ASSESSMENT OF LONG-TERM AIR POLLUTION IMPACTS ON SOIL PROPERTIES IN THE VICINITY OF ARNOT POWER STATION ON THE SOUTH AFRICAN HIGHVELD

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ABSTRACT

Atmospheric pollution on the South African highveld is perceived as a concern because of the combination of heavy industry and climatic features that prevail in the region. The frequent occurrence of surface inversions (80 - 90 % of days in the winter months), permits the accumulation of pollutants near ground level. Although industrial stacks, and those of power stations in particular, are generally able to emit gaseous and particulate pollutants above the boundary layer, looping and fumigation of plumes may occur under convective conditions. Under such circumstances, the concentration of pollutants at ground level may be high, especially within 4 km of the stack.

Since considerable damage to European and North American ecosystems has occurred as a result of atmospheric pollution, concerns were first raised in a report by Tyson, Kruger and Louw in 1988, that similar effects may be taking place on the eastern highveld region of South Africa. The current study was prompted in direct response to these concerns. The first major objective was to establish long-term monitoring sites whereby changes in the pedosphere in response to atmospheric inputs could be detected. The second objective was to characterise the soil collection and to determine whether any impacts are detectable at this early stage.

Arnot power station was selected as the focal point of the study as it is a base-load power station, is the most distant from the industrial centres of Witbank, Middelburg and Gauteng and has been in operation for over twenty years. Fifteen sampling sites located in an arc ranging ENE to SE downwind of the power station were selected. Both topsoil and subsoil were sampled at each site. Details of geographical co-ordinates and site features were noted to enable reproducible resampling. Sampling took place in August 1996, but three sites were visited again in October and resampled to test the reproducibility of sampling. Although not statistically comparable, the soils of each site showed similar results for key analyses, which included EC, pH, organic carbon, and acid neutralising capacity. However, one of these three soils showed almost a doubling of anion concentrations in saturated paste extracts (e.g. sulphate concentration rose from 19.8 to 42.8 $mg.L^{-1}$), with a concomitant rise in EC (144 $\mu S.cm^{-1}$ to 210 $\mu S.cm^{-1}$). These preliminary results indicate the need for a more stringent test of the sampling protocol in which within-site variability and sampling variability are evaluated.

The accurate determination of key variables such as sulphate is pivotal to the value of long-term monitoring. The determination of phosphate-extractable sulphate was investigated using two techniques - turbidimetry and ion chromatography. Turbidimetry is widely used, but is acknowledged to be inaccurate because of interference from the phosphate extractant. The application of ion chromatography represents a novel approach to the determination of phosphate-extractable sulphate. The high phosphate concentration required to displace sulphate must be diluted in order to avoid overloading the ion exchange column with the assumed result that the sulphate component is diluted to levels below detection. However, ion chromatography is sufficiently sensitive to permit the detection of low sulphate concentrations (<0.5 $mg.L^{-1}$). The sulphate concentrations obtained by turbidimetry were generally

underestimated compared with those obtained by ion chromatography. In some soils turbidimetric analysis recorded no phosphate-extractable sulphate despite the fact that water-soluble sulphate was present. Water-soluble sulphate determined by both turbidimetry and ion chromatography gave comparable sulphate estimates. The findings of the current study suggest that ion chromatography may prove a viable and more accurate alternative to turbidimetry for the determination of phosphate-extractable sulphate.

The soil collection was described in terms of pH in water, KCl and K_2SO_4. Ca and Mg were extracted in 1 M KCl and determined by atomic absorption spectrometry, while extractable acidity was determined by potentiometric titration. Acid neutralizing capacity (ANC) was estimated by pH measurement of a soil suspension in an acetate buffer solution which correlates well with ANC estimated by serial incubation with HCl. Organic carbon was determined by wet oxidation, particle size distribution by sedimentation using the hydrometer method, and minerals in the sand, silt and clay fractions by X-ray diffractometry. Oxides of iron, aluminium and manganese were determined using citrate-bicarbonate-dithionite extraction. Major and trace elements in the bulk soil were determined by wavelength dispersive X-ray fluorescence spectrometry.

With one exception the soils are generally acidic (pH in water ranging between 5 and 6.3) and dominated by kaolinite in the clay fraction. The exception, a black clay soil, measured pH(water) of 7.1, is smectite-rich and represents a subsoil derived from doleritic parent material. Extractable acidity of all the soils ranged from 0.2 to 10.6 $mmol_c.kg^{-1}$ and acid saturation between 0.07 and 52 %. The soils are either sandy loams, loamy sands or sandy clays. The highest clay content (30%) was recorded for the black clay soil. The soils are dominated by negative charge. Citrate-bicarbonate-dithionite extractable Fe and Al range from 0.3 to 2.7 % and 0.06 to 0.37 % respectively. An index of sulphate retention was calculated using the expression [kaolinite content + 5(Fe content) - 10(organic carbon content)] which not only separates topsoils from subsoils but exhibits a significant linear relationship with phosphate-extractable sulphate for the subsoils when considered as a separate group.

No evidence of changes in concentration with distance from the power station was found for any of the trace elements, major elements or soil acidity parameters. However, water-extractable sulphate showed slightly elevated concentrations in the topsoils (13.6 to 15.4 $mg.kg^{-1}$) within 4-6 km of the power station, declining to 4.7 to 9.8 $mg.kg^{-1}$ at a 20 km distance from the power station. This incipient gradient should be re-examined with a greater sampling density to establish the worth of regular monitoring of long-term changes.

The relationship between organic carbon and total sulphur also revealed an apparently higher background concentration of inorganic sulphur when compared to soils from regions relatively unaffected by atmospheric pollution. Whether this finding is attributable to the parent material or to the atmospheric deposition of sulphur compounds is another area of research requiring more detailed investigation.

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INTRODUCTION

Concerns about atmospheric pollution on the South African highveld were raised in the landmark report by Tyson *et al.* in 1988. The eastern highveld region is rich in coal seams which fuel power stations providing 72 % of South Africa's primary energy source. Industries such as ferro-alloy smelters, petrochemical works and foundries also rely on coal to meet their energy and raw material requirements. Tyson *et al.* (1988) highlighted concerns that the concentration of heavy industry and the unique climate in this region promote the accumulation of atmospheric pollutants.

Although there may be considerable debate as to the exact mechanisms involved (Sverdrup *et al.*, 1992) there is little doubt that air pollution from smelters, power stations and other industries has contributed to the acidification of soils and waters in industrialised regions. In particular, Scandinavia and Central European countries have borne the brunt of poor atmospheric pollution control. In the 1920s, the effects of anthropogenic acidification were first noted in freshwater ecosystems of Southern Norway - where both fish diversity and the yield of salmonid fishes declined. Although acidification steadily increased it was only in the period from 1950 to 1980 that large scale deterioration of aquatic environments became apparent (Brodin and Kuylenstierna, 1992). The decline of coniferous forests in the mountainous regions of Germany, Poland and Czechoslovakia was believed to be caused by soil acidification and high airborne concentrations of sulphur dioxide and ozone. Recent forest health surveys have recorded symptoms such as crown thinning, needle loss, and needle yellowing in the Nordic countries - symptoms which parallel those found before the widespread forest decline in Central Europe (Sverdrup *et al.*, 1992).

In South Africa the effects of atmospheric pollution on human health, soils, surface waters, forests, agricultural crops and the materials used for buildings and other structures have received research attention (Scholes *et al.*, 1996; Kempster *et al.*, 1996; Fey *et al.*, 1996; Gnoinski *et al.*, 1996 and Terblanche *et al.*, 1996). It is the European and North American experience that forested ecosystems are most affected by atmospheric deposition, yet in South Africa, there is no conclusive evidence of tree damage attributable to atmospheric deposition (Scholes *et al.*, 1996). Reuss and Johnson (1986) did warn, however, that the effects of acidification may not be apparent in short- to medium-term experiments, but that long-term consequences are nevertheless likely.

In Europe, international co-operation to manage atmospheric pollutants has brought about substantial reductions in the emissions of pollutants such as sulphur dioxide. Although acidification from SO_2 is no longer as threatening, other pollutants such as ozone and nitrogen compounds are receiving greater attention. In addition, there is growing concern over the impacts which industrial growth in developing countries of the Far East and Africa will have on environmental resources (Yagishita, 1995; Kuylenstierna *et al.*, 1995).

The commitment by Eskom, the major electricity generator in South Africa, to produce the cheapest electricity in the world, has raised the question of how realistic the price of electricity is, since the wide range of external costs to society have not fully been taken into account. Van Horen (1996) has attempted to identify some of these costs but often found that insufficient information hampered his efforts. One such arena where more information was required was the valuation of the impacts caused by acidification through atmospheric pollution. At a recent international workshop, the need for further research in South Africa was considered "of paramount importance if the ecological damage now recognised in North America and Europe is to be avoided" (Bell, 1996).

The power generation industry has a brief history in South Africa and the landscape has consequently not been exposed to high levels of atmospheric pollution for more than about thirty years. Indubitably, impacts such as those apparent in the Northern hemisphere are still possible in South Africa. Acknowledging that time delays in soil responses may be operative, it would be valuable to establish baseline data against which changes in soil chemistry can be assessed.

The recognition of the need for more information provided the impetus for the current study. This project seeks to establish a baseline data set against which long-term changes can be compared. The study site selected is located on grassland so that the acidifying effects of agricultural harvesting or afforestation are minimal if not absent. Owing to the prevailing climatic conditions on the highveld, atmospheric deposition events may be most intense in the near-field of power stations. The study sites were established along an hypothesized deposition gradient since spatial comparisons along the gradient may allow some early inferences to made about possible impacts. Finally, some of the parameters determining the sulphate retention ability of soil will be investigated.

The broad aims outlined above can be crystallised into four key questions:

Is the sampling of baseline monitoring sites repeatable?
Are the analytical methods employed valid and repeatable ?
Is there an observable soil acidification gradient in the vicinity of an "acid source"?
Does soil sulphur, or some labile fraction of soil sulphate, decrease with distance from a power station ?

By answering some or all of these questions, a start will be made towards assessing the impacts of atmospheric pollution on the highveld. If no impacts are apparent, the data will in any event constitute baseline information for future studies.

CHAPTER 1

AIR POLLUTION IMPACTS ON SOIL CHEMICAL PROPERTIES - A LITERATURE REVIEW

1.1 Introduction

The deposition of air pollutants on the soil gives cause for concern because of the possible impact on agricultural productivity and water quality. The eastern highveld was identified by Tyson *et al.* (1988) as an area of special concern because of the combination of heavy industry and climatic conditions which promote the accumulation of atmospheric pollutants. The fate of these pollutants rests on atmospheric processes which will determine whether the pollutants are dispersed or deposited. The link between atmosphere and pedosphere is therefore the focus of this chapter.

1.2 The climate of the southern sub-continent

The emission of primary industrial pollutants is relatively constant throughout the year. Consequently it is the meteorological conditions in the region that control the concentration of secondary pollutants such as sulphate. Parameters such as temperature, humidity, hours of sunshine and wind are all determinants of secondary pollutant formation, transportation and dispersion (Held *et al.*, 1996a). Some background information on key climate factors will be presented in order to facilitate an understanding of the potential extent and impacts of air pollution in the highveld region.

1.2.1 General atmospheric circulation

An anticyclone is a system of winds rotating outwards from an area of high barometric pressure which results in fine stable weather. In general, the atmospheric circulation over southern Africa is anticyclonic above 700 hPa. The frequency of the anticylonic circulations reaches a maximum in the winter - occurring on 65 % of days or more. The stable conditions that prevail during an anticyclone allow large-scale elevated temperature inversions to form which prevent the vertical dispersion of pollutants. Inversions play an important role in pollutant dispersion and therefore warrant some further discussion.

1.2.2 The development of temperature inversions

Convection lowers the temperature of the earth's surface because a parcel of warm air at the surface will rise, carrying heat away from the surface. As the parcel rises, it expands and the work done causes it to cool adiabatically, i.e. there is no exchange of energy with the outside air. For the atmosphere of the earth, the lapse rate is calculated as - 9.8 $K.km^{-1}$ for dry air. However, the measured rate is - 6.5 $K.km^{-1}$ because air bears moisture which condenses as it rises and releases latent heat (Brimblecombe, 1986).

If the actual change in temperature in the ambient air is greater than the lapse rate, then a rising air parcel is at a higher temperature than the surrounding air. The parcel will have a greater tendency to rise and causes "unstable conditions" because convective mixing takes place. Under neutral conditions, the environmental lapse rate is similar to that expected under adiabatic expansion. If the environment cools less rapidly with height than the adiabatic lapse rate, then an "inversion" has formed. Radiation inversions form at night when the ground cools more rapidly than the air, but may break up during the day when the sun warms the ground (Brimblecombe, 1986).

Elevated inversions are caused either by the subsidence of an air mass or by the frontal movement of air masses. According to Held *et al.* (1996b), the base heights of these inversions on the South African highveld are at 1 700 m above ground level in the winter but in summer can range from 2 000 to 3 000 m above ground level. In the summer months, cyclonic circulations occur at the 850 hPa level allowing troughs to develop over the central plateau of the country which destroy the inversions. In the winter months, the stable anticyclonic conditions also allow surface-based inversions to develop at night. On the highveld, surface-based inversions can range in strength from 3 to 11°C and in depth from less than 100 m to 400 m above ground level. The surface inversion depths in summer are similar to those in winter but rarely exceed 2 °C in strength. These inversions create a stable boundary layer which prevents the dispersion of low level emissions. Nocturnal inversions occur with a frequency of 80 - 90 % during the highveld winter, and so exert a strong influence on pollutant dispersion. However, a nocturnal low level wind maximum, known as a Low-Level-Jet (LLJ) often develops above the surface inversions. It forms under highly stable nocturnal conditions, with speeds ranging from 5 - 15.5 $m.s^{-1}$, and serves as an efficient dispersant in the first few hundred metres above ground level (Held *et al.*, 1996b).

1.2.3 Atmospheric stability and pollutant plume behaviour

The stability of the atmosphere determines pollutant plume behaviour and dispersion characteristics (Figure 1.1). Under unstable conditions, the pollution plume may loop violently when it encounters strong convective eddies. High ground-level concentrations of pollutants then result. Turner (1996) reports that although the typical position for maximum plume

impact is about ten stack lengths downwind of the source, plume strikes have been recorded within two stack heights of the source. Fumigating plumes, which occur when the air is stable above the emission point also result, in high concentrations of pollutant at ground level. Coning occurs under near-neutral conditions and leads to equal dispersion in the horizontal and vertical directions. Fanning occurs in very stable conditions, such as an inversion, leading to much horizontal dispersion but little vertical dispersion. Lofting occurs when the emission is just above an inversion layer and disperses pollutants both vertically and horizontally (Held *et al.*, 1996b; Brimblecombe, 1986).

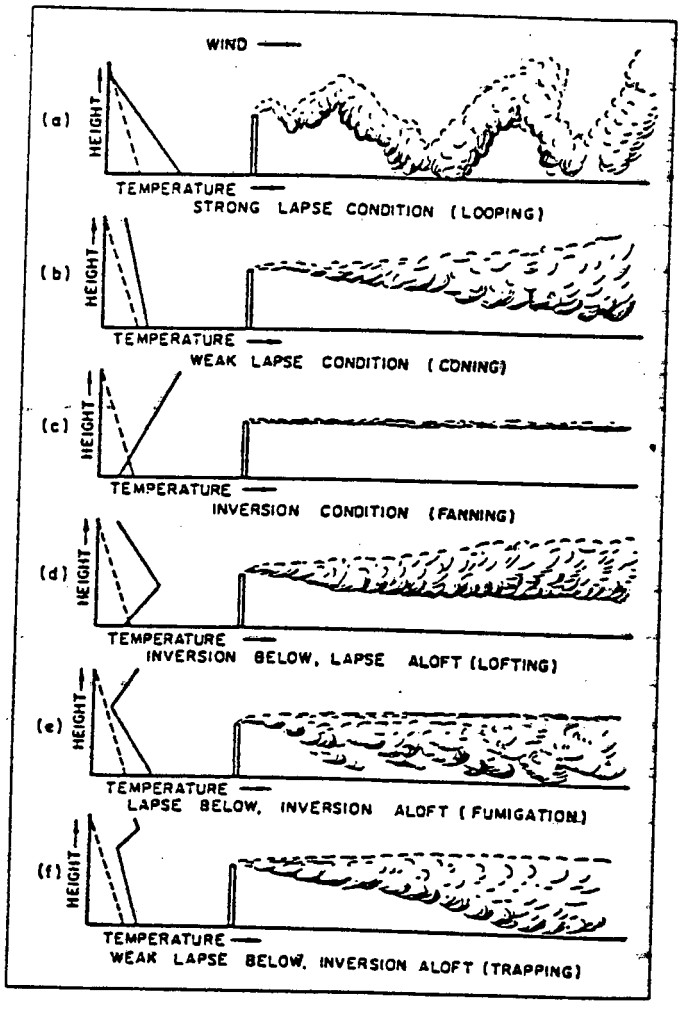


Figure 1.1 The effect of lapse rate on pollution plume behaviour. The dry adiabatic lapse rate (DALR) is indicated by a broken line while the environmental lapse rate (ELR) is indicated by a solid line (from Pretorious *et al.*, 1986).

The plumes from the Eskom power stations are reported as amongst the most bouyant in the world (Turner, 1996). Such buoyant plumes are generally able to break through the stable boundary layer that develops at night and are dispersed in the overlying neutral layer or are carried off by the LLJ. The boundary layer prevents the plumes from mixing down to ground

level. During the day, however, the convective boundary layer encourages strong looping behaviour which results in high pollutant concentrations near to the plume source. Modelling of plume behaviour under such extremes of stability and instability is difficult - particularly because the peak concentrations often occur when the mean wind velocities are low.

1.3 Atmospheric deposition

Wind-entrained dust, smoke from biomass burning, marine salts and air pollutants all contribute to atmospheric deposition. Although a variety of compounds are deposited on the soil surface, it is the acidifying compounds, trace elements and heavy metals derived from industrial processes which generally cause environmental damage.

Apart from the impacts associated with the gaseous compounds of N and S, power station emissions in South Africa are unlikely to cause any serious pollution problems. Compared with coals from the United States, Australia, Belgium and Germany, South African coal was found to be generally low in trace elements such as Pb, As, Zn and Ni (Willis, 1983; Willis, 1987).

Sulphuric, nitric, carbonic, hydrochloric, phosphoric or organic acids may all enter an ecosystem through atmospheric deposition processes. Of these, sulphuric and nitric acids are the most common anthropogenic acids and the ones which give the most cause for concern. Nitrogen is often limiting as a plant nutrient and its deposition as nitric acid serves to fertilize ecosystems that are N-poor. The biological interactions involving N are quite complex and beyond the scope of this review. For discussion of nitrogen transformations as acidifying processes, I refer the reader to Reuss and Johnson (1986).

Although South African coal is low in S (0.4 - 1.6 %) compared with coals from Europe (Willis, 1983), S emissions are significant because of the large quantities of coal that are burnt annually on the South African highveld, both for industrial purposes and as a domestic fuel source. In the past, the burning of coal discard dumps was a substantial source of low level emissions of sulphur dioxide although such sources are now largely controlled (Wells *et al.*, 1996).

1.4 Atmospheric deposition processes

Three processes of atmospheric deposition can be distinguished. Wet deposition occurs in precipitation - generally rainfall or snowfall. In dry deposition processes, gaseous and particulate matter is directly deposited from the atmosphere to the surface. Mist deposition is usually treated separately because the surface is exposed for long time periods and to relatively concentrated solutions. The semi-arid climate of the South African highveld, compared with many similarly affected northern hemisphere landscapes, means that wet

deposition is not the predominant means of pollutant deposition. Close to the pollutant source, dry deposition is most likely dominated by gaseous components whereas further from the source aerosols will dominate (Held *et al.*, 1996a).

The measurement of dry deposition is both difficult and expensive and very little work has consequently been done on this aspect in South Africa. Nevertheless, the flux of acid pollutants to the surface by dry deposition either equals or exceeds that by wet deposition. Dry deposition is calculated as follows:

$$\text{Flux to surface } (Q) = V_d C$$

where C = concentration of species (gas molecule/particle/aerosol) in the air
and V_d = deposition velocity - which depends on factors such as time of day, surface chemistry, surface moisture and vegetation type.

The measurement of dry deposition is presently receiving much attention in the highveld region especially since estimates range from the same magnitude as wet deposition to six times as much (Turner *et al.*, 1996).

Deposition through mist is generally more acidic than rainfall, and contains higher concentrations of dissolved chemical species. For example, a study by Olbrich (1993) found that mist samples contained almost double the sulphate concentration than rain. Since mists are generally of greater duration, they can potentially have greater impacts - especially in forested areas. However, except for on the Drakensberg escarpment, and high lying areas near Dullstroom, mist events are rare on the highveld.

1.5 Emission, conversion and deposition of sulphur compounds

1.5.1 Sulphur dioxide

Sulphur dioxide is a primary pollutant emitted directly from sources such as coal-fired power stations, biomass burning, and industries such as ferro-alloy works, steelworks and foundries. Estimates of temporal variation in SO_2 concentrations depend on the sources being considered. On a seasonal basis, domestic space heating coupled with lower mixing heights of the boundary layer contribute to elevated SO_2 levels in the winter months. On the other hand sulphur dioxide derived from power stations is emitted at a relatively constant rate. The concentrations of SO_2 due to low level sources are greatest at night because of nocturnal inversions whereas daytime atmospheric mixing and advection have the capacity to disperse SO_2 accumulations from the previous night. Thus multi-day accumulations of SO_2 near ground-level do not occur (Annegarn *et al.*, 1996).

Turner (1990 - cited in Annegarn *et al.*, 1996), summarised the findings of a five year study conducted in the industrial highveld region. He found that the concentrations of SO_2 in both rural and urban areas of the highveld seldom exceeded the 24-hour average guideline of 100 ppb set by the Department of Environmental Affairs and Tourism. At most monitoring sites the guideline values were not even approached while the monthly and yearly guideline values were never exceeded. Annegarn *et al.* (1996) concluded that the ground level concentrations of sulphur dioxide are adequately controlled and did not pose a threat to either human health or the environment. However, they did make an exception for areas close to tall stacks (within a 4 km radius) because the plumes may reach ground level under conditions of turbulent convective mixing, resulting in peak concentrations close to elevated sources. Thus, under circumstances of atmospheric turbulence, dry deposition of sulphur dioxide may be quite considerable in the near-fields of power stations and similar industrial plants.

There is a clear gradient of both decreasing concentration and decreasing frequency of short term high SO_2 concentrations from the industrialised part of the Mpumalanga highveld. Regional air recirculation is also suggested to result in widespread episodes of high pollution concentrations. This hypothesis was tested using the existing SO_2 data set maintained by Eskom[1]. However, no inter-site correlations between daily mean SO_2 concentrations were found. Annegarn *et al.* (1996) concluded that neither pollution episodes caused by stagnation nor the recirculation of air occurred regularly in the region. Alternatively, if such episodes do occur, then the episodes are of short duration.

1.5.2 Transformation of sulphur dioxide to secondary pollutants

Factors such as sunlight, atmospheric oxidation and interactions between different pollutants drive the formation of secondary pollutants from sulphur dioxide. Ultimately, the atmospheric conversion rates will largely dictate in what form the pollutant is deposited (Held *et al.*, 1996a). Four main processes have been defined by Pienaar and Helas (1996a,b), which may be summarised as :

Gas-phase reactions: Although the oxidation of SO_2 to SO_3 is thermodynamically favourable, the reaction is so slow that it can be ignored (about 5% per hour in summer). However, if SO_3 is formed in the presence of a catalyst, it then reacts immediately with water vapour to form sulphuric acid (H_2SO_4).

Photo-oxidation reactions: The photo-oxidation of SO_2 is considered to be unimportant in the troposphere. Although the reaction of hydroxyl radicals with SO_2 is the main oxidation process, it is very slow. The 24-hour averaged rate of SO_2 oxidation is estimated at 0.7 % per hour under cloudless summer conditions in a fairly clean

[1] Eskom is the major electricity generator in South Africa.

atmosphere. The resultant series of chemical reactions that gives rise to H_2SO_4 is thus limited by the slow oxidation rate.

Heterogeneous processes: Although particles of fly ash, ferric oxide, dust and soot are reported to enhance the oxidation of SO_2 (Saxena *et al.* 1995), the work of Pienaar and Helas (1996a) did not find this to be the case.

Aqueous phase processes: In polluted atmospheres, aqueous phase reactions are the major contributors to atmospheric acidification. Tropospheric pollutants such as ozone, H_2O_2, peroxyacetyl nitrate (PAN) and peroxyacetic acid dissolve in cloud water and then readily oxidise dissolved SO_2. In the gas-phase such reactions do not occur at measurable rates. The rates of aqueous phase oxidation depend on the gas-phase concentrations, solubility and rate of mass transfer of the oxidising agents such as ozone, hydrogen peroxide and the hydroxyl and peroxyl radicals (Pienaar and Helas, 1996b).

Despite the various reaction pathways, most of the sulphur deposited on the soil surface will ultimately form H_2SO_4. Even if subject to various delays because of biological transformations, Reuss and Johnson (1986) assume that most sulphur will reach the soil solution within the same annual cycle in which it was deposited. However, this assumption might be questionable in the less humid climate of South Africa. Nevertheless, whether deposited directly in the gas phase or following conversion to the particulate phase, sulphur dioxide is an acidifying compound (Annegarn *et al.*, 1996).

1.5.3 Dispersion and deposition of sulphate

The mean rainfall composition for seven highveld sites is presented in Table 1.1. Rainfall in equilibrium with atmospheric CO_2 has a pH of 5.6 (Galloway *et al.*, 1976) thus the mean pH of 4.9 reported for rainfall on the highveld is not unduly acidic. Rainfall in industrialised regions can be less acidic than anticipated because of neutralisation by base cations. Base cations may originate from industrial processes, dust from unpaved roads or tillage practices, or wind erosion (Hedin *et al.*, 1994; Schlesinger, 1991). The inputs of base cations in deposition, whether from soil dust or from industrial emissions, is an aspect that has received very little attention, and one which Kuylenstierna (1996) believes could be significant in South Africa.

Table 1.1 Weighted mean composition of bulk precipitation from seven highveld sites (reported in $mg.L^{-1}$) (Data from the Hydrological Research Institute and adapted from Fey and Guy, 1993).

Cations		Anions	
Na^+	0.72	F^-	0.08
Mg^{2+}	0.30	Cl^-	0.97
Ca^{2+}	1.15	SO_4^{2-}	2.89
NH_4^+	0.65	PO_4^{3-}	0.09
K^+	0.40	NO_3^{2-}	0.51
Si^{4+}	0.25	Total alkalinity	5.07
pH	4.94		

Long term monitoring has shown sulphate to be the most abundant anion in rainfall - whether in the industrial highveld region or the more rural Northern province. Figure 1.2 shows the seven year mean sulphate concentrations over the highveld area and these are comparable to those reported for similar regions in the United States. However, the central highveld receives less rain (between 600 - 700 mm per year), so that typical annual deposition loads in rainfall are estimated at 17kg $SO_4^{2-}.ha^{-1}$ on the central highveld, which is approximately half of the maximum load reported for the US (Turnet *et al.*, 1996). Inputs of sulphate through dry deposition have not been included in either the US or South African estimate. As mentioned earlier, estimates of dry deposition range from being equal to wet deposition to six times as much.

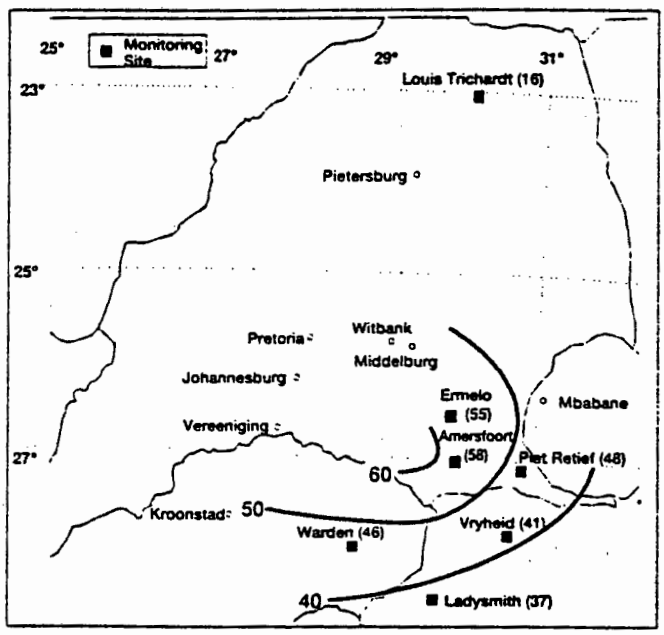


Figure 1.2 The seven year mean sulphate concentrations in rainfall in $\mu eq.L^{-1}$ over the highveld region (1985 - 1992) (After Turner *et al.*, 1996).

Sulphate concentrations collected from mist samplers located in the escarpment region were found to be almost double those for rainfall (Olbrich, 1993). Deposition through this mechanism is restricted largely to the escarpment regions of the highveld and would rely heavily on canopy interception.

The dry deposition of sulphate aerosols was monitored over seven years on the highveld and mean concentrations of particulate sulphate were found to be low and fairly evenly distributed (Figure 1.3). Such distribution is accounted for by the uniform distribution of sources of SO_2 and the slow conversion and deposition rates of sulphate.

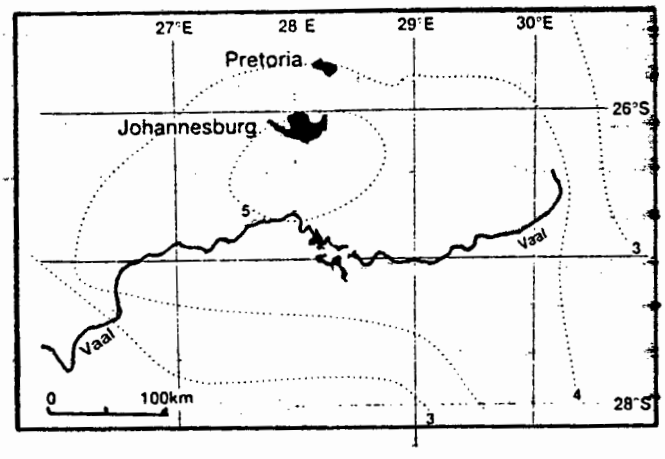


Figure 1.3 Isolines of equal sulphate (total concentration, $\mu g.m^{-3}$) measured from 1982 - 1992 (After Held *et al.*, 1996b).

