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Investigating the long-term effects of air pollution on soil properties in the vicinity of the Arnot power station

Joanne Lynne Reid

A research report submitted to the Faculty of Science, University of the Witwatersrand, in partial fulfilment of the requirements for the degree of

Master of Science (Coursework and Research Report)

Johannesburg, October 2007

Declaration

I declare that this is my own, unaided work. It is being submitted in partial fulfillment for the Degree of Master of Science (Coursework and Research Report) at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

_____

(Signature of candidate)

_____ day of October 2007

Abstract

A study was conducted in 2006 to investigate the long-term effects of air pollution on soil properties in the vicinity of the Arnot power station, Mpumalanga, South Africa. Fifteen sites were re-sampled and the soil chemical properties compared to baseline data gathered in 1996, resulting in a ten year period after which changes in soil properties were investigated. A spatial gradient was incorporated into the study in order to better understand the deposition of pollutants with increasing distance from the power station. The study indicates that long-term acidic deposition has led to detectable changes in soil chemical properties. Three chemical properties, namely the concentrations of calcium and magnesium in both the topsoils and the subsoils, as well as the effective cation exchange capacity in the subsoils showed a significant increase since 1996. However, five soil chemical properties, namely soil pH (K_2SO_4), the concentration of hydrogen and aluminium and total sulphur in both the topsoils and the subsoils, as well as extractable sulphate in the topsoils and soluble sulphate in the subsoils, all show that the soils have become more acidic over the ten years. The acidic components in the soil override the basic components, as shown by the ratio of basic cations to acidic cations in the soils. The spatial gradient generally indicates that at approximately 8 km from the power station, there is a decrease in the concentration of acidic soil properties and one explanation for this may be a reduction in the acidic components of atmospheric deposition at this site. However, this needs further investigation. Two significant relationships with distance were found, namely a significant negative relationship with soluble sulphate and a significant positive relationship with acid neutralising capacity.

This research will form part of a database for other long-term monitoring programmes and will allow data to be compared to other data from this area of research. It will also provide information to important industry leaders such as Eskom.

Acknowledgements

I would like to thank my supervisor, Professor Mary Scholes, for her supervision of this research and for her guidance and suggestions for improvement.

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I would like to thank Greg for his patience with me and for trying to help me better understand statistics.

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Chapter 1: Introduction

A source of energy is arguably the single most important commodity for people across the globe and is probably the key driver of the global economy. Electricity generation is a major user of primary energy, burning pulverised coal to produce steam which in turn drives large turbines to produce electricity for the grid. Internationally, coal is currently the most widely used primary fuel, accounting for approximately 36% of the world's electricity production (Eskom 2006).

With the start of the Industrial Revolution in the late 18th and early 19th centuries came a shift in the way resources were used. In the industrialising world, an economy based on the use of manual labour was slowly beginning to be replaced by an industry driven by machinery powered by fossil fuels, predominantly coal. However, with this revolution and the increased use of fossil fuels, came many real and potential impacts on the natural environment. For example, since the Industrial Revolution 150 years ago, carbon dioxide (CO_2) levels in the atmosphere have increased by more than 35% (Midgley *et al.* 2001), resulting in an enhanced greenhouse effect.

Currently, global change is the overriding environmental issue concerning scientists and the public across the world (Vitousek 1994), the evidence for which is overwhelming and the potential impacts frightening (Steffen *et al.* 2004). Global environmental change occurs as a number of interacting components that alter the structure and function of the Earth as a system (Vitousek 1994). The issues surrounding global change require urgent attention, however, this is difficult due to the magnitude of the problem. Global change is more than just climate change. It is a function of changes in land cover, ozone depletion, acid rain and global climate change (Steffen *et al.* 2004).

Of these, global climate change is probably the best recognised. It is an area of much contention, with many different schools of thought surrounding global climate change issues (Lomborg 2001). Although not as obvious, the effects of land use change are just as sinister as those associated with climate change and global warming. Land use change

is a broad topic and includes a change in the cover of the land as well as a change in the use of the land. A change in soil properties as a result of the burning of fossil fuels can be considered land use change since, in the long-term, soils may not be able to sustain their productivity due to changes in their physical and chemical properties.

The gaseous components emitted during the combustion of coal, such as sulphur dioxide and nitrogen oxides, are the precursors of fine particulate sulphates and nitrates and these are known to cause acid deposition (Held *et al.* 1996a). Acid deposition is highly variable in both space and time; it links air pollution to both aquatic and terrestrial ecosystems and alters the interactions of many elements, such as hydrogen, sulphur, nitrogen, calcium, magnesium and aluminium (Driscoll *et al.* 2001). Acid deposition has contributed to the acidification of soils and waters in industrialised regions (Van Tienhoven 1997), and in South Africa, the effects of air pollution on soils, human health, surface waters, forest, agricultural crops and building materials have been researched (Fey and Netch 1996; Kempster *et al.* 1996; Scholes *et al.* 1996).

Coal-fired power stations are generally concentrated around the coal seams in order to keep production costs to a minimum. Approximately 84% of South Africa's total coal production originates in the Mpumalanga Province (Mpumalanga DACE 2003) and this concentration of coal reserves limits the construction of coal-fired power stations in other areas. As a result, eight of the eleven of Eskom's South African base-load coal-fired power stations are found on the Highveld in the Mpumalanga province, as shown in Figure 1.

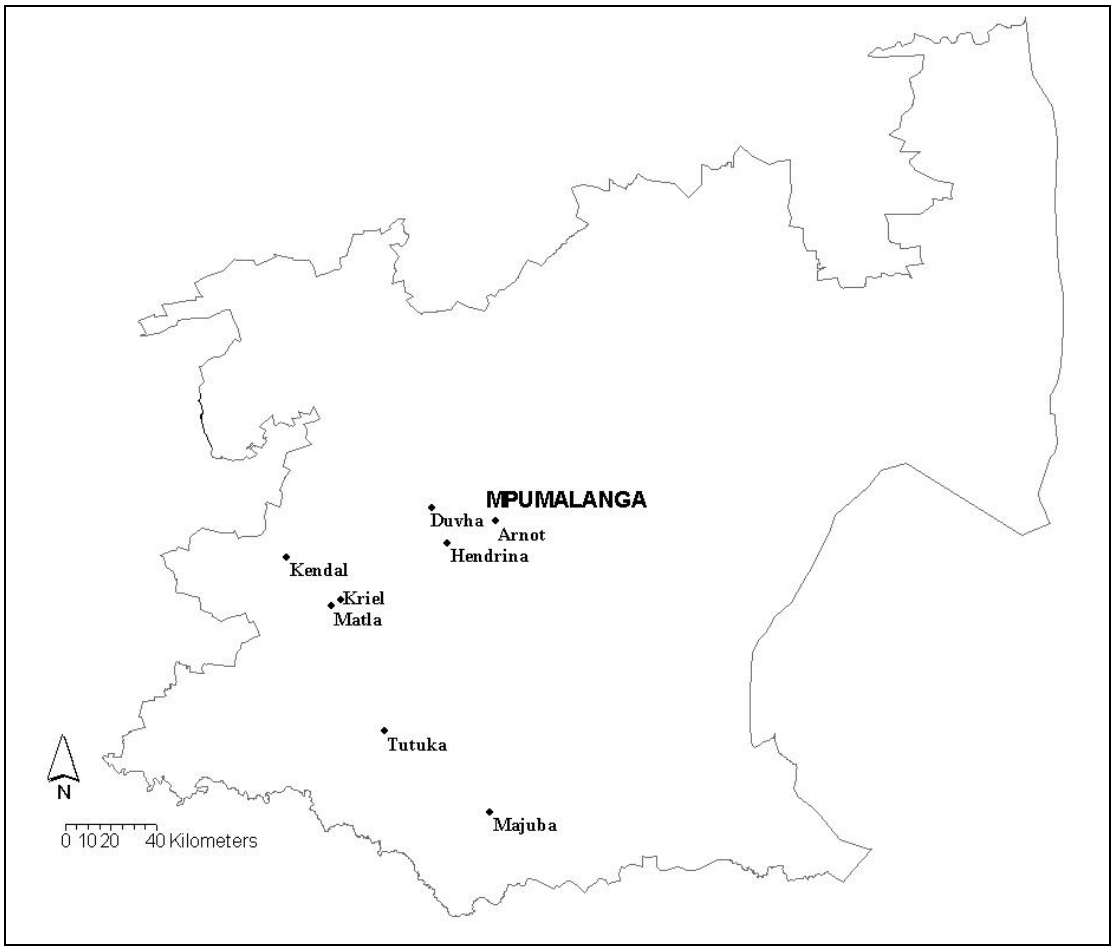


Figure 1: Location of the eight base load power stations within the Mpumalanga Province.

The Mpumalanga Province is naturally divided into three physiographic zones, namely the Escarpment, the Lowveld and the Highveld. The Highveld forms the bulk of south-western Mpumalanga and comprises flat, gently undulating terrain at high altitude. It is within this zone that the eight base load coal-fired power stations within the Province are situated, namely the Arnot, Duvha, Hendrina, Kendal, Kriel, Majuba, Matla and Tutuka power stations.

The Arnot power station forms the focal points for this study and was chosen by Van Tienhoven (1997) for several reasons. Firstly, Arnot is the most easterly of these eight power stations, situated approximately 35 km south-east of Middleburg. It is the furthest from the industrial hubs of Gauteng, Witbank and Middelburg, and for this reason, background pollution levels are assumed to be low. Secondly, the Arnot power station is

one of the oldest power stations in South Africa and was fully operational by 1975. This relatively long history of air pollution and therefore deposition, coupled with the assumed low background pollution levels, makes the Arnot power station an ideal location to monitor the long-term impacts of air pollution on soil properties.

Although there are various sources of pollution in the vicinity of the Arnot power station such as vehicle emissions, the power station itself is likely to be the dominant contributor of dry deposition within the study area. However, wet deposition within the study area is unlikely to be due to the Arnot power station since the mechanism of wet deposition involves the deposition of pollutants via rainfall which is generally formed some distance away and later transported to the area through winds.

The transport and subsequent deposition of air pollutants emitted from power stations is a function of many complex factors such as atmospheric stability, stack height, the rate of emission as well as the rate of transport and transformations that occur. All these factors influence the distance from the source where the pollutants will be deposited. It is therefore important to incorporate a distance gradient into any study that deals with air pollution. For this reason, soils were sampled at fifteen different sites between 1 km and 20 km away from the power station.

Aim

This research was aimed at gaining a better understanding of the link between the atmosphere and the pedosphere, specifically the long-term effects of air pollution on soil properties in the vicinity of the Arnot power station. The monitoring of long-term changes against a baseline is the best way of assessing effects of pollution and since Van Tienhoven (1997) established a baseline in August 1996, this study assessed the effects of air pollution on soil chemical properties ten years later.

Key Questions and Hypotheses

Several key questions were explored. The following questions were key to understanding the changes in the soil properties in the topsoils and the subsoils as well as the impacts on the soil through long-term monitoring.

i) How has the concentration of base cations (calcium, magnesium and ECEC) changed since the baseline study in both the topsoils and the subsoils and is there a relationship with distance from the power station?

ii) What is the change in the concentration of aluminium in the soil since 1996 in both the topsoils and the subsoils and how is this related to distance from the power station?

iii) How does the concentration of sulphur (total sulphur, extractable sulphate and soluble sulphate) change with distance from the power station and does this differ between the topsoils and the subsoils?

iv) How has the acidity of the soils changed at each of the sites since the baseline study? This will be analysed for both the topsoils and the subsoils and will be determined by analysing soil pH, extractable acidity, acid neutralising capacity (ANC) and base saturation.

v) What is the change in the concentration of soluble NH_4^+ and NO_3^- since the baseline study and what is the relationship with distance?

Hypotheses were formulated based on the distance from the power station, sampling depth and the long-term changes in soil properties. The following hypotheses were tested:

1. The greatest total sulphur and therefore sulphate levels in the soil are found within 10 km of the power station.
2. The concentration of extractable aluminium has increased while the concentration of exchangeable base cations, specifically calcium and magnesium has decreased at all sites and across both soil depths as a result of prolonged atmospheric deposition.
3. The soil pH has decreased at all of the sites due to increased soil acidification.

This research has been written up to achieve three objectives:

Chapter 2 – to provide a comprehensive literature review of the area of research

Chapter 3 – to present all findings in the format of a manuscript that could be submitted for publication. I prepared the original draft with further interpretation and discussion by Professor Mary Scholes. I made an 80 % contribution, with a 20 % contribution by Professor Mary Scholes.

Chapter 4 – a general discussion, which allows for an examination of the results with regards to published literature

This format has led to some repetition but will hopefully lead to rapid publication of this work.

Chapter 2: Literature Review

General Soil Properties

1. Introduction

Soil is essential to life on Earth and forms the interface between the atmosphere and lithosphere as well as the lithosphere and the hydrosphere (White 1997). Soil is a natural body, having both mineral and organic components, as well as physical, chemical and biological properties (Kabata-Pendias and Pendias 2001). According to the classic theory by Jenny (1994), soil is formed by an interaction between time, climate, vegetation, topography and parent material, being predominantly weathered rocks (Singer and Munns 1987; Sposito 1989; Miller and Donahue 1990; Kay 2000). Soils therefore have elements representative of the material from which they are formed and include essential plant nutrients such as nitrogen, sulphur, calcium, iron, magnesium, manganese, zinc, and chlorine (Singer and Munns 1987; Miller and Donahue 1990). Although the parent material from which a soil is derived has important implications for soil processes by virtue of its properties, soil texture is equally important.

2. Soil Texture

Soil texture is determined by the distribution of the particles sizes within the soil (White 1997) and is defined by the relative proportions of sand, silt and clay (Singer and Munns 1987; Miller and Donahue 1990; White 1997). Minerals with different compositions will have different properties (Singer and Munns 1987) and soil texture is one of the most stable of these properties (White 1997). The distribution of sand, silt and clay fractions within the soil profile in influenced by a number of factors, including topography. Clays in the surface soil layers are carried downward by water and are deposited in soil layers at depths ranging from 15 to 60 cm (Miller and Donahue 1990).

3. Charge

Soils have an inherent charge, allowing many interactions to occur within the soil. Negative electrostatic charges in soil are derived in three ways (Singer and Munns 1987):

1. edge charge where crystals end;
2. internal charge due to isomorphous substitution, and
3. variable charge due to protonation or deprotonation.

This charge can be either permanent or pH dependant. Negative charge as a result of isomorphous substitution within the lattices of soil minerals is permanent charge (Rhoades 1982; Singer and Munns 1987; Hendershot *et al.* 1993; Alloway and Ayers 1997) and occurs when one ion is substituted by another ion with a lower valency (Miller and Donahue 1990; Alloway and Ayers 1997). Isomorphous substitution replaces one atom with another of similar size within the crystal lattice, but the size of the crystal structure of the mineral does not change. The substituted cations are held loosely on the surface and many of these cations are important soil nutrients involved in cation exchange (Singer and Munns 1987). On the other hand, negative charge derived from hydrolysis reactions on broken mineral edges, external surfaces of oxides and hydroxides and organic colloids (Alloway and Ayers 1997) are all pH-dependant (Rhoades 1982; Singer and Munns 1987; Miller and Donahue 1990; Hendershot *et al.* 1993).

4. Soil Nutrients and Nutrient Cycles

Nutrient cycles are important for the addition of nutrients to the soil. As nutrient ions are removed from the soil solution by adsorption, they are replenished from several sources including decomposition and cation exchange (Miller and Donahue 1990). Decomposition of organic matter by bacteria, fungi and actinomycetes makes these nutrients available for adsorption by plants (Miller and Donahue 1990). Elements needed by plants that are obtained from the soil include nitrogen (N), phosphorus (P), sulphur (S), potassium (K), calcium (Ca), magnesium (Mg), copper (Cu), iron (Fe), manganese

(Mn), zinc (Zn) and chlorine (Cl). The most important soil nutrients and processes are outlined below.

4.1 Soil Organic Matter

Soil organic matter (SOM) is one of the most important components of soils and has an influence over many soil processes. Soil organic matter is an important component of the pH buffering capacity of soils (Bloom 2000). The main constituents of SOM are carbon, oxygen, hydrogen and nitrogen (Sparks 1995).

4.2 Aluminium

Aluminium (Al) comprises approximately 8 % of the Earth's crust, making it the third most abundant element in the Earth's crust after oxygen and silicon (Singer and Munns 1987; Slattery *et al.* 1999). Chemically active soil aluminium can have many different forms which are controlled primarily by the pH and the mineralogical composition of the system (Barnhisel and Bertsch 1982). The dominant species of aluminium is Al^{3+} for clay minerals at low pH. As the pH increases, Al^{3+} is hydrolysed and is removed from cation exchange sites (Hochman *et al.* 1992). Aluminium becomes increasingly soluble below a soil pH 5 (du Toit 1993; Paul *et al.* 2003) and exchangeable aluminium (Al^{3+}) is positively correlated to soil pH (Hochman *et al.* 1992; Paul *et al.* 2003).

