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THE NITROGEN AND SULFUR STATUS AND ISOTOPES OF SOILS WITHIN THE VICINITY OF A COAL-FIRED POWER STATION IN SOUTH AFRICA

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0401554T

A dissertation submitted to the Faculty of Science, University of Witwatersrand, in fulfilment of the requirements for the degree of Masters of Science

Johannesburg, 2012

DECLARATION

I declare that this dissertation is my own, unaided work. It is submitted for the degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any other degree or examination at any other university.



29th day of March 2012 in Witbank, South Africa

ABSTRACT

Amplified loads of sulfate and nitrate have caused increased stress on soil systems in many areas of the world, as both are dominant components of acid rain. This is a critical environmental stress due to the damage caused to soil, water quality and ecosystem functioning. Issues concerning the rising emissions of these elements from local industries have begun to attract increasing attention in South Africa, as the rates of deposition in the Mpumalanga Highveld region alone is comparable to those experienced in First World countries. This study sought to investigate the use of natural stable isotopes of sulfur and nitrogen to identify the process transformations that these species undergo in environmental cycles. Total $\delta^{34}S$, $\delta^{15}N$ and $\delta^{13}C$ isotope signature of soils in the Mpumalanga region were combined with total elemental concentrations to determine the effect of deposition on the soil system. Soil samples from two soil depths (0 – 10 cm and 20 – 40 cm) were taken along a distance gradient from an identified pollution source, the Majuba power station. Long-term air quality data from the study area were also obtained from Eskom's air quality monitoring stations, as well as sulfur and nitrogen deposition data from selected literature.

Elemental concentrations decreased with soil depth as expected, while sites located approximately 25 km downwind of the power station were seen to contain higher concentrations of both soil sulfur and nitrogen. The mean per site soil sulfur concentration across all depths ranged from 0.009 % to 0.048 %, while the mean per site nitrogen concentration across all depths ranged from 0.056 % to 0.346 %. The mean soil carbon concentration in the top-soils ranged from 0.97 % to 7.93 %, and decreased in the sub-soils to 0.490 % to 3.270 %.The mean $\delta^{34}S$ value for the top-soils was found to be 8.28 ‰ and increased to 10.78 ‰ in the sub-soils. Soil $\delta^{15}N$ also increased with soil depth from 6.55 ‰ to 8.28 ‰. Soil $\delta^{13}C$ values were seen to increase from -12.83 ‰ in the top-soils to -11.90 ‰ in the sub-soils. Lighter $\delta^{34}S$ values at the surface may be due to anthropogenic deposition. The positive $\delta^{34}S$ shift was attributed to a two-source mixing model (atmospheric deposition and bedrock) and isotopic fractionation processes that occur within the soil profile. The $\delta^{15}N$ values of the top-soil were higher than what is expected if all nitrogen was derived from atmospheric nitrogen gas fixation. The increase in $\delta^{15}N$ with depth suggested that isotope fractionation occurred during nitrogen export due to the faster reaction rate of ^{14}N compared to ^{15}N. The soil $\delta^{13}C$ values indicated a typical C4 grassland system. New carbon at the top-soil depths was enriched in ^{13}C due to the slower decay of ^{13}C-depleted lignin; whereas in the sub-soils microbial recycling of carbon dominates and explained the higher ^{13}C content of the older carbon. The conceptual framework presented for this project involves simultaneous processes of deposition and export in the soil system. This was particularly true for sulfur, where sites with lower isotope values had lower soil sulfur concentrations and vice versa.

This indicates that high levels of deposition correspond to high net export. The sulfur and nitrogen isotopic signatures could not be used to as a direct means of source identification; however, the effectiveness of isotopes in elucidating transfer of these nutrients in the soil system was illustrated.

DEDICATION

I dedicate this project to my students: past, present and future. You have taught me that intelligence is not a final destination but a life long journey.

"…To strive, to seek, to find, and not to yield."

Alfred Lord Tennyson

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1 INTRODUCTION

Increased human activity including the combustion of fossil fuels has enhanced the rate and transformation of natural processes. Petrochemical refineries, the combustion of coal by power stations and the increasing numbers of vehicles on the road, have caused increasing amounts of sulfur (S) and nitrogen (N) to be released into the atmosphere. Species of these two elements are emitted via a pollution plume and 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. This is a critical environmental stress (Driscoll *et al.,* 2001) due to the damage caused to soil, water quality and ecosystem functioning. This damage can have considerable economic consequences. The decreasing water quality impacts on industrial and domestic use, which causes water demand and treatment costs to rise. Issues concerning the rising emissions of S and N from local industries have begun to attract increasing attention in South Africa. In the Mpumalanga Highveld region alone, the mass of deposition of atmospheric loads of sulfur oxides (SO_x) and nitrogen oxide (NO_x) species per unit area of land is comparable to those experienced in First World countries (Tyson *et al.,* 1988). Moreover, atmospheric transfer models that have been used to calculate transfer and deposition of sulfur (using emissions for 1990 and a projection for 2050) have shown increasing soil acidification risk in South Africa (Van Tienhoven *et al.,* 1995; Kuylenstierna *et al.,* 2001). This is due to the location of power stations and petrochemical plants, proximity to large coal reserves and being under the influence of unique air circulation patterns resulting in the pollutants being trapped (Tyson *et al.,* 1988). The fate of these emitted pollutants and their effect on the soil-water system is still unclear and potential exists to fill the necessary knowledge gaps of the South African situation. The occurrence of natural stable isotopes of S, N and oxygen in sulfate (SO_4^{-2}) and nitrate (NO_3^-) can be used to identify the sources of S and N as well as process transformations in environmental cycles. Specific sources and transformation pathways often yield identifiable signatures compromising the relative abundance and occurrence of species in relation to one another (Dawson *et al.,* 2002). Identifying sources of S and N input and processes affecting their export from an ecosystem are critical in determining the extent of nutrient cycling locally and for global cycles. In addition, carbon (C) isotopes can also be utilized in conjunction with S and N, as the fractionation of C isotopes that occurs during ecosystem processes makes C stable isotopes an ideal tool in understanding terrestrial ecosystem pathways (Balesdent and Mariotti, 1996).

This project aims to quantify S, N and C isotopes in order to better understand nutrient cycles in grassland ecosystems receiving S and N inputs via deposition. The implementation of isotopic analysis of S and N compounds in South Africa could indeed broaden our understanding of the use of

stable isotopes in discriminating between various pollution sources and whether this is an avenue for future research. At present, the expertise required to carry out such an investigation is not yet readily available in South Africa. This project contributes to building the expertise that is currently lacking and adds to the technological advancements made in the field of environmental science.

2 AIMS AND OBJECTIVES

The main aim of this study was to obtain a baseline of the total $\delta^{34}S$ and $\delta^{15}N$ isotope signature of soils in the Mpumalanga region. Soil $\delta^{13}C$ values were also determined, in order to better understand the S and N data. This study combined the measurements of total elemental concentrations in the soil system, as well as isotopic measurements of S, N and C to determine the effect of deposition on the soil system in the Mpumalanga Highveld, South Africa.

Air quality data from air quality stations around the Majuba Power station in Mpumalanga as well as S and N rates of deposition were also assessed in conjunction with the soil isotope and elemental data. This aided in evaluating the effect of these pollutants on the soil system.

Additional, this project also aimed to provide a screening set of samples and analysis in order to illustrate the effectiveness of isotopes in documenting transformations of S, N and C in the soil system. By doing so, this study will aid in elucidating which of the many species of S and N are worth further investigating by means of isotopic analysis.

This project is part of a much larger deposition project currently being carried out by the University of KwaZulu-Natal, University of the Witwatersrand, Airshed Planning Professionals and Umfula Wempilo Consulting, aimed at evaluating the impacts of acid deposition on soil and water quality in the Mpumalanga region. This project is funded by Sasol and Eskom. The larger-funded project aspires to assess the magnitudes of atmospheric deposition over the Eastern regions of South Africa, to investigate the processes and paths by which S and N pollutants move through the environment and to evaluate the damage that has been caused by these pollutants to date. It is envisioned that if the potential impact of atmospheric deposition can be forecast, management measures can be implemented in time to avert possible substantial damage.

The objectives of this study were:

1. to obtain $\delta^{34}S$, $\delta^{15}N$ and $\delta^{13}C$ isotope measurements of soils in the region of the Majuba Power Station in Mpumalanga, South Africa, and
2. to compare these isotope measurements with soil S, N and C concentrations along a gradient from a known pollutant source

Key questions addressed in connection with the proposed objectives were:

1. What is the $\delta^{34}S$ signal and concentration of total soil S with increasing distance from an identified pollution source, the Majuba Power Station?
2. What is the $\delta^{15}N$ signal and concentration of total soil N with increasing distance from an identified pollution source, the Majuba Power Station?
3. What is the $\delta^{13}C$ signal and concentration of total soil C with increasing distance from an identified pollution source, the Majuba Power Station?
4. How are $\delta^{34}S$, $\delta^{15}N$ and $\delta^{13}C$ isotope measurements of soils and elemental concentrations of the nutrients correlated?
5. How do the isotopic ratios compare with potential source ratios in the published literature and is it possible to identify sources of S and N in the Mpumalanga region?

3 LITERATURE REVIEW

3.1 THE EMISSION OF SO_X AND NO_X FROM COAL BURNING POWER STATIONS

Mankind is living in a world totally dependent on electricity. In many countries electricity production is provided by coal burning power stations, and for many years coal has been the only fuel for raising steam (England, 1979). Even today, coal burning accounts for approximately 36 % of the world's electricity production (Eskom, 2006), however, in providing economical and reliable supplies of electricity, mankind must be aware of the detrimental effects our activities have on the environment.

Coal contains hydrogen-rich compounds, which can be burnt in oxygen to release energy. However, in doing so reduced S and N compounds that are present as impurities in the coal are also oxidized to acidic forms (Kennedy, 1986). These waste products are discharged into the atmosphere, where they are transported across a region by atmospheric circulation before being re-deposited on the land surface. It is the emission, production and deposition of these oxides that are of most concern. Sulfur and N compounds fulfil similar biological and chemical roles in the biosphere. They are important oxidation and reduction agents, providing energy for growth; both S and N are contained in amino acids and in structural components of cells, where they form conspicuous elements of the nucleic acids (Kennedy, 1986). Since S and N are so prominent in the metabolism and structure of all life forms, it is not surprising that they are also involved in the utilization of fossilized biological materials such as coal, oil and natural gas. The combustion of these fossil fuels has therefore resulted in an alteration of the S and N cycles. Gains and losses of particular forms of S and N in a particular locality can strongly affect the local balance of rates of interconversion of substances. The addition of excess S and N to the environment can thus drastically change the rate of one phase of an environmental cycle and can certainly introduce a temporary imbalance (Kennedy, 1986). This may ultimately lead to significant ecosystem degradation, especially of vulnerable ecosystems unable to restore the natural balance.

Power stations and industrial operations release SO_2 into the atmosphere where it is oxidized to form SO_4^{-2}. Once formed, sulfur-oxide pollutants (SO_x) may be dispersed thousands of kilometres from their source. Sulfur oxide pathways are dependent on topography, meteorology and the rate of conversion of SO_2, which can vary from 1 % to 4 % per hour. Depending on atmospheric moisture, up to 80 % of emitted SO_2 can be oxidized to SO_4^{-2} (Scorgie, 2006). Sulfate is the precursor of sulfuric acid (H_2SO_4), an important component of acid rain. Fossil fuel combustion also produces nitrogen oxides (NO and NO_2, together denoted as NO_x). Nitric oxide (NO) is first oxidized in the presence of O_2 to nitrogen dioxide (NO_2) within a few seconds, and then to nitric acid (HNO_3) and NO_3^- particles

(Lovett, 1992; Webb and Hunter, 1998). Nitrate oxides are important because of their potential to produce acid deposition and because they act 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). A number of sources contribute to NO emissions, however, overall 80 % or more of all NO emissions globally are human-caused (Vitousek *et al.*, 1997). Thus, the transformation of SO_x and NO_x into H_2SO_4 and NO_3, constitute the basis of the acid rain and soil acidification phenomena that are causing increasing impacts on vulnerable ecosystems.

Dispersion by atmospheric turbulence enables the plume from the stationary source to mix with surrounding clean air carrying oxidants which transform the major primary pollutants (SO_2 and NO) into secondary pollutants (SO_4^{-2} and NO_2, NO_3^- etc.). Dispersion may even bring an elevated plume down to ground where some of the pollutants may undergo gradual deposition because of sedimentation, impaction or chemical adsorption - a process known as *dry* deposition (Smith, 1989). Dispersion is also partially responsible for drawing pollution into precipitating clouds, where through numerous processes it may finally be removed by a process known as *wet* deposition. Wet deposition was modelled and was found to contribute between 50 % and 70 % of the total global SO_x deposition (Blight *et al.,* 2009). The relative importance of wet and dry deposition for removal of NO_x varies significantly among models, with globally between 40 % and 70 % of NO_x removed by wet deposition (Blight *et al.,* 2009).

3.2 IMPACTS OF ACID DEPOSITION

One of the major concerns of fossil fuel burning is the release of gases into the atmosphere that not only have negative effects on air quality but extended effects on the biosphere and the important systems that it encompasses. These effects include damage to aquatic and terrestrial ecosystems, human health and corrosion of engineering material and global climate change (Rhode *et al.,* 1995). Coal fired power plants are notoriously known for the high levels of air pollutants released per unit of power they generate. A comparison of emissions factors (pounds of emissions per megawatt hour of power generation) based on 2004 data reveal that the average coal fired power plant emits more than twelve times as much sulfur dioxide (SO_2) and 6 times as much nitrogen dioxide (NO_2) as the average non-coal fired power plant (Kahn, 2008). It is also widely known that ambient pollution levels are higher in countries with coal-fired power plants (Levy *et al.,* 2002a).

A great deal is known about the presence of pollutants within the fuel and their behaviour in the industrial plant, and a reasonable working knowledge of the diffusion process in the atmosphere does exist. However, there is a need for a more objective knowledge about the impacts caused by these pollutants when they reach the lower atmosphere and the biosphere (Clarke, 1979). In order to implement effective control standards it is crucial that a broader knowledge of the actual impacts that the flue-gases released cause in the environment is acquired, so that appropriate methods for monitoring and mitigation can be effectively way.

Acid deposition is deposition of acidifying compounds, dissolved either in precipitation (also known as acid rain) or directly in "dry" form (Slanina and Davis, 2008). Both the precursors (SO_2, NO_x, and ammonia (NH_3)) and the products (H_2SO_4, HNO_3 and ammonium (NH_4^+)) of acid forming species can be transported over large distances (up to 1,500 km) depending on meteorological conditions, speed of conversion, and removal by deposition processes (Slanina and Davis, 2008). Acid deposition is a critical environmental stress that undermines the integrity of the ecosystem on which it is deposited (Brodin and Kuylenstierna, 1992, Bobbink and Reolofs, 1995; Fenn *et al.*, 2003). 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 (H) , S, N, calcium (Ca), magnesium (Mg) and aluminium (Al) (Driscoll *et al.,* 2001). In industrial regions, acid deposition has caused excessive nutrient concentrations in soils and can result in water pollution problems known as eutrophication. Nitrate and NH_4^+ are essential, for development in vegetation, but in concentrations that are too high, these species lead to a diversity loss, especially in oligotrophic ecosystems adapted to low nutrient availability (Stevens *et al.,* 2004, Slanina and Davis, 2008).

Processes that lead to soil acidification include those that lead to an increase in the number of negative charges and acidic cations in the soil, such as the accumulation of organic matter, clay formation, and the removal of basic cations (Reuss and Johnson, 1986). The loss of base cations from the soil may be due to plant uptake or to leaching. Loss of cations, by leaching from the soil, can only occur if there is an associated mobile anion (Reuss and Johnson, 1986). Under acidic conditions, these anions include NO_3^- and SO_4^{-2} from atmospheric deposition. It has been shown that increased inputs of SO_4^{-2} accelerate leaching of acidic cations (H^+ and $A1^{3+}$), base cations (potassium (K^+), sodium (Na^+, calcium (Ca^{2+}) and magnesium (Mg^{2+})), and nutrient elements and subsequently acidify terrestrial and aquatic systems (e.g. Richter *et al.,* 1983; Reuss and Johnson, 1986).

3.3 THE MAJOR BIOGEOCHEMICAL CYCLES

3.3.1 The sulfur system

3.3.1.1 Emissions

Natural emissions of S to the atmosphere include biogenic sources, sea spray, volcanic emissions, biomass burning and wind-raised dust. The magnitudes of all natural sources are highly uncertain and exhibit high spatial and temporal variability. Estimates of global anthropogenic S emissions range from 60 to 110 Tg (S) yr^{-1} (2 to 3 T.mol.yr^{-1}) for the years 1976 to 1985 (Möller, 1984; Hameed and Dignon, 1988), comparable to but probably somewhat larger than natural emissions (excluding sea salt spray). The combustion of fossil fuels accounts for 80 to 85 % of the total anthropogenic S emissions, with the remainder originating from the smelting of ores and other industrial processes and burning (Howarth *et al.,* 1992). Evidence is accumulating that ambient S concentrations and deposition are decreasing in Western Europe (Leck and Rodhe, 1989; Mylona, 1989) and in North America (Dillon *et al.,* 1988). However, emissions from Asia, South America, and Africa may well increase dramatically (Galloway, 1989). From 1990 to the year 2000, S emissions in Europe fell by about 37 % and in the USA by about 17 %, but in China over the same period emissions increased by about 30 % (Kuylenstierna *et al.,* 2001).

3.3.1.2 Transport and transformations

Sulfur dioxide, the gaseous precursor of the SO_4^{-2} aerosol, is released as a result of anthropogenic activity (fossil fuel and biomass burning) and from natural sources (volcanic gases and dimethyl sulfide) (Penner *et al.,* 2001). Other species emitted from natural sources include hydrogen sulfide, dimethyl sulfide, dimethyl disulfide, carbonyl sulfide, carbon disulfide and methyl mercaptain. The reduced S compounds undergo oxidation in the atmosphere to SO_2. The expected atmospheric residence time of most (primary) species is a day or less. Sulfur dioxide undergoes oxidation in the gas phase, primarily with the hydroxyl radical, on the surface of particles, or in precipitation elements, through oxidation with the peroxyl radical or ozone, or in the presence of metal catalysts. The product in all cases is the SO_4^{-2} form either in particles or in cloud and precipitation droplets. Residence times for these various S species in the atmosphere vary depending on the chemical and meteorological regime in the region of the world in question. The chemical form in which S exists in the atmosphere has a significant influence on the efficiency with which it is removed to the surface of the earth (Whelpdale, 1992; Penner *et al.,* 2001).

Sulfur constituents in the atmosphere can be brought to the surface by a variety of processes. Gases, such as SO_2, can dissolve in cloud and raindrops or adsorb on to frozen precipitation elements. Sulfate particles are efficient condensation nuclei and are incorporated into precipitation by nucleation

or as a result of scavenging by cloud droplets and falling drops. The efficiency of wet removal of S species depends on the form (SO_4^{-2} is more efficiently removed than SO_2), and on the characteristics of the precipitation in a given location (Stewart and Howarth, 1992). Those deposition processes, which do not involve precipitation, are collectively termed dry deposition. Particles larger than about 10 μm in diameter may be removed by gravitational sedimentation. Smaller particles and gases, however, are more efficiently brought to the near-surface region by turbulent atmospheric motions, where they may subsequently be brought into contact with surface elements by molecular-scale processes. Actual uptake is accomplished by chemical reaction, dissolution, adsorption, etc. Sulfur dioxide is dry deposited more efficiently than particulate SO_4^{-2} because it is more readily taken up at the surface location (Stewart and Howarth, 1992).

3.3.1.3 The influence of acid deposition on soil sulfur cycling

Much consideration has been given to the influence of acid deposition on S cycling. In many soils, SO_4^{-2} is the most abundant divalent anion and is often the most abundant anion of any charge. As such, its abundance can influence the movement and adsorption of basic and acidic cations. In reducing environments, sulfides and polysulfides precipitate and complex with a variety of metals, often controlling the chemistry of the metals. Indirectly, precipitation of metal sulfides can control the availability of other elements, such as phosphorus (Stewart and Howarth, 1992). The extent of atmospheric SO_4^{-2} retention in the soil is of the utmost importance to cationic nutrient transport, acidification processes, and aluminium mobilization. The cation leaching effects of SO_4^{-2} are controlled by biological and sorption processes. As defined by Prenzel and Meiwes (1994), SO_4^{-2} sorption is the process of reversibly storing both S and acidity in the soil matrix, thereby delaying and adjusting the acidification of the soil solution. Sposito (1989), defined sorption as the solid retention of SO_4^{-2} that can be recovered by desorption with the addition of water and/or exchangeable anions. Kinetically, the adsorption of SO_4^{-2} is very rapid (Zhang *et al.,* 1987; Curtin and Syers 1990a) with nearly complete adsorption in minutes (Sparks, 2000). Following rapid sorption, additional removal of SO_4^{-2} from solution continues at a very low rate, perhaps due to diffusive penetration of the SO_4^{-2} into solid particles (Barrow, 1985), precipitation of aluminium sulfate compound(s) (Nordstorm, 1982; Khanna *et al.,* 1986), or microbial immobilization **(**Freney *et al.,* 1971).

Sulfate sorption reduces the ability of atmospheric inputs of S to cause the leaching of ions from the soil solution by reducing the concentration of SO_4^{-2} in the soil solution (Singh and Johnson, 1986; Inskeep 1989). When a soil is subjected to acid deposition the concentration of SO_4^{-2} in the soil solution increases. Since adsorption is concentration dependent, adsorption will also increase. Thus, sorption and biological processes can delay the cation leaching effects. Other factors such as soil pH, clay type, SO_4^{-2} residence time in the soil, anion competition and the presence of oxides of Fe and Al

can also influence the degree of adsorption (Fey and Guy, 1993; Tabatabai, 2005). Sulfate may be retained in the soil by sorption to amorphous oxides and hydroxides of aluminium (Al) and iron (Fe) (Abrahamsen 1984; Van Stempvoort *et al.,* 1990). In aerated acidic forest soils, mobilization mechanisms include the conversion of organic soil S to inorganic forms under aerated conditions, a process that is referred to as mineralization (David and Mitchell, 1987). In forest floor and humic mineral soils, the decomposition of both major forms of organic S, the mineralization of carbon-bonded S and the hydrolysis of organic SO_4^{-2}, are microbially mediated (Mayer *et al.,* 1995). Sulfate can be immobilized in the soil if it is incorporated into organic matter, however, adsorption may be a more important process than biological immobilization (Reuss and Johnson, 1986). An understanding of the capacity of a soil to adsorb and retain SO_4^{-2} is important for determining the effect of acid deposition on a given ecosystem (Singh and Johnson, 1986; Comfort *et al.,* 1992).

In the subsoil, desorption can supply SO_4^{-2} to the soil solution (Figure *1*) (Mitchell *et al.,* 1998). This process is dependent upon the degree to which the soil has previously adsorbed SO_4^{-2}, the concentration of SO_4^{-2} in incoming solutions relative to the concentration with which the soil was previously equilibrated (Johnson and Todd, 1983), changes in soil pH, and the reversibility of SO_4^{-2} adsorption (Mayer *et al.,* 1995). Sulfur that was previously stored in the soil may be released, which will cause cation leaching and further lead to acidification of soils and adjacent water bodies.

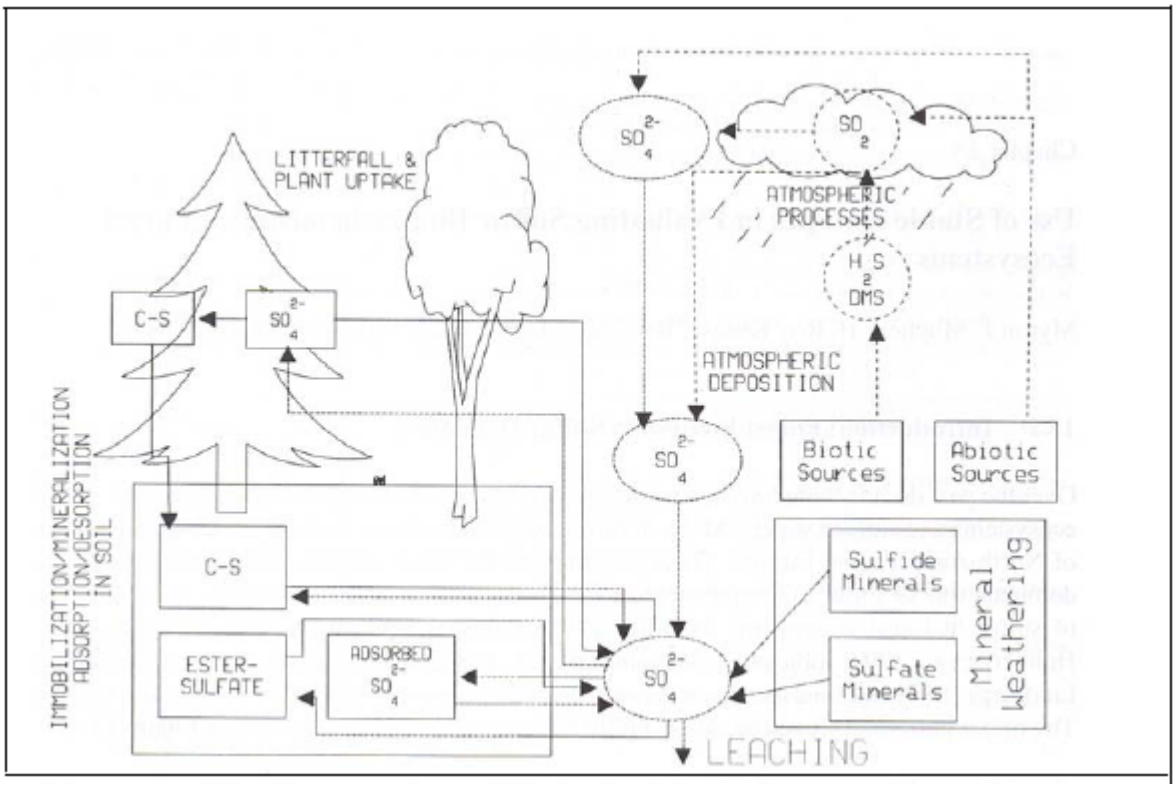


Figure 1: Schematic representation of the S cycle affecting S isotope composition (Mitchell *et al.*, 1998).

3.3.2 The nitrogen system

The biosphere contains a complex mixture of N compounds. The large number of compounds with different physical and chemical properties makes the picture for N flows and conversions very complex and variable. Although N is an element that is abundant on earth, only a very small proportion of it enters into the biogeochemical N cycle at significant rates. The unavailability of the 99.96 % occurring as N gas, combined with the major role played by N-containing substances in all forms of life, has caused N to be one of the key elements limiting the primary production on which humans depends for food, fodder, fibre, and fuel (Rosswall, 1981).

The high energy required to break the N-N bond and the inability of most living species to utilize molecular N results in a high demand for already fixed forms of this essential element. Ecological systems are therefore, to a great extent, adapted to the recycling of the more easily available forms. Globally, 90 – 97 % of the N content of net primary production of plant biomass derives from the recycling of forms other than N_2, leaving only about 3-10 % as annually fixed from the molecular N pool (Eriksson and Rosswall, 1976).

3.3.2.1 Nitrogen components

Nitrogen is present in the environment in a wide variety of chemical forms including organic N, NH_4^+, NO_3^-, nitrous oxide (N_2O), NO or inorganic nitrogen gas (N_2). Organic N may be in the form of a living organism, humus or in the intermediate products of organic matter decomposition.

Atmospheric N_2 fixation can occur via various pathways, which include biological fixation, industrial N-fixation (in the manufacturing of fertilizers) and the combustion of fossil fuels (which release various forms of NO_x). On a global scale, a source of major concern is the extent to which human activities have increased the emission of N_2O into the atmosphere (Crutzen, 1972). An increase of 1.00 % in the emission rate of nitrous oxide will cause a 0.20 % decrease in stratospheric ozone, influencing the penetration of ultraviolet light (Crutzen, 1974).

3.3.2.2 Nitrogen deposition and effects on soil nitrogen cycling

The major sink for NO_x in the atmosphere is the oxidation to HNO_3, which readily dissociates into NO_3^- where it can be deposited as wet deposition. Dry deposition can also contribute significant loads of atmospherically derived N to ecosystems as dry gases, such as NH_3 and NO_2 (Kendall *et al.,* 2007). Nitrate is weakly adsorbed onto soils and is readily leached. Ammonium, that is not biologically assimilated, is oxidized by microorganisms to NO_3^- (Figure 2). The nitrification of NH_4^+ is an important contributor of acidity to the soil as H^+ ions are produced (Kennedy, 1986). The form of N

in acid precipitation also influences the amount of acidity generated and effects on cation leaching, as do uptake and leaching processes (Reuss and Johnson, 1986). If leaching occurs in non-N limited systems, especially those subject to anthropogenic inputs, acidification will occur. Leaching of base cations accompanies the leaching of acid anions (Ulrich, 1983). As calcium is depleted, the leaching of toxic inorganic aluminium is increased (Vitousek *et al.,* 1997). Nitrate that leaches through the soils to stream water and groundwater, causes soil mineral depletion, soil acidification and alters downstream freshwater and coastal marine ecosystems (Likens *et al.,* 1996, Nixon *et al,.* 1996).

Concerns have arisen regarding the effects of N deposition on forest health and downstream ecosystems after observations of significant increases in NO_3^- concentrations in some lakes and streams (Grennfelt and Hultberg, 1986; Henriksen and Brakke, 1988; Stoddard, 1994). Numerous experiments have shown that where increased N additions led to increased NO_3^- mobility, the NO_3^- losses also led to losses of nutrient cations and increases in soil and water acidity (McNulty and Aber, 1993; Boxman *et al*., 1995; Emmett *et al.,* 1995). Indeed, increased uptake of N from acid deposition has been suggested as a mechanism of forest decline in North America and Europe (Friendland *et al.*, 1984).

