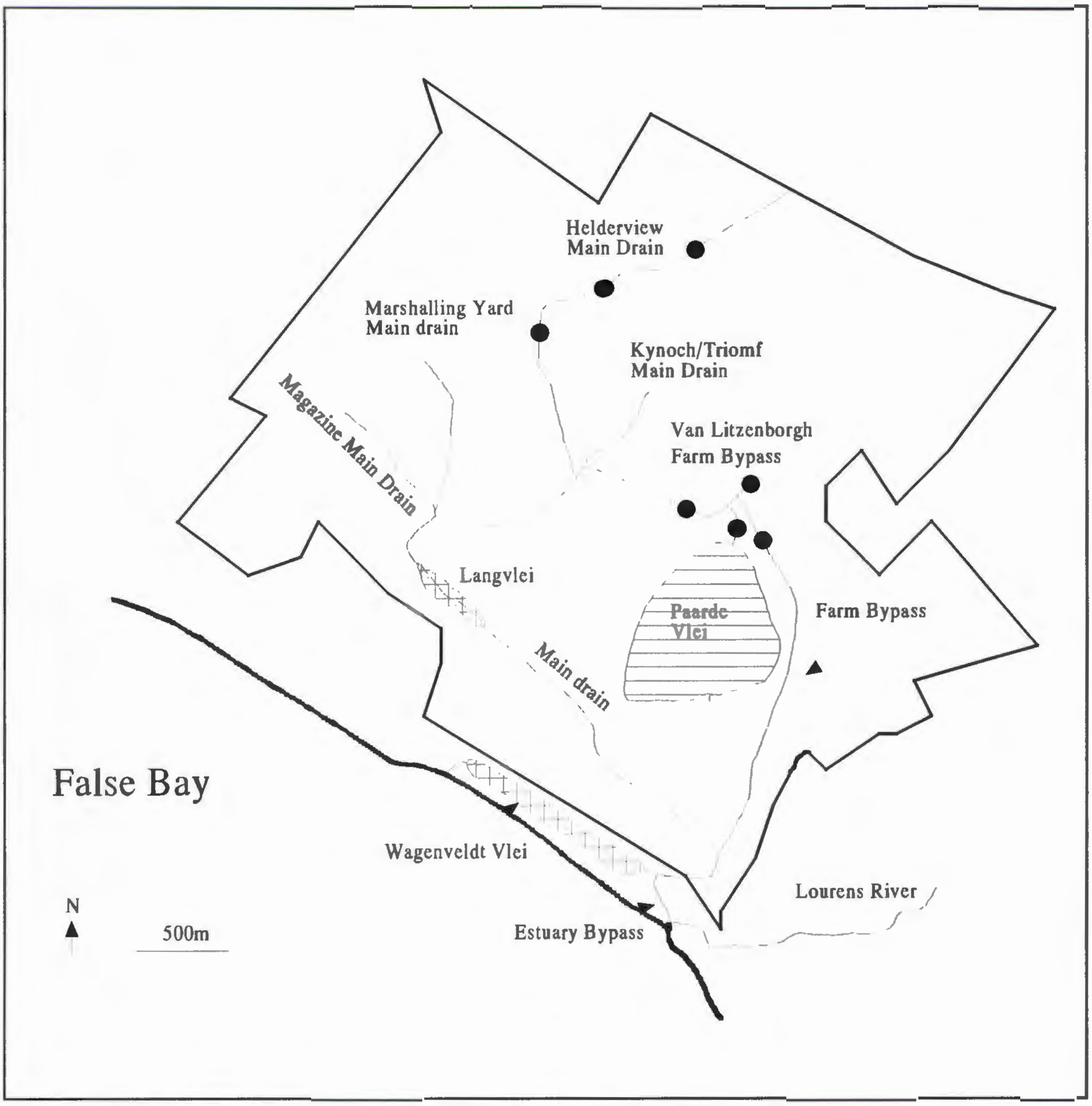


Figure 6.1. Recommended locations for background samples if further work is to be performed again.

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APPENDIX 1. ANALYTICAL APPRAISAL

1.1. Charge balance

Calculating the charge balance is the ultimate test of the quality of data as it is known that it is not possible for a charge imbalance to occur because for every positively charged ion in solution there must be a negatively charged ion balancing that charge. Using *MINTEQA2* (Allison *et al.*, 1985) it is possible to calculate the charge balance prior to and post speciation. The important balance is the post speciation charge balance. This is because the post charge balance takes complexation into account. It is known that on complexation there may be a change in the valance of a species (Allison *et al.*, 1991). Furthermore, pH may effect which species is present *eg.* at a low pH phosphate exists as $H_2PO_4^-$ whereas at a high pH it exists as HPO_4^{2-}. The charge balance that was calculated for the water samples is given in Table A1.1, while the charge balance that was calculated for the sediment extracts is given in Table A1.2. A good charge balance is considered to be one in which the imbalance is $< \approx 10$ %.

Table A1.1. Charge balance calculated for the analyses conducted on the water samples.

Sample Number	Unspeciated (%)	Speciated (%)
1	-22	-12
2	-14	-1.1
3	-21	-13
4	-18	-7.0
5	-10	-7.0
6	+8.1	+5.9
7	-24	-14
8	+15	+8.0
9	+9.7	+5.8
10	-12	+7.6
11	-19	-20
12	-14	-3.1
13	-2.3	-4.1
14	-10	-7.6
15	+2.9	+6.7
16	+6.4	-3.6
17	+37	+5.5

Table A1.2. Charge balance calculated for the analyses conducted on the sediment extracts.

	Top layer		Bottom layer	
Sample Number	Unspeciated (%)	Speciated (%)	Unspeciated (%)	Speciated (%)
1	-21	+23	-24	-16
2	+3.6	+3.7	+10	+12
3	-22	-12	-11	-2.1
4	-15	-17	-27	-14
5	+7.5	+10	+3.7	+8.5
6	+17	+18	+7.6	-2.0
7	+7.3	+9.8	+34	-9.1
8	-5.8	-0.9	-24	-17
9	-9.6	+9.7	+2.0	+10
10	-3.2	+0.005		
11	-6.4	+4.3	+0.26	+3.4
12	+2.9	+6.0	+40	+56
13	-1.2	+2.2	+1.9	+6.3
14	-2.4	+8.6		
15	-13	+8.0	-15	-10
16	+3.5	-1.1		
17	+2.7	-12	+2.1	-13

For the charge balance calculated for both the water samples and the sediment extracts, a number of samples had a charge balance greater than 10 %. A select number of these samples were re-analysed, but it did not effect the charge balance. It is hypothesised that the large charge balance that exists for sample 12B occurs because it is expected that there may be relatively large concentrations of Ba in this sample. This hypothesis is made based on the findings that during the bulk elemental analysis (by XRF) large concentrations of Ba were detected. The large charge imbalance that exists in the other samples has been attributed to analytical inaccuracy or bias.

1.2. Precision

The results presented here are those of multiple readings conducted on various samples to determine the precision of the technique. Precision was determined by running either duplicate or triplicate analyses on a number of samples (approximately every fifth sample analysed). In some cases where budgetary restrictions prevented multiple readings being obtained, precision is taken from the relevant literature. In the case where the same technique was performed on both water and sediments, the following discussion will be relevant to both sets of results. Table A1.3 reports the precision determined for the elements analysed using HPIC. Table A1.4 reports precision on the results obtained from ICP-OES. Table A1.5 reports the precision determined for this study on results that were obtained using equipment other than the HPIC, ICP-OES or XRF. Precision, accuracy and machine set-up conditions for XRF are those reported by Willis (1995). See page A1.8 of this Appendix.

The values reported in these tables were calculated by determining the mean, standard deviation and relative standard deviation (RSD = {mean ÷ standard deviation} x 100) for the samples on which multiple analyses were performed. The lowest and highest RSD are those that are reported in the tables.

For the various analytical techniques it appears that the precision that was obtained was within that reported in the literature

Table A1.3. The minimum and maximum relative standard deviations obtained from the duplicate samples analysed on HPIC.

Analyte	Relative Standard Deviation (%)	Detection Limit (mg/l)[1]
Cations		
Ca^{2+}	0.8 - 5.1	1
Na^{+}	0.01 - 9.3	1
K^{+}	0.5 - 3.9	1
NH_4^{+}	2.1 - 29	1
Mg^{2+}	0.6 - 7.4	1
Anions		
Cl^{-}	0.3 - 3.1	1
Br^{-}	2.9	1
NO_2^{-}	8.9	1
NO_3^{-}	1.3 - 5.3	1
SO_4^{2-}	0.08 - 9.5	1

[1] Willis (1996 pers.comm.).

Table A1.4. Detection limits and precision of the ICP-OES JOBY YVON 70 C instrument.

Table A1.4. Detection limits and precision of the ICP-OES JOBIN YVON 70C instrument.