4.3 Ammonium

Under moderate to low pH conditions (pH < 8), ammonia (NH_3) exists as ammonium (NH_4^+) which has a strong affinity for negatively charged clay and organic matter particles (Groffman 2000). Ammonium may compete with base cations for cation exchange capacity sites. Enhanced NH_4^+ deposition has been shown to cause substantial mobilisation of base cations, leading to more direct and rapid leaching of base cations from upper horizons with subsequent accumulation in lower horizons (White and Cresser

1998). This results in a redistribution of base cations within the soil profile, effectively decreasing the exchangeable cation status of the soil (White and Cresser 1998).

4.4 Calcium and Magnesium

Calcium (Ca) and magnesium (Mg) are both essential plant nutrients (Aitken and Scott 1999; Bruce 1999). Calcium is the fifth most abundant element and the third most abundant metal after iron and aluminium in the Earth's crust (Bruce 1999). Both calcium and magnesium occur in soils mainly in mineral forms, and they help the soil to form aggregates (Sparks 2000). Exchangeable calcium (Ca^{2+}) concentrations are highly variable in soils, and high amounts are found in neutral and alkaline soils where values reach 30-40 $cmol_c\ kg^{-1}$ when carbonate is present (Bruce 1999). However, acid soils have lower levels of exchangeable Ca^{2+} and values of less than 5 $cmol_c\ kg^{-1}$ are common (Bruce 1999).

5. Transport Processes

Transport processes are important to soil systems and these vary in scale and speed (Singer and Munns 1987). Nutrients are primarily transported in the soil in solution. On a global scale, the transport of solutes is critical in terms of environmental pollution as well as general soil quality and fertility (Warrick 2000). The concentration of a particular ion in the soil solution and the ability of solid components in soils to re-supply depleted ions are important properties of soils (Singer and Munns 1987). The concentration of ions in the soil solution is determined by the interacting processes of oxidation, reduction, adsorption, precipitation and desorption (Alloway and Ayers 1997).

6. Acidifying Reactions

Acidifying processes are important for determining the level of acidification of the soil prior to acid deposition. Acidifying reactions include redox reactions and leaching. The process of removing base cations through leaching is known as podzolisation and results

in the formation of acidic soils (du Toit 1993). These usually form in humid areas under conditions of high rainfall and good drainage which causes intense weathering and leaching of basic cations from the upper horizons to the lower horizons, where they accumulate (Miller and Donahue 1990). The base cations most commonly removed are sodium (Na^{+}), potassium (K^{+}), calcium (Ca^{2+}) and magnesium (Mg^{2+}) (Miller and Donahue 1990; White 1997).

Soil Chemical Properties

1. Soil pH

Soil pH is probably the single most important chemical characteristic of the soil (Bloom 2000) and is used as the benchmark for the interpretation of soil chemical processes (Slattery *et al.* 1999). Soil pH exerts a major influence on many other soil properties and affects the mobility of trace metals within the soil. With increasing pH, the solubility of most trace cations will decrease (Kabata-Pendias and Pendias 2001).

2. Cation Exchange

Once cations have been adsorbed, they resist being removed via leaching from the soil matrix but can be replaced, or exchanged, by other cations in solution (Singer and Munns 1987; Miller and Donahue 1990). Exchangeable cations are the main reserve of calcium and magnesium in most soils and of potassium in many soils (Singer and Munns 1987). According to charge balance, the uptake of ions from the soil solution must be electrically balanced (Singer and Munns 1987). These charges attract counter (exchangeable) ions and form the exchange complex (Hendershot *et al.* 1993). The sources of cation exchange in soils are clay minerals, organic matter and amorphous minerals (Reuss and Johnson 1986; Singer and Munns 1987; Sparks 1995). The dominant exchangeable cations are classed as either basic (K^{+}, Ca^{2+} and Mg^{2+}) or acidic (aluminium (Al^{3+}) and hydrogen (H^{+}) (Anderson and Ingram 1993).

2.1 Cation Exchange Capacity

The capacity of the soil to retain cations is known as the cation exchange capacity (CEC) of the soil (Singer and Munns 1987; White 1997). The CEC is a measure of the negative charge on soils, expressed as the quantity of cations that can be adsorbed by the soil (Rhoades 1982; Singer and Munns 1987; Hendershot *et al.* 1993). The CEC is usually measured in centimoles of charge (positive or negative) per kilogram of dry soil ($cmol_c\ kg^{-1}$) (Miller and Donahue 1990; White 1997).

2.2 Effective Cation Exchange Capacity

The effective cation exchange capacity (ECEC) is a measure of the cation exchange capacity of the soil near its natural pH, however, ECEC can only be used for soils that are not base saturated, in other words, where soil pH which is less than 7 (Anderson and Ingram 1993). The ECEC is calculated as the exchangeable bases subtracted from the exchangeable cations and this value is added to the exchangeable acidity (Anderson and Ingram 1993). The ECEC of many soils has been shown to be pH related (Hochman *et al.* 1992) and generally decreases with a decrease in pH (Hochman *et al.* 1992; du Toit 1993). However, du Toit (1993) found that this effect is largely neutralized by an increase in organic matter, and therefore an accumulation of soil organic matter should increase the ECEC (du Toit 1993). In forest soils, exchangeable Al^{3+} generally accounts for more than 75% of ECEC (Richter *et al.* 1992).

3. Acid Neutralising Capacity

The acid neutralizing capacity (ANC) is a measure of the ability of the soil to neutralize inputs of strong acids and is largely the result of terrestrial processes such as mineral weathering, cation exchange and the immobilization of sulphate and nitrogen (Driscoll *et al.* 2001). It is a measure of the buffering capacity of the soil (du Toit 1993) and thus the ability of the soil to resist a change in pH (Miller and Donahue 1990). It follows that there is a strong positive correlation between ANC and soil pH (Costigan *et al.* 1981; Van

Breemen *et al.* 1983; Sposito 1989; Miller and Donahue 1990). An increase in ANC as a result of an increase in pH results in an increased capacity of solution components to bind and therefore neutralize protons (Sposito 1989).

The ANC of most soils is associated with silicate minerals (Van Breemen *et al.* 1983) and the weathering of silicon and carbonate minerals result in a decrease in ANC. Inputs of strong acids to the soil can decrease the soil ANC by displacing base cations, while weak acids can only change the ANC indirectly through the leaching of base cations in solution (du Toit 1993).

Atmospheric deposition of sulphur dioxide (SO_2) generally oxidises to sulphuric acid, H_2SO_4, representing an irreversible input of H^+ that will directly reduce the ANC of the soil (Van Breemen *et al.* 1983). Based on the parent rock from which soil is derived, as well as the degree of weathering it has undergone, a soil may be inherently acidic or basic in its reaction (du Toit 1993). If the weathering rate of the parent material does not keep up with the rate of acid deposition into a system, the ANC of the soil will be reduced, leading to soil acidification through the leaching of base cations from the soil and their subsequent replacement with protons (H^+) and acidic cations (Van Breemen *et al.* 1983; Mayer 1998).

Major Biogeochemical Cycles

1. The Sulphur Cycle

The sulphur cycle is a complex interaction of inputs, transformations, internal reservoirs and outputs (Reuss and Johnson 1986). The total sulphur pool is divided into two forms, namely organic and inorganic forms, with organic sulphur generally being the major contributor to total sulphur (Roberts and Bettany 1985). In well-aerated soils from humid and semi-humid regions, approximately 90 % to 95 % of the total soil sulphur is organic; however, it is the total sulphur pool as well as the inorganic fraction that is of interest in this research, as shown in Figure 2. The inorganic fraction is predominantly in the form

of sulphate (SO_4^{2-}). (Tabatabai 1982; Lewis 1999; Sparks 2000). Sulphate is the oxidised form of sulphur and is both soluble and relatively mobile and as such is easily leached down the soil profile by rainfall (Miller and Donahue 1990). Sulphate levels have also been shown to be well correlated with percentage carbon in the soil (Singh and Johnson 1986).

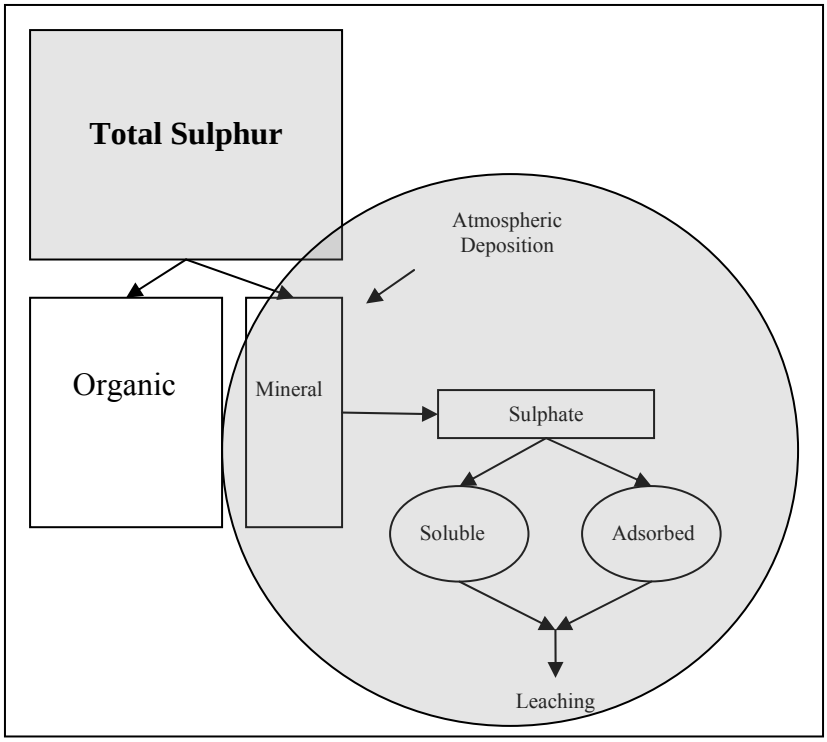


Figure 2: The sulphur cycle with the portions of interest shaded.

Topography plays a major role on the concentration of elements in the soil and total sulphur is known to increase downslope from upper to lower slope positions (Roberts and Bettany 1985). Both total and soluble sulphate generally increases with soil depth, whereas Roberts and Bettany (1985) found organic sulphur decreased significantly with depth as did the proportion of organic sulphate. The topsoils of most well drained soils contain small amounts of water-soluble sulphate due to leaching of sulphate down the soil profile. In contrast, larger quantities of water soluble sulphate are found in soils of arid regions (Tabatabai 1982) since these are not subjected to leaching. The concentration of water-soluble sulphate in the soil solution is affected by mineralisation, leaching and plant uptake of sulphate as well as by acid deposition (Tabatabai 1982). Since plants take

up sulphur mainly in the form of sulphate ions, extractable sulphate can give an indication of atmospherically deposited sulphur (Palomino *et al.* 2005).

Subsoils generally contain more sorbed sulphate and have greater sulphate retention capacities than topsoils (Fey and Guy 1993). The reason for this is thought to be due to the generally higher clay content and lower pH of subsoils. This highlights the importance of sampling soils at different depths (Fey and Guy 1993) and for this reason, the influence of topography needs to be considered when choosing sampling sites. For this study, sampling sites were chosen on the upper and mid-slopes, with no sampling on the lower slopes, and these sites were sampled at two depths, namely topsoils sampled from 0 – 10 cm and subsoils sampled from 20 – 40 cm.

1.1 Adsorption of sulphate

The sulphate anion, SO_4^{2-}, may be retained in the soil by sorption to amorphous oxides and hydroxides of aluminium (Al) and iron (Fe) (Abrahamsen 1984). Sulphate can be immobilised in the soil if it is incorporated into organic matter, however, adsorption may be a more important process than biological immobilisation (Reuss and Johnson 1986). An understanding of the capacity of a soil to adsorb and retain sulphate is important for determining the effect of acid deposition on a given ecosystem (Singh and Johnson 1986; Comfort *et al.* 1992). Sulphate sorption reduces the ability of atmospheric inputs of sulphur to cause the leaching of ions from the soil solution through a reduction in the concentration of sulphate in the soil solution (Singh and Johnson 1986; Inskeep 1989). As defined by Prenzel and Meiwes (1994), sulphate sorption is the process of reversibly storing both sulphur and acidity in the soil matrix, thereby delaying and adjusting the acidification of the soil solution. Kinetically, the adsorption of sulphate is very rapid (Zhang *et al.* 1987; Curtin and Syers 1990a) with nearly complete adsorption in minutes (Sparks 2000).

2. The Nitrogen Cycle

Nitrogen is an essential nutrient vital for plant growth and is limiting in most ecosystems across the globe, thereby controlling ecosystem productivity (Miller and Donahue 1990; Van Miegroet *et al.* 1992a; Vitousek 1994; Bobbink and Roelofs 1995; Vitousek *et al.* 1997; Strong and Mason 1999; Galloway *et al.* 2004; Güsewell 2004). Nitrogen in the soil includes both organic and inorganic forms in the soil (Blackmer 2000). The accumulation of nitrogen is primarily regulated by biological reactions, with the uptake of nitrogen by plants, decomposition of litter in soil and the immobilization of nitrogen in SOM forming a tight nitrogen cycle (Nissinen and Hari 1998). As with sulphur, the mineral component of nitrogen is of interest.

2.1 Mineral Component of Nitrogen in the Soil

The predominant mineral forms are ammonium and nitrate (NO_3^-) (Strong and Mason 1999; Baisre 2006) and either form can be used by plants. Both are common components of acid deposition (Reuss and Johnson 1986; Driscoll *et al.* 2001) and for this reason, ammonium and nitrate are considered the most important forms of nitrogen (Rayment and Higginson 1992; Shaffer and Ma 2001). Ammonium and nitrate usually make up less than 1% of the total soil nitrogen pool (Falkengren-Grerup *et al.* 1998).

Nitrate is highly soluble and since it is weakly held by soils, it is easily leached (Abrahamsen 1984; Reuss and Johnson 1986; Sparks 1995; Groffman 2000). It is readily transported in surface runoff and precipitation and as a result is the primary cause for eutrophication in aquatic ecosystems (Groffman 2000). Nitrate is the preferred form of nitrogen by plants and it is usually the most abundant form that can be taken up in well-aerated soils (Blackmer 2000). It is naturally produced by mineralization (the conversion of organic N to NH_4^+) and nitrification (the conversion of NH_4^+ to NO_3^-) processes within the soil (Bielek 1998).

The concentration of nitrogen within the soil is influenced by both topography and soil texture. Burke *et al.* (1995) and Schimel *et al.* (1985) found higher nitrogen pools at the bottom of slopes compared to the middle or top. Callesen *et al.* (2003) showed that soil carbon storage depends on soil texture and may also be true for nitrogen storage in the soil profile since carbon and nitrogen are closely linked. The concentration of nitrogen in the soil is also influenced by soil depth (Crowe *et al.* 2004) and generally increases with decreasing depth.

3. Human Alteration of the Biochemical Cycles

3.1 Source

Many ecosystems are exposed to extensive human impact which results in various types and amounts of environmental change (Diekmann and Falkengren-Grerup 2002), most notably the alteration of the biogeochemical cycles of the Earth (Aber *et al.* 1989; Vitousek *et al.* 1997). The most pronounced impact on the atmosphere and the biosphere has come from the combustion of fossil fuels (Aber *et al.* 1989; Vitousek 1994; Goulding *et al.* 1998). Fossil fuels became the primary energy supplier at the start of the 20th century (Bobbink and Roelofs 1995; Galloway *et al.* 2004) concurrent with the start of the industrial revolution. The major atmospheric pollutants associated with coal-combustion are oxides of sulphur and nitrogen oxides (Cowling and Linthurst 1981; Annegarn *et al.* 1996) which are transferred from long-term geological reserves to the atmosphere (Galloway *et al.* 2004). These two pollutants are equally important in their impact on ecosystems (Vitousek 1994; Bobbink and Roelofs 1995; Vitousek *et al.* 1997; Bobbink *et al.* 1998; Galloway 1998; Goulding *et al.* 1998; Galloway *et al.* 2004; Baisre 2006).

The pollution pathway concept put forward by Holdgate (1979) states that all pollution events have a pollutant, a source, transport medium and a target. However, the modelling of pollutants is more complex than just these four factors and a good pollution model includes the factors shown in Figure 3.