Most monitoring sites recorded concentrations between 3 and 5 $\mu g.m^{-3}$. The crucial factors defining the concentrations of sulphate on the highveld were the type of air mass, the pressure system determining the intensity and direction of the air mass flow, the depth of the mixing layer and the oxidation chemistry (Held *et al.*, 1996b). The sulphate aerosol is reasonably well correlated with temperature and humidity but not with wind speed. In the warmer months the movement of moist, warm air masses over the sub-continent results in higher sulphate concentrations. Thus sulphate concentrations are higher in summer and lower during winter, although this general trend is overlain by high sulphate episodes throughout the year.

At high elevations (above 300 m above ground level) sulphate concentrations are higher - for example 71 $\mu g.m^{-3}$ was recorded at the top of Verkykkop and 51 $\mu g.m^{-3}$ at the top of the Kendal power station stack (before Kendal came into operation) (Held *et al.*, 1996a). Such high concentrations occur either because of accumulation of particulates at higher altitudes or because of recirculation of air masses on a regional scale. Aerosol layering in the middle troposphere has recently been confirmed by the study by Held *et al.* (1996c).

Episodes of high sulphate aerosol concentrations at ground level can occur when the postulated pool of pollutants at higher altitudes is mixed down towards the surface. At ground level, the highest sulphate concentrations seldom exceeded the 25 $\mu g.m^{-3}$ limit laid down by the California Air Resources Board. Held *et al.* (1996b) estimated that such episodes occur on average 19 times per year and each lasts a few days. Episodes of low sulphate concentrations occur, on average, 17 times per year, also lasting a few days.

The tall stack policy adopted by Eskom appears to have controlled the ground level concentrations of both primary and secondary pollutants. However, this policy, together with the local meteorological conditions, has brought about high concentrations of secondary pollutants, such as sulphate aerosols, at elevated layers (Held *et al.*, 1996a; Held *et al.*, 1996c).

1.6 Impacts of atmospheric deposition on soil

Acid deposition acts to increase the exchangeable acidity of soil and reduces the fraction of exchangeable bases (Koptsik and Mukhina, 1995). The exchangeable acidity is either directly increased through the inputs of H^+ or by the increase in exchangeable aluminium through the reaction of H^+ with soil minerals. The aluminium species replace the base cations on the soil exchange complex and the base cations are then leached from the system in tandem with strong acid anions such as sulphate (Reuss and Johnson, 1986).

According to Reuss and Johnson (1986), sulphate leaving a system must be accompanied by an equivalent amount of cations because of charge balance considerations. The export of the base cations will tend to acidify the system, although the time scale over which acidification will occur is strongly dependent on the nature of the soil affected. In alkaline or neutral soils, the negative exchange surface is dominated by the basic cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) whereas H^+ is the dominant exchangeable cation in organic acid soils. Aluminium species, such as Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ which have formed from the dissolution of soil minerals, dominate in acid mineral soils. In strongly acid soils, the high levels of aluminium that may result may be toxic to plants although susceptibility will depend on the plant species, and the composition of the soil solution.

The effects of increased proton loading on the vast range of heterotrophic soil organisms, particularly the microbial population, are poorly understood (Wolters and Shaefer, 1994). The effects on soil biota may be caused directly through proton toxicity or indirectly, through factors such as nutrient imbalances, mobilization of toxic metals or changes in the structural habitat of the soil. Processes like humification and nitrogen fixation could be halted at low pH values and rates of litter decomposition could also change. Changes in the community of soil organisms can affect chemical and nutritional properties or soil structure and texture, and, ultimately these changes could affect both the structure and functioning of terrestrial ecosystems.

The deposition of sulphur compounds from the atmosphere also results in an increase in the concentration of sulphate in the soil solution. Concerns that sulphate deposition may be increasing the solute load in runoff and thereby salinizing the major water supply of Gauteng prompted a one-year study of the soils of the Vaal Dam catchment (Fey and Guy, 1993). On average, the soils of the Vaal catchment had double the concentration of sulphate in solution found for comparable soils from southern Natal. Skoroszewski (1995), in another short term study, measured sulphate outputs from a small catchment in the Suikerbosrand Nature Reserve, near Johannesburg, and the results suggested that between 9 and 17 % of the measured sulphate inputs through deposition were being retained in the soils. The remaining sulphate was being removed in surface runoff.

According to Reuss and Johnson (1986), the response of the soil solution to increased sulphur inputs will depend on factors such as biological uptake and the ability of many soils to retain sulphate on soil surfaces. Although sulphur is an essential plant nutrient, the plant requirements for sulphur are soon met. Thus sulphate retention on soil surfaces, particularly sesquioxides, is an important buffer mechanism in the soil. In this way, the secondary effects of acid deposition - such as base cation removal, aluminium mobilization and decreased alkalinity of the soil solution - may be delayed by years or even decades.

It must be stressed that the acidification of soil is a natural process in many systems - particularly in humid climates where water accelerates reactions (McBride, 1994). In systems unaffected by acid deposition, base cations are leached out in association with organic acids or bicarbonate (HCO_3^-). The net accumulation of basic cations into the biomass also acidifies the soil over time. In natural systems the base cations will ultimately be returned to the soil via the processes of decomposition but where biomass is harvested, the base cations are exported and then can only be replaced through mineral weathering or artificial fertilizers (Reuss and Johnson, 1986; McBride, 1994).

McBride (1994) cites two other mechanisms of natural acidification: the oxidation of sulphides in soils with fluctuating water tables, and nitrogen transformations such as nitrification. In both processes, the time scale at which the system is considered is important since the acidification may be reversed once the reducing conditions return or the denitrifying bacteria are activated.

In view of its importance in mediating the impacts of sulphate-laden pollution on soil chemical properties, sulphate retention by soil will form the focus of the remainder of this review.

1.7 Sulphate sorption in soil

Isomorphous substitution of ions in clay lattices (such as Mg^{2+} for Al^{3+}, and Al^{3+} for Si^{4+}), is primarily responsible for the net negative charge carried by most soil surfaces (Alloway, 1995). However, positively-charged sites may exist within a soil having a net negative charge (McBride, 1994). This obviously has important implications for the sorption of sulphate as an anionic species. Before exploring how positively charged surfaces arise in soils, it is useful to consider the interaction between the soil surface and soil solution in a little more detail.

In the simplest view, the negative charge on the clay minerals is smeared out over the planar surfaces of the crystals (White, 1979; Wild, 1993). Each surface charge is neutralised by a mobile ion of opposite charge to give an alignment of charges in two planes which is termed a Helmholtz double layer. However, the spatial distribution of the ions is dictated by two opposing forces: i) a diffusive force which drives the mobile cations away from the high concentration near the negatively-charged clay surface to the outer solution, and ii) the electrostatic forces attracting the cations towards the charged surface. The result is a diffuse distribution of cations and anions in solution which, together with the surface charge, is termed the Gouy layer.

A more realistic model of charge distribution is represented by the Stern model which combines the concepts of the Helmholtz and Gouy models (White, 1979). The Stern model can accommodate ions of greater valency, does not regard the ions as point charges and, importantly, recognises other forces between the ions and the mineral surface beside simple electrostatic attraction. Essentially, the solution component of the double layer is split into two components: i) The Stern layer, which is a plane of cations of finite size located close to the clay's negative surface. In this region the electrical potential decays in a linear fashion with distance from the clay surface. ii) The diffuse layer of cations, across which there is an exponential decrease in the electrical potential. The inner surface of the diffuse layer contacts the Stern layer and is termed the outer Helmholtz plane (White, 1979).

1.7.1 Positively charged soil surfaces

Positive sites on a soil surface are accounted for by the uptake of protons from solution on to suitable sites - particularly under acidic conditions - when NH_2 and OH groups are protonated to NH_3^+ and OH_2^+ (Mott, 1981; White, 1979). Sulphate sorption by soils is strongly pH-dependent, especially when dealing with variably charged soils which can reversibly adsorb H^+ ions. The sites of pH-dependent charge are responsible for most of the positive charge present in soils.

The sulphate anion interacts with soil minerals which possess these surface hydroxyl groups. Such minerals include the poorly crystalline aluminosilicates (allophanes), the oxides of Fe, Al and Mn and the edge sites of the layer silicate clays (McBride, 1994). Kaolinite has been identified as an effective adsorbent for aqueous SO_4^{2-} (Kooner *et al.*, 1995; Mott, 1981). Although sulphate is highly desorbable from kaolinite, this is not the case for desorption from hydrous oxides of Fe and Al (Mott, 1981). Quartz lacks Al and Fe exchange sites on the mineral surface and so has low SO_4^{2-} sorption capacity (Lükewille *et al.*, 1995).

1.7.2 Adsorption

Ions in the diffuse layer (sometimes referred to as the diffuse ion swarm) are free to move about in the soil solution and are fully dissociated from surface functional groups (Sposito, 1989). The soil surface charge is neutralised only in a delocalised sense, by simple electrostatic attraction. There is no electron transfer or sharing between ion and crystal (Sposito, 1989; Mott, 1981). The monovalent anions, Cl^- and NO_3^-, are non-specifically adsorbed anions forming part of the diffuse-ion swarm. Another type of electrostatic bonding which has been recognised, is termed "outer-sphere surface complexation", in which at least one water molecule is interposed between the positive surface group and the complexed anion.

Both diffuse ion association and outer-sphere complexation can be described as non-specific adsorption. Sposito (1989) considers that the SO_4^{2-} anion adsorbs mainly as a part of the diffuse-ion swarm and as an outer-sphere complex species. His conclusion is based on the observed readily exchangeable character of the anion and is supported by several subsequent studies cited by Gustafsson (1995).

Specific adsorption corresponds to what is sometimes termed inner-sphere surface complexation, which may involve ionic as well as covalent bonding (Sposito, 1989). According to Mott (1981), the sulphate ion falls into the class of specifically adsorbed anions which are adsorbed by chemical bonding at specific sites to form a ligand. Most often the mechanism for this coordination is ligand exchange for hydroxl ions. Such adsorption is termed "chemisorption" and is often thought of as being irreversible. McBride (1994) lists four criteria for recognising ligand exchange or chemisorption:

i) The release of OH^- into solution;
ii) A high degree of specificity of the surface towards particular anions;
iii) The reaction is non-reversible, or desorption is considerably slower than adsorption;
iv) A change in the measured surface charge to a more negative value following adsorption.

Most studies have concluded that SO_4^{2-} is a specifically adsorbed (chemisorbed) anion (studies cited in Zhang *et al.*, 1987 and in Guadalix and Pardo, 1991). Evidence for this is provided

by the fact that SO_4^{2-} displaces OH^- in a ligand exchange-type reaction which results in the release of OH^- ions to the soil solution, and a subsequent increase in solution pH. Thus the pH of soils equilibrated with SO_4^{2-} is higher than that of soils equilibrated with Cl^- or NO_3^-, since these latter ions are adsorbed without the release of OH^- ions. The increase in cation adsorption which results is due to the net increase of surface negative charge associated with sulphate adsorption (Curtin and Syers, 1990a).

Adsorption of SO_4^{2-} is typically found to increase with a decrease in pH (Zhang *et al.*, 1987; Kooner *et al.*, 1995). According to the latter authors, the adsorption of SO_4^{2-} is restricted to the positive side of the zero point of charge, via either inner- or outer-sphere adsorption mechanisms, so that SO_4^{2-} adsorbs primarily to those mineral surface sites which are positive or neutral. The adsorption of SO_4^{2-}on oxide surfaces results in the release of OH^- and/or H_2O ligands (Inskeep, 1989). Having displaced the OH^- and OH_2 ligands , the SO_4^{2-} is then adsorbed to either one or two Al or Fe atoms. Kooner *et al.* (1995) refer to these mechanisms of SO_4^{2-} adsorption as monodentate - or bidentate inner-sphere complexes, respectively. The bidentate inner-sphere complexes are supposedly less stable than the monodentate inner-sphere complexes, because each sulphur atom is shared between two surface sites which places a strain on the bonds with the surface (Kooner *et al.*, 1995). On the other hand, McBride (1994), who terms such adsorption a "binuclear bridging mechanism" states that adsorption would be non-reversible, since desorption would require two bonds to be broken simultaneously.

In studies of this type it is important to consider the solution pH at which the adsorption process occurs. At low pH, the OH ligands would be protonated to OH_2, which, when replaced by the sulphate ligand, is simply given off as water and would not reflect an increase in pH. Thus, Zhang *et al.* (1987) found that the ratio of OH^- released to SO_4^{2-} adsorbed was very low at pH 5.

Numerous studies have shown SO_4^{2-} adsorption to be fully reversible (studies cited in Freney and Williams, 1983; Novák and Přechová, 1995). This suggests that the adsorption of SO_4^{2-} does not meet the criteria set by McBride (1994) that chemisorption be non-reversible or have a slower rate of desorption than adsorption.

Mott (1981) describes low-affinity specific adsorption for those ions which are attracted to a surface to a greater extent than would be expected from diffuse layer theory, yet are not bound to the surface. Curtin and Syers (1990a) have used this idea to explain how SO_4^{2-} was quantitatively removed by extraction with an indifferent electrolyte solution. They reasoned that if SO_4^{2-} is chemically bonded to surface metal atoms, then it is unlikely that adsorbed SO_4^{2-} would be completely removed by an indifferent electrolyte such as NaCl. Since the SO_4^{2-} could be extracted, it was suggested that the SO_4^{2-} is adsorbed in a plane closer to the surface than are monovalent ions (which are attracted purely by electrostatic forces) but is not chemically bound to the metal surface. Instead, it was proposed that the SO_4^{2-} is adsorbed into

the Stern layer, where further positive charge is induced on the surface by OH^- release. Adsorption of SO_4^{2-} into the Stern layer diminishes the capacity of the diffuse layer to hold anions electrostatically, while cations are held in larger numbers. This type of interaction has been termed "low-affinity specific adsorption" to distinguish it from chemisorption. Accordingly, although the forces involved will be other than purely electrostatic, SO_4^{2-} does not become chemically co-ordinated to the surface metal atoms as do chemisorbed anions such as phosphate (Curtin and Syers, 1990b).

1.7.3 Precipitation reactions

Some studies have suggested that SO_4^{2-} retention by soils is inadequately explained by adsorption alone. An alternative mechanism involves the precipitation of aluminium sulphate minerals such as jurbanite ($AlOHSO_4.5H_2O$), alunite ($KAl_3(SO_4)_2(OH)_6$) and basaluminite ($Al_4(OH_{10})SO_4.5H_2O$) (Lükewille *et al.*, 1995; Fey and Guy, 1993; Sposito, 1989). Formation of aluminium sulphate minerals is possible in high sulphate, low pH environments where the resultant minerals are more stable than existing aluminium solids such as gibbsite and kaolinite (Fey and Guy, 1993). The low pH is necessary to ensure that there is sufficient Al in solution to enable the precipitation reactions to proceed (Sposito, 1989; Lükewille *et al.*,1995).

Although the precipitation of such minerals is supported by solubility data, no direct evidence for their formation has yet been presented, except in special cases such as acid sulphate soils (Curtin and Syers, 1990a). Recent attempts at modelling sulphate sorption and desorption in soils have either been based on adsorption isotherms or have incorporated the chemical equilibria of these minerals. The studies by Lükewille *et al.* (1995) and Alewell *et al.* (1995) found that the data were more accurately described by a model based on the Langmuir isotherm than one based on the solubility products of jurbanite and alunite.

On the other hand, in a similar attempt to model SO_4^{2-} sorption and desorption, Prenzel and Meiwes (1994) found that their results could not be adequately described by adsorption isotherm models. A model based on the solubility product of jurbanite ($AlOHSO_4$) was more successful in describing the soil solution data. The authors were careful to point out that the appropriateness of their model did not prove the formation of the aluminium sulphate minerals in the soil. Rather, they viewed the use of solubility equilibria as an appropriate basis for explaining the interaction between the soil solution and soil surface.

From the above discussion it is evident that the retention of sulphate on soil surfaces is not amenable to simple description. Sulphate does not always behave as a conventional, specifically adsorbed anion, since sorption is apparently reversible on kaolinites but not oxides. Several studies have been cited which imply that the sulphate does not reach the inner Helmholtz plane and so is not involved in ligand exchange or chemisorption. Yet, the anion is clearly attracted more readily to the surface than an electrostatically bound ion such as Cl^-.

In summary, Mott (1981) describes sulphate as "in some ways the most puzzling of all the anions with respect to sorption".

1.7.4 Factors influencing sulphate sorption

The soil properties most commonly correlated with SO_4^{2-} sorption are pH, ionic strength, extractable Fe and Al, organic matter and clay content, although the relationships between these properties and SO_4^{2-} sorption are not necessarily simple, linear functions. Adsorption of sulphate is negligible above pH 6.5 and increases with decreasing pH below this value (Tabatabai, 1982). Bolan *et al.* (1986) found that sulphate sorption always decreased with increasing solution ionic strength. The importance of one soil property over another in dictating sorption behaviour will also vary between different soils (Comfort *et al.*, 1992).

Ligand exchange of SO_4^{2-} for OH^- or H_2O occurs at the surfaces of Fe or Al oxides or kaolinite - depending on the surface charge of the edge sites. Of these, Tabatabai (1982) considers Al to be the most important in sulphate adsorption. The adsorption of sulphate by different constituents occurs at a number of energetically different reaction sites.
The amount of sorbed SO_4^{2-} is negatively correlated with the organic matter content of the soil because of the competition between SO_4^{2-} and organic anions for Al binding sites on soil minerals and oxides (Comfort *et al.*, 1992; Inskeep, 1989, Kooner *et al.*, 1995; Courchesne *et al.*, 1995; Guggenberger and Zech, 1992). Lükewille *et al.* (1995) found less sorption in upper soil horizons and attributed this to a higher organic matter content. Organic acids containing carboxylic or phenolic functional groups can bind to oxide surfaces, thereby reducing the amount of surface sites available for anions such as SO_4^{2-}. Inskeep (1989) stresses that it is the quantity of functional groups available for surface binding that is important, rather than the amount of total carbon present. An experiment on a podsolic soil showed that the efficiency of organic matter in displacing SO_4^{2-} is controlled by the extent of proton dissociation from the functional groups of the organic matter. The dissociation of acidic groups should increase from pH 3.2 to pH 4.2, thus increasing the net negative charge of humic acid molecules and enabling them to compete with SO_4^{2-} for positively charged sites (Courchesne *et al.*, 1995).

1.7.5 Kinetic aspects of sulphate sorption

The release of OH^- from the soil provides a useful basis for estimating the rate of adsorption of SO_4^{2-}. Zhang *et al.* (1987) found that adsorption proceeded rapidly - with approximately 80 % of the total displaced OH^- being released within 4 minutes. Similar results were reported by Bolan *et al.* (1986, cited in Novák and Přechová, 1995) and Rajan (1978, cited in Inskeep, 1989). On the other hand, the study by Kooner *et al.* (1995) found that the adsorption of SO_4^{2-} was a time-dependent process which only reached equilibrium within 4 days.

The soils used by Zhang *et al* (1987) were described as predominantly kaolinitic whereas those of Kooner *et al.* (1995) contained appreciable quantities of Fe and Mn oxides in addition to kaolinite. These differences could account for the marked differences in sulphate sorption rates, with sulphate being sorbed fastest on the kaolinite soil. However, this explanation contradicts the earlier finding that sulphate adsorption on Al and Fe oxides is instantaneous (Novák and Prechová, 1995). Tabatabai (1982) also mentions that sulphate sorption on kaolinite is weak relative to that on Fe and Al oxides.

Broad comparisons of this nature should be made with caution since different experimental protocols, soil types and analytical methods may conspire to produce an apparently confusing picture. Nevertheless, present evidence would suggest that different mechanisms may operate on different mineral surfaces in the soil for the retention of sulphate. This idea was mentioned earlier by Mott (1981), when pointing out the discrepancies in adsorption/desorption behaviour in oxides and kaolinites.

Recent studies have shown that atmospheric SO_4^{2-} deposition in Europe has decreased, with the result that concentration of SO_4^{2-} in soil solutions and runoff has also decreased. However, the observed rate of SO_4^{2-} decrease in soil solutions has not been proportional to the decrease in SO_4^{2-} deposition (Matzner and Murach, 1995; studies cited in Giesler, 1996), which again suggests some degree of slow reversibility in sulphate retention. Alewell (1995, cited in Matzner and Murach, 1995) showed that most soil SO_4^{2-} is reversibly bound and will thus be mobilised if SO_4^{2-} deposition decreases. Thus, the reversal of acid deposition impacts will be retarded by SO_4^{2-} desorption - with the rate of desorption being dependent on the amount of SO_4^{2-} stored on the soil surface and the steepness of the desorption isotherm. Since sulphate isotherms may exhibit a degree of hysteresis (Gustafsson, 1995; Courchesne *et al.*, 1995), the adsorption isotherms cannot be used to predict desorption.

In general, the SO_4^{2-} concentrations in the soil solution of European soils at present indicate that the desorption isotherms are fairly flat. Preliminary data from the Solling Roof Project in Germany show that although SO_4^{2-} inputs are decreasing, only small amounts of SO_4^{2-} are being released into the soil solution. In the Solling Roof experiment, atmospheric deposition on a forest stand has been excluded by a plexiglass roof since 1991. Instead of rainfall the stand has been irrigated with a solution of a pre-industry composition, yet there has been no dramatic response in the sulphate concentration of the soil solution (Alewell *et al.*, 1995).

The present prediction is that considerably greater reductions in SO_4^{2-} deposition are needed before the rate of desorption will increase. Matzner and Murach (1995) have suggested that, in soils with high SO_4^{2-} content, it will take several decades before the SO_4^{2-} concentration in the soil solution will reflect the reduced SO_4^{2-} input through deposition.

1.8 Conclusions

The combination of heavy industry and prevailing climatic conditions on the South African highveld results in the accumulation of air pollutants. The stable boundary layer that occurs with an 80 - 90 % frequency during the winter months traps low-level pollutant emissions, but generally allows the emissions from tall stacks to escape. However, under strong convective conditions, looping plumes may result in high pollutant concentrations at ground level within 4 kilometers of the stack.

Sulphur emissions from industry are ultimately deposited to the soil. Typical loads of sulphate in rainfall are 17 kg $SO_4^{2-}.ha^{-1}.yr^{-1}$. Dry deposition is not included in this estimate and may be double to six-fold the wet deposition. The deposition of sulphate results in an accumulation of sulphate in soil solution and increased leaching of base cations from the soil profile. The extent to which sulphate inputs are buffered are determined by soil properties such as pH and sesquioxide and organic matter content.

In Chapter 2 the soil sampling protocol is critically appraised, while the accurate determination of sorbed sulphate is the focus of Chapter 3. Finally, the chemical properties of soils sampled near a power station on the South African highveld are investigated in Chapter 4.

CHAPTER 2

SELECTION AND SAMPLING OF SOIL MONITORING SITES

2.1 Introduction

Reuss and Johnson (1986) recognised the prediction of the effects of acid deposition on terrestrial and aquatic ecosystems as being one of the most pressing challenges facing environmental science. The only meaningful way of addressing the challenge is through environmental monitoring. Environmental monitoring principles and procedures are briefly introduced in this chapter with special reference to the use of deposition gradient studies to assess impacts. The establishment of monitoring sites near a power station is described, with emphasis on the sampling protocol. A preliminary attempt to validate this protocol is also described.

The provision of such information is intended to provide a baseline data set for comparison with data to be collected at various times in the future. The insights gained from the European experience should facilitate early detection of impacts and allow the timely implementation of appropriate control strategies in South Africa.

2.2 Environmental monitoring

Acid rain research follows five main approaches in studying the effects of acid inputs to soil each of which experimental approaches has its own inherent limitations are summarised by Wolters and Schaefer (1994). The approaches are:

1) Monitoring of long-term changes (Falkengren-Grerup *et al.*, 1987; Stuanes *et al.*, 1995);
2) Comparison of sites at varying stages of pollution (Vogt *et al.*, 1995; Schaaf *et al.*, 1995);
3) Gradient analyses within one site (Kashulina *et al.*, 1995; Mesanza *et al.*, 1995);
4) Application of simulated acid rain - both in the field and in the laboratory (Koptsik and Mukhina, 1995);
5) The exchange of soil cores between different sites (Raubuch *et al.*, 1995).

The monitoring of long-term changes in acid-polluted soils is viewed as the best and most direct way of assessing pollutant effects. The drawback to this approach is the extended time scales over which monitoring may be necessary. For example, Falkengren-Grerup *et al.* (1987) found noticeable differences in pH and base cation concentrations in both forested and heathland soils sampled 30 years apart. Information gathered from pollution gradients can

overcome the time constraint but in turn are limited by possible within-site variability that may confound the results. Nevertheless the use of deposition gradients has proved extremely useful in a number of studies. A few recent deposition gradient studies are described below, together with factors determining their success or failure as monitoring tools.

High levels of smelter pollutants were found in bulkfall and rainfall collections near to a nickel-copper smelter by Freedman and Hutchinson (1980), who calculated that between 42 to 52 % of the Ni, Fe and Cu emissions but less than 3 % of the sulphur emissions were deposited within 60 km of the smelter. Sulphate deposition amounted to 1.2×10^6 kg.yr^{-1} within the 60 km radius of the smelter (approximately 0.1kg sulphate.ha^{-1}.yr^{-1}). Studies on the litter component showed similar elevations of Ni, Cu and SO_4 close to the smelter. However, soil pH showed no distance effect, probably because of soil buffering factors. Similarly, Hogan and Wotton (1984) found that metal concentrations in the soil were correlated with distance from the smelter whereas soil pH was not, even though deposition of sulphate was occurring. In this case Zn oxides, which are also emitted by the smelter, may have been buffering the effects of sulphur deposition.

A more recent deposition study in the Kola region of Russia by Koptsik and Mukhina (1995) showed a significant, increasing trend of exchangeable acidity in the organic horizon, and exchangeable aluminium in the E-horizon, of a podzolic soil with distance from a nickel smelter. High concentrations of Ca and Mg in soils close to the smelter were explained by high inputs of these elements in dust emissions.

Schaaf *et al.* (1995) studied three Scots pine ecosystems along a deposition gradient in north-eastern Germany. The soils at each site are derived from glacial outwash sediments and, according to the authors, their present-day chemical status is clearly a reflection of their different deposition histories. In brief, high concentrations of Ca and SO_4 in the soil solution were found at the site with the greatest deposition loads of Ca and SO_4 (20 kg Ca.ha^{-1}.yr^{-1} and 25 kg S.ha^{-1}.yr^{-1} respectively) but these decreased along the deposition gradient.

The scale at which deposition gradients are studied can vary from hundreds of kilometers to within 5 kilometers of a pollution source. The natural variation attributable to both climate and mineralogical factors can cloud data quite markedly, especially if a gradient line is lengthy. Nevertheless, Raitio *et al.* (1995) found a clear connection between the atmospheric SO_2 concentrations and foliar sulphur concentrations (total, organic and inorganic S) over a 450 km pollution gradient from smelters on the Kola Peninsula of Russia.

A study of gardens up to 25 km from the Plock oil refinery (Central Poland) showed that the sulphate sulphur concentration in both soils and groundwaters did not depend significantly on the distance to the refinery. However, the dominant wind direction was from the west while the area under consideration was located south or south east of the refinery. Despite the sample sites receiving only a low direct inflow of air pollutants from the refinery, above

normal sulphate concentrations were found for all receptors examined - soils, groundwaters and various vegetables. For soils, a sulphate sulphur content of more than 0.004 % was considered excessive (Mikula, 1995).

Many gradient studies (Li and Landsberg, 1975; Jylhä, 1996; Patrinos *et al.*, 1983) have focused on the composition of washout as an indicator of pollution. Washout refers to the removal of aerosols by raindrops as they fall through a pollution plume. Li and Landsberg (1975) found that the values of H^+ concentration clearly decreased concentrically from a pollution source while Patrinos *et al.* (1983) found that sulphur, hydrogen and chloride concentrations in plume washout were elevated above background levels. These studies also demonstrated the importance of meteorological conditions in studying deposition phenomena. For example, Li and Landsberg (1975) found that when rainfall events were accompanied by winds, the increased H^+ concentration of the washout was reflected in the appropriate wind direction. On the other hand, Jylhä (1996) failed to verify modelled sulphate deposition within a 10 km radius of a power station because the distribution of precipitation collectors failed to match the path of the pollution plume.

Besides meteorological conditions, factors such as background atmospheric concentrations and transformation rates are all significant determinants of plume washout composition. Ten Brink *et al.* (1988) not only found that plume washout of SO_2 showed strong day-to-day variation despite constant SO_2 emissions, but also that deposition of S compounds was negligible above the high background levels prevalent in the area. Dry deposition was suggested to be a more efficient SO_2 deposition process than plume washout - even during rain episodes.

The importance of dry deposition was re-emphasized in a study by Ayers *et al.* (1995). Wet-only deposition at sites located upwind, amongst and downwind of 5 power stations exhibited no clear signal of sulphur and nitrogen emissions. The high-speed winds which often accompanied the rainfall events were hypothesized to quickly ventilate the valley in which the stations were located. Modelled estimates suggested that dry deposition may be the dominant deposition process in operation.

As demonstrated by the studies of Jylhä (1996) and Mikula (1995) the prediction of plume behaviour is often uncertain, particularly when plume washout is measured on an event basis. For long term studies, the general meteorological trends are more critical than the real-time behaviour of a plume.

2.3 Site selection and characteristics

2.3.1 Locality

Arnot power station, located near Middelburg, Mpumalanga, was chosen as the focal point for the study for a number of reasons. Arnot is the most easterly of South Africa's power stations and is one of seven base load power stations that is fired by coal in the Mpumalanga province of South Africa (Figure 2.1). It is also the most distant from the industrial complexes of Gauteng, Witbank and Middelburg; background pollutant levels are therefore assumed to be low. Finally, Arnot is one of the oldest power stations - its first unit came into operation in 1971 and the last in 1975. At present only three units are operating but the station is anticipated to be fully operational again in 1998. Production data for Arnot since 1986 are presented in Table 2.1 (Eskom, 1995). Unpublished data implicates a 2.0 % sulphur content for the number 1 coal seam at Arnot and 1.1 % sulphur content for the number 2 seam. The estimates of sulphur emissions in Table 2.1 are nevertheless based on the published range of S contents for South African coals (Willis, 1983). Thus, since it was commissioned in 1971, Arnot power station has emitted between 452 000 to 1 807 920 tons of sulphur, assuming complete conversion to sulphur dioxide. Eskom reports coal burning in coal-fired power stations to have totalled 79 377 000 tons of coal for 1995.