Element	Residual Standard Deviation (mg/l)	Detection limit (mg/l)
Ca	3.0	0.05
Mg	0.27	0.03
Na	0.24	1.0
Fe	0.33	0.1
Al	4.5	0.5
Cu	1.38	0.2
Cr	0.6	0.1
Mn	0.39	0.04
Ni	38	0.2
Si	4.5	0.09
Co	4.5	0.1
Pb	26.7	1.0
Zn	3.6	0.1
Cd	12	0.06

Table A1.5: The precision of the various techniques, other than HPIC, ICP-OES and XRF, that was used in the study. In some cases where precision and accuracy have been reported in the literature, they are recorded here.

	Range of value obtained in this study[*]	Values from the literature		
Analysis	RSD (%)	Precision[1]	Accuracy[2]	Reference
pH	0.22 - 7.34	1.37 %	≈ 0.02 pH units	Franson, 1985
EC	0.12 - 4.0	8.3 %	4.8 %	Franson, 1985
Alkalinity	0.1 - 15.7	≈ 10 %	nvr[#]	Franson, 1985
Phosphorus	3 - 11	6.2 %	nvr	Franson, 1985
Fluoride	2.1 - 5.2	0.03 mg/l	nvr	Franson, 1985
Organic Carbon	0.75 - 18	nvr	nvr	---
Carbonate		2-4 %	2-10 %	Birch, 1982
Extractable Acidity	0 - 4.3	nvr	nvr	---

[*] RSD calculated as described above.

[1] These values are either reported as a standard deviation, in the units of measurement or they are reported as a relative standard deviation (coefficient of variation) as a percent.

[2] Accuracy is reported as a percent of the actual value or the deviation from the actual value.

[#] nvr = No value reported in the literature

1.3. Accuracy

As a result of time and equipment limitations, it was not possible to determine the accuracy of all the techniques that were used. It was, however, possible to get an idea of the accuracy of the Na, K, Mg and Ca values by comparing the results obtained from ICP-OES and those obtained from HPIC. For both the water and sediments samples the correlations were statistically significant; however, there was no 1:1 correlation (see Figure A1.1 and A1.2).

This result could be attributed to the fact that ICP is determining total elemental concentrations whereas HPIC is only determining the concentration of ions in solution. If this was occurring it is expected that the icp analyses would give concentrations that are consistently larger than those detected by HPIC. This is not a finding of this study and therefore, it is concluded that the lack of 1:1 correlation occurs as a result of analytical inaccuracy or bias. It is not, however, possible to attribute this inaccuracy to one technique. Therefore, it is concluded that both techniques contain inherent inaccuracies.

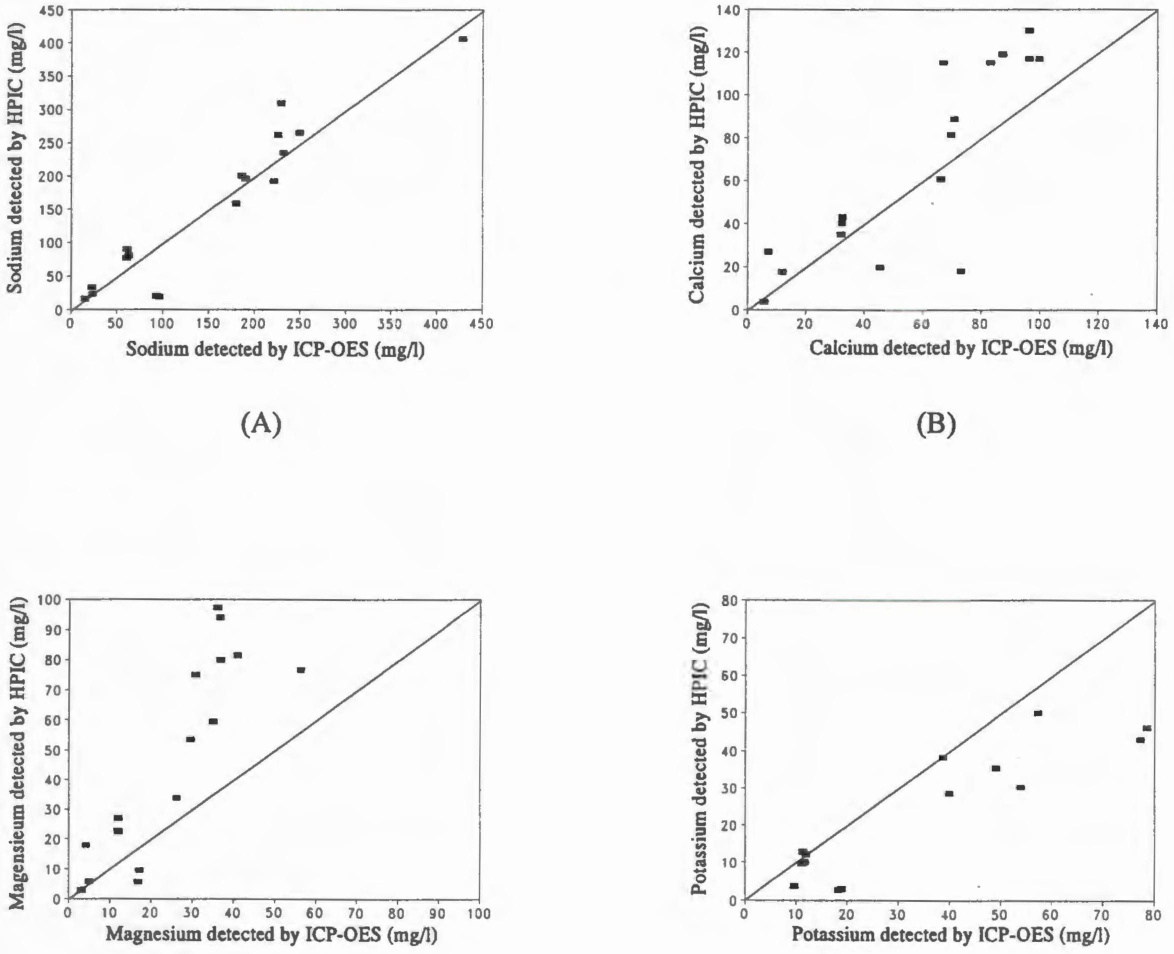
A further test of the accuracy of the HPIC analyses is to compare the concentrations that are reported as being in a standard to the concentration that is know to be in the standard (see Table A1.6).

Table A1.6. Concentrations in the standard solutions used to calibrate the HPIC instrument. Values in bold are the values that the machine reported as being in the standard during the calibration procedure.

STD	Ca2$^+$	Na$^+$	K$^+$	NH_4^+	Mg^{2+}	Cl^-	NO_{2-}	NO_{3-}	SO_{42-}
1	6.25	6.25	1.25	1.25	1.25	0.90	0.50	0.50	1.00
	6.28	**6.21**	**1.26**	**1.26**	**1.26**	**1.27**	**0.53**	**0.47**	**1.03**
2	12.5	12.5	2.50	2.50	2.50	1.90	1.00	1.00	2.00
	13.1	**12.9**	**2.60**	**2.56**	**2.57**	**2.01**	**1.05**	**0.93**	**2.11**
3	25.0	25.0	5.00	5.00	5.00	4.70	2.50	2.50	5.00
	25.3	**25.0**	**4.92**	**5.13**	**5.06**	**4.84**	**2.43**	**2.40**	**5.15**
4	50.0	50.0	10.0	10.0	10.0	9.40	5.00	5.00	10.0
	50.6	**50.9**	**10.1**	**10.2**	**10.1**	**9.02**	**4.60**	**4.79**	**9.70**

T-tests for dependant samples performed by the computer package STATISTICA indicate that the concentrations detected by HPIC do not significantly differ from the concentrations that are known to be in the samples.

For the other techniques that were used, careful attempts were made to accurately calibrate the instruments that were being used against a set of standards with known concentrations.