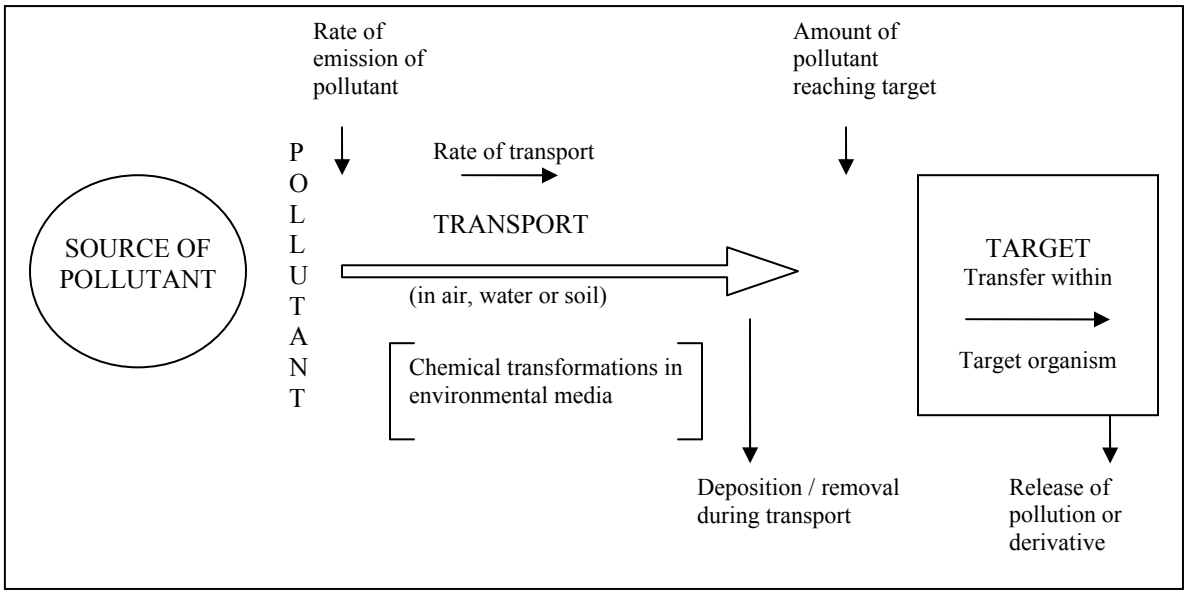


Figure 3: A simplified model of environmental pollution (Holdgate 1979).

Although human alteration of biochemical cycles is not new (Delwiche 1970), the magnitude of the alternation is new (Galloway 1998), particularly within the nitrogen cycle (Dalton and Brand-Hardy 2003). This alteration has many negative consequences on all ecosystems and at all ecosystem levels (Fenn *et al.* 1998), both spatially and temporally. Spatially, impacts may range from local to global, with temporal changes evident in both the short- and long-term (Vitousek 1994).

3.2 Transport

The transport of pollutants depends on many factors, including the height they reach in the atmosphere, their particle size and climatic factors (Alloway and Ayers 1997). The rate at which pollution will accumulate in the atmosphere depends on the state of the atmosphere, particularly in the boundary layer which is subject to turbulence (Taylor 1922).

Most air pollutants are emitted into the boundary layer and airflow in the boundary layer is subject to turbulence due to the roughness of the surface of the Earth (Taylor 1922). Air pollutants tend to be transported by the wind and mixed with surrounding air until

their concentration in the boundary layer is fairly homogeneous, however, pollution spikes may still be noticeable (Alloway and Ayers 1997). In South Africa, wind and turbulence are the main dispersal agents for pollutants (Mphepya 2002).

The use of tall stacks at most power plants allows extensive mixing of emissions in the atmosphere, resulting in both chemical and physical interactions and transformations of atmospheric particles, aerosols and gases (Cowling and Linthurst 1981). In South Africa, a stack height of 300 m usually emits emissions above inversion layers and above the stable boundary layer to enable wide dispersion of these pollutants (Van Tienhoven and Scholes 2003), and areas downwind from these high stacks will generally be less affected by atmospheric pollution (Alloway and Ayers 1997). Plumes emitted from tall stacks during stable conditions, primarily at night, can be transported up to thousands of kilometres downwind of the source before reaching ground-level, often in a well diluted state (Turner *et al.* 1996b). However, strong convection currents during the daytime transport plumes upwards and downward while drifting downwind and pollutants reach ground-level close to the emission source (Turner *et al.* 1996b). These pollutants are generally well diluted due to convective mixing (Turner *et al.* 1996b). Plume dispersion depends primarily on the wind-speed as well as the stability and height of the atmosphere (Webb and Hunter 1998).

Meteorological conditions in the Highveld determine both the extent and the duration of air pollution in the region (Van Tienhoven and Scholes 2003) and semi-permanent continental anti-cyclones dominate 20 % of the time in summer and between 70 % and 90 % of the time in winter (Tyson *et al.* 1988; Held *et al.* 1996b; Tyson and Preston-Whyte 2000; Mphepya 2002). The stable atmospheric conditions associated with anti-cyclones give rise to fine and hot weather conditions and reduce vertical mixing, resulting in reduced transport and relatively high ambient concentrations of pollutants in the atmosphere (Mphepya 2002).

3.3 Transformation

The sulphur dioxide and nitrogen oxides that are emitted from power stations are in the form of reduced or partly oxidised molecules (Pienaar and Helas 1996; Webb and Hunter 1998) and these atmospheric pollutants need to undergo chemical transformations in order to be removed from the atmosphere. These are generally oxidation processes and the main oxidizing agent in the atmosphere is the hydroxyl (OH^-) radical (Jacob 1986). However, photochemical transformation of these pollutants are also important and South Africa has a high frequency of sunny days that promote the photochemical transformation of many of these pollutants (Van Tienhoven and Scholes 2003).

Emissions of sulphur dioxide (SO_2) and nitrogen oxides (NO_x) interact with water vapour in the atmosphere and once deposited on the soil surface are ultimately oxidized to SO_4^2 and NO_3^- respectively (Van Breemen *et al.* 1983; Fey and Guy 1993; Galloway 1995; Mphepya 2002). These processes release equal amounts of H^+ into the environment (Cowling and Linthurst 1981; Van Breemen *et al.* 1983; Galloway 1995).

Sulphur

In soils subject to acid deposition, sulphate is usually the dominant anion in soil horizons (Mayer 1998). Sulphur is deposited on the surface on the Earth in the form of sulphur dioxide (SO_2). Given that all SO_2 deposited is eventually oxidized to sulphate, effectively all sulphur input becomes sulphate in the soil (Reuss and Johnson 1986). This is important since the conversion is irreversible (Van Breemen *et al.* 1983; Mphepya 2002). It is thought that most sulphur reaches the soil solution within the same annual cycle as it was deposited (Reuss and Johnson 1986), with the distance from the pollution source determining the amount of sulphur deposited (Sparks 2000).

Nitrogen

Both ammonium (NH_4^+) and nitric oxide (NO) are important from an environmental perspective (Olivier *et al.* 1998; Groffman 2000; Shaffer and Ma 2001). Nitric oxide is primarily formed in the atmosphere and can undergo many transformations before it is deposited. Once emitted, NO is oxidised in the presence of O_2 and is converted to NO_2 within a few seconds (Lowman 2003) and then to nitric acid (HNO_3) and nitrate particles (Lovett 1992; Webb and Hunter 1998). Nitrogen oxides (NO + NO_2, together denoted as NO_x) are waste products of fossil fuel combustion (Galloway 1998) and are found close to anthropogenic sources (Bytnerowicz *et al.* 1987). NO_x is important because of its potential to produce acid deposition and because it acts as a precursor of both acid rain (Groffman 2000; Galloway *et al.* 2004), and the formation of ground level and tropospheric ozone, known as photochemical smog (Furiness *et al.* 1998; Olivier *et al.* 1998; Groffman 2000; Dalton and Brand-Hardy 2003; Galloway *et al.* 2004).

3.4 Deposition

Acid deposition is defined as the transfer of strong acids and acid-forming substances from the atmosphere to the surface of the Earth (Driscoll *et al.* 2001) and can occur via wet, dry or mist deposition. Acid deposition is a critical environmental stress (Driscoll *et al.* 2001) which undermines the integrity of the ecosystems on which it is deposited (Abrahamsen 1984; Brodin and Kuylenstierna 1992; Fenn *et al.* 2003). It is a dominant feature of anthropogenic changes in the chemical climate of the Earth (Cowling and Linthurst 1981). As with all atmospheric related problems, acid deposition is an issue that ignores political boundaries since it can stem from transboundary air pollution and has the potential to affect large geographical areas (Driscoll *et al.* 2001). Ground-level concentrations of pollutants are of interest from an environmental point of view (Bennett 1995). Plumes from elevated sources mix to ground level only when there is sufficient turbulence in the lower atmosphere occurring at a height high enough to include the emitted plume (Webb and Hunter 1998; Mphepya 2002). Soils acts as a sink for

pollutants through adsorption processes which bind inorganic and organic pollutants to the surface of soil colloids (Alloway and Ayers 1997).

4. Distance from Source

The distance between emissions source and deposition point can vary greatly (Furiness *et al.* 1998) and according to conventional distance model predictions, the highest concentration of pollutants due to power generation are found from tens to hundreds of kilometres from tall stacks, these being over 300m in height (Annegarn *et al.* 1996). Many authors have however found that generally, airborne concentrations of pollutants decrease with distance from the main emission sources (Tørseth and Semb 1998) and in the western United States, pollution gradients decline steeply with distance from the pollution source (Fenn *et al.* 2003). On the Mpumalanga Highveld, Lowman (2003) found that high, medium and low ambient concentrations of nitrogen dioxide reflected distance from the pollution source. Skiba *et al.* (1998) linked increased nitrogen deposition to increased soil available NH_4^+ and NO_3^- concentrations in a linear relationship away from the source. It is reasonable to assume that the highest deposition of pollutants will occur in the areas of highest air-borne concentrations. The distance from the pollution source of greatest environmental concern will therefore be the distance that receives the most deposition and this needs to be identified.

Granat and Rodhe (1973) investigated the long-term average wet acid deposition due to an oil-fired power plant in Sweden. Results showed that increased acid input due to power generation would not be greater than 10-15% within 15 km of the plant (Granat and Rodhe 1973). In a study investigating rainwater pH, Li and Landsberg (1975) found the highest pH values occurred about 2 km away from the power station. However, subsequent studies have indicated that the greatest environmental impact from power generation appears to be within 10 km to 15 km from the source (Freedman and Hutchinson 1980; Annegarn *et al.* 1996; Ek *et al.* 2001).

The impacts of atmospheric deposition resulting from a large nickel-copper smelter in Canada were investigated by Freedman and Hutchinson (1980), and although no clear gradient of rainfall acidity with distance from the source was found, wet deposition was the most acidic within 10 km of the smelter (Freedman and Hutchinson 1980). Annegarn *et al.* (1996) investigated the concentration of air pollutants on the Mpumalanga Highveld and found that peak concentrations can occur within 1 to 10 km of a tall stack, despite conventional distance model predictions. More recently, in a study investigating the sulphur dioxide emissions from a copper mine by Ek *et al.* (2001), the most heavily polluted area and the associated acidification was found to be within 12 km from the mine. These studies highlight the need to incorporate a distance gradient into any investigation of the impacts of pollution emitted from tall stacks.

5. Impacts of Acid Deposition

Scientists in the developed countries of Europe and North America have paid much attention to the problems caused by the atmospheric deposition of excess nutrients and acidifying substances (Hogg *et al.* 1995; Bobbink *et al.* 1998; Fenn *et al.* 1998; Diekmann and Falkengren-Grerup 2002; Fenn *et al.* 2003). Acid deposition has impacts on the atmosphere, ecosystems and nutrient cycles and these impacts are profound (Aber 1992; Brodin and Kuylenstierna 1992; Bobbink and Roelofs 1995; Bobbink *et al.* 1998; Fenn *et al.* 1998; Goulding *et al.* 1998; Nissinen and Hari 1998; Tietema *et al.* 1998; Driscoll *et al.* 2001; Dalton and Brand-Hardy 2003; Galloway *et al.* 2004). Impacts may be direct or indirect (Cowling and Linthurst 1981; Driscoll *et al.* 2001) and may be both positive and negative, depending on the ecosystem concerned. However, the time scale over which these impacts manifest must be considered (Galloway 1995). Increased deposition of nitrogen and to a lesser degree, that of sulphur, may have a fertilization effect and increase growth in forests in the short-term (Abrahamsen 1984), however, this is counteracted in the long-term by the leaching of cations from the soil (Cowling and Linthurst 1981). The requirements for nitrogen are usually higher than those for sulphur and therefore the effects of nitrogen deposition are usually more significant (Abrahamsen 1984; Galloway 1998; Dalton and Brand-Hardy 2003).

The impact of acid deposition on ecosystems depends on both the magnitude of the deposition and the sensitivity of the ecosystem (Kuylenstierna *et al.* 1995), as well as abiotic factors such as soil nutrient status and the buffering capacity of the soil (Bobbink *et al.* 1998).

5.1 Impacts on Soils

In soil, acid deposition may have three effects (Abrahamsen 1984):

- a fertilizer effect due to the deposition of nitrogen (and potentially also of sulphur) since the nitrogen deposited through acid deposition is generally in the same form as that of fertilizer;
- an acidification effect caused by the increased leaching of SO_4^{2-} and NO_3^- as well as base cations such as Mg^{2+}, Ca^{2+}; and
- an aluminium toxicity effect when soil acidity is increased

Leaching of base cations

The deposition of acids from the atmosphere is linked to soil acidification through leaching of base cations. Exchangeable cations are leached from the upper horizons to the lower horizons (Richter *et al.* 1992; White and Cresser 1998) thereby redistributing them within the soil profile (Singer and Munns 1987). Nutrient cations, primarily calcium and magnesium, tend to be leached downwards first, followed by an increase in the concentration and mobility of hydrogen ions and inorganic aluminium (Aber 1992; Fenn *et al.* 1998). Once base cations have been leached from the soil, the soil pH drops to a point where aluminium can be mobilised (Fey and Guy 1993), which is toxic to many plants and organisms (Cowling and Linthurst 1981).

Aluminium Mobilisation

Aluminium mobilisation and soil pH are closely linked (Reuss and Johnson 1986; Van Miegroet *et al.* 1992a; Van Miegroet *et al.* 1992b; Fenn *et al.* 1998). High concentrations of sulphates and nitrates in soil solution as a result of atmospheric deposition reduce the pH and increase the mobilisation of aluminium in the soil, thereby increasing aluminium ion (Al^{3+}) concentrations (Fenn *et al.* 1998). This increased mobility of aluminium is detrimental to ecosystem functioning and affects these systems both directly and indirectly. Directly, aluminium is toxic to many plants and organisms (Cowling and Linthurst 1981; Scholes *et al.* 1996) and increased aluminium mobilisation may indirectly adversely affect root activity and uptake (Van Miegroet *et al.* 1992b).

6. Retention of Acid Deposition

The capacity of the soil to retain sulphate and nitrogen is important because it determines the impact of atmospheric deposition on the soil (Curtin and Syers 1990b).

6.1 Sulphate Retention

Sulphate retention is related to aluminium and iron sesquioxide content in soils, solution pH, ionic strength and soil organic matter (Courchesne *et al.* 1995), as well as calcium content in acidic soils (Sparks 2000). There is a strong correlation between the sulphate retention index and the degree of acid saturation of the exchangeable cations (Fey and Guy 1993).

6.2 Nitrogen Retention

There is a fundamental lack of understanding of how and why the processes that retain nitrogen vary among systems and how they have changed and will change in time (Galloway *et al.* 2004). Nitrogen deposition to many European forests exceeds the capacity of these systems to retain nitrogen (Gundersen *et al.* 1998; Sparks 2000).

Chronic nitrogen deposition causes a syndrome of ecosystem responses described by the nitrogen saturation hypothesis (Aber *et al.* 1989). The nitrogen saturation hypothesis was put forward by Aber (1989) to describe ecosystem responses to chronic nitrogen inputs, such as those from deposition and can be defined as the availability of ammonium and nitrate in excess of total combined plant and microbial nutritional demand (Aber *et al.* 1989). Once a system reaches nitrogen saturation, increasing nitrogen inputs will result in increases in nitrate leaching (Van Miegroet *et al.* 1992a). Although sulphur emissions have decreased in many parts of the world, particularly in developed countries, Fenn *et al.* (1998) point out that nitrogen emissions have continued to increase, suggesting that nitrogen saturation of ecosystems across the globe may become more common.

7. Deposition Amounts

7.1 Sulphur

Industry accounts for 35 % of global atmospheric sulphur emissions (Sparks 2000). Globally, the atmospheric deposition of sulphur in polluted areas is generally more then than 10 kg S ha $^{-1}$ yr $^{-1}$, but can be as high as 80 kg S ha $^{-1}$ yr $^{-1}$ in heavily polluted regions (Reuss and Johnson 1986). Although the impacts of acid deposition have been well researched in Europe and North America, South African data are limited. The primary mode by which sulphur dioxide emitted from tall stacks reaches the surface of the Earth on the Mpumalanga Highveld is dry deposition (Held *et al.* 1996a).

Dry deposition of sulphate over a forested is estimated as being 1.7 kg S ha $^{-1}$ yr $^{-1}$ and that of a grassland being 0.4 kg S ha $^{-1}$ yr $^{-1}$. However, closer to an industrialized area dry deposition estimates range between 16.3 kg S ha $^{-1}$ yr $^{-1}$ and 27.0 kg S ha $^{-1}$ yr $^{-1}$ (Piketh and Annegarn 1994, cited in Van Tienhoven *et al.* 1995). These estimates are higher than those obtained by Mphepya (2002). Mphepya (2002) undertook a study to investigate precipitation chemistry in South Africa. Sites on the Highveld were chosen that represented industrial (Amersfoort and Elandsfontein) and rural (Louis Trichardt) environments. Dry deposition of sulphur ranged between 0.52 kg S ha $^{-1}$ yr $^{-1}$ and

9.36 kg S ha $^{-1}$ yr $^{-1}$ at all the sites. Skoroszewski (1995) studied sulphur deposition in the Gauteng province in South Africa and found dry deposition accounted for between 39 % and 90 % of total deposition.