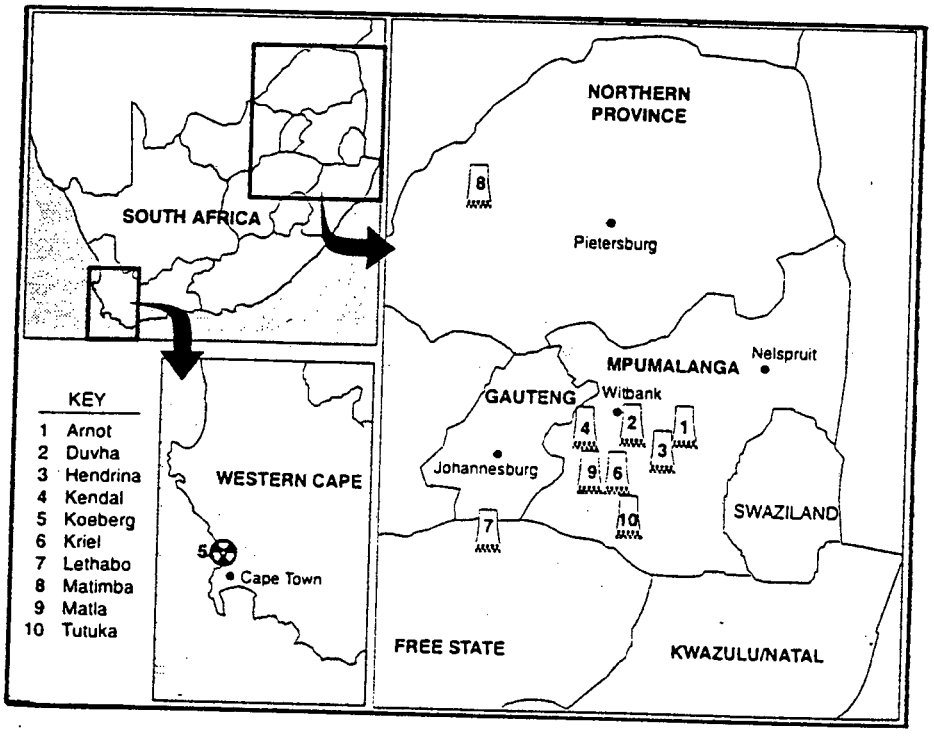


Figure 2.1 Location of Eskom's base load stations in South Africa, including the nuclear facility, Koeberg, in the Cape Province.

Table 2.1 Electricity production and coal consumption for Arnot power station, together with estimates of sulphur emissions based on the extremes of sulphur content reported for South African coals.

	Total since commissioned	1995	1994	1993	1992	1991	1990	1989	1988	1987	1986
Energy sent out by 31-12-1995 (GWh)[1]	230 604	3 863	4 558	4 089	7 426	10 839	10 845	11 601	10 806	11 699	11 458
Mass of coal burnt by 31-12-1995 (tons)[2]	112 995 000	1 892 870	2 233 420	2 003 610	3 638 740	5 311 110	5 314 050	5 684 490	5 294 940	5 732 510	5 614 420
Sulphur content (tons) at 0.4 %	451 980	7 572	8 934	8 014	14 555	21 244	21 256	22 738	21 180	22 930	22 458
Sulphur content (tons) at 1.6 %	1 807 920	30 286	35 735	32 058	58 220	84 978	85 025	90 952	84 719	91 720	89 831

[1] Eskom (1995)

[2] Average coal consumption for Arnot = 490 tons .GWh^{-1} (Eskom, 1995).

2.3.2 Meteorological factors

The behaviour of a pollution plume depends on the prevailing climatic conditions. Factors such as the magnitude of the source, wind speed, rapidity of vertical and lateral dilution and the effective source height will determine the ground level concentrations of air pollutants (Bennet, 1995, cited in Fey *et al.*, 1996).

Details on meteorology, source configuration and topography are required as inputs for pollutant dispersion models. Dispersion models are used for two purposes: i) to predict the concentration of pollutants from sources and ii) to understand the mechanisms that result in particular concentration characteristics. However, the application of such models on the highveld is limited by the extremes of stability and instability that frequently occur (Turner, 1996). Under conditions of atmospheric turbulence, emissions are mixed throughout the boundary layer, resulting in peak concentrations near ground level and close to elevated sources. This finding flouts the predictions of conventional dispersion models that ground contact of emissions from 300 m high stacks would only occur tens or hundreds of kilometers away from the source (Annegarn *et al.*, 1996). Under convective conditions, Lidar scanning by Bennet (1995, cited in Fey *et al.*, 1996) showed a looping plume structure within a deep boundary layer. The plume moved close to ground level at least 2.5 kms from the source. Under more strongly convective conditions, Bennet (1995) suggested that a touch-down model for plume behaviour would be more appropriate. Thus under circumstances of atmospheric turbulence, dry deposition of sulphur dioxide may be quite considerable in the near-fields of power stations and similar industries.

Instead of invoking pollutant dispersion models, local meterological factors were used to decide on the general sampling area - using Arnot power station as the focal point. In general, the maximum mid-day mixing depth in winter varies between 1 000 and 2 000 m above ground level but may exceed 2 500 m above ground level in summer (Held *et al.*, 1996b). The daytime surface winds of the Mpumalanga highveld are predominantly north to north-westerly while easterly winds are the next most frequent. In winter, the frequency of south westerly winds increases. However at night north-easterly winds predominate with easterly and south easterly winds (Held *et al.*, 1996).

The prevailing wind direction recorded at Arnot was a determining factor in the selection of sampling points. Over a 24 hour period the wind is most frequently from the east (13.2 %; Table 2.2). However, Turner (1996) noted that meteorological conditions on the highveld are very different between night and day. At night, the surface inversions which develop result in a stable boundary layer. Plumes from tall stacks, such as those from Arnot (195 m each), can escape the stable boundary layer and are dispersed.

Table 2.2 Percentage frequency of occurrence and mean wind speed for each of the 16 wind directions at Arnot power station from 1 April 1979 to 31 March 1984 (adapted from Pretorius *et al.*, 1986).

	24-hour period 00h00-24h00		Day-time period 06h00-18h00		Night-time period 18h00-06h00	
Wind direction	Frequency of occurrence %	Mean wind speed ($km.h^{-1}$)	Frequency of occurrence %	Mean wind speed ($km.h^{-1}$)	Frequency of occurrence %	Mean wind speed ($km.h^{-1}$)
N	8.7	12.7	3.7	14.3	13.7	12.2
NNE	5.7	11.1	3.0	12.2	8.3	10.7
NE	7.4	13.6	3.8	14.1	11.0	13.4
ENE	11.6	16.4	8.5	17.9	14.7	15.6
E	13.2	18.3	11.6	19.4	14.7	17.5
ESE	5.9	15.3	5.9	16.1	5.9	14.6
SE	2.9	12.3	3.6	13.0	2.2	11.0
SSE	1.7	9.5	2.0	9.9	1.3	8.8
S	2.2	8.9	2.9	9.0	1.4	8.7
SSW	2.6	9.9	3.8	10.3	1.5	8.7
SW	3.9	11.3	5.5	11.7	2.2	10.3
WSW	3.9	12.1	**5.6**	13.1	**2.3**	**9.8**
W	3.3	12.9	**4.7**	14.7	1.8	8.4
WNW	7.2	15.8	**11.9**	**17.2**	2.6	9.2
NW	10.3	15.9	**15.2**	**18.0**	5.4	10.1
NNW	9.6	13.8	8.2	6.5	11.0	11.8

During the day, however, the stable conditions are disturbed by convective currents. A convective boundary layer develops which is unstable and encourages the plume to adopt strong looping behaviour. On such occasions the ground level concentrations of pollutants are increased. Although the typical position for maximum plume impact is about ten stack lengths downwind of the source, plume strikes have been recorded within two stack heights of the source (Turner, 1996). At Arnot, the most frequent wind direction during the day is from the NW (15.2 %) followed by WNW (11.9 %; see bold font in Table 2.2). Thus the plume is likely to strike the ground most frequently in the direction SE and ESE of the power station. Turner *et al.* (1992), however, report that for high SO_2 concentration events, the measured hourly averaged wind direction is not a good indicator of the plume travel direction.
Sampling was ultimately conducted in an arc ranging ENE to SE of the power station since the wind blows in this region with a 37.4 % frequency (Figure 2.2).

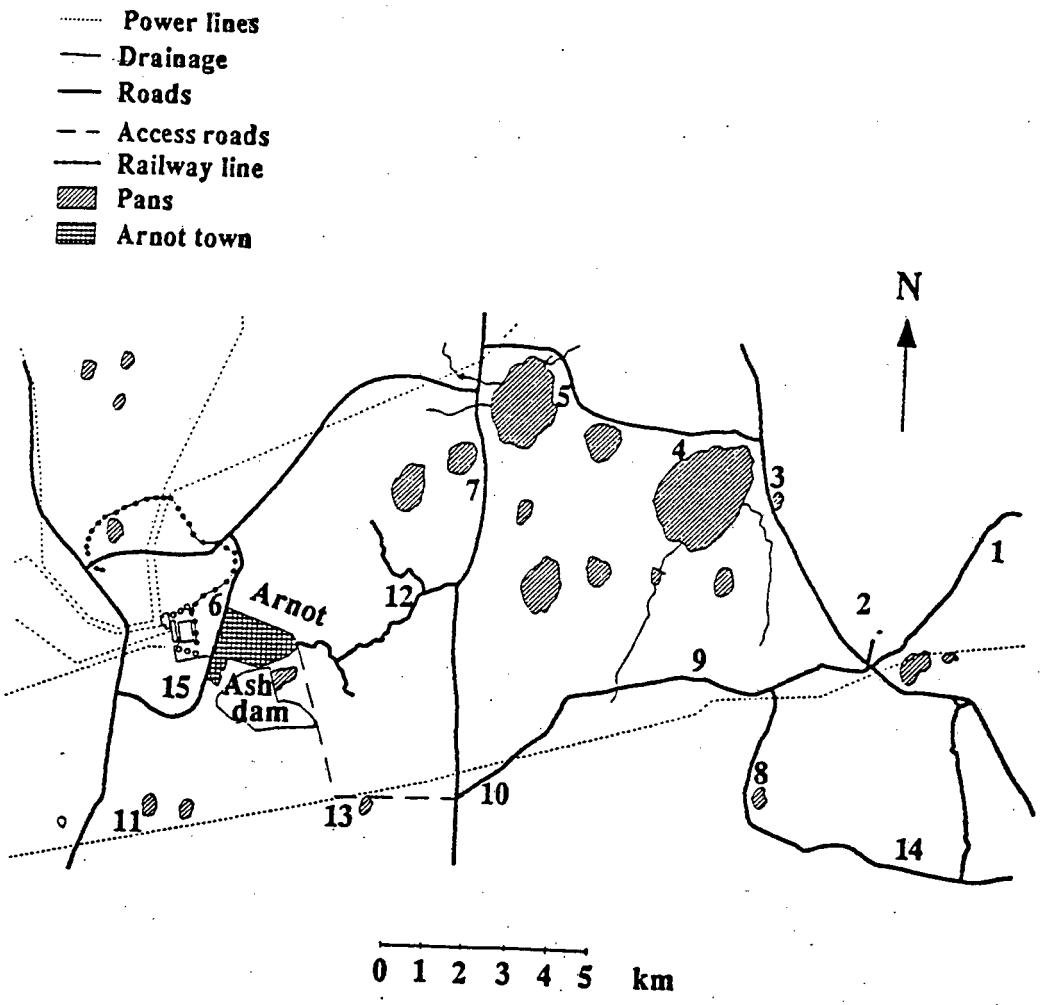


Figure 2.2 Location of soil sampling sites in relation to Arnot power station.

A detailed study of SO_2 dispersion at Matimba power station showed the importance of wind speed in determining plume behaviour (Turner *et al.*, 1992). Episodes of high SO_2 concentrations at ground level and closest to the source were generally experienced during very light wind conditions (less than 3.6 $km.h^{-1}$ at 96 m above ground level). The data presented in Table 2.2 show that for the selected WSW to NW wind directions, the mean wind speeds are high (between 13 and 18 $km.h^{-1}$ at 10 m above ground level). Wind speed generally increases with altitude, so the pre-condition of light winds for maximum looping close to the source would not apply in the selected wind directions. Presumably ground contact of the plume under high wind speed conditions would simply be further from the source than the 2.5 km touch down point reported by Turner *et al.* (1992).

2.3.3 Land use

Coal mining and agriculture are the main land uses in the region. Maize cultivation, and to a limited extent, livestock farming, are the major agricultural activities. Sampling sites were restricted to natural grassland showing minimal evidence of recent, intensive grazing by livestock, wherever possible (Figure 2.3).

Figure 2.3 Photograph of site 1 - facing SE at a distance of 19.9 km from Arnot power station. Note short grass and denuded patches indicating heavy grazing impacts.

Figure 2.4 In contrast, site 10 (facing W, 8.3 km from Arnot power station) has a thick grass sward, indicating that the site has either not been subject to recent grazing or fire, or was cultivated in the past and has returned to a *Hypparhenia sp.*-dominated grassland. The survey beacon (altitude 1718.5 mamsl, 363 m ground height) is discernible through the right-most *Acacia mearnsii* tree.

2.3.4 Land Type and topography

Much of the South African landscape has been classified into terrain units which serve as indicators of agricultural potential. The terrain units are delineated on the basis of uniformity of terrain form, pedosystems and finally climate zones. The area surrounding the Arnot power station is primarily occupied by a *plinthic catena* (Land Type Memoirs 2528 Pretoria, 1987) which is further separated into two terrain units, Ba and Bb, on the basis of a pedological/terrain form boundary. The unit Ba indicates land in which red and/or yellow apedal soils (Hutton, Bainsvlei, Avalon, Glencoe and Pinedene forms) that are dystrophic and/or mesotrophic predominate over red and/or yellow soils that are eutrophic. Red soils occupy more than a third of the area. The Bb land unit differs only in that the red soils are not widespread. As a consequence of the similarity of the landtypes sampling sites could be selected which fell on either Ba or Bb. For the record, sites 1, 6, 10, 11, 12, 13, and 15 fall within land unit Ba while the remaining sites (sites 2, 3, 4, 5, 7, 8, 9 and 14) fall within land unit Bb. Note that the soils described above follow the classification of MacVicar *et al.* (1977). In all units the valley bottoms are occupied by gley soils such as the Rensburg form. Site 10 is, however, an exception to the general description of the landscape as it was occupied by a Rensburg soil of the Phoenix series (non-calcareous in the G-horizon) and was situated on a hill crest (Figure 2.4).

The general topography of the area is characterised by gently rolling hills with a midslope length ranging between 500 - 1 500m and a maximum slope of 15 % (Land Type Memoirs 2528 Pretoria, 1987). The undulating nature of the landscape is evident in Figure 2.5.

Roberts and Bettany (1985 - cited in Fey *et al.*, 1996) showed that topography influenced the form and amount of sulphur within a soil profile. Soils in the lower landscape had more soluble sulphate and organic sulphur, and greater sulphate accumulation at depth, than soils in higher positions on a slope. The accumulation of sulphate in bottomlands due to processes of illuviation down a slope would confound interpretations with respect to sulphate of atmospheric origin. Thus sampling was restricted to the upper- and midslopes; bottomlands were not sampled at all.

The higher portions of the landscape are also more likely to intercept pollution plumes than the valley bottoms. Annegarn *et al.* (1996) found a greater concentration of sulphur dioxide at a monitoring site that was elevated 150 m above the surrounding terrain. Thus sampling of the upper slopes increases the likelihood of intercepting plume touchdown.

Figure 2.5 Site 7 viewed when facing W towards Arnot power station (8.1 km distant). The pollution plume is evident as is the gentle topography of the landscape.

2.3.5 Accessibility

Ease of access to the sampling sites was an additional criterion for selection although not an overriding one. Wherever possible, sites were selected on either Eskom or Amcoal property as land use on these properties are unlikely to change in the foreseeable future. Eskom is the major electricity generator in South Africa, while Amcoal is the mining division of Anglo-American which supplies coal to Eskom. When sites were located on private land, permission from the landowner was always sought.

2.3.6 Geology

Although parent material is a primary determinant of the nature of soil, geological features were not used as criteria, especially since the geology is fairly uniform. The sampling area is primarily underlain by interbedded shale, shaly sanstone, sandstone, grit and conglomerates of the Ecca formation, and interbedded tillite and shale of the Dwyka formation; both formations are of the Karoo sequence. These sedimentary rocks are intruded by coarse-grained dolerite. Some outcrops of Steenkampsberg quartzite and sub-ordinate shale of the Pretoria group are located in the easterly portion of the sampling area (Department of Mines, 1978; 2528 Pretoria 1:250 000 Geological Series map, Government Printer, Pretoria). Specific information with respect to rock type is provided for each sampling site (Appendix 1).

2.4 Sample collection and preparation

Having identified the area south-east and east-south-east of the power station as the most appropriate for sampling, specific sites were selected using a combination of orthophotographs, a 1:50 000 topocadastral map (Chief Directorate: Surveys and Land Information 2529DD Arnot, 1986) and a preliminary reconnaissance. The location of sampling sites is shown in Figure 2.2. Sampling was conducted from 5 to 9 August 1996.

Once a sampling site was selected using the criteria outlined in section 2.3, a centrepoint was selected at random. Care was taken to ensure that the entire sampling area was clear of features such as roads, tracks, kraal sites, stock feeding sites or rock ridges. Smaller features such as animal burrows and termite mounds could not be avoided but we ensured that soil samples were not taken near these. Notes were made of site features such as approximate distance to fences, windpumps, trees, farmgates and other landmarks. Each site is described in this manner in Appendix 1.

Since the establishment of baseline monitoring sites is an objective of this study, the exact location of each site must be known so that the correct sites can be resampled in the future. A GARMIN GPS 45 navigator was used to locate the position of the centrepoint of each sampling site. The Geographical Positioning System (GPS) is operated by the government of the United States of America, which is solely responsible for its accuracy and maintenance. The system is currently under development and is subject to changes which could affect the accuracy and performance of all GPS equipment. Thus, supplementary information from local maps and describing site-specific features was essential to ensure that each site could be relocated in the future.

The GARMIN GPS 45 features a MultiTrac8™ receiver which tracks and uses up to eight satellites simultaneously. Position accuracy ranges from 5 to 15 meters. The map datum field used as the default setting is the World Geodetic System 1984 (GARMIN GPS 45 Instruction Manual).

The centrepoint can be considered the hub of a wheel with a radius of 25 m (Figure 2.6). A soil sample was taken at the end of each of eight spokes which were roughly equal distances apart. Two additional samples were taken on opposite spokes 12 m from the centre - to give a total of 10 samples which were combined to give one composite sample for each site. The area sampled thus covered an area of about 1 970 m^2.

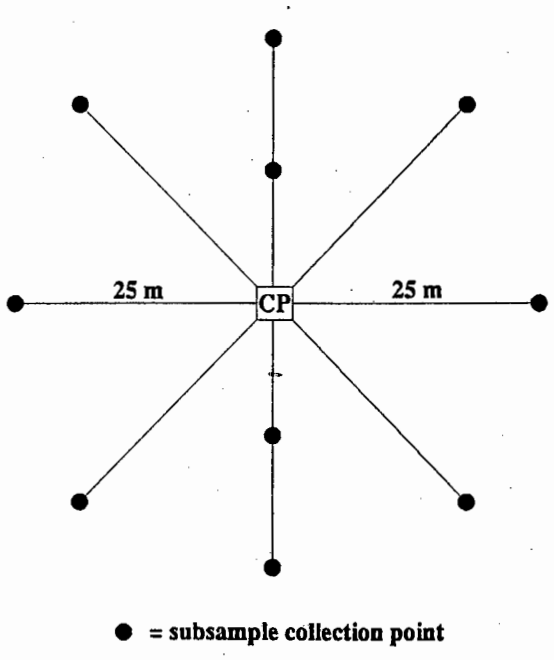


Figure 2.6 Sampling wheel showing the relative positions of samples to each other. Samples were combined to form one composite sample for each site.

At each point a topsoil and subsoil sample were taken. Topsoil was collected as follows: The soil surface was scraped clean of vegetation and loose material with a spade. A square of spade width (250 mm) was chopped into the soil surface to a depth of 10 cm. Once lifted, the soil clod was then quartered and taken to the centrepoint where it was deposited on a thick plastic sheet. Once all ten topsoil samples were collected, the clods on the plastic sheet were broken down, large roots and stones discarded and the soil well mixed to give a single composite sample. A two liter plastic screw-top bottle was filled with soil, as was a large, clear plastic bag. Both bottle and bag were labelled and sealed with masking tape. Approximately 4 kg soil was taken for each sample. Subsoil was sampled by augering deeper into the existing hole, until the auger tip was at a depth of 20 cm. Any soil in the auger blades was discarded. Further augering, to a depth of 40 cm, resulted in a sub-soil sample from 20 - 40 cm in the soil profile. As with the topsoil sample, the subsoil was broken down, mixed, bagged and labelled as a composite sample for that site.

Each site was sampled only once in this manner. Time and labour constraints did not allow more samples to be taken and this limitation must be considered during data interpretation. Sampling the top- and subsoil samples will give an indication of the geochemical feasibility of establishing long-term monitoring sites in the vicinity of Arnot. Based on the preliminary findings, the sites could be revisited to allow the description and classification of soil profiles for each site.

2.5 Validation of sampling protocol

The information gathered in this exercise is intended to provide the baseline data with which future work can be compared. However, within-site variability can be quite high, and some indication of the variability inherent at a site is thus necessary.

An attempt to validate the sampling protocol was made by revisiting three sites and repeating the sampling. Ideally, someone without any previous knowledge of the site should have performed the resampling - using a GPS, the topographical map and site descriptions to identify the sites. However, this was not feasible so I revisited three sites myself and tested the repeatability of sampling.

2.5.1 Materials and methods

A different GPS navigator unit was used but of the same make (GARMIN 45 GPS). Since I had prior knowledge of the site I could easily find the site and remembered the location of the centrepoint of the sampling wheel and recorded the position given by the GPS without knowing beforehand what they should be. The co-ordinates for both visits are presented in Table 2.3. Soils were resampled according to the original protocol. The three sites were revisited on 20 October 1996 and sampled in the same way. Time constraints limited sample collection to the topsoil only.

Preliminary air-drying and sieving was done at the CSIR laboratories in Nelspruit. The measurement of pH in water, KCl and K_2SO_4, and EC, was performed in the Geology Department at the University of Cape Town. Organic carbon by wet oxidation, ANC and anions in saturated paste solutions were also determined. Details of each method are given in Appendix 2. Only a few analyses were performed in order to get an impression of repeatability of the sampling.

2.5.2 Results and discussion

Finding the sites with the use of the maps and site descriptions was simple but the position of the centrepoint was not as easy to find, even though I was familiar with the site. While exploring the site, the original sampling holes could be found and were used as guides to estimate the location of the centrepoint. At the centrepoint the GPS reading was recorded, and can be compared with the original position (Table 2.3). The greatest discrepancy was recorded for latitude at site 6 - a difference of 0.027′ - which amounts to approximately 46 m. However, the identification of this site was less certain than the other two sites sampled. The smallest discrepancy was 2 m from the original centrepoint. The GPS has a recognised error of 15 m, so the general repeatability of the GPS for the remaining sites is either within or slightly over that error margin.

Subsamples were taken near to the original sampling holes and pooled to give a composite sample. The results presented in Table 2.3 show that, to a large extent, the findings for the different sampling times are quite similar. Despite the 46 m discrepancy in the latitudinal position of the site 6 centrepoint, the values obtained for anions, pH, organic carbon and ANC were very similar. However site 13 showed a doubling in the concentration of Cl, NO_3, and SO_4, which is also reflected in the higher value for electrical conductivity. The extracts were repeated to ensure that analytical error was not the cause of the differences. The estimates of percentage organic carbon also show some range in values. Obviously more replicates are necessary for a statistically valid comparison and more sites should be included. By collecting composite samples over a large area it was hoped that within-site variability would be minimised.

Freedman and Hutchinson (1980) found with-in site variability to be high in their study of a deposition gradient from a nickel-copper smelter in Sudbury. Six samples from a site had been combined to form one composite sample for the Subury site whereas ten samples made up the composite sample in the present study. A far more intensive sampling strategy was employed by Stuanes *et al.* (1995) in a similar study were soils were sampled from 50 points in a grid of 10 m by 20 m in size. Sampling was repeated four times for each grid. Unfortunately the authors gave no information on within-site variability. These two examples from the literature illustrate that sampling intensity should be given careful consideration. The most efficient and effective sampling strategy will depend on the inherent variation of each site.

Table 2.3 Comparison of selected analytical data for samples taken in August and October for three sites.

	Site 6		Site 13		Site 15	
	August	October	August	October	August	October
Position co-ordinates	25°56.142'S 29°47.892'E	25°56.169'S 29°47.909'E	25°58.740'S 29°49.948'E	25°58.749'S 29°49.947'E	25°57.345'S 29°47.087'E	25°57.342'S 29°47.077'E
Anions in saturated paste solution ($mg.L^{-1}$)						
Cl	23.3	27.3	8.5	18.1	24.3	27.3
NO_3	1.9	1.3	0	1.0	0.5	1.2
SO_4	40.6	43.0	19.8	42.8	48.6	51.2
EC ($\mu S.cm^{-1}$)	291	245	144 (n=2)	210 (n=2)	273	288
pH (water)	5.2	5.2	5.8	5.7	5.9	5.9
pH (KCl)	4.1	4.1	4.4	4.4	4.5	4.6
pH (K_2SO_4)	4.6	4.6	4.8	4.8	4.9	5.0
Organic carbon (%)	2.3	2.2	1.8	2.1	2.2	2.8
ANC ($cmol_c.L^{-1}$)	2.5	2.6	2.9	2.9	3.7	4.1

Ideally, the validation of a sampling protocol should be far more comprehensive than the approach adopted in this study. Ramsey *et al.* (1995) have shown that the principles of the collaborative trial, where the performance of an analytical method is assessed, can be applied to sampling strategies. In a collaborative trial a number of workers would independently follow the sampling instructions for a particular site; the collected samples would then be analysed under repeatable conditions (i.e. in a single run in one laboratory) to avoid confounding analytical variations with sampling variations. Such an exercise allows estimates to be made of the uncertainties associated with the sampling method. The suitability of the sampling protocol can then be evaluated.

Seasonal variation can be an important confounding factor in studies which require resampling. Tabatabai (1982) states that the sulphur status of soil will vary on a seasonal basis. The sampling period for this study extended over the dry winter months when sulphate movement in rainwater leachate is minimal. To achieve reproducibility, resampling for long-term monitoring purposes should be done in the dry season.

2.5.3 Conclusions

The sampling procedure described above represents a preliminary stage in the establishment of long-term monitoring sites near a power station. The repeatability of the sampling protocol appears to be satisfactory. The method of testing was, however, based on a superficial examination of the results obtained for a few analytical procedures. The reproducibility of the sampling protocol, in which several workers independently sample the site in a predetermined fashion, should be tested by the application of a collaborative trial approach, as advocated by Ramsey *et al.* (1995). A more rigorous assessment of the sampling protocol is essential if the data are to contribute to a long-term monitoring programme.

In addition, the number of sites to be sampled at some future time may be reduced if geochemical evidence indicates unusual sites which warrant exclusion from the data set. The provision of accurate geographical information and site descriptions enables each site to be revisited for more detailed description and classification of soil profiles at any time in the future.

CHAPTER 3

DETERMINATION OF SOIL SULPHATE

3.1 Introduction

Sulphur is a key element operating in biogeochemical cycles and exists in a variety of forms and oxidation states. In terms of global reservoirs, most of the sulphur at any time is found in the lithosphere. The weathering of sulphide-bearing minerals in rocks releases sulphur as sulphate. Since sulphur is a necessary nutrient for all forms of life, much of the sulphate is incorporated into the biomass through plant uptake and microbially mediated reactions. The organically bound sulphur is then released back to the soil through decay and mineralisation reactions (Freney and Williams, 1983; Charlson *et al.*, 1992). Under certain climatic conditions, the decay processes may be arrested and the subsequent accumulation of organic matter be converted to coal, peat or petroleum gas. The anthropogenic combustion of these fossil fuels accelerates the transfer of sulphur between the lithosphere and the atmosphere.

Sulphur in soils can be broadly grouped into organic sulphur, accounting for over 95 % of the total sulphur in soils, and inorganic sulphur. The inorganic fraction is dominated by sulphate in oxidising environments and occurs as water soluble salts, in insoluble forms or as sulphate adsorbed onto soil colloids (Tabatabai, 1982). The term labile sulphate refers to both the water-soluble and sorbed fractions.

The accurate determination of soil sulphate is an essential requirement in evaluating whether or not anthropogenic impacts from the oxidation of fossil fuels are occurring. A long-term monitoring system established to detect impacts requires reliable baseline data and a consistent method of analysis in order to make valid comparisons between present and anticipated conditions. In the following chapter, two methods for the chemical analysis of labile sulphate are compared and the suitability of each method to meet these requirements is assessed.

3.2 Methods of sulphur determination

Much of the sulphur in soil is bound in the organic fraction which is normally estimated from the difference between total sulphur values and the inorganic sulphate values (Tabatabai, 1982). Total S is usually determined by the conversion of the various sulphur forms by oxidation to one form - such as sulphate - which is then determined by colorimetry, gravimetry, turbidimetry or by ion exchange. Total S can also be accurately determined by x-ray fluorescence spectroscopy (XRFS) (Tabatabai, 1982).

Sulphate is the most common form of inorganic sulphur in soils, particularly in well-drained and well-aerated soils. Freney (1961, cited in Tabatabai, 1982) estimates the amount of reduced sulphur compounds at < 1 % under such conditions. No attempts were therefore made in the current study to convert reduced S-compounds to sulphate prior to determination. Since sulphate can be sorbed onto soil surfaces, the amount that is measurable depends on the fraction that is released by the soil surface. The capacity of a variety of solutions to extract sulphate is reviewed by Tabatabai (1982). The water soluble sulphate fraction can be extracted with water while various chloride and phosphate salts are suggested for extraction of the adsorbed fraction. Fox *et al.* (1964, cited in Tabatabai, 1982) found 0.01 M $Ca(H_2PO_4)_2.H_2O$ to be most effective; the phosphate in the solution, in the concentration of about 500 $mg.L^{-1}$ P, is able to displace most of the adsorbed sulphate of many soils and the resultant extract is easier to filter than an extractant such as KH_2PO_4. The sulphate can then be determined by colorimetry, turbidimetry, titrimetry, gravimetry or ion chromatography. Tabatabai (1982) recommends the colorimetric method developed by Johnson and Nishita (1952) as the most accurate means of determining sulphate. However, the method requires specialised glassware and reagents and is labour intensive. Of the methods listed, turbidimetry and ion chromatography are discussed further since these were the two techniques exploited in the present study.