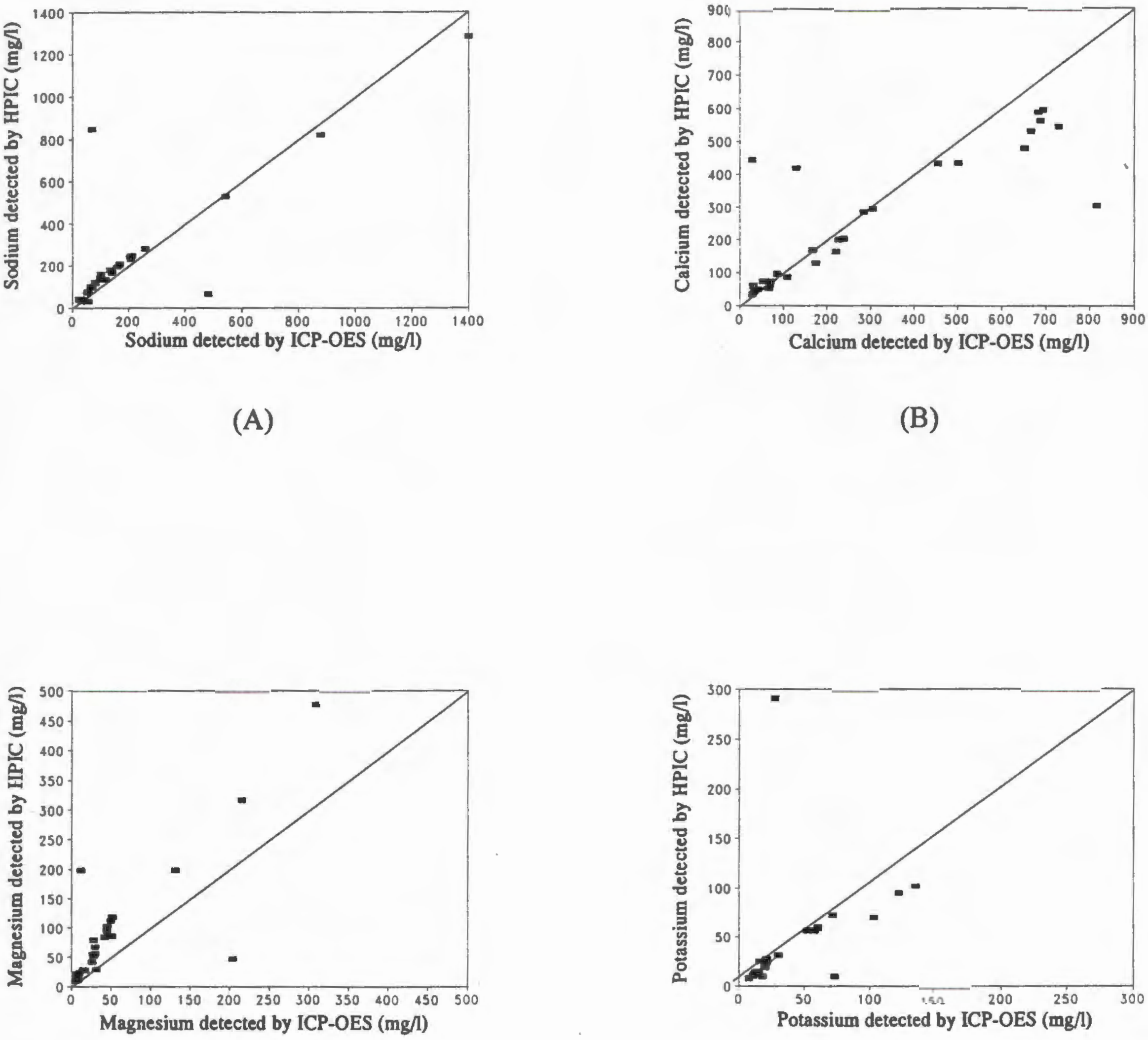
(A)

(B)

(C)

(D)

Figure A1.1 Correlation between the data obtained using ICP-OES and HPIC. (A) Sodium. (B) Calcium. (C) Magnesium. (D) Potassium.



(A)

(B)

(C)

(D)

Figure A1.2 Correlation between the data obtained using ICP-OES and HPIC. (A) Sodium. (B) Calcium. (C) Magnesium. (D) Potassium.

1.4. Precision, Accuracy and Instrumental set-up for the XRF analysis

Document compiled by J.P.Willis (1995).

1.4.1. Major elements

Nine major elements, Fe, Mn, Ti, Ca, K, P, Si, Al and Mg (with Ni and Cr when Ni and Cr concentrations exceed ~2000 ppm) are determined using fusion disks prepared according to the method of Norrish and Hutton (1969). The disks are analyzed on a Philips PW1480 wavelength dispersive XRF spectrometer with a Mo/Sc x-ray tube. Fe, Mn and Ti are measured with the tube at 100 kV, 25 mA. The other elements are determined with the tube at 40 kV, 65 mA. Peak only measurements are made on the elements Fe through Mg. Sodium is determined using powder briquettes, the x-ray tube at 40 kV, 65 mA, and with backgrounds measured at −2.00 and +2.00°2θ from the peak position. Analytical conditions are given in Table 1.

Fusion disks made up with 100% Johnson Matthey Specpure SiO_2 are used as blanks for all elements except Si. Fusion disks made up from mixtures of Johnson Matthey Specpure Fe_2O_3 and $CaCO_3$ are used as blanks for Si. Intensity data are collected using the Philips X40 software. Matrix corrections are made on the elements Fe through Mg using the de Jongh model in the X40 software. Theoretical alpha coefficients used in the de Jongh model for all other elements on the analyte element are calculated using the Philips on-line ALPHAS programme. Na_2O is not included in the matrix corrections in de Jongh model, and no matrix corrections are made to the sodium intensities.

Table A1.7. Analytical conditions for determination of major elements using a Philips PW1480 WDXRF spectrometer.

Element/line	Collimator	Crystal	Detector	PHS		Counting time (s)	Concentration range *	RMS	No. of standards
				LWL	UPL				
FeKα	F	LiF(220)	FL	16	70	150	0 - 17	0.118	14
MnKα	F	LiF(220)	FL	15	70	150	0 - 0.22	0.005	14
TiKα	F	LiF(200)	FL	28	70	150	0 - 2.75	0.020	14
CaKα	F	LiF(200)	FL	36	70	20	0 - 12.5	0.037	14
K Kα	F	LiF(200)	FL	36	70	50	0 - 15.5	0.057	14
P Kα	C	GE(111)	FL	25	75	100	0 - 0.36	0.008	14
SiKα	C	PE(002)	FL	32	74	100	0 - 100	0.408	14
AlKα	C	PE(002)	FL	25	75	80	0 - 17.5	0.136	14
MgKα	F	PX-1	FL	30	74	150	0 - 46	0.095	14
NaKα	F	PX-1	FL	30	78	200	0 - 9	0.189	15

* = all concentrations expressed as wt% oxide

$$RMS = \sqrt{\frac{1}{n - k} \sum \left(Conc_{given} - Conc_{calc} \right)}$$

where

n = no. of standards

k = no. of calibration coefficients, *i.e.* 2, the slope and intercept of the calibration line.

$Conc_{given}$ = recommended concentration for an element in a standard

$Conc_{calc}$ = concentration of an element calculated from the best-fit calibration line

First order calibration lines, with intercept, are calculated using all data points, including blanks. Calibration plots for Fe_2O_3, CaO, SiO_2 and MgO are given in Figures 1 - 4.

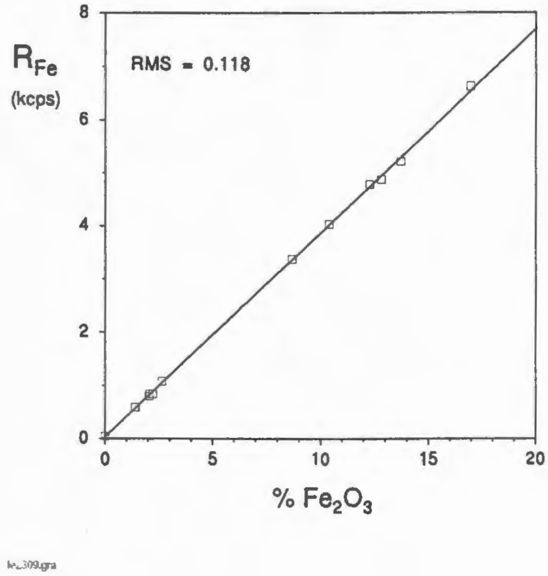


Figure A1.3. Calibration plot for Fe_2O_3 using "Norrish" fusion disks.

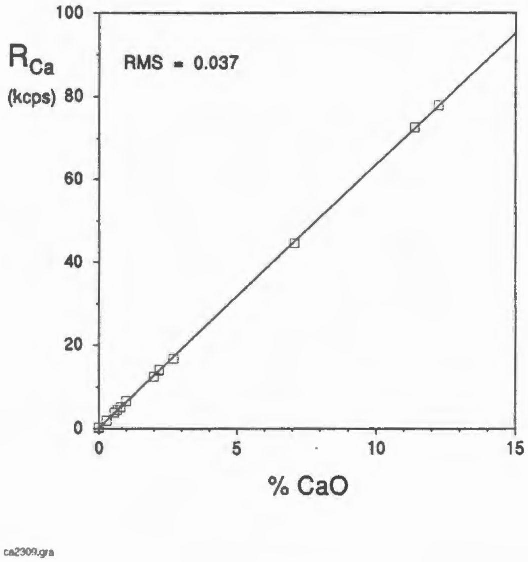
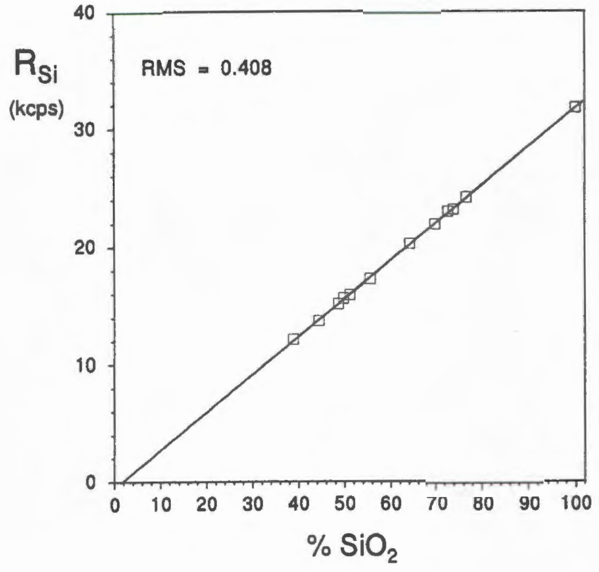
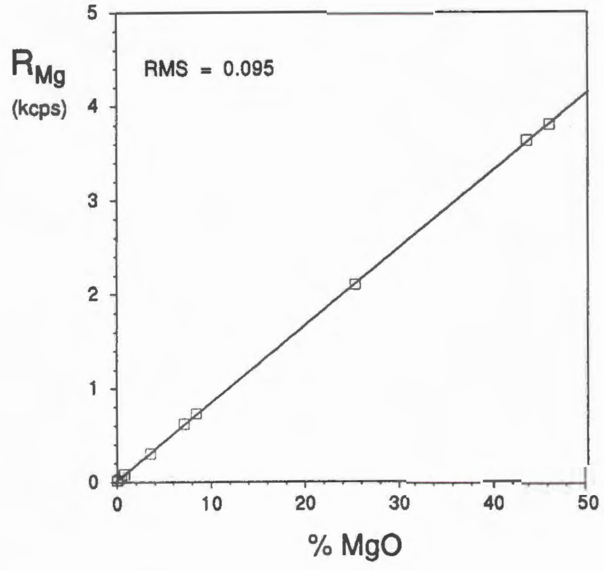