7.2 Nitrogen

Globally, rates of atmospheric deposition of nitrogen range from 5 kg N ha $^{-1}$ yr $^{-1}$ to more than 20 kg N ha $^{-1}$ yr $^{-1}$ (Groffman 2000). There have been few deposition studies in South Africa relative to those in Europe and North America, and two studies (Mphepya 2002; Lowman 2003) are of particular interest. Mphepya's (2002) study investigated nitrogen deposition, dry deposition of nitrogen ranged between 0.1 – 1.00 kg N ha $^{-1}$ yr $^{-1}$ for these sites (Mphepya 2002). Wet deposition of nitrogen, predominantly in the form of nitrate averaged 0.38 mg l $^{-1}$, this being smaller than the deposition of sulphur at the same site. The data from Mphepya (2002) indicate the strong influence of industrial activities on precipitation chemistry, with sulphur, being more important as a pollutant than nitrogen at most sites, particularly sites exposed to industrial pollution.

A study by Lowman (2003) found that total deposition on the Mpumalanga Highveld shows a strong seasonal variance, with deposition in forests approximately three times that of grasslands. Total wet deposition amounts of nitrogen for the Mpumalanga Highveld were found to range between 6.5 kg N ha $^{-1}$ yr $^{-1}$ and 10.6 kg N ha $^{-1}$ yr $^{-1}$ (Lowman 2003), with an average of 7.84 kg N ha $^{-1}$ yr $^{-1}$ (Lowman 2003). Ammonium and nitrate are the most important ions and nitrate is slightly dominant over ammonium, comprising 53 % and 47 % of the total respectively (Lowman 2003). Of the total nitrogen deposition in grasslands, wet deposition accounted for 7.8 kg N ha $^{-1}$ yr $^{-1}$ (31%) and dry deposition for 7 kg N ha $^{-1}$ yr $^{-1}$ (28 %) (Lowman 2003).

8. Emissions within a South African Context

In South Africa, coal accounts for 77% of the primary energy source for the country and is predominantly used for electricity production. Globally, coal accounts for

approximately 36% of the world's total electricity production, while in South Africa; coal-fired power stations generate almost 90% of the electricity. Eskom is the primary electricity provider for South Africa, providing 95% of South Africa's electricity needs: electricity that is among the cheapest in the world.

Eskom burns approximately 100 000 kilo tons of coal per annum, with an average ash content of 30 % (Eskom 2006). Although this coal has a low sulphur content, this high ash content in comparison to coals from around the world (Wells *et al.* 1996) results in high particulate emissions (Van Tienhoven and Scholes 2003). Table 1 provides a summary for the average Eskom emissions for 1996 to 2006. The factors influencing gaseous emissions include the amount of coal burned, sulphur and nitrogen content of the coal, the burner set-up, maintenance and operation of the milling plant and the thermal efficiency of the plant (Eskom 2006).

Table 1: Average Eskom emissions for all power stations, 1996 – 2006 (Eskom 2006).

Coal Burnt kt	Particulate emissions kt	Ash Content %	Nitrous Oxide (N_2O) kt	Sulphur Dioxide (SO_2) kt	Nitrogen Oxide (NO_x) as NO_2 kt
100000.0	68.0	29.0	2400.0	1600.0	740.0

The average surface concentration of NO_2 emissions for all emission sources at the Arnot power station is approximately 5 μg m^{-3}, while the average surface concentration of SO_2 is 20 μg m^{-3}. Particulate emissions at the Arnot power station have been reduced from more than 2.0 kg $(MWh)^{-1}$ in the 1990's to 0.19 kg $(MWh)^{-1}$ for the reporting period 2005 to 2006. This is attributed to the fitting of bag filters at the station (Eskom 2006).

Chapter 3: Investigating the long-term effects of air pollution on soil properties in the vicinity of the Arnot power station

Abstract

The effects of acid deposition on soil properties were investigated in the vicinity of the Arnot power station, Mpumalanga, South Africa. This investigation formed part of a long-term monitoring programme for which the data for the baseline study were collected in 1996, resulting in a ten year period after which changes in soil properties were investigated. A spatial gradient was incorporated into the study in order to better understand the deposition of pollutants with increasing distance from the power station. The study indicates that long-term acidic deposition has led to detectable changes in soil chemical properties. Three chemical properties, namely the concentrations of calcium and magnesium in both the topsoils and the subsoils, as well as the effective cation exchange capacity in the subsoils showed a significant increase since 1996. However, five soil chemical properties, namely soil pH (K_2SO_4), the concentration of hydrogen and aluminium and total sulphur in both the topsoils and the subsoils, as well as extractable sulphate in the topsoils and soluble sulphate in the subsoils, all show that the soils have become more acidic over the ten years. The acidic components in the soil override the basic components, as shown by the ratio of basic cations to acidic cations in the soils. The spatial gradient generally indicates that at approximately 8 km from the power station, there is a reduction in the acidic soil properties. However, this needs further investigation. Two significant relationships with distance were found, namely a significant negative relationship with soluble sulphate and a significant positive relationship with acid neutralising capacity. This research will form part of a database for other long-term monitoring programmes and will allow data to be compared to other data from this area of research. It will also provide information to important industry leaders.

Keywords acid deposition · air pollution · coal-fired power station · long-term monitoring · soil acidity · spatial gradient · sulphates

1. Introduction

Many ecosystems are exposed to extensive human impact that results in various types and amounts of environmental change (Diekmann and Falkengren-Grerup 2002), most notably the alteration of the biogeochemical cycles of the Earth (Aber *et al.* 1989; Vitousek *et al.* 1997). This alteration has many negative consequences on all ecosystems and at all ecosystem levels (Fenn *et al.* 1998), both spatially and temporally. The most pronounced impact on the atmosphere and the biosphere has come from the combustion of fossil fuels (Aber *et al.* 1989; Vitousek 1994; Goulding *et al.* 1998), resulting in acid deposition and subsequent soil acidification. Acid deposition is a critical environmental stress (Driscoll *et al.* 2001) which undermines the integrity of the ecosystems on which it is deposited (Abrahamsen 1984; Brodin and Kuylenstierna 1992; Bobbink and Roelofs 1995; Fenn *et al.* 2003) and is a dominant feature of anthropogenic changes in the chemical climate of the Earth (Cowling and Linthurst 1981). Acid deposition has impacts on the atmosphere, ecosystems and nutrient cycles and these impacts are profound (Aber 1992; Brodin and Kuylenstierna 1992; Bobbink and Roelofs 1995; Bobbink *et al.* 1998; Fenn *et al.* 1998; Goulding *et al.* 1998; Nissinen and Hari 1998; Tietema *et al.* 1998; Driscoll *et al.* 2001; Dalton and Brand-Hardy 2003; Galloway *et al.* 2004).

Fossil fuels became the primary energy supplier at the start of the 20th century (Bobbink and Roelofs 1995; Galloway *et al.* 2004) concurrent with the start of the industrial revolution. The major atmospheric pollutants associated with coal-combustion are oxides of sulphur and nitrogen (Cowling and Linthurst 1981; Annegarn *et al.* 1996) which are emitted into the atmosphere via a pollution plume. These pollutants are transferred from long-term geological reserves to the atmosphere (Galloway *et al.* 2004) where they undergo transformations and are subsequently deposited on the surface of the Earth in the form of acid deposition. These two pollutants are equally important in their impact on ecosystems (Vitousek 1994; Bobbink and Roelofs 1995; Vitousek *et al.* 1997; Bobbink *et al.* 1998; Galloway 1998; Goulding *et al.* 1998; Galloway *et al.* 2004; Baisre 2006), with the dominant forms being sulphate (SO_4^{2-}), ammonium (NH_4^+) and nitrate (NO_3^-) (Reuss and Johnson 1986; Rayment and Higginson 1992; Driscoll *et al.* 2001; Shaffer and Ma

2001). In South Africa, the primary source of energy is coal, with coal-fired power stations generating almost 90% of the country's electricity. Eskom is the primary electricity provider for South Africa, providing 95% of South Africa's electricity needs: electricity that is among the cheapest in the world (NUS Consulting Group 2005). In order to keep production costs to a minimum, coal-fired power stations are generally concentrated around the coal seams and approximately 84% of South Africa's total coal production originates in the Mpumalanga Province (Mpumalanga DACE 2003). This has resulted in a concentration of coal-fired power stations in the region, with Eskom having eight of their eleven of base-load coal-fired power stations situated on the Mpumalanga Highveld.

Meteorological conditions in the Highveld determine both the extent and the duration of air pollution in the region (Van Tienhoven and Scholes 2003) and semi-permanent continental anti-cyclones dominate 20 % of the time in summer and between 70 % and 90 % of the time in winter (Tyson *et al.* 1988; Held *et al.* 1996; Tyson and Preston-Whyte 2000; Mphepya 2002). The stable atmospheric conditions associated with anti-cyclones reduce vertical mixing, resulting in reduced transport and relatively high ambient concentrations of pollutants in the atmosphere (Mphepya 2002). These stable conditions are also ideal for the formation of surface based temperature inversions (Held *et al.* 1996). Surface inversions are usually formed during the evening and these inversions do not allow the emitted pollution plumes to reach the surface of the Earth, reducing the deposition of pollutants. During the day, however, these inversions breakdown and convective mixing allows deposition of pollutants to the surface of the Earth (Tyson & Preston-Whyte 2000).

Once the emitted pollutants are deposited on the surface of the Earth, they are oxidized to sulphates (SO_4^{2-}) and nitrates (NO_3^-) (Van Breemen *et al.* 1983; Fey and Guy 1993; Galloway 1995; Mphepya 2002). The process of removal of particles from the atmosphere depends on the size of the particle (Fowler *et al.* 1999) and deposition can either occur via wet, dry or mist deposition. The relative importance of these deposition mechanisms is dependant on the local climatic conditions (Turner *et al.* 1996; Eugster *et*

al. 1998; Baisre 2006). As with all atmospheric related problems, acid deposition is an issue that ignores political boundaries since it can stem from transboundary air pollution and therefore has the potential to affect large geographical areas (Driscoll *et al.* 2001).

The distance between the emissions source and the deposition point can vary greatly (Furiness *et al.* 1998) and according to conventional distance model predictions, the highest concentration of pollutants due to power generation are found from tens to hundreds of kilometres from tall stacks, these being over 300m in height (Annegarn *et al.* 1996). However, many authors have found that generally, airborne concentrations of pollutants decrease with distance from the main emission sources (Tørseth and Semb 1998; Fenn *et al.* 2003). On the Mpumalanga Highveld, Annegarn *et al.* (1996) predict that the highest concentrations of pollutants can occur within 1 to 10 km of tall stacks and this has implications for soil chemical properties.

Acid deposition is linked to soil acidification through leaching of exchangeable cations. Exchangeable cations are leached from the upper horizons to the lower horizons (Richter *et al.* 1992; White and Cresser 1998) thereby redistributing them within the soil profile (Singer and Munns 1987). Nutrient cations, primarily base cations calcium (Ca^{2+}) and magnesium (Mg^{2+}), tend to be leached downwards first, followed by an increase in the concentration and mobility of hydrogen ions (H^{+}) and inorganic aluminium (Al^{3+}) (Aber 1992; Fenn *et al.* 1998). Once base cations have been leached from the soil, the soil pH drops to a point where aluminium can be mobilised (Fey and Guy 1993).

Policymakers can play a key role in minimising the environmental change caused by the combustion of fossil fuels through the formation of policy to reduce emissions in order to lessen our burden on the environment (Ek *et al.* 2001). However, although policymakers may call for reduced emissions, understanding and predicting the response of ecosystems to anticipated reductions in emissions is increasingly difficult in light of climate change (Driscoll *et al.* 2001), and scientists are faced with a complex task to present the scenario with the greatest certainty to policymakers.

This research was aimed at gaining a better understanding of the impacts of acid deposition on the structure and functioning of ecosystems, specifically soil properties. Several key questions were explored and soil properties were analysed at two depths and compared with samples taken in 1996. The acid and base statuses of the soils were of primary concern as were changes in distance from the source.

2. Materials and Methods

2.1 Site Description

The Arnot power station is located approximately 35 km south-east of Middleburg in the Mpumalanga Province, South Africa. The Province is naturally divided into three physiographic zones, namely the Escarpment, the Lowveld and the Highveld. The Highveld forms the bulk of south-western Mpumalanga and comprises flat, gently undulating terrain at high altitude. Mean annual rainfall ranges from 500 to 900 mm and the mean annual temperature is 12°C.

The Arnot power station was chosen by Van Tienhoven (1997) as the focal point for the study for several reasons. Of the eleven base load coal-fired power stations owned by Eskom in South Africa, eight of them are situated in the Mpumalanga province. Arnot is the most easterly of these power stations, and is the furthest from the industrial hubs of Gauteng, Witbank and Middelburg and background pollution levels were therefore assumed to be low. The Arnot power station was fully operational by 1975, making it one of the oldest power stations in South Africa, and this relatively long history of air pollution and deposition on the soil surface, coupled with the low background pollution levels, makes the Arnot power station an ideal location to monitor the long-term impacts of air pollution on soil properties.

2.2 Sampling Methodology

Sample points were located at varying distances from the power station in order to incorporate a distance gradient into the study and ranged from 1.3 km to 19.9 km

downwind of the power station (Figure 4). Pretorius *et al.* (1986), cited in Van Tienhoven (1997), found that during the day, the most frequent wind direction is from the north-west (15.2 %), followed by west-north-west (11.9 %). The plume is therefore most likely to strike the ground most frequently in the direction south-east to east-south-east and sampling was conducted in an arc ranging from south-east to east-south-east as the wind blows in this direction with a 37.4 % frequency. As part of a long-term monitoring strategy for the area, samples were taken from the same points as those in the baseline study. Location of the sampling points was determined by Van Tienhoven (1997) and both local meteorological conditions as well as land use were taken into consideration during site selection and sampling sites were restricted to natural grasslands.

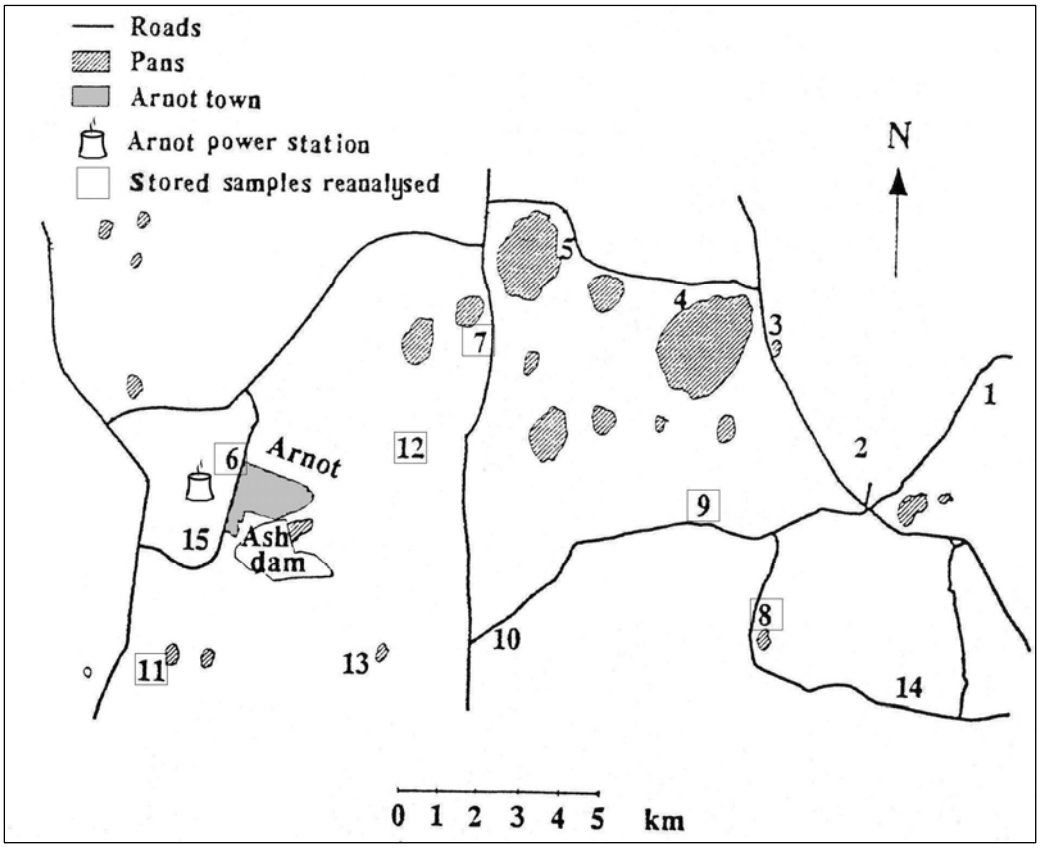


Figure 4: Location of sampling sites in relation of the Arnot power station (Van Tienhoven 1997).