Turbidimetric determination of extractable sulphate is a widely practised technique employed by many laboratories, although a number of problems are associated with the method. In principle, sulphate in solution reacts with an excess of barium chloride which forms insoluble barium sulphate. The turbidity of the resultant solution is measured by the amount of light attenuated through scattering by the precipitate, and is then determined spectrophotometrically. High variability plagues turbidimetric determinations, and there can be considerable uncertainty concerning the accuracy of the results (Adams *et al.*, 1984). Variability can stem from interference from other solutes or incomplete precipitation reactions. Despite these flaws, turbidimetry is widely used because it is a simple and rapid means of analysing for sulphate in aqueous solutions.

Ion chromatography is a relatively modern technique for the determination of sulphate inorganic ions in aqueous solution. Ion chromatography (IC) separates ions in a sample on the basis of differential affinity for an ion exchange surface. The sample is carried by a mobile phase - the eluent - through an ion exchange resin which represents the stationary phase. The dense packing of resin beads in the exchange column requires that the eluent be under high pressure in order to pass through the column. The ions progress through the column at different rates and therefore enter the detector at different times. The ions are detected by the increase in electrical conductivity of the mobile phase and are reported as conductivity peaks on a chromatogram. The elution time is specific to a particular ion and the peak area or peak height is proportional to concentration, which is determined after appropriate calibration with standard solutions (Willard *et al.*, 1988).

Ion chromatography is a method which has been extensively evaluated and can be regarded as reliable as well as recommended for the determination of common ions such as sulphate. It is well recognised as being a sensitive technique with detection limits, accuracy and precision being instrument dependent (Fifield, 1995; Watson, 1994, Method No. W75, pg 537 & 617). Although recognized as having wide potential applications, to my knowledge, the general literature reports no instances where IC has been used for the determination of phosphate-extractable sulphate. The high concentration of phosphate in the extract would generally require dilution in order to avoid overloading the anion exchange column and sulphate is consequently anticipated to be diluted beyond detection. Thus the use of IC for the determination of phosphate-extractable sulphate represents a novel application of the technique.

3.3 Materials and methods

3.3.1 Extraction of water-soluble sulphate

An aqueous extract of each soil was prepared from 500g of soil saturated to field capacity, using the method of Rhoades (1982a), details of which are given in Appendix 2. The extract was filtered through a 0.45 μm filter to remove colloids, followed by a Dionex On-Guard-P cartridge for removal of organic compounds.

3.3.2 Extraction of the adsorbed sulphate fraction

The extraction of adsorbed sulphate was performed in the laboratories of the Grain Crops Institute at Cedara, Pietermaritzburg, KwaZulu-Natal. Sulphate was extracted with 0.01 M $Ca(H_2PO_4)_2.H_2O$ containing 10 mL Superfloc per litre. A 2.50 g sample of air-dry soil (< 2 mm fraction) was weighed into soil cups, to which 25 mL of the calcium phosphate solution was added by automatic dispenser. The solution was then stirred for 30 minutes on an automated stirring apparatus. Solution and soil were filtered through approximately 2 g of sulphur-free carbon held in Whatman No. 1 filter paper to remove any organic colouration from the extract prior to turbidimetric analysis.

3.3.3 Sulphate determination by turbidimetry

Turbidimetric analysis for sulphate was also performed in the Grains Crop Institute laboratories at Cedara, using an auto-analyzer method. Solutions for the auto-analyzer were prepared according to the directions given by Wall, Gerhrke and Suzuki (1986). Calibration standards of 0, 5, 10, 15 and 20 ppm S were prepared in the soil extracting solution. A batch of 43 samples could be analyzed at a time, but these included calibration standards, distilled

water blanks, extractant blanks and a control soil of known sulphate concentration. Determinations of the control soil and the calcium phosphate extraction blank were each repeated three times during each analytical run and the 10 ppm S calibration standard was repeated twice. The concentration of sulphate was determined from a calibration curve, after which the extractant blank value was subtracted from the sample value.

Five extractions and analytical runs were performed, giving at least three determinations of extractable sulphate for each sample; in some cases four were obtained. Two samples of saturated paste extracts were also analyzed but the small solution volume permitted only one determination of the water-soluble sulphate.

3.3.4 Sulphate determination by ion chromatography

Each sample was diluted appropriately to achieve an electrical conductivity less than 100 $\mu S.cm^{-1}$ in order to avoid over-loading the exchange column. For the saturated paste extracts the dilution factor was either two or five, whereas the calcium phosphate extracts required a tenfold dilution. All samples were filtered prior to analysis as described in section 3.3.1.

A DIONEX 300 ion chromatography system and associated software was used for the determination of sulphate. The determination was performed on a Dionex HPIC-AS4A-SC anion exchange column with carbonate/bicarbonate eluent and conductivity detection, using peak area as the basis for determination. The run conditions were as follows:
Sample loop volume: 50 µL
Guard column: Dionex HPIC-IonPac AG4A
Separator column: Dionex HPIC-IonPac AS4A-SC
Eluent: 1.80mM Na_2CO_3 and 1.70 mM $NaHCO_3$
Eluent flow rate: 2.0 $mL.minute^{-1}$

3.4 Results and discussion

The concentrations of sulphate in saturated paste extracts are presented in Table 3.1. Where possible a repeat determination was performed, but samples and replicates are insufficient to allow a full statistical comparison. Analyses performed on the same day were highly repeatable (samples indicated by n=2 or n=3).

Table 3.1 shows the similar concentrations of sulphate obtained by both IC and turbidimetry for the two saturated paste extracts (5T and 7T).

Table 3.1 Concentrations of water soluble sulphate in saturated paste extracts determined by ion chromatography and turbidimetry (mg $SO_4^{2-}.L^{-1}$). Topsoils are designated by -T and subsoils by -S.

Sample	Ion chromatography				Turbidimetry
	Assay on 9/9/1996	Assay on 27/9/1996	Mean	s[1]	
1T	32.1 (n=3, s=0.07)				
2T	22.7				
3T	35.0				
4T	24.2	28.2			
5T	33.8	29.7	31.8	2.9	30.3
6T	40.6				
7T	34.2	29.5	31.9	3.3	34.0
8T	41.9	38.3			
9T	41.5				
10T	25.0				
11T	62.0				
12T	46.2 (n=2, s=0.02)				
13T	19.9				
14T	19.1				
15T	48.6				
1S	18.4	17.5			
2S	31.7				
3S	25.2				
4S	18.9 (n=2, s=0.03)				
5S	25.2				
6S	42.3				
7S	15.5 (n=2, s=0.06)				
8S	24.7				
9S	17.4				
10S	41.1				
11S	51.7				
12S	38.9	34.8			
13S	20.3				
14S	17.0	15.2			
15S	21.6 (n=2, s=0.06)				

[1] s = one sample standard deviation

The results for the determination of extractable sulphate by turbidimetry are presented in Table 3.2, together with the values obtained for the control soils and the extractant blanks. The results of the turbidimetric determination are highly variable: for some soil samples the repeatability of analysis was good (eg 12T and 5S), whereas others displayed a wide range of sulphate concentration (eg 3T, 7T and 2S). Sample means and standard deviations are presented in Table 3.2.

Table 3.2 Phosphate extractable sulphate determined by turbidimetry. Each analytical run is individually presented to demonstrate the variability of control soils and blanks between different runs. Topsoils are designated by -T and subsoils by -S.

Sample	Phosphate extractable sulphate (mg sulphate. kg soil^{-1})					Mean	Standard deviation	Relative standard deviation
	4/10/1996	10/9/1996a	10/9/1996b	10/9/1996c	9/9/1996	(x)	(s)	%
1T	21.1	16.9		21.3		19.7	2.5	12.6
2T	22.0	2.2		15.9		13.4	10.1	75.7
3T	23.6	2.5		9.1		11.7	10.8	92.2
4T	11.7	20.8		19.5		17.3	4.9	28.4
5T	22.0	26.4	26.6	26.4		25.4	2.2	8.8
6T	29.0	28.9	29.8	34.3		30.5	2.6	8.4
7T	19.2	9.1		13.3		13.9	5.1	36.8
8T	31.6	48.2	48.3	38.2		41.6	8.2	19.6
9T	17.6	25.8	25.7	18.2		21.8	4.5	20.7
10T	11.9	11.2	11.2	8.9		10.8	1.3	12.1
11T	19.2	20.4	20.8			20.1	0.8	3.9
12T	28.3	26.7	27.2	28.7		27.7	1.0	3.5
13T	14.6	20.7	22.4		7.8	16.4	6.6	40.4
14T	20.4			20.3	15.5	18.8	2.8	14.8
15T	20.5			23.3	13.0	18.9	5.3	28.2
1S	0.0	0.0		0.0		0.0	0	-
2S	50.7	19.6		21.4		30.6	17.4	57.0
3S	5.5	6.2		5.4		5.7	0.5	8.1
4S	21.6	21.2		12.4		18.4	5.2	28.2
5S	80.1	79.2	80.8	82.5		80.6	1.4	1.7
6S	66.0	60.0	60.4	62.0		62.1	2.7	4.4
7S	3.4	4.7	4.7	5.9		4.7	1.0	21.9
8S	59.6	60.6	63.0	49.4		58.1	6.0	10.3
9S	0.0	0.0	0.0	0.0		0.0	0	-
10S	21.5	23.2	26.2	17.1		22.0	3.8	17.3
11S	19.7	23.4	23.5	23.1		22.4	1.8	8.0
12S	0.0	0.6	4.5		0.0	1.3	2.1	169.8
13S	25.3	21.9	22.0		15.2	21.1	4.3	20.2
14S	48.3			52.3	45.5	48.7	3.5	7.1
15S	70.2			63.8	68.1	67.4	3.3	4.9
Control soils		123.4	126.7	124.3	131	126.4	3.4	2.7
Extractant blanks		2.7	2.5	2.5	4.0	2.9	0.7	24.7

Samples 1S and 9S repeatedly recorded zero values of extractable sulphate while sample 12S recorded very low values of sulphate. Yet the absence of any extractable sulphate in samples 1S and 9S seems unlikely since both were found to have water-soluble sulphate, albeit in low concentrations (Table 3.1). The explanation for this anomaly may lie in the subtraction of the calcium phosphate blank, particularly for samples where the initial extractable sulphate concentration is low. Fox *et al.* (1987 - cited in du Toit, 1993b) suggest that small amounts of calcium phosphate can interfere with the precipitation of barium sulphate. Sulphate can be underestimated in some soils because unknown constituents of the soil solution prevent the precipitation of the barium sulphate. Fox *et al.* (1987) name soluble silica as one possible culprit. The co-precipitation of barium phosphate may also be problematic, especially at low sulphate concentrations when barium sulphate is minimal compared with barium phosphate (du Toit, 1993b). These observations are supported by the more consistent results obtained for the control soil, which has considerably more sulphate than any of the soils sampled. Another explanation may be offered for soils with a large sorbing capacity for phosphate. If phosphate is sorbed onto the soil surface in large amounts, the initial high phosphate concentration that was accounted for in the blank may no longer be applicable to the sample. By subtracting the calcium phosphate blank in these soils, an overcorrection would be effected, resulting in negative values for sulphate. That interference from the calcium phosphate extractant may occur is further substantiated by comparison of the water-soluble sulphate concentrations which were determined by both IC and turbidimetry (samples 5T and 7T in Table 3.1). In this case the extractant used was distilled water and the results for both determinations are quite similar.

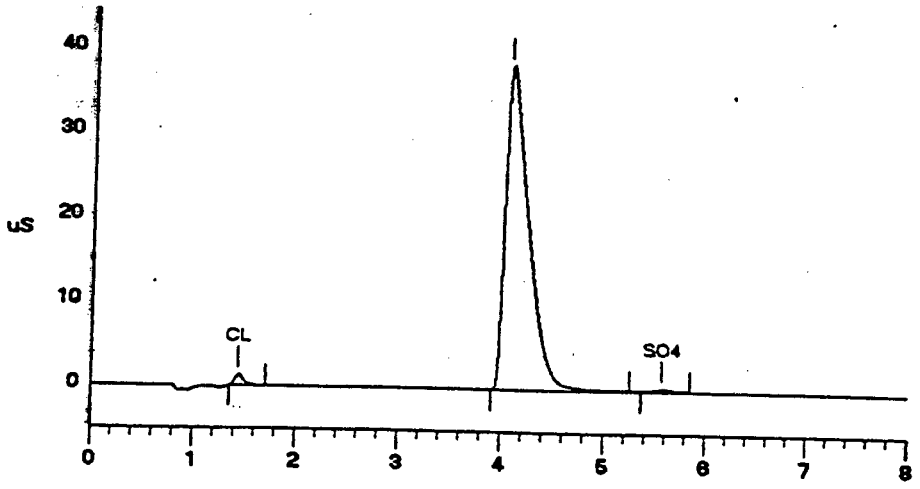
The soil extracts prepared on 4 October 1996 were used for direct comparison with ion chromatography. To the author's knowledge, the use of ion chromatography to determine phosphate-extractable sulphate has not been reported in the scientific literature. After extraction and determination of the labile sulphate fraction at Cedara, the remaining solution was couriered to the University of Cape Town for determination by IC. The values obtained by IC were considerably higher than those obtained by turbidimetry (Table 3.3). To account for the discrepancies the IC chromatograms were scrutinised more closely. Inspection of the chromatograms revealed that, despite the apparent separation of peaks, there was still a degree of overlap between the phosphate and sulphate peaks. The IC data were then reprocessed to allow more accurate calculation of the area under the sulphate curve (Figure 3.1). At low concentrations of sulphate the adjustment could reduce the measured concentration by as much as 7 %. Once dilution factors (10x) had been accounted for and the concentrations had been related to the soil mass (soil:extractant ratio = 1:10), the absolute error was magnified a hundredfold. The original and processed IC data are presented in Table 3.3 along with the results for turbidimetry.

Table 3.3 Concentration of extractable sulphate (mg $SO_4^{2-}.kg^{-1}$ soil) in the soil collection determined by turbidimetry and ion chromatography (IC). Topsoils are designated by -T and subsoils by -S.

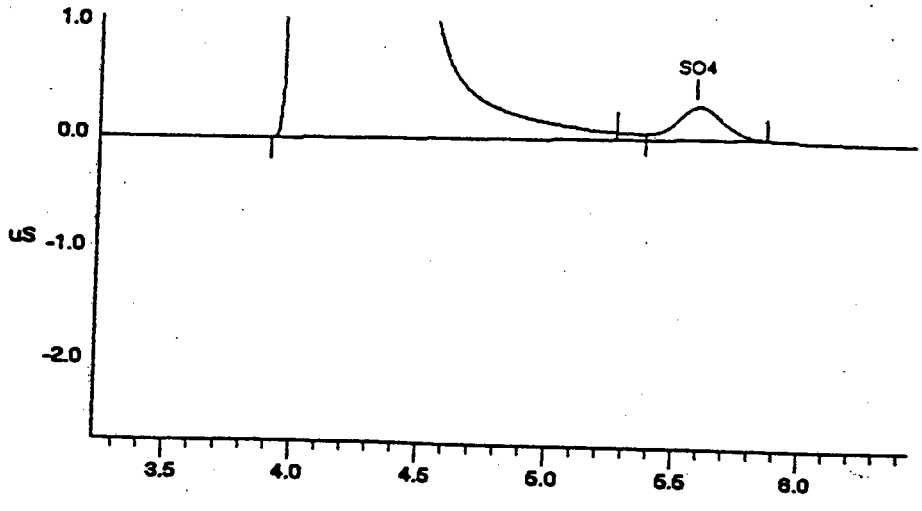
Sample	Turbidimetry	IC - uncorrected*	IC - corrected*
1T	21.1	63.4	59.1
2T	21.6	82.6	77.4
3T	23.1	74.1	68.6
4T	12.1	67.9	63.2
5T	22.2	95.8	91.1
6T	28.3	89.8	84.6
7T	18.8	103.3	97.2
8T	31.0	95.4	90.1
9T	17.4	84.5	79.3
10T	12.0	57.7	53.4
11T	19.0	87.5	81.9
12T	28.0	90.6	85.5
13T	14.2	52.9	48.6
14T	19.9	61.7	57.2
15T	20.0	58.8	54.0
1S	0.0	89.8	85.5
2S	49.7	113.6	106.8
3S	5.3	56.2	52.3
4S	22.0	96.1	91.6
5S	79.6	142.7	138.2
6S	64.4	146.5	140.8
7S	3.3	73.6	68.8
8S	58.1	146.6	140.1
9S	0.0	85.3	81.4
10S	21.8	88.5	83.8
11S	19.2	87.9	82.6
12S	0.0	85.6	80.9
13S	24.6	72.9	68.0
14S	47.1	104.5	99.7
15S	68.4	121.7	116.2

* Correction involved accounting for the tailing of the phosphate peak under the sulphate peak as is shown in Figure 3.1b.

a).



b).



c).

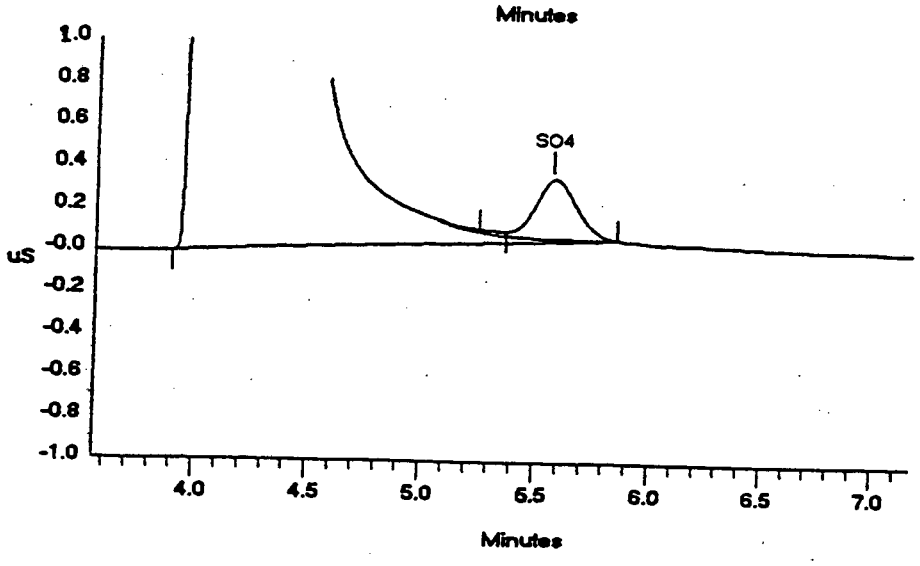


Figure 3.1 Chromatogram for sample 14T showing a) the apparent separation of the phosphate peak (unlabelled) and sulphate peak, giving a sulphate concentration of 0.61 ppm sulphate. Closer inspection b) shows the overlap between the phosphate and sulphate peak. Reprocessing of the software parameters shows the phosphate tail under the sulphate curve in c). The area above the phosphate tail is recalculated to give a concentration of 0.57 ppm sulphate.

Phosphate-extractable sulphate values from Table 3.3 are plotted against the total sulphur determined by XRFS in Figure 3.2. The discrepancy in the values of extractable sulphate determined by IC and turbidimetry is readily apparent.

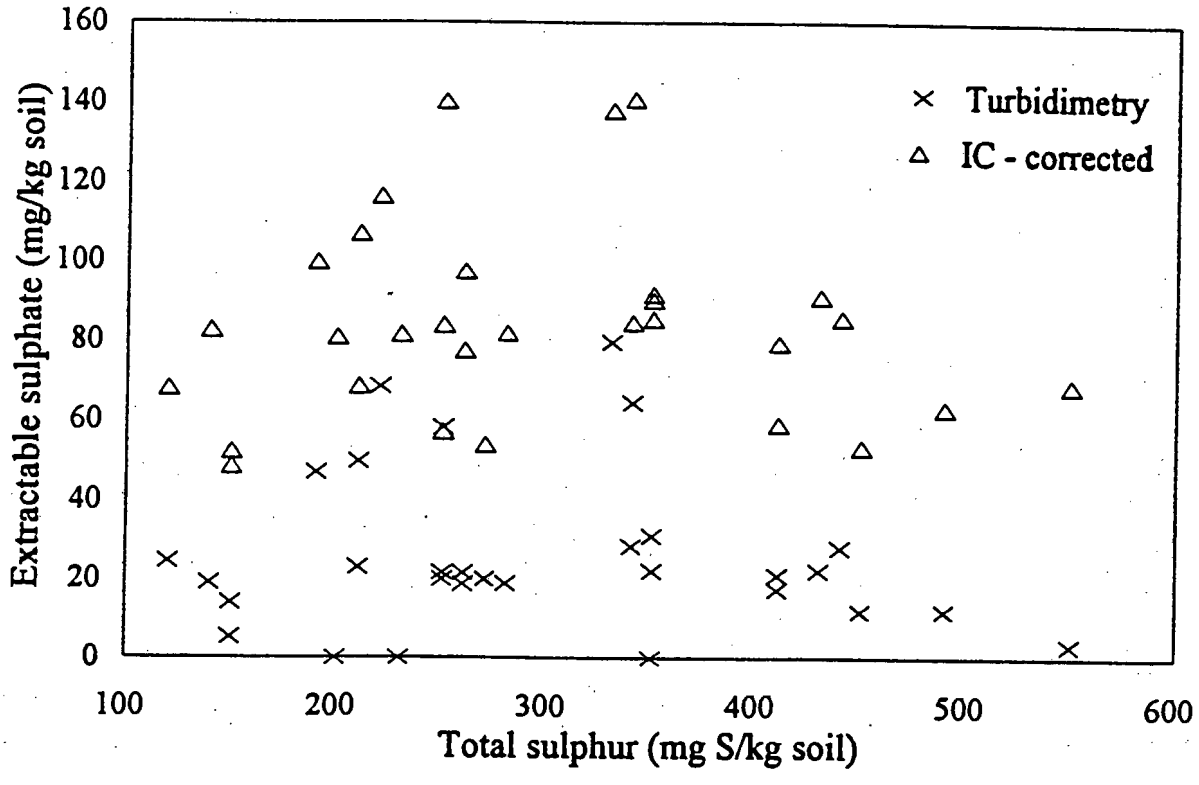


Figure 3.2 Extractable sulphate determined by turbidimetry and IC plotted against total sulphur determined by XRFS.

A significant correlation was found between the results obtained by turbidimetry and IC (r^2 = 0.64, 28 d.f.) (Figure 3.3). Interestingly, the slope of the regression relationship between the two methods is very close to one, suggesting that the overall difference between the two is relatively constant, although the weakness of the regression also indicates that there is considerable random variation in this difference among the soils.

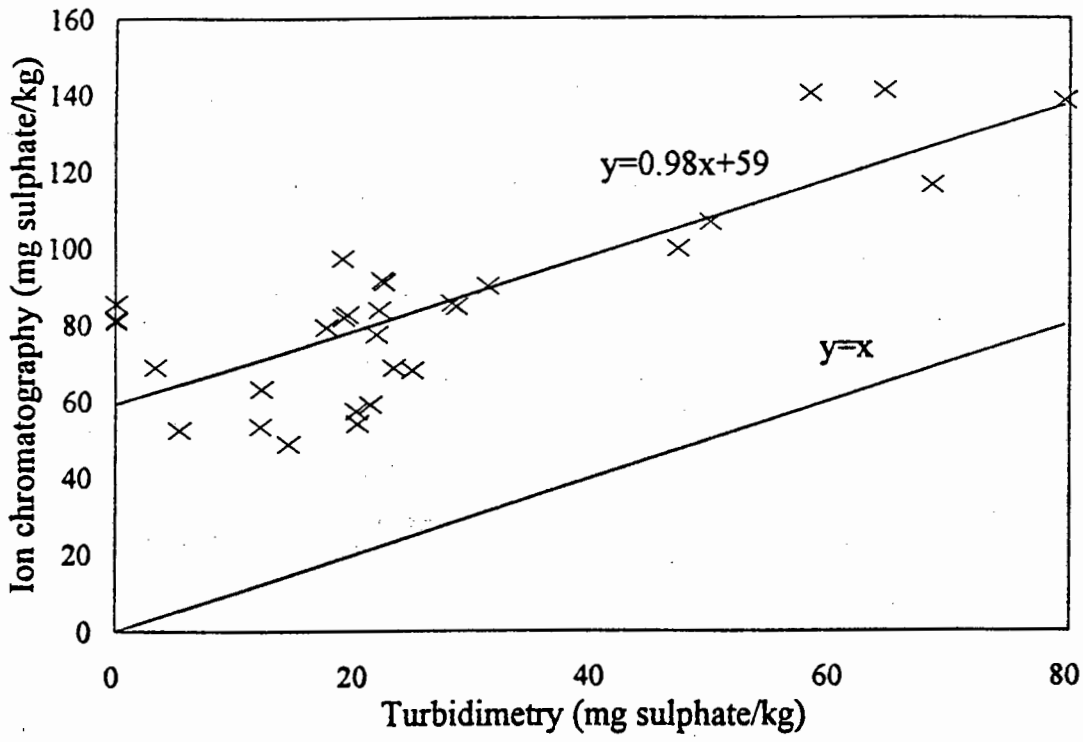


Figure 3.3 The relationship between the extractable sulphate determined by IC and turbidimetry ($y=0.98x+59$, $r^2=0.64$, 28 degrees of freedom); the equivalence line ($y=x$) is plotted for comparison.

Wall *et al.* (1986) found the precision of the automated turbidimetric method to be excellent, reporting a relative standard deviation of 2.28 % for three independent analyses done in duplicate on six soil samples. On the other hand, Adams *et al.* (1984) found turbidimetry to be the least reliable of four methods used for the determination of soil sulphate. Turbidimetry overestimated the sulphate added as a spike and generally gave higher values of sulphate compared with other methods. Although based on the same principle of $BaSO_4$ precipitation, the findings of Adams *et al.* (1984) are not directly comparable to the present study. Adams *et al.* (1984) used the standard method for sulphate determination recommended by The American Public Health Association (1971) and there are considerable differences in the composition of the buffer solutions and experimental procedure compared with the method used in the laboratories at Cedara.

The present results show a large degree of variability and an apparent underestimation of extractable sulphate by turbidimetry, possibly attributable to incomplete precipitation reactions. Poor sulphate determination could also be caused by removal of more sulphate from standards than samples by the decolorising charcoal, contamination of the charcoal by sulphate or incomplete removal of colloidal particles by filtration (MC du Toit, 1993; Adams *et al.*, 1984). Despite its simplicity and ease of use, the automated turbidimetric method for sulphate determination does not appear to be suited to the accurate determination of sulphate, particularly at low concentrations.

The high phosphate concentration (500 $mg.L^{-1}$ P) of the extractant solution limits the sensitivity of IC for the determination of sulphate since the soil extract must be diluted to avoid overloading the exchange column. The sulphate present in the extractant solution is consequently diluted to low concentrations (as low as 0.5 $mg.L^{-1}$ sulphate), nearing the lower limits of reliable detection for the sulphate anion (about 0.2 $mg.L^{-1}$; JP Willis, personal communication).

Clearly, neither method is without its drawbacks. The strength of the extracting solution could be reduced so that less dilution is required for IC. A concentration of approximately 200 $mg.L^{-1}$ P might prove strong enough to displace sulphate from soil surfaces and would require less dilution, effectively increasing 2.5-fold the sensitivity of the IC method for phosphate-extractable sulphate detection. A longer extraction time might also be effective. In addition, a slower elution rate could be used so that anion peaks are narrower and more easily measured off the chromatogram. The determination of extractable sulphate could be done quite reliably provided there is careful processing of the IC data to eliminate peak overlap. An added advantage of IC is that anions such as chloride, nitrite and nitrate can be determined simultaneously - taking only eight minutes per sample to do so.

The data presented above suggest that the determination of extractable sulphate by turbidimetry is inaccurate at low concentrations, confirming the findings of MC du Toit (1993), whereas IC is generally acknowledged to be a reliable technique. Since water extractable sulphate was measured in all samples by IC, the zero values obtained by turbidimetry for phosphate-extractable sulphate show turbidimetry to be inappropriate for determinations of this nature. Turbidimetry may be satisfactory to establish relative quantities of soil sulphate but remains suspect in terms of its accuracy.

3.5 Conclusions

Comparison of phosphate-extractable sulphate values showed those determined by turbidimetry to be consistently below those determined by IC. The phosphate extractant solution appears to be primarily responsible for the high variability and inaccuracies associated with the turbidimetric determination, especially at low concentrations of sulphate. The subtraction of the extractant blank may result in an over-correction for soils with a high phosphate-sorbing capacity. Thus turbidimetry is not only inaccurate at low concentrations of sulphate but also inconsistent as soils differ in their capacity to retain phosphate. Further work with turbidimetry should focus on experimenting with soils of various phosphate sorption capacities to establish the subsequent effect on the accuracy of sulphate determination.

The use of ion chromatography for the determination of phosphate-extractable sulphate has not been reported in the literature. Nevertheless, the preliminary results presented here suggest that IC is potentially a viable, and probably more accurate method compared to turbidimetry, for phosphate-extractable sulphate determination. Further evaluation of this new application of ion chromatography is recommended, especially with relation to possible modification of the extraction conditions and instrumental operation to improve both sensitivity and accuracy.

CHAPTER 4.

PROPERTIES OF SOILS IN THE VICINITY OF ARNOT POWER STATION WITH SPECIAL REFERENCE TO POTENTIAL AIR POLLUTION IMPACTS

4.1. Introduction

The monitoring of long-term changes has been identified by Wolters and Schaefer (1994) as the best and most direct way of quantifying the effects of atmospheric deposition. During the establishment of long-term monitoring sites, the collection and characterization of the baseline data is of primary importance and should be performed according to a range of standard physical, chemical and mineralogical methods. Special emphasis should be placed on those soil properties most likely to be impacted by atmospheric pollution - such as parameters related to soil acidity and soil sulphur status. Finally, wherever possible, relationships between various soil properties should be identified as these may provide a firmer basis for future comparison and possibly allow a comparison with sites elsewhere.

In this chapter, the suite of soils collected in the vicinity of Arnot power station is described and the relationships between a range of parameters are explored.