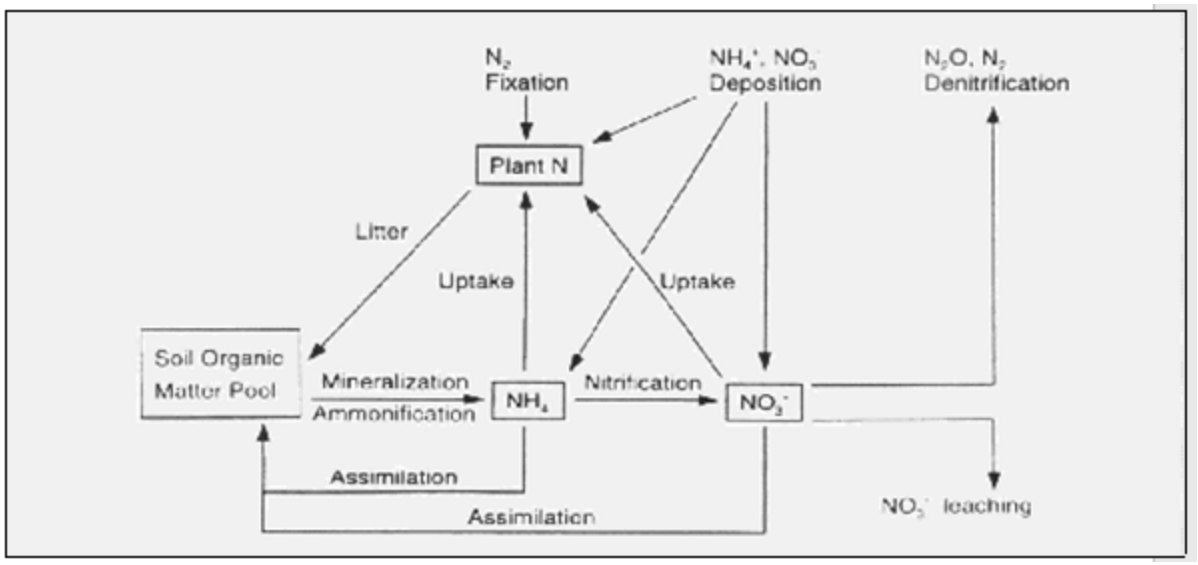


Figure 2: Nitrogen transformations and processes affecting $\delta^{15}N$ vales in forest ecosystems (Nadelhoffer and Fry, 1994).

3.3.3 The carbon system

The reservoirs of C consist of the atmosphere, the terrestrial biosphere (which usually includes freshwater systems and non-living organic material, such as soil C), the oceans and the sediments (which include fossil fuels). Exchanges occur between these reservoirs, because of various chemical, physical, geological, and biological processes. The global C budget is the balance of these exchanges (incomes and losses) between the C reservoirs. Over the past 200 years, humans have introduced ca.

400 petagrams of C (PgC, where 1 petagram = $1x10^{15}$ metric tons) to the atmosphere through deforestation, biomass burning and the burning of fossil fuels (Sabine *et al.,* 2004).

The C cycle is driven by the exchange of C between the land, ocean and atmosphere. The main flux from the atmosphere to the biota is expressed by the primary productivity, and this represents an important link in the C cycle (Ajtay *et al.,* 1979). Primary productivity of an ecological system can be defined as the rate at which radiant energy is stored by photosynthetic and chemosynthetic activity of producer-organisms, chiefly green plants, in the form of organic substances which can be used as food materials (Odum, 1971).

3.3.3.1 Soil organic matter

Soil organic matter (SOM) is a very important component of the C cycle, and accurate data on this reservoir are still lacking in South Africa (du Preez, 2010). The term SOM has been used to encompass all organic materials found in soil (Stevenson, 1994), excluding charcoal (Oades, 1988), or excluding non-decayed plant and animal tissues, their partial decomposition products and the living soil biomass (MacCarthy *et al.*, 1990). More formally, Baldock and Nelson (1998) defined SOM as the sum of all natural and thermally altered biologically derived organic material found in the soil or on the soil surface irrespective of its source, whether it is living or dead, or stage of decomposition, but excluding the above ground portion of living plants.

SOM represents a large organic C reservoir and is the result of a delicate balance between biomass accumulation by photosynthesis and oxidation by respiration. In natural systems soil organic C levels tend towards an equilibrium value, however continued alteration of management and cropping practices create a system where these levels are always in a state of flux (Baldock and Skjemstad, 1999). Loss of soil C, which has been established as the largest terrestrial C reservoir, can be caused by decreased inputs from net primary production, accelerated decomposition, and increased losses from erosion and combustion (Sabine *et al.,* 2004). Indeed, through increased decomposition as a result of clearing and cultivation, soil C content is said to be decreasing in many parts of the world (Ajtay *et al*., 1979). As the impact of mankind on soil C continues to increase, the study of dead organic matter including humus, in the study of biological productivity of natural ecosystems requires further attention.

3.4 THE SOUTH AFRICAN SITUATION

Due to large-scale industrial emissions and agriculture, atmospheric pollution on the South African Highveld is perceived as a concern. Coal fired power stations generate 90 % of the country's electricity, with Eskom (the primary electricity provider) supplying 95 % of the country's needs. The

Mpumalanga Highveld is often referred to as the powerhouse of South Africa (Tyson *et al.,* 1988), due to the large concentration of coal reserves and thus coal fired power stations in the area. Indeed 84 % of South Africa's total coal production originates in the Mpumalanga Highveld (Figure 3) (Mpumalanga DACE 2003). Of the 1.1 Mt of S emitted in southern Africa, 66 % originates in South Africa of which an estimated 90 % is released from the Mpumalanga Highveld (Sivertsen *et al.,* 1995). In a study of the emissions from the Mpumalanga Highveld it was shown that atmospheric pollution emissions are comparable to, if not higher, than emissions from the northern hemisphere power stations (Tyson *et al.,* 1988). Other industrial sources of atmospheric emissions in this region include petrochemical plants, ferro-alloy works, brick works, steel works and fertilizer plants. Domestic fuel burning and vehicle emissions also contribute a small fraction to the emission inventory (Blight *et al.,* 2007). In South Africa anthropogenically induced atmospheric deposition of S and N is large compared to natural export via run-off, and of comparable magnitude to that experienced in first world countries (Blight *et al.,* 2007). The effects of atmospheric pollution on human health, soils, surface waters, forests, agricultural crops and forests have received research attention (e.g. Scholes *et al.,* 1996; Terblanche, 1996). However, substantial gaps exist in the knowledge base of the South African situation.

A study conducted on the long-term effects of air pollution on soil properties near the Arnot Power Station, Mpumalanga, showed that the soils have indeed become more acidic over time (Reid, 2007). In addition, the concentrations of calcium and magnesium in both the top-soils and the sub-soils, as well as the effective cation exchange capacity in the sub-soils showed a significant increase since 1996. Soluble SO_4^{-2} in the sub-soils showed a significant negative relationship with distance from the power station. The concentration of total S has significantly increased in both the top-soils and the sub-soils; extractable SO_4^{-2} showed a significant increase in the top-soils and soluble SO_4^{-2} showed a significant increase in the sub-soils. However, approximately 8.1 km downwind from the power station, the concentration of total S was lowest in both the top-soils and the sub-soils, while extractable $SO_4^{-2}$was lowest in the top-soils. This could possibly be as a result of lowered deposition of acidic components at this site. However, other studies have found 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).

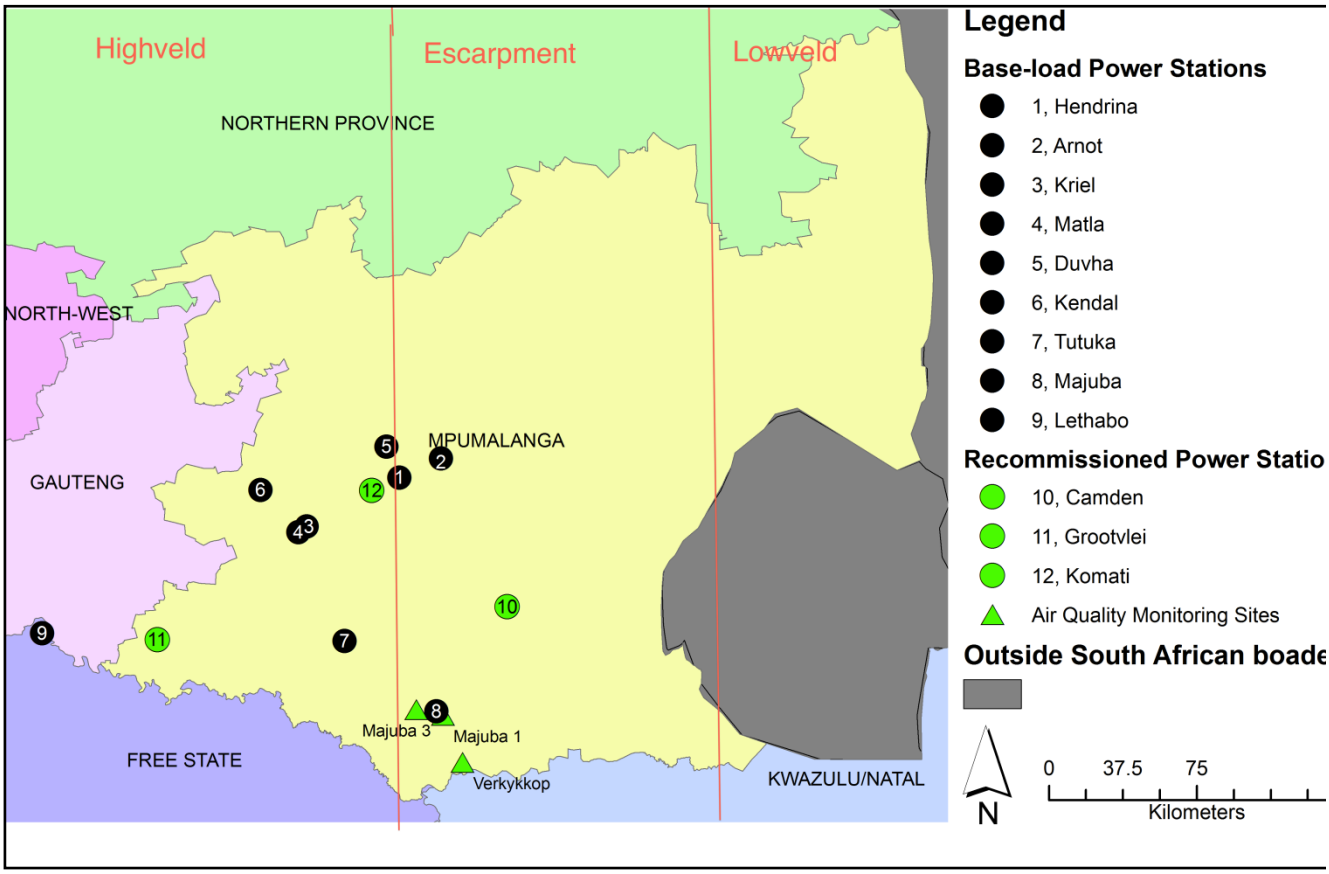


Figure 3. : Location of the 11 base-load power stations within the Mpumalanga Province.

Grasslands

Parts of Mpumalanga fall within the grassland biome, a region where the average annual precipitation is very variable. Shallow soils, high fire frequency and frost limit the distribution of trees. Arid or semi-arid grasslands are fragile ecosystems in which the organic C and N pools are relatively smaller compared with those in some other ecosystems. As a result, these grassland ecosystems are more sensitive to climate change and the disturbances of human activities (Rutherford and Westfall, 1986).

3.5 THE USE OF STABLE ISOTOPES IN ECOLOGICAL STUDIES

Assessing the effects of chronic levels of SO_x and NO_x as well as the consequences of SO_4^{-2} and NO_3^- deposition poses a challenge for environmental scientists. Environmental factors such as the availability of water and nutrients, can affect air pollution absorption and their effects on plants, thereby contributing to the complexity of the problem (Winner and Atkinson, 1986). A wide range of

ecological specialists suggest the use of stable isotopes of S and N to quantify the absorption of SO_x and NO_x from atmospheric sources and to reveal the mechanisms that underlie the effects of acid deposition on S and N systems (e.g. Winner *et al.,* 1989; Dawson, 2002).

Stable isotopes offer tremendous potential for new approaches on research on a wide variety of ecological processes (Rundel *et al.,* 1989). The occurrence of natural stable isotopes of S, N and oxygen in SO_4^{-2} and NO_3^- can be used to identify the sources of S and N as well as process transformations in environmental cycles. Specific sources and transformation pathways often yield identifiable signatures compromising the relative abundance and occurrence of species in relation to one another (Elliott, 2006). Natural differences in the stable isotope composition of biological and abiotic compounds of ecological interest result from differences in a variety of predictable factors that influence fractionation. These include source effects, diffusional constraints, enzyme selectivity, and interactions between compounds (Rundel *et al.,* 1989). Thus, the use of stable isotope investigations can provide new insights into the source and pathways of environmental pollutants, as well as the fluxes between different compartments in the abiotic environment. The use of stable isotope techniques in ecological research has grown steadily during the past two decades. Stable isotope information has provided insights across a range of spatial scales from the cell to the plant community, ecosystem, or region and over temporal scales from seconds to centuries. The elegance of stable isotope methods derives from the fact that the behaviour of stable isotopes in ecological systems and biogeochemical cycles is reasonably well understood owing to the pioneering work of isotope chemists and geochemists (Dawson *et al.,* 2002).

Most elements of biological interest have two or more stable isotopes, with one isotope usually present in far greater abundance. Isotopic composition is measured by determining the ratio of the two most abundant stable isotopes present in the sample (Rundel *et al.,* 1989). Isotope effects are usually small and fractional differences in isotope ratios (δ values) are usually expressed in parts per thousand (‰) relative to a standard. For example, the natural stable S isotope composition of a sample (in ‰) is given as:

$$\delta^{34}S = \left[\frac{\left(\frac{^{34}S}{^{32}S} \right)_{sample}}{\left(\frac{^{34}S}{^{32}S} \right)_{standard}} - 1 \right] \times 1000$$

3.5.1 Sulfur isotopes

The stable isotope abundance determination for S is usually restricted to ^{32}S and ^{34}S, as the ratio of $^{34}S/^{32}S$ reflects the ratio of the two most abundant isotopes (Krouse, 1989). Meteoritic iron sulfide (FeS) has been accepted as an international standard because of its isotopic consistency and composition close to the mean of the terrestrial range (Krouse, 1989; Mook, 2000). A $\delta^{34}S$ value of zero indicates that the sample and meteor reference have the same $\delta^{34}S/^{32}S$ ratios (Winner *et al.,* 1989). Pollutant S can be traced isotopically through the biosphere if it differs in isotopic composition from environmental receptors and subsequent fractionation processes are not extensive (Krouse, 1989). Sources of pollution often have a distinct $\delta^{34}S$ signature, which can be used to follow transect pathways and resistance times of S in terrestrial ecosystems (Krouse *et al.,* 1984). Sulfur isotope data can also indicate whether S has found its way into a given soil horizon from atmospheric fallout or by transportation in solution from subsurface waters (Krouse and Case, 1981). The large variation in $\delta^{34}S$ values between pollutant S and natural plant and soil S has led to the important use of S isotope ratios as tracers of pollutant transfer (Krouse, 1989). In addition, the analysis of stable S isotope distributions can be helpful in documenting the fate of SO_2 in various ecosystems (Winner *et al.,* 1989), as there are distinct isotopic differences between anthropogenic and background S (Krouse, 1987). Isotopic ratios can thus be used as source tracers if the various sources are isotopically different from each other and if changes in isotopic composition during pollution transport and transformation are small. Fortunately, the latter criterion is known to be met, e.g. in the case of S oxidation in the atmosphere (Hitchcock and Black, 1984; Krouse, 1987).

3.5.1.1 Atmospheric sources of sulfur

Sulfur isotope analysis of atmospheric aerosols is a well-established tool for identifying sources of S in the atmosphere, estimating emission factors, and tracing the spread of S from anthropogenic sources through ecosystems. Primary SO_4^{-2} particles, such as sea salt, mineral dust, fly ash or industrial dust are directly emitted with S in the form of SO_4^{-2}. Therefore, the isotopic composition of primary sulfate particles can be interpreted directly as a source signature. Five particle types dominate primary particles: biological particles, mineral dust, industrial dust, resuspended road dust and fly ash. Sulfur in plant tissue mostly reflects the isotopic composition of the atmospheric input (dry and wet deposition); unless other sources such as artificial fertilizer or local geology dominate the S input into soil (Krouse and Grinenko, 1991; Gebauer *et al.*, 1994; Novak *et al.*, 2000, Zhao *et al.*, 2003).

Anthropogenic sulfates exhibit a wide range of $\delta^{34}S$ values, depending on regionally varying sources [combustion, fossil fuel refining, gypsum processing, ore smelting (Table 1) (Nielsen, 1974; Krouse and Grinenko, 1991)]. The $\delta^{34}S$ value of sea spray is approximately 20 ‰; the average of all

volcanic emissions is around 5 ‰ while most of the biogenic emissions are isotopically lighter (Pichlmayer *et al.,* 1998)

Table 1. $\delta^{34}S$ values (‰) for a selection of natural and anthropogenic sources.

Source	Compounds	Mean $\delta^{34}S$ value (‰)	Reference
Sea-spray	SO_4^{-2}	+21	Rees (1970)
Volcanic activity	Total S	+4.7	Lein (1968)
Flue gas from coal combustion		-1 to +3	Nielsen (1974)
Combustion and refining of oil and gas	H_2S	+10	Pankina (1983)

3.5.1.2 Lithospheric sources of sulfur

The entire S contributed to our environment by natural processes and human activity originates from reservoirs in the earth's crust. In many cases, the $\delta^{34}S$ can serve as a 'fingerprint' to identify sources of S and trace its fate in the environment (Nielson *et al*., 1991).

Gypsum ($CaSO_4.2H_2O$) is one of the most common evaporitic minerals occurring in terrestrial, lacustrine and marine sedimentary environments and can be found along most of the hyper-arid coastline from South Africa through to Angola (Watson, 1979). The origin of southern Africa's most extensive gypsum accumulation is still unclear, while Cagle (1975) proposed a bedrock source which could be significant for gypsum in South Africa (Visser, 1963). Bedrock sulfides from the Damaran Orogen have a $\delta^{34}S$ from -4.1 to +13.8 ‰, (mean +4.8 ‰), with average $\delta^{34}S$ isotopic composition for potential source rocks such as the Matchless Amphibolite Belt mean at +8.7 ‰, the Rösing Formation mean at +3.5 ‰ and the Karibib Formation mean at +3.8 ‰ (Shannon and Hugo, 1974; Pirajno *et al*., 1992; Eckardt and Spiro, 1999). Weathering of these sulfides would produce SO_4^{-2} with $\delta^{34}S$ values similar to their source sulfide. Reimer (1986) found South African playa gypsum to have a mean $\delta^{34}S$ of 15.1 ‰, while the S isotopic composition for terrestrial gypsum in the Namib dessert is slightly lower at mean 13.9 ‰ (Eckardt and Spiro, 1999). Gypsum from the organic-rich marine sediments,

acting as a marine atmospheric H_2S proxy, have lighter isotopic S values of -34.8 to -4.5 ‰, which are typical for organic-rich, sulfate-reducing upwelling sediments (Kaplan and Ritterberg, 1964).

Sulfide ores such as pyrite, chalcopyrite, polymetallic and copper-nickel deposits are a major source of anthropogenic S (Grinenko and Grinenko, 1991). The global mean $\delta^{34}S$ value for pyrite-chalcopyrite deposits ranges from -2.0 to +5.0 ‰. The average isotope composition of S compounds released during sulfide ore processing is slightly enriched in ^{34}S and the average $\delta^{34}S$ value has been taken as +3.4 ‰ (Grinenko and Grinenko, 1991).

The extent of S contribution to the environment from the mining and utilization of coal is well known. Although SO_2 is the main form in which S is released into the atmosphere by coal utilization, S may also be introduced into the environment as SO_4^{-2} during the mining of coal or from the weathering of coal stockpiles and waste dumps (Smith and Bates, 1974). Sulfur in coal occurs in several chemical forms, as Fe sulfide, as organic S, as SO_4^{-2} and as elemental S, while pyrite and organic S are the most abundant forms. Mach *et al.* (1999) measured $\delta^{34}S$ ratios of 70 samples of coal from all stratigraphic levels in the Northern Czech Republic, arriving at a mean value of 2.0 ‰. This $\delta^{34}S$ signature of the pollution source differs from $\delta^{34}S$ of the forest floor (3.4 ‰) by only 1.4 ‰. Hortsmann *et al*. (2001) measured ten sulfide concentrates (pyrite) from coal samples from the Witbank coalfield and the results are given below (Table 2). Their study concluded that the source of S in the studied coal was likely to have been a combination of original plant S and ^{34}S depleted S from bacterial reduction of dissolved SO_4^{-2} in (ground) water.

Table 2. Total S concentration (%) and $\delta^{34}S$ (‰) value for South African coal (Horstmann, 2001).

	Total S (%)	**$\delta^{34}S$ (‰)**
Low-S coal	0.9 - 1.1	Pyrite: -30 to +17
Intermediate–S coal	1.8	SO_4^{-2}: –11 to +5.3 Organic S: -2.5 to +4.9

Within-seam variations in the isotopic composition of coal seam components have been firmly established (Smith and Batts, 1974; Price and Shieh, 1979) and according to Smith and Bates (1974), isotopic data for total S in coal cannot be used to assess the isotopic composition of emissions to the

atmosphere due to the numerous fractionation processes that occur. It has been suggested that a more extensive global assessment of the isotopic composition of coals should be undertaken.

3.5.1.3 Sulfate isotopic composition

The large variations in the S isotopic composition ($\delta^{34}S$ values from ca. −50.0 to ca.+30.0 ‰) in the lithosphere, and the additional spatial–temporal dependence of oxygen isotopic composition of precipitation, results in dissolved SO_4^{-2} having a remarkable fingerprint (e.g. Clark and Fritz, 1997). Sulfate isotopic composition has thus been used in many studies to examine the SO_4^{-2} sources and processes affecting its content during the hydrological cycle. An investigation was carried out on the SO_4^{-2} content, as well as $\delta^{34}S$ and $\delta^{18}O$ of dissolved SO_4^{-2} in a crystalline massif located in the Sudety Mountains, Poland, in order to assess the amount of the SO_4^{-2} delivered to the surface and groundwater systems by modern atmospheric precipitation (Szynkiewicz *et al*., 2008). Approximately one third of the SO_4^{-2} delivered to the surface and groundwater by modern precipitation was attributed to anthropogenic pollution. The $\delta^{34}S$ (SO_4^{-2}) values in the precipitation had a small range of variations from 3.27 to 7.6 ‰, with an average of 5.7 ‰. These values were slightly higher, on average by 1.2 ‰, than $\delta^{34}S$ (SO_4^{-2}) values in surface water and groundwater (average 4.6 ‰). These values were in agreement with results for freshwater SO_4^{-2} and suggest that SO_4^{-2}, affected by biological transformation, was probably the most important constituent of sulfate in the catchment under study.

3.5.1.4 The use of sulfur isotopes to document fractionation processes in the sulfur cycle

Chemical and biological isotope fractionation processes cause variations in the natural abundance of S isotopes in the S cycle (Mitchell *et al.,* 1998*).* The former may be extremely slow and therefore difficult to observe, while biological processes are known to accelerate kinetic isotope fractionation (Mitchell *et al.,* 1998). Two processes suspected to cause 'overall' S fractionations are assimilation of S by plants and mineralization of organic S in the soil (Krouse and Grinenko, 1991).

In general, ^{34}S is enriched in sulfate and depleted in sulfide (Kemp and Thode, 1968). This effect is observed during SO_4^{-2} reduction, from S^{6+} to S^{2-}. Indeed, the most important aspect of the S cycle in soils and sediments is the reduction of SO_4^{-2} by microorganisms. In the dissimilatory reduction of SO_4^{-2} to form H_2S with the subsequent oxidation of organic matter, large isotopic fractionation occurs (Jackson and Gough, 1989). It is this primary fractionation process in nature that enables the use of stable isotope ratios to elucidate anthropogenic influences in the S cycle. As S is reduced in anaerobic sediments, H_2S becomes isotopically depleted in ^{34}S, while the residual SO_4^{-2} becomes enriched in ^{34}S (Nielson, 1974).

Soil sorption/desorption of SO_4^{-2} buffers the short-term variation in the concentration of SO_4^{-2} in water draining from soils as well as the isotopic composition of the dissolved SO_4^{-2} (Fuller *et al.,* 1985; Van Stempvoort 1989). If isotope techniques are to be used to trace the effect of SO_4^{-2} deposition, it is essential to examine any fractionation effects. In strongly polluted soils, soil $\delta^{34}S$ values have known to shift by approximately 20 ‰ (Krouse and Case, 1981). However, based on field studies of the upland forest soil B-horizon in the Plastic Lake watershed, Ontario, there was no significant fractionation of S and O isotopes in SO_4^{-2} by soil sorption, including mineral adsorption (Van Stempvoort *et al*., 1990). According to Van Stempvoort *et al.,* (1990) mere adsorption and desorption of inorganic SO_4^{-2} does not cause S isotope fractionation. The $\delta^{34}S$ pattern of inorganic SO_4^{-2} is site-specific because it is controlled by two site- specific processes:

(i) Existence/non-existence of preferential pathways for fast seepage of unaltered atmospheric SO_4^{-2} to deeper soil horizons, and

(ii) Mixing of atmospheric S (primary SO_4^{-2} with newly mineralized organic S (secondary SO_4^{-2})

Van Stempvoort *et al. (*1990) details two-fractionation scenarios for total soil S in unploughed forested sites: the first isotope effect is discrimination of the heavier isotope ^{34}S during assimilation of atmogenic S by spruce; the second biological S isotope shift is caused by mineralization of organic soil S. With increasing soil depth, the older, more mature organic residues become enriched in the heavier isotope whereas the soil water becomes enriched in the lighter isotope, which is preferentially mineralized and removed (Van Stempvoort *et al.,* 1990).

In a study on the isotope compositions of SO_4^{-2} in bulk precipitation near Munich (Germany) and seepage water and soil SO_4^{-2} in acid forest soils representative of southern Germany, similar results were found (Mayer *et al.,* 1995). The $\delta^{34}S$ values of inorganic SO_4^{-2} at the depth of 50-60 cm were nearly identical to the $\delta^{34}S$ values of seepage water SO_4^{-2} from the lysimeters prior to irrigation. This supports findings of Van Stempvoort *et al.* (1990) in the Plastic Lake watershed (Canada), indicating that S isotope fractionation between adsorbed and aqueous SO_4^{-2} in soils is negligible. Laboratory studies using synthesized goethite, an important sulfate-sorbing phase in soils, gave similar results (Mayer *et al.,* 1995). Some SO_4^{-2} $\delta^{34}S$ data from previous studies of soils and organic-poor marine sediments also indicate negligible isotope effects associated with sorption. Thus, biological redox cycling of S remains the only known Earth-surface process that strongly fractionates (>3.0 ‰) S and O isotopes in SO_4^{-2} (Van Stempvoort *et al.,* 1990).

A study by Norman *et al.* (2002) measured S isotope fractionation under conditions approaching gross mineralization. Laboratory incubation–extraction experiments were performed on samples from the Oh and Ah horizons of a Black Forest soil in a catchment near Schluchsee, Germany.

Changes in $\delta^{34}S$ values for SO_4^{-2} extracted every three days with deionized-distilled water over a three week incubation period were found to be small (<1.5 ‰). A second experiment used the addition of dilute ammonium sulfate solution, enriched in ^{34}S relative to soil S, to demonstrate unequivocally that SO_4^{-2} adsorption and desorption during the incubation were negligible. This study concluded that the leaching of soils led to a loss of isotopically light organic SO_4^{-2} from the organic S pool. This process was considered responsible for progressively heavier $\delta^{34}S$ values for organic S with depth in undisturbed forest soils (Norman *et al.,* 2002).

The analysis of natural abundance ratios of stable isotopes can provide a useful approach to elucidate the biogeochemical S cycle. A study was conducted in two catchments in the Black Forest (Germany) in order to determine the isotope compositions of S compounds in the two-forested catchments, for which S fluxes and pool sizes of all major S sources were known (Mayer *et al.,* 1995). Whereas S isotope measurements should allow the identification of S sources in different ecosystem compartments, oxygen isotope ratios in SO_4^{-2} were used as a potential indicator for redox reactions. The isotopic composition of SO_4^{-2} in bulk precipitation, canopy throughfall, and seepage water at three different soil depths, stream water, and groundwater were monitored. Isotope measurements on aqueous SO_4^{-2} were complemented by $\delta^{34}S$ -analyses on SO_2 in the air, total S and inorganic SO_4^{-2} in the soil, and bedrock S. The similarity in $\delta^{34}S$-values between precipitation and throughfall SO_4^{2-} suggested that dry deposition of S compounds, isotopically similar to those of bulk precipitation, was the reason for the observed increase in S fluxes in the study area**.** The slight variations in $\delta^{34}S$ values of atmospheric S constituents over time was believed to be caused by seasonal variability in S sources with different isotopic signatures such as burning of oil and coal (Nielsen 1974), emissions from automobile exhaust (Grey and Jensen, 1972), or marine S sources (Nriagu *et al.,* 1991; Newman *et al.,* 1991; Wadleigh *et al.,* 1994). The mass weighted mean $\delta^{34}S$ value for bulk precipitation and throughfall $S0_4^{-2}$ in both catchments was found to be +2.1 ‰ over the entire observation period of the study. This value was interpreted as the isotopic signature of long-range transported S of anthropogenic and natural origin, since the study sites in the Black Forest are remote with only minor emissions from local industrial sources. The soil S isotope data indicated that atmospheric deposition was the dominant source of SO_4^{-2} throughout the mineral soil horizons of the two catchments, whereas lithogenic S derived from mineral weathering was rather insignificant. In addition, it was found that microbial transformations were not only responsible for the depletion in the $\delta^{18}O$ values of seepage water SO_4^{-2}, but they also explained variations in the $\delta^{34}S$ values of different S compounds in different soil horizons. These variations did not indicate multiple sources of S in this ecosystem but *in situ* isotope fractionation during S mineralization and immobilization in the soil (Mayer *et al.,* 1995).