Van Tienhoven (1997) established a baseline in August 1996 and in principle, the sampling strategy adopted for this study was the same as that implemented for the

baseline study. The GPS co-ordinate recorded for each site by Van Tienhoven (1997) formed the centre-point of an equilateral triangle with the sampling points of the triangle located 25 m apart. At each of the sample points, three samples were taken for both the topsoils and the subsoils and these were combined to give a composite sample per point. Topsoil was collected from the soil surface to a depth of 10 cm, while subsoil was collected from 20 – 40 cm in the soil profile. Soil samples were oven dried at 60° C for 48 hours, sieved (2 mm sieve), and sent to BEMLab (Pty) LTD in Cape Town for soil analyses to be performed. Stored soils (topsoils and subsoils) collected in 1996 from six sampling sites, namely sites 6, 7, 8, 9, 11 and 12 were also sent to BEMLab (Pty) LTD for analysis. These six sites are marked by numbered squares in Figure 4. The methods of analyses for the 1996 soils and the 2006 soils were the same; however, the analyses were conducted at different laboratories. Although data from 1996 were available, it was felt that re-testing the 1996 soil at the same laboratory and under the same conditions would give a more accurate description of the change in soil properties.

2.3 Lab Methods

Soils underwent a suite of analyses as given in Table 2.

Table 2: Suite of soil analyses performed by BEMLab (Pty) LTD.

Analysis	Reagent	Procedure	Reference
Soil pH	▪ Distilled water ▪ 1 M KCl ▪ 1 M K_2SO_4	pH meter	McLean (1982) Soil and Plant Analysis Council (1998)
Acid Neutralizing Capacity (ANC)	1 M KCl	Titrate with 2M NaOH (calcium carbonate equivalent)	Rayment and Higginson (1992)
Extractable base cations (Ca^{2+} ; Mg^{2+})	1 M ammonium acetate extraction	ICP-OES	Chapman (1965) Soil and Plant Analysis Council (1998)
Extractable acidity	Standard NaOH	Titration	Reeve and Sumner (1971)
Organic carbon		Loss on Ignition	Davies (1974)
Extractable Fe, Mn , Al	citrate-bicarbonate-dithionite (CBD) extraction	ICP-OES	Kunze (1965) Mehra and Jackson (1958)
Soluble anions and cations	Distilled water	Saturated paste extracts, ICP-OES	Clesceri *et al.* (1998)
Electrical Conductivity (EC)	Distilled water	Saturated paste extract	United States Salinity Staff (1954) Soil and Plant Analysis Council (1998)
Soil texture		Hydrometer	Day (1956)
Total sulphur	Aqua regia digestion	ICP-OES	Soil and Plant Analysis Council (1998)
Extractable sulphate	0.01 M calcium phosphate extraction (pH 4)	ICP-OES	Soil and Plant Analysis Council (1998)
Total nitrogen		Leco FP528 Nitrogen analyser	Horneck and Miller (1998)

From these data, the effective cation exchange capacity (ECEC) of the soils was calculated as the sum of Ca^{2+}, Mg^{2+}, H^{+} and Al^{3+}, while acid saturation was calculated as the sum of H^{+} and Al^{3+} divided by the ECEC, expressed as a percentage.

2.4 Data Analyses

The 1996 data had no replicates and as a result statistical analyses on these data were limited. The re-tested 1996 soils were labelled as 1996/1 in order to differentiate them from original 1996 data. Although statistical analyses were performed on both the 1996

data and the re-tested 1996/1 data, only the 1996/1 data was plotted against distance from the power station. The relationship between soil properties and distance from the power station was analysed using regressions and significant differences between the re-tested soils and the 2006 soils were determined using a paired t-test at a significance level of 0.05.

3. Results

Soil chemical data for the 2006, 1996/1 and 1996 soils are given in Table 3 for the topsoils and the subsoils. Data from all fifteen sampling sites were used for both 2006 and 1996 soils, while 1996/1 soils were used from six sites. Highlighted cells indicate either a significant increase (+) or a significant decrease (-) from the 1996/1 soils or the 1996 soils. No percentage change is given for soil pH since this would not be meaningful but rather a significant increase or decrease is indicated by the sign, + or – respectively. Soils were predominantly classed as either sandy loam or loamy sand. Soil chemical properties that showed a significant difference between the 2006 and the 1996/1 data were plotted against distance from the power station. Table 4 gives an indication of the mean soil texture across both the topsoils and the subsoils for the six sites used as a comparison to the 2006 data. The soil texture does not appear to be significantly different between sites.

Table 3: Minimum, maximum and mean values for soil chemical properties for the 2006, 1996/1 and 1996 for two soil depths. Highlighted cells indicate a statistically significant change between the data.

		pH (KCl)			pH (water)			pH (K_2SO_4)			Ca 2+ ($mmol_c\ kg^{-1}$)			Mg 2+ ($mmol_c\ kg^{-1}$)			H + ($mmol_c\ kg^{-1}$)		
		2006	1996/1	1996	2006	1996/1	1996	2006	1996/1	1996	2006	1996/1	1996	2006	1996/1	1996	2006	1996/1	1996
	Minimum	4.0	4.0	4.2	3.7	4.0	5.3	4.5	4.7	4.7	2.9	3.6	7.8	1.4	1.6	9.3	6.9	2.5	0.9
	Maximum	5.3	5.0	4.6	5.4	4.9	6.0	5.7	5.6	5.0	49.6	33.7	18.0	23.5	18.3	20.0	23.6	6.0	6.2
	Mean	4.5	4.5	4.4	4.5	4.4	5.7	4.9	5.0	4.9	13.8	10.9	12.3	7.5	5.8	14.1	13.1	3.8	2.9
Topsoils	Change (%)		0.1	+		2.0	-		-	+		26.6	11.7		30.1	-46.5		247.0	355.6
	Minimum	4.0	4.0	4.1	3.5	3.9	5.0	4.4	4.8	4.7	0.6	1.9	3.0	0.7	1.1	7.4	5.9	2.5	0.6
	Maximum	5.0	4.8	4.8	5.1	5.0	6.3	5.5	5.4	5.4	11.8	6.8	13.0	14.3	5.0	17.0	18.2	7.6	10.3
	Mean	4.3	4.3	4.4	4.2	4.3	5.7	4.8	5.0	4.9	5.3	3.9	7.0	4.4	2.9	11.4	12.0	5.0	4.8
Subsoils	Change (%)		0.0	-		-3.1	-		-	-		35.7	-24.6		52.9	-61.6		138.6	151.8

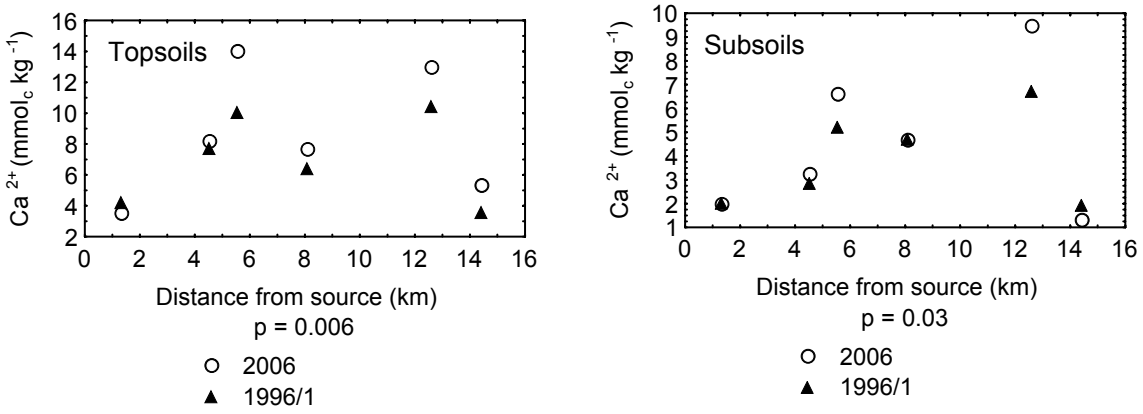
		Al $^{3+}$ ($mmol_c\ kg^{-1}$)			ECEC ($mmol_c\ kg^{-1}$)			Acid Saturation (%)			Base Saturation (%)			ANC (%)		ANC ($cmol_c\ L^{-1}$)	EC ($mS\ m^{-1}$)		
		2006	1996/1	1996	2006	1996/1	1996	2006	1996/1	1996	2006	1996/1	1996	2006	1996/1	1996	2006	1996/1	1996
	Minimum	12.4	11.4	29.6	33.1	23.5	53.6	28.1	21.8	56.8	4.2	9.5	10.9	0.2	0.3	2.1	7.1	8.9	21.0
	Maximum	90.4	51.5	133.3	112.7	66.5	156.6	95.8	90.5	89.1	71.9	78.2	43.2	0.9	1.0	4.0	125.1	14.7	46.0
	Mean	53.2	25.0	66.1	87.6	45.4	95.3	74.9	64.2	68.5	25.1	35.8	31.5	0.5	0.4	3.0	18.5	11.6	33.0
Topsoils	Change (%)		112.7	-19.5		92.8	-8.1		16.7	9.3	-29.9		-20.2		25.4			58.9	-44.1
	Minimum	16.7	13.2	29.6	30.2	23.5	49.5	64.0	66.7	58.4	1.3	4.5	7.0	0.1	0.3	2.4	4.5	6.7	12.0
	Maximum	109.8	82.0	133.3	137.9	94.9	154.4	98.7	95.5	93.0	36.0	33.3	41.6	0.6	0.8	3.7	20.2	10.6	30.0
	Mean	67.0	40.1	66.1	88.7	51.8	89.2	87.9	83.4	75.8	12.1	16.6	24.2	0.3	0.5	3.0	8.4	8.0	20.3
Subsoils	Change (%)		67.3	1.5		71.1	-0.6		5.4	16.0	-27.3		-50.0		-44.8			5.6	-58.6

		Total S ($mg\ kg^{-1}$)			Extractable SO_4^{2-} ($mg\ kg^{-1}$)			Soluble SO_4^{2-} ($mg\ l^{-1}$)			Total N (%)			NH_4^+ ($mg\ l^{-1}$)			NO_3^- ($mg\ l^{-1}$)		
		2006	1996/1	1996	2006	1996/1	1996	2006	1996/1	1996	2006	1996/1	1996	2006	1996/1	1996	2006	1996/1	1996
	Minimum	60.0	8.6	150.0	8.0	7.8	79.0	0.0	9.5	39.0	0.1	0.1	ND	0.1	1.1	2.5	0.02	0.3	0.00
	Maximum	199.1	30.6	200.0	34.3	17.8	97.0	474.4	14.9	82.6	0.2	0.2	ND	6.0	3.4	7.9	11.2	0.5	8.7
	Mean	104.4	15.6	175.0	16.6	13.7	86.5	39.9	12.3	57.4	0.2	0.1	ND	1.7	2.5	5.7	1.4	0.3	2.1
Topsoils	Change (%)		571.2	-40.4		21.5	-80.8		223.5	-30.3		27.3			-33.9	-70.6		314.4	-34.4
	Minimum	25.9	4.2	50.0	5.8	4.8	69.0	5.9	5.0	20.5	0.1	0.04	ND	0.0	1.0	1.1	0.01	0.3	0.00
	Maximum	80.9	36.9	300.0	32.7	32.4	141.0	19.0	14.4	69.1	0.2	0.1	ND	1.2	1.9	4.1	5.7	0.4	25.4
	Mean	60.0	16.1	141.7	15.2	17.7	99.2	10.9	9.5	41.4	0.1	0.1	ND	0.3	1.6	2.5	0.8	0.3	6.1
Subsoils	Change (%)		271.8	-57.7		-13.9	-84.7		15.1	-73.6		88.6			-79.3	-87.0		127.3	-87.4

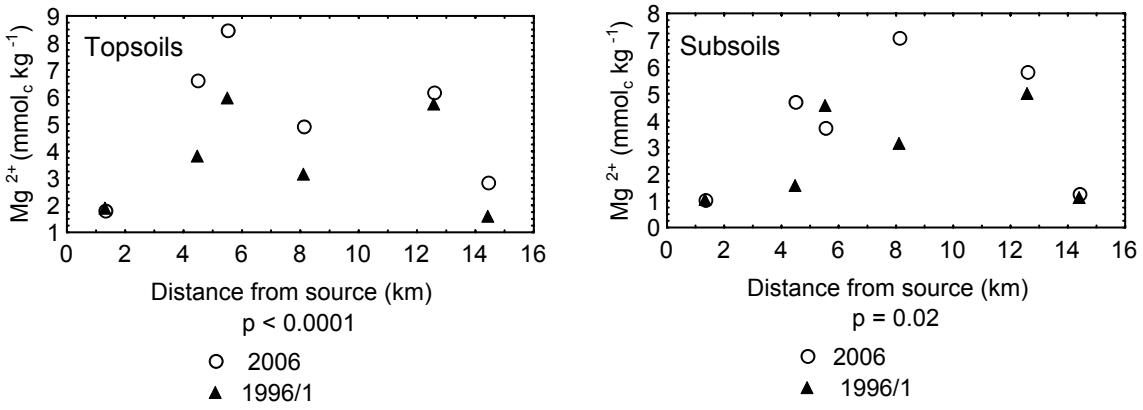
Table 4: Mean soil texture data at six sites across two soil depths

	Topsoils				Subsoils			
Site	**Clay (%)**	**Silt (%)**	**Sand (%)**	**Classification**	**Clay (%)**	**Silt (%)**	**Sand (%)**	**Classification**
6	**7.3**	**7.4**	**85.3**	Loamy sand	**11.8**	**5.4**	**82.8**	Sandy loam
7	**5.7**	**5.3**	**88.9**	Sand	**13.6**	**2.7**	**83.7**	Loamy sand
8	**4.7**	**6.2**	**89.1**	Sand	**12.9**	**1.7**	**85.4**	Loamy sand
9	**3.1**	**5.7**	**91.1**	Sand	**5.9**	**7.4**	**86.7**	Loamy sand
11	**5.7**	**7.2**	**87.1**	Sand	**14.9**	**6.0**	**79.1**	Sandy loam
12	**2.7**	**7.1**	**90.2**	Sand	**11.9**	**5.5**	**82.7**	Loamy sand

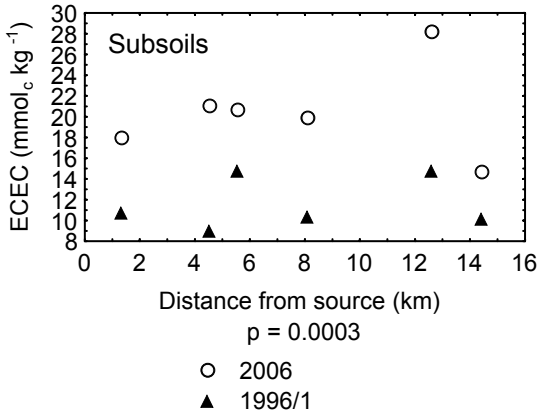
Base cations Ca^{2+} and Mg^{2+} showed a significant increase in both the topsoils (Ca^{2+} $p = 0.006$; Mg^{2+} $p < 0.0001$) and subsoils (Ca^{2+} $p = 0.03$; Mg^{2+} $p = 0.0229$) since 1996. The ECEC increased significantly ($p = 0.0003$) in the subsoils (Figure 5). The ANC showed a significant decrease in the subsoils since 1996 (Figure 6).



a)



b)



c)

Figure 5: The concentration of a) calcium and b) magnesium in the topsoils and the subsoils and c) the ECEC in the subsoils.

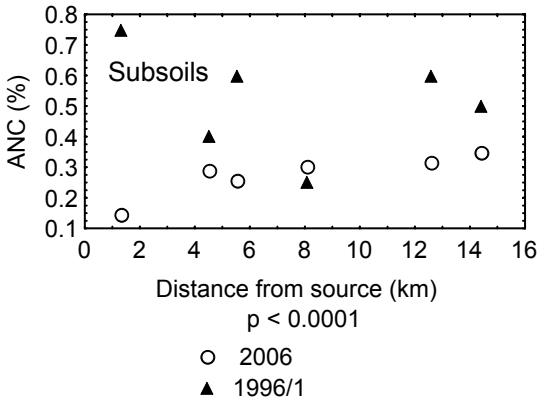


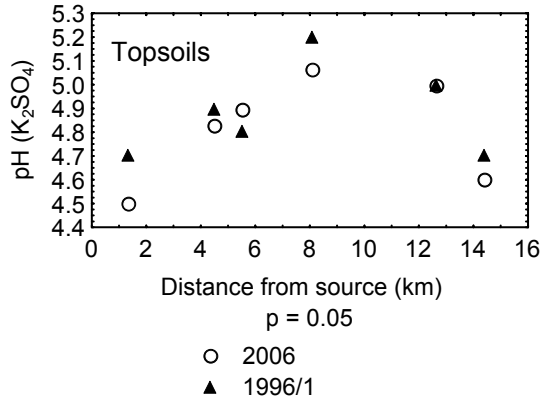
Figure 6: The ANC in the subsoils plotted against distance from the power station.

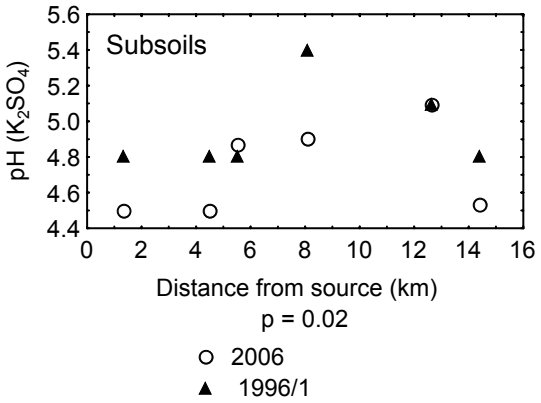
The concentration of base cations is greater in the topsoils than the subsoils. However, the ECEC is similar for both the topsoils and the subsoils. Since the ECEC is calculated as the sum of Ca^{2+}, Mg^{2+}, H^{+} and Al^{3+}, the concentration of either H^{+} or Al^{3+} must be higher in the subsoils than the topsoils for similar ECEC results in both the topsoils and the subsoils. The concentration of H^{+} is not significantly different between soil depths, however, the concentration of Al^{3+} is greater in the subsoils than the topsoils, resulting in no overall difference between the ECEC in the topsoils and the subsoils.