Figure A1.4 Calibration plot for CaO using "Norrish" fusion disks



si2309.gra

Figure A1.5 Calibration plot for SiO_2 using "Norrish" fusion disks.



mg2309.gra

Figure A1.6. Calibration plot for using MgO "Norrish"fusion disks

1.4.2. Trace elements

Trace elements are determined on powder briquettes using a series of x-ray tubes. Analytical conditions are listed in Tables 2 and 3.

Table A1.8. X-ray tubes and tube and x-ray path settings for the determination of trace elements using a Siemens SRS303AS and Philips PW1480 WDXRF spectrometer.

Spectrometer	**Element/line**	**X-ray tube**		**X-ray path**
		Target	**kV - mA**	
SRS303AS	RhKαC	Rh	60 45	Vacuum
SRS303AS	MoKα	Rh	60 45	Vacuum
SRS303AS	NbKα	Rh	60 45	Vacuum
SRS303AS	ZrKα	Rh	60 45	Vacuum
SRS303AS	Y Kα	Rh	60 45	Vacuum
SRS303AS	SrKα	Rh	60 45	Vacuum
SRS303AS	U $L\alpha_1$	Rh	60 45	Vacuum
SRS303AS	RbKα	Rh	60 45	Vacuum
SRS303AS	Th$L\alpha_1$	Rh	60 45	Vacuum
SRS303AS	Pb$L\beta_1$	Rh	60 45	Vacuum
PW1480	ZnKα	Au	60 45	Vacuum
PW1480	CuKα	Au	60 45	Vacuum
PW1480	NiKα	Au	60 45	Vacuum
PW1480	CoKα	W	50 55	Vacuum
PW1480	MnKα	W	50 55	Vacuum
PW1480	CrKα	W	50 55	Vacuum
PW1480	V Kα	W	50 55	Vacuum
PW1480	Ba$L\alpha_1$	Cr	50 55	Vacuum
PW1480	ScKα	Cr	50 55	Vacuum

Table A1.9. Instrumental conditions for determination of trace elements using a Siemens SRS303AS and Philips PW1480 WDXRF spectrometer.

Element /line	Collimator	Crystal	Detector	PHS		Counting time (s)	Background position(s) relative to peak position	Concentration range *
				LWL	UPL			
RhKαC	F	LiF(220)	SC	0.6	1.5	200		
MoKα	F	LiF(200)	SC	0.7	1.7	160	−0.8 +0.65	0 - 5.2
NbKα	F	LiF(200)	SC	0.5	1.6	160		0 - 268
ZrKα	F	LiF(200)	SC	0.5	1.6	160		0 - 1210
Y Kα	F	LiF(200)	SC	0.5	1.6	160	−0.61 +0.54	0 - 143
SrKα	F	LiF(200)	SC	0.5	1.6	160	+0.60	0 - 440
U Lα_1	F	LiF(200)	SC	0.5	1.6	160		0 - 15
RbKα	F	LiF(200)	SC	0.5	1.6	160	+0.53	0 - 530
ThLα_1	F	LiF(200)	SC	0.5	1.6	160		0 - 51
PbLβ_1	F	LiF(200)	SC	0.4	1.4	160	+1.27	0 - 40
ZnKα	F	LiF(220)	FS	20	80	200	−1.08 +4.24	0 - 235
CuKα	F	LiF(220)	FS	20	80	200	+4.44	0 - 227
NiKα	F	LiF(220)	FS	20	80	200	+2.52	0 - 630
CoKα	F	LiF(220)	FL	15	75	200	+1.00	0 - 116
MnKα	F	LiF(220)	FL	15	75	200	−2.30 +4.70	0 - 1700
CrKα	F	LiF(220)	FL	15	75	200	−4.10 +2.90	0 - 465
V Kα	F	LiF(220)	FL	13	67	200	+3.40	0 - 640
BaLα_1	F	LiF(200)	FL	25	75	200	−5.20	0 - 2680
ScKα	F	LiF(200)	FL	25	75	200	−2.78	0 - 54

* = all concentrations expressed as part per million (ppm or mg.kg^{-1})

The RhKα Compton peak is used to determine the mass absorption coefficients of the specimens at the RhKαC wavelength (Figure 5) and the calculated 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 and Sc analyte wavelengths are calculated from major element compositions using the tables of Heinrich (1986). Mass absorption coefficient corrections are 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 are 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.

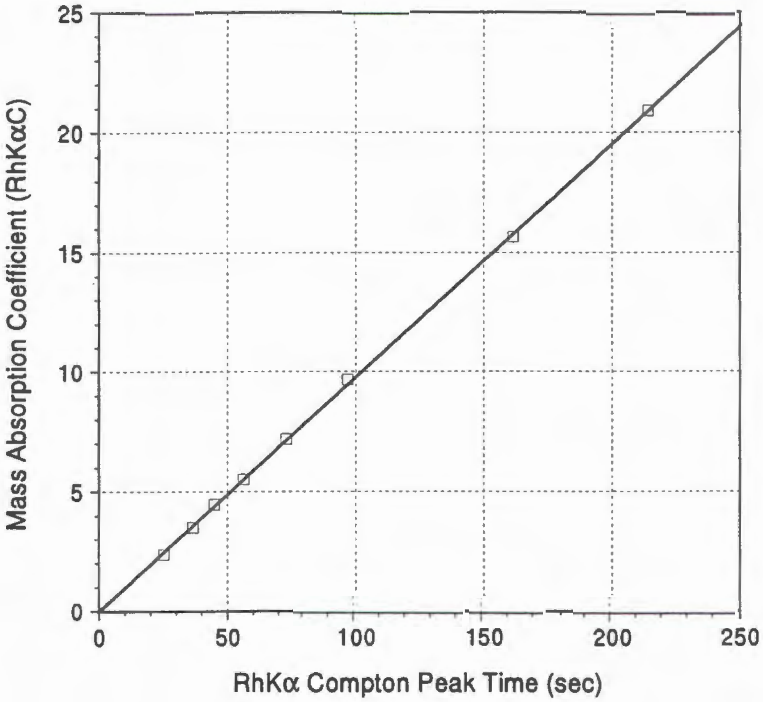


Figure A1.7. Calibration line for determination of mass absorption coefficients at the RhKαC wavelength. RhKαC peak time is the time required to accumulate 400 000 counts on the RhKαC peak using the fixed count method.

Measured intensity data are 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 are calculated using six or more international rock standard reference materials (SRMs) for each element. The one standard deviation ($1\,\sigma$) error due to counting statistics and the lower limit of detection is calculated for each element in each specimen.

Table 4 lists the given and calculated concentrations for selected elements in a number of rock SRMs, which gives an indication of the accuracy of the trace element data. Table 5 lists the one standard deviation counting error and lower limit of detection for each of the elements in an acidic (low Fe, Ca and Mg, high Si) rock and in a mafic (high Fe, Ca and Mg, low Si) rock. Because of the difference in mass absorption coefficients between the two types of specimen the counting error and lower limit of detection will be slightly higher in mafic rock specimens. The two examples given cover the range of mass absorption coefficients found in the majority of geological rock, soil and sediment specimens.

The counting error and lower limit of detection are calculated using the following formulae:

$$1\,\sigma \; error \; (in \; ppm) = Conc \times \frac{\sqrt{\dfrac{I_p}{T_p} + \dfrac{I_b}{T_b}}}{I_n}$$

and $$LLD \; (in \; ppm) = \frac{6}{m}\sqrt{\frac{I_b}{T_{total}}}$$

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} = $T_p + T_b$

N.B. I_b is the calculated background *plus* any corrections for spectral interference, and is equal to $I_p - I_n$.