3.5.2 Nitrogen isotopes

Two stable isotopes of N occur, ^{14}N and ^{15}N, the former being the most abundant (Mook, 2000). The ratio of these two stable N isotopes for N_2 in air is constant, which makes atmospheric N_2 useful as the standard in the convention used in stable isotope analysis. Isotopic composition is expressed in parts per thousand deviation from the atmospheric N as defined by the following equation:

$$\delta^{15}N = \left[\frac{\left(\frac{^{15}N}{^{14}N} \right)_{sample}}{\left(\frac{^{15}N}{^{14}N} \right)_{standard}} - 1 \right] \times 1000$$

A wide range of oxidation states exhibited by N compounds leads to a wide range of $^{15}N/^{14}N$ ratios being present in compounds of differing natural origins. This is useful for identifying sources and pathways of N in the environment (Kendall and McDonnel, 1998).

3.5.2.1 Tracing anthropogenic inputs of nitrogen to ecosystems

The identification of actual N sources and the understanding of the processes affecting local NO_3^- concentrations can aid in the development of effective water quality and land-use management practices. In many circumstances, N isotopes offer a direct means of source identification because different sources of NO_3^- often leave distinct isotope compositions (Kendall *et al.,* 2007). In addition, biological cycling of N often changes isotope ratios in predictable and recognizable directions. N isotope studies often include the analysis of the oxygen isotope of NO_3^- ($\delta^{18}O$), especially in the studies of the role of atmospheric deposition in watersheds (Kendall and McDonnel, 1998).

Air pollution sources have been distinguished using $\delta^{15}N$ analysis of NO_x for the past several decades. Generally, anthropogenic NO_x sources have positive $\delta^{15}N$ values (Kendall *et al.,* 2007), and existing studies suggest that natural NO_x sources, including lightning, have lower $\delta^{15}N$ values than anthropogenically derived NO_x from fossil fuel combustion. It has also been documented that relatively pristine sites usually have lower $\delta^{15}N$ (NO_2) values than highly polluted or heavily travelled sites (Moore, 1977). NO_x emissions from coal-fired power stations have been reported in the range of +6‰ to +13‰, (Heaton, 1990) while that of vehicle exhaust is reported in the range of +3.7‰ to +5.8 ‰ (Moore, 1977; Pearson *et al.,* 2000). In both vehicle and stationary source fossil fuel combustion, the isotopic value of the resulting NO_x is suggested to be a function of the N present in the original fuel, the N_2 pumped through the engine and the fractionations associated with the thermal NO_x

production. Since thermally produced NO_x is presumed to have lower $\delta^{15}N$ values than fuel-derived NO_x, it is assumed that vehicle NO_x emissions have lower $\delta^{15}N$ values compared with that of stationary sources (Kendall *et al.,* 2007). As for biogenic soil emissions and biomass burning, $\delta^{15}N$ values are expected to be <0 ‰ due to the preferential volatilization of ^{14}N.

Soil N composition can be used to identify and trace sources of atmospheric input into ecosystems. Heaton (1987) measured the $\delta^{15}N$ of oxidized and reduced N gases. The $\delta^{15}N$ values ranged from -150.0 ‰ for oxidized N gases (from the stack of a HNO_3 plant) to 5.2 ‰ for emissions from a coal-burning power station. Formation of HNO, by the incremental solution of NO, in water absorption towers, if accompanied by a large exchange isotopic fractionation, could leave NO, with this low $\delta\ ^{15}N$ value. The $\delta^{15}N$ value of the HNO_3 was found to be -6.0 ‰. As mentioned previously, power stations and vehicles produce NO, chiefly by oxidation of atmospheric N ($\delta^{15}N$ = 0.0 ‰,) and partly from the fuel [$\delta^{15}N$ of coal = - 2.0 to + 3.0 ‰ (Wlotzka, 1972)]. Since the oxidation is rapid and occurs at high temperatures relatively little fractionation is envisaged; $\delta^{15}N$ values for pollutant NO, may therefore be expected to be close to 0.0 ‰. However, the $\delta^{15}N$ of atmospheric deposition can vary significantly depending on the N form and season. Weighted values for wet and dry deposition estimated the $\delta^{15}N$ of total atmospheric deposition to be -3.0 ‰ for NO_3^- and NH_4^+ (Heaton, 1986). However, significant temporal variation is known to be common.

Bragazza *et al*. (2004) integrated temporal and source changes at 16 sites across 11 European countries, and identified sources of atmospheric deposition by measuring the $\delta^{15}N$ of mosses. Moss $\delta^{15}N$ varied from -8 to -3 ‰ across the gradient. The $\delta^{15}N$ values were not correlated with total deposition, annual temperature, or annual precipitation. Instead, the isotopic compositions were significantly correlated with the ratio of reduced to oxidized N (NH_x/NO_x) in the deposition. Mosses located in areas with greater emissions of NH_3 from agriculture activities had lower $\delta^{15}N$ values than those more heavily influenced by NO_x emissions from industrial activity.

3.5.2.2 The use of nitrogen isotopes to document processes in the soil nitrogen cycle

Fractionation during mineralization results in small isotopic differences and it is assumed that the observed discrimination is negligible (Evans, 2007). In light of the changing understanding of soil N cycling and technological advances, further research is needed on the processes and fractionation events that produce organism-available N. It is believed that the overall rate of soil N cycling is limited by the rate of depolymerisation of amino acids from soil organic matter that occurs at localized microsites within the soil (Schimel and Bennett, 2004). In addition to the uptake of inorganic N, organic N uptake may occur either directly by plants or through mycorrhizae (Schimel and Bennett,

2004). For this reason, bulk soil values may provide little information on the $\delta^{15}N$ of N assimilated by organisms.

Studies on $\delta^{15}N$ of inorganic reduced N compounds compared with oxidized forms are becoming more important because 70 % of atmospheric NH_3 originates from volatilization of NH_4^+. The observed discrimination with volatilization can be large because the formation of gaseous NH_3 from NH_4^+ involves several steps and each can discriminate against ^{15}N (Evans, 2007). The first of these reactions is the formation of NH_3 from NH_4^+, which induces an isotopic effect of ca. 20 ‰. Final volatilization of NH_3 into the atmosphere results in an observed discrimination of 30 ‰, depending on the concentration gradient between the soil and atmosphere (Högberg, 1997).

A constant pattern across ecosystems is that the soil $\delta^{15}N$ increases and N content decreases with soil depth (Shearer and Kohl, 1986; Fry, 1991; Högberg, 1997). Possible mechanisms for this observation include (Nadelhoffer and Fry, 1988):

- discrimination during decomposition,
- differential preservation of components enriched in ^{15}N and
- illuviation of ^{15}N enriched organic matter in deeper soil horizons.

The most likely mechanisms for the increase with depth are inputs of litter at the soil surface that are isotopically lighter than organic matter and overall isotopic fractionation during microbial processing of organic matter during decomposition and N loss (Figure 4) (Nadelhoffer and Fry, 1988; Kramer *et al*., 2003). Fractionation for each N transformation that occurs with increasing soil depth causes the remaining soil N to become progressively enriched in ^{15}N as N moves down the soil profile (Figure 4).

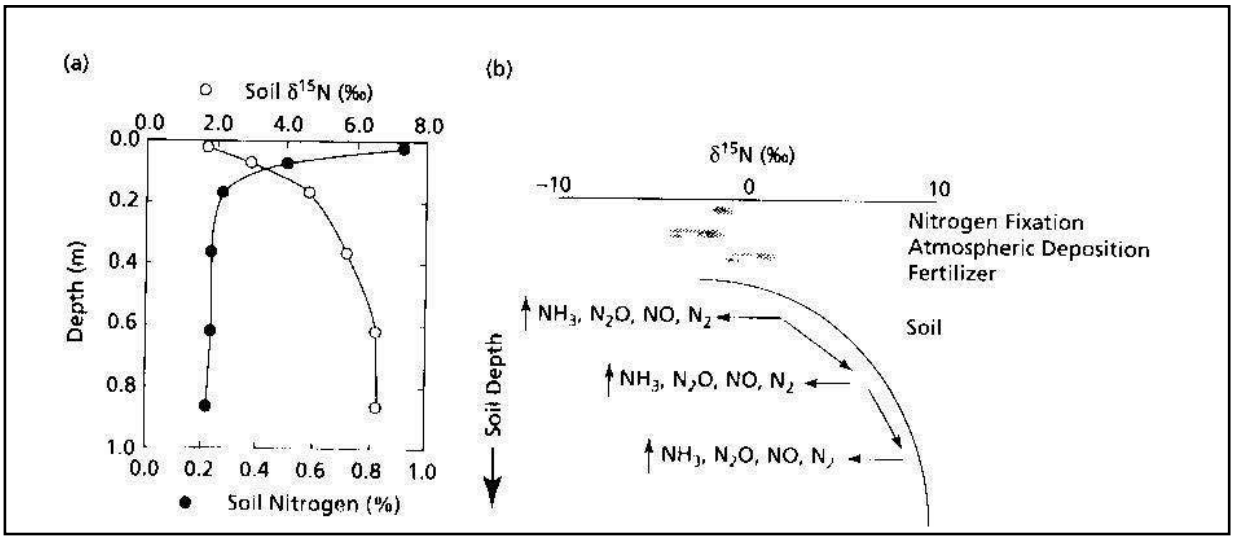


Figure 4 (Left panel) Soil $\delta^{15}N$ and nitrogen content of a typical soil profile (from Sperry *et al.*, 2006). Closed symbols are soil nitrogen content and open symbols are soil $\delta^{15}N$. (Right panel) Conceptual model based on Nadelhoffer & Fry (1988, 1994) proposing the mechanisms for the increase in soil $\delta^{15}N$ with depth. Horizontal arrows represent mineralization and nitrification; vertical arrows represent gaseous nitrogen loss. Fractionation during each transformation causes the remaining soil nitrogen to become progressively enriched in ^{15}N as nitrogen moves down the soil profile.

Simultaneous analysis of both soil N content and N isotopic composition can provide information on N sources to the ecosystem. Soil N content decreases during decomposition because of net mineralization of SOM and subsequent gaseous loss by volatilization and denitrification. As previously mentioned, these decreases in soil N content are accompanied by a corresponding increase in the soil $\delta^{15}N$ (Nadelhoffer and Fry 1988). This process follows Rayleigh distillation kinetics (Mariotti *et al.,* 1982; Nadelhoffer and Fry, 1988) and can de described by:

$$\delta^{15}N_t = \delta^{15}N_0 + \varepsilon \ln\left(\frac{C_t}{C_0}\right) \qquad (3)$$

where $\delta^{15}N_t$ is the isotopic composition of the substrate at time t, $\delta^{15}N_0$ is the isotopic composition of the substrate at the start of the reaction and C_t/C_0 is the fraction of the substrate remaining after time t. When $\delta^{15}N_t$ is plotted against C_t/C_0, the slope of the linear relationship (ε) is equal to the fractionation associated with decomposition (Mariotti *et al.,* 1981). Extrapolation back to $C_t/C_0 = 1$ yields the expected isotopic composition of the original N source.

If values of ε were similar among soils, then differences in the y-intercept between soils would indicate sources of different isotopic composition. The isotopic composition and concentration of the original substrate are seldom known and so Equation (3) is rewritten as:

$$\delta^{15}N_t = k + \varepsilon \ln([N]) \quad (4)$$

Where $\delta^{15}N_0$ and C_t/C_0 in Eq. (1) are replaced by a constant k, and soil N concentration ([N]) respectively (Fustec *et al.,* 1991).

In arid ecosystems, cyanobacteria and lichens that are capable of N fixation dominate the primary source of N input in the biological soil crust. Surface disturbance can be widespread in these systems and eliminates biological soil crusts and N fixation. Therefore identifying whether N input is dominated by physical (atmospheric deposition) or biological (N_2 fixation) processes is important to determine the potential affects of surface disturbance on ecosystem N cycling. Evans and Ehleringer (1993) used a Rayleigh relationship to assess the relative contribution of physical and biological processes (Figure 5). The predicted linear relationship between soil δ ^{15}N and the natural log of soil N content was established. Values for the biological soil crust fell immediately along this relationship while values for atmospheric deposition fell well off the relationship. Evans and Belnap (1999), who observed lower soil N contents, confirmed these results and greater soil δ ^{15}N values in disturbed versus undisturbed sites.

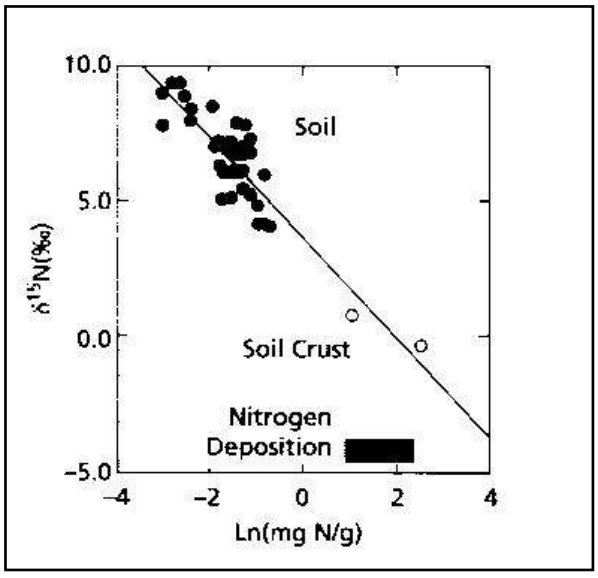


Figure 5. Relationship between soil δ ^{15}N and Ln. (soil nitrogen content) in soils and in two potential sources of N in cold dessert ecosystems (Evans and Ehleringer, 1993).

Measurements of natural abundance ^{15}N have been used increasingly as an indicator of change in the N

cycling of forests (Dawson, 2002). Elevated levels of N availability can lead to increased rates of N cycling. This increase in turn results in ^{15}N enrichment of each soil pool as the lighter ^{14}N isotopes are preferentially lost through leaching and denitrification. Other studies have used natural abundance ^{15}N and ^{18}O within NO_3^- simultaneously to examine whether N deposited onto a forest is cycled within plants and microbes or directly passes through the forest into nearby streams without biological processing, an indicator that the system may have reached N saturation (Durka *et al.,* 1994).

3.5.3 Carbon isotopes

The fractionation of C isotopes that occurs during ecosystem processes makes stable isotopes an ideal tool in understanding terrestrial ecosystem pathways. Much of the C isotope work has focused on C3 vs. C4 plant dynamics because of the substantial difference in ^{13}C discrimination in these photosynthetic pathways. Carbon isotope data are usually expressed as $\delta^{13}C$, which is defined as the relative difference between the isotope ratios of sample and standard. The international standard is Vienna-Pee Dee Belemnite (V-PDB). The present $\delta^{13}C$ value of the atmosphere is -8.0 ‰. C3 plants show a $\delta^{13}C$ ranging from -32.0 ‰ to -22.0 ‰ (mean of -27 ‰) and C4 plants have values of -16.0 ‰ to -9.0 ‰ (mean of -13.0 ‰) (Balesdent and Mariotti, 1996; Boutton, 1996).

The $\delta^{13}C$ value of SOM reflects the relative proportion of C3 to C4 plant material present (Ludlow *et al*., 1976; Martin *et al*., 1990). On this basis, natural ^{13}C abundance in SOM has been used as a proxy to estimate the turnover rates of SOM when the original vegetation was replaced by plants with a different photosynthetic pathway (Martin *et al.,* 1990; Trouve *et al.,* 1994). It has also been utilized as a tracer of paleoecological vegetation changes in many parts of the world. This includes Africa (Bond *et al*., 1994; Schwartz *et al.,* 1986), India (Mariotti and Peterschmitt, 1994), South America (Guillet *et al*., 1988; Volkoff and Cerri, 1987), Central America (Johnson and Wedin, 1997), and western North America (Dzurec *et al.,* 1985; McPherson *et al.,* 1993; Steuter *et al.,* 1990).

3.5.3.1 Using variation of $\delta^{13}C$ with depth to estimate soil carbon pools

SOM can be distinguished into two pools according to their mean residence time: ‘active soil carbon’ with turnover rates of 25 years and ‘passive soil carbon’ with turnover rates on the order of hundreds to thousands of years (Balesdent and Guillet, 1982; Connin *et al.,* 1997; Harrison, 1996). It is still not clear what properties of SOM determine what material makes up each category. $\delta^{13}C$ values differ for each soil fraction, with the coarser, sandier fractions containing less C with lower in ^{13}C values than the clay-rich fraction (Balesdent *et al*., 1988; Bird *et al.,* 2000; Gregorich *et al.,* 1995; Martin *et al.,* 1990). It may be that physical protection by the clay minerals rather than chemical differences distinguish the two categories (Hsieh, 1997) or selective preservation of fine particulates with increased fire frequency (Bird *et al.,* 2000).

The $\delta^{13}C$ of SOM generally increases with depth in soil that has remained under the same plant community for an extended period of time (O'Brien and Stout, 1978; Desjardins *et al.,* 1994). In the tropics, several authors (e.g. Volkoff et al., 1982; Desjardins et al., 1991) have reported increases of 2 to 4 ‰ within the upper meter. This trend appears to be independent of soil physical and chemical conditions (Balesdent *et al.*, 1993). This pattern of increasing $\delta^{13}C$ values with depth is attributed to isotopic fractionation during decomposition of plant material and humification (Ågren *et al.,* 1996). Soil $\delta^{13}C$ values increase when the size of physical SOM fractions decrease (Cerri *et al.,* 1985;Vitorello *et al.,* 1989; Desjardins *et al.,* 1991; Feigl *et al.,* 1995). The increase of $\delta^{13}C$ during humification is probably due to preferential decomposition of organic compounds depleted in ^{13}C, conversion of humic to fulvic acids (Nadelhoffer and Fry, 1988; Balesdent *et al*., 1993), or incorporation of older, depleted soil organic matter (Wedin *et al.,* 1995). Flexor and Volkoff (1977) studied changes in $\delta^{13}C$ values of the humus chemical fractions of a humic ferralitic soil profile under a Brazilian tropical forest. They showed that the humic fraction had a more negative $\delta^{13}C$ values than the others fractions, but selective preservation of specific groups of compounds such as lignin does not explain the pattern of $\delta^{13}C$ with increased SOM age in all cases (Wedin *et al*., 1995).

3.5.4 Conclusion

Amplified loads of NO_3^- and SO_4^{-2} have caused increased stress on soil and water systems in many areas of the world, as both are dominant components of acid rain. Excess deposition of these nutrients have negative impacts on ecosystem health and services such as loss of biodiversity (Sala *et al.,* 2000; Stevens *et al.,* 2004), eutrophication and N saturation (Aber *et al.,* 1998), soil acidification (Richter and Markewitz, 2001), and increased susceptibility to secondary stresses (Aerts and Bobbink, 1999; Witzell and Shevtsova, 2004). Future climate changes may exacerbate the situation by affecting biogeochemical controls on the transport of water, nutrients and other materials from land to freshwater ecosystems (Kendall *et al.,* 2007).

In order to make effective progress in environmental management, it is essential that the understanding of the processes that affect local N and S concentrations is broadened and more sophisticated ways to identify actual N and S sources are developed. Stable isotope studies can offer a means to better understand these nutrient cycles and their interactions. In addition, isotope studies enables source identification, as anthropogenic and natural sources of S and N often have distinct isotopic compositions, and the processes that occur in the cycling of these elements yield recognizable and predictable isotope ratios. Thus, the analysis of $\delta^{34}S$ and $\delta^{15}N$ values from various sources can aid in tracing the origin of these pollutants and their fate in the environment.

4 METHODS AND MATERIALS

4.1 STUDY SITE SELECTION

The Mpumalanga province is naturally divided into three physiographic zones (**Error! Reference source not found.**), 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 area of interest falls into the climatological transition region between the Highveld and the nearby escarpment. The nearest representative long-term climatological observations are from Ermelo, about 90 km north north-east of Amersfoort (SAWB, 1986). The mean annual precipitation there is 755 mm, with January (126 mm) and November (131 mm) having the highest mean monthly rainfall. Rain is recorded on 96.7 days.yr^{-1} (≥0.1 mm), of which on average 24 days receive ≥10 mm.day^{-1}. However, from May to August the average monthly rainfall totals are ≤20 mm (Mphepya *et al.,* 2004).

The Majuba Power Station is one of Eskom's youngest power stations, having been operational since 2001. It is situated between Amersfoort and Volksrust, about 55 km from Standerton, Mpumalanga (Figure 6). Majuba is the most southern of the 11 functional Eskom coal fired power stations, and is approximately 200 km south-east of Johannesburg and 50–100 km south-east to south-south-east of the major industrial activities, which also includes the main centre of electric power generation in the Mpumalanga Highveld area. The area around Majuba was selected as the sampling site as background pollution levels are assumed to be low due to its distance from densely populated and industrial sites. A map of the estimated annual SO_x ground level concentrations in the Mpumalanga area illustrates how the area of sampling was not impacted by high SO_x concentrations which occur further north and west of the sampling site (**Error! Reference source not found.**). Thus, the area selected was considered a good indication of local and combined impacts of these power stations.

As part of the strategic ambient air quality-monitoring network, Eskom has constructed air quality monitoring stations within 6 km of the Majuba power station to assess the local impacts on air quality resulting from the emissions of the station. This site is equipped to monitor SO_2, NO_x and fine particulate matter (Eskom Environmental Report 2000). Thus, relatively long-term ambient air quality data from the study area can be assessed in conjunction with the isotope data. The monitoring stations that fall within the selected study site include Majuba 1, Majuba 2, Majuba 3 and Verkykkop.

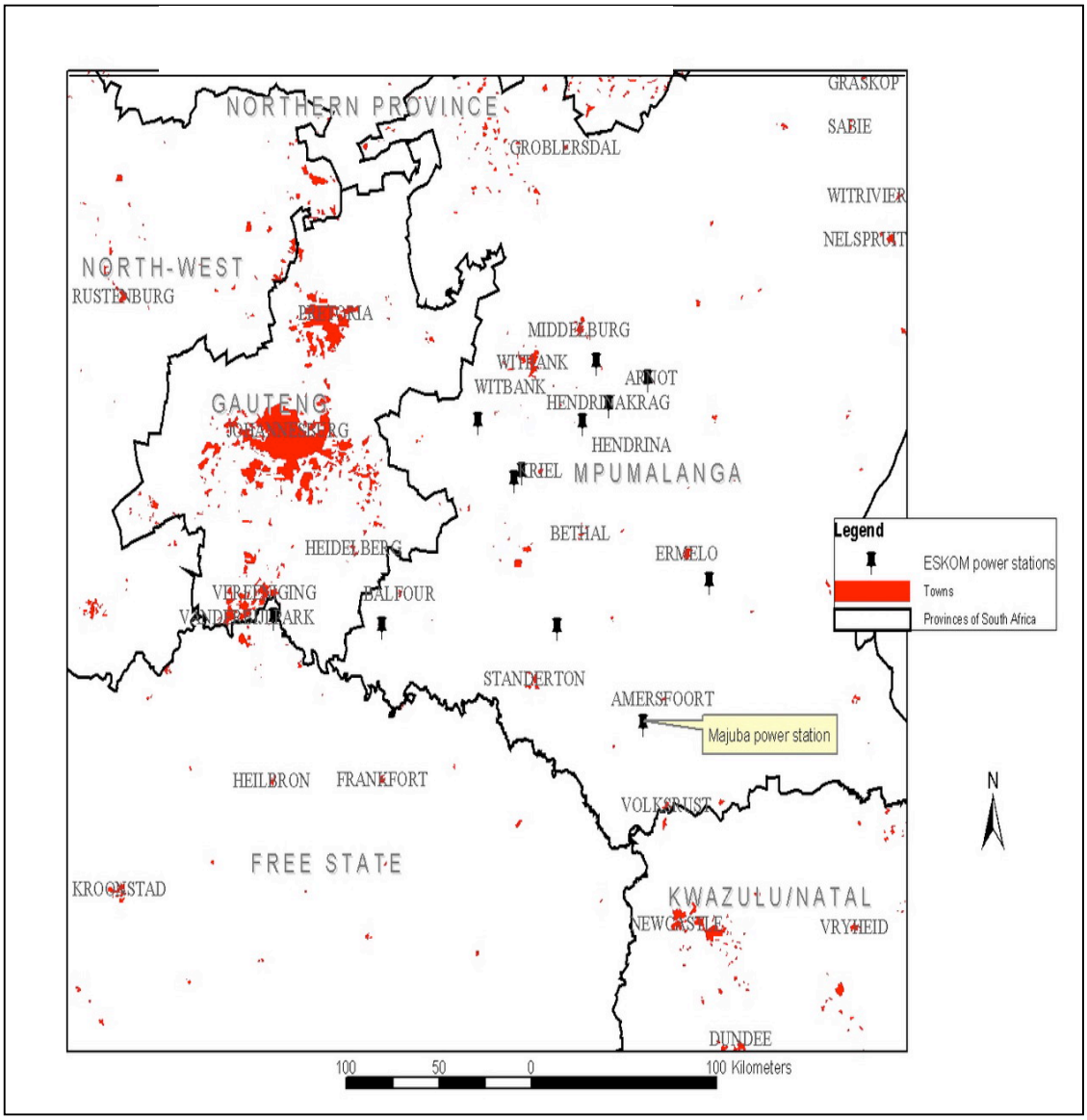


Figure 6. Location of the Majuba Power Station in relation to other power stations and towns. Soils and air quality data were collected in the immediate vicinity of the Majuba Power Station.

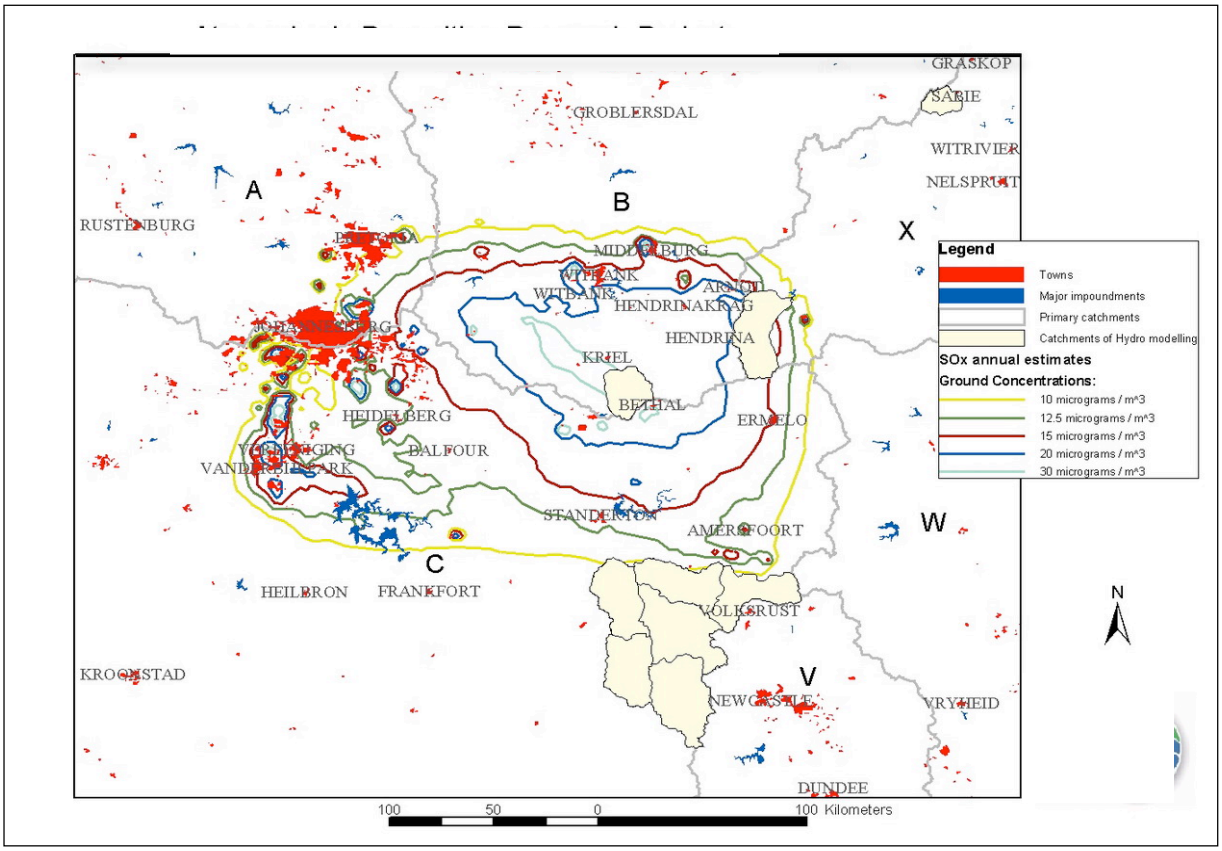


Figure 7. Map showing estimated annual SO_x ground level concentrations across the Mpumalanga and Gauteng area

4.2 AMBIENT AIR QUALITY DATA

The air quality data were collected at the Eskom air quality-measuring station within 6 km of the Majuba Power Station, referred to as Majuba 1. Air quality and weather parameters measured at this station include particulate matter, SO_2 concentrations, and meteorological parameters comprising wind speed, wind direction and ambient temperature (Table 3). The time span for these data range from December 1994 to 2005. These parameters are measured on a frequent basis (approximately every 10 minutes), but only hourly averages are logged. Aggregated data and wind rose data were taken directly from Eskom Environmental Database-driven Web-enabled Integrated System (EDWEIS) for Environmental Observations and Analysis (accessed 2009).

Table 3. Location of the Majuba air quality monitoring station, including the parameters measured and dates of measurement, used in this study.

Air quality measuring station	GPS coordinates	Parameters measured	Dates of measurement
Majuba 1	29º 48' 00.8'' E 27º 06' 46.2'' S	PM10[1] (BTA)	Apr 1995 – 2005
		TMP[4], SO_2,WDR[5],WSP[6],WVL	Dec 1994 – 2005
		NO_2; NO; NO_x[3]	Dec 1994 – Dec 1997

PM10[1] – Particulate matter ($\mu g.m^{-3}$)
TMP[4]-Ambient temperature (°C)
SO_2[2]-Sulfur dioxide concentrations (ppb)
WDR[5] – Wind direction (taken from the centre of the wind rose)
WSP[6] – Wind speed ($m.s^{-1}$).
WVL[7] – Wind velocity ($m.s^{-1}$).
NO_2, NO, NO_x[3] - Nitrogen dioxide, nitric oxide and nitrogen oxide (ppb)

4.3 SULFUR AND NITROGEN DEPOSITION DATA

Data on S and N deposition rates were taken from the literature review and modelling of acid deposition over the Highveld area compiled by Airshed Planning Professionals Pty Ltd as part of a study entitled 'Investigation into the Effects of Atmospheric Pollutants on the Soil-Water-Ecosystem continuum in the Eastern Regions of South Africa'. This study was part of an Eskom – Sasol Joint Committee project. From this report, total S and N deposition rates for the Amersfoort site were used, due to its proximity to the Majuba Power Station near where the soil samples were collected (Figure 6).