Soils across the globe have been affected by acid deposition and in comparison, the concentration of Ca^{2+} (topsoils: 2.9 – 49.5 $mmol_c\ kg^{-1}$; subsoils: 0.6 – 11.8 $mmol_c\ kg^{-1}$) is significantly lower in the Arnot soils than those reported by Singh *et al.* (1995) in soils around coal-fired power stations in India, where concentrations of between 112.5 and 175.0 $mmol_c\ kg^{-1}$ were reported. This is also true for the Ca^{2+} concentration of 80.0 $mmol_c\ kg^{-1}$ reported by Reeve and Sumner (1971) in Natal Oxisols. The concentration of Mg^{2+} (topsoils: 1.38 – 23.46 $mmol_c\ kg^{-1}$; subsoils: 0. 7 – 14.3 $mmol_c\ kg^{-1}$) is low in comparison to the soils tested by Bühmann *et al.* (2006) in the Eastern Cape region that were found to have an average Mg^{2+} concentration of 15.6 $mmol_c\ kg^{-1}$ in the topsoils and 13. 7 $mmol_c\ kg^{-1}$ in the subsoils.

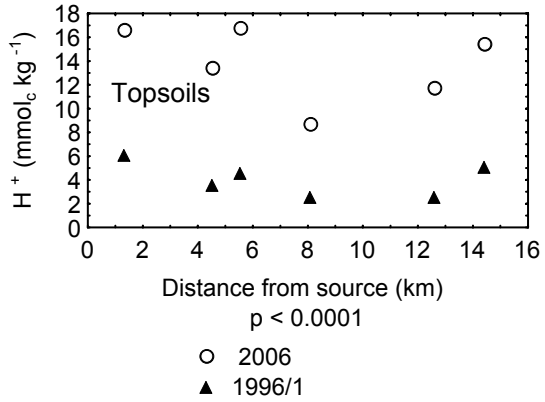
Similar ranges for base cation concentration for soils subjected to acid deposition were reported by Madeira *et al.* (2003) for soils in the Azores of between 3.8 and 131.1 $mmol_c\ kg^{-1}$ for Ca^{2+} and between 1.1 and 33.3 $mmol_c\ kg^{-1}$ for Mg^{2+}. Similarly, Stutter *et al.* (2003) reported Ca^{2+} concentrations to range between 0.2 and 40.9 $mmol_c\ kg^{-1}$ for the topsoils and between 0.09 and 26.9 $mmol_c\ kg^{-1}$ in the subsoils, and Mg^{2+} concentrations of between 0.3 and 14.2 $mmol_c\ kg^{-1}$ for the topsoils and 0.09 – 13.4 $mmol_c\ kg^{-1}$ for the subsoils in north-eastern Scotland. Sullivan *et al.* (2006) reported that concentration of exchangeable base cations and base saturation is generally low in soils subject to acid deposition, with a mean Ca^{2+} concentration of 5.1 $mmol_c\ kg^{-1}$, a mean Mg^{2+} concentration of 1.2 $mmol_c\ kg^{-1}$ and a mean base saturation of less than 10.3 %. These results are very similar to those reported for the Arnot soils.

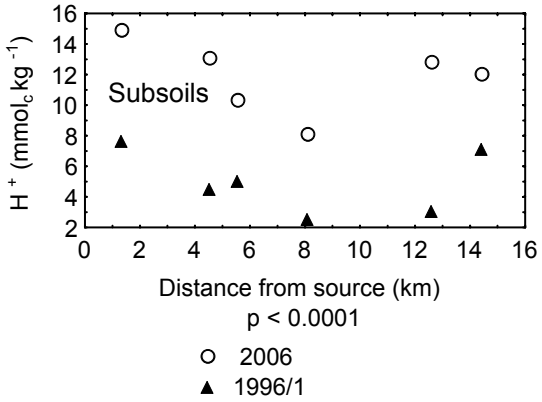
The acidity of the soil has increased since the baseline study, as shown by the significant increase in the concentration of H^+ (topsoils: $p < 0.0001$, subsoils: $p < 0.0001$) and Al^{3+} (topsoils: $p < 0.0001$, subsoils: $p < 0.0001$) in the soil (Figure 7). Extractable Al^{3+} concentration showed a significant increase over the ten year period, with an increase of 113 % and 67 % in the topsoils and subsoils respectively (Figure 7). The increased soil acidity is also shown by the significant decrease in soil pH (K_2SO_4) (topsoils: $p = 0.05$, subsoils: $p = 0.02$) (Figure 8).



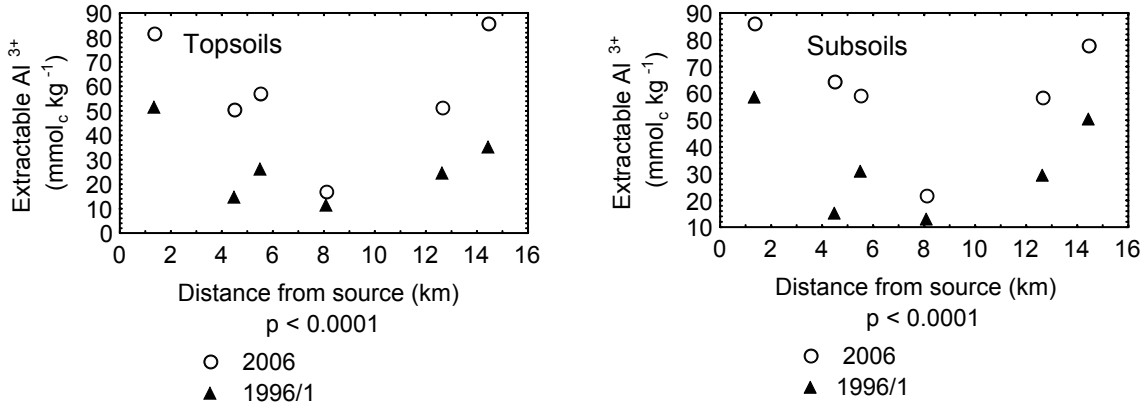


a)





b)



c)

Figure 7: Soil chemical properties of a) pH (K_2SO_4); b) hydrogen ion concentration and c) extractable aluminium concentration plotted against distance from the power station.

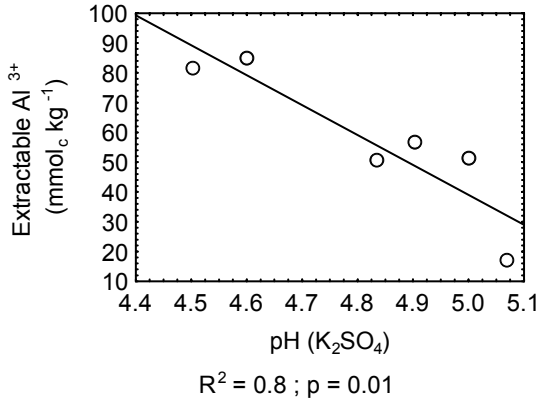


Figure 8: Significant negative relationship between extractable aluminium and pH (K_2SO_4) for the 2006 topsoils.

Although soil pH (water) and pH (KCl) were also measured, only pH (K_2SO_4) showed a significant change since the baseline study. The difference between pH (water) and pH (salt) is referred to as delta pH (Δ pH). Although the pH (salt) is usually KCl, the same trends should be observed when the salt used is K_2SO_4. However, these trends may not be as marked. This difference (Δ pH) gives an indication of the mineralogy of the soil. Delta pH ranged between - 0.3 and - 0.8 for the 2006 topsoils, and between - 0.3 and - 1.0 for the 2006 subsoils. If Δ pH is small or negative, a strongly sesquioxide colloidal soil fraction with relatively large anion exchange capacity is indicated (Fey and Guy 1993). Delta pH is also widely known to be related to the proportion of positive to negative surface charge.

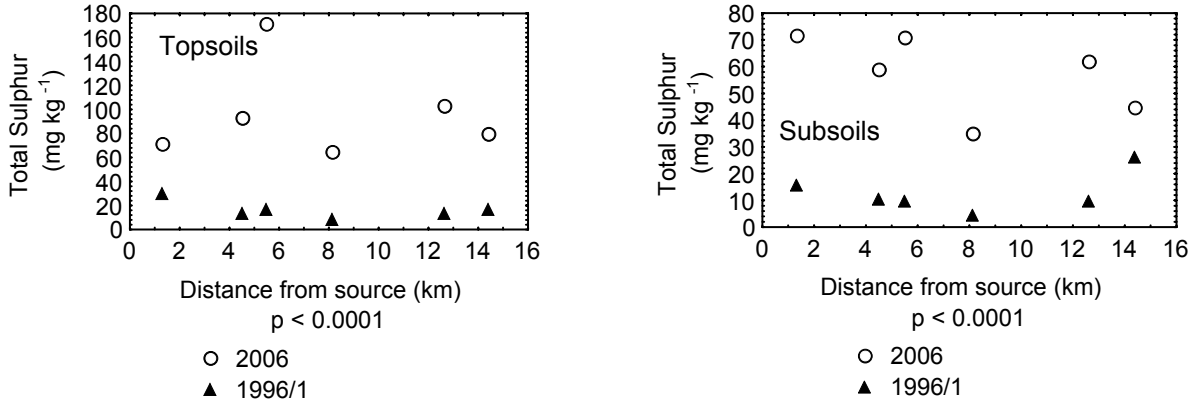
The greater the absolute magnitude of Δ pH, the greater the extent of mixed mineralogy. This can also give an indication of the weathering of the soil. The absolute values indicate that topsoils therefore have a more mixed mineralogy and are more weathered than the subsoils.

The soil pH (K_2SO_4) is lower (topsoils: mean pH 4.9; subsoils: mean pH 4.8) than reported by Fey and Guy (1993) for soils in the Vaal catchment. The Arnot soils are therefore more acidic in comparison to the soils from the Vaal catchment. Soil pH (K_2SO_4) is based on a logarithmic scale. Extractable acidity is a measure of the H^+ concentration in the soil and appears to be within the range reported by Sullivan *et al.* (2006) for the north-eastern USA, as well as Kram *et al.* (1997) for the Czech Republic. Both of these studies were undertaken in soils subjected to air pollution and acid deposition.

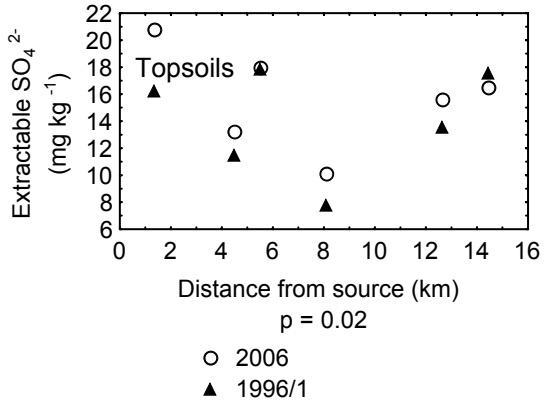
The topsoils were found to have a lower average extractable Al^{3+} concentration than that reported by Kram *et al.* (1997) of 72.6 $mmol_c\ kg^{-1}$. Extractable Al^{3+} in the topsoils (12.4 – 90.4 $mmol_c\ kg^{-1}$) was found to be similar to that recorded by Xue *et al.* (2003), with a range of between 28.0 – 54.0 $mmol_c\ kg^{-1}$ for soils in China. In soils in the Eastern Cape, Bühmann *et al.* (2006) also found similar concentrations of extractable Al^{3+} as in the 2006 Arnot soils, with a mean of approximately 86.0 $mmol_c\ kg^{-1}$ and these were consequently classified as moderately acidic. However, the concentration of Al^{3+} for these soils appears to be high in comparison to other soils subject to acid deposition, as reported by Hochman *et al.* (1992), Kram *et*

al. (1997), McLaughlin and Phillips (2006) and Oulehle *et al.* (2006). Hochman *et al.* (1992) showed that the Al^{3+} concentration of soils ranged between 0.7 – 38.9 $mmol_c/kg$ in New Zealand and between 0.8 – 53.0 $mmol_c\ kg^{-1}$ for soils in Australia. The subsoils show a higher mean than the 55.3 $mmol_c\ kg^{-1}$ reported for soils in the Czech Republic by Kram *et al.* (1997). McLaughlin and Phillips (2006) reported Al^{3+} concentrations of between 29.9 – 37.2 $mmol_c\ kg^{-1}$, while Oulehle *et al.* (2006) report averages of 21.4 $mmol_c\ kg^{-1}$ and 10.0 $mmol_c\ kg^{-1}$ for the topsoil and subsoils respectively for soils in the Czech Republic. In the subsoils, the extractable Al^{3+} concentration (16.7 – 109.8 $mmol_c\ kg^{-1}$) is approximately double that recorded by Xue *et al.* (2003) for soils in China. According to Xue *et al.* (2003), when considering the soil pH (water), base saturation and exchangeable Al^{3+} concentration of the soil, the soils under investigation can be classed as moderately acidic.

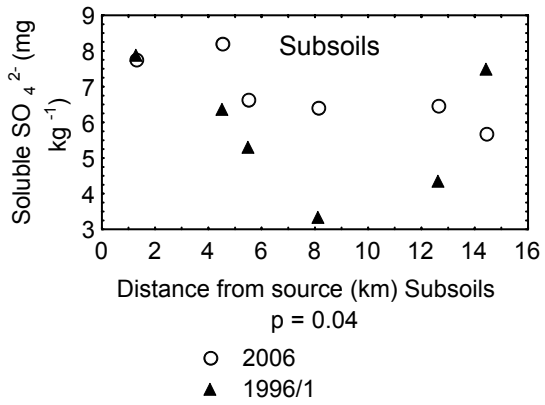
There was a significant increase in total sulphur in the topsoils ($p < 0.0001$) and the subsoils ($p < 0.0001$), while extractable sulphate increased significantly in the topsoils ($p = 0.02$) and soluble sulphate increased significantly in the subsoils ($p = 0.04$) (Figure 9).



a)



b)



c)

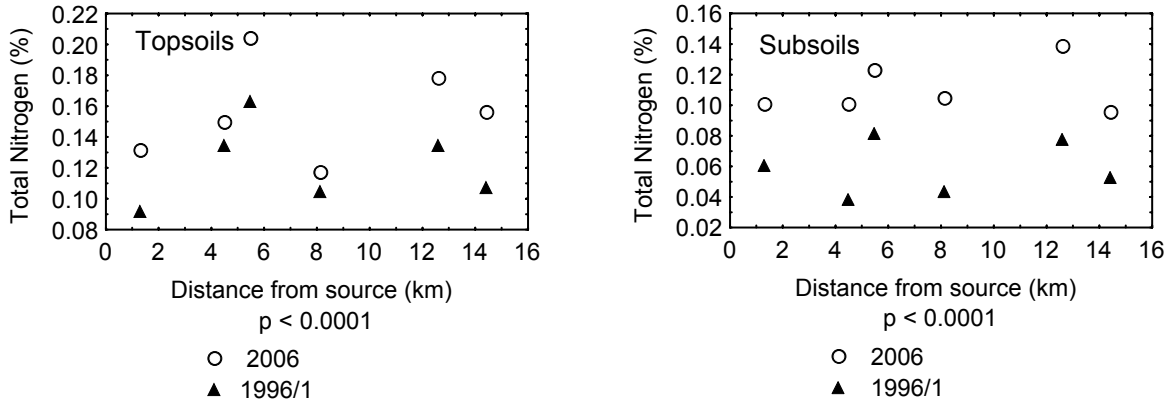
Figure 9: Sulphur content of the soil given by a) total sulphur in the topsoils and the subsoils b) extractable sulphate in the topsoils and c) soluble sulphate in the subsoils plotted against distance from the power station.

In the 2006 study, total sulphur increased significantly in the topsoils and subsoils, while extractable SO_4^{2-} increased significantly in the topsoils and soluble SO_4^{2-} increased significantly in the subsoils. A significant positive relationship between total sulphur and extractable sulphur was expected; however, although a positive relationship between the two variables was found, this relationship was not significant.