4.2. Materials and methods

Details of the methods employed are provided in Appendix 2 or are cited from general texts. The pH in distilled water, KCl and K_2SO_4 was determined for each soil, using a 1:2.5 soil:solution ratio. Acid neutralizing capacity (ANC) was determined according to the method of du Toit and Fey (1994) and du Toit (1993a). Extractable base cations (Mg and Ca) and extractable acidity were determined in 1 M KCl (Thomas, 1982). Extractable bases were determined by atomic absorption spectrometry, while extractable acidity was determined by potentiometric titration. Effective cation exchange capacity was calculated as the sum of extractable acid and base cations. Acid saturation was then derived as extractable acidity*100/ECEC.

Organic carbon by the Walkley-Black wet oxidation method, and citrate-bicarbonate-dithionite (CBD) extractable Fe, Mn and Al were determined according to the methods outlined by Nelson and Sommers (1986), and Jackson *et al.* (1986), respectively.

Saturated paste extracts were prepared by wetting 500 g of soil to field capacity then extracting the soil solution by suction (Rhoades, 1982). Concentrations of anions and cations in the soil solution were determined by ion chromatography, as described in Chapter 3. Although phosphate-extractable sulphate was determined turbidimetrically (Wall *et al.*, 1986), only those values of extractable sulphate determined by ion chromatography were used. Chapter 3 outlines the rationale for this decision and presents a description of the method employed.

The major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, S and P, reported as oxides) were determined for all soils by XRFS using Norrish fusion discs. Powder briquettes were prepared for the determination of trace elements (Mo, Nb, Zr, Y, Sr, U, Rb, Th, Pb, Zn, Cu, Ni, Co, Mn, Cr and V) by XRFS.

The mineralogical study on the sand, silt and clay fractions was performed by X-ray diffractometry by the ISCW in Pretoria. Particle size analysis was performed by sedimentation using the hydrometer method.

4.3. Results and discussion

4.3.1. General soil properties

Table 4.1 shows the solid phase properties that were measured for each of the sampled soils. The majority of the soils are classed as sandy loams or loamy sands, although 5 subsoils fall into the sandy clay textural class. The highest clay content (30%) was recorded for the subsoil on site 10.

The most widespread parent material is the Ecca group of shales and sandstones, with intrusions of dolerite dykes and sills. The sandstone influence is reflected in the dominance of quartz in the silt and sand fractions. Less than 10 % feldspar occurs in 60 % of the soils sampled. With one exception (site 10), the clay fraction is dominated by the 1:1 layer silicate, kaolinite, followed by mica. The soils of site 10 have an almost equal ratio of smectite to kaolinite - a reflection of the doleritic parent material found in this region of the highveld (Bühmann, 1986). Although the goethite fraction is reported in Table 4.1 it is regarded as an overestimation, as comparison with the total Fe_2O_3 determined by XRFS will show.

The dominance of quartz in the sand and silt fractions, and kaolinite and mica in the clay fractions, indicates a moderate stage of soil development - according to the Jackson and Sherman sequence of soil development (1953, cited in McBride, 1994).

Table 4.1 Textural, chemical and mineralogical characteristics of the soil collection

Sample	Distance *	Clay	Silt	Sand	Gravel	Organic carbon	CBD extractable			Minerals in clay fraction					Minerals in silt fraction				Sand fraction	
		(< 2mm fraction)					Fe	Al	Mn	Mica	Kaolin.	Goet.	St.	Is.	Mica	Kaolin.	Quartz	Feld.	Quartz	Feld.
	(km)	%	%	%	%	(%)	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Topsoil																				
1	19.9	20	10	70	7.5	4.5	2.70	0.23	0.063	12	72	16					100		100	
2	16.9	14	4	82	0.5	2.3	0.83	0.32	0.005		86	14					98	2	100	
3	14.8	7	3	90	1.0	0.9	0.34	0.11	0.014	13	87						96	4	99	1
4	12.8	19	11	70	4.7	3.8	2.10	0.36	0.047	8	86	6					100		100	
5	10.7	22	10	68	1.7	3.2	1.40	0.34	0.008	3	94	3				2	92	6	98	2
6	1.3	15	7	78	7.2	2.3	1.60	0.32	0.009	3	90	7				4	94	2	100	
7	8.1	7	5	88	0.1	1.5	0.26	0.08	0.012	9	91						97	3	96	4
8	14.4	9	7	84	1.1	2.9	1.30	0.37	0.008	7	80	13					100		100	
9	12.6	16	8	76	0.5	3.6	1.10	0.27	0.020	9	72	19					100		100	
10	8.3	21	8	71	0.7	3.3	0.66	0.08	0.058	19	36		44				96	4	100	
11	4.5	8	5	87	4.5	2.8	0.51	0.12	0.011	6	91	3					96	4	100	
12	5.5	14	11	75	5.4	4.0	0.86	0.19	0.008	13	66	21					100		100	
13	5.8	10	8	82	3.4	1.8	0.46	0.12	0.010	25	53	10		12			93	7	99	1
14	18.8	16	5	79	0.3	1.8	0.90	0.25	0.008		80	20					96	4	100	
15	1.0	16	6	78	0.0	2.2	1.00	0.24	0.008	5	86	9				2	96	2	100	
Subsoil																				
1	19.9	25	7	68	20.1	2.3	2.60	0.35	0.052	9	76	15			2	5	93		100	
2	16.9	15	5	80	2.0	0.8	0.77	0.25	0.002	7	81	12					96	4	100	
3	14.8	9	3	88	1.0	0.4	0.26	0.06	0.011	12	88						97	3	100	
4	12.8	29	9	62	6.9	2.1	2.30	0.35	0.038	7	87	6					98	2	100	
5	10.7	29	9	62	4.0	1.4	1.70	0.33	0.005	3	95	2				3	91	6	100	
6	1.3	21	6	73	25.9	1.4	2.20	0.36	0.007	1	94	5				3	97		100	
7	8.1	10	3	87	0.1	0.6	0.26	0.08	0.007	8	90	2					95	5	94	6
8	14.4	18	6	76	3.1	1.1	1.60	0.21	0.002	3	85	12					100		100	
9	12.6	22	6	72	2.7	1.6	1.30	0.16	0.010	9	81	10					100		100	
10	8.3	30	8	62	16.8	2.3	0.77	0.08	0.270		45		35	20			98	2	98	2
11	4.5	14	6	80	3.8	0.9	0.42	0.09	0.003	6	94						94	6	99	1
12	5.5	19	7	74	13.8	1.3	0.92	0.17	0.004	12	75	13					98	2	100	
13	5.8	12	5	83	8.4	0.7	0.90	0.11	0.008	24	45	7		24			96	4	100	
14	18.8	16	6	78	0.9	0.7	0.95	0.27	0.003	3	81	16					97	3	100	
15	1.0	19	7	74	0.1	0.9	1.00	0.19	0.004	5	91	4					100		100	

Kaolin. = kaolinite St. = smectite Is. = interstratified kaolinite/mica Goet. = goethite Feld. = feldspar

* Distance refers to the distance of each sampling site from the Arnot power station

Table 4.2 shows the major element composition while trace elements are shown in Table 4.3. Although the elemental composition, mineralogy and particle size of soils can generally be related to parent material (McBride, 1994), the work of Bühmann (1986) on soils of the highveld showed that dolerite and upper Ecca shale weather to soils with very similar properties. The influence of parent material is still reflected in the elemental composition of some of the soils, for example, the soil on site 10 is high in MnO, MgO, CaO and NaO compared with the other sites. Although not as apparent as on site 10, the soils on site 1 also have elevated levels of MnO, MgO, CaO and NaO compared with the other sites. Elevated levels of trace elements such as Mn, Co, V, Ni and Cu also occur on site 10, followed by sites 1 and 4.

The surface and solution properties of each soil are tabulated in Tables 4.4 and 4.5. The pH in water of the soils ranges from 5 to 7.1 (Table 4.4) and falls within the acid class (pH 4 - 7) of Thomas and Hargrove (1984). According to the Soil Classification Working Group (1991) most of the soils would be classed as moderately acidic (pH 5.5 - 6.5), there is one alkaline soil and the remainder are strongly acidic (between pH 4.0 - 5.4).

Exchangeable Ca^{2+} and Mg^{2+} are elevated in the soils of site 10 and less markedly so for the soils of site 4 (Table 4.4). Exchangeable acidity at both sites is low compared with the remaining soils. The acid saturation ranges from 0.07 to 52 % for all the soils sampled, with soils of sites 4 and 10 being less than 0.68 % acid saturated.

The parent material of each site was identified from the 1:250 000 Geological Series map (2528 Pretoria)(see Appendix 1 - Site descriptions). The inconsistencies between the apparent parent material of each site and its geochemical characteristics indicate that through weathering and transport processes the original signature of the parent material is less marked, supporting the findings of Bühmann (1986). The soils of site 10 are, however, an exception. It is apparent from the data that these soils are uncharacteristic of the general suite of soils collected. The doleritic parent material has evidently played a major role in determining the mineral assemblage of the site 10 soils. Dolerite is reported by Bühmann (1986) to have a uniform mineral assemblage dominated by plagioclase and pyroxene, although quartz may occur in small quantities. Since phyllosilicates are absent from the original rock, the present clay suite is likely to have been formed during secondary weathering processes. McBride (1994) suggests that the type of environment under which smectites form is alkaline as a result of restricted drainage and/or evaporative salt accumulation of normally mobile ions such as Ca and Mg. Both Ca and Mg are present in greater amounts in the smectite-rich soil at site 10.

Table 4.2 Total chemical analysis (major elements) of the soil collection

Sample	SiO2 %	TiO2 %	Al2O3 %	Fe2O3 %	MnO %	MgO %	CaO %	Na2O %	K2O %	P2O5 %	SO2 %	1l2O %	LOI %	TOTAL %
Topsoil														
1	76	0.68	7.2	6.9	0.10	0.05	0.07	0.03	0.38	0.08	0.04	0.88	6.7	98.91
2	88	0.41	4.1	1.7	0.01	0.03	0.03	0.03	0.24	0.04	0.03	0.41	3.6	98.95
3	88	0.42	4.1	1.7	0.01	0.03	0.03	0.03	0.24	0.04	0.02	0.41	3.6	98.64
4	72	0.85	7.7	5.2	0.06	0.11	0.12	0.06	0.86	0.08	0.05	4.64	7.0	98.47
5	77	0.69	9.3	3.3	0.02	0.07	0.06	0.07	1.20	0.06	0.04	0.55	6.8	98.92
6	82	0.63	6.4	4.0	0.02	0.02	0.04	0.02	0.27	0.07	0.03	0.32	5.1	99.22
7	88	0.42	4.3	1.2	0.02	0.01	0.05	0.14	1.80	0.03	0.03	0.51	3.1	99.19
8	77	0.69	9.3	3.3	0.02	0.07	0.06	0.07	1.20	0.06	0.04	0.55	6.8	98.78
9	86	0.46	4.2	2.5	0.03	0.01	0.08	0.04	0.47	0.05	0.04	0.37	5.1	99.26
10	80	0.66	5.4	4.4	0.15	0.32	0.92	0.31	0.78	0.15	0.05	0.48	6.0	99.20
11	89	0.27	3.1	1.8	0.02	0.02	0.05	0.09	0.90	0.05	0.03	0.96	3.3	99.21
12	84	0.44	4.4	2.3	0.02	0.02	0.07	0.05	0.54	0.05	0.04	1.80	5.6	99.11
13	91	0.33	2.7	1.7	0.02	0.04	0.04	0.06	0.85	0.04	0.02	0.42	2.0	99.41
14	89	0.47	3.6	2.0	0.02	0.02	0.03	0.02	0.24	0.05	0.03	0.33	3.1	99.05
15	87	0.47	5.2	1.8	0.02	0.03	0.05	0.03	0.30	0.07	0.03	0.44	3.9	99.22
Subsoil														
1	75	0.66	7.7	8.3	0.10	0.04	0.03	0.02	0.35	0.06	0.04	1.34	5.6	98.99
2	89	0.42	4.2	1.7	0.01	0.04	0.02	0.02	0.23	0.03	0.02	0.65	2.8	99.26
3	90	0.49	3.8	1.3	0.02	0.01	0.04	0.12	1.40	0.03	0.02	0.42	1.7	99.29
4	71	0.89	9.0	6.0	0.06	0.13	0.09	0.05	0.90	0.07	0.04	3.97	6.4	98.39
5	75	0.72	10.5	3.7	0.02	0.07	0.03	0.07	1.36	0.05	0.03	1.62	5.8	98.95
6	79	0.63	7.1	6.1	0.03	0.02	0.02	0.02	0.25	0.08	0.03	0.76	4.8	99.20
7	89	0.42	4.4	1.1	0.02	0.01	0.04	0.04	0.13	1.80	0.06	0.02	0.5	99.13
8	88	0.42	4.5	2.4	0.01	0.03	0.01	0.02	0.23	0.04	0.03	0.64	2.9	99.10
9	86	0.49	5.0	2.7	0.02	0.01	0.04	0.04	0.49	0.04	0.02	1.06	3.6	99.01
10	65	0.73	9.4	7.2	0.84	0.88	1.68	0.30	0.70	0.06	0.03	4.99	6.4	98.63
11	90	0.28	3.6	1.5	0.01	0.03	0.02	0.08	0.93	0.02	0.01	0.40	1.8	99.08
12	87	0.41	4.5	2.4	0.01	0.01	0.03	0.05	0.49	0.03	0.02	0.85	3.1	98.89
13	89	0.47	5.2	1.8	0.01	0.04	0.01	0.06	0.27	0.04	0.01	0.30	1.6	99.27
14	90	0.43	3.5	1.9	0.01	0.04	0.01	0.02	0.20	0.03	0.02	0.40	2.4	98.94
15	90	0.32	2.8	1.8	0.01	0.05	0.02	0.03	0.82	0.05	0.02	0.49	3.0	99.24

* LOI = loss on ignition

Table 4.3 Total chemical analysis (trace elements) of the soil collection

Sample	Mo ppm	Nb ppm	Zr ppm	Y ppm	Sr ppm	U ppm	Rb ppm	Th ppm	Pb ppm	Zn ppm	Cu ppm	Ni ppm	Co ppm	Mn ppm	Cr ppm	V ppm
Topsoil																
1	<1.2	9.3	395	12	8.0	<2.4	40	6.2	23	26	34	42	31	865	234	156
2	<1.1	7.3	401	11	6.3	<2.1	24	5.4	4.8	14	10	18	3.4	99	89	41
3	<1.1	8.2	417	14	41	<2.2	53	5	13	12	8.5	11	5.4	260	92	33
4	2.4	12	477	19	26	<2.4	56	6.7	20	31	30	45	25	584	218	120
5	1.4	14	532	26	52	3.5	69	13	20	32	15	25	9.7	169	132	75
6	<1.2	11	472	15	37	3.0	23	11	20	24	16	22	6.7	211	172	80
7	1.6	7.8	356	12	55	<2.1	64	7.3	17	11	7.6	11	2.4	225	59	30
8	<1.1	7.2	354	9.4	8.8	<2.1	22	4.8	9.1	16	13	18	5.2	121	93	56
9	1.1	7.7	316	11	15	<2.2	35	5	9.9	17	15	17	8.7	294	119	62
10	<1.2	7.1	343	13	46	3.5	37	5.4	12	27	27	25	32	1422	158	169
11	2.8	5.4	329	9.3	28	<2.1	40	4.8	10	14	13	14	4.8	181	77	35
12	1.4	9.0	403	13	17	<2.1	43	6.3	7.1	18	12	18	4.7	162	92	49
13	4.2	6.5	412	9.1	26	<2.2	36	8.3	8.6	9.5	11	15	3.7	167	131	30
14	<1.1	6.8	358	9.9	7.2	<2.1	22	3.9	7.5	14	12	24	5.3	150	135	45
15	<1.1	8.6	322	11	28	<2.1	27	7.4	13	20	11	19	8.3	125	87	56
Subsoil																
1	1.4	9.4	364	12	4.8	<2.5	40	7.3	28	26	41	48	41	880	320	205
2	1.4	6.7	371	10	4.8	<2.1	24	5.8	5.3	13	11	19	3.5	71	94	46
3	<1.1	8.3	428	15	40	<2.2	53	6.1	12	12	9.4	14	6.0	207	92	35
4	1.8	12	433	20	24	<2.4	63	7.7	23	34	30	46	31	610	218	142
5	1.3	15	523	27	55	3.7	75	13	20	33	15	26	11	117	133	80
6	1.2	11	453	15	38	3.9	23	10	24	23	19	23	6.1	190	242	128
7	1.3	8.1	356	12	54	2.2	64	5.9	15	9.2	7.9	12	4.8	154	56	29
8	1.4	8.1	353	14	6.7	<2.2	21	5.5	7.5	15	12	20	4.9	71	91	63
9	1.7	8.3	362	12	13	<2.2	40	5.4	8.5	17	16	21	7.2	169	115	65
10	<1.3	7.3	265	17	56	<2.5	39	<2.8	13	50	68	95	130	7809	199	292
11	1.4	5.8	270	9.9	25	<2.1	44	4.6	9.9	11	8.2	13	3.0	74	70	39
12	2.1	8.0	379	13	12	<2.2	40	6.3	7.3	15	13	20	5.2	109	93	52
13	2.8	6.4	352	8.6	22	<2.2	34	6.2	14	7.7	8.1	10	4.3	125	151	42
14	1.9	7.4	312	9.5	3.4	<2.1	19	4.8	4.8	13	10	23	4.1	85	135	42
15	1.8	7.9	267	12	21	<2.1	26	7.7	12	15	12	19	5.0	87	91	58

The unique qualities of site 10 therefore allow its exclusion from the data set on occasions where relationships are being sought between soil properties. The smectitic, base-rich character of this soil places it in a similar category to soils from topographic depressions. As mentioned at the study outset, such depressions were avoided as likely accumulators of soluble salts which would confound effects from atmospheric deposition.

The soil solution data for the saturated paste extracts are presented in Table 4.5, together with estimates of phosphate-extractable sulphate. In both topsoils and subsoils, the dominant cation in solution was Mg^{2+}, followed by Ca^{2+} and K^{+}. Chloride was the dominant anion in most topsoils (in 9 out of 15 topsoils sampled) while SO_4^{2-} dominated in almost all of the subsoils. However, requirements of charge balance (i.e. < 10 % difference between sums of cations over anions) were not met for 11 of the subsoil solutions and for 14 of the topsoil solutions. In general, an excess of cations over anions was apparent which is not unexpected since neither dissolved organic carbon nor HCO_3^- alkalinity were determined as there was insufficient sample solution to permit further analysis. Fey *et al.* (1996) found a strong correlation ($r^2 = 0.84$) between dissolved organic carbon and excess positive charge in soils from grassland sites similar to the soils sampled in the present study. In this case, however, the pH range of the soils (pH in water > 5 and typically close to a value of 6) suggests that HCO_3^- would probably account for the deficit of anions relative to cations in the extracts. Although both NO_2^- and PO_4^{3-} were measured the amounts were negligible, except for four subsoils where NO_2^- ranged from 0.01 to 0.10 $mmol_c.L^{-1}$ and three subsoils for which PO_4^{3-} ranged between 0.02 to 0.15 $mmol_c.L^{-1}$.

Further consideration of data in Tables 4.1 to 4.5 pertinent to the objectives of this study will be made in Section 4.3.2 - Deposition gradients, Section 4.3.3 - Soil acidity and Section 4.3.4 - Soil sulphate.

Table 4.4 Surface properties (acidity & ion exchange characteristics) of the soil collection

Sample	Distance (kms)	pH water	pH KCl	pH K2SO4	KCl exchangeable cations (mmolc/kg soil) acidity	Ca	Mg	ECEC (mmolc/kg)	Acid saturation %	ANC (cmolc./L)
Topsoil										
1	19.9	6.0	4.7	5.1	1.0	17	22	40	2.6	4.7
2	16.9	5.3	4.2	4.7	6.7	6.2	8.9	22	31	2.5
3	14.8	6.1	4.8	5.3	0.5	10	10	21	2.5	3.3
4	12.8	6.0	4.8	5.2	0.4	27	27	55	0.68	4.7
5	10.7	5.6	4.3	4.8	2.7	14	19	36	7.4	3.2
6	1.3	5.3	4.2	4.7	6.2	7.8	9.3	23	27	2.5
7	8.1	5.9	4.6	5.0	1.0	10	13	24	4.1	3.3
8	14.4	5.4	4.2	4.7	5.5	8.1	10	24	23	2.4
9	12.6	6.0	4.6	5.0	1.0	18	18	37	2.7	3.7
10	8.3	6.3	5.0	5.5	0.3	61	53	115	0.22	6.1
11	4.5	5.9	4.5	4.9	0.9	12	14	26	3.5	2.5
12	5.5	5.6	4.4	4.8	2.7	18	20	41	6.6	3.6
13	5.8	5.9	4.5	5.0	1.8	11	9.9	22	7.8	2.9
14	18.8	5.6	4.4	4.9	3.9	10	11	24	16	3.0
15	1.0	5.9	4.6	5.0	1.4	11	11	24	5.9	3.7
Subsoil										
1	19.9	5.8	4.5	5.1	3.1	7.1	16	27	12	5.1
2	16.9	5.0	4.1	4.6	10.6	2.6	7.3	20	52	2.1
3	14.8	6.2	4.5	5.1	1.0	7.9	9.9	19	5.3	2.3
4	12.8	6.3	5.0	5.5	0.2	23	27	51	0.51	5.6
5	10.7	5.3	4.3	4.8	6.5	7.0	14	27	24	3.4
6	1.3	5.0	4.1	4.7	10.3	3.4	7.4	21	49	2.7
7	8.1	6.3	4.8	5.4	0.6	8.5	13	22	2.9	3.2
8	14.4	5.2	4.2	4.7	8.7	3.0	7.7	19	45	2.6
9	12.6	6.1	4.6	5.1	1.1	13	17	30	3.7	4.0
10	8.3	7.1	5.4	5.9	0.1	115	113	228	0.065	10.0
11	4.5	5.8	4.2	4.8	3.6	4.3	8.3	16	22	2.1
12	5.5	5.9	4.3	4.9	4.3	9.8	15	29	15	3.4
13	5.8	5.6	4.3	4.9	4.2	7.1	9.3	21	20	2.5
14	18.8	5.1	4.1	4.7	7.7	2.6	6.4	17	46	2.2
15	1.0	5.0	4.1	4.6	7.2	3.3	6.8	17	41	1.8

Table 4.5 Solution composition and extractable sulphate in the soil collection

Sample	SOLUBLE CATIONS (mmol c/L)					SOLUBLE ANIONS (mmol c/L)							Extractable sulphate (mg/kg)	
Topsoil	Na	NH4	K	Mg	Ca	Cl	NO3	SO4	Sum of anions*	Sum of cations	Sodium adsorption ratio	EC (extract) mS/cm	water	phosphate
1	0.25	0.19	0.57	0.89	0.59	1.06	0.00	0.67	1.75	2.48	0.29	0.24	9.8	59
2	0.09	0.22	0.45	0.35	0.27	0.52	0.09	0.47	1.11	1.38	0.16	0.16	5.5	77
3	0.32	0.45	0.77	0.92	0.61	0.61	0.06	0.73	1.61	3.08	0.37	0.28	9.0	69
4	0.11	0.07	0.40	0.69	0.41	0.74	0.01	0.59	1.34	1.68	0.14	0.18	7.5	63
5	0.55	0.13	0.60	1.01	0.69	1.08	0.08	0.62	1.87	2.98	0.59	0.29	11.0	91
6	0.35	0.31	0.49	0.96	0.82	0.66	0.06	0.85	1.95	2.93	0.38	0.29	9.9	85
7	0.07	0.35	0.55	0.47	0.36	0.45	0.00	0.61	1.10	1.81	0.11	0.21	7.4	97
8	0.16	0.44	0.91	0.97	0.78	1.82	0.14	0.80	2.79	3.26	0.17	0.37	10.0	90
9	0.13	0.32	0.68	0.84	0.50	0.81	0.00	0.86	1.75	2.47	0.16	0.26	10.3	79
10	0.14	0.00	0.21	0.96	0.67	0.63	0.00	0.52	1.16	1.98	0.15	0.17	8.0	53
11	1.29	0.14	1.11	1.06	0.79	1.68	0.00	1.29	3.02	4.39	1.34	0.46	13.6	82
12	0.28	0.35	0.78	1.20	0.97	1.53	0.00	0.96	2.64	3.58	0.27	0.39	15.4	86
13	0.08	0.14	0.25	0.38	0.11	0.24	0.00	0.41	0.69	0.96	0.16	0.12	4.5	49
14	0.13	0.21	0.35	0.52	0.40	0.59	0.00	0.40	1.01	1.60	0.19	0.17	4.7	57
15	0.45	0.26	0.56	0.61	0.48	0.68	0.02	1.01	1.73	2.36	0.61	0.24	11.8	54
Subsoil														
1	0.10	0.10	0.32	0.29	0.16	0.24	0.21	0.36	0.83	0.96	0.20	0.11	5.3	85
2	0.21	0.21	0.55	0.83	0.55	1.02	0.00	0.66	1.72	2.35	0.26	0.25	6.9	107
3	0.13	0.09	0.10	0.48	0.34	0.20	0.00	0.52	0.78	1.14	0.20	0.13	5.2	52
4	0.10	0.10	0.18	0.49	0.00	0.24	0.00	0.39	0.81	0.87	0.21	0.11	5.8	92
5	0.38	0.07	0.28	0.66	0.33	0.69	0.00	0.52	1.22	1.73	0.54	0.18	8.5	138
6	0.08	0.23	0.41	0.63	0.55	0.63	0.00	0.88	1.53	1.91	0.10	0.20	11.0	141
7	0.25	0.20	0.24	0.48	0.29	0.22	0.06	0.32	0.68	1.46	0.40	0.14	2.9	69
8	0.16	0.14	0.39	0.61	0.37	0.47	0.41	0.51	1.43	1.66	0.22	0.18	6.4	140
9	0.09	0.09	0.33	0.38	0.00	0.28	0.00	0.36	0.68	0.88	0.20	0.12	4.5	81
10	0.96	0.00	0.07	1.28	0.94	0.50	0.11	0.86	1.62	3.25	0.91	0.27	22.4	84
11	0.53	0.06	0.56	0.52	0.31	1.00	0.02	1.08	2.21	1.97	0.82	0.30	9.5	83
12	1.57	0.10	0.41	0.47	0.30	0.73	0.10	0.73	1.63	2.85	2.53	0.28	12.0	81
13	0.10	0.06	0.18	0.34	0.26	0.22	0.00	0.42	0.71	0.95	0.18	0.10	3.7	68
14	0.11	0.10	0.22	0.21	0.17	0.22	0.05	0.32	0.61	0.82	0.26	0.09	3.7	100
15	0.53	0.18	0.34	0.40	0.32	0.48	0.20	0.45	1.14	1.78	0.88	0.20	5.5	116

* NO2 and PO4 not present in topsoils and negligible in subsoils except for 4S = 0.15 mmol c/L PO4 and 11S = 0.1 mmol c/L NO2

4.3.2. Deposition gradients

A number of soil chemical parameters were plotted against distance from the power station in order to establish whether any trends were evident. The relationship between distance and some key properties which might be expected to vary with the intensity of atmospheric pollution impacts, such as soil pH measured in water and various sulphur fractions (phosphate-extractable sulphate, water-soluble sulphate and total sulphur) are shown in Figure 4.1. Although no clear trends are evident, close inspection of Figure 4.1b does show a decline in the concentration of water-soluble sulphate with distance. The high sulphate concentration in the subsoil of site 10 (at 8.3 km from the power station) can be disregarded because the soil is unusually high in smectitic clay and therefore could be expected to accumulate solutes compared with the other sites. The trend is probably not significant, but may demonstrate an early indication of heightened water-soluble sulphate levels in the near-field of the power station. The greatest concentrations are apparent about 4-6 km of the power station (excluding site 10). As mentioned in Chapter 1, Section 1.5.1, Annegarn *et al.* (1996) stated that high SO_2 concentrations were unlikely to pose an environmental threat except within 4 km of a tall stack. Turner (1992) predicted that plume touch down would occur at a distance of 2.5 km from a tall stack. Since the position of plume touch down is reliant on the local meteorological conditions and the stack configuration such predictions cannot be broadly applied. Nevertheless, the data in Figure 4.1(b) suggest that heightened sulphate concentrations are evident within 4-6 km of Arnot power station. The soluble sulphate calculated as a fraction of the total dissolved solids in solution was also plotted against distance but no relationship was evident.

There was no evidence of heightened trace element concentrations in the vicinity of the power station, supporting the prediction by Willis (1987), based on chemical data, that trace elements from coal-burning power stations should not constitute an environmental problem.

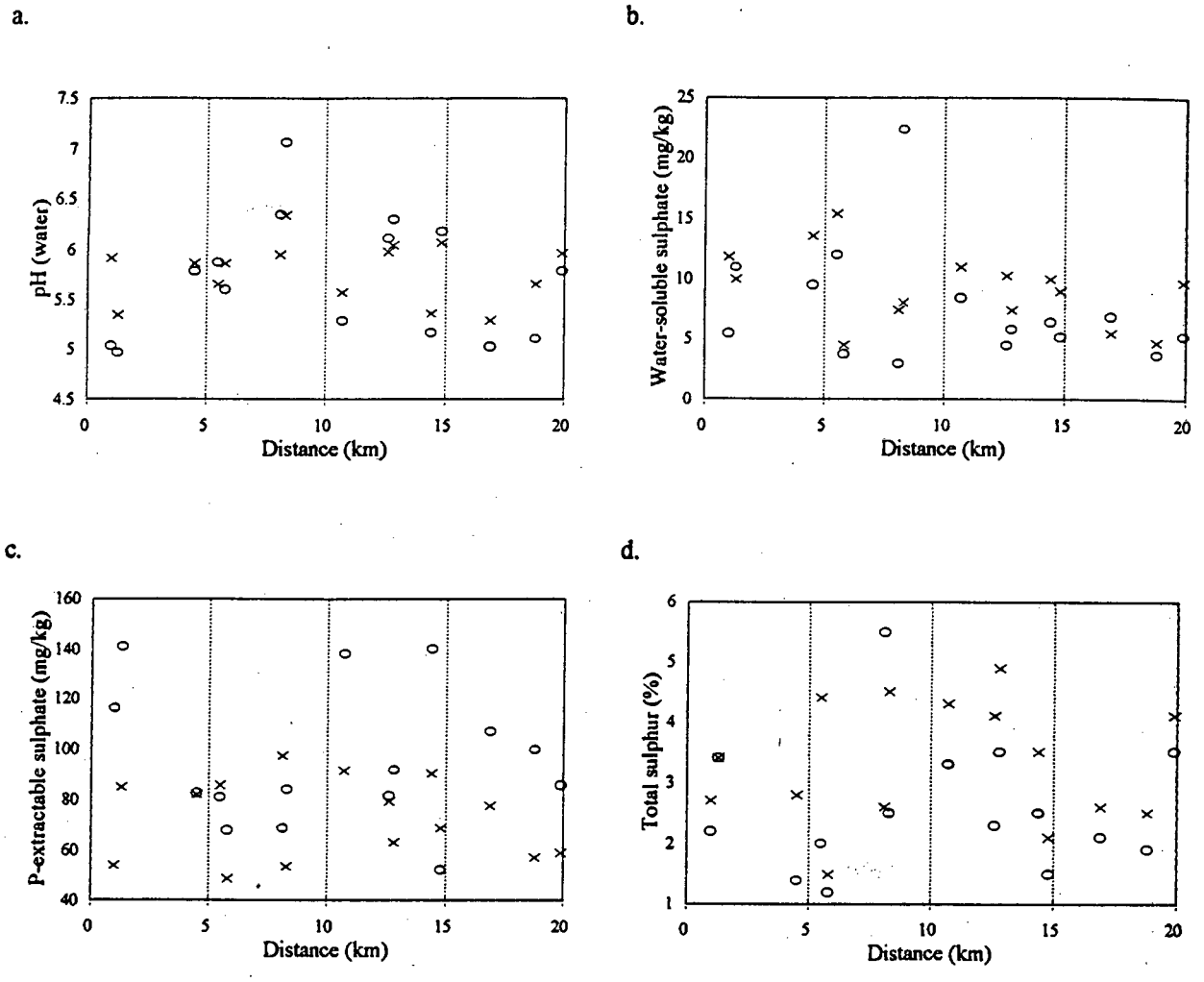


Figure 4.1 Parameters plotted as a function of distance of sampling from the Arnot power station a). pH(water), b). water-soluble sulphate c). phosphate-extractable sulphate and d). total sulphur. Topsoils are indicated by a cross and subsoils by an open circle.