Table A1.10. Given and calculated trace element data (all values in ppm) for some rock SRMs.

Element	QLO-1		BHVO-1		W-2		STM-1		BIR-1	
	Given	Calc	Given	Calc	Given	Calc	Given	Calc	Given	Calc
Mo	2.6	3.5	1.0	0.8	(0.6	0.5	5.2	3.1	(0.5	<0.8
Nb	10	11	19	19	7.9	7.4	268	267	0.6	0.9
Zr	185	190	179	181	94	95	1210	1220	16	19
Y	24	25	28	28	24	23	46	47	16	17
Sr	336	329	403	395	194	195	700	689	108	109
U	1.9	2.3	0.4	<1.6	0.5	<1.2	9.1	8.8	0.01	<1.2
Rb	74	71	11	9.7	20	20	118	114	0.3	<0.6
Th	4.5	4.0	1.1	1.8	2.2	2.7	31	31	0.03	<1.5
Pb	20	20	2.6	3.1	9.3	8.5	18	17	3	3.1
Zn	61	61	105	106	77	79	235	242	71	69
Cu	29	25	136	139	103	108	(4.6	2.1	126	132
Ni	(5.8	1.8	121	127	70	72	(3	1.7	166	170
Co	7.2	7.6	45	44	44	43	0.9	<1.9	51	52
Mn	720	690	1300	1290	1260	1240	1700	1600	1320	1280
Cr	(3.2	3.6	289	312	93	100	(4.3	3.2	382	404
V	54	44	317	314	262	257	(8.7	<1.6	313	306
Ba	1370	1430	139	138	182	191	560	589	7.0	10
Sc	8.9	10.3	31.8	33.9	35	36	0.6	0.5	44	39

(n.n = value given for information only

Table A1.11. Calculated trace element data, 1 σ counting error and lower limit of detection (all values in ppm) for two rock specimens having different mass absorption coefficients.

Element	JR-2			JB-1a		
	Calc	**1 σ**	**LLD**	**Calc**	**1 σ**	**LLD**
Mo	4.1	0.2	0.6	1.8	0.3	0.7
Nb	19	0.1	0.4	28	0.2	0.5
Zr	87	0.1	0.3	152	0.2	0.4
Y	51	0.2	0.6	24	0.2	0.6
Sr	8.2	0.1	0.4	444	0.3	0.5
U	11	0.3	0.9	2.3	0.4	1.2
Rb	303	0.2	0.4	39	0.2	0.6
Th	34	0.4	1.1	9.8	0.5	1.4
Pb	24	0.5	1.3	7.5	0.6	1.8
Zn	28	0.2	0.6	84	0.4	0.9
Cu	1.1	0.3	0.8	55	0.5	1.1
Ni	1.3	0.3	0.8	139	0.7	1.3
Co	<1.2	0.4	1.2	37	0.9	2.3
Mn	878	1.7	1.2	1100	2.0	1.8
Cr	1.6	0.4	1.3	406	1.5	2.0
V	1.7	0.4	1.2	193	1.4	3.0
Ba	28	0.6	1.5	523	1.8	3.3
Sc	6.0	0.2	0.5	26	0.4	0.9

In order to test the quality of the data that were generated by the XRF analysis, correlation coefficients were calculated to determine whether Ca and Sr and K and Rb are significantly correlated. These correlations were performed because it has been empirically determined that theses elements will often be correlated with each other (Willis, 1985 and Krauskopf, 1979). The association between Ca and Sr occurs because these two elements have similar ionic radii, which results in Sr being able to substitute for Ca in a number of minerals. A similarity in ionic radius between Rb and K means that Rb can substitute for k in a number of minerals.

The correlation tests that were performed indicates that Ca and Sr (Figure A1.8) are strongly correlated and that Rb and K (Figure A1.9) are strongly correlated. This result would indicate that the quality of the XRF data is reasonably good.

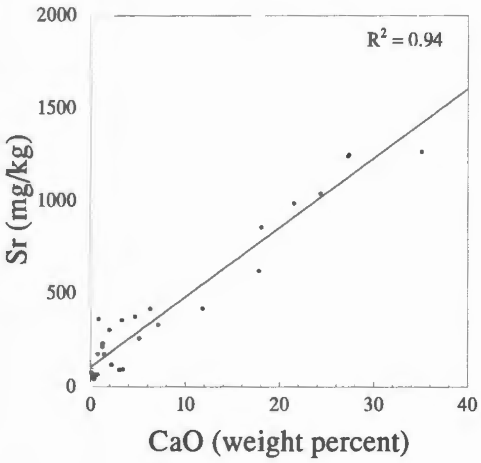


Figure A1.8 Correlation between the concentration of Sr and Ca in the bulk sediment samples.

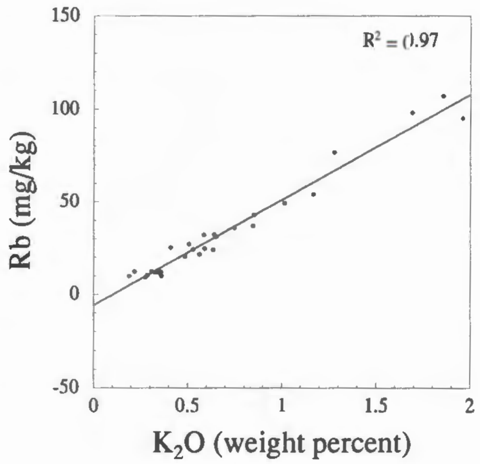


Figure A1.9 Correlation between the concentration of Rb and K in the bulk sediment samples.

APPENDIX 2. DETAILED DESCRIPTION OF ANALYTICAL METHODS

2.1 pH

pH measurement is the determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode.

2.2 Electrical conductivity

Electrical conductivity was measured using a Crisons Micro electrical conductivity meter.

2.3 Alkalinity

Apparatus/reagents:
Hydrochloric acid (HCl), 0.1 *N*.
Automatic potentiometric titrator.

Procedure:
A known aliquot of sample was titrated against hydrochloric acid until an end point of pH 4.5 was reached. The titration was performed using an automatic titration assembly.

2.4 KCl Extractable Acidity

Apparatus/reagents:
0.01 M KCl
Sodium hydroxide (NaOH), 0.01 *M*.
Automatic potentiometric titrator.

Procedure:

1) Weigh out 5g of sample,
2) Add 12.5 ml of KCl (ratio 1:2.5),
3) Shake for 30 mins and then allow to settle for 10 mins,
4) Filter through Whatman's No. 1 filter paper,
5) Titrate filtrate against NaOH, using automatic titration assembly, until an end-point of 8.3 is reached.

2.5 High Performance Ion Chromatography (HPIC)

HPIC is used for the separation and determination of a variety of cations and anions. This is achieved by measuring the conductivity of the solution, or by measuring the intensity of colour complexes formed by the ions to be measured. Ions in a solution are separated using a stationary phase ion exchange resin contained in a column. In-line detection of the ions of interest is carried out. Detection of the common anions and cations was by conductivity with auto- suppression of the eluent.

The analysis was carried out by means of a Dionex conductivity DX300 series suppressed IC system coupled to the AI-450 chromatography software package. A Dionex AG4A guard column was used with a Dionex AS4A-SC separator column for anion determination, while a Dionex CG12A guard column was used with a Dionex CS12A separator column for cation determination.

Ions are moved through an ion exchange column within a mobile phase or eluent. The eluent used to determine anions was a 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3 solution.

Run time was approximately 15 minutes at a flow rate of 1 ml/min for cations and 8 minutes for anions at a flow rate of 2 ml/min.

Sample preparation:

1) Filter samples through 0.2 μm filter paper using Millepore apparatus.
2) Dilute samples until conductivity is less than 100 μS/cm.

2.6 Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)

Free analyte atoms formed in a plasma (temperature = 6000-10 000K) rise to excited electronic states. The atoms then return to the ground state by emission of energy at a characteristic wavelength. The emission signal is proportional to the concentration of the analyte.

The analyses were made on a JOBIN YVON 70C(JY70C) inductively coupled plasma atomic emission spectrometer.

Instrument settings

Power: 1Kw
Pressure - Ar gas: 3.4 bar
R.F.: 27.12 MHz
Flow rate: 2.0 ml/min
Aerosol gas flow: 0.4/min and 0.8/min (Na and K)
Plasma gas flow: 0.1 ml/min
Coolant gas flow: 16 ml/min

2.7 Phosphate determination: the Ascorbic Acid Method

Principles:

Ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form a heteropoly acid, phosphomolybdic acid that is reduced to intensely coloured molybdenum blue by ascorbic acid.

Apparatus:

Turner 340 Spectrophotometer (with a light filter for the range 420-900nm).