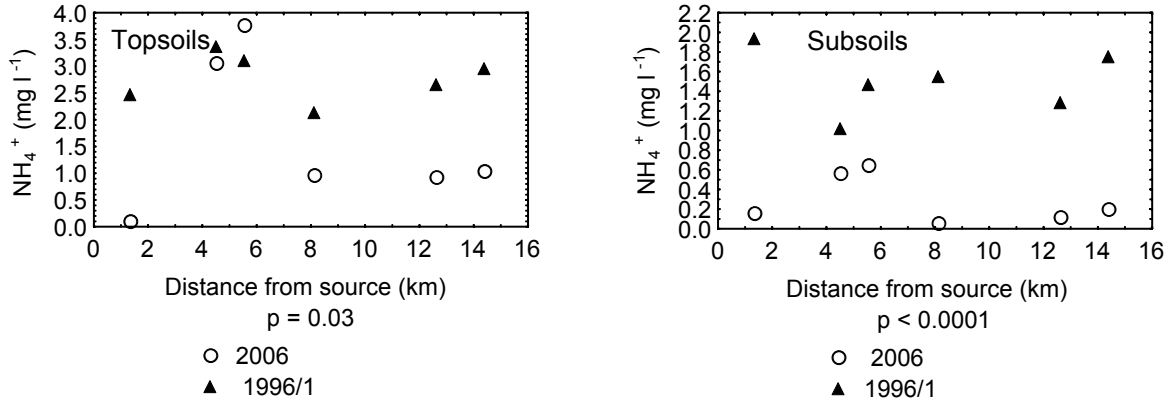
Since plants take up sulphur mainly in the form of sulphate ions, extractable SO_4^{2-} can give an indication of atmospherically deposited sulphur (Palomino *et al.* 2005). Extractable SO_4^{2-} showed a significant increase since the baseline study (topsoils: 8.0 – 34.3 mg kg^{-1}; subsoils: 5.8 – 32.7 mg kg^{-1}). Gallardo-Lara *et al.* (1990) found extractable SO_4^{2-} levels averaged 14.9 mg/kg in acid soils from Spain, and this is

similar to the extractable SO_4^{2-} content of the soils under investigation. Extractable SO_4^{2-} was found to be within the range reported by Fey and Guy (1993) for soils in Natal of between 2.0 and 55.0 mg kg $^{-1}$ and those reported by Sullivan *et al.* (2006) of between 7.6 – 150.9 mg kg $^{-1}$. However, the concentration of extractable SO_4^{2-} is above that reported by Singh *et al.* (1995), who reported a range of between 0.03 – 0.05 mg kg $^{-1}$ in soils around a coal-fired power plant in India.

Total nitrogen increased significantly in the topsoils ($p < 0.0001$) and subsoils ($p < 0.0001$), while NH_4^+ concentrations showed a significant decrease of 34 % in the topsoils ($p = 0.03$) and 80 % in the subsoils ($p < 0.0001$) since the baseline study (Figure 10). However, there was no significant difference in the concentration of NO_3^- in either the topsoils or the subsoils.



a)



b)

Figure 10: Soil nitrogen content given by a) total nitrogen and b) ammonium concentration in both the topsoils and the subsoils plotted against distance from the power station.

The total nitrogen content (topsoils: 0.09 – 0.2 %; subsoils: 0.1 – 0.2 %) was below the range of 1.0 -1.1 % reported McLaughlin and Phillips (2006) for soils in the north-eastern USA. Total nitrogen was found to be within the range reported by Sullivan *et al.* (2006) of 0.1 – 0.4 % for soils in the north-eastern USA and Schaaf *et al.* (1995), with reported values of 0.02 – 0.1 % for soils in north-eastern Germany. However, the total nitrogen content of the soils is above the range reported by Singh *et al.* (1995) of 0.04 – 0.05 % for soils within the vicinity of a coal-fired power plant in India. The deposition of nitrogen affects both the pH and the nitrogen content of the soil and Diekmann and Falkengren-Grerup (2002) assume that these two variables are positively correlated since the simultaneous deposition of acidifying substances and nitrogen affects both the pH and the nitrogen content of the soil. This assumption appears to be supported by these data, since a significantly positive relationship was found between the total nitrogen content of the soil (%) and pH (K_2SO_4) for the 2006 subsoils, as shown in Figure 11. It also seems to be supported by data presented by Richards *et al.* (1997) for soils in the Western Cape vegetated by fynbos.

The concentration of NH_4^+ ranged between 0.08 mg l^{-1} and 6.0 mg l^{-1} and showed a decrease of 34 % in the topsoils and 80 % in the subsoils. Microbial processes alter both NH_4^+ and NO_3^-, however; the role of microbial processes has not specifically been identified in this study. The transient nature of both these soil chemicals makes it difficult to detect and measure actual changes in the concentration of these chemicals in the soil since they change rapidly and this makes it difficult to detect a trend.

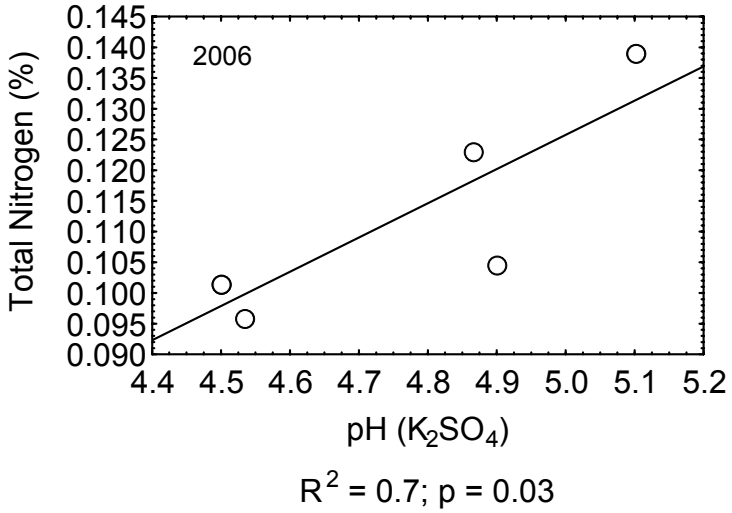


Figure 11: The relationship between total nitrogen (%) and pH (K_2SO_4) and in the 2006 soils.

Generally, airborne concentrations of pollutants decrease with distance from the main emission sources (Tørseth and Semb 1998; Fenn *et al.* 2003) and soluble SO_4^{2-} and ANC in the 2006 subsoils were found to have a significant spatial relationship, as shown in Figure 12.

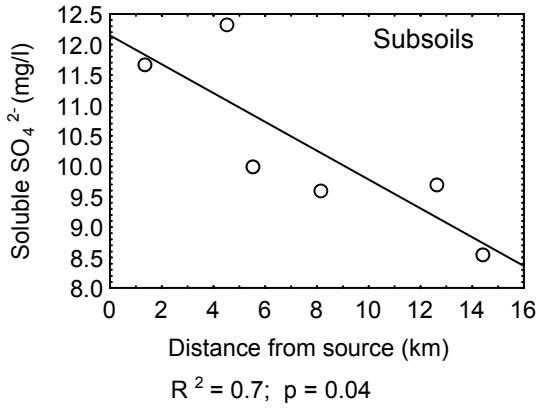


Figure 12: The relationship between soluble sulphate and distance from the power station for the 2006 subsoils.

The relationship between ANC and distance from the power station is best explained by a logarithmic relationship which indicates that there is a rapid increase in ANC as distance from the power station increases, however, this relationship begins to flatten out (Figure 13).

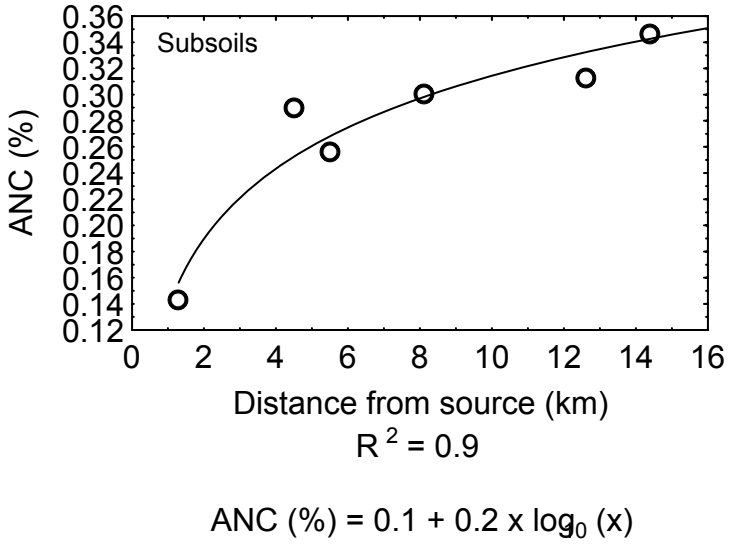


Figure 13: The relationship between the ANC and distance from the power station for the 2006 subsoils.

4. Discussion

4.1 Conceptual Framework

A conceptual framework has been used to explain the trends in the data. This framework is based on the rates of input to the system, throughput within the system and output from the system of the acidic and basic components of deposition. These rates can be used to explain overall trends such as soil acidification, or trends significant in either the topsoils or the subsoils. Input into the system is made up of deposition, while leaching results in throughput from the topsoils to the subsoils. Soil chemicals are retained within the soil via cation exchange and through binding to soil components. Output from the system is primarily due to leaching from the subsoils deeper into the soil horizon.

4.2 Potential Errors of Caution

It is important to note that there are some discrepancies between the data sets used as a base with which to compare the 2006 soils (either 1996 or 1996/1 soils). The storage of the 1996 soils may have resulted in some chemical changes occurring in these soils. However, the soils were oven dried and sieved using a 2 mm sieve before they were

stored. The soils were packed in airtight plastic containers and were finally packed into storage boxes. These were stored at room temperature. Since the soils were exposed to neither excessive moisture nor heat during the ten years that they were stored, few chemical changes are expected to have occurred in these soils and they are therefore regarded as representative of the original 1996 soils.

Differences in analytical resolution are also important to consider. A comparison between the 1996 soils and the 2006 soils shows a decrease in the concentration of basic cations, while a comparison between the 1996/1 soils and 2006 soils shows an increase in these same chemical properties. A comparison between the 1996 soils and the 2006 soils shows a significant decrease in the concentration of Ca^{2+}, Mg^{2+} and Al^{3+} since the baseline study, as well as a significant decrease in the ECEC of the soils. The data also show a significant decrease in the concentration of total sulphur, extractable sulphur and soluble sulphur since 1996. The reason for these differences may be due to the different rates of input to the system, throughput within the system and output from the system. The 1996 data indicates that the rate of input was less than the rate of output, therefore reflecting a decrease in many of the soil chemical properties. However, the 1996/1 data indicates that the rate of input of pollutants is greater than the rate of output and therefore reflects an increase in these soil chemical properties. However, in both cases, the overall results show a decrease in soil pH, as well as an increase in the concentration of H^{+} in the soil. Regardless of the data set used as a comparison to the 2006 soils, the net effect remains the same. The reason for this is due to the absolute concentrations of cations in the soil. The absolute values show that for the 1996, 1996/1 and 2006 soils, the concentration of base cations in the soil is significantly lower than the acidic components, as shown by the ratio between basic cations and acidic cations in the soil. The sum of acidic cations is greater than the sum of basic cations, and has resulted in the overall acidification of the soil. These data are shown in Table 5.

Table 5: Sum of basic cations and acidic cations for two soil depths at six sites

	Topsoils			Subsoils		
	1996	**1996/1**	**2006**	**1996**	**1996/1**	**2006**
Sum of Basic Cations Ca^{2+}; Mg^{2+} (mmolc kg^{-1})	26.4	10.8	13.9	18.4	6.7	8.5
Sum of Acid Cations H^{+}; Al^{3+} (mmolc kg^{-1})	86.2	31.2	71.3	70.8	38.0	73.5

In each of the data sets, the acidic cations were greater than the basic cations, and this was greatest in the subsoils. In the topsoils, the ratio of basic cations to acidic cations is 1:3 for the 1996 soils, 1:3 for the 1996/1 soils and 1:5 for the 2006 soils. In the subsoils, the ratio of basic cations to acidic cations is 1:4 for the 1996 soils, approximately 1:5 for the 1996/1 soils and almost 1:9 for the 2006 soils. Therefore, the subsoils are more acidic than the topsoils, with the 1996/1 and 2006 subsoils being approximately twice as acidic as the topsoils. This indicates that the rate of throughput of acidic and basic components in the system is greater than the rate of output, leading to acidification of the soil. Although the absolute values are within the same order of magnitude between the 1996 soils and the 1996/1 soils for the majority of the chemical properties, some are markedly different. These include Ca^{2+}, Mg^{2+}, Al^{3+}, total sulphur, extractable SO_4^{2-}, soluble SO_4^{2-} and NH_4^{+}. Current methods to analyse soil properties may account for certain differences in the absolute values between data due to the differences is analytical resolution.

The concentration of Ca^{2+} and Mg^{2+} in the soil was determined using KCl as an extractant, while in 1996/1 these were extracted using ammonium acetate. The data from these two methods of extraction should be comparable; however, the concentration in 1996 was determined by atomic adsorption spectroscopy, while in 1996/1 the method used was ICP-OES. The concentration of CBD-extractable Al^{3+} in the 1996 soils was calculated as a percentage based on the amount of dissolved compound in the extraction. However, modern techniques use ICP-OES to determine the concentration of CDB-extractable Al^{3+} in the soil and this was used to determine the concentration of Al^{3+} in the 1996/1 soils. The modern technique of ICP-OES is a more accurate and efficient way

to determine the concentration of chemicals in the soil and this may account for these differences.

The total sulphur content of the 1996 soils was not specifically determined, but rather was determined as a percentage of sulphur dioxide (SO_2) in the soil and the total sulphur concentration was then determined from these data. However, total sulphur was specifically determined for the 1996/1 and 2006 soils and these data therefore give a better reflection of the total sulphur content of the soils.

In comparison to other studies such as the studies by Gallardo-Lara *et al.* (1990) and Fey and Guy (1993) previously mentioned, the mean concentration of extractable SO_4^{2-} for the 1996 topsoils of 86.5 mg kg^{-1} appears to be high, while the mean concentrations for 1996/1 (14.1 mg l^{-1}) and 2006 (15.7 mg l^{-1}) are similar. This indicates that the reported 1996 data may be inaccurate.

The concentration of extractable sulphate was determined by extraction with calcium phosphate in both the 1996 and the 1996/1 soils; however, the procedure used was different. Van Tienhoven (1997) used ion chromatography to determine the concentration of extractable SO_4^{2-} in the soil, and according to Van Tienhoven (1997), this procedure had not been used before and therefore represented a novel approach to determine extractable sulphate. However, in a trial to test this method, Van Tienhoven (1997) found that the values obtained via ion chromatography were considerably higher than those obtained by the conventional method of turbidimetry. The results from this trial showed a mean extractable sulphate concentration of 20.6 mg l^{-1} for the topsoils and 30.9 mg l^{-1} for the subsoils determined by turbidimetry, and a mean of 72.7 mg l^{-1} and 95.8 mg l^{-1} for the topsoils and subsoils respectively determined by ion chromatography. This represents values of 3.5 times higher in the topsoils and 3 times higher in the subsoils for extractable SO_4^{2-} determined by ion chromatography versus turbidimetry and may explain the significantly higher extractable SO_4^{2-} concentrations for 1996 soils. If the extractable SO_4^{2-} levels for the 1996 soils were scaled down by a factor of 3.5, although

the values would still be higher than the 1996/1 or 2006 data, the data would be within the same range.

The absolute values for soluble SO_4^{2-} and NH_4^+ for the 1996 soils are considerable lower than the for the 1996/1 soils and this can also be explained by the analytical procedures. Soluble SO_4^{2-} and NH_4^+ were determined using saturated pastes for both the 1996 and for the 1996/1 soils. Whereas in 1996, ion chromatography was used to determine the concentration of cations and anions in the soil solution, the concentrations for the 1996/1 soils were determined using ICP-OES. Since ICP-OES is a more accurate and reliable modern technique, this may explain the higher concentration of soluble SO_4^{2-} and NH_4^+ reported for the 1996 soils.

The analytical techniques used in 2006 are more accurate and reproducible than those used in 1996 and this could have resulted in different absolute amounts recorded for each of the soil chemicals analysed. For this reason, the comparison between the re-tested 1996/1 soils and the 2006 soils would be a better representation of the actual change in soil chemical properties rather than analyse a change in the analytical procedures used to determine these chemical properties.

4.3 Base Cations

The ECEC gives the cation exchange capacity of the soil near its natural pH (Anderson and Ingram 1993) and has been shown to be positively correlated with pH in many soils (Hochman *et al.* 1992; du Toit 1993), decreasing as the soil becomes more acidic. The ECEC has important implications in terms of acid deposition since the ECEC of a soil significantly contributes to the ability of the soil to buffer against acidic inputs. An increase in base cations, especially Ca^{2+} and Mg^{2+}, may be attributed to deposition such as dust from an alkaline soil and fly ash (du Toit 1993; Singh *et al.* 1995; Gbondo-Tugbawa and Driscoll 2003). Increased concentrations of base cations in the soil could also be as a result of mobilisation and leaching of cations further down into the soil profile. The significant increase in the ECEC in the subsoils may be evidence for this mobilisation.

The increased concentration of Al^{3+} in the subsoils may be linked to the soil pH, since below pH 5.5, aluminium becomes increasingly soluble (Fenn *et al.* 1998). Soil pH (K_2SO_4) is lower in the subsoils, thereby resulting in more acidic subsoils and a subsequent increase in the solubility of extractable Al^{3+}. This was reflected in the negative relationship found between Al^{3+} and pH (K_2SO_4) and is discussed later.