4.3.3. Parameters related to soil acidity

4.3.3.1. Soil pH

The suspension pH of each soil measured in water, KCl and K_2SO_4 (Table 4.4) and the relationships between these parameters are shown in Figure 4.2. The difference in pH measured in water and pH in an electrolyte solution can be either positive, neutral or negative, depending on the net charge on the soil colloids (Aitken and Moody, 1991). In all the soils

sampled, the relationship between these measures of pH followed the order pH(water) > pH(K_2SO_4) > pH(KCl).

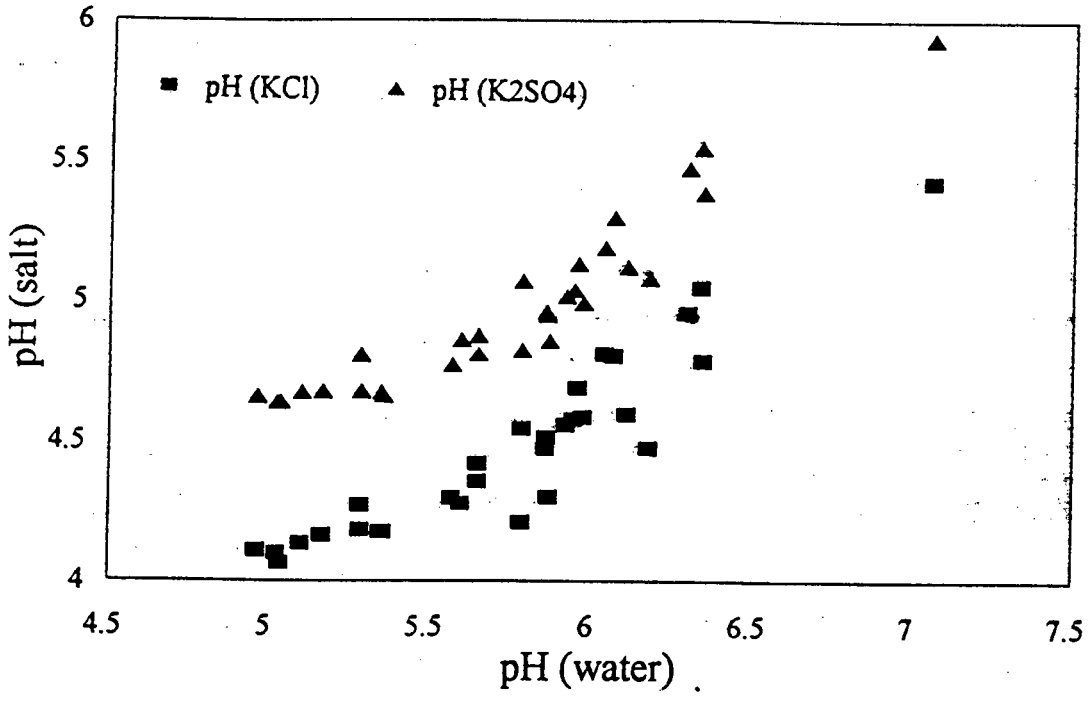


Figure 4.2 Relationship of pH measured in KCl or K_2SO_4 (pH_{salt}) to pH measured in water for the 30 soils based on data in Table 4.4.

A comparison of pH values in salt solution shows a consistent difference of 0.4 to 0.6 pH units between pH measured in KCl and pH in K_2SO_4. This linear relationship is strongly linear even in the low pH range (r^2=0.97, 28 degrees of freedom).

When the pH in salt solution is lower than in water, it is usually taken to indicate that negative charge dominates the soil exchange surfaces (Parfitt, 1980). H^+ and Al^{3+} ions are displaced from the negative exchange sites by the K^+ ion, resulting in a decreased pH relative to that in water. In soils that are strongly sesquioxidic, only small reductions or even increases in pH may result on the addition of salts - especially phosphate and sulphate salts. The anions exchange for OH^- from the positively charged sesquioxides resulting in a rise in pH (Thomas and Hargrove, 1984). Accordingly, the data in Figure 4.2 indicate that all the soils have a net negative charge. Inspection of Figure 4.2 also reveals an apparent departure from the general trend of linearity in the low pH(water) range (< pH 5.5) for the relationships of both sulphate and chloride pH values with pH (water).

In the low pH range, the concentration of H^+ in solution is already high and is therefore pH is not as affected by the concentration of H^+ released by the displacing salts. Consequently, although pH may decrease in salt solution relative to that in water, the corresponding pH value in salt solution is less depressed than at higher pH values - resulting in the curvilinear trend at lower pH values (Figure 4.2). Aitken and Moody (1991) have demonstrated that the fitting of a curvilinear function to similar data resulted in higher correlation coefficients than those obtained for a linear fit. The difference in pH values measured in water and an electrolyte solution also decreases as the pH decreases towards the pH value at which charge is no longer generated on the soil surface, termed *point of zero charge* (PZC) (McBride, 1994; Sposito, 1989). The solution pH and the electrolyte concentration determine the charge on sesquioxide surfaces and whether these surfaces will adopt acidic or basic characteristics. Figure 4.3 shows that the general trend is for ΔpH (i.e. pH(KCl) - pH(water)) to decrease with decreasing pH - a phenomenon which Aitken and Moody (1991) indicate should be expected for a suite of soils which possess variable charge but which are net negatively charged.

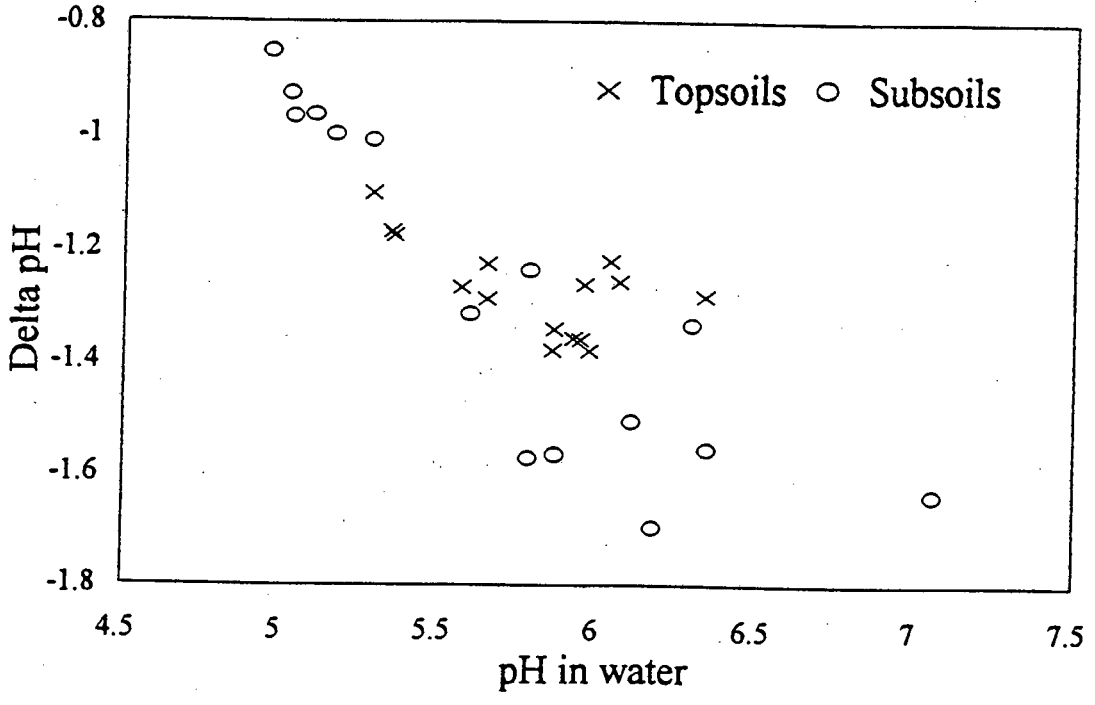


Figure 4.3 Relationship between pH measured in water and ΔpH (i.e. pH(KCl)-pH(water)), based on data in Table 4.4.

4.3.3.2. Extractable acidity

The extractable or exchangeable acidity is measured as the moles of titratable protons per unit mass displaced by an unbuffered KCl solution. For the soil collection, the exchangeable acidity ranges between 0.3 and 10.6 $mmol_c.kg^{-1}$ (Table 4.4). The exchangeable acidity in soils is primarily attributable to the readily exchangeable forms of Al^{3+} ions (Thomas and Hargrove, 1984; Sposito, 1989). The K^+ ion replaces the Al species on the mineral surface, which then hydrolyse in solution to release protons which are measured as exchangeable acidity. In Figure 4.4 the ratio of exchangeable acidity to effective cation exchange capacity (ECEC) is plotted against pH in KCl, and the data clearly conform to the classical relationship between acid saturation of the exchange surfaces and soil pH, described by Sposito (1989, p. 214).

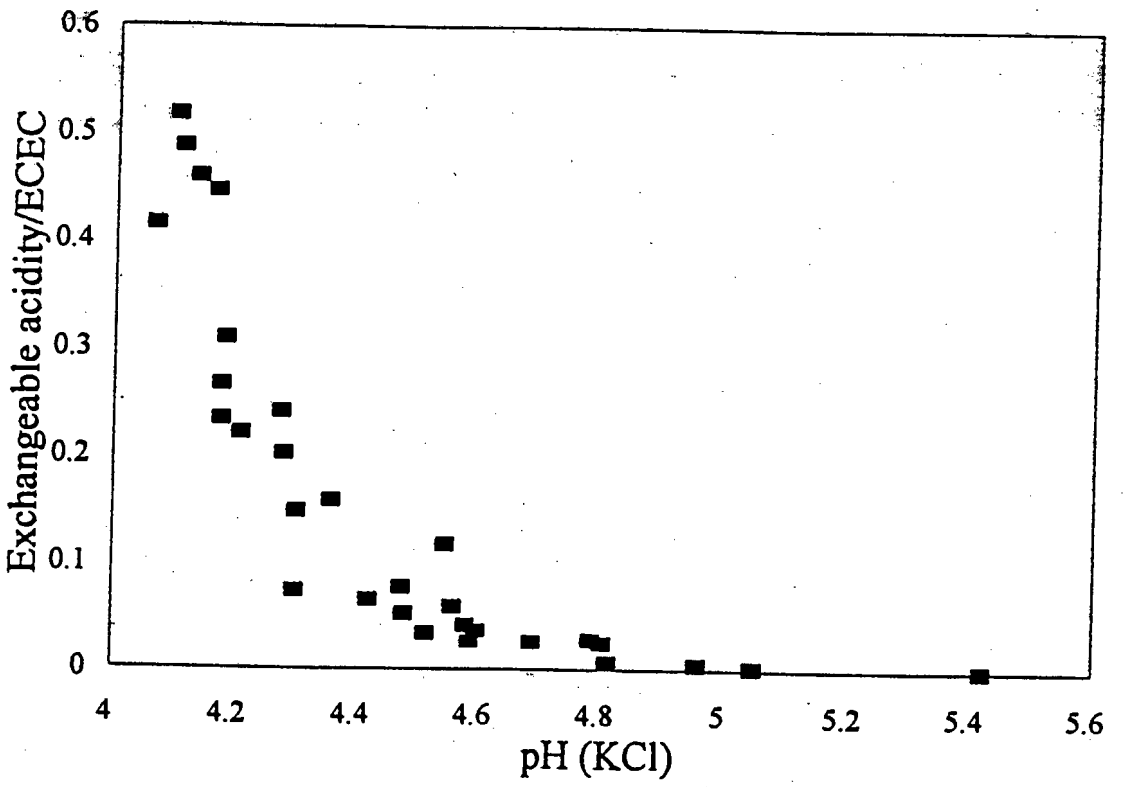


Figure 4.4 The relationship between the acid saturation of the effective cation exchange capacity (ECEC) and pH measured in KCl, based on data in Table 4.4

4.3.3.3. Acid neutralising capacity

Calculation of the ANC of a soil takes into account the buffer system of that soil when measuring the quantity of acid with which a soil will react before the soil pH drops below a particular reference pH value (in this case a pH value of 3.5). An ANC of 1 $cmol_c.L^{-1}$ is equivalent to about 1 ton of $CaCO_3.ha^{-1}$ to a depth of 20 cm. Soils at sites 1, 4 and 10 displayed the greatest acid neutralising capacity (> 4.7 $cmol_c.L^{-1}$) of the suite of soils (Table 4.4). The ANC calculated by the buffer method of du Toit and Fey (1994) was fairly well correlated with the pH measured in water (r^2=0.56, df=28). This finding corresponds with that of Fey *et al.* (1995) who used a dataset comprising 127 soils. Du Toit (1993a) found a weak correlation (r^2=0.137, df=18) between pH in KCl and ANC whereas the present data, shown in Figure 4.5, are strongly correlated (r^2=0.749, df=28).

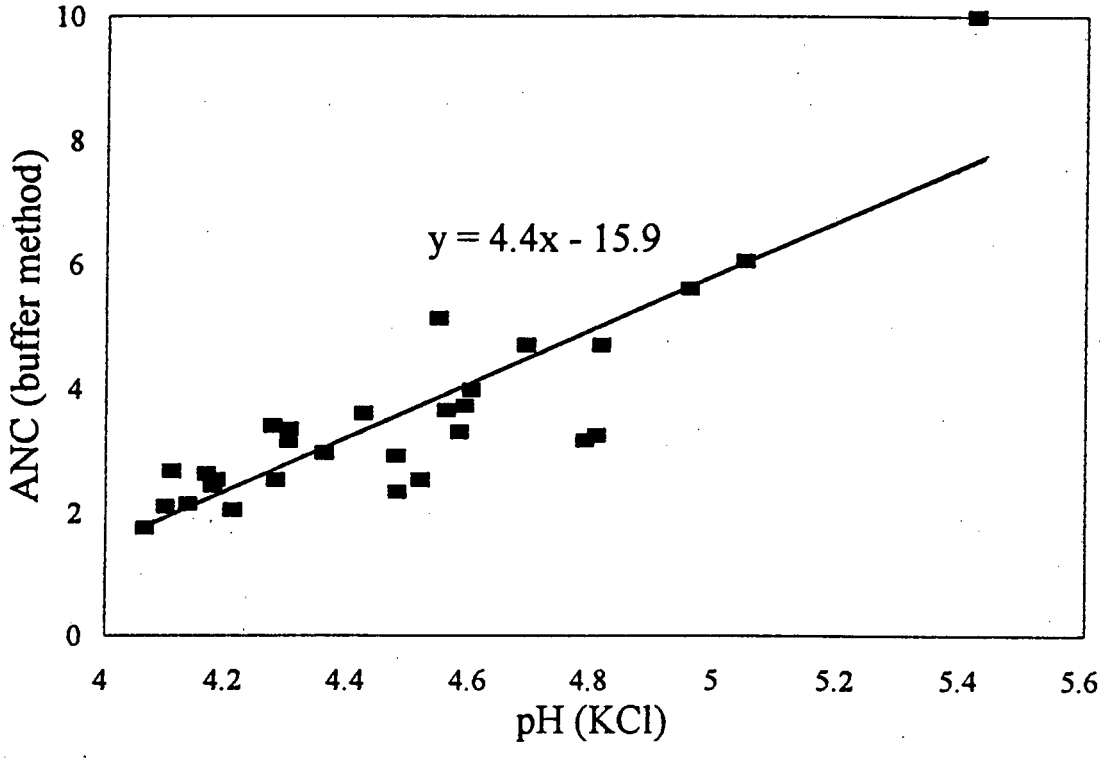


Figure 4.5 The relationship between acid neutralising capacity (units = $cmol_c.L^{-1}$) and pH measured in KCl, based on data in Table 4.4. Sample 10S was included in the regression analysis.

According to van Breemen *et al.* (1983), the ANC of most soils is associated with silicate minerals which have very slow dissolution kinetics. Van Breemen *et al.* (1983) used the method of component composition to calculate the ANC of the soil, where the soil is considered to include all inorganic matter including soil solution, solid particles and adsorbed ions. ANC is calculated using total elemental analyses, but the method does not consider the kinetics of mineral weathering. Nevertheless, du Toit (1993a) found significant relationships between ANC calculated by component composition, serial titration with HCl and the ANC buffer method described in Appendix 2. Of these methods, component composition was selected as the least satisfactory method for comparison with the ANC buffer method. As a consequence, ANC by component composition was not calculated in the present study.

4.3.4. Soil sulphate

Sulphur compounds are the major atmospheric pollutants to which the soils in the vicinity of Arnot are exposed, yet, as was demonstrated in Section 4.3.2, no relationships between the various sulphur fractions and distance from the sulphur source are readily apparent. However, Chapter 1 made clear that a number of factors influence the behaviour of sulphur, and in particular sulphate, in soils. The capacity of soil to retain sulphate depends on factors such as the sesquioxide content, clay content and organic matter.

Fey and Guy (1993) suggested that the difference in pH measured in K_2SO_4 and that measured in KCl could be used as an easily measured index of the sulphate sorption capacity of soils. The increased pH is supposedly related to the release of OH^- ions displaced by ligand exchange with the sulphate anion (Curtin and Syers, 1990a). The sulphate anion is specifically adsorbed in contrast to the indifferent chloride anion (Mott, 1981). The pH difference (calculated as $pH(K_2SO_4)$ - pH(KCl)) should provide an indication of OH^- release which can be attributed to sulphate sorption. As is evident in Figure 4.6 there is no clear relationship between this index of sulphate sorption and phosphate-extractable sulphate. However, there is a distinct separation of the topsoils from the subsoils. The small pH difference manifested for the topsoils is attributable to the greater organic matter content in the topsoil horizons. In the lower horizons, there is a lower concentration of humic substances to block positively charged sites on the sesquioxide surfaces. As is apparent in Figure 4.6, the pH difference between pH measured in K_2SO_4 and that measured in KCl would not serve as a reliable indicator of phosphate-extractable sulphate.

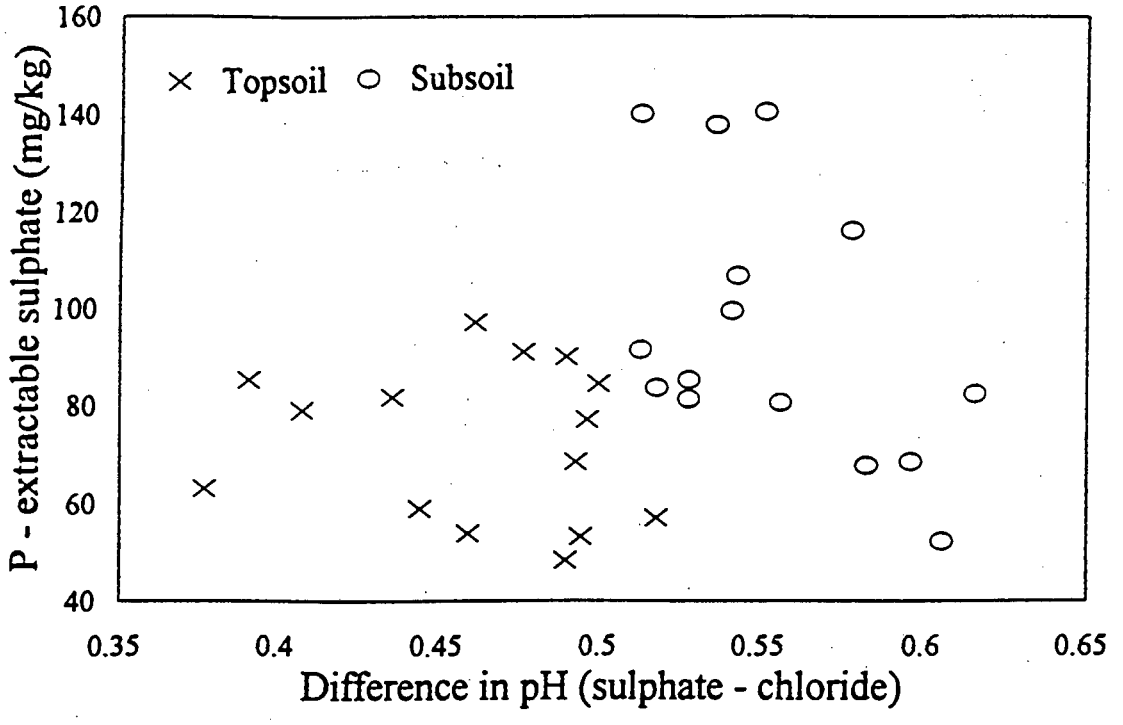


Figure 4.6 The relationship between difference in pH(K_2SO_4 - KCl) and phosphate-extractable sulphate based on data presented in Tables 4.4 and 4.5.

The relationships between both water- and phosphate-extractable sulphate and a number of other soil properties known to influence sulphate sorption were also explored. Parameters included clay and, specifically, kaolinite content, CBD-extractable Mn, Fe and Al, organic carbon, ANC, acid saturation and ECEC, as well as pH in water, KCl and K_2SO_4. No clear relationships or correlations were apparent between any of these individual parameters and the various sulphate fractions. Although the dependence of sulphate sorption on soil properties such as sesquioxide content and pH is theoretically apparent, these relationships are not simple linear functions. Sulphate retention would appear to depend more on the interplay between the various factors. For this reason an attempt was made to derive an expression which relates the various factors to one another in such a way as to provide an estimate of extractable sulphate. Such an expression might be termed a sulphate retention index. An example of such an index is plotted against extractable sulphate in Figure 4.7. Factor weightings were chosen based on an intuitive estimate of the relative importance of each factor in contributing (either positively or negatively) to the retention of sulphur in soil.

The sulphate retention index was calculated as follows:

SRI = kaolinite content + 5(Fe content) - 10(organic carbon content)

where the contents are expressed as %. Kaolinite is calculated from the clay content and the % kaolinite in the clay fraction (by XRD) while the Fe content is that extracted with citrate-bicarbonate-dithionite.

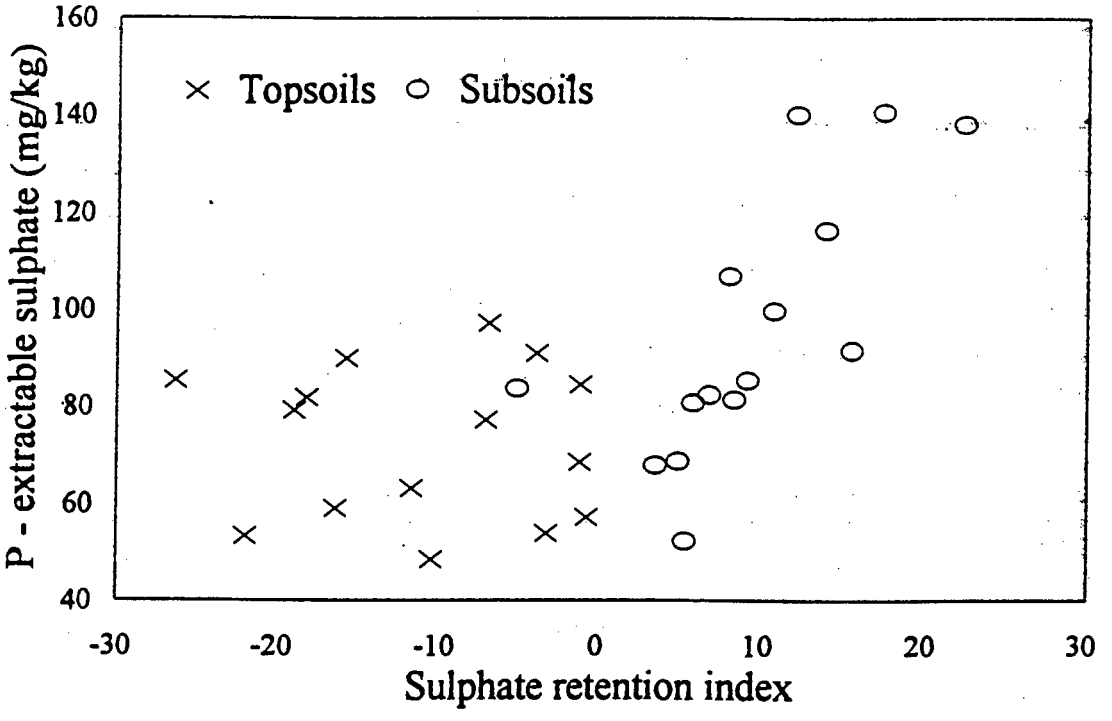


Figure 4.7 The relationship between the index of sulphate retention (SRI) and phosphate-extractable sulphate.

Figure 4.7 shows a clear separation of topsoils from subsoils - primarily on the basis of organic matter content. The subsoil 10S is an exception as, as stated previously, it is characterised by a smectitic mineralogy. The calculated SRI for the subsoils considered separately, demonstrates a linear relation (r^2 = 0.68, df = 12, 10S excluded from regression calculation) with the phosphate extractable sulphate. For the subsoils, the equation of the line is: P-extractable sulphate = 4.3(SRI) + 53. There is no relationship evident for the topsoils. The topsoils and subsoils (except the smectitic 10S) are fortuitously separated into positive and negative sectors, with topsoils being sulphate-repelling and subsoils sulphate-retaining.

Although this index is a crude estimate of the relative importance of the factors influencing sulphate retention, it could be further developed into a potentially useful tool for the assessment of geochemical responses to atmospheric pollution impacts. Changes in either the slope or intercept or both, of the relationship between extractable sulphate and the subsoil SRI, could provide some indication of an accumulation of sulphate which might be more reliable than extractable sulphate alone. Such comparisons may not only facilitate the assessment of sulphate accumulation but also may prove useful in comparing sites in different regions of the sub-continent.

The importance of organic carbon in governing sulphate accumulation in soils has been implicitly demonstrated in both Figure 4.6 and 4.7. Organic carbon is widely recognised as being negatively correlated with extractable sulphate (Comfort *et al.*, 1992 and references cited in Section 1.7.3.) To a certain extent this assertion is supported by the present data, as shown in Figure 4.8. Again, the separation between topsoils and subsoils on the basis of organic matter is evident. The higher organic carbon fractions in the topsoil horizons imply a greater proportion of humic substances which compete with sulphate for sorption sites. Sulphate that is not bound to the soil surface is lost through leaching, resulting in a low extractable sulphate fraction. The data conform to the generalisation made by Tisdale *et al.* (1985) that there is an accumulation of adsorbed SO_4^{2-} in deeper soil horizons - supposedly as a result of eluviation or leaching of sulphates from the upper horizons.

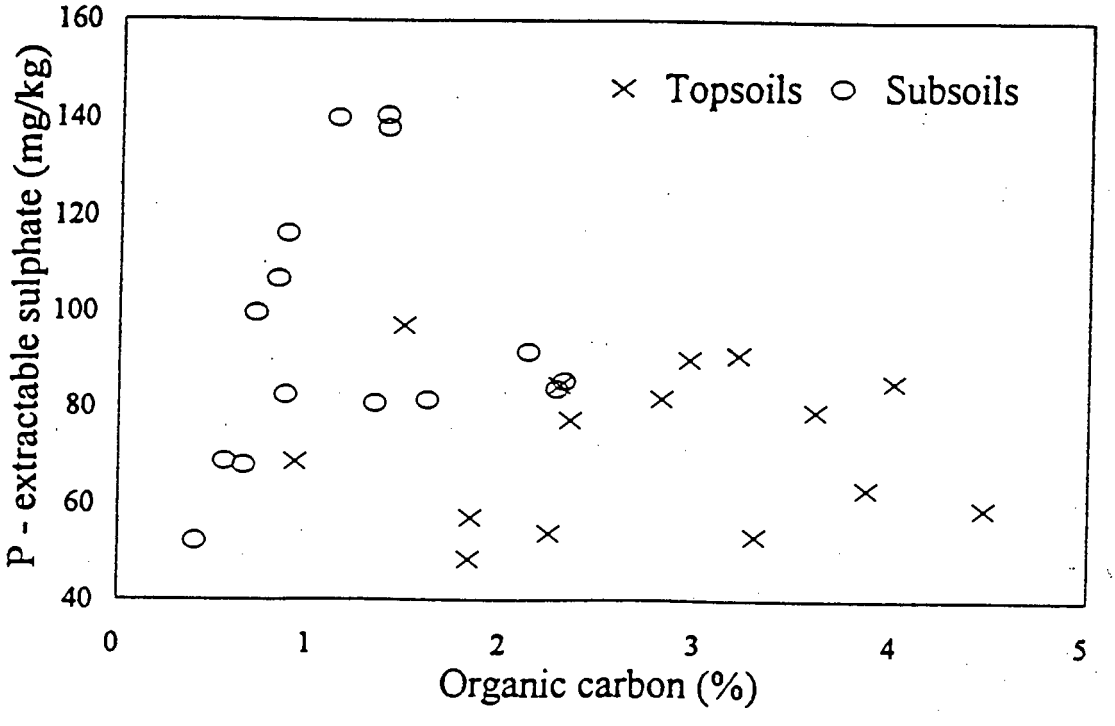


Figure 4.8 Phosphate-extractable sulphate as a function of soil organic carbon, based on data in Tables 4.1 and 4.5.