Reagents:

1) Potassium antimonyl tartrate solution: 1.3715g $K(SbO)C_4H_4O.1/2H_2O$ was dissolved in 400ml distilled water in a 500-ml volumetric flask and diluted to volume,
2) Ammonium molybdate solution: 20g $(NH_4)_6Mo_6O_{24}.4H_2O$ was dissolved in 500ml distilled water,
3) Ascorbic acid: 0.01*M*: 1.76g ascorbic acid was dissolved in 100ml distilled water,
4) Sulphuric acid, 5*N*: 70ml concentrated H_2SO_4 was diluted with 500ml distilled water,
5) Combined reagent: 50mL sulphuric acid, 5ml potassium antimonyl tartrate, 15ml ammonium molybdate solution and 30ml ascorbic acid solution were mixed together in the order given.
6) Stock phosphate solution: 219.5g of KH_2PO_4 dissolved in 1000ml of water,
7) Standard phosphate solution: 50.0ml stock phosphate solution was diluted to 1000ml with distilled water, 1.00ml = 2.50μg P.

Procedure:

Sample treatment: 25.0ml sample was pipetted into a dry, clean test tube. 4.0ml mixed reagent was added and the resultant solution was mixed thoroughly. After 15 minutes the absorbance of each sample/standard was measured, using reagent blank as the reference solution at a wavelength of 880nm.

Calibration curve preparation: a series of six standards was used to prepare a calibration curve: absorbance was plotted vs phosphate concentration to give a straight line passing through the origin.

The equation for the standard curve was given as:

$$\text{ABS} = 0.624\ (\text{STD P}) + 0.004$$

Calculation:

$$\text{mg P/L} = (\text{mg P (final volume)} * 1000)\ /\ \text{ml sample}$$

2.8 Fluoride by ion selective electrode

Apparatus:

A Corning ion analyzer coupled with a fluoride ion selective electrode and a Calomel reference electrode 255 was used for the determination of F^-.

Reagents:

1) Stock fluoride solution: Dissolve 221.0mg anhydrous sodium fluoride in 1000ml distilled water,
2) Standard fluoride solution: Dilute 100ml stock fluoride solution to 1000ml with distilled water
3) Fluoride buffer: Add 57ml glacial acetic acid, 58g NaCl and 4.0g of cyclohexylenediaminetetraacetic acid to 500 mlof distilled water, and stir to dissolve,
4) NaOH crystals

Procedure:

1) Once the fluoride buffer has been made up, place in a water bath to cool and then slowly add NaOH until a pH of between 5.3 and 5.5 is reached. After attainment of pH dilute to a volume of 1000ml,
2) Prepare a set of standards containing 0.1, 1.0 and 10.0 mg F/ℓ,
3) Pipette sample and standard, using a ratio of 1:1, into a suitable container
4) Analyse with ion analyser

2.9 Organic Carbon: Walkley-Black Method (1935)

Principle:

Organic matter in soil may be oxidised by treatment with a hot mixture of $K_2Cr_2O_7$ and sulphuric acid, according to the equation:

$$2Cr_2O_7^{2-} + 3C + 16H^+ = 4Cr_3^+ + 3CO_2 + 8H_2O$$

After completion of this reaction, the excess dichromate is titrated with iron (II) ammonium sulphate hexahydrate. The reduced dichromate is assumed to be equivalent to the organic C present in the sample, assuming that soil organic matter has an average valence of zero.

Reagents:

1) Potassium dichromate 0.167 mol/l,
2) Concentrated sulphuric acid,
3) Concentrated ortho-phosphoric acid,
4) Iron (II) ammonium sulphate (0.5 mol/l),
5) Indicator: barium diphenylamine sulphonate.

Method:

1) Grind sediments to pass through a 0.35mm sieve, using a porcelain mortar and pestle.
2) To 0.5g of ground sediments, add 10ml $K_2Cr_2O_7$ solution, swirl gently to disperse the sediments in suspension,
3) Rapidly add 20ml of concentrated sulphuric acid, and then swirl the flask until the sediments and reagents have mixed,
4) Allow flask to cool on a protected surface for 30 min, and then add 150ml deionised water and 10ml concentrated ortho-phosphoric acid,
5) Add 1cm^3 indicator and titrate the excess dichromate with iron (II) ammonium sulphate solution. The colour change involved at the end-point is dark violet to green.

Calculations:

Concentration of $Fe(NH_4)_2(SO_4)_2$ mol dm^{-3} =

$$\frac{10ml\ K_2Cr_2O_7\ X\ 0.167\ X\ 6}{ml\ Fe(NH_4)_2(SO_4)_2}$$

Organic carbon % =

$$\frac{ml\ Fe(NH_4)_2(SO_4)_2\ blank\ -\ ml\ Fe(NH_4)_2(SO_4)_2\ sample\ X\ 0.3\ X\ M\ X\ f}{soil\ mass}$$

where f = 1.3 and M = concentration of $Fe(NH_4)_2(SO_4)_2$ in mol.l

2.10 Carbonate content (Karbonat-bombe, Birch (1922))

Procedure:

1) Determination of calibration curve

   1.1. One gram of $CaCO_3$ was weighed out (2 dec places) into a plexiglass cylinder of the karbonat-bombe.

   1.2. 5ml concentrated HCl was placed into the small plastic bucket and lowered carefully into the plexiglass cylinder without spilling.

   1.3. The lid was tightly screwed onto the gasket, and the pressure release screw was closed securely. The sample was immersed in the acid by tipping the plexiglass cylinder and shaking gently to ensure all the powder came in contact with the acid.

   1.4. The manometer was read when effervescence had ceased.

   1.5. An aliquot of 0.5 g was used to provide a second point on the calibration curve.

2) Sample analysis

   Steps 1.1 to 1.4 are repeated with an accurately weighed sample of dried and crushed powder.

2.11 Clay Content (Pipette method)

Principle:

Soil particles are discrete units comprising the solid phases of the soil. They generally cluster together as aggregates, but can be separated from each other by chemical and physical means. Once aggregates have been separated, the soil particles can be separated from each other by pipetting of fractions that have known sedimentation times (based on Stockes law).

Apparatus:

1) 1 l, glass sedimentation cylinders,
2) Hand stirrer consisting of a 50cm long brass rod joined to the centre of a circular brass plate 1.5mm thick,
3) 25 ml Lowy pipette and stand.

Reagents:

1) Calogen dispersing solution: Dissolve 35.7g sodium hexametaphosphate and 7.94g sodium carbonate in 1l deionised water,

Procedure:

1) Add 10ml of Calogen dispersing solution to pretreated oven dried soil, and transfer quantitatively to a 250ml centrifuge bottle. make up to volume of ± 150ml with deionised water and shake overnight,
2) Fill sedimentation cylinder to the 1ℓ mark. Cover cylinder with watch glass and allow to equilibrate with the ambient temperature.
3) Stir suspension thoroughly with hand stirrer for 30 seconds. Note time when stirring terminated.
4) After 5 hours and 30 mins lower the pipette to a depth of 7 cm and suction of 25ml and then discharge the sample into a tarred evaporating dish.

Calculations:

Percent clay (%) =

$$\frac{(A - B) X 1000 X 100)}{C X 25}$$

where A = mass (g) of pipetted clay

B = mass (g) of correction of dispersing agent

C = mass (g) of pretreated oven dried sample

2.12 Separation of clay fraction

Reagents:

1) 30 % hydrogen peroxide,
2) 1 *M* NaOH,
3) Dilute Na_2CO_3 solution (pH 10)
4) 1*M* HCl
5) NaCl crystals

Procedure:

1) Approximately 50g of sample is weighed into 500ml beakers. 25ml of H_2O_2 is added. After initial effervescence has subsided, add further aliquots of H_2O_2 until effervesce has completely ceased,
2) Quantitatively transfer sample to 250ml centrifuge bottle, fill to within 3cm of top and adjust pH, using NaOH, to a pH of ± 9.
3) Shake slurry for 4 hours,
4) Transfer contents to a 2l plastic container and fill with Na_2CO_3 solution. Allow to stand for 16 hours,
5) Siphon supernatant to a depth of 18cm, collecting the supernatant in a 5l bucket,
6) Repeat steps 4 and 5 until a clear supernatant is recovered,
7) Adjust pH of supernatant to $> 5 < 7$ with a few drops of 1*M* HCl, and add NaCl to promote flocculation,
8) After flocculation collect flocculant and concentrate by centrifugation,
9) Dialyse sample in fresh water for 48 hours and in deionised water for 48 hours. Once Cl^- can no longer be detected with silver nitrate added to the dialysing solution, concentrate clay by centrifugation,
10) Pipette 2 ml of clay solution onto a glass slide.

2.13 X-Ray Diffraction

Principles:

When a given crystalline substance is irradiated by monochromatic X-rays, a pattern is obtained which is characteristic for that material. In this way any crystalline compound may be identified. The sample usually consists of small crystallites (ground solids or particles in suspension), whose random orientation ensures that every possible reflection plane is presented parallel to the surface by some crystallites.

Procedure:

Scan over a two theta range of 4-80 degrees (X ray tube running at 25mA, 40kV).