Meteorological modelling undertaken in this project utilized the US-EPA CALMET modelling for three base case years selected by the hydrological specialists. In addition, hourly CALPUFF modelling of NO_x and SO_x emissions to simulate wet, dry and total deposition of $SO_4^{-2}$and NO_3^- species for the base case and break point years were applied. The outputs included:

- Hourly deposition rates for the average rainfall year (2000) for selected discrete receptor points.
- Annual deposition rates for the base case average wet (1995) and dry (2006) year scenarios for the entire modelling domain (1.7 km grid resolution).

- Annual deposition rates for the historical and projected future break point years for the entire modelling domain (using meteorological data for an average rainfall year).

4.4 SOIL SAMPLING METHODOLOGY

Sample points were located at varying distances from the power station in order to incorporate a distance gradient into the study, ranging from 1.4 km to 41 km downwind of the power station (Figure 7). Sites were chosen on the basis of the emission plume and thus sampling was conducted in an arc ranging from east-south-east to south-east. Land type, as well as land use, was taken into consideration during site selection and sampling sites were restricted to natural grasslands (Land Type Survey Staff, 2002).

The sampling methodology implemented in similar studies by Van Tienhoven (1997) and Reid (2007) was used in this study. The GPS co-ordinate for each site formed the centre-point of an equilateral triangle with the sampling points at the apexes of the triangle located 25 m apart. At each of the sample points, three samples were combined to give a composite sample, for both the top-soils and the sub-soils. Top-soils were collected by hand augur (10 cm diameter) from the soil surface to a depth of 10 cm, while sub-soils were collected from 20 – 40 cm in the soil profile. Ten sites were sampled, with three replicate soil samples collected at each site at the two soil levels. A sub-soil sample from site 1 could not be obtained as the soil was too hard to sample via soil augur, this resulted in 59 soil samples (top-soils n = 30, sub-soils n = 29).

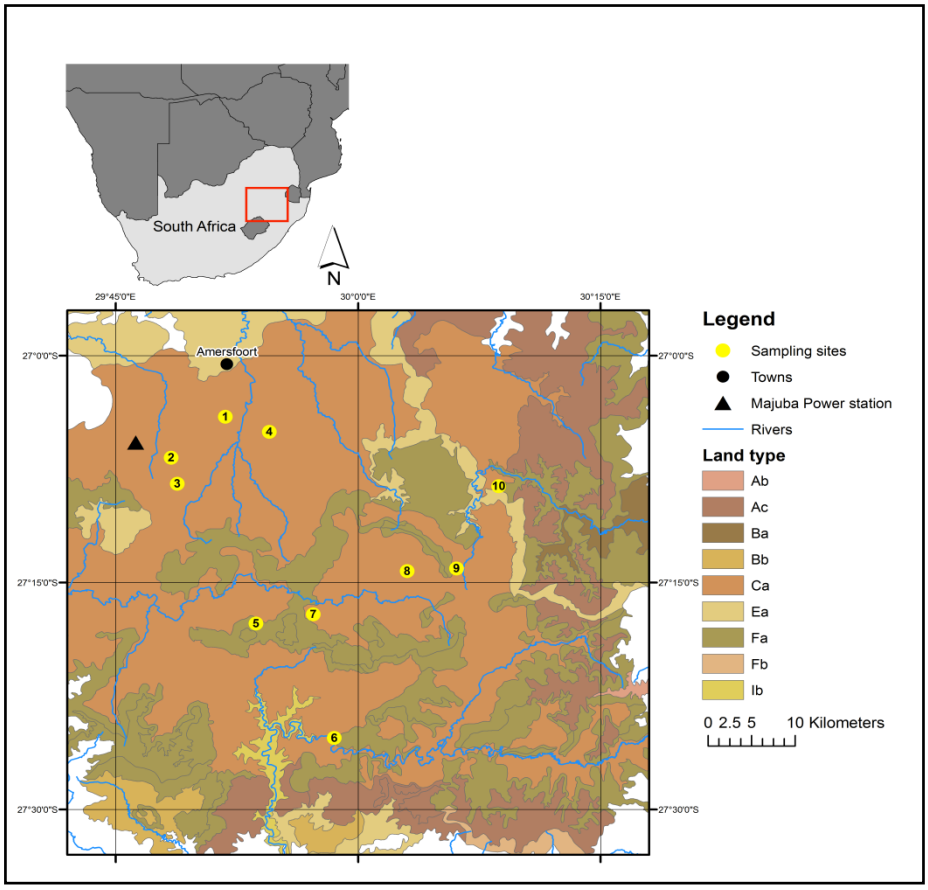


Figure 7. Location of sites sampled for isotope studies, including the position of the power station and the air quality stations.

4.5 LABORATORY METHODS

The soil samples were air-dried to prevent any significant isotope fractionation, sieved (2 mm sieve), and ground to a homogenous powder. The soils were also pre-treated with dilute 1% hydrochloric acid to remove carbonates and dried overnight at 50°C. Iso-Analytical Limited[1] in the United Kingdom performed the $\delta^{34}S$ analysis of total sedimentary S, including total S content. The soil $\delta^{15}N$ and $\delta^{13}C$, as well as total soil N and C analyses, were undertaken at the CSIR[2] in South Africa.

All the isotope analyses were performed using an IRMS coupled with an elemental analyser (EA), with an overall precision better than 0.5 %. Analysis was performed using a standard protocol for each instrument, which includes blanks and certified standards

[1] Iso-Analytical Limited http://www.iso-analytical.com Tel: +44 (0)1270 766771

[2] Council for Scientific and Industrial Research http://www.csir.co.za Tel: + 27 12 841 2911

Sulfur isotope analysis

The three steps in S isotope analysis are (1) the extraction of the S compound(s) of interest, (2) the preparation of the measurement gas and (3) isotope ratio mass spectrometry (Mayer and Krouse, 2004). The most frequently practiced procedure to measure S isotope abundances is using SO_2 in an electron impact source isotope ratio mass spectrometer (IRMS). Since few techniques can handle raw sample specimens, extracting various forms of S from raw materials and converting them to pure SO_4^{-2} or SO_4^{-2} precipitates are a pre-requisite and a major challenge in S isotope abundance studies. In order to extract dissolved SO_4^{-2} from water, the sample was filtered through a 0.45µm membrane, and converted to barium sulfate ($BaSO_4$) by addition of barium chloride ($BaCl_2$) solution. Ion exchange techniques were successfully employed for this purpose (Mayer and Krouse, 2004). Thermal decomposition of $BaSO_4$ then results in SO_2 formation. Pure $BaSO_4$ requires a temperature near 400 ºC for decomposition, which is close to the softening temperature for quartz. The SO_2 produced is purified chemically, separated in a GC column and swept by an inert carrier gas via an open slit through an ion source of a mass spectrometer. The changing ion currents are then recorded with multiple collectors. For the S isotope analysis of the cola sample, approximately 5 mg samples were weighed into pre-cleaned tin capsules and combusted on-line in a Flash EA. This involved the normal coupling to the MS via a ConFloIV. The coal samples were combusted with vanadium pentoxide powder to ensure full oxidation. Samples were referenced against the international standard, NZ1, and sulfanilamide was used as a running standard.

Nitrogen isotope analysis

EA-IRMS (elemental analyser isotope ratio mass spectrometry) was the technique used for N and C isotope analyses. In brief, tin capsules containing appropriate amounts of samples or reference materials (equivalent to ca. 20 µg N for the NH_4^+ on resin and 100 µg N for the silver nitrate), were loaded into an automatic sampler on a Europa Scientific elemental analyser. Here, samples are dropped in sequence into a furnace held at 1000 °C, where they are combusted in an oxygen rich environment. The tin capsules flash combust, raising the temperature in the region of the sample to ~ 1700 °C. The gases produced on combustion are swept in a helium stream over combustion catalyst (Cr_2O_3), copper oxide wires (to oxidize hydrocarbons), and silver wool to remove S and halides. The resultant gases, N_2, NO_x, H_2O, O_2, and CO_2 are swept through a reduction stage of pure copper wires held at 600 °C. This step removes O_2 and converts NO_x species to N_2. A magnesium perchlorate chemical trap was used to remove H_2O (Barrie and Prosser, 1996).

For ^{15}N analysis, CO_2 was removed using a chemical trap (Carbosorb) and the N focused on a packed column gas chromatograph held at an isothermal temperature of 100 °C. The resultant

chromatographic peak of N_2 enters the ion source of a Europa Scientific 20-20 IRMS where it is ionized and accelerated. Gas species of different masses are separated in a magnetic field then simultaneously measured using a Faraday cup collector array at masses of 28, 29 and 30. Both references and samples are converted to gases and analysed using this method.

Coal isotope analysis

The coal S isotope signal was measured using the standard routine. Three c.a. 5 mg samples were weighed into pre-cleaned tin capsules and combusted on-line in a Flash EA. The normal coupling to the MS via a ConFlo IV was used. The coal samples were combusted with vanadium pentoxide powder to ensure full oxidation. Samples were referenced against an international standard called NZ1 and sulfanilamide was used as a running standard. Reproducibility was 0.5 ml^{-1} (S Woodburn, 2012 pers. comm.)

Particle size distribution

Particle size analysis is a measurement of the size distribution of the individual particles in a soil sample. The major features of this method are the dispersion or destruction of soil aggregates into discrete units by chemical and/or mechanical means and the separation of particles according to size limits by sieving and sedimentation. Dispersion was accomplished using a 4 % sodium hexametaphosphate solution buffered with sodium carbonate (Anderson and Ingram, 1996). Texture was determined using a hydrometer. Soil texture was classified using a texture triangle according to the USDA (United States Department of Agriculture) classification scheme.

4.6 DATA ANAYSIS

A two-way factorial analysis of variance (ANOVA) was used to analyse the six response variables; percentage elemental S, percentage elemental N, percentage soil organic C, $\delta^{34}S$, $\delta^{15}N$ and $\delta^{13}C$ values using the SAS 9.1. The two factors considered were, soil depth (0 – 10 cm and 20 – 40 cm) and sample site. If the overall ANOVA test was shown to be significant, then multiple comparison tests were used to show where the differences lay. The Bonferroni procedure was used as this test is in between the most conservative and the least conservative comparison tests. Since the number of observation per group/treatment differs, the type III sum of squares ANOVA table was consulted. In the case where the overall model was non-significant, the non-significant interactions were removed from the model, and the test rerun, leading to an improvement of the overall ANOVA model.

In order to meet the assumptions of the ANOVA test, the data were tested for:

- Normality: This was evaluated using graphical analysis (boxplots and histograms), as well as a goodness of fit test.
- Homogeneity of variances: This was checked by plotting the residuals against the predicted values.

The data were shown to approximate normality, and no transformations of the data were undertaken. Statistical significance was accepted for $p < 0.05$.

5 RESULTS

Before exploring, the results found in this study, this brief introduction serves to explain the structure of the results reported.

This study aims to quantify soil S and N concentrations as well as isotopes in order to better the understanding of nutrient cycles in the grassland ecosystem. In order to achieve this a number of different types of data were collected, some personally collected in the field and analysed in the laboratory whereas other have been extracted from the literature in order to answer the key questions of this study.

Firstly, data from the wind and pollution roses obtained from the Majuba 1 air quality monitoring station are presented. The data were collected from 2000 - 2005 and are presented as wind speed and direction as well as SO_2 concentrations. The data on S and N rates of S and N deposition have been extracted from the Eskom-Sasol project report (Blight et *al.,* 2009). This is followed by the elemental and isotopic soil data for S, N and C for Majuba soils.

The key findings in the S, N and C data show the relationship between the elemental concentrations and the isotope ratios with soil depth and sample site. The relationships for each element have been reported in a systematic way to allow for a comparison. Statistical groups were identified as described in Chapter 3 Section 3.5. The elemental and isotope values for each element were plotted against sample site. In all cases, except for soil N concentration, the mean ± standard error for top-soil and sub-soil value per site is indicated in the figure, even though the statistical grouping was based on the mean value per site, irrespective of depth. In all these figures, the sites have been ordered according to the elemental concentration values in the top-soils.

The results obtained regarding the S, N and C concentration and isotope ratios for a composite coal sample obtained for Majuba power station are reported.

5.1 RESULTS COLLECTED BY OTHERS IN COLLABORATIVE PROJECTS

5.1.1 Wind fields

The wind rose and pollution rose data were collected from the Majuba 1 air quality monitoring station during the period 2000 – 2005. Figure 8 and Figure 9 show wind direction, but the pollution rose (Figure 8) shows pollution concentration while the wind rose (Figure 9) shows wind speeds. The Majuba 1 station monitors ambient SO_2 and NO_x concentration, although NO_x wind fields were not available for analysis. The centre of the wind rose depicts the air quality monitoring station. The position of the spokes in the polar diagram represents directions from which the wind was blowing. The length of the segment indicates the percentage of the time the wind blew from that direction. Each arc in the wind/pollution rose represents a 3.0 % interval. The pollution concentration (ppb) or speed ($m.s^{-1}$) in the various categories are denoted by colours and width. So, for example, the SO_2 pollution rise (Figure 8) shows that winds blow from the west 17 % of the time, and SO_2 concentrations are less than 2 ppb for 4.5 % of that time. The centre of the Majuba 1 wind rose depicts that calm winds (0 – 0.5 $m.s^{-1}$) prevailed for 6.0 % of the time.

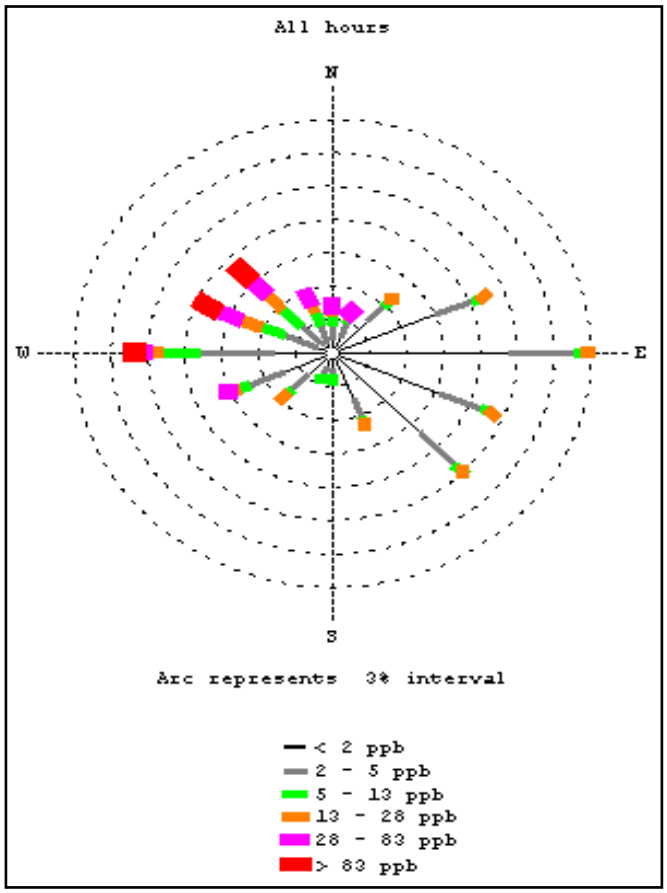


Figure 8. Sulfur dioxide pollution rose for all hours. Data collected from Majuba 1 air quality monitoring station during the period 2000 – 2005.

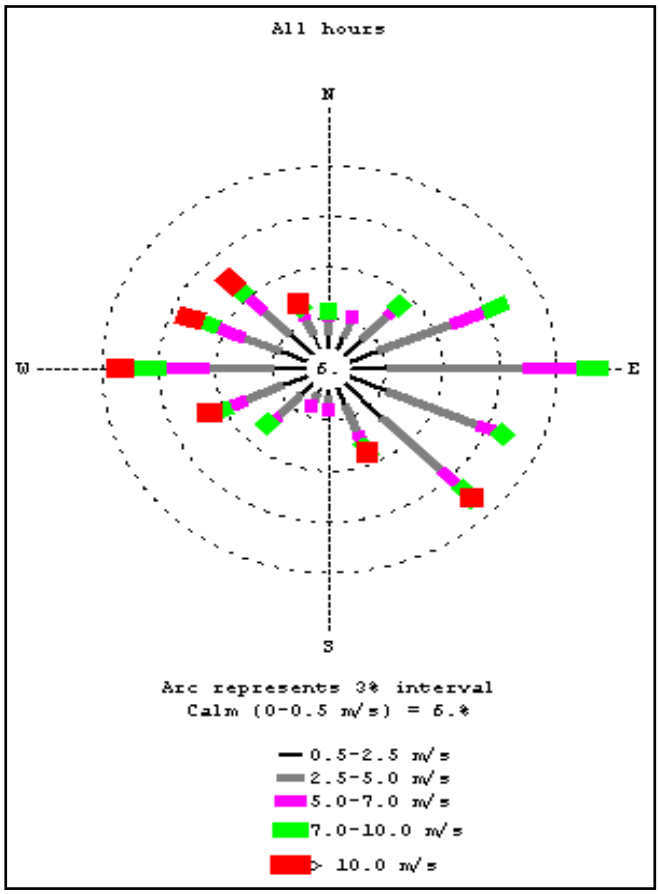


Figure 9. Wind rose for all hours. Data collected from Majuba 1 air quality monitoring station during the period 2000 –

The SO_2 pollution rose shows high concentrations of SO_2 (greater than 83.0 ppb for 3.0 % of the time) from the north-westerly direction (Figure 8). Data from the wind rose (Figure 9) show high wind speeds coming from the north-westerly direction. High wind speeds are also seen to be coming from the east and southeast, however the concentration of SO_2 from these directions is far lower. The strong winds coming from the southeast have low SO_2 concentrations (< 2.0 ppb for 9.0 %, 2 - 5 ppb for 4.5 % and between 13.0 and 28.0 % ppb for approximately 1.0 % of the time).

The variance in the hourly mean SO_2 concentration with season taken from the Majuba 1 air quality monitoring station is shown below (Figure 10). SO_2 concentration is seen to peak during the spring and winter months, at approximately mid-day. This may be due to high demands and stable atmospheric conditions during these times.

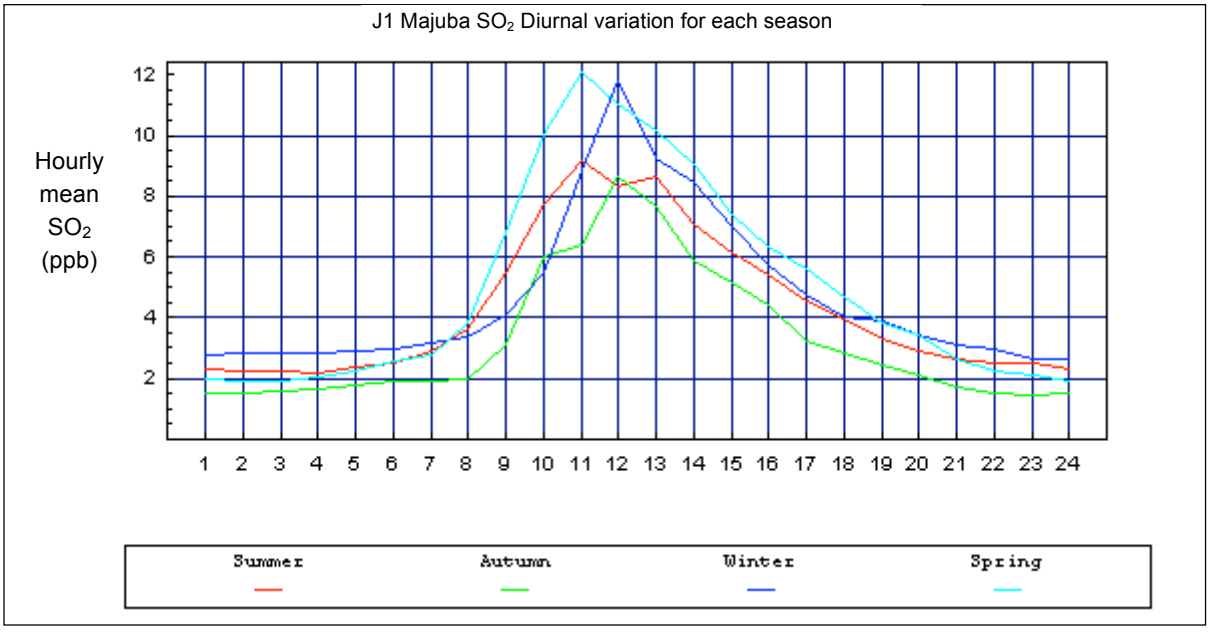


Figure 10. Variance in the hourly mean SO_2 concentration (ppb) with season, taken from the Majuba 1 air quality control station during the period 1995 - 2000.

5.1.2 Ambient air concentrations and deposition rates of sulfur and nitrogen for a range of Highveld sites

Ambient air pollution concentrations and deposition rates modelled at discrete receptor points for an average rainfall meteorological year (2000/2001) is given below (Table 4).

Table 4. Ambient air pollution concentrations and deposition rates for discrete receptor points for an average rainfall meteorological year (Blight *et al.*, 2009).

Receptor site	Annual average ambient air concentration ($\mu g/m^3$)					Total annual deposition rate ($kg.ha^{-1}.yr^{-1}$)	
	SO_2	SO_4	NO	NO_2	NO_3	Total S	Total N
Amersfoort	9.8	1.8	0.4	3.3	1.4	11.4	5.6
Majuba 1	9.9	1.9	0.4	3.3	1.5	23.3	5.6
Majuba 3	9.6	1.9	0.4	3.2	1.5	10.0	5.3
Verkykkop	7.5	1.7	0.3	2.5	1.3	7.6	3.9

The S ambient air concentration is seen to be dominated by SO_2 across all receptor sites during wet, dry and average rainfall years with little difference in the SO_2 contribution across years (Table 4). According to Blight *et al.* (2009), the overall sulfur deposition rate largely followed regional SO_2 concentration gradients. Since SO_2 concentrations are high it is feasible that they will contribute large proportions to S deposition. The highest percentage contribution of SO_2 deposition to total S deposition was predicted to occur in the immediate vicinity (downwind) of high stack releases (e.g. Majuba 1 site 94 %). At other sites, the percentage contribution of SO_2 deposition was projected to be typically 80 % to 90 % of total S deposition (Blight *et al.,* 2009).

Total N deposition was modelled and measured to be dominated by wet deposition of NO_3^- and NH_4NO_3 (~50 %), with total wet deposition accounting for over 60 % of the total deposition (Blight *et al.,* 2009).

5.1.3 Measured and modelled S and N deposition rates for the Amersfoort region

Total S and N deposition rates are given from published results from previous measurement and modelling studies. Mphepya and Held (1999) used the NOAA inferential model to indirectly measure dry S deposition for the 1996 – 1998 period. Hourly concentrations of SO_2, NO_x, O_3 and SO_4^{-2}, as well as meteorological parameters (temperature, relative humidity, rainfall, wind speed and direction, sigma theta and total radiation) were used as input variables for the modelling.

Galy-Lacaux *et al.* (2003) presented measurements of N deposition for Amersfoort for the 1996 - 1998 period. Total N deposition at Amersfoort has been measured as 15 kg $N.ha^{-1}.yr^{-1}$

comprising 63 % wet deposition (9.5 kg $N.ha^{-1}.yr^{-1}$) and 37 % dry deposition (5.6 kg $N.ha^{-1}.yr^{-1}$). Based on Blight *et al*. (2009) measured and modelled values at Amersfoort, N deposition was found to comprise: 37 % dry deposition of gases (NO, NO_2, HNO_3, NH_3), 33 % wet deposition of ammonium nitrate (NH_4NO_3), 24 % wet deposition of $(NH_4)_2SO_4$ and HNO_3 and <1 % dry deposition of NH_4NO_3

Table 5. Summary of measured and modelled total S and N deposition rates obtained from literature for a similar period 1996 – 2001.

Station	Measured and modelled total S deposition ($kg.ha^{-1}.yr^{-1}$)	Measured and modelled total S deposition ($kg.ha^{-1}.yr^{-1}$)	Measured total N deposition ($kg.ha^{-1}.yr^{-1}$)	Measured and modelled total N deposition ($kg.ha^{-1}.yr^{-1}$)
Amersfoort	7.5	11.4	16.47	5.61
Reference	Mphepya and Held, 1999 (1996 – 1998)	Blight et *al.,* 2009 (2000 – 2001)	Galy-Lacaux *et al*., 2003 (1996 – 1998)	Blight et *al.,* 2009 (2000 – 2001)

Modelled output by Blight *et al.* (2009) for total S deposition was a factor of 1.5 higher than that published by Mphepya and Held (1999). The higher values are due to higher predictions for wet S deposition. The wet S deposition was predicted for the period 2000 – 2001, which had a rainfall of 720 mm compared to the average 1996 - 1998 rainfall of 510 mm (Blight et *al.,* 2009). Thus, the modelled total S deposition by Blight *et al.* (2009) was higher than the measurement deposition at the Amersfoort station (Table 5).

Predicted total N deposition at Amersfoort was lower than the total measured N deposition rates published for Amersfoort. About 30 % of this difference is due to dry deposition of NH_3 gas not having been accounted for in the predictions made by Blight et *al.,* (2009). Dry deposition of gaseous NH_3 is given as accounting for 33 % of the total N deposition at Amersfoort (Blight et *al.,* 2009). Excluding gaseous NH_3, predicted N deposition comprised 50 % of that measured at Amersfoort (Table 5).

5.1.4 Spatial variation in ambient concentration and deposition rates

Spatial variations in ambient concentrations and deposition rates for an average rainfall year taken from the Eskom-Sasol Airshed report are also reported (Figure 11 and Figure 12), taken from Blight *et al.,* (2009).

The highest total annual S deposition was predicted to occur over the central Highveld receptor sites, with >80 kg.ha^{-1}.yr^{-1} being projected for Kendal 2 and between 20 and 30 kg.ha^{-1}.yr^{-1} for the Elandsfontein and Leandra sites. Total S deposition rates were less than 15 kg.ha^{-1}.yr^{-1} at Volksrust and Amersfoort (Figure 11).

The total N deposition maximum was predicted to occur at a more eastern location compared to the S deposition maximum (centred between Bethal and Ermelo) (Figure 12). Total N deposition was predicted to be dominated by wet deposition of NO_3^- and NH_4NO_3, with time taken for formation of these products and spatial variations in rainfall accounting for the deposition maximum being located more remotely from significant NO_x source areas. Higher rainfall generally occurred over the eastern regions, while the lowest rainfall occurred over the south-western Mpumalanga Province, bordering Gauteng Province (Blight et *al.,* 2009). This area of minimum rainfall coincides with the area of elevated ambient NO_3^- concentrations, with the reduced wet removal likely to have contributed to the peak ambient ground level NO_3^- concentrations (Blight *et al.,* 2009).

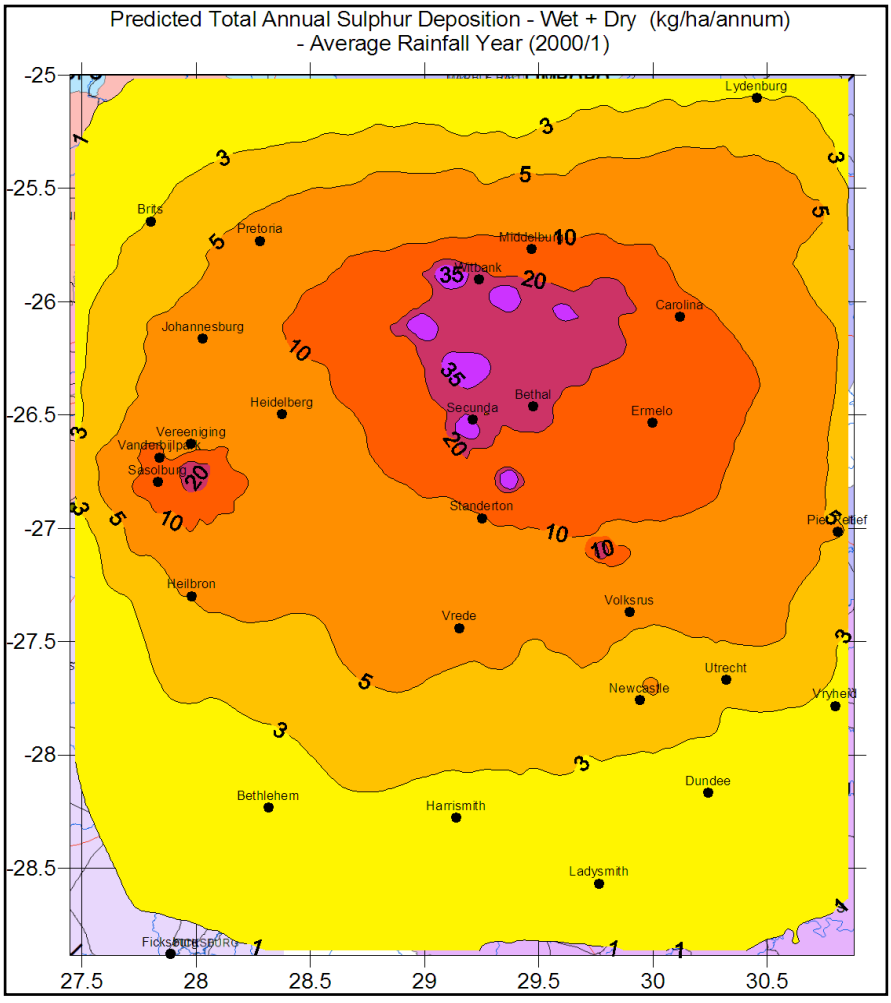


Figure 11. Predicted total annual S deposition for average rainfall year kg.ha^{-1}.yr^{-1} (2000/1).