Conversely, there is a weak but positive relationship between organic carbon and the concentration of water-soluble sulphate in the soil solution, shown in Figure 4.9 ($r^2 = 0.29$; df=27). This result is not unexpected as organic matter will enhance the desorption and thus the solubility of sulphate. The outlier represented by the subsoil of site 10 was excluded in the calculation of the regression. The quantities of soluble sulphate in soils fluctuate seasonally and on a year-to-year basis. The variation is a consequence of the interaction between environmental and seasonal factors on the mineralization of organic sulphur, the fluxes of soil moisture and sulphate uptake by plants. When plant and animal residues are returned to the soil, microbial metabolism is responsible for converting the organically bound sulphur to sulphate (Tisdale *et al.*, 1985). Most of the sulphur remains organically bound in the soil humus.

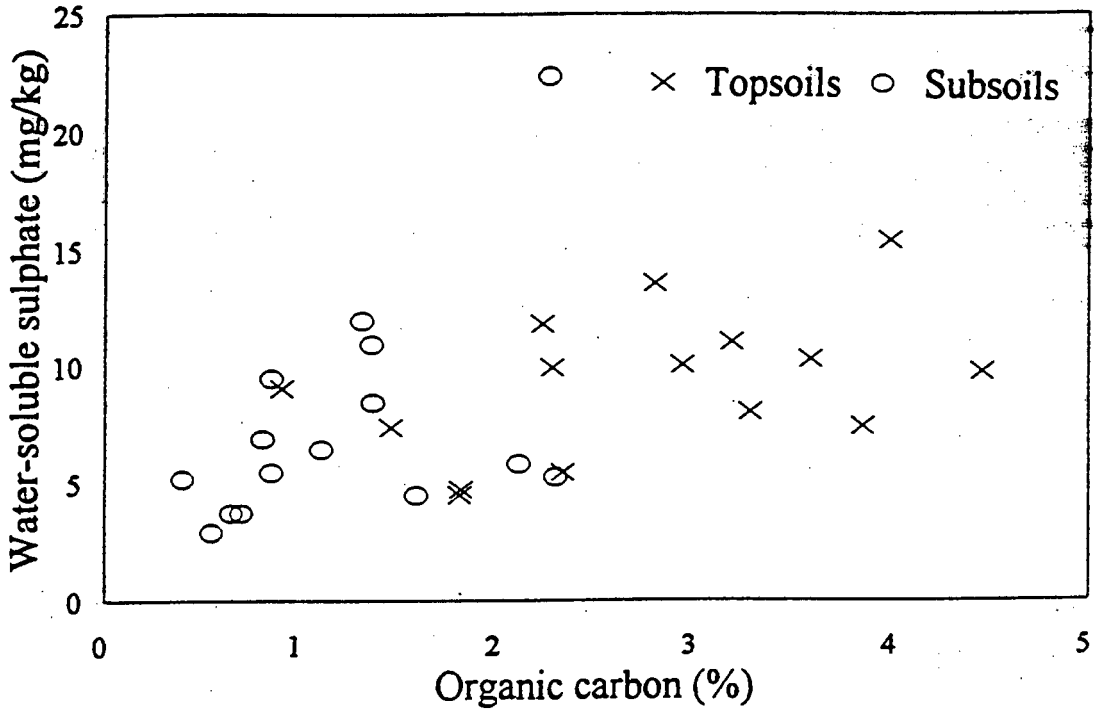


Figure 4.9 Relationship between water-soluble sulphate and organic C, based on data in Tables 4.1 and 4.5.

Tabatabai (1982) stressed the importance of organic matter in influencing the amount and form in which sulphur occurs in the soil. A strong relationship (r=0.85, df=27) (Figure 4.10) exists between the fraction of organic carbon present in soil and the total sulphur content of the soil, confirming that the greatest fraction of sulphur in the soil is usually organically bound. Tisdale *et al.* (1985) state that in excess of 90 % of the sulphur in noncalcareous soils

exists in organic form. In Figure 4.10 the y-intercept represents the sulphur in the soil that is not in association with organic matter. Background levels of sulphur in soils can be attributed to S-bearing minerals in the parent rock. The parent material in the Arnot area could be high in sulphide-bearing minerals such as pyrite. This hypothesis is tentatively supported by the unpublished data (Willis, pers. comm.) for the sulphur content of coal from the Arnot coal seams. The number 1 seam has an S-content of 2.0 % while the number 2 seam bears 1.1 % sulphur. These values exceed or approach the upper limit of the reported range for South African coal ((0.4 - 1.4 %; Willis, 1983). Thus it is feasible that the soils in the vicinity have inherited a high sulphur content from the parent material. In the long-term, however, most of this additional sulphur would be expected to become incorporated pedogenically in the humus fraction.

Jacks *et al.* (1994) traced sulphur sources in soils and waters using sulphur isotope ratios and concluded that the mobilisation of sulphur through bedrock weathering is negligible. Jacks *et al.* (1994) studied gneisses and charnockites and whether their results are applicable to teh shales and dolerites of the Arnot area is an aspect that requires further investigation.

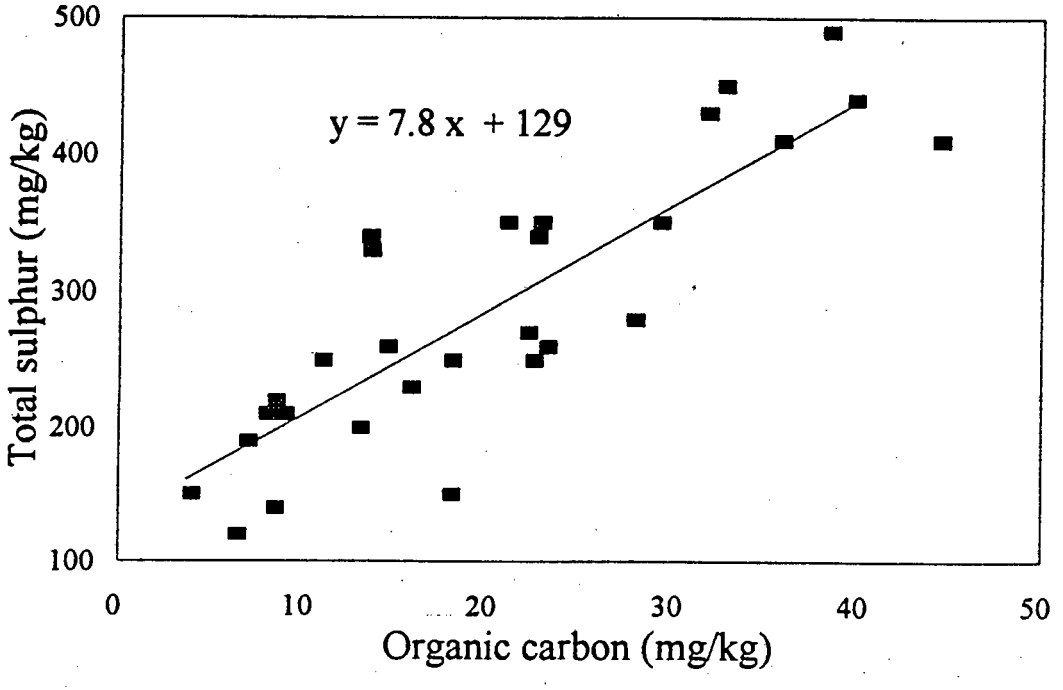


Figure 4.10 Relationship between total S and organic C for the soil collection, based on data from Tables 4.1 and 4.2. The regression was performed without the outlier (10S), giving an r^2 of 0.73 (df=27).

An alternative source of inorganic sulphur, besides that derived from parent material, is through the atmospheric deposition of sulphur compounds. Five datasets, comprising soils from different parts of South Africa and including Arnot, were compared with respect to their organic carbon and total sulphur relationships. The soil data of du Toit (1993b) were predominantly sampled from sites in the northern Orange Free State, but also included a few soils from the Eastern Cape and the highveld. Of this data set only seven soils were situated in areas likely to be subjected to atmospheric pollution. Du Toit's data were split into a presumably more polluted highveld component (defined according to the geographical boundaries) and the remaining soils from the OFS and Cape province. In addition, unpublished data from East Griqualand, an area unaffected by industrial emissions, and the industrialised Vaal Dam catchment (Fey and Guy, 1993) were compared. The relationship between organic carbon and total sulphur were defined for each region and details of the regression parameters are given in Table 4.6. The regression equation is of the form $S = aC+b$, where S = total sulphur ($mg.kg^{-1}$) and C = organic carbon ($g.kg^{-1}$) and a and b are constants.

Table 4.6 Regression data for soil data sets from different parts of South Africa.

	Arnot	Vaal Dam Catchment (Fey & Guy, 1993)	du Toit data (1993b)[1]		East Griqualand (Fey, unpublished data)[2]
			Highveld	Excluding highveld	
r^2 value	0.73	0.71	0.76	0.90	0.42
Number of observations	29	11	7	43	24
a ($mg.g^{-1}$)	7.8	5.9	5.4	9.1	5.2
b ($mg.kg^{-1}$)	129	142	82.5	6.7	74

1 The regression was calculated using data for soils not subject to cultivation.

2 Unpublished total sulphur and organic carbon data for both the Vaal Dam Catchment and East Griqualand are provided in Appendix 3.

The relationships presented in Table 4.6 are illustrated in Figure 4.11. In general the slopes of the relationships are quite similar - the exception being the soils of du Toit (1993b) which exclude the highveld samples (i.e. the Cape and OFS). Many of these soils, which originate in more arid parts of the interior of South Africa, are very low in organic carbon content. At

such low concentrations the determination of organic carbon (and, for that matter, total S) is less accurate, which suggests that, despite the large number of soils in this collection by comparison with the other sets, the relationship should be treated with more circumspection.

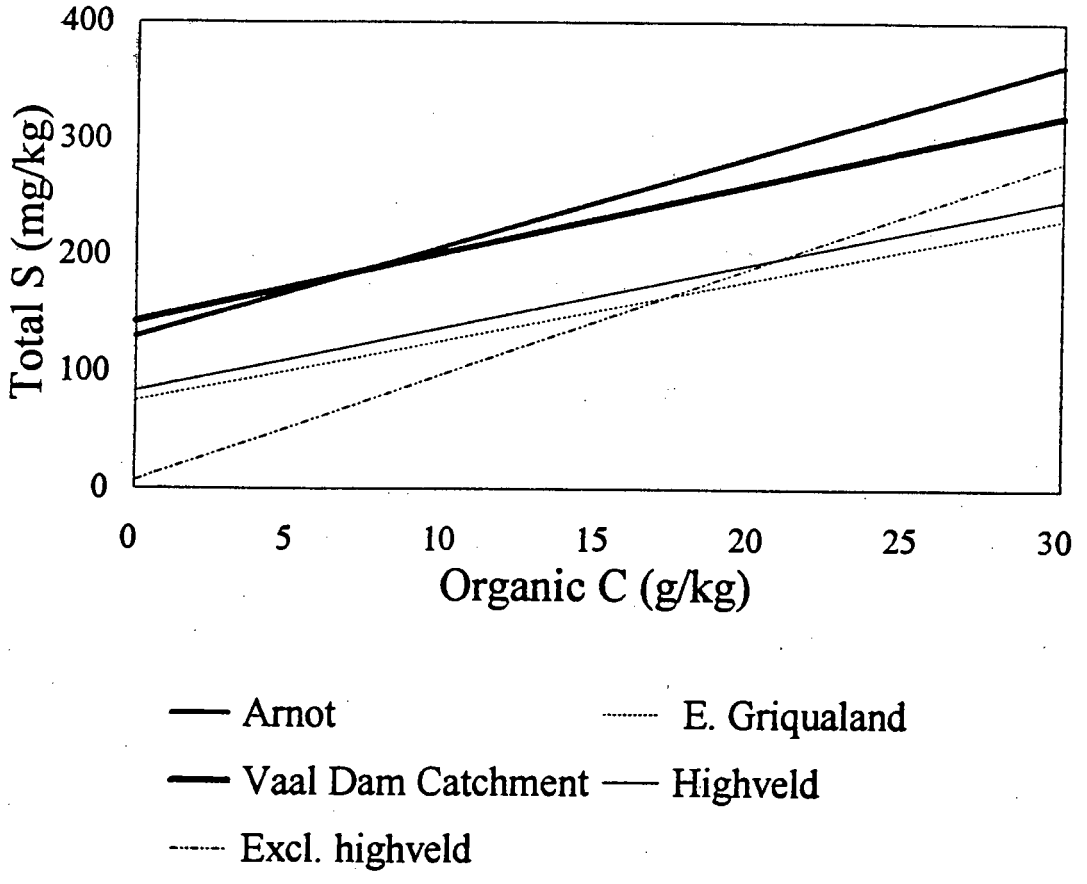


Figure 4.11 Relationship between organic carbon and total sulphur for various parts of South Africa. Solid lines indicate areas affected by atmospheric pollution. Sources of data and regression analyses are presented in Table 4.6.

Although the slopes of the equations are similar, the intercept values vary considerably. It is noteworthy that the industrial areas subject to air pollution, such as Arnot, the Vaal Dam catchment and the highveld soils of du Toit (1993b), have a higher y-intercept value i.e. a higher background value, ostensibly representing inorganic sulphur. The implication is either that the inorganic sulphur fraction in the soils of these areas is derived from atmospheric deposition of sulphur compounds or that the parent material and soils are higher in sulphur than those of East Griqualand and du Toit's soils from the Cape and OFS, and that this sulphur has yet to be incorporated in soil organic matter.

Before any conclusions can be drawn concerning these findings, more extensive information on the composition of the parent material is required, particularly with reference to the sulphur-bearing mineral component. In addition, data sets from other parts of southern Africa should be established and the relationships between organic carbon and total sulphur compared. Nevertheless, the data presented above suggest that soils subject to atmospheric deposition of sulphur compounds may possess a higher inorganic sulphur component than soils unaffected by atmospheric pollution.

Although the relationship between carbon and sulphur in the organic fraction falls within a fairly narrow range, Tisdale *et al.* (1985) report marked differences between the C/N/S ratios among and between types of world soils. Such variation is attributable to variations in parent material and other soil-forming factors such as climate, drainage and vegetation. A close association is reported for the sulphur and nitrogen components of soil organic matter thus Tisdale *et al.* (1985) suggest that total nitrogen and organic sulphur are more closely correlated than organic carbon and organic sulphur. The C:S ratio for humins, humic acids and fulvic acids range between 36 to 145 whereas the N:S ratio ranges between 2.7 to 8.3 (Sparks, 1995). Since the N/S ratio in most whole soils falls within the narrow range of 6 to 8:1 (Tisdale *et al.*, 1985) the relationship between nitrogen and sulphur may be a more valuable one to utilize in the quest for indications of sulphur deposition from atmospheric pollution.

4.4. Conclusions

The soils in the vicinity of Arnot power station are moderately acidic sandy-loams or loamy-sands. The soils are variably-charged, dominated by negative charge. Kaolinite is the dominant mineral in the clay fraction with the exception of the site 10 soil which has an equal proportion of smectite. In all the soils, Fe dominates the sesquioxidic fraction.

No trends in major or trace elements with distance from the power station were apparent. Measures of pH in water, KCl and K_2SO_4 as well as phosphate-extractable sulphate against distance showed no relationships. Water-soluble sulphate is an exception as it appears to be elevated within 6 km of the power station.

Since sulphate retention on soil depends on a combination of factors such as soil pH and sesquioxide content rather than a single factor, two indices of sulphate retention were explored. An index of sulphate retention calculated from the pH difference between pH measured in KCl and that in K_2SO_4 did not show a correlation with the phosphate-extractable sulphate, although the subsoils and topsoils were separated into two distinct groups. A sulphate retention index calculated as [kaolinite content + 5(Fe content) - 10(organic carbon content)] not only separated topsoils from subsoils but revealed a linear relationship between phosphate-extractable sulphate and the SRI for the subsoils. No relationship was apparent for the topsoils which suggests that the relatively high concentration of humic substances in the topsoils blocks the sorption of sulphate on the sesquioxide surfaces.

The presence of organic matter in soil is acknowledged to play an important role in sulphate retention. The relationships between organic carbon and total sulphur were therefore explored for five areas, two of which are relatively unaffected by emissions from industrial activity. Preliminary findings suggest that inorganic sulphur levels are higher in areas affected by atmospheric deposition compared with areas in which no atmospheric pollution from industry is apparent. Further investigation to isolate the contribution from the parent material and that hypothesized to originate from atmospheric deposition is strongly recommended. The relationship between nitrogen and total sulphur could be used rather than organic carbon and total sulphur as the N:S ratio is apparently more narrowly defined. In the long-term, a change in the N:S relationship may reflect whether or not sulphur is accumulating as a consequence of atmospheric deposition.

GENERAL DISCUSSION AND CONCLUSIONS

The thirty soils collected during the course of this study provide a baseline data set for long-term monitoring of atmospheric deposition impacts to soils. The geographical co-ordinates of each site which was sampled are provided and site features are described to facilitate resampling in the future. Soil samples collected during the present study are stored at two locations in South Africa and will provide historical samples for future comparison. A preliminary attempt to test the repeatability of the sampling protocol suggests that a more rigorous approach should be adopted. Ramsey *et al.* (1995) provide guidelines for statistically valid tests of the repeatability and reproducibility of sampling protocols.

Of all the analytical techniques employed in this study, only the determination of phosphate-extractable sulphate was critically investigated. The use of turbidimetry for accurate determination of phosphate-extractable sulphate is questionable as the high phosphate concentration required to displace sulphate from the exchange sites interferes with the determination. Although generally considered inappropriate, ion chromatography is suggested as a viable alternative to turbidimetry for the determination of phosphate-extractable sulphate.

The relationships between soil chemical features and the amount of sulphate sorbed on soil surfaces were investigated. An index of sulphate retention, calculated as [kaolinite + 5(Fe content) - 10(organic carbon content)], was found to give a satisfactory separation of topsoils from subsoils. The relationship between the sulphate retention index and phosphate-extractable sulphate was found to be linear for the subsoils only, suggesting that once the competition for positively charged sites from organic matter is reduced, sulphate retention is controlled by the free Fe oxide and kaolinite contents of the clay fraction.

Preliminary results suggest that evidence of impacts of atmospheric deposition may be appearing in the soils near Arnot power station. Arnot has been burning fossil fuels for electricity production since 1971, and there is an indication that concentrations of water-soluble sulphate may be elevated in the soils near the power station. The highest concentrations of water-soluble sulphate (13.6 - 15.4 $mg.kg^{-1}$) were found within 4-6 km of the power station. However, sampling was only conducted in an arc extending ENE to SE of the power station as this area was assumed to be most frequently subjected to looping pollution plumes. Efforts to verify these results should focus on an area upwind of the prevailing wind direction and should sample soils beyond 20 km of the power station to establish more reliable background values of water-soluble sulphate in the local soils. Apart from water-soluble sulphate there is no indication of a deposition gradient for any of the trace elements, the major elements or parameters linked to soil acidity.

The relationship between total sulphur and organic carbon described for the soils in the vicinity of Arnot suggests an elevated background concentration of inorganic sulphur compared with soils from regions likely to be less polluted. The relationships derived for soils originating in supposedly polluted areas (the Vaal Dam catchment, highveld soils and the immediate surrounds of Arnot power station) generally revealed a higher background concentration of inorganic sulphur than that derived for soils of unpolluted regions (East Griqualand, Eastern Cape and Orange Free State). Whether this inorganic sulphur is a legacy of the parent material or a consequence of atmospheric deposition of sulphur compounds is an aspect that requires further research. Further research should focus on gathering data from various regions of southern Africa to establish whether background levels of inorganic sulphur can be attributed to atmospheric deposition of sulphur compounds or to the parent material. Additional work is required to assess whether total nitrogen would prove more suitable than organic carbon in establishing background inorganic sulphur concentrations, as the N:S ratio is generally more restricted than the C:S ratio.

The evidence so far suggests that long-term monitoring of soil chemistry in the vicinity of Arnot power station is essential. Long-term monitoring will permit impacts to be detected at a reasonably early stage and allow the timely implementation of appropriate control strategies. To this end the establishment of a reliable monitoring system, in which both the sampling and analytical techniques employed are repeatable and accurate, is imperative. In particular, a study of the manner in which the interrelationships between parameters, rather than simply the parameters themselves, are altered, could prove fruitful in the detection of impacts of atmospheric pollution on the pedosphere.

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APPENDIX 1 - SITE DESCRIPTIONS

The position of each of the sampling sites was accurately marked on a 1:50 000 topographical sheet of the Arnot area, as well as on appropriate 1:10 000 orthophotos. Reference to the 1:50 000 2529 DD Arnot (second edition, 1986) topographical map is essential. The map resources are housed in the Department of Geological Sciences, University of Cape Town, Cape Town. Additional features of each site are provided in the in the following section (Adapted from the original manuscript prepared by H Dodds). Soil samples are archived in two localities: The Department of Geological Sciences, University of Cape Town, Rondebosch, Cape Town, and The Division of Water, Environment and Forestry Technology, CSIR, Nelspruit.

Site 1

Date of sampling	6 August 1996
Latitude	25° 55′ 05.1″ S
Longitude	29° 59′ 18.2″ E
Orthophoto No.	2529 DD 20 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Quartzite and shale, or diabase
Distance from power station	19.9 km, east-north east of the power station
Soil samples taken by	M van Tienhoven, H Dodds, C Koekemoer, L Schoeman
Sample storage	Plastic bottles and plastic bags
Access	The public road crosses over Witkloofspruit approximately 500m before the sampling site. Access to the site is through a farm gate opposite the entrance to the farm "Blesbokspruit".

Observations

The landowner is Mr Stoffel Venter. The slope of the site had a south-west aspect, was gentle and slightly convex. The sample was taken from the upper midslope in heavily grazed grassveld. An old kraal site was situated about 30 m to the south west. No erosion, mechanical disturbance or sign of a water table was evident. The soil was moist and the transition from topsoil to subsoil was not distinct. A rocky ridge was evident on the eastern side of the site.

Site 2

Date of sampling	6 August 1996
Latitude	25° 56′ 16.5″ S
Longitude	29° 57′ 22.4″ E
Orthophoto No.	2529 DD 20 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Shale
Distance from power station	16.9 km, east of the power station
Soil samples taken by	M van Tienhoven, H Dodds, C Koekemoer, L Schoeman
Sample storage	Plastic bottles and plastic bags
Access	The site was situated in grazing land, north of an ephemeral vlei but south-west of a grove of wattle trees (*Acacia mearnsii*). Access is either via the farmstead "Goedehoop", or through a gate off the main road, which was kept locked by the farmer.

Observations

The land owner was Mr Stoffel Venter. The sample was taken from a tract of natural veld wedged between *Eragrostis curvula* grazing lands, about 1 km from the tar road, and had been recently burnt. The site was very slightly convex, but with no aspect. No evidence of erosion, mechanical disturbance, surface rock or sign of a water table was observed. The soil was moist. Wattle stands were present at a short distance to the north and east. The remnants of an old pan were evident at some distance to the south. The *Eragrostis* had been fertilised with K and N in the 1980's.

Site 3

Date of sampling	6 August 1996
Latitude	25° 54′ 46.9″ S
Longitude	29° 55′ 55.2″ E
Orthophoto No.	2529 DD 19 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Basalt and andesite
Distance from power station	14.8 km, north east of the power station
Soil samples taken by	M van Tienhoven, C Koekemoer, L Schoeman
Sample storage	Plastic bottles and plastic bags
Access	Access was gained through a gate off the main road and by following a farm track which ran parallel to a fence line. The site was located north of a pine and wattle stand between the road and Otterpan.

Observations

The landowner (Mr Van der Merwe) had recently passed away, and permission to sample was obtained from Mr Stoffel Venter. The sample was taken from the crest of a flat, straight slope with no aspect, about two thirds up from the shore to the mielie land fence. No evidence of erosion, or sign of a water table was observed. Although not in the sampling area, animal mounds were evident in the vicinity, and the possibility exists of mechanical disturbance of the soil by burrowing. Samples were taken in thick grassveld, at the northern end of the Otterpan catchment. Maize cultivation was apparent on the slope crest to the north and east. The sampled area was surrounded by grazing land (sheep). The soil was moist.

Site 4

Date of sampling	6 August 1996
Latitude	25° 54′ 15.3″ S
Longitude	29° 54′ 34.1″ E
Orthophoto No.	2529 DD 19 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Basalt and andesite, or shale
Distance from power station	12.8 km, north east of the power station
Soil samples taken by	M van Tienhoven, C Koekemoer, L Schoeman
Sample storage	Plastic bottles and plastic bags
Access	The site was accessed through an informal gate in the fence between two kraals close to the road. The sampling site was located to the right hand side towards a farmstead, and slightly downslope in the direction of the northern extent of a wattle stand. The samples were taken to the north-west of Grootpan, on the western side of the wattle thicket.

Observations

Samples were taken midslope of a south-west facing, straight slope with gradient about 30°. Two dwellings were upslope, one to the east and one to the west of the site. No evidence of a water table, erosion, or mechanical disturbance of the soil was observed. The site had a thick grass cover, interspersed with *Tagetes minuta*, and appeared to be underlain by dolerite. Only nine subsamples were taken, as rock was struck at a shallow depth on one occasion.

Site 5

Date of sampling	6 August 1996
Latitude	25° 53′ 23.1″ S
Longitude	29° 52′ 47.7″ E
Orthophoto No.	2529 DD 13 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Shale
Distance from power station	10.7 km, east-south east of the power station
Soil samples taken by	M van Tienhoven, C Koekemoer, L Schoeman
Sample storage	Plastic bottles and plastic bags
Access	Permission to sample was obtained at the farmstead (Mr Combrink) situated north east of the Klippan. Access to the site was gained through large double gates, about 1 km to the south of the farmstead. A farm track leads south but we left the track and headed north towards the farmstead.

Observations

The soil sampling site was located about three quarters upslope between the water's edge and the road, to the south of a large, tree-covered rock outcrop. A dolerite outcrop extended around one fifth of the pan. The rest of the pan was surrounded by grazing land, with maize crops near the north-western and south-eastern shore. Marshy areas were present to the north and south of the pan. The sampling site was sloped at about 35°, convex, with a western aspect and covered by grassveld. The soil was clayey and moist, with some evidence of mottles. No evidence of a water table, erosion or mechanical disturbance was observed.

Site 6

Date of sampling	6 August 1996
Latitude	25° 56′ 08.5″ S
Longitude	29° 47′ 53.3″ E
Orthophoto No.	2529 DD 16 & 17 (1st editions, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Shale
Distance from power station	1.3 km, north east of the power station
Soil samples taken by	M van Tienhoven, H Dodds
Sample storage	Plastic bottles and plastic bags
Access	A dirt road ran from the tar road to the east of the power station, and could be followed to the railway line, where access to the site was gained by climbing over a collapsed fence.

Observations

The site was situated in a wedge of land hemmed in by the railway line, the road and ESKOM land which possibly served as a coal stockpile area in the past. Maize fields and a stand of oak trees were directly upslope of the site, and grazing land was immediately downslope. Samples were taken from the upper midslope position, on a straight, roughly 25° slope covered by grassveld and subject to cattle grazing. No evidence of erosion or sign of a water table was observed. The openings of subterranean termite tunnels were abundant, and mechanical disturbance of the soil by these animals was a possibility. The soil was dry and the surface was quite sandy and stony.

Site 7

Date of sampling	7 August 1996
Latitude	25° 54′ 30.6″ S
Longitude	29° 51′ 34.5″ E
Orthophoto No.	2529 DD 18 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Shale
Distance from power station	8.1 km, south east of the power station
Soil samples taken by	M van Tienhoven, C Koekemoer, L Schoeman
Sample storage	Plastic bottles and plastic bags
Access	The site was situated on mine land. A gate (signposted 'Refuge Bay 9') led directly onto a dirt track which was navigable by car, provided a sharp lookout was kept for fugitive barbed wire.

Observations

Samples were taken from a site on the eastern shore of the pan, with a wattle stand about 100 metres to the south and a large wattle thicket about 300 metres to the north. The pan was surrounded by grazing land (horses) with maize lands on the southern crest, and there was evidence of excavation on the eastern shore (failed dam?), about half way between the road and the water. A dolerite outcropping occured to the north, and a stand of blue gum trees to the north east. The site was situated on a slightly concave, roughly 20° slope with a north-west aspect, and samples were taken from the upper midslope. The soil was sandy and was covered by thick, heavily grazed grassveld with sparsely dispersed khakibos (*Tagetes minuta*). No evidence of erosion or sign of a watertable was observed, but small termite mounds and an old road were apparent in the vicinity, and could indicate potential mechanical disturbance of the soil.

Site 8

Date of sampling	7 August 1996
Latitude	25° 58′ 35.9″ S
Longitude	29° 55′ 38.0″ E
Orthophoto No.	2529 DD 24 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Shale
Distance from power station	14.4 km, east-south east of the power station
Soil samples taken by	M van Tienhoven, C Koekemoer, L Schoeman
Sample storage	Plastic bottles and plastic bags
Access	The site was situated on mine land, and could be entered through a gate leading directly off the road and signposted 'W3'.

Observations

A stand of wattle trees lay to the south west of the pan, while maize fields were present to the north, east and south and were interspersed with grazing veld. Soil samples were taken on the north-eastern side of the pan, about 30 metres from a large, single wattle tree. An outcrop of possibly sandstone emerged close to the pan. The sampling site was situated on the upper midslope to crest of a straight, roughly 10° slope with a south east aspect. The soil was moist and sandy and had a good grass cover dominated by *Eragrostis*. Some animal burrows and slight depressions were evident in the vicinity of the site, and there was no evidence of erosion or sign of a water table. Only 9 subsoil subsamples were taken, as rock was repeatedly struck in one of the subsample sites.

Site 9

Date of sampling	6 August 1996
Latitude	25° 57′ 11.1″ S
Longitude	29° 54′ 36.9″ E
Orthophoto No.	2529 DD 24 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Dolerite
Distance from power station	12.6 km, east of the power station
Soil samples taken by	M van Tienhoven, H Dodds, C Koekemoer, L Schoeman
Sample storage	Plastic bottles and plastic bags
Access	The site was situated on mining land. Access was gained through a farm gate marked 'W8' located opposite Klipfontein farm.

Observations

The sampling site was roughly in line with the western post of the gate, about 50 metres from the road, and was covered by grazed grassveld. On entry through the gate there was a disused concrete threshing floor 10 m in diameter located on the right hand side. Samples were taken from the midslope of a approximately 15° slope with a north east aspect. There was no evidence of erosion or signs of a water table, although patches of damp, dark soil were observed. Termite or dung beetle burrows were also observed. Surface rock outcrops were evident.