2.14 X-ray Fluorescence Spectrometry (XRF)

Characteristic X-ray spectra are produced by irradiation of a sample with a beam of sufficiently short wavelength X-rays. Interaction of the primary electrons with atoms of the sample causes excitation of the atom with ejection orbital electrons. During the subsequent electronic rearrangement by which the atoms de-excite to the ground state, fluorescence X-rays of energy characteristic of that element are emitted. The emission intensity of the characteristic radiation is measured with a suitable X-ray spectrometer and compared with that from a standard sample (Potts, 1992).

A wavelength dispersive spectrometer consists of five principal components: a diffracting crystal, an x-ray detector (gas flow proportional or scintillation counter or both), beam defining collimators, goniometer and an X-ray tube. The goniometer is a device which maintains the correct angular and spatial relationship between the components.

A portion of the scattered fluorescence is collimated by the entrance slit of the goniometer and directed onto the plane surface of the analysing crystal. The spectral lines reflected according to the Bragg relation, pass through an auxiliary collimator to the detector where the energy of the x-ray quanta is converted into electrical impulses (counts). The primary slit, analyzer crystal and secondary slit are placed on the focal circle so that Bragg's law is always satisfied as the goniometer is rotated (Potts, 1992).

A sample is irradiated with an unfiltered beam of primary X-rays. This causes the elements present to emit characteristic fluorescence lines. A portion of the emitted fluorescence is collimated by the entrance slit of a goniometer and directed onto a plane surface of the analysing crystal.

A Philips X'Unique II (PW 1480) wavelength dispersive XRF spectrometer was used in the analyses.

Samples were prepared by first being air dried and then milled for approximately three minutes in a carbon steel Siebtechnik swing mill, reducing grain size to below 50μm diameter. 6g of the powdered sample was then mixed with 4% mowiol solution using a mortar and pestle, before being mechanically pressed into briquette form under a pressure of ±10t. The resulting briquettes were then placed under vacuum for 1 hour in order to desiccate them and to prevent fracture from occurring in the XRF machine (under vacuum conditions).

APPENDIX 3: RESULTS PERTAINING TO THE WATER SAMPLES COLLECTED FROM THE DRAINAGE SYSTEM.

Table A3.1: Ratio of sodium to chloride at the different sample sites.

Sample #	Na-Cl
1	0.65
2	0.74
3	0.43
4	0.44
5	0.44
6	0.61
7	0.53
8	0.65
9	0.51
10	0.52
11	0.52
12	0.59
13	0.50
14	0.59
15	0.75
16	0.72
17	0.50

Table A3.2. Selected results of the analysis of groundwater sampled on site.

	ABH5b	ABH6	KFBH3	KFBH8	FBH2
Potassium as K mg/ℓ	14	230	470	20	120
Sodium as Na mg/ℓ	590	87	110	1500	400
Calcium as Ca mg/ℓ	260	850	340	560	220
Magnesium as Mg mg/ℓ	57	89	140	1100	130
Ammonium as N mg/ℓ	0.4	49	180	2.5	6.9
Sulphate as SO_4 mg/ℓ	680	70000	940	1500	330
Chloride as Cl mg/ℓ	880	500	440	5400	780
Alkalinity as $CaCO_3$ mg/ℓ	250		30	120	120
Nitrate as N mg/ℓ	<0.1	1600	320	5	130
Phosphate as P mg/ℓ	<0.1	91	<0.1	<0.1	<0.1
Nitrite as N mg/ℓ	<0.1	27	0.6	0.3	0.3
Iron as Fe mg/ℓ		10000			10
Fluoride as F mg/ℓ (Field)	0.8	0.3	2.9	1	13
Conductivity mS/M (Lab)	390	12000	600	1500	400
pH (Lab)	7.7	0.9	6.4	6.3	6.4
Saturation pH (pH 20 °C)	6.8		7.6	6.9	7.3
Total Hardness as $CaCO_3$ mg/ℓ	890	2500	1500	6000	1100
% Difference	0.2	0.05	4.8	0.1	3.7
CATIONS meq/l	44	1600	58	190	43
ANIONS meq/l	44	1600	56	190	41
Cadmium as Cd mg/ℓ	<0.1	0.01	<0.01	<0.1	<0.1
Chromium as Cr mg/ℓ	<0.05	5.5	<0.05	<0.05	<0.05
Copper as Cu mg/ℓ	<0.05	<0.05	0.16	<0.05	<0.05
Iron as Fe mg/ℓ	0.06	10000	7.7	0.6	13
Lead as Pb mg/ℓ	<0.05	4.1		0.06	<0.05
Zinc as Zn mg/ℓ			0.3	<0.05	0.3
Sulphides as S mg/ℓ	0.07	3.8			
Mercury as Hg mg/ℓ	<0.002	0.3		<0.002	<0.002
Boron as B mg/ℓ	0.5	0.8		<0.2	<0.2
Nickel as Ni mg/ℓ	<0.05	2.2		0.21	0.07
Manganese as Mn mg/ℓ	0.21	11		1.0	1.0
Acidity as $CaCO_3$ mg/ℓ		58000		0.03	
Arsenic as As mg/ℓ	0.03	0.03		0.026	0.005
Cyanide as CN mg/ℓ	<0.05			<0.05	<0.05
Molybdenum as Mo mg/ℓ					
Aluminium as Al mg/ℓ	0.7			0.5	3.0

ABH5 = Acids area ABH 6 = Sampled next to the main drain KFBH3 = Downgradient of the factory
KFBH8 = Kynoch Fertilizers FBH2 = Downgradient and southeast of Kynoch Fertilizers

Table A3.3 Saturation indices of minerals that have the potential to precipitate from the water collected at different locations in the Main Drain (*ie.* SI > 1). Structural formula given in Table A3.4.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Ferrihydrite	2.1	2.4		2.6	2.4	0.9			1.3		1.3	2.1	1.4	1.7			
Goethite	6.5	6.7	2.5	7	6.8	5.3			5.7		5.7	6.5	5.8	6			
Fe(OH)$_2$.7Cl	6.9	7.2		7.7	7.6	6.5			6.7		6.8	6.9	6.6	6.9			
Maghemite	7.6	8.1		8.7	8.2	5.2			5.9		6.1	7.6	6.2	6.8			
Strengite	2.8		3.3	0.5	0.9	3.4			3.5					2.8			
Magferrite	7.4	8.7		10.5	9.8	3.5			4.9		5	7.8	4.9	6			
Lepidocrocite	5.6	5.9	1.7	6.2	5.9	4.4			4.8		4.9	5.6	4.9	5.2			
Hematite		18.5	10.1	19.1	18.6	15.6			16.3		16.5		16.6	17.2			
Alunite			2.6			4.1				0.2							
Diaspore			0.2			2.8	1.1		1.6	1.7	2.1						
Jarosite-Na			1	1.5	2.4	3.1			2.7		2.8	0.2	1.5	2.13			
Jarosite-K			4	3.7	4.1	5.8			5.4		5.6		4.2	4.8			
Jarosite-H			0.2			0.2											
Kaolinite			0.1			5.3	2		2.6	2.7	3.37						
MnPO$_4$			1.8			2.9	4	3.6	3.1	3.3	3.4		2.3	2.3		2.3	
Na-Nontronite			8.4			15.2			15.1			15.2					
K-Nontronite			9.2			15.9			15.9			15.9					

Table A3.3 Saturation indices of minerals that have the potential to precipitate from the water collected at different locations in the Main Drain (*ie.* SI > 1). Structural formula given in Table A3.4.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Ca-Nontronite			15			21.7			21.7			21.7					
Mg-Nontronite			14.7			21.4			21.4			21.4					
Boehmite						1.1					0.3						
Gibbsite						1					0.2						
Halloysite						2					0.1						
Leonhardite						6.4	1		1.8		3.2						
Muscovite						6.5	2		2.7		3.9						
Pyrophyllite						4.2	1.1		1.3		1.9						
Montmorillonite						3.4					1.8						
Hydroxyapatite	3.6	2.4		5.9	5.1	1.8	5.7	5.9	4.3	4.5	5.2		1.6	11	1.6	2.6	
Fluorite						0.7	0.6	0.6	0.2	0.12							
Carbonate-fluorapatite	9.3	6.6		17.5	15.9	10.7	17.9	18.1	14.7	15.2	16.7				9.4	10.6	
Aragonite				0.2													
Calcite				0.4													
Dolomite				0.6													

Table A3.4. Structural formulae of the minerals that have the potential to precipitate from solution.