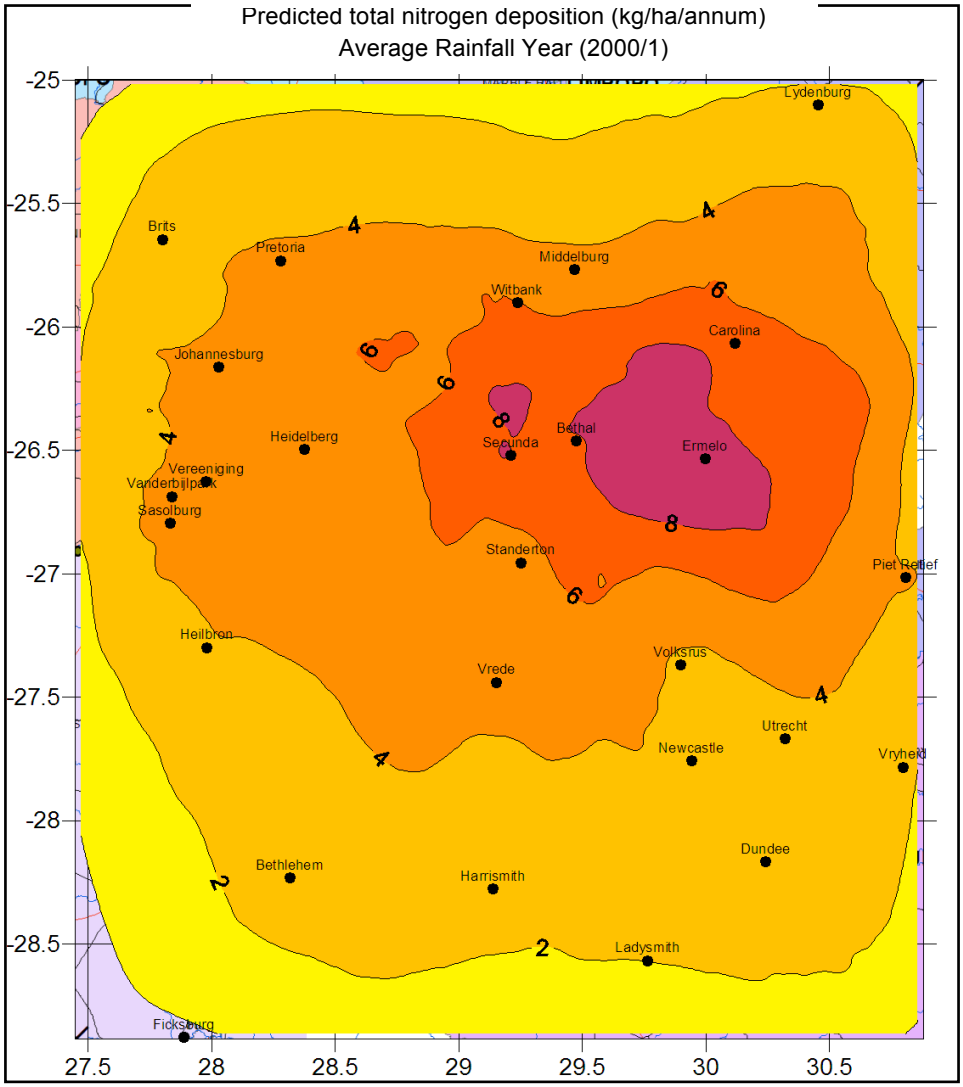


Figure 12. Predicted total N deposition for an average rainfall year kg.ha^{-1}.yr^{-1} (2000/1).

5.2 RESULTS COLLECTED PERSONALLY AS PART OF THIS RESEARCH

5.2.1 Sulfur

5.2.2 Total soil sulfur

The total soil S concentration was found to be higher in the top-soil (0 – 10 cm) than the sub-soil (20 – 40 cm) depths (Figure 13). The mean per site (n = 3) soil S concentration across all depths ranged from 0.009 % to 0.048 % and both soil depth and sample site were shown to significantly affect the concentration of S in the soil ($F = 112.83$, $p < 0.0001$; $F = 41.72$, $p < 0.0001$ respectively), while no statistical interaction was found to exist between these 2 factors.

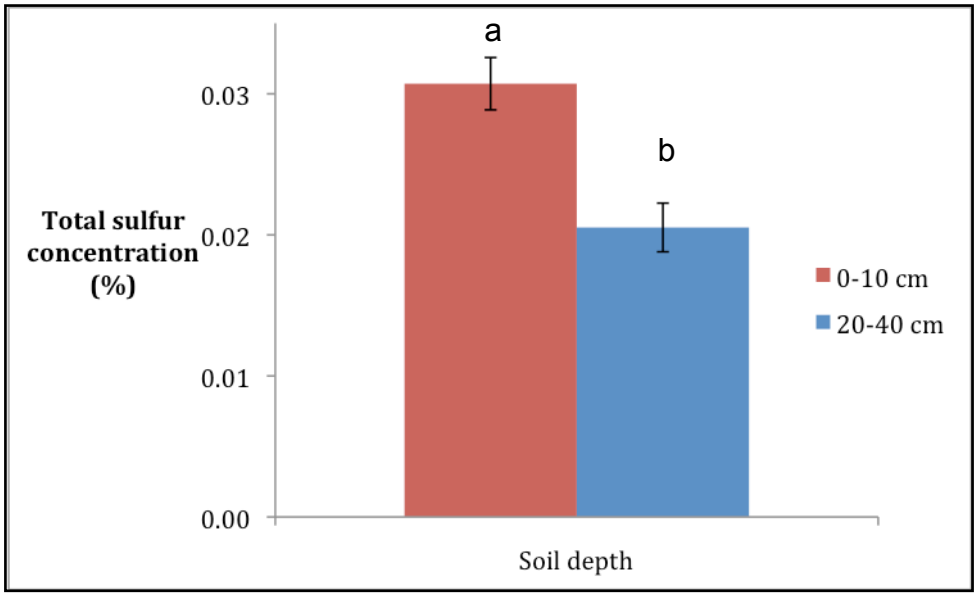


Figure 13. Mean percentage soil S concentration (± standard error) found in the Majuba soils for all 10 sites, representing both top (n = 30) and sub-soil (n = 29) depths. Means associated with different letters are statistically different ($p \leq 0.05$).

When the soil S concentrations were compared across the ten sites, three major groups were identified. Sites 2, 3, 4 and 6 had a lower percentage of soil S than the remaining six sites (Figure 14). The spatial pattern observed shows sites 5 and 7, which are situated 22.45 km and 25.70 km downwind from the Majuba Power Station to have higher soil S content than those situated closer to the power station (Figure 15). However, site 1, which is 9.58 km northeast of Majuba, also shows a relatively high soil S concentration.

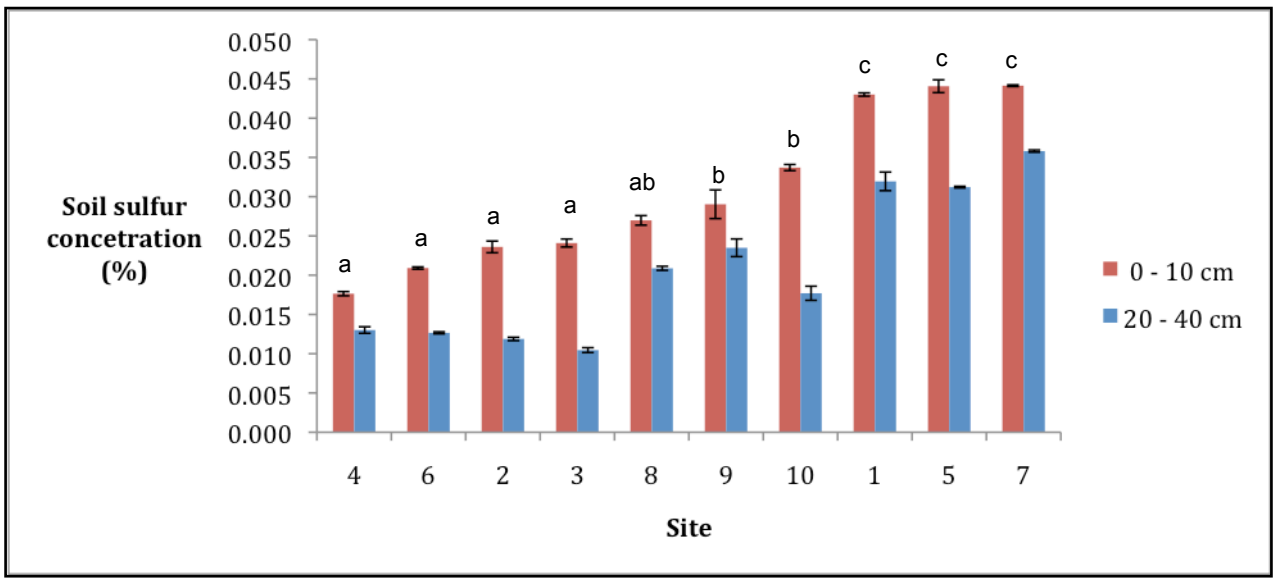


Figure 14. Soil S concentration found in the Majuba soils across the two soil depths and the 10 sites sampled. Means associated with the different letters are significantly different ($p \leq 0.05$).

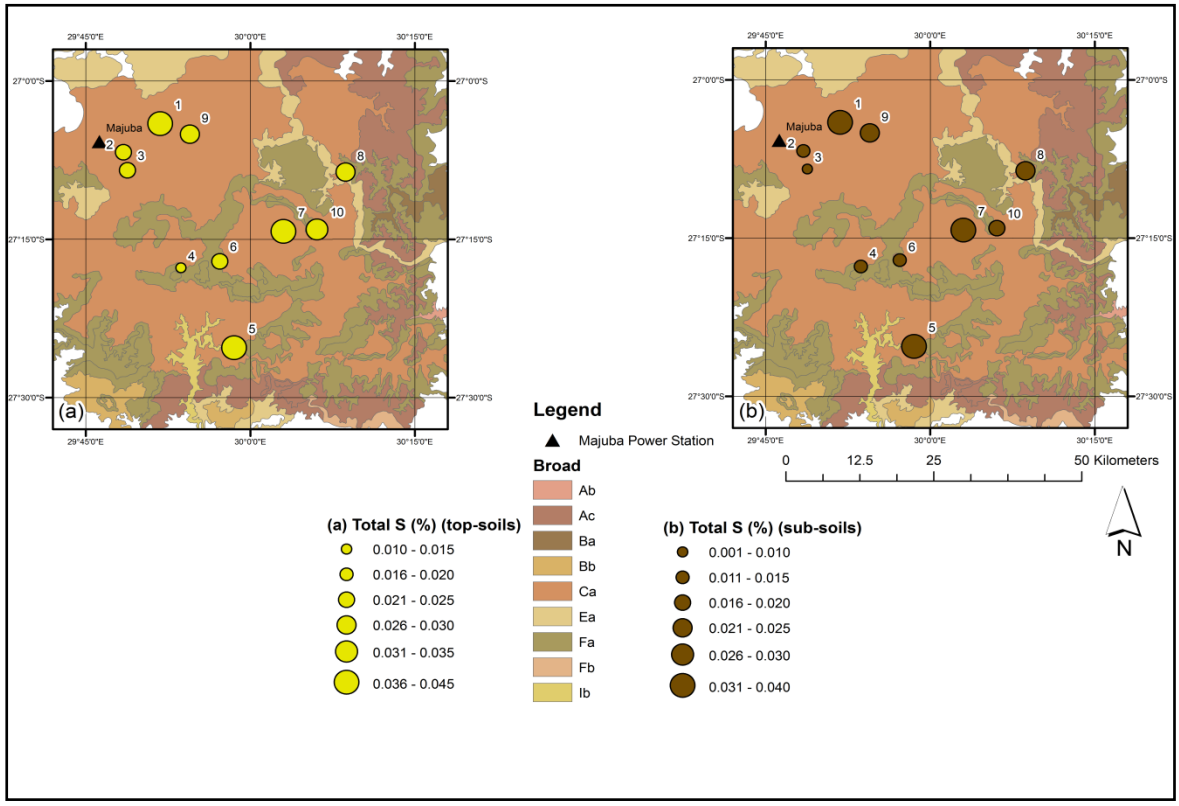


Figure 15 Map of sample sites showing spatial variation in percentage soil S, showing both top-soil (n = 29) and sub - soil depths (n = 30) for Majuba soils.

The SO_2 pollution rose from the Majuba 1 air quality monitoring station shows high concentrations of SO_2 coming from the north-westerly direction (Figure 8). This could explain the high concentrations of soil S found at sites 5 and 7, southeast of the power station.

5.2.3 Soil sulfur isotopes

The $\delta\ ^{34}S$ values were found to be higher in the sub-soil than top-soil depths (Figure 16). The top-soils ranged from 4.72 to 15.32 ‰, while the sub-soils ranged from 7.28 to 19.07 ‰. The $\delta^{34}S$ values were compared across all sample sites and soil depths and both soil depth and sample site were shown to significantly affect the $\delta\ ^{34}S$ value in the soil ($F = 49.90$, $p < 0.0001$; $F = 18.59$, $p < 0.0001$).

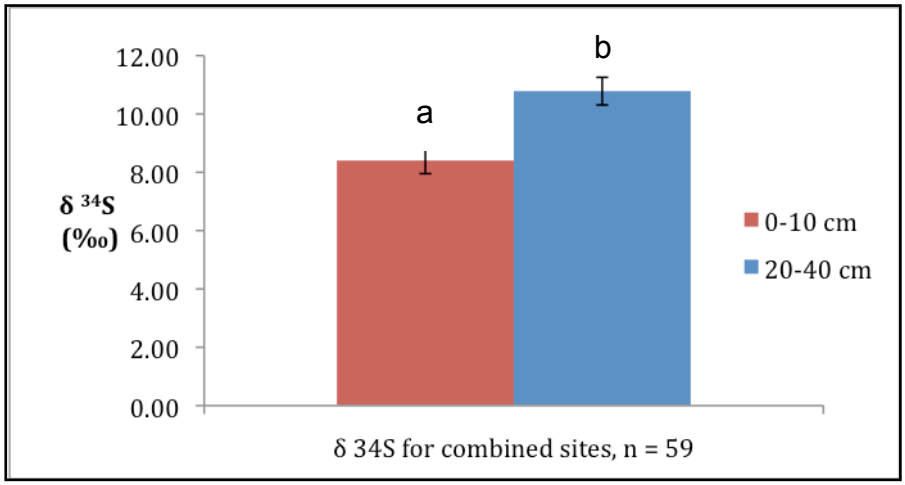


Figure 16. Mean ± standard error $\delta^{34}S$ ‰ values for Majuba soils for all ten sites, representing top (n = 30) and sub (n = 29) soil depths. Means associated with different letters are statistically different ($p \leq 0.05$).

The sites were grouped together according to similarity in the mean isotope signature. Site 5, 7, 8 and 9 are all in close proximity to each other with similar isotope signals, as are sites 1, 2, 3 and 4 (Figure 17). Site 10, on the north east of the Sandspruit catchment is an outsider with statistically higher S isotope signal than the remaining nine sites (Figure 18). The $\delta^{34}S$ value across the ten sites appears to follow a similar pattern as the soil S concentrations. In general, sites with higher S concentrations had higher $\delta^{34}S$ values.

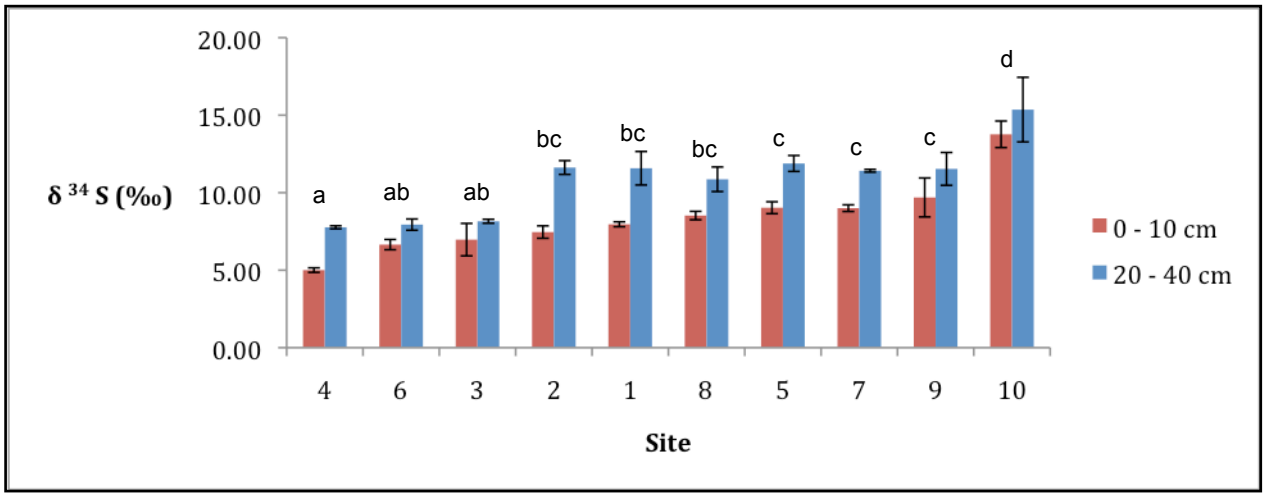


Figure 17. Mean ± standard error $\delta^{34}S$ (‰) values for Majuba soils, for both top-soils (n = 30) and sub-soils (n = 29), across the ten sampled sites. Means associated with a different letter are significantly different ($p \leq 0.05$).

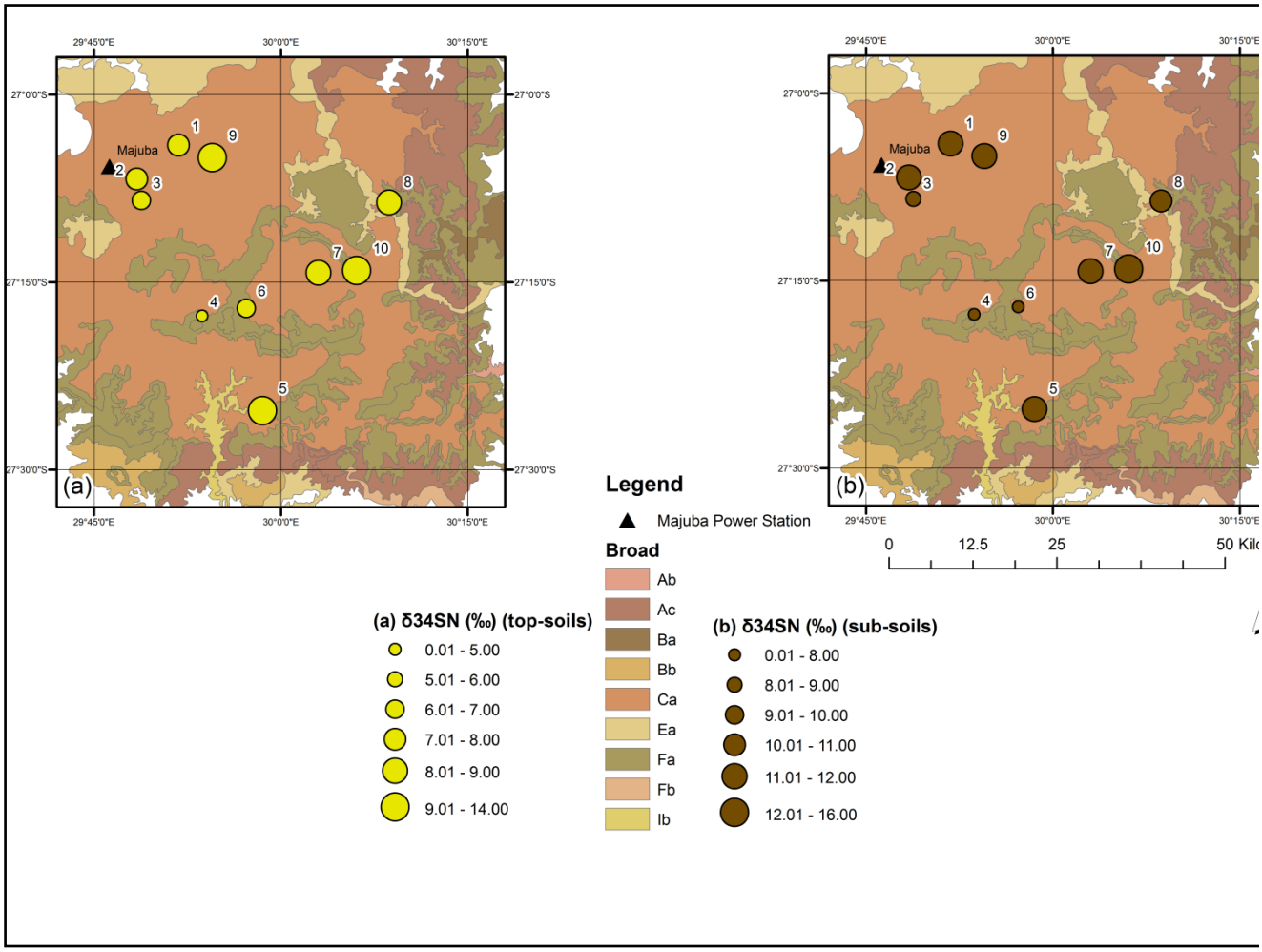


Figure 18. Map of sample sites showing spatial variation in the mean $\delta^{34}S$ (‰) signal, showing both top-soil (n = 29) and sub-soil depths (n = 30) for Majuba soils.

A weak correlation ($r^2 = 0.237$ for top-soils and $r^2 = 0.183$ for sub-soils) was established between mean soil $\delta^{34}S$ signal and S concentration (Figure 19). Site 10 again appears as an outlier, and does not fall along a linear relationship between soil $\delta^{34}S$ signal and S concentration.

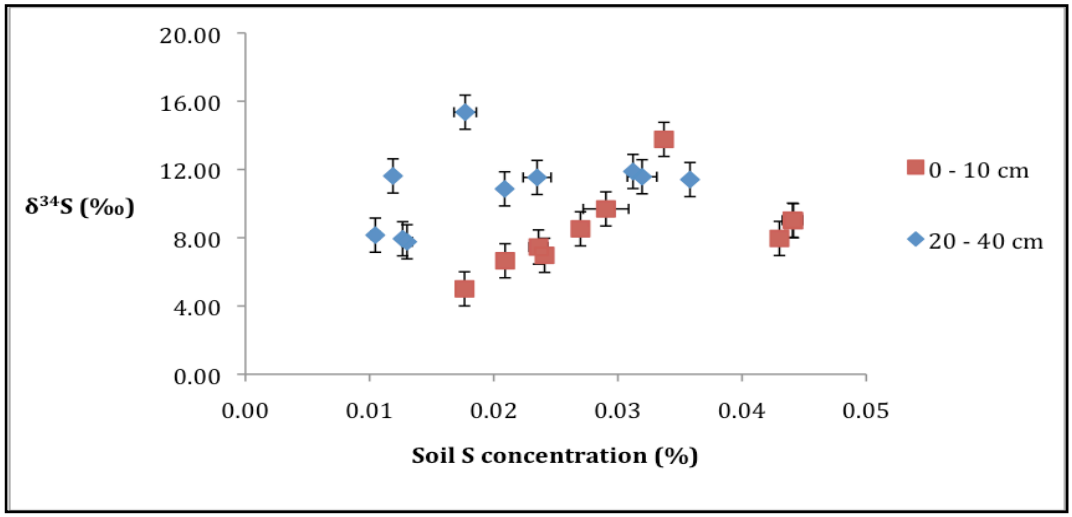


Figure 19. Graph showing mean soil $\delta^{34}S$ (‰) signal versus mean S concentration for both top-soils ($r^2 = 0.237$) and sub-soil depths ($r^2 = 0.183$) for Majuba soils.

5.3 NITROGEN

5.3.1 Total elemental nitrogen

Nitrogen concentrations were found to be higher in the top-soil than in the sub-soil depths (Figure 20). The mean per site (n = 3) percentage elemental N concentration across all depths ranged from 0.056 % to 0.346 %.

The total soil N concentrations were also compared across all sample sites and soil depths. The percentage N was found to be affected by both soil depth and sample site ($F = 102.11$, $p < 0.0001$, $F = 21.00$, $p < 0.0001$ respectively), while a weak statistical interactive effect was also found to exist between these two factors ($F = 2.26$, $p = 0.0382$)

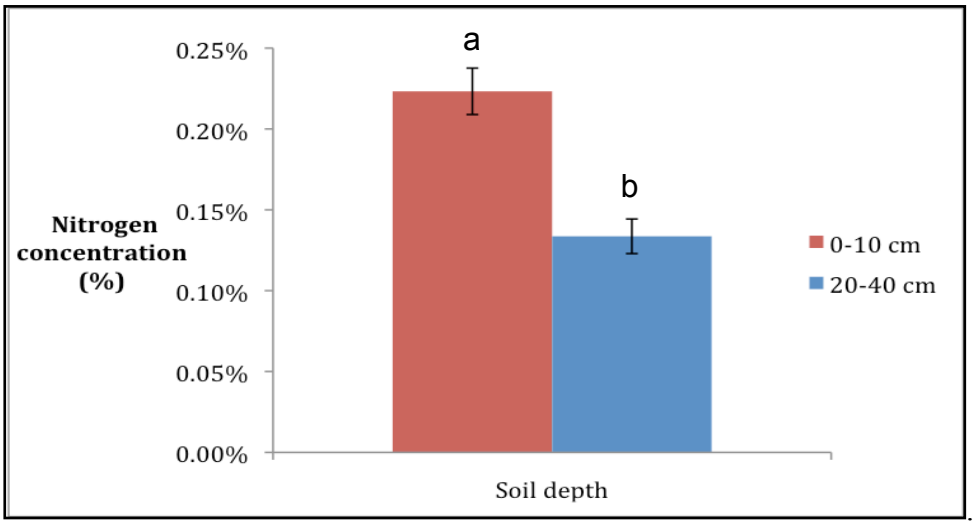


Figure 20. Mean percentage soil N values (± standard error) for all sites, representing both top-soil (n = 30) and sub-soil (n = 29) depths. Means associated with different letters are statistically different ($p \leq 0.05$).

A Bonferroni post-hoc test was then carried out across the ten sites to see where the differences in elemental N values occurred. The sites were grouped together, irrespective of soil depth, according to significant similarity in percentage N (Figure 21), and two groups were identified. The sites showed similar grouping to the S concentrations, with sites 2, 3, 4 and 6 having the lowest percentage of soil N (Figure 22). The higher N values occurred at sites 5 and 7, located approximately 25 km from the Majuba power station.

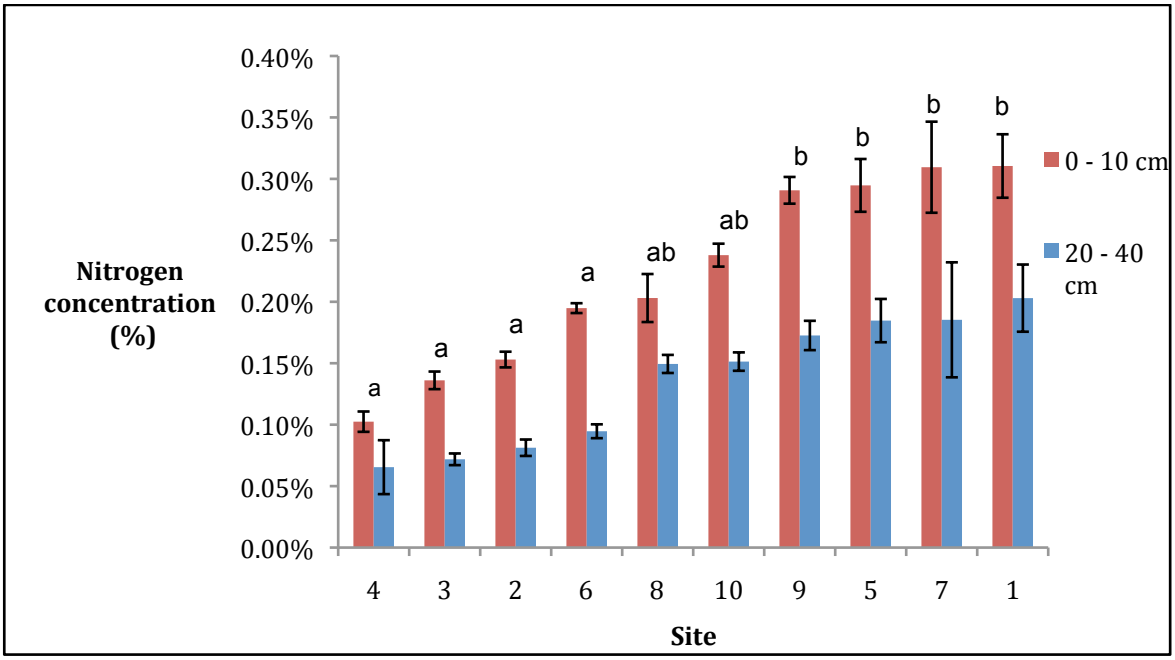


Figure 21. Nitrogen concentration (%) found in the Majuba soils across the two soil depths (0-10 cm and 20-40 cm) and the 10 sites sampled. Means associated with the different letters are significantly different ($p \leq 0.05$).

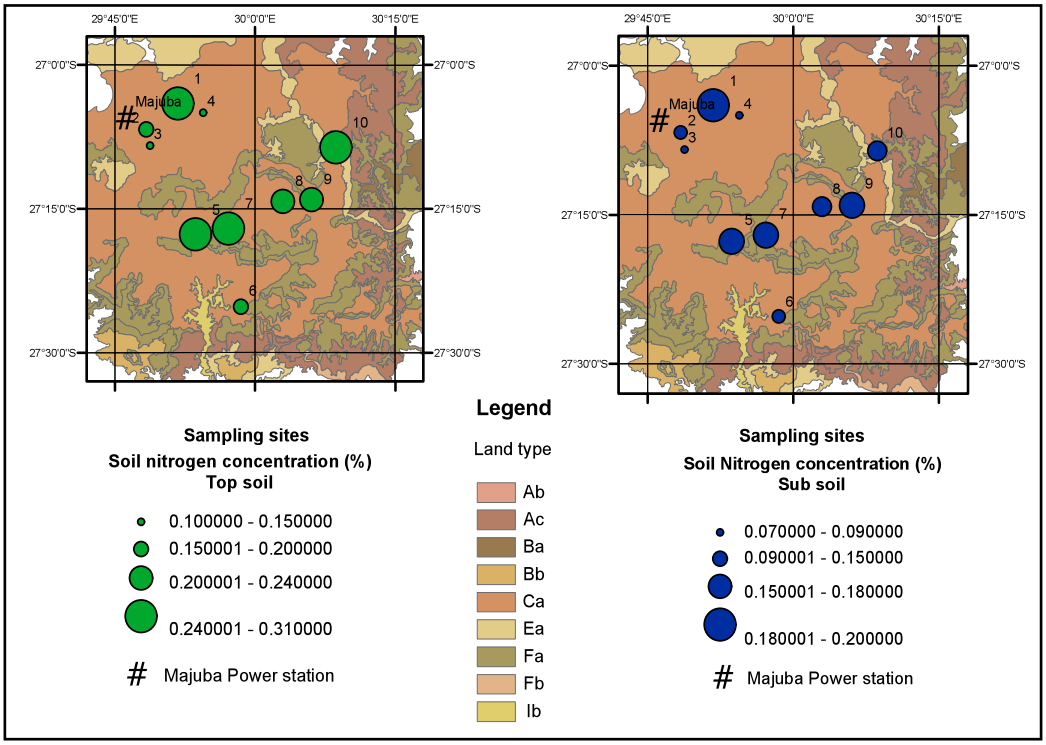


Figure 22. Map of sample sites showing spatial variation (significant interaction between site and depth, ($F = 2.26$, $p = 0.0382$) in percentage soil N, for top-soil ($n = 30$) and sub-soil ($n = 29$) depths for Majuba soils.