Site 10

Date of sampling	7 August 1996
Latitude	25° 58′ 29.8″ S
Longitude	29° 51′ 55.3″ E
Orthophoto No.	2529 DD 23 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Dolerite
Distance from power station	8.3 km, east-south east of the power station
Soil samples taken by	M van Tienhoven, H Dodds, C Koekemoer, L Schoeman
Sample storage	Plastic bottles and plastic bags
Access	The site was accessed through a driveway with large, ornate, concrete posts on either side. A side gate led into the paddock directly from the driveway. The nearby homestead "Leeupan" is distinguished by two large palm trees. The house was close to the road.

Observations

The sampling site lay 40m to the north-east of a survey beacon, roughly 100 m to the north of the farmstead, and was covered by thick, waist-high grassland with some *Themeda*. Some evidence of grazing was observed, but this was neither intensive nor recent. The site was situated on the crest of a very slightly concave slope of about 5 to 10° and with a north aspect. There was no evidence of erosion, mechanical disturbance or sign of a water table. The soil was a moist, heavy, black clay, and contained very dark to black concretions of about 3 mm diameter.

Site 11

Date of sampling	7 August 1996
Latitude	25° 59′ 02.4″ S
Longitude	29° 47′ 03.5″ E
Orthophoto No.	2529 DD 21 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Shale
Distance from power station	4.5 km, south west of the power station.
Soil samples taken by	M van Tienhoven, C Koekemoer, L Schoeman
Sample storage	Plastic bottles and plastic bags
Access	The site was accessible by a service road for the power line which runs through the area. Access to this route is from the public road but through a series of locked gates the keys to which were supplied by Mr Koekemoer.

Observations

The sampling site lay directly to the south of the nearby pan, with an avenue of oak trees and powerlines south of the site. The soil was moist and sandy and was well covered by grassveld, predominantly "kweekgras", which appeared to be grazed by cattle. The site was situated in the upper midslope of a slightly concave, south facing slope of gradient about 10°. There was no evidence of erosion, mechanical disturbance or sign of a water table.

Site 12

Date of sampling	8 August 1996
Latitude	25° 55′ 55.2″ S
Longitude	29° 50′ 28.0″ E
Orthophoto No.	2529 DD 17 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Shale
Distance from power station	5.5 km, east-north east of the power station
Soil samples taken by	M van Tienhoven, H Dodds
Sample storage	Plastic bottles and plastic bags
Access	The site was situated on mine land and could be accessed using a dirt road which ran to the east of Rietkuil, and then turning off onto a farm road. During the week of sampling, minor detours were encountered along this route, possibly because of the movement of test drill rigs which were shifted from site to site. It is possible that further modification of these roads may occur in the future.

Observations

The site was covered by grassveld and subject to sheep and cattle grazing. Soil was sampled from the midslope position of a straight, south-west facing slope with a gradient of about 15°, north of a windmill. No evidence of erosion nor sign of a water table was observed. Animal burrows and tracks were evident.

Site 13

Date of sampling	8 August 1996
Latitude	25° 58′ 44.4″ S
Longitude	29° 49′ 56.9″ E
Orthophoto No.	2529 DD 22 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Shale
Distance from power station	5.8 km, south-west of the power station
Soil samples taken by	M van Tienhoven, H Dodds
Sample storage	Plastic bottles and plastic bags
Access	The site was accessed by driving along the dirt road which ran parellel to the ash dam, turning to the east at a large, fenced off area which marked the junction of underground water mains and is termed "Picadilly circus". Head into the veld to the south of a fence post which marks the beginning of an east-running farm fence. It was possible to drive a car over the flat terrain. The land is privately owned, and Mr Koekemoer obtained permission for sampling.

Observations

The site was situated on lightly-grazed grassveld on the north-eastern side of the nearby pan, and immediately upslope of a broad band of low-growing bush (possibly *Stoebe vulgaris*) which extended downslope towards the shore. Extensive khakibos establishment was also evident on the eastern side of the pan. A rural settlement was situated to the north-north east, behind a wattle thicket. Soil was sampled from the upper midslope to crest of a slightly convex, south-east facing slope with a gradient of roughly 10°. No sign of erosion or a water table was evident. The soil was moist. Animal burrows and cattle tracks were observed.

Site 14

Date of sampling	8 August 1996
Latitude	25° 59′ 36.9″ S
Longitude	29° 58′ 10.1″ E
Orthophoto No.	2529 DD 25 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Quartzite and shale, or tillite and shale
Distance from power station	18.8 km, east-south east of the power station
Soil samples taken by	M van Tienhoven, H Dodds
Sample storage	Plastic bottles and plastic bags
Access	The landowner, Mr Combrink, was approached for permission to sample on his land. The farmstead "Goedehoop" was about 1 km from the main dirt road, on the western side of the farm access road. The site itself was further to the west, in a paddock which lay directly next to the main dirt road. A road beacon labelled "1/D248" lay parallel to the sampling site. The site was located downslope of the road and access required climbing through the fence.

Observations

The site was covered by well-established grassveld, with a very diverse species composition and very lightly grazed by antelope. The last time the soil had been ploughed was about 50 years ago. Animal burrows and tracks were evident, but were very sparse. Soil was collected from midslope of a straight, north facing slope with a gradient of about 10°. There was no evidence of erosion or a water table.

Site 15

Date of sampling	9 August 1996
Latitude	25° 57′ 20.7″ S
Longitude	29° 47′ 05.2″ E
Orthophoto No.	2529 DD 21 (1st edition, 1986) 1:10 000
Topographical map No.	2529 DD Arnot (2nd edition, 1986) 1:50 000
Lithology	Shale
Distance from power station	1.0 km, south-south west of the power station
Soil samples taken by	M van Tienhoven, H Dodds
Sample storage	Plastic bottles and plastic bags
Access	A public tar road runs south of the power station. Large white brick walls flanked an access road which runs north towards the power station. The turnoff to the access road was also marked by a stand of pine trees. The access road forked, and the right hand fork was followed for about 50 metres, until immediately before a farmstead surrounded by a large, high security fence. The site lay about 40 meters to the south of the road and could be entered by climbing over the fence.

Observations

The site was located in a tract of natural veld which was not extensively grazed, and which was wedged in between the farmstead and a maize field to the east and south east, and a housing development to the north, directly upslope. Soil samples were taken midslope of a straight, south-west facing slope with a gradient of about 15°. No evidence of erosion or sign of a water table was observed. A few animal burrows were noted.

APPENDIX 2 - ANALYTICAL METHODS

1. Geographical Positioning System A2-1
2. Sample preparation A2-1
3. Determination of pH in water, KCl and K_2SO_4 . . . . . A2-1
4. Determination of acid neutralising capacity A2-3
5. Determination of exchangeable cations A2-4
6. Determination of exchangeable acidity A2-4
7. Determination of exchangeable calcium and magnesium A2-4
8. Preparation of saturated soil paste extracts A2-5
9. Determination of soluble ions by ion chromatography A2-5
10. Determination of organic carbon A2-6
11. Determination of soil moisture content A2-7
12. Particle size analysis A2-7
13. Determination of extractable iron, aluminium and manganese: dithionite-citrate-bicarbonate. A2-8
14. Determination of mineralogical composition of sand, silt and clay fractions A2-9
15. Sample preparation for XRF spectrometry A2-9
16. Routine analysis of trace and major elements by wavelength dispersive X-ray fluorescence spectrometry A2-10
    16.1. Major elements A2-10
    16.2. Trace elements A2-11

APPENDIX 2 - ANALYTICAL METHODS

Many of the analytical techniques described in the following section are standard techniques which are readily available in standard texts or from the scientific literature. However, if valid comparisons are to be made between the data collected in this study and data to be collected in the future, the methods employed must be repeatable. Thus, wherever possible, details of each method have been noted.

1. Geographical Positioning System

A GARMIN GPS 45 navigator was used to locate the position of the sampling sites. The Geographical Positioning System (GPS) is operated by the government of the United States of America, which is solely responsible for its accuracy and maintenance. The system is currently under development and is subject to changes which could affect the accuracy and performance of all GPS equipment. Thus, supplementary information from local maps and site-specific features were noted to ensure that each soil sampling site could be relocated in the future.

The GARMIN GPS 45 features a MultiTrac8™ receiver which tracks and uses up to eight satellites simultaneously. Position accuracy ranges from 5 to 15 meters. The map datum field used as the default setting is the World Geodetic System 1984 (GARMIN GPS 45 Instruction Manual).

2. Sample preparation

Each soil sample was poured out into a clean, dry soil tray and left to air dry indoors for three to four days. Once dry the soil was ground to pass through a 2 mm soil sieve, then stored in plastic jars with airtight screw-on lids. Unless otherwise stated airdried, sieved soil was used in all analyses. Reference samples are kept by both the CSIR (Nelspruit) and the Department of Geological Sciences, University of Cape Town, Cape Town.

3. Determination of pH in water, KCl and K_2SO_4

The pH in distilled water, 1 M KCl and 0.5 M K_2SO_4 was determined for each soil according to the method of McLean (1982). A 1:2.5 ratio of soil:solution was used. The soils were shaken for 10 minutes on a reciprocal shaker and left to stand for 30 minutes prior to pH measurement. The pH was measured with a glass electrode paired with a calomel (Hg-Hg_2Cl)

reference electrode, using a Crison micropH 2001 pH meter. The pH meter was calibrated daily with buffers pH 4.01 and pH 7.00. The electrode was lowered into the solution until the tip was just above the settled soil layer. The pH was recorded once the digital reading was stable for at least 10 seconds. In the case of pH in distilled water, the electrode was immersed for a minute before the reading was taken.

Instrument precision was tested by 3 non-consecutive measurements of the same extract. The details for extracts of samples 5T and 13S are shown in Table A2.1 - for pH in water, KCl and K_2SO_4.

Table A2.1 Precision of pH measurements for extracts of samples 5T and 13S - determined by 3 non-consecutive measurements of the extract (n=3). Results are shown for pH in water, KCl and K_2SO_4.

	pH (water)			pH (KCl)			pH (K_2SO_4)		
Sample	x	s	RSD[1]	x	s	RSD	x	s	RSD
5T	5.47	0.006	0.1%	4.30	0.006	0.1%	4.75	0.006	0.1%
13S	5.49	0.036	0.7%	4.26	0.006	0.1%	4.82	0	0%

[1] RSD = relative standard deviation

In general there was far more variation in the measurements of pH in water than for those made in either KCl or K_2SO_4.

The repeatability of the extractions was also tested by performing six repeats of each extraction on samples 6T and 13T. Results are presented in Table A2.2.

Table A2.2 Repeatability of extractions in water, KCl and K_2SO_4 performed for samples 6T and 13T (n=6).

	pH (water)			pH (KCl)			pH (K_2SO_4)		
Sample	x	s	RSD[1]	x	s	RSD	x	s	RSD
6T	5.23	0.016	0.3%	4.11	0.021	0.5%	4.60	0.027	0.6%
13T	5.79	0.037	0.6%	4.43	0.014	0.3%	4.85	0.037	0.8%

[1] RSD = relative standard deviation

Note that it is mathematically incorrect to average pH values (since pH = - log $[H^+]$). Yet converting the pH values of a few samples to the H^+ concentrations, finding the mean and converting back to pH, revealed no difference in the pH averages. For the sake of efficiency all subsequent pH values were averaged without converting to $[H^+]$.

4. Determination of acid neutralising capacity

The acid neutralising capacity (ANC) of soil estimates the extent to which acidifying activities, such as cropping or atmospheric deposition, are held in check before the soil is seriously degraded. Thus, ANC provides an indication of the resilience or buffering capacity of the ecosystem to acid inputs.

Two methods of determining ANC are generally employed - both approaches are time-consuming and costly. The method of van Breemen *et al.* (1983) requires a full assay of the total basicity present while the second method involves a serial titration and equilibration with strong acids (Nätscher and Schwertmann, 1991, cited in du Toit, 1993a). A more efficient means of determining ANC was developed by B du Toit (1993) and du Toit and Fey (1994), whereby the same chemical principles used to determine the base neutralising capacity of soils (BNC) or lime requirement were adapted to the determination of ANC.

A buffer mixture of 0.01 moles HOAc, 0.001 moles KOAc and 0.1 moles (11.1g) of $CaCl_2$ was made up to 1 liter and adjusted to pH 3.5. Five mL of soil were mixed with 15 mL of the buffer solution and the suspension shaken for 15 minutes. After shaking, the suspension was allowed to settle for 15 minutes before the pH of the supernatant solution was recorded. ANC was calculated as follows:

$$ANC\ (cmol_c.L^{-1}) = 9.624\ (pH) - 34.13$$

where an ANC of 1 $cmol_c.L^{-1}$ is equivalent to 1 t $CaCO_3.ha^{-1}$.20 cm.

Du Toit (1993a) found an excellent correlation ($r^2 = 0.96$) between the pH of the soil-buffer solution and soil ANC derived by the method of Nätscher and Schwertmann (1991).

The ANC was determined on duplicates for each soil sample in the present study but for some samples the determination was repeated 3 or 4 times to test precision. The results are reported in Table A2.3.

Table A2.3 Repeatability of ANC determinations

Sample	n	Average (x) ($cmol_c.L^{-1}$)	Sample standard deviation (s)	Relative standard deviation
1T	4	4.70	0.17	3.5%
6T	4	2.51	0.05	1.9%
7S	3	3.18	0.15	4.6%

5. Determination of exchangeable cations

Exchangeable cations and acidity were determined according to the potassium chloride method described by Thomas (1982). Exchangeable acidity was determined by titration and exchangeable calcium and magnesium by atomic absorption spectrometry.

6. Determination of exchangeable acidity

A 5 mL volume of the 1 N KCl extract was titrated against 0.01 M NaOH to an endpoint pH of 8.3. An automatic titrator (DTS 8000 Radiometer Multititration System with a TTT titrator and ABU autoburette) was used with a delay of 10 seconds. Each sample was titrated twice, and the average acidity, in units of $mmol.L^{-1}$, calculated for each sample. In order to test the precision of the titration, the titration was repeated 6 times on one extraction sample. Similarly, the repeatability of the extraction procedure was tested by performing 5 extractions on one sample. The results are reported in Table A2.4.

Table A2.4 Precision of extraction method and automatic titrimetric determination of exchangeable acidity.

Sample	Number of repeats n	Average ($mmol_c.L^{-1}$) x	Sample standard deviation s	Relative standard deviation	Range
a). Extraction and determination of two soil samples with 1N KCl solution.					
5T	4	0.17	0.02	8.6%	0.16-0.19
13S	4	0.28	0.01	4.2%	0.27-0.29
b). Determination of exchangeable acidity by repeated titration of one extract.					
13S	6	0.27	0.005	2.1%	0.26-0.27

7. Determination of exchangeable calcium and magnesium

Extracts in 1N KCl were submitted to the Department of Chemical Engineering, University of Cape Town for determination by atomic absorption spectrometry.
Precision of the determination is given in Table A2.5.

Table A2.5 Repeatability of extraction method and determination of calcium and magnesium by atomic absorption spectrometry.

Sample	n	Sample mean (x) ($mg.kg^{-1}$ soil)	Sample standard deviation (s)	Relative standard deviation
Calcium				
5T	5	276.0	5.7	2.1%
13S	5	141.4	10.5	7.5%
Magnesium				
5T	5	220.2	2.5	1.2%
13S	5	112.9	5.5	4.9%

Cation exchange capacity (CEC) is normally expressed as mmoles charge per kg of soil. It is a measure of the quantity of readily exchangeable cations neutralising the negative charge in the soil. CEC is estimated by taking the sum of exchangeable cations present in the leachate after exposure to a saturating salt solution - termed the summation method as (Rhoades 1982b). The effective cation exchange capacity (ECEC) is calculated from the concentrations of Ca^{2+}, Mg^{2+} and H^{+} cations extracted by 1N KCl.

8. Preparation of saturated soil paste extracts

Preparation of the saturated paste extracts was performed by the Agricultural Research Council in Nelspruit according to the procedure outlined by Rhoades (1982a). Soil pH of the fresh extract was not recorded. Once extracted the solution was refrigerated and frozen. During transportation from Nelspruit to Cape Town the extracts were kept as cool as possible but considerable thawing nevertheless occurred.

The saturated paste extracts were filtered through a 0.45 µm filter and the electrical conductivity of each solution was determined.

The concentrations of soluble salts in the saturated paste extracts were determined by ion chromatography. Dilution of the extracts was often necessary to prevent damage to the ion chromatography column. Extracts were diluted to achieve an electrical conductivity below 100 $\mu S.cm^{-1}$.

9. Determination of soluble ions by ion chromatography

All soil solutions were filtered through a 0.45 µm filter and a Dionex On-Guard-P cartridge for the removal of organic colloids.

A DIONEX 3000 ion chromatograph and DIONEX API-450 software were used for the determination of anions and cations. Cation separation was achieved using a DIONEX HPIC-CS5 exchange column with 20mM methyl-sulphonic acid eluent. Flow rate was 1.0 $mL.min^{-1}$. Conductivity was measured from peak height and compared with standards for Na, K, Mg and Ca. Anions were determined using a Dionex HPIC-IonPac AS4A-SC ion exchange column using 1.80 mM Na_2CO_3 and 1.70 mM $NaHCO_3$ eluent. Flow rate was 2.0 $mL.min^{-1}$. Conductivity was measured using peak area and compared with standards of Cl, NO_3, PO_4 and SO_4. MicroMembrane™ cation and anion autosuppresors were used. Details of precision are given in Table A2.6.

Table A2.6 Repeatability of anion and cation determination by ion chromatography. Ion concentrations are reported in $mg.L^{-1}$

	Same day		Repeat on different day
Anions			
Cl^-	8.4	8.2	8.4
SO_4	17.5	17.5	18.4
Cations			
Mg^{2+}	11.2	11.2	nd
K^+	30.5	30.0	nd

nd = no data

10. Determination of organic carbon

Organic carbon was determined according to the Walkey-Black procedure outlined in Nelson and Sommers (1982) and the Handbook of Standard Soil Testing Methods for Advisory Purposes (1990). The recovery factor (f = 1.3) as determined by Nelson and Sommers (1982), was applied.

The determination of organic carbon was performed in duplicate for each sample and in triplicate for five samples in order to test the repeatability and precision of the method (Table A2.7). Corrections were made for soil moisture content.

Table A2.7 Reproducibility of the Walkley-Black determination of organic carbon. Values given are % organic carbon (without soil moisture correction).

Sample	n	Sample mean (x)	Sample standard deviation (s)	Relative standard deviation	Range
1T	3	4.3	0.1	2.3 %	4.2-4.4
1S	4	2.3	0.4	15.6%	1.9-2.6
5S	3	1.3	0.1	8.7%	1.2-1.4
9S	3	1.6	0.1	3.7%	1.5-1.6
12S	3	1.3	0	0%	-

11. Determination of soil moisture content

Exactly 30 g of airdried soil, sieved to pass through a 2 mm sieve, were weighed out into a pre-weighed glass petri dish. The dishes were placed in an oven at 90 °C for 72 hours until a constant mass (y) was achieved. The mass was determined immediately on removal from the oven to reduce moisture uptake from the air by the soil. Percentage moisture content was calculated as below:

$$\% \text{ moisture content} = \frac{(30 \text{ g air dry soil} - y)}{30 \text{ g}} \times 100$$

Percentage moisture estimates are based on only one determination per sample.

12. Particle size analysis

The mass of the bulk soil sample was measured before sieving through a 2 mm soil sieve. After sieving, the mass of the gravel fraction remaining in the sieve was measured and reported as a fraction of the bulk soil.

The sand, silt and clay fractions of each soil were determined according to the standard methods employed by the Institute for Tropical and Sub-tropical Crops (Agricultural Research Council) in Nelspruit, Mpumalanga. The method is based on Stoke's Law which is well outlined in basic soil texts such as Kohnke (1968).

Air dry soil, sieved to pass through a 2 mm sieve, was poured into a 250 mL glass beaker. For fine-textured soils 50 g of material were used, whereas 100 g were used for sandy soils. Approximately 200 mL of distilled water were added to the soil in the beaker together with 5 mL of 1N sodium hexametaphosphate. The sodium hexametaphosphate acts to disperse the

clay by removing or complexing polyvalent cations and replacing these with the monovalent sodium cation (Kohnke, 1968). The mixture was left to equilibrate overnight.

The slurry was then decanted into a stainless steel mixing flask, rinsing the original beaker thoroughly with distilled water to ensure that all the soil was transferred. The mixing flask was then filled with distilled water to make a total volume of about 500 mL. Clay soils were mixed for 15 minutes while sandy soils required only ten minutes. After mixing, the flask was removed from the mixer, ensuring that any soil on the mixing shaft was rinsed into the flask. The slurry was decanted into a standardised de Bouyoucos soil cyclinder and distilled water added almost to the mark (1130 mL for 50 g of clay soils or 1205 mL mark for 100 g of sandy soils). The soil hydrometer was placed into the cyclinder and allowed to settle before the cylinder was filled completely to the appropriate mark. Two or three drops of pure amyl alcohol were added to ensure that organic matter did not stick to the hydrometer and interfere with its operation. The hydrometer was removed, the lid placed on the cylinder and the cylinder inverted ten times to ensure good mixing. Once shaken the cyclinder was immediately placed on a firm surface, the lid removed and the hydrometer gently immersed in the solution. Reading A was taken exactly 4 minutes after shaking (sand fraction). The cylinder was left undisturbed for a further two hours before taking reading B (clay fraction). A ZEAL hydrometer was used for all of the determinations. The particle size fractions were calculated as follows:

% sand	= 100 - (Reading A/mass of soil used)
% clay	= Reading B/mass of soil used
% silt	= 100 - (% sand + % clay)

where the fractions are defined as sand: 2.00 - 0.002 mm
silt: 0.02 - 0.002 mm
clay: < 0.002 mm

Only one determination was performed per sample.

13. Determination of extractable iron, aluminium and manganese: dithionite-citrate-bicarbonate.

Free iron and aluminium oxides in the soils were determined by the Institute for Soil, Climate and Water according to the method prescribed by Jackson, Lim and Zelazny (1986) and the Handbook of Standard Soil Testing Methods for Advisory Purposes (1990). Once the free iron, aluminium and manganese hade been extracted, their concentrations were determined by atomic absorption spectrometer.

14. Determination of mineralogical composition of sand, silt and clay fractions

Mineral identification in the sand, silt and clay fractions was performed by X-ray diffraction by the Institute for Soil, Climate and Water.

15. Sample preparation for XRF spectrometry

Powder briquettes and fusion discs for analysis by X-ray fluorescence spectrometrywere prepared according to the standard method employed by the Department of Geological Sciences, University of Cape Town.

A 50 g mass of each soil was milled in a Sieb swing mill with a carbon steel vessel for 2 minutes at the fast setting. Plastic gloves and a clean wooden spatula were used to transfer the milled soil to a plastic bag which was then sealed. The Sieb mill was cleaned between samples by milling with quartz for one minute. The milled quartz was discarded and the mill cleaned with compressed air under an extraction fan to reduce dust contamination. The milled was then washed under tap water, rinsed with distilled water, dried off and finally rinsed and dried with acetone.

Preparation of powder briquettes for trace element determination:
Six grams of the milled soil were mixed with 6 drops of 4 % Mowial using an agate pestle and mortar. Once mixed the powder was pressed into a briquette using boric acid as the binder.

Preparation of Norrish fusion discs for major element determination:
The method of Norrish and Hutton (1969) was employed for the preparation of fusion discs. Additional details of the preparation of glass discs and a discussion of the potential sampling errors and contamination problems are given by Claisse and Willis (1995).

16. Routine analysis of trace and major elements by wavelength dispersive X-ray fluorescence spectrometry

The following information is taken directly from Willis (1996) and provides details of the XRF instrument parameters and calculations performed in estimating major and trace element data.

16.1. 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 or 0.2 %) 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 dual target 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 A2.8.

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 A2.8. Analytical conditions for determination of major elements using a Philips PW1480 WDXRF spectrometer.

Element/ line	Collimator	Crystal	Detector	PHS LWL	PHS UPL	Counting time (s)	Concentration range *	RMS	No. of standards
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

16.2. Trace elements

Trace elements were determined on powder briquettes in a series of analytical runs using a number of different x-ray tubes. Analytical conditions are listed in Tables A2.9 and A2.10.

The RhKα Compton or the MoKα Compton peak is used to determine the mass absorption coefficients of the specimens at the RhKαC wavelength or the MoKαC wavelength, and the Compton peak mass absorption coefficient values are used to correct for absorption effects on the Mo, Nb, Zr, Y, Sr, U, Rb, Th, Pb, Br, Se, Bi, As, W, Zn, Cu and Ni analyte wavelengths. Primary and secondary mass absorption coefficients for the Co, Mn, Cr, V, La, Ce, Nd, Ba, Sc, S and F 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.

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 σ) error due to counting statistics and the lower limit of detection is calculated for each element in each specimen.

Table A2.9 X-ray tubes and tube and x-ray path settings for the determination of trace elements using a Philips PW1480 WDXRF spectrometer.

Element/line	X-ray tube		X-ray path
	Target	kV - mA	
MoKαC	Mo/Sc	90 30	Vacuum
MoKα	Rh	80 35	Vacuum
NbKα	Rh	80 35	Vacuum
ZrKα	Rh	80 35	Vacuum
Y Kα	Rh	80 35	Vacuum
SrKα	Rh	80 35	Vacuum
U $L\alpha_1$	Rh	80 35	Vacuum
RbKα	Rh	80 35	Vacuum
Th $L\alpha_1$	Rh	80 35	Vacuum
Pb $L\beta_1$	Rh	80 35	Vacuum
ZnKα	Au	60 45	Vacuum
CuKα	Au	60 45	Vacuum
NiKα	Au	60 45	Vacuum
CoKα	Au	50 55	Vacuum
MnKα	Au	50 55	Vacuum
CrKα	Au	50 55	Vacuum
V Kα	Au	50 55	Vacuum
S Kα	Mo/Sc	40 65	Vacuum
F Kα	Mo/Sc	40 70	Vacuum

Table A2.10 Instrumental conditions for determination of trace elements using a Philips PW1480 WDXRF spectrometer.

Element /line	Collimator	Crystal	Detector	PHS LWL	PHS UPL	Counting time (s)	Concentration range *
MoKαC	F	LiF(220)	SC	32	74	200	
MoKα	F	LiF(200)	SC	30	74	200	0 - 280
NbKα	F	LiF(200)	SC	30	74	200	0 - 268
ZrKα	F	LiF(200)	SC	30	74	200	0 - 1210
Y Kα	F	LiF(200)	SC	30	74	200	0 - 143
SrKα	F	LiF(200)	SC	30	74	200	0 - 440
U $L\alpha_1$	F	LiF(200)	SC	30	74	200	0 - 15
RbKα	F	LiF(200)	SC	30	74	200	0 - 530
Th $L\alpha_1$	F	LiF(200)	SC	30	74	200	0 - 51
Pb $L\beta_1$	F	LiF(200)	SC	30	74	200	0 - 40
ZnKα	F	LiF(220)	FS	20	80	200	0 - 235
CuKα	F	LiF(220)	FS	20	80	200	0 - 227
NiKα	F	LiF(220)	FS	20	80	200	0 - 630
CoKα	F	LiF(220)	FL	15	75	200	0 - 116
MnKα	F	LiF(220)	FL	15	75	200	0 - 1700
CrKα	F	LiF(220)	FL	15	75	200	0 - 465
V Kα	F	LiF(220)	FL	13	67	200	0 - 640
S Kα	C	Ge(111)	FL	32	72	100	

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

Table A2.11 lists the one standard deviation counting error and lower limit of detection for each of the elements in two of the soils used in this study. The difference in mass absorption coefficients between the two types of specimen result in different counting errors and lower limits of detection.

Table A2.11 Calculated trace element data, 1 σ counting error and lower limit of detection (all values in ppm) for two soil samples.

Element	1T			1S		
	Calc	1 σ	LLD	Calc	1 σ	LLD
Mo	<1.2	0.4	1.2	1.4	0.4	1.3
Nb	9.3	0.4	1.0	9.5	0.4	1.1
Zr	395	0.9	1.1	364	0.9	1.1
Y	12	0.4	1.2	13	0.5	1.3
Sr	8.0	0.4	1.2	4.8	0.4	1.2
U	<1.2	0.8	2.4	<2.3	0.9	2.3
Rb	40	0.5	1.3	40	0.6	1.3
Th	6.2	0.9	2.7	7.3	1.0	2.8
Pb	23	1.3	3.6	28	1.4	3.8
Co	33	1.2	3.1	41	1.3	3.3
Mn	864	2.6	2.5	880	2.6	2.6
Cr	233	1.6	2.7	320	1.9	2.9
V	157	1.7	3.3	204	1.8	3.5

APPENDIX 3 - TOTAL SULPHUR AND ORGANIC CARBON DATA

	Total sulphur		Organic carbon	
	%	mg/kg	%	g/kg
EAST GRIQUALAND				
2a	0.010	100	0.85	8.5
3a	0.025	250	2.54	25.4
4a	0.023	230	1.75	17.5
5a	0.018	180	1.21	12.1
6a	0.010	100	0.92	9.2
7a	0.014	140	1.5	15
8a	0.009	90	0.29	2.9
9a	0.012	120	0.49	4.9
10a	0.013	130	0.49	4.9
11a	0.016	160	1.35	13.5
12a	0.019	190	1.06	10.6
13a	0.022	220	2.27	22.7
14a	0.022	220	2.13	21.3
15a	0.008	80	0.86	8.6
16a	0.007	70.1	0.89	8.9
17a	0.016	156.7	1.84	18.4
18a	0.014	137.3	1.95	19.5
19a	0.013	126.9	0.98	9.8
20a	0.013	128.4	1.66	16.6
21a	0.018	177.6	0.92	9.2
22a	0.007	67.2	1.5	15
23a	0.007	65.6	0.69	6.9
24a	0.011	108.8	0.49	4.9
25a	0.015	148.8	2.55	25.5
VAAL DAM CATCHMENT				
	0.039	390	0.9	9
	0.024	240	1.12	11.2
	0.02	200	0.8	8
	0.021	210	0.7	7
	0.031	310	3.01	30.1
	0.023	230	1.55	15.5
	0.027	270	2.17	21.7
	0.023	230	0.81	8.1
	0.021	210	1.1	11
	0.013	130	0.39	3.9
	0.014	140	1.39	13.9
	0.035	350	3.13	31.3