The acid neutralizing capacity (ANC) is a measure of the buffering capacity of the soil (du Toit 1993) and is therefore a measure of the soil's ability to resist a change in pH (Miller and Donahue 1990). Inputs of strong acids to the soil can decrease the soil ANC by displacing base cations (du Toit 1993). Atmospheric deposition of sulphates generally represent an irreversible input of H^+ that will directly reduce the ANC of the soil (Van Breemen *et al.* 1983). According to du Toit (1993), an increase in the ECEC should lead to increased ANC, however, the reverse was found. The ECEC significantly increased in the subsoils, while the ANC of the soils has significantly decreased by approximately 45 % in the subsoils since the baseline study. A possible explanation for this may be due to the increased concentration of Al^{3+} in the subsoils.

Within a South African context, according to Bühmann *et al.* (2006), the concentration of Ca^{2+} is within the same range as those of soils from the Eastern Cape, with an average of 10.1 $mmol_c/kg$ and 12.6 $mmol_c/kg$ for subsoils and topsoils respectively. However, the source of these cations is completely different.

The concentration of base cations in the Arnot soils is higher than those from heavily acidified sites. At heavily acidified sites, the Ca^{2+} and Mg^{2+} concentrations, as well as base saturation have been found to be low due to the leaching of base cations from these soils. McLaughlin and Phillips (2006) found that Ca^{2+} concentrations in soils in the north-eastern USA ranged between 0.9 and 8.2 $mmol_c\ kg^{-1}$ and Mg^{2+} concentrations between 0.9 and 1.5 $mmol_c\ kg^{-1}$. Oulehle *et al.* (2006) reported ranges of Ca^{2+} and Mg^{2+} of 0.4 – 1.6 $mmol_c\ kg^{-1}$ and 0.2 – 1.0 $mmol_c\ kg^{-1}$ respectively for soils in the Czech Republic. The concentration of Mg^{2+} in the subsoils was significantly higher than the mean subsoil Mg^{2+} concentration reported by Kram *et al.* (1997) of 0.4 $mmol_c\ kg^{-1}$ in the

Czech Republic. The percentage change between the 1996/1 soils and the 2006 soils was found to be higher for Mg^{2+} than for Ca^{2+} and a possible reason for this, as suggested by Bühmann *et al.* (2006) is that Mg-bearing minerals are easily weathered and Mg^{2+} is removed from the soil more readily than Ca^{2+}. The concentration of Ca^{2+} is therefore generally higher than the concentration of Mg^{2+} in the soil, as pointed out by Thomas (1982).

Koptsik and Mukhina (1995) investigated soils also subjected to acid deposition in the Kola Peninsula in northern Russia and, according to their results, which showed base saturation to range between 6.6 and 33 % in the topsoils and between 13.9 and 22.9 % in the subsoils, the base saturation of the Arnot soils (topsoils: 4.2 – 71.9 %; subsoils: 1.3 – 36.0 %) is low. The base saturation is within that reported by Xue *et al.* (2003) of between 10.6 – 34.9 % in the topsoils and between 9.6 – 29.0 % for the subsoils in southern China, as well as that found by Schaaf *et al.* (1995) in north-eastern Germany of between 4 – 74 %. However, the mean base saturation is higher than the mean of 7.5 % in the topsoils and 5.6 % in the subsoils reported by Oulehle *et al.* (2006) in the Czech Republic for soils subjected to long-term acid deposition.

Generally, the ECEC is not significantly different to other soils subject to acid deposition. The ECEC of the Arnot soils (topsoils: 33.1 – 112.7 $mmol_c\ kg^{-1}$; subsoils: 30.2 – 137.9 $mmol_c\ kg^{-1}$) is slightly lower than the range reported by Hochman *et al.* (1992) of between 80.2 – 200.2 $mmol_c\ kg^{-1}$ for soils in New Zealand. Similar ECEC ranges were reported by Hochman *et al.* (1992) of between 52.4 – 191.1 $mmol_c\ kg^{-1}$ for soils in Australia and those reported by Sullivan *et al.* (2006) for soils in north-eastern USA of between 38.1 – 136.9 $mmol_c\ kg^{-1}$, with a mean of 83.0 $mmol_c\ kg^{-1}$. The ECEC is slightly above the range reported by McLaughlin and Phillips (2006) of between 42.1 – 93.2 $mmol_c\ kg^{-1}$ for soils in the north-eastern USA . However, the mean ECEC for the subsoils is almost double that recorded by Xue *et al.*(2003) who recorded a mean ECEC of 45.0 $mmol_c\ kg^{-1}$ for subsoils impacted by acid deposition in China.

4.4 Acids

Soil pH has a major influence on many other soil properties, and decreasing pH is closely linked to the solubility and mobilisation of Al^{3+} (Reuss and Johnson 1986; Van Miegroet *et al.* 1992a; Sparks 1995; Fenn *et al.* 1998). A significant negative relationship was found between extractable aluminium and pH (K_2SO_4) (Figure 8).This was expected since as the pH of the soil decreases and the soil becomes more acidic, aluminium is mobilized into the soil solution thereby increasing aluminium ion concentrations (Fenn *et al.* 1998). This significant negative relationship between extractable Al^{3+} and pH (K_2SO_4) was also found by Hochman *et al.* (1992), Reeve and Sumner (1971) as well as Paul *et al.* (2003). The concentration of extractable Al^{3+} was higher in the subsoils and in the topsoils, as was the acidity of the soils measured by pH (K_2SO_4). This may be linked to the greater ANC of the topsoils than that of the subsoils, as well as the significant decrease in the ANC of the subsoils since the baseline study.

Although the concentration of Al^{3+} is significantly higher than found in other studies, it appears that the concentration of Al^{3+} in the Arnot soils is similar to other South African soils, such as reported by Bühmann *et al.* (2006) for soils from the Eastern Cape. However, there has still been a significant increase in the Al^{3+} concentration of 113 % in the topsoils and 67 % in the subsoils since the baseline study, and this change is important.

The total sulphur concentration as well as the extractable sulphur and soluble sulphur concentrations were higher in the topsoils than the subsoils. This may be because the topsoils receive sulphur deposition directly from the atmosphere; the subsoils receive sulphur as throughput from the topsoils. The increase in soluble SO_4^{2-} in the subsoils may be due to a significant increase in both total sulphur and extractable SO_4^{2-} in the topsoils and therefore increased throughput of soluble sulphate from the topsoils to the subsoils. Although there is a source of nitrogen into the soil, it is difficult to determine what is happening to this nitrogen in the soil due to the complexities associated with the mass

balance of nitrogen. Only two forms of nitrogen have been measured in this study and the data would need to be converted if mass balance was to be calculated.

The concentration of calcium, ANC and total sulphur in the topsoils are all approximately double the concentrations of these same elements in the subsoils, while the acid saturation is almost 1.5 times higher in the subsoils than the topsoils. This can be attributed to the concentrations of acids versus bases in the topsoils and the subsoils. In the topsoils, the sum of Ca^{2+} and Mg^{2+} (13.9 $mmol_c\ kg^{-1}$) is five times less than the sum of Al^{3+} and H^{+} (71.3 $mmol_c\ kg^{-1}$). In the subsoils, the sum of the bases (8.5 $mmol_c\ kg^{-1}$) is approximately 9 times lower than the concentration of acids (73.5 $mmol_c\ kg^{-1}$). The reason for the difference between the topsoils and the subsoils may be due to calcium, since the concentration of Ca^{2+} in the topsoils (8.7 $mmol_c\ kg^{-1}$) is approximately double that in the subsoils (4.6 $mmol_c\ kg^{-1}$). The concentration of Ca^{2+} in the topsoils can also be linked to the ANC capacity of the topsoils, which is approximately double that of the subsoils. The source of the Ca^{2+} is probably fly ash. This replenishes the buffering capacity of the soils, which offsets the acidic deposition. The high concentration of acids in both the topsoils and the subsoils can be attributed mainly to the concentration of Al^{3+}, with a mean concentration of 57.4 $mmol_c\ kg^{-1}$ in the topsoils and 61.6 $mmol_c\ kg^{-1}$ in the subsoils. The mean concentration of H^{+} (topsoils: 13.8 $mmol_c\ kg^{-1}$; subsoils: 12.0 $mmol_c\ kg^{-1}$) for the six sites is within the same range as the mean concentration Ca^{2+} and Mg^{2+} (topsoils: 5.2 $mmol_c\ kg^{-1}$; subsoils: 3.9 $mmol_c\ kg^{-1}$) for the same six sites.

4.5 Spatial Gradient

Two significant spatial relationships were found at the 1.0 – 20.0 km scale of this study, namely soluble SO_4^{2-} and ANC, both in the subsoils of the 2006 soils. It is interesting that both the significant spatial relationships were found only in the subsoils. No significant spatial relationships were found between soil chemical properties and distance from the power station for the topsoils. The data shows that although the concentration of Ca^{2+}, Mg^{2+} and $H^{+}$is higher in the topsoils, the ECEC is not significantly different

between the topsoils and the subsoils, and this can be attributed to the higher concentration of Al^{3+} in the subsoils than the topsoils. The pH (K_2SO_4) is also lower in the subsoils, and these two factors are a sign that the subsoils are more acidic than the topsoils. This is also reflected in the ratio between basic and acidic cations between the topsoils and the subsoils for the 2006 soils. The topsoils show a basic cation to acidic ratio of 1:5, while for the subsoils, this is closer to 1:9. It is therefore likely that the significant spatial relationships found for soluble SO_4^{2-} and ANC, and distance from the power station for the subsoils is linked to the increased acidity of the subsoils relative to the topsoils.

Certain soil properties were found to be linked at site 7, situated approximately 8.1 km in a north-easterly direction downwind from the power station. The concentration of H^+ and extractable Al^{3+} was the lowest in both the topsoils and the subsoils at this site. This can be linked to the soil pH, since pH (K_2SO_4) was the highest in the topsoils and one of the highest in the subsoils at this site, meaning that the soils were the least acidic at this site. Similarly, this trend was found in the sulphur content of the soils, since the lowest total sulphur content for both the topsoils and the subsoils, as well as for the extractable SO_4^{2-} content in the topsoils was found at this site. Total nitrogen was also found to be lowest in the topsoils, while the concentration of NH_4^+ was lowest in the subsoils at site 7. Neither soil texture nor the soil moisture content of the soils were significantly different at this site when compared to the other sites.

These findings indicate that there is decrease in the concentration of acidic soil properties at approximately 8 km from the power station which could possibly be as a result of lowered deposition of acidic components at this site. However, this disagrees with other studies that have indicated that the greatest environmental impact from power generation appears to be within 10.0 km to 15.0 km from the source (Freedman and Hutchinson 1980; Annegarn *et al.* 1996; Ek *et al.* 2001).

An investigation of the prevalent winds in the vicinity of the Arnot power station shows that winds are predominantly north-westerly to northerly and south-easterly. The winds

are seldom from the south-west and therefore atmospheric deposition at site 7 should be lower than other sites. However, wet deposition should be uniform across the extent of the study area and the differences in deposition may not be the only reason for the lowered concentrations of acidic soil properties at site 7. However, the data from this study do not allow any strong conclusions to be drawn and further investigations would be needed in order to explain the large differences found at this site.

If a larger spatial gradient was incorporated into this study, more trends that are significant may have become apparent as pollutants may be transported over large spatial gradients, according to conventional distance models. Trajectory modelling, deposition fields and the use of stable isotopes to identify the source of pollutants all have the potential to give a broader understanding of these spatial gradients. Since air pollutants are able to be transported over a large spatial gradient, the assumption of low background pollution levels in the vicinity of the Arnot power station may not hold since the potential transportation of pollutants into the area from other highly polluted regions such as Witbank and Middelburg may be significant. This could be investigated through the use of detailed trajectory and dispersion modelling for pollutants from these areas and would be a necessary next step in this line of research.

5. Conclusion

The study indicates that long-term acidic deposition has led to detectable changes in soil chemical properties, regardless of whether the original 1996 data or the re-tested 1996 soils data are used for the comparison between the baseline study and the soils collected and analysed in 2006. However, the re-tested soils, labelled as 1996/1 are considered more representative of the changes in the soil chemical properties since these were tested using identical laboratory methods as the 2006 soils. Five important soil chemical properties, namely pH (K_2SO_4), the concentration of hydrogen (H^+) and extractable aluminium (Al^{3+}), total sulphur and extractable SO_4^{2-} indicate that atmospheric deposition in the vicinity of the Arnot power station appears to have significantly acidified the soils in the region during the ten year period from 1996 to 2006. There is an

indication that distance from the power station may be important in more acidic soils. It appears that the increased acidity of the subsoils relative to the topsoils was responsible for the significant spatial relationships found between soluble SO_4^{2-} and ANC and distance from the power station. There was also an indication that at approximately 8.0 km from the power station there is a reduction in the acidic components of atmospheric deposition. This finding however needs further investigation. This research will form part of a database for other long-term monitoring programmes and will allow data to be compared to other data from this area of research. It will also provide information to important industry leaders such as Eskom.

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Chapter 4: General Discussion

In order to answer the key questions and hypotheses for this research, the re-tested 1996/1 soils were used as a comparison to the 2006 soils.

Key Questions

i) How has the concentration of base cations (calcium, magnesium and ECEC) changed since the baseline study in both the topsoils and the subsoils and is there a relationship with distance from the power station?

The concentration of Ca^{2+} and Mg^{2+} has significantly increased since the baseline study in both the topsoils and the subsoils, while the ECEC has significantly increased in the subsoils only. No significant spatial relationship was found for these soil chemical properties.

ii) What is the change in the concentration of aluminium in the soil since 1996 in both the topsoils and the subsoils and how is this related to distance from the power station?

A significant increase in the concentration of extractable Al^{3+} was found in both the topsoils and the subsoils since the baseline study; however, no significant spatial relationship was identified.

iii) How does the concentration of sulphur (total sulphur, extractable sulphate and soluble sulphate) change with distance from the power station and does this differ between the topsoils and the subsoils?

Only one significant spatial relationship for sulphur was found, namely soluble SO_4^{2-} in the subsoils, which showed a significant negative relationship with distance from the power station. The concentration of total sulphur has significantly increased in both the

topsoils and the subsoils, extractable SO_4^{2-} showed a significant increase in the topsoils and soluble SO_4^{2-} showed a significant increase in the subsoils. However, at site 7, situated approximately 8.1 km downwind from the power station, the concentration of total sulphur was lowest in both the topsoils and the subsoils, while extractable sulphate was lowest in the topsoils.

iv) How has the acidity of the soils changed at each of the sites since the baseline study? This will be analysed for both the topsoils and the subsoils and will be determined by analysing soil pH, extractable acidity, acid neutralising capacity (ANC) and acid saturation.

There was a significant decrease in the soil pH (K_2SO_4) in both the topsoils and the subsoils, indicating that the soils have become more acidic. Extractable acidity, as determined by the concentration of H^+ in the soil, showed a significant increase in both the topsoils and the subsoils, while the ANC showed a significant decrease in the subsoils. There was no significant change in acid saturation since the baseline study. A significant positive relationship was found between the ANC in the subsoils and distance from the power station.

v) What is the change in the concentration of soluble NH_4^+ and NO_3^- since the baseline study and what is the relationship with distance?

Soluble NH_4^+ showed a significant decrease since the baseline study in both the topsoils (34 %) and the subsoils (80 %). However, no significant change was found in the concentration of soluble NO_3^-. Neither of these two soil chemical properties showed a significant spatial relationship.

Hypotheses

Hypotheses were formulated based on the distance from the power station, sampling depth and the long-term changes in soil properties. The following hypotheses were tested:

1. The greatest total sulphur and therefore sulphate levels in the soil are found within 10 km of the power station.

The greatest concentration of total sulphur in both the topsoils and the subsoils, extractable SO_4^{2-} in the topsoils and soluble SO_4^{2-} in the subsoils were all greatest within 10 km from the power station and this hypothesis therefore appears to be supported. However, the lowest concentration of total sulphur in both the topsoils and the subsoils as well as the extractable SO_4^{2-} concentration in the topsoils was found at site 7, situated 8.1 km from the power station.

2. The concentration of extractable aluminium has increased while the concentration of exchangeable base cations, specifically calcium and magnesium has decreased at all sites and across both soil depths as a result of prolonged atmospheric deposition.

The concentration of extractable Al^{3+} did significantly increase in both the topsoil and the subsoils as indicated by the six sites that were investigated; however, the concentration of Ca^{2+} and Mg^{2+} also showed a significant increase in both the topsoil and the subsoils since the baseline study. This may be due to the deposition of base cations from fly ash. However, the overriding acidic cation components in the soil resulted in the soils becoming more acidic.

3. The soil pH has decreased at all the sites due to increased soil acidification.

The soil pH (K_2SO_4) did show a significant decrease since the baseline study and has resulted in the soils becoming more acidic.

Recommendations

This study could have been improved buy including work on stable isotopes in order to identify the source of the pollution since not all the pollution can be attributed to the power station and may come from other sources such as vehicle emissions, biomass burning and windborne dust. Investigating the pollution over a larger spatial gradient may highlight more relationships that are significant since according to conventional distance model predictions, pollutants may be transported over large spatial gradients.

Long-term monitoring is key to understanding the impacts of acid deposition on an ecosystem and further monitoring at these same sites would allow interesting and worthwhile comparisons in order to better understand the effects and impacts of acid deposition.

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