5.3.2 Soil nitrogen isotopes

The soil $\delta^{15}N$ values ranged from 3.15 ‰ to 9.64 ‰ and were found to be higher in the sub-soil than top-soil depths (Figure 23).

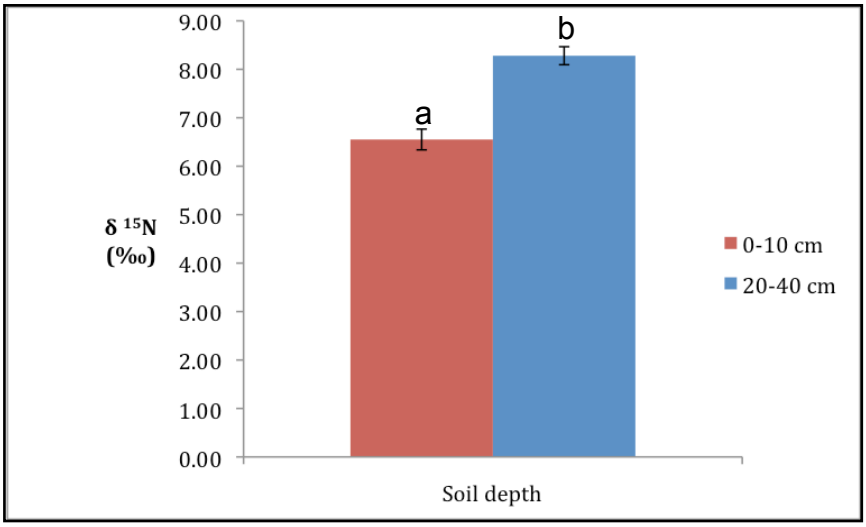


Figure 23. Mean ± standard error $\delta^{15}N$ ‰ values for Majuba soils for all ten sites, representing top (n = 30) and sub (n = 29) soil depths. Means associated with different letters are statistically different ($p \leq 0.05$).

The $\delta\ ^{15}N$ values were found to be significantly affected by both soil depth and sample site ($F = 4.64$, $p < 0.0001$, $F = 8.46$, $p < 0.0001$), while no statistical interaction was found to exist between these two factors.

The $\delta^{15}N$ values were compared across the ten sites, and grouped together according to statistical similarity (Figure 24). There appears to be a slight similarity between the grouping of the $\delta^{15}N$ and $\delta^{34}S$ values across sites. Site 5, 7, 8 and 9 are all close to each other with similar mean isotope signals. Site 1, 2, 3 and 4 are in close proximity to the Majuba power station and to each other, and display statistically similar $\delta^{15}N$ signals (Figure 25). As seen in the $\delta^{34}S$ data, site 10 on the north east of the Sandspruit catchment is an outsider with its own unique S and N isotope signature. In this case, the $\delta^{15}N$ signal is significantly lower than the other nine sites. A similarity in the grouping of sites for the S and N isotope values and the S and N elemental concentrations is also seen to exist.

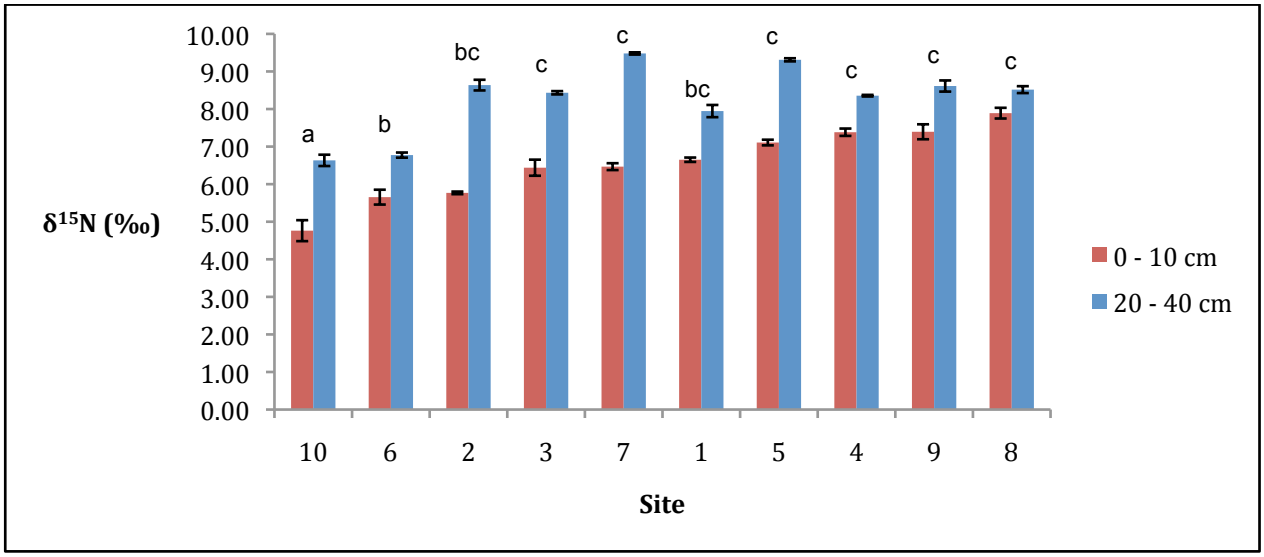


Figure 24. Mean ± standard error $\delta^{15}N$ (‰) values for Majuba soils, for both top-soils (n = 30) and sub-soils (n = 29), across the ten sampled sites. Means associated with a different letter are significantly different ($p \leq 0.05$).

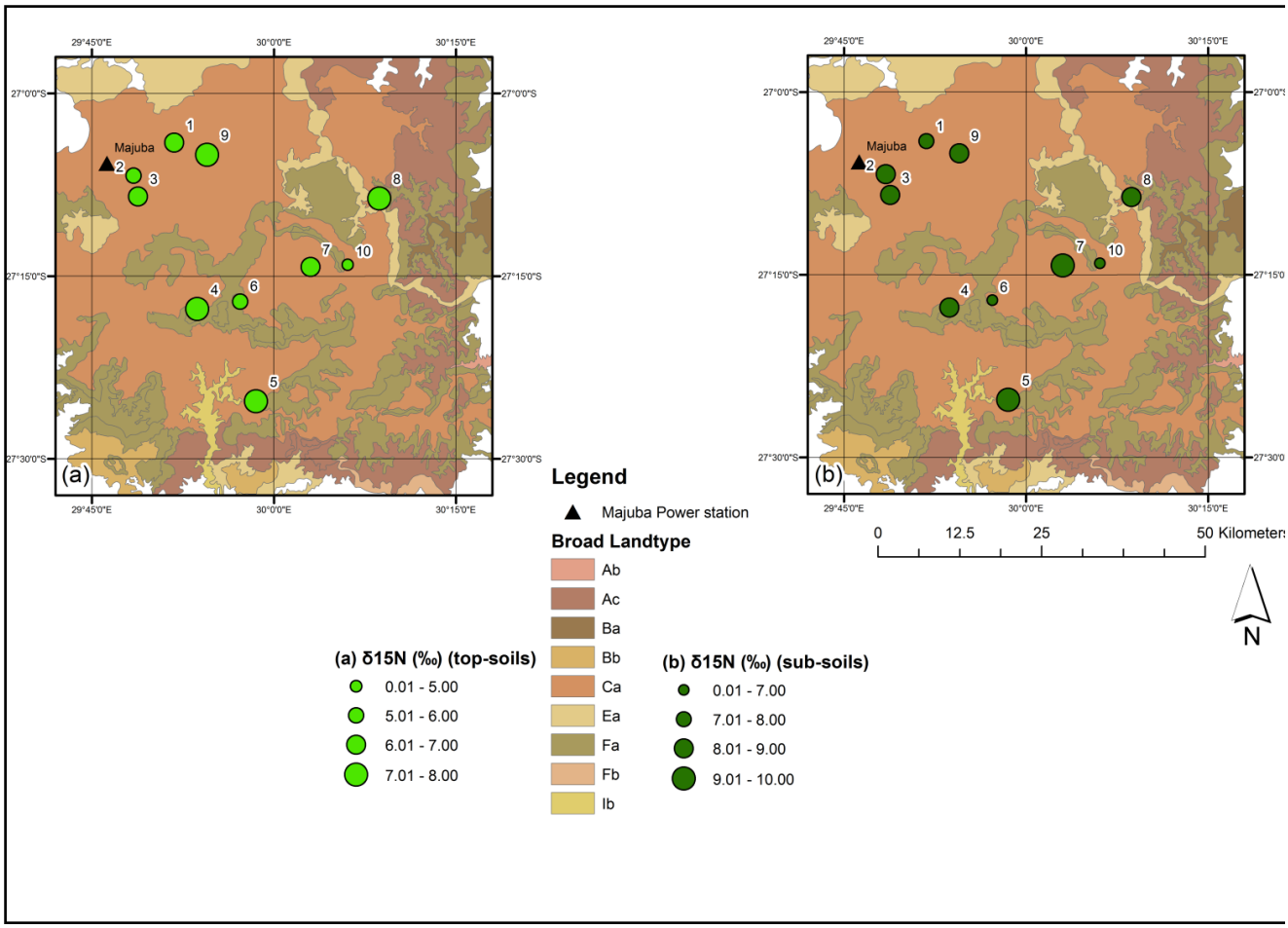


Figure 25. Map of sample sites showing spatial variation in $\delta^{15}N$ (‰), for both soil depths combined (n = 59) for Majuba soils.

The mean N concentration for each site was then plotted against the $\delta^{15}N$ value at each soil depth. There is a very weak correlation between these two variables in the top-soils ($r^2 = 0.026$) compared to the sub-soil ($r^2 = 0.055$) depths. A diffusion gradient can be established, as the sub-soil depths is seen to have lower N levels than the top-soils (Figure 26).

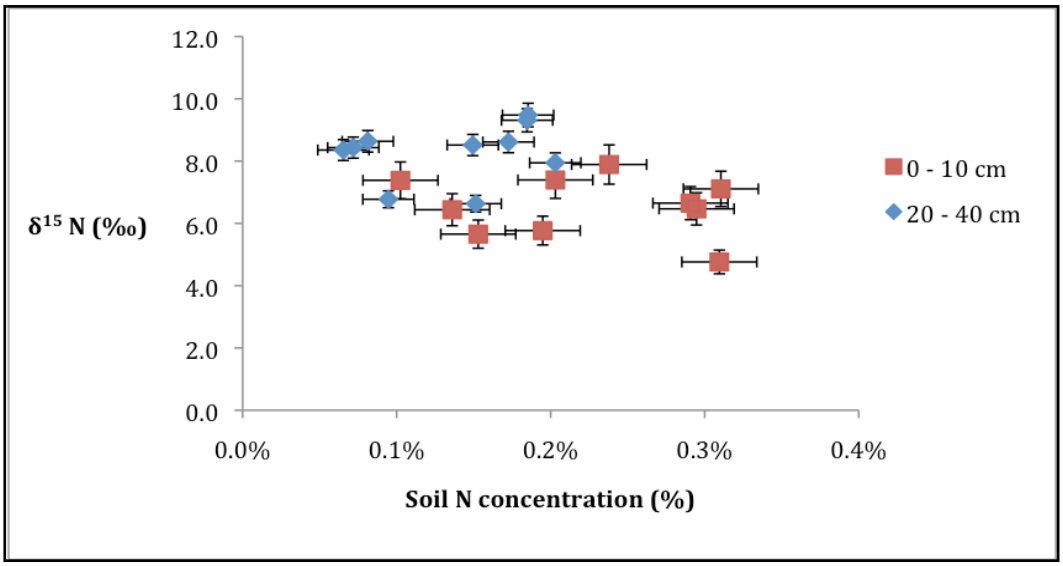


Figure 26. Graph showing mean soil $\delta^{15}N$ signal versus mean N concentration for both top-soils ($r^2 = 0.026$) and sub-soil depths ($r^2 = 0.055$) for Majuba soils.

In order to utilize the Rayleigh distillation model on Majuba soils, $\delta^{15}N$ versus the natural log of soil N content was plotted (Figure 27). A weak correlation was found between these factors ($r^2 = 0.14$) and the linear relationship was extrapolated back to Ln %N = 0, to yield a $\delta^{15}N$ value of approximately 1.14 ‰. Thus, according to the Rayleigh distillation model, the N isotope signal of the original N source is 1.14 ‰.

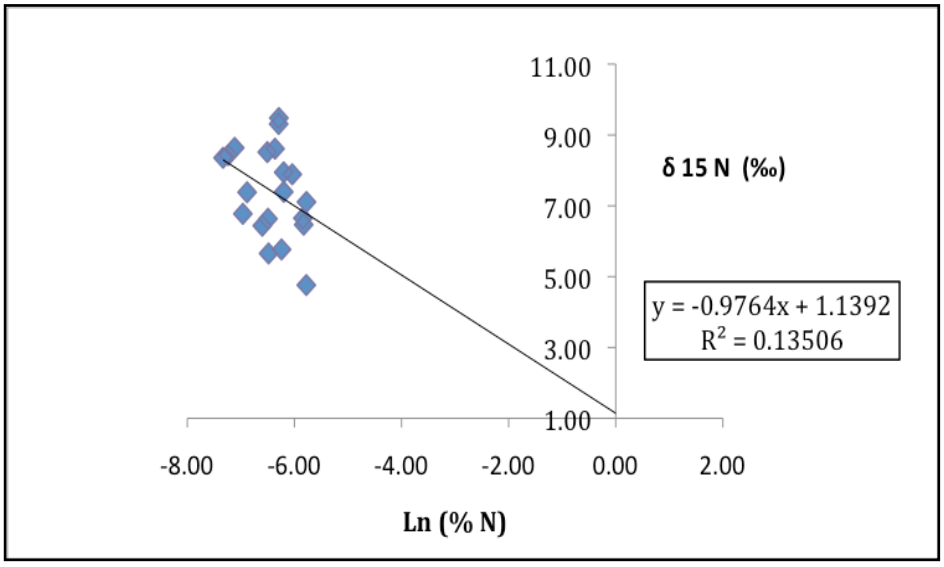


Figure 27 Graph showing mean soil $\delta^{15}5N$ versus natural long mean N concentration for the pooled data for Majuba soils.

5.4 CARBON

5.4.1 Total elemental carbon

The concentration of total soil C was found to be statistically higher in the top-soil than the sub-soil depths ($F = 18.45$, $p = 0.000112$), as expected (Figure 28). The top-soils ranged from 0.97 % to 7.93 %, while the sub-soils ranged from 0.49 % to 3.27 %.

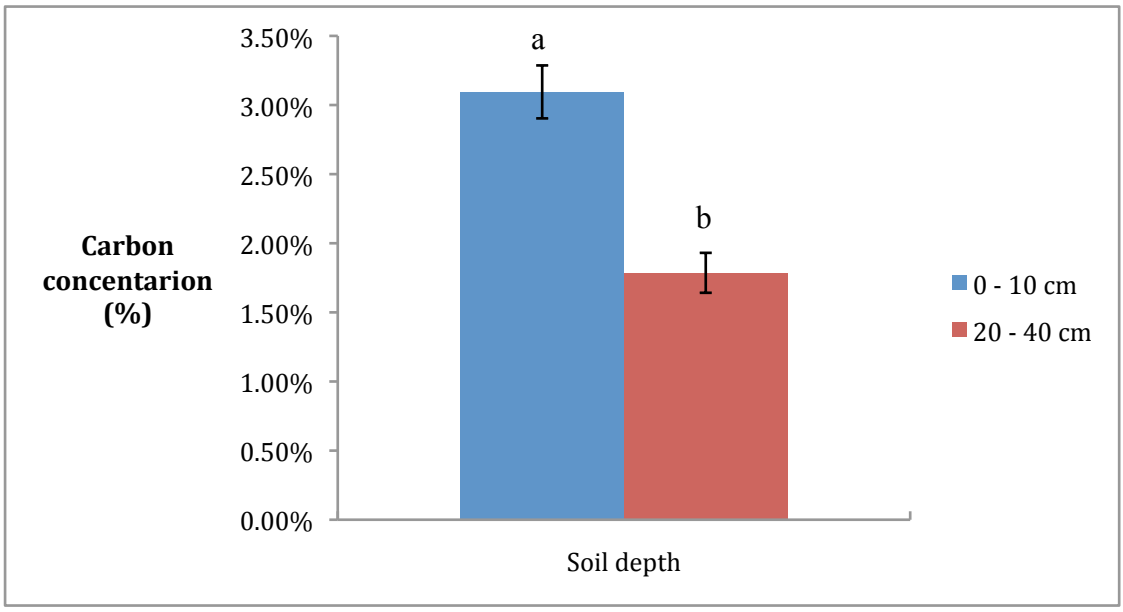


Figure 28. Mean percentage soil C concentration (± standard error) found in the Majuba soils for all 10 sites, representing both top (n = 30) and sub-soil (n = 29) depths. Means associated with different letters are statistically different ($p \leq 0.05$).

A significant difference in the C concentration across the ten sites was found ($F = 3.22$, $p = 0.0051$), but only the Bonferoni pair-wise comparison was able to establish where this difference occurred. Two groups were established, with a large degree of overlap in statistical similarity in mean soil C concentration (Figure 29). Site 7 was significantly different to site 1, 2 and 3. The spatial variation shows sites 2 and 3, which are in close proximity and downwind to the Majuba power station, as well as site 6, which is approximately 37.41 km downwind of the power station having the lowest percentage of soil C (Figure 30).

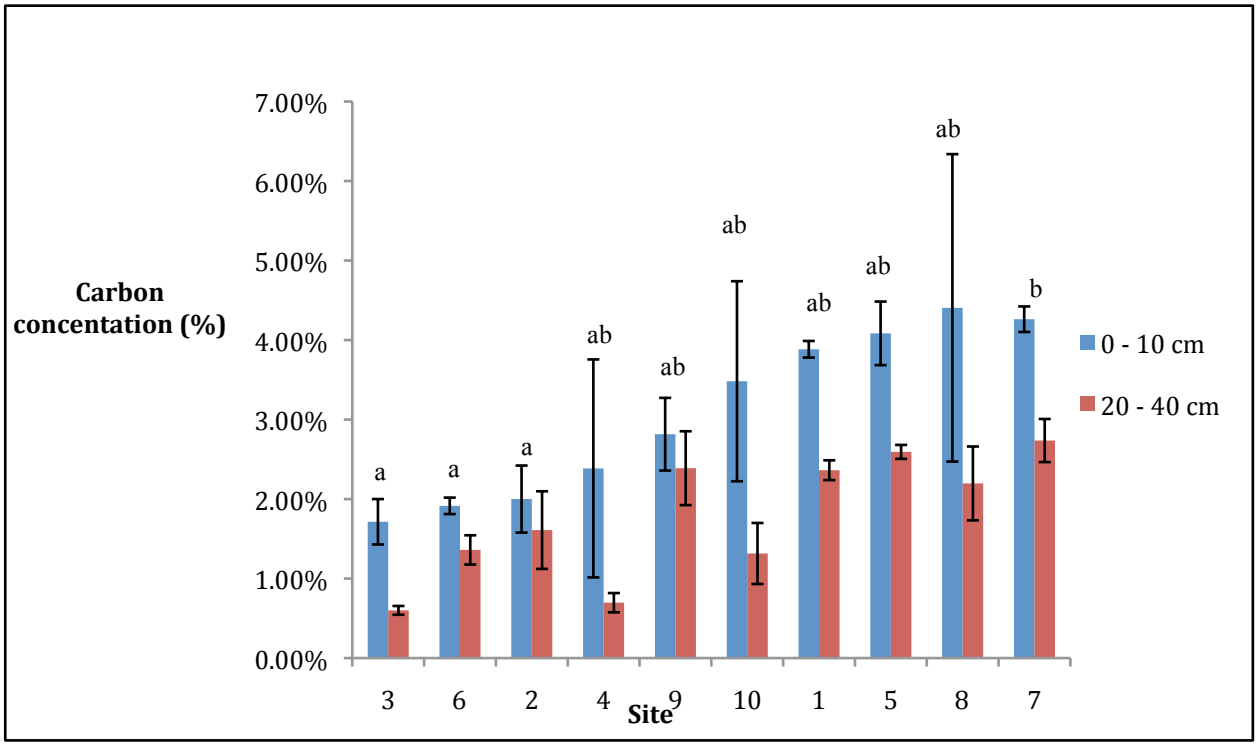


Figure 29. Mean ± standard error soil C concentration (%) values for Majuba soils, for both top-soils (n = 30) and sub-soils (n = 29), across the ten sampled sites. means associated with a different letter are significantly different ($p \leq 0.05$).

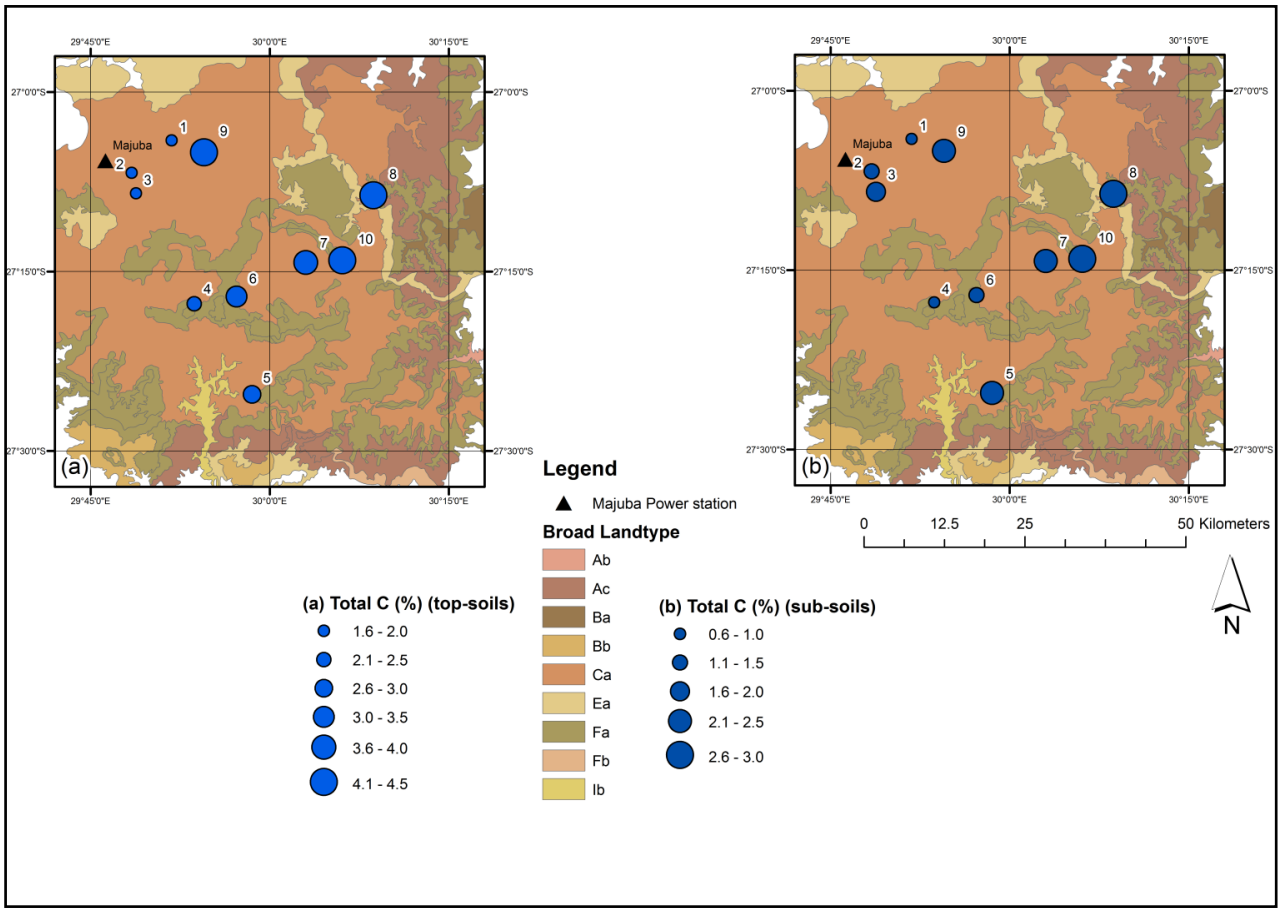


Figure 30. Map of sample sites showing spatial variation in C concentration (%), showing both top-soil (n = 29) and sub-soils (n = 30) for Majuba soils.

5.4.2 Soil carbon isotopes

Top-soils were found to be more depleted in $\delta^{13}C$ than the sub-soil depths (Figure 31). The top-soils ranged from -16.27 to -10.93 ‰, while the sub-soils ranged from -10.28 to -5.44 ‰.

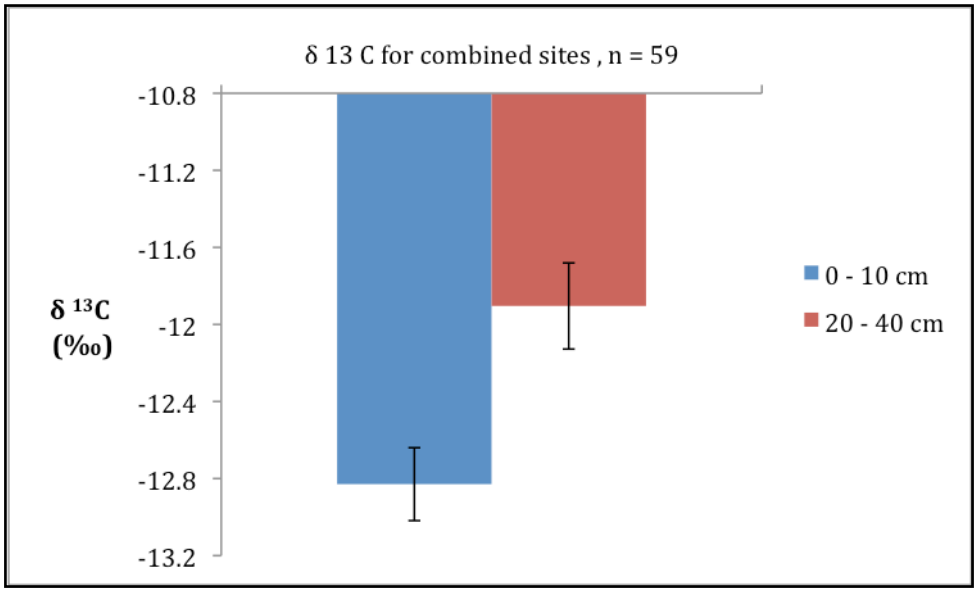


Figure 31. Mean ± standard error $\delta^{13}C$ ‰ values for Majuba soils for all ten sites, representing top (n = 30) and sub (n = 29) soil depths ($p \leq 0.05$).

Both soil depth and sample site were shown to significantly affect the $\delta^{13}C$ value in the soil ($F = 7.31$, $p = 0.009$; $F = 5.30$, $p = 0.025$ respectively), while no interaction was found to exist between these two factors. The sites were grouped together according to similarity in the isotope signature across both soil depths. Sites 1, 2, 3, 5, 7 and 9 are not significantly different (Figure 32), while Site 10 on the north east of the Sandspruit catchment again appears to have a unique C isotope signature, which is only statistically similar to 3 other sites. This outcome was also observed in the N and S isotope data for site 10. It appears that site 10 was a consistent outlier (both mathematically and statistically) due to difference in topography and potential difference in land types.

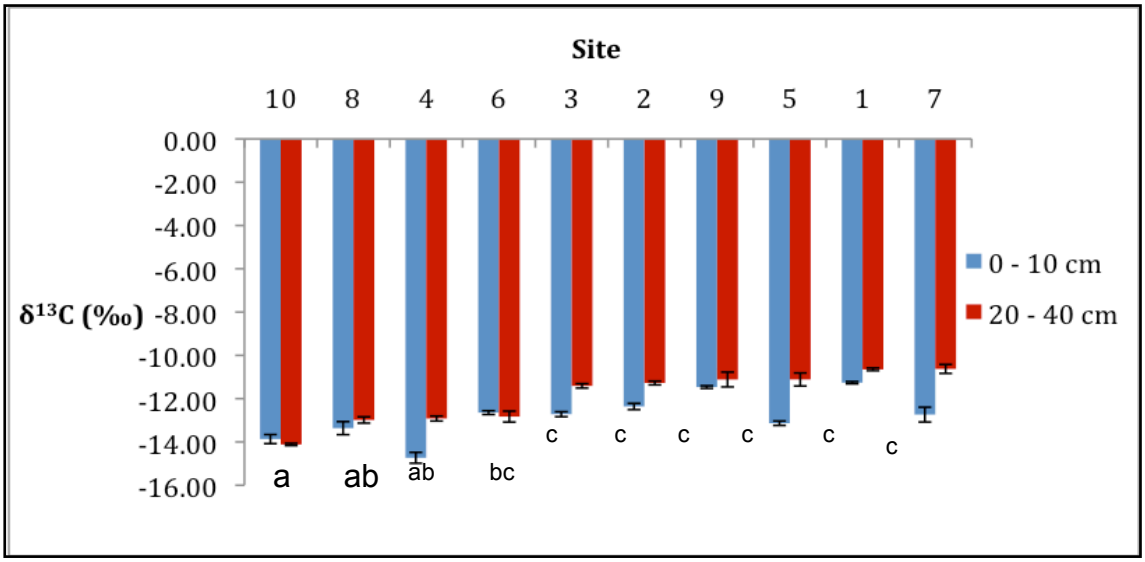


Figure 32. Mean ± standard error $\delta^{13}C$ (‰) values for Majuba soils, for both top-soils (n = 30) and sub-soils (n = 29), across the ten sampled sites. Means associated with a different letter are significantly different ($p \leq 0.05$).