Mineral name	Structural Formula
Ferrihydrite	α-FeOOH
Goethite	FeOOH
Maghemite	γ-Fe_2O_3
Strengite	$FePO_4.H_2O$
Lepidocrocite	$Fe_2O_3.H_2O$
Hematite	α-Fe_2O_3
Alunite	$(K,Na)_2O.3Al_2O_3.4SO_3.6H_2O$
Diaspore	AlOOH
Jarosite-Na	$Na_2O.3Fe_2O_3.4SO_3.6H_2O$
Jarosite-K	$K_2O.3Fe_2O_3.4SO_3.6H_2O$
Jarosite-H	$H_2O.3Fe_2O_3.4SO_3.6H_2O$
Kaolinite	$Al_2O_3.2SiO_2.2H_2O$
Na-Nontronite	$NaO.3Fe_2O_3.10SiO_2.9H_2O$
K-Nontronite	$KO.3Fe_2O_3.10SiO_2.9H_2O$
Ca-Nontronite	$CaO.3Fe_2OO_3.10SiO_2.9H_2O$
Boehmite	α-$Al_2O.H_2O$
Gibbsite	$Al_2O_3.H_2O$
Halloysite	$Al_2O_3.2SiO_2.4H_2O$
Muscovite	$H_2KAl_3Si_3O_2$
Pyrophyllite	$Al_2O_3.4SiO.H_2O$
Montmorillonite	$MgO.Al_2O_3.5Si_2.nH_2O$
Hydroxyapatite	$10Ca.3P_2O_5.H_2O$
Fluorite	CaF_2
Carbonate-fluorapatite	$(Ca,Mg,Na)_{10}.[(P,C)O_4]_6(OH,F)_2$
Aragonite	$CaCO_3.2H_2O$
Calcite	$CaCO_3$
Dolomite	$(Mg,Ca)CO_3$

APPENDIX 4. DETAILED TABLES OF RESULTS PERTAINING TO THE SEDIMENT SAMPLES

Table A4.1a. Trace and Major elements, detected by XRF, in the top layer of the sediments collected from the drainage system.

		1T	2T	3T	4T	5T	6T	8T	9T	10T	11T	12T	13T	14T	15T	16T	17T
Trace Elements (mg/kg)	Zn	39	4.6	48	36	20	110	61	32	94	40	120	550	150	78	130	4.8
	Cu	10	3.9	55	23	11	85	110	26	51	41	160	320	44	240	210	4.4
	Ni	19	2.3	19	15	12	23	12	16	21	18	28	42	17	13	19	3.8
	Co	16	bdl*	5.9	3.9	2.9	8.0	3.9	3.9	7.5	4.0	7.9	33	3.9	bdl	8.1	bdl
	Mn	310	35	120	110	94	120	180	110	120	90	130	690	110	65	110	33
	Cr	55	28	90	59	43	100	61	57	110	81	130	81	48	190	230	21
	V	77	bdl	110	33	19	120	24	26	34	22	60	33	15	66	90	6.6
	Mo	2.4	1.7	3.2	3.1	2.7	3.5	5.5	5.7	4.1	3.8	5.9	4.6	2.8	22	67	0.15
	Y	25	5.3	32	16	11	40	22	10	10	9.2	21	26	8.0	14	16	9.4
	Rb	54	12	110	32	25	77	10	31	12	12	25	20	12	22	32	9.2
	Nb	5.5	1.3	16	7.2	6.0	13	7.1	7.6	5.4	5.0	12	7.8	2.4	6.0	7.7	3.5
	Sr	330	1300	67	91	67	210	380	53	420	260	310	620	990	180	230	1000
	Th	7.5	3.3	24	8.1	5.1	37	11	5.2	6.5	5.9	12	8.0	3.5	8.4	13	2.8
	Zr	170	30	240	310	320	120	180	210	82	130	350	190	100	100	120	280
	U	1.3	1.1	5.6	0.95	0.87	8.0	3.9	1.7	2.9	0.69	4.7	3.8	1.2	5.5	5.5	0.91
	Pb	26	5.3	60	36	11	76	33	170	320	260	1300	1400	16	410	530	5.9
Major Elements (Weight percent)	Fe_2O_3	6.5	0.50	9.3	2.7	1.3	13	2.6	2.7	2.6	1.9	3.9	7.0	2.6	23	30	0.50
	TiO_2	0.30	0.06	0.88	0.30	0.16	0.70	0.36	0.31	0.22	0.19	0.52	0.32	0.11	0.37	0.46	0.14
	BaO	0.03	0.01	0.05	0.01	0.01	0.05	0.02	0.02	0.05	0.03	0.11	1.4	0.01	0.07	0.07	0.01
	CaO	7.1	27	0.43	3.0	0.69	1.3	4.7	0.37	6.3	5.1	1.9	18	22	1.4	1.3	24
	K_2O	1.2	0.36	1.9	0.59	0.41	1.3	0.36	0.65	0.31	0.35	0.59	0.49	0.33	0.56	0.64	0.28
	Cl	0.01	0.23	0.09	0.06	0.31	0.19	0.27	0.02	0.11	0.08	0.19	0.09	0.05	0.29	0.51	0.05
	S	0.07	0.16	0.12	0.06	0.08	0.18	0.52	0.06	4.3	5.4	2.4	2.5	0.17	0.52	0.92	0.16
	P_2O_5	0.17	0.11	2.4	0.10	0.22	6.1	2.4	0.21	0.48	0.36	1.2	1.1	1.1	9.4	10	0.13
	SiO_2	65	44	54	76	61	36	68	87	52	59	51	31	46	23	21	45
	Al_3O_2	6.6	0.87	18	6.2	2.9	19	3.5	3.7	4.2	2.9	8.3	6.1	1.8	6.0	7.3	0.63
	MgO	1.2	1.3	1.0	0.80	0.67	0.96	0.34	0.39	0.39	0.20	0.33	0.50	0.96	0.48	0.66	0.86
	Na_2O	0.48	0.53	0.25	0.26	0.27	0.27	0.43	0.26	0.22	0.19	0.19	0.26	0.35	0.19	0.26	0.36

*: Indicates that analyte concentration is below detection limits

Table A4.1b. Trace and Major elements, detected by XRF, in the bottom layer of the sediments collected from the drainage system.

		1B	2B	3B	4B	6B	7B	9B	11B	12B	13B	15B	17B
Trace Elements (mg/kg)	Zn	49	40	18	27	43	13	55	150	160	570	78	15
	Cu	13	15	47	19	69	20	24	180	190	1900	270	16
	Ni	28	13	12	14	23	17	13	2200	2300	43	17	6.3
	Co	30	4.9	3.3	2.8	7.0	bdl*	bdl	15	14	29	4.6	bdl
	Mn	540	130	86	100	120	120	100	790	810	1000	84	48
	Cr	73	56	63	52	100	59	50	170	160	32	160	30
	V	120	21	55	23	100	23	24	110	110	bdl	96	7.1
	Mo	2.8	3.7	9.4	3.7	4.5	6.5	3.3	10	11	2.0	8.2	2.1
	Y	42	11	18	15	28	8.2	14	23	25	19	24	6.4
	Rb	95	24	49	27	98	9.9	24	36	37	12	43	10
	Nb	8.1	4.3	13	6.4	16	3.4	4.8	12	12	3.9	8.0	2.8
	Sr	120	860	44	94	77	62	420	360	360	1300	180	1200
	Th	12	5.7	16	6.1	23	4.8	6.2	17	18	1.9	12	2.6
	Zr	140	110	360	330	200	100	170	0.94	230	78	170	78
	U	2.7	bdl	4.3	1.9	6.3	0.22	4.4	1.1	8.2	1.1	4.8	1.8
	Pb	37		49	27	71	18	150	2.6	2700	1000	340	22
Major Elements (Weight percent)	Fe_2O_3	10	2.0	4.0	2.1	10	1.9	2.5	8.2	19.7	7.3	20	0.70
	TiO_2	0.43	0.19	0.57	0.26	0.87	0.15	0.20	0.73	0.48	0.13	0.49	0.09
	BaO	0.05	0.01	0.04	0.01	0.05	0.03	0.01	0.23	0.07	4.5	0.08	0.01
	CaO	2.2	18	0.34	3.4	0.06	0.24	12	3.3	0.82	35	0.75	27
	K_2O	1.9	0.64	1.0	0.51	1.7	0.19	0.53	0.75	0.85	0.22	0.85	0.29
	Cl	0.004	0.30	0.06	0.02	0.23	0.07	0.01	0.16	0.41	0.04	0.28	0.04
	S	0.04	0.45	0.11	0.05	0.18	0.04	0.08	1.8	0.39	2.9	0.36	0.19
	P_2O_5	0.14	0.15	1.4	0.08	2.1	0.50	0.27	1.2	7.9	0.52	8.0	0.29
	SiO_2	67	52	74	78	51	88	64	41	29	13	28	43
	Al_2O_3	11	3.3	6.9	4.9	18	1.3	3.8	11	10	3.1	10	1.0
	MgO	1.8	1.2	0.49	0.63	0.95	0.12	0.81	0.48	0.65	0.42	0.63	1.2
	Na_2O	0.52	0.60	0.24	0.22	0.31	0.09	0.26	0.15	0.24	0.05	0.20	0.38

*: Indicates that analyte concentration is below detection limits

Table A4.3. pH of sediments prior to oxidation and after oxidation.

Sample	Initial pH	Final pH
3B	4.82	3.09
4B	7.65	5.94
5B	5.58	3.65
6B	3.79	3.14
8B	6.32	4.15
9B	7.64	7.86
10W	7.18	7.58
11B	2.65	1.17
12B	3.81	1.53
13B	7.39	7.28
15B	3.95	2.98
16W	4.80	2.78