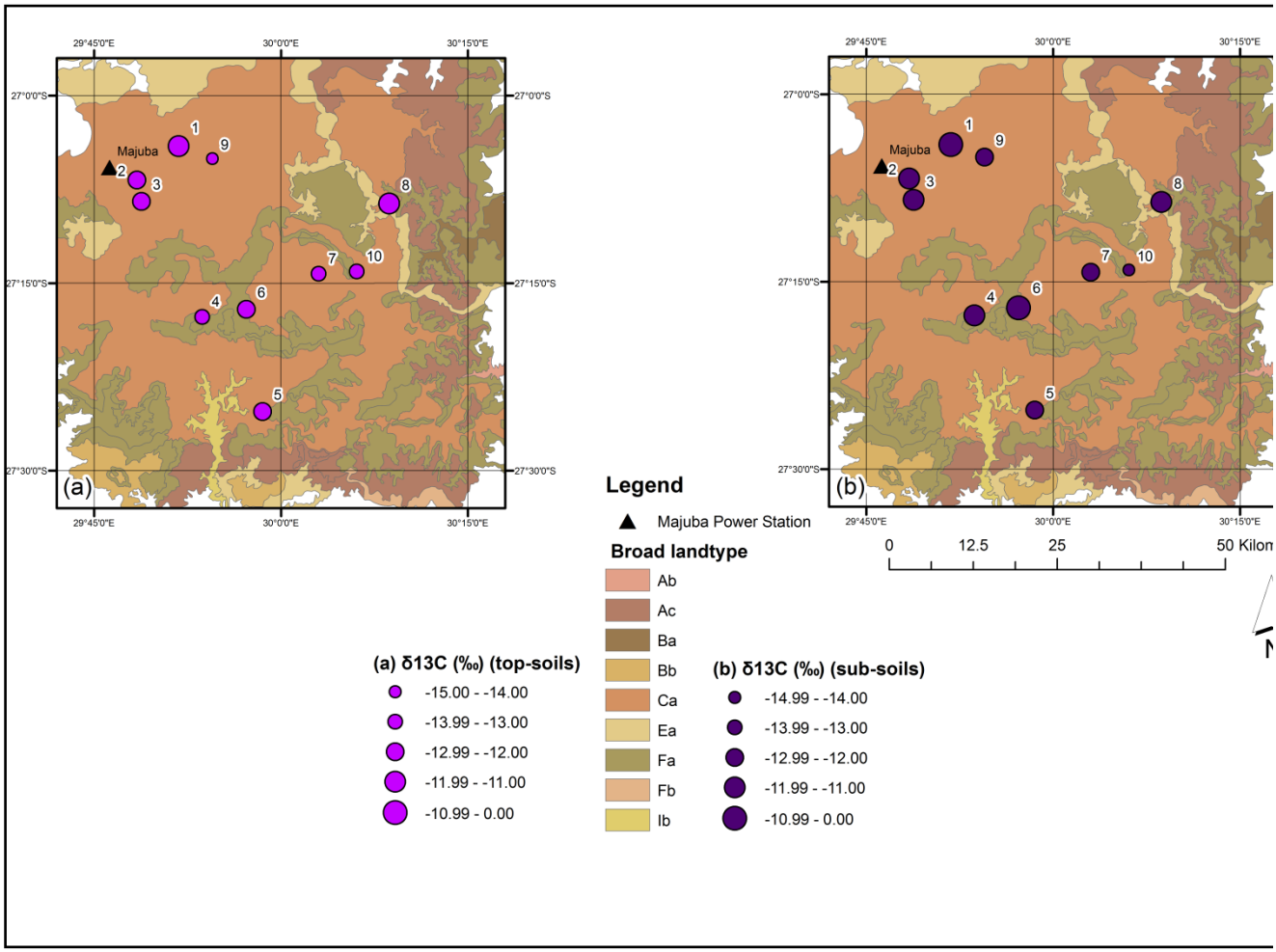


Figure 33. Map of sample sites showing spatial variation in $\delta^{13}C$ (‰), for both soil depths combined (n = 59) for Majuba soils.

A very weak correlation was established between mean soil $\delta^{13}C$ signal and soil C concentration at the top-soil ($r^2 = 0.035$) and sub-soil ($r^2 = 0.053$) depths. Site 10 only appears as an outlier in the sub-soils (Figure 34) while site 1, in close proximity to the power station, is an outlier in the top-soil depths.

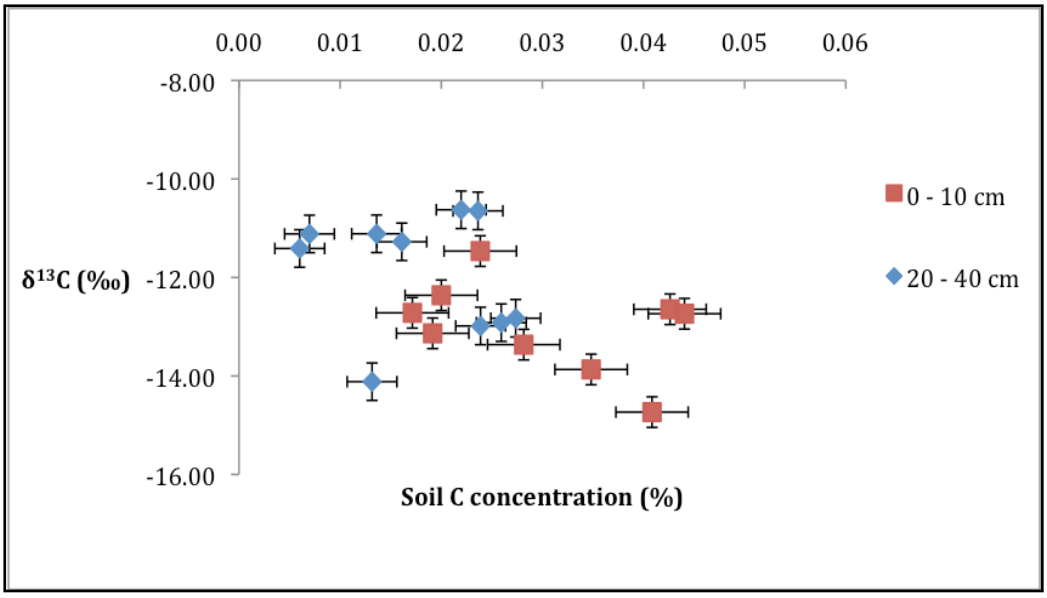


Figure 34. Graph showing mean soil $\delta^{13}C$ signal versus mean C concentration for both top-soils ($r^2 = 0.035$) and sub-soil ($r^2 = 0.053$) for Majuba soils.

5.5 CORRELATIONS

The mean soil N concentration was plotted against the mean soil C concentration at both depths (Figure 35). A very weak correlation is seen to exist ($r^2 = 0.002$) for the top-soil, while no correlation is present in the sub-soil depths ($r^2 = 0.000$). Site 4 and site 6 do not fall on the best-fit line, and can be described as outliers. A very similar pattern is observed in the soil S concentration versus C concentration plot (Figure 36). The sub-soils, however, have a higher correlation ($r^2 = 0.01$) than the top-soils ($r^2 = 0.006$).

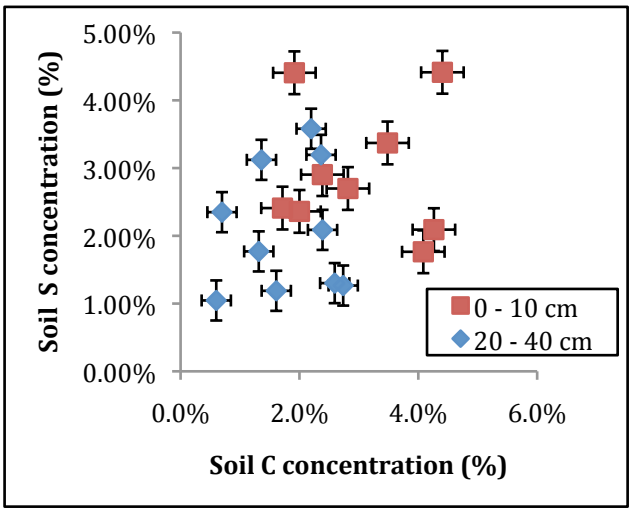


Figure 36. Graph showing mean soil sulfur concentration versus mean carbon concentration for both top-soils (r^2 = 0.006) and sub-soil depths (r^2 = 0.01) for Majuba

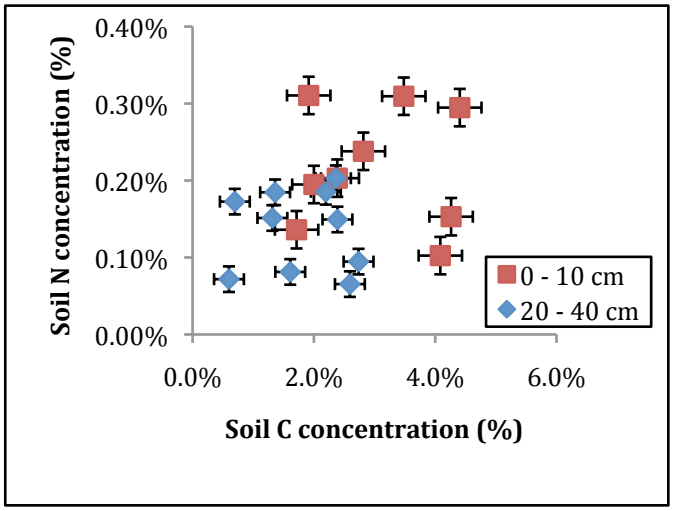


Figure 35. Graph showing mean soil nitrogen concentration versus mean carbon concentration for both top-soils (r^2 = 0.002) and sub-soil depths (r^2 = 0.000) for Majuba soils.

The relationship between soil N and S concentration was also investigated. A strong correlation is seen to exist between these two nutrients in both the top-soil (r^2 = 0.814) and sub-soil (r^2 = 0.851) depths (Figure 37).

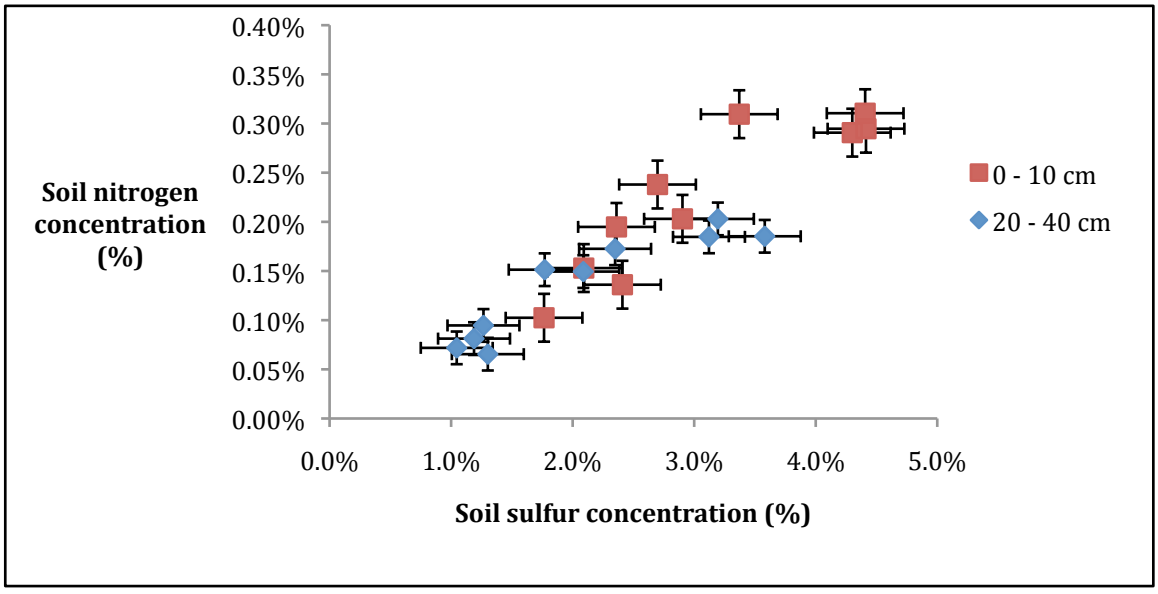


Figure 37. Graph showing mean soil N concentration versus mean S concentration for both top-soils (r^2 = 0.814) and sub-soil depths (r^2 = 0.851) for Majuba soils.

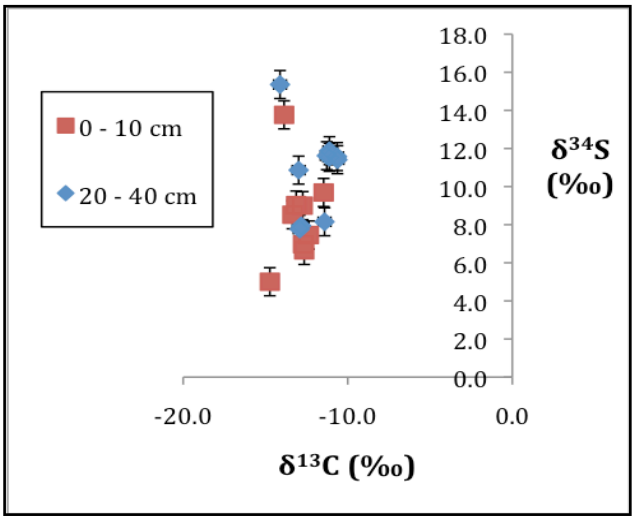


Figure 39. Graph showing mean soil $\delta^{34}S$ signal versus mean soil $\delta^{13}C$ signal for both top-soils ($r^2 = 0.007$) and sub-soil depths ($r^2 = 0.006$) for Majuba soils.

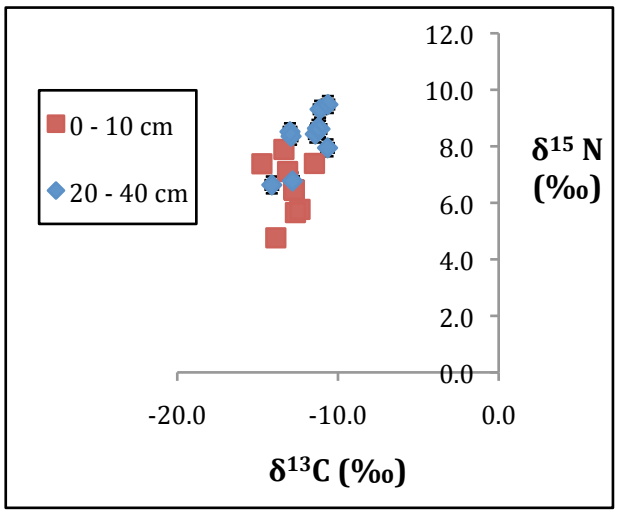


Figure 38: Graph showing mean soil $\delta^{15}N$ signal versus mean soil $\delta^{13}C$ signal or both top-soils ($r^2 = 1x10^{-05}$) and sub-soil depths

The mean soil $\delta^{15}N$ signal was plotted against the mean soil $\delta^{15}C$ signal for both depths (Figure 38). No correlation is seen for the top-soil (r^2 = 1E-05), with site 10 being the major outlier. The correlation is drastically improved when this outlier is removed from the series. A slight correlation is present in the sub-soil depths (r^2 = 0.501) with site 1 lying off the correlation gradient. The soil $\delta^{34}S$ versus $\delta^{15}C$ signal plot has a comparable weak correlation in both the top (r^2 = 0.007) and sub (r^2 = 0.006) soil depths, with site 10 being the foremost outlier in both soil depths (Figure 39).

There appears to be a very weak relationship between the mean soil $\delta^{15}N$ and $\delta^{34}S$ signals in both the top-soil depth (r^2 = 0.178). Site 8 and 9 are outliers in this series, and were outliers in the soil S and N concentration plot. The correlation between soil $\delta^{15}N$ and $\delta^{34}S$ signals in the sub-soil depth is very week (r^2 = 0.007), and again site 10 is responsible for the weak relationship (Figure 40).

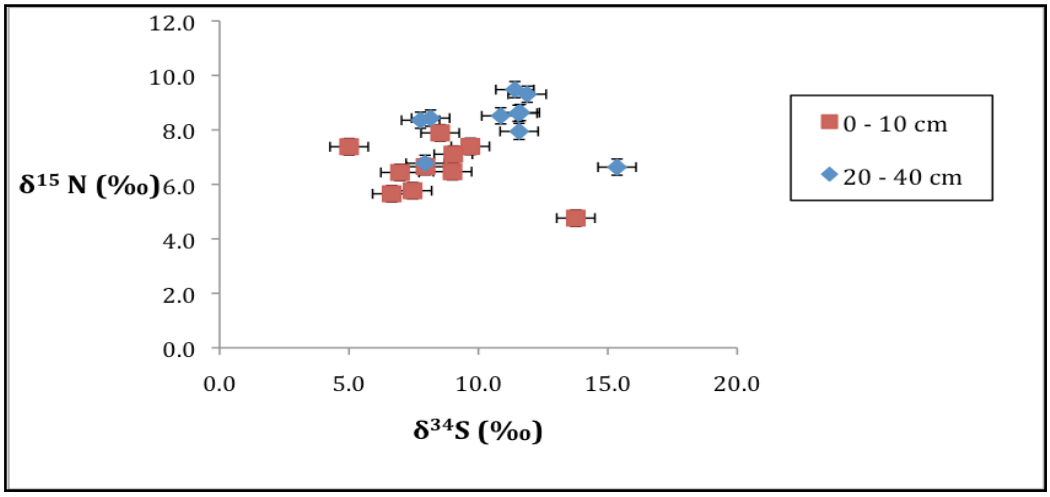


Figure 40. Graph showing mean soil δ^{15} N signal versus mean soil δ^{34}S signal for both top-soils (r^2 = 0.178) and sub-soil depths (r^2 = 0.007) for Majuba soils

The range in the C:N ratio for both the top-soils and sub-soils is shown below (Table 6).

Table 6. Table of C:N ratios ±standard errors obtained for both top-soils (n = 30) and sub-soils (n = 29) for Majuba soils

Soil depth	Mean ± standard error C:N
0 – 10 cm	8.06 ± 1.44
20 – 40 cm	9.61 ± 2.40

5.6 COAL

A composite sample of the coal burnt at Majuba power station was also analysed and the results are given in Table 7. The total N and C concentration is higher than that analysed in the soil samples, while the δ^{15}N and the δ^{13}C value of the coal sample were far lower.

Table 7. Mean ± standard error for total S, N and C concentration (%), as well as δ^{34}S, δ^{15}N and δ^{13}C (‰) for a composite coal sample from Majuba power station

Total S (%)	Total N (%)	Total C (%)	δ^{34}S (‰)	δ^{15}N (‰)	δ^{13}C (‰)
0.44 – 0.66%	1.20 ± 0.08	53.77 ± 2.75	3.80 ± 0.50	0.73 ± 0.27	-23.42 ±0.15

5.7 PARTICLE SIZE DISTRIBUTION

The particle size distribution showed that soils contained higher percentages of clay, followed by silt and sand. The sub-soils had higher percentages of clay than the top-soils, while percentages of silt and clay were higher in the top-soils (Figure 41).

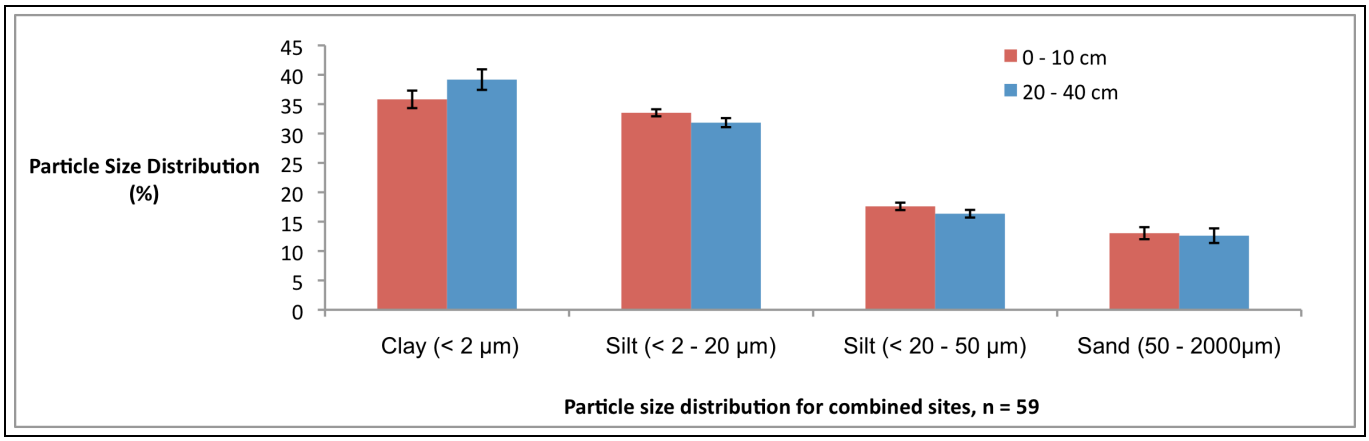


Figure 41. Graph showing particle size distribution for all 10 sites combined, indicating both top-soil (n = 29) and sub-soil (n = 30) depth for Majuba soils.

6 DISCUSSION

Sulfur, N and C play an important role in the functioning of terrestrial ecosystems and are essential for life. Studies of the interactions between these nutrients can provide a valuable means of understanding the structure and functioning of ecosystems. Increased S and N deposition to systems may enhance the rate and transformation of natural processes (Figure 42). Identifying sources of S and N input and processes affecting their export from an ecosystem are critical in determining the extent of nutrient cycling locally and for global cycles.

This study combined the measurements of total elemental concentrations in the soil system, as well as isotopic measurements of S, N and C to determine the effect of deposition on the soil system in the Mpumalanga Highveld, South Africa.

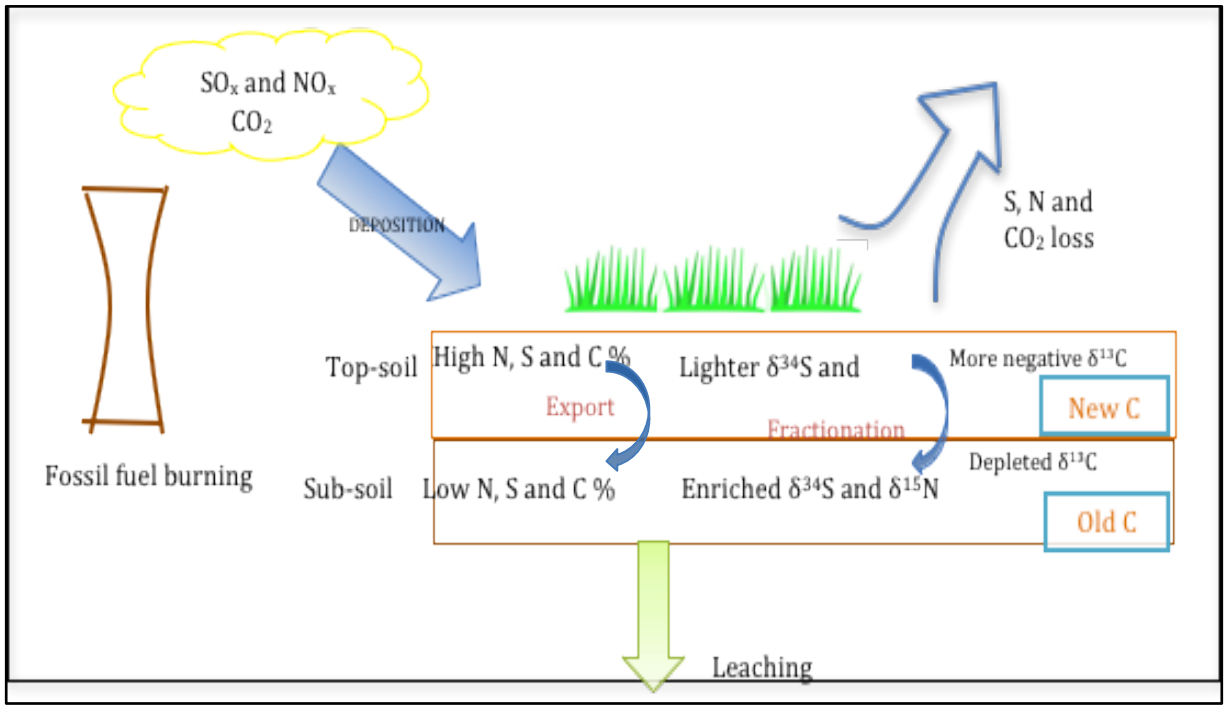


Figure 42. Schematic diagram illustrating the pathway of S, N and C from the atmosphere to the soil system.

6.1 CONCEPTUAL FRAMEWORK

The interpretation of the presented conceptual framework (Figure 43) requires an understanding of the simultaneous processes of deposition and export in the soil system. S and N are deposited on the surface and loss from the top-soils to the sub-soil occurs through export. The rate at which these processes of deposition and transfer occur, will determine the net concentrations and

isotopes measured at the time of sampling. The theory proposed relates specifically to S since the N data does not support this theory. This may indicate that biological and chemical fractionation occurs at different rates in the N and S soil system.

High isotopic values indicate a higher ratio of the heavier isotope. During fractionation, the $\delta^{34}S$ isotope value will increase if the reaction favours the lighter isotope, and vice versa.

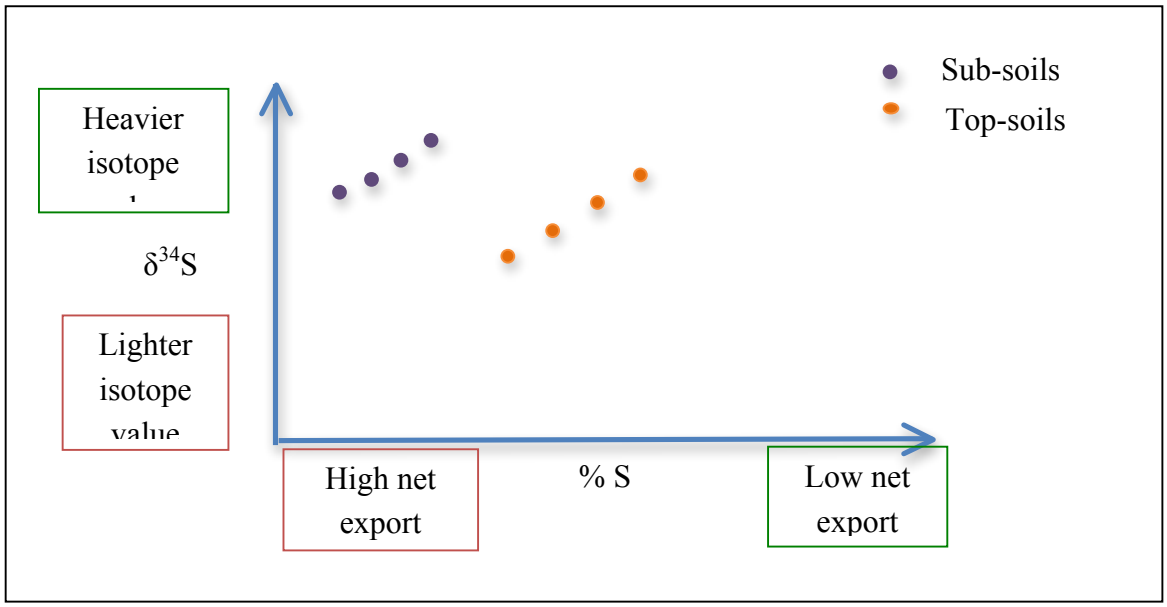


Figure 43. Conceptual diagram illustrating the correlation between $\delta^{34}S$ and % S in the top-soil and sub-soil depth.

Sulfur is deposited on the surface soil by the process of deposition. The deposited S from anthropogenic sources has a lighter $\delta^{34}S$ isotope value than that of natural sources. Large amounts of S deposition results in an increase in S export, which then decreases the percentage of S in the top-soils. More export also implies shorter residence times allowing for less biological fractionation and maintaining lower S isotopic signatures in the top-soils. As the net export decreases, the percentage of S in the top-soils increases. Since export has decreased, the S has a longer soil residence time, allowing natural biological processes to occur. These biological processes favour the lighter S isotope, which will then be incorporated into biological material. Thus, fractionation occurs and the soil becomes enriched in the heavier S isotope resulting in a heavier isotope value.

In the sub-soils, the percentage of S decreases due to lower SOM concentrations (Figure 13) and net export of S. The S in the sub-soils will then have a heavier isotopic signal, because of biological fractionation and the fact that the S does not necessarily originate from atmospheric deposition on the soil surface. The heavier isotopic signal in the sub-soils could be a mixture of natural bedrock S (with heavier $\delta^{34}S$ values) and the deposited S (with lighter $\delta^{34}S$ values) and biologically transformed S. Thus the origin of the S in the sub-soils is not necessary the same as that of the top-soils.

6.1.1 Limitations of conceptual framework

The main aims of this study were to obtain a baseline of the total $\delta^{34}S$ and $\delta^{15}N$ isotope signatures of soils in the Mpumalanga region, and to compare these S and N concentrations at various soil depths with these isotope values. Therefore, in order to meet this objective at an achievable cost, only total soil S, N and C isotope values and soil concentrations were measured.

Isotopic signatures of various possible S and N sources in the study area were not measured (other than the coal sample), and direct tracing of S and N through the system, from the atmosphere to the soil cannot be made. However, comparison between the S and N isotope signature in the Majuba coal sample and soil values can be inferred. Oxygen isotopes were also not measured, thus oxidation processes and transfer of NO_3^- and SO_4^{-2} species cannot be documented. Patterns of mineralization and transfers between organic and inorganic pools were not analysed, and inorganic S and N isotopes were also not measured.

Variations in the soil S, N and C isotopes will now be discussed, followed by an interpretation of the soil S, N and C concentrations. Finally, correlations between the various elements will be examined.

6.2 SOIL ISOTOPES

6.2.1 Sulfur

The mean ± standard error $\delta^{34}S$ in the top-soils was found to be 8.28 ± 0.18 ‰ and increased in the sub-soils to 10.78 ‰ ± 0.47 (Figure 16). A variety of natural and anthropogenic sources of S results in a wide range of $\delta^{34}S$ values. Common natural sources of S include sea-spray and volcanic emissions, while anthropogenic sources may consist of flue gas from coal combustion and combustion and refining of oil and gas (Table 1). The wide range in $\delta^{34}S$ values can be attributed to essentially three processes, which vary with locality. These are

(a) local weathering of rocks containing evaporates and sulfide ores, (sub-soils),

(b) inputs of sulfate from the atmosphere (top-soils), and

(c) bacterial sulfate reduction in less aerobic environments leading to differentiation of $\delta^{34}S$ values with soil depth (internal).

Other studies from a coal fired power plant in Spain that utilized South African coal, measured $\delta^{34}S$ for SO_2 in the stack emissions of a coal-powered plant to be -2.8 ± 0.5 ‰ (Puig *et al*., 2008). The same study found the $\delta^{34}S$ in bulk precipitation at the polluted sites to increase to +3.3 ‰. For the polluted atmosphere in Bologna, Panettiere *et al*. (2000) reported a mean $\delta^{34}S$ value of +3.2 ‰ (range +0.4 to +6.2 ‰). Atmospheric SO_4^{-2} from polluted areas in central Europe had a measured $\delta^{34}S$ values ranging from close to +4 to +5 ‰ (Querol *et al*., 2000). Novak *et al.* (1996) found SO_2 $\delta^{34}S$ near a cluster of coal-fired power stations in central Europe to vary between 0.2 – 0.3 ‰ in the winter and 2.5 – 4.8 ‰ in the summertime.

In addition to anthropogenic S, natural sources (sea salt sulfate, marine DMS, and crustal evaporates and gypsum) could also influence S isotope ratios in the atmosphere, eventually affecting those of precipitation and throughfall. Majuba power station is located approximately 500 km from the Indian Ocean and marine aerosols are known to have very high positive $\delta^{34}S$ values (+20 ‰) (Newman *et al*., 1991). Mphepya *et al.,* (2004) calculated the sum of marine contributions to the total ionic content of Amersfoort to be 11 %. Galpin and Turner (1999) found that the 73.5 % of the variance in rainfall signatures in Amersfoort could be explained by industrial, oceanic with overland path, biomass combustion and soil and surface material (in order from most important factor to least important factor). Thus, it is possible that a marine component could contribute to the higher than expected $\delta^{34}S$ values at Majuba.

Sulfur is known to have two fractionation processes: the assimilation of S by plants and the mineralization of organic S in the soil (Krouse & Grinenko 1991). Both are associated with an increase in soil $\delta^{34}S$. The $\delta^{34}S$ values were found to be higher in the sub-soil than top-soil depths (Figure 8). This is in line with other studies that show an increase in $\delta^{34}S$ ratios from top-soil to mineral soil, regardless of the distance from major point sources of atmospheric pollution (Novak *et al.,* 1996; Novak *et al.*, 2001). The positive $\delta^{34}S$ shift may result from

i) mixing of S from two isotopically distinct sources (bedrock and atmosphere) and/or
ii) isotope fractionation processes within the soil profile.

Sulfate precursors of gypsum and dissolved sulfate include bedrock sulfides and decompositional marine biogenic H_2S. The $\delta^{34}S$ value of bedrock sulfide in the Central Namib dessert has been known to vary from -4.1 – 13.8 ‰ (Eckardt and Spiro, 1999), the large variation accounted for differences in geology and varying sulfide species (such as chalcocite, bornite and pyrite). Reimer (1986) measured the $\delta^{34}S$ of southern African playa gypsum to be slightly higher at 15.1 ‰. Thus, it is possible that a two-source mixing model is responsible for the higher $\delta^{34}S$ values found in the Majuba sub-soils.

The $\delta^{34}S$ value for the Majuba coal sample was measured at +3.8 ± 0.5 ‰ (Table 7) and has an S concentration of 0.44%. Several studies have shown that *low-S* (≤ 1% S) coal contains mostly syngenetic organic sulfur with rather homogeneous $\delta^{34}S$ values reflecting primary plant S (e.g. Smith and Batts, 1974; Price and Shieh, 1979, Smith *et al*., 1982; Hackley and Anderson, 1986; Spiker *et al*., 1994). Hortsmann *et al*., (2001) measured the $\delta^{34}S$ of organic S in a South African coal to range from -2.5 – 4.9 ‰. The results found in our study fall within the higher end of this range. This may explain the higher $\delta^{34}S$ values found in the Majuba soil, compared to those published.

6.2.2 Nitrogen

The $\delta^{15}N$ values of total N ranged from 3.15 ‰ to 9.64 ‰ and were seen to increase with soil depth, as N concentration decreased (Figure 23). The isotopic composition of atmospheric N_2 is considered globally uniform, within analytical precision, with a ^{15}N abundance of 0.37 % (Junk and Svec, 1958; Sweeney *et al*., 1978; Mariotti, 1983). $\delta^{15}N$ values for terrestrial N compounds generally fall in the range -15 to + 20 ‰ (Heaton, 1986). The $\delta^{15}N$ values of the Majuba top-soils (6.55 ± 1.21 ‰) were higher than what is expected if all N was derived from atmospheric N_2 fixation. If this were the case, the $\delta^{15}N$ signature would be approximately 0 ‰ (Nadelhoffer & Fry, 1994). Heaton (1986) reported $\delta^{15}N$ originating from dry deposition in non-cultivated areas to usually be in excess of 5 ‰. In Utah, surface soil $\delta^{15}N$ values ranged from 0 to 4 ‰ in undisturbed sites (Evans & Ehleringer, 1993; Evans & Belnap, 1999). In forest mineral soils in Japan, $\delta^{15}N$ values of total soil N ranged from 1.0 to 6.8 ‰ (Koba *et al.,* 1997). Heaton (1986) found that NO_3^- in soil water had a similar $\delta^{15}N$ signature as total soil organic N, which is in the range of +4 to +8 ‰.

The higher positive values of $\delta^{15}N$ in Majuba soils indicate that the soil N is affected by other processes of the N cycle, which could include coupled nitrification/denitrification, NH_3 volatilization, or atmospheric deposition of enriched NO_3^- or NH_4^+. An increase in isotope abundances may result from the effects of human activities such as domestic grazing and cultivation (Aranibar *et al.*, 2004). These activities tend to fractionate the N within the system thus, favouring exports of ^{14}N in the harvested or consumed plants. A considerable number of isotopic surveys found $\delta^{15}N$ values of greater than 10 ‰, and these were interpreted as representing localised pollution by animal or sewage waste (Heaton, 1986). Thus, land use intensity could explain the high $\delta^{15}N$ values in Majuba soils, although effort was made not to sample near sewage or animal waste.

In addition, the high $\delta^{15}N$ values may verify that the Majuba area is not N-limited. Nitrogen impoverished areas are known to experience lower mineralization and nitrification rates and smaller N gas losses to the atmosphere (Neill *et al.*, 1997). In contrast, N rich systems will have more N losses

than N-poor systems, which will lead to the former having higher $\delta^{15}N$ values. As N is lost, the N left behind will undergo biological fractionation leading to isotopic enrichment (Högberg 1997).

It is worthwhile to note that soil N isotope values are known to be highly seasonal (Woodburn, 2011 pers. comm.; Heaton, 1986). Aranibar *et al.* (2004) also investigated N cycling in the soil and plant system along a precipitation gradient in the Kalahari sands (South Africa) and concluded that $\delta^{15}N$ values increase as aridity increases. Since seasonal $\delta^{15}N$ data for the Majuba study area are not available, care should be taken in comparing $\delta^{15}N$ values with other studies that might differ in amount and seasonality of precipitation. However, with that in mind, a comparison of the $\delta^{15}N$ values in Majuba soils, (which has a mean annual rainfall of 1008mm) to the wettest site sampled in the Kalahari (Lukulu, with a mean annual rainfall of 970mm), reveals that the Majuba site has a slightly higher mean $\delta^{15}N$ value for top-soils (6.33 ‰) than Lukulu (5.10 ‰). This is therefore contradictory to the findings made by Aranibar *et al.*, (2004).

The increase with depth suggests that isotope fractionation occurred during N export due to the faster reaction rate of ^{14}N compared to ^{15}N (Koba *et al.*, 1997). A similar pattern is observed in the total soil S and $\delta^{34}S$ data (Figure 13 and Figure 16). This increase with depth could also be due to inputs of plant litter at the soil surface that are isotopically lighter than soil organic matter and overall isotopic fractionation during microbial processing of organic matter during decomposition and N loss (Nadelhoffer and Fry, 1988; Kramer *et al.*, 2003). Fractionation for each N transformation that occurs with increasing soil depth causes the remaining soil N to become progressively enriched in ^{15}N as N moves down the soil profile.

The $\delta^{15}N$ value for the composite coal sample from Majuba power station (0.73 ± 0.27 ‰) was found to be within the lower range reported in the literature. In Australia, $\delta^{15}N$ values of coal samples ranged from 0.5 to 2.7 ‰, while a coal sample from Beaver Lake in the Antarctic was reported as 3.00 ‰ (Rigby and Batts, 1985). Since very little isotopic fractionation is envisaged at the high temperatures of combustion, $\delta^{15}N$ of emitted NO_x, is expected to be similar to that of the N which was oxidized (atmospheric N_2, $\delta^{15}N = 0$; fuel N, $\delta^{15}N = -1$ to $+5$ %) (Heaton, 1986). Furthermore, the $\delta^{15}N$ value obtained for the Majuba composite coal sample was not far off the valued obtained via the Rayleigh distillation model, which estimated the N isotope signal of the original N source to be 1.14 ‰.

6.2.3 Carbon

The $\delta^{13}C$ values increased from -12.83 ± 0.19 ‰, in the tops soils to -11.90 ± 0.22 ‰, in the sub-soil depths (Figure 29). These values indicate a typical C4 grassland system, as C4 plants exhibit a $\delta^{13}C$ value of -13.00 ± 2 ‰ (Lajtha and Marshall, 1994). The $\delta^{13}C$ values for Majuba soils are higher than those found in a semi-arid grassland in south eastern Arizona where the $\delta^{13}C$ in SOM was measured at -16.5 ‰ (Biggs *et al.,* 2002) and a typical savanna where the C isotope signal varies between -26 and -14 ‰ (Martinelli *et al.*, 2007).

The increase in $\delta^{13}C$ with soil depth was also documented by Balesdent *et al.* (1993) at 14 forested sites, as well under savanna like vegetation in southeast Brazil (Roscoe, 1999). Various mechanisms have been proposed to account for increasing $\delta^{13}C$ ratios with increasing soil depth. Balesdent and Mariotti (1996) suggested a conceptual model for the $\delta^{13}C$ ratios of soil organic matter distinguishing between early and later stages of C decay. In the early steps, ^{13}C enrichment in soil due to microbial respiration is more or less balanced by the slower decay of ^{13}C-depleted lignin, whereas later microbial recycling of C dominates and explains the higher ^{13}C content of old C. In addition, the higher ^{13}C content of pre-industrial atmospheric CO_2 may account for some of the ^{13}C enrichment in older soil organic matter (Balesdent and Mariotti, 1996).

$\delta^{13}C$ values are also known to differ for each soil fraction, with the coarser fractions containing less C and always lower in ^{13}C than the clay-rich fractions (Balesdent *et al.,* 1988; Bird *et al*., 2000; Gregorich *et al.,* 1995; Martin *et al.,* 1990). It has been suggested that physical protection by the clay minerals rather than chemical differences distinguish the two categories (Hsieh, 1997) or selective preservation of fine particulates with increased fire frequency (Bird *et al*., 2000). In the Majuba study, top-soils contained lower $\delta^{13}C$ values than sub-soils. This could be an indication that top-soils are dominated by coarser soil fractions than sub-soils. According to the particle size distribution data, the top-soils did contain more sand than the sub-soils, but this difference was not statistically significant.

6.3 SOIL CONCENTRATIONS

6.3.1 Sulfur

Sulfur content of grassland soils usually ranges between 0.010 and 0.05% with an average of 0.03% (Clark *et al.,* 1980). The S percentages in Majuba soils fell within this range, at 0.031 % in the top-soils to 0.021 % in the sub-soils. However, it was higher than the S percentages found near the Arnot power station, South Africa, where total soil S values ranged from 0.0104 % in the top-soils to 0.006 % in the lower soil depths (Reid, 2007). In the Great Plains of North America, total organic S in bulk soils of the native grassland sites ranged from 0.019 % to 0.085%, with an average of 0.044 % (Wang *et al*., 2006). Total S in the soils of the Ethiopian Rift Valley ranges from 0.01% of the

subsurface layers of the Fluvisol, to 0.046% of the Andosol at a depth of 70–100 cm from the surface (Itanna, 2005). The S content of Majuba soils was higher than of selected virgin South African soils, which range from 0.0032 to 0.03% (du Toit and du Preez, 1995). The variations in soil S concentrations may also be due to differences in soil organic matter (SOM) levels resulting from differences in vegetation, climate and soil types.

The study conducted by Reid (2007) found an increase in total S during a ten-year period, in both soil depths, as the acidity of the soil increased due to acid deposition. Similarly, it is feasible that under high acid deposition conditions, Majuba soils contain high percentages of soil S.

The total soil S values were also seen to decrease with soil depth (Figure 13), as expected. This may be because the top-soils receive S deposition directly from the atmosphere; the sub-soils receive sulphur as throughput from the top-soils (Reid, 2007). Roberts and Bettany (1985) also found organic sulphur to decrease significantly with depth as did the proportion of organic sulphate. The carbon-bonded S fraction is highly labile, and remineralizes the immobilized SO_4^{-2} (Freney *et al.,* 1971; Saggar *et al.,* 1981; Maynard *et al.,* 1984). Thus, as SO_4^{-2} is known to generally increase with depth in the soil profile, the total carbon-bonded S decreases with depth. A study investigating sulphur in soils of the central-northern part of the Zambian copper belt-mining district also found concentrations of total S to be higher in top-soil relative to subsurface soil (Kříbek *et al*., 2010). The Zambia study concluded that the high content of sulphur in top-soil might be a result of S emissions from mining operations.

Sites 5 and 7, approximately 22.45 and 25.70 km downwind from the Majuba Power Station showed the highest percentages of soil S (Figure 14 and Figure 15). Data from the wind and pollution roses collected from the Majuba 1 air quality monitoring station indicate high wind velocities with high S concentrations in the direction east-north-east to south-east (Figure 8 and Figure 9). Thus, it would appear that due to the prevailing winds and the height of the stack, the pollution plume does not affect the sites near the power station, and the S deposition is falling onto sites located approximately 25 km from the power station. However, some studies have shown the greatest impact from power generation to be within 10 – 15 km from the source (Freedman and Hutchinson 1980; Annegarn *et al.* 1996; Ek *et al.* 2001; Reid, 2007). A pollution gradient study in the Kola Peninsula (Russia) found a correlation between percentage of S in the top-soils and S deposition (Koptsik and Alewell, 2007). This correlation was found to be strongest up to 16 km from the source with S contents appearing to be rather unaffected for distances greater than 20 km. Thus, the high concentrations of S that were found at such large distances from the Majuba Power Station may be due to low net export of S rather than high deposition loads at those sites. As explained in the conceptual framework, reduced amounts of S

deposition may result in lower net S exports, resulting in higher percentages of S compared to higher S deposition sites.

High percentages of soil S were also measured at site 1, only 9.58 km slightly north east of the power station. Since the wind roses do show high velocity winds in that direction, it is possible that this site is directly influenced by high deposition loads from the pollution plume.

6.3.2 Nitrogen

The higher soil clay content found in Majuba soils (36 ± 1.5 % in the top-soils increasing to 39 ± 1.7 % in the sub-soil depths) could account for the higher S, N and C percentages. The total soil N ranged from 0.22 % in the top-soils depths to 0.13% in the sub-soils (Figure 20). These values are higher than results reported for savanna soils in the Kruger National Park (0.024 % ± 0.002 % to 0.052 % ± 0.007 %) (Janse, 2007), but comparable to values reported by Reid (2007) near the Arnot Power station (0.20 % in the top-soils and 0.10 % in the sub-soil depths). In grassland soils in the eastern escarpment of South Africa, the total N ranged from the minimum of 0.23 % to a maximum of 0.94 %, with a median N concentration and standard deviation of 0.37 and 0.16 % (Ndala *et al*., 2006). Total N 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 N content of the soils is above the range of 0.04 – 0.05 % reported by Singh *et al.* (1995) for soils within the vicinity of a coal-fired power plant in India. The relatively high values of N found in the Majuba soils may be due to increased N deposition.

The total soil N values were seen to decrease with soil depth, as seen in the soil S values. Again, this may be due to top-soils receiving N deposition directly from the atmosphere as well as organic inputs from plant material; while the sub-soils receive N as throughput from the top-soils (Reid, 2007). The decrease in total N with soil depth is congruent with other studies, including forest soils in Japan (Koba *et al*., 1997), as well as savanna soils (Janse, 2007) and grassland soils (Reid, 2007).

The total N in both the top-soil and sub-soil depths showed a similar spatial variation as seen in the total soil S values (Figure 21 and Figure 22). The higher N values at sites located approximately 25 km from the Majuba power station may also be explained by low net export of N at these sites or the ability of pollutants to be transported over large spatial gradients, according to conventional distance models.

6.3.3 Carbon

The soil C concentration in the top-soils was 3.09 ± 0.002 % and decreased to 1.79 ± 0.001 % in the sub-soils (Figure 28). According to a generalized organic C map for virgin top-soils in South Africa, organic C in the Mpumalanga province under grassland varies from 0.09 % to 12.53 % (with a median of 2.51 %) (Barnard, 2000). The percentage organic C in non-cultivated grassland soils in Harrismith, South Africa, was found to be 2.6 % in bulk soils and 3.32 % in the coarse soil fraction (Birru 2002). The spatial distribution of soil C seen in Figure 20 shows high within site variability, which is a common characteristic of undisturbed systems (Barnard, 2000).

6.4 CORRELATION BETWEEN SOIL ISOTOPES AND SULFUR, NITROGEN AND CARBON CONCENTRATIONS

6.4.1 δ^{15}N:% N

A weak correlation was seen to exist between δ^{15}N and % N (Figure 26). A diffusion gradient can be established, as sub-soils did contain lower N levels than the top-soils. If a Rayleigh distillation model is used to access the relative contribution of physical and biological processes on N content in soils, a linear relationship between soil δ^{15}N and soil N content would indicate N from natural processes (Figure 5). Values that fall off this line indicate N from atmospheric deposition (Evans and Ehleringer, 1993). The relationship between δ^{15}N and % N in Majuba soils indicates that of a natural undisturbed system (Figure 27).

6.4.2 C:N ratio

The C:N ratio in Majuba soils were in the range expected for grassland soils (approximately 10) (Table 6) (Schimel *et al.*, 1994) and increased from the top-soil to the sub-soil depths. This is also comparable to the C:N ratio found in desertified grasslands of Inner Mongolia, China (Yu-Chun *et al.,* 2010). The large variability in C:N ratio across the ten Majuba sites may be due to local differences in organic matter across the landscape, indicating the relative rates of turnover. The amount (stock) of organic matter in a given soil can increase or decrease depending on numerous factors, and even when stocks are at equilibrium, SOM is in a continual state of flux (Paul, 1984). SOM turnover is mainly dependent on primary production and soil microbial activity (Jenny, 1980), which could differ greatly across the ten sites leading to variability in the C:N ratios in Majuba soils.

While a weak correlation was found to exist between δ^{15}N and δ^{13}C in the Majuba soils, this may be due to certain sites identified as outliers in the series (Figure 38). Martinelli *et al*., (2007) found a direct correlation between δ^{15}N and δ^{13}C in the soils under *terra firme* forests in the Brazilian Amazon

Region. The correlation observed can be explained by a progressive isotopic enrichment in the direction to deeper soil layers due to the decomposition of organic matter.

6.4.3 δ^{34}S:% S

A strong correlation is seen to exist between soil S content and δ^{34}S value (Figure 19). In general, sites with higher S concentrations had higher δ^{34}S values. This result is contrary to the observation found in the Teepee Creek area of Alberta, where more negative δ^{34}S values of soil specimens were found for higher S contents (Krouse and Case, 1981). This was also the case in forest soils in Europe, where sites receiving the largest amounts of S from the atmosphere had the highest S concentration at the top-soil depth. Sites receiving the smallest amount of S from the atmosphere had the lowest S concentration. It appears that S retention in the organic-rich forest floor increases with atmospheric S loads. This may not the case with grassland soils near an S deposition source. Sites that contained the smallest percentages of soil S had lighter isotopic values. According to the conceptual framework proposed in this study, sites with low S percentages experience high net S export. This idea is similar to that found in N-rich areas, were additional N results in high N losses (Hoğberg 1997). The lighter δ^{34}S values for these sites that are experiencing high S losses indicate S deposition. Thus, a coupling of the two processes of net export and deposition is needed to explain the correlation between soil S content and δ^{34}S.

Site 10, on the north east of the Sandspruit catchment does not fit within this framework, as it has a higher soil S isotope signal, but a low soil S concentration. Specifically, there is a substantial decrease in soil S concentration in the sub-soil compared to the top-soil. This may be due to site specific factors, such as land type, resulting in an increases export of S, with little soil residence time for significant fractionation to occur resulting in a higher than expected δ^{34}S value.

6.4.4 δ^{34}S:δ^{15}N

A strong correlation can be seen between soil N and S concentration (Figure 37), as well as soil δ^{15}N and δ^{34}S values (Figure 40). While the correlation between N and C were indicative of a natural system, and the S data pointed towards deposition, the coupling of N and S indicate that processes in the N cycle are also related to deposition. It becomes difficult to separate the natural processes from deposition when the N and S results are so highly correlated.

7 CONCLUSION

The findings of this research can be summarised in response to the key questions posed at the beginning of this study.

1. *What is the $\delta^{34}S$ signal and concentration of total soil S with increasing distance from an identified pollution source, the Majuba Power Station?*

   The mean $\delta^{34}S$ in the top-soils was found to be 8.28 ‰ and increased in the sub-soils to 10.78 ‰. The mean soil S concentration was 0.031 % in the top-soils and decreased to 0.021 % in the sub-soils. In general, sites situated 22 – 27 km downwind from the Majuba Power Station had higher soil $\delta^{34}S$ and total soil S than those situated closer to the power station.

2. *What is the $\delta^{15}N$ signal and concentration of total soil N with increasing distance from an identified pollution source, the Majuba Power Station?*

   The mean $\delta^{15}N$ values ranged from 3.15 ‰ to 9.64 ‰ and were seen to increase with soil depth, as N concentration decreased. The total soil N ranged from 0.22 % in the top-soils depths to 0.13% in the sub-soils. Higher total soil N concentrations were found at sites located approximately 25 km from the Majuba power station.

3. *What is the $\delta^{13}C$ signal and concentration of total soil C with increasing distance from an identified pollution source, the Majuba Power Station?*

   The $\delta^{13}C$ values increased from -12.83 ‰, in the tops soils to -11.90 ‰, in the sub-soil depths. The total soil C concentration decreased from 3.09 % in the top-soils to 1.79 % in the sub-soils. No real relationship was seen in the $\delta^{13}C$ values and total soil C with increasing distance from the Majuba power station.

4. *How are $\delta^{34}S$, $\delta^{15}N$ and $\delta^{13}C$ isotope measurements of soils and elemental concentrations of the nutrients correlated?*

   A strong correlation was seen to exist between soil S content and $\delta^{34}S$ value. In general, sites with higher S concentrations had higher $\delta^{34}S$ values. This supports the conceptual framework proposed in this study. A weak correlation was seen to exist between $\delta^{15}N$ and total soil N concentrations. A diffusion gradient was established, as sub-soils did contain

lower N levels than the top-soils. The relationship between $\delta^{15}N$ and total soil N concentrations in Majuba soils indicates that of a natural undisturbed system.

5. *How do the isotopic ratios compare with potential source ratios in the published literature and is it possible to identify sources of S and N in the Mpumalanga region?*

After comparison with identified pollution source ratios, the lighter $\delta^{34}S$ values at the surface were suggested to be from anthropogenic deposition. The positive $\delta^{34}S$ shift was attributed to a two-source mixing model (atmospheric deposition and bedrock) and natural isotopic fractionation processes that occur within the soil profile. The $\delta^{15}N$ values of the top-soil were higher than what is expected if all nitrogen was derived from atmospheric nitrogen gas fixation. The higher positive values of $\delta^{15}N$ in Majuba soils indicate that the soil N is affected by other processes of the N cycle, which could include coupled nitrification/denitrification, NH_3 volatilization, or atmospheric deposition of enriched NO_3^- or NH_4^+. An increase in isotope abundances may result from the effects of human activities such as domestic grazing and cultivation. The sulfur and nitrogen isotopic signatures could not be used to as a direct means of source identification; however, the effectiveness of isotopes in elucidating transfer of these nutrients in the soil system was illustrated.

8 REFERENCES

Aber, J. D., Magill, A., McNulty, S. G., Boone, R. D., Nadelhoffer, K. J., Downs, M. and Hallett, R. (1995) Forest biogeochemistry and primary production altered by nitrogen saturation. *Water Air and Soil Pollution,* **85** pp 1665–1670.

Aber, J.D. McDowell, W. Nadelhoffer K. Magill A,. Berntson, G. Kamakea, M. McNulty, S. Currie, W Rustad, L. Fernandez I. (1998) Nitrogen saturation in temperate forest ecosystems: hypotheses revisited *Bioscience,* **48** pp 921–934.

Abrahamsen, G. (1984) Effects of acid deposition on forest soil and vegetation. *Philosophical Transactions of the Royal Society of London, B* **305** 1124 pp 369-382.

Aerts, R. Bobbink R. (1999) Chapter 4: the impact of atmospheric nitrogen deposition on vegetation processes in terrestrial, non-forest ecosystems In Langan, S.J. (Ed), *The Impact of Nitrogen Deposition on Natural and Semi-natural Ecosystems*, Kluwer Academic Publishers, The Netherlands, pp 88.

Ågren, G.I., Bosatta, E., Balesdent, J., (1996). Isotope discrimination during decomposition of organic matter: a theoretical analysis. *Soil Science Society of America Journal,* **60** pp 1121–1126.

Ajtay, G.L., Ketner, P. and Duvigneaud, P., (1979) Terrestrial Primary Production and Phytomass, In Bolin, B., Degens, E.T., Kempe, S. and Ketner, P. (Eds) SCOPE 13 - The Global Carbon Cycle, John Wiley & Sons Ltd., Chichester, U.K, pp 301–367.

Aranibar, J.N., Otter, L., Macko, S.A., Feral, C.J.W., Epstein, H.E., Shugart, H.H. and Swap, R.J., (2004). Nitrogen cycling in the soil-plant system along a precipitation gradient in the Kalahari sands. *Global Change Biology,* **10** pp 359–373.

Annegarn, H.J., Turner, C.R., Helas, G., Tosen, G.R. and Rorich, R.P. (1996). Chapter 6 - Gaseous Pollutants. In: Held, G., Gore, B.J., Surridge, A.D., Tosen, G.R., Turner, C.R. and Walmsley, R.D. (Eds) *Air pollution and its Impacts on the South African Highveld*. Environmental Scientific Association, Cleveland.

Baldock, J.A. and Nelson, D.W. (1998) Soil Chemistry In Malcolm, E.S. (Ed) *Handbook of Soil Science*, CRC Press LLC, Florida pp 103.

Baldock, J.A. and Skjemstad, J.O. (1999) Soil Organic Carbon/Soil Organic Matter In Peverill, K.I., Sparrow, L.A and Rueter, D.J. (Eds) *Soil Analysis: An interpretation Manual*, CSIRO Publishing, Collngwood.

Balesdent, J., Girardin, C., Mariotti, A. (1993) Site-related d13C of tree leaves and soil organic matter in a temperate forest. *Ecology,* **74** pp 1713–1721.

Balesdent, J., Wagner, G.H., Mariotti, A. (1988) Soil organic matter turnover in long-term field experiments as revealed by carbon-13 natural abundance. *Soil Science Society of America Journal,* **52** pp 118–124.

Balesdent, J. and Mariotti, A. (1996) Site- related ^{13}C of tree leaves and soil organic matter in a temperate forest, *Ecology* **74** pp 1713–1721.

Barnard, R.O. (2000) Carbon sequestration in South African soils. ARC-ISCW Report No GW/A/2000/48.

Barrie, A., Prosser, S.J. (1996) Automated analysis of light element stable isotope ratio mass spectrometry In Boutton, T.W. and Yamasaki, S.I. (Eds) *Mass Spectrometry of Soils,* Marcel Dekker, London, pp 1-46

Barrow, N. J. (1985) Reactions of anions and cations with variable charge soils. *Advances in Argronomy,* **38** pp 183-230.

Roberts T. L. and Bettany J. R., (1985) The influence of topography on the nature and distribution of soil sulfur across a narrow environmental gradient. *Canadian Journal of Soil Sci*ence, **65** pp 419-434.

Biggs, T.H., Quade, J. and Webb, R.H. (2002) y13C values of soil organic matter in semiarid grassland with mesquite (Prosopis) encroachment in southeastern Arizona. *Geoderma,* **110** pp 109–130.

Birru, T.C. (2002) Organic matter restoration by conversion of cultivated land to perennial pasture on three agro-ecosystems in the Free State. M.Sc. dissertation. (University of the Free State: Bloemfontein)

Bird, M.I., Veenendaal, E.M., Moyo, C., Lloyd, J., Frost, P. (2000) Effect of fire and soil texture on soil carbon in a sub-humid savanna (Matopos Zimbabwe). *Geoderma,* **94** pp 71–90.

Bird, T. and Scholes, M. (2008) Is atmospheric pollution damaging South Africa's ecosystem? *Water and Sanitation Africa,* **3**:5 pp 56–58

Blight, J., Bester, C., Bird, T., Herold, C., Idowu, O. Lorenz, S., Scholes, M., Snyman, N. and Titshall, L. (2007) Knowledge Review: An investigation into the effects of atmospheric pollutants on surface water quality in the eastern regions of South Africa. Prepared for the Water Research Commission

Blight, J., Cornelius, G., Herold, C., Lorentz, S., and Scholes, M., (2009). An investigation into the effects of atmospheric pollution on the soil-water-ecosystem continuum in the eastern regions of South Africa - Phase 0 research report. Report number: RES/RR/09/30350, Eskom Holdings Limited, Rosherville, South Africa.

Bobbink, R. and Roelofs, J.G.M. (1995) Nitrogen critical loads for natural and semi-natural ecosystems: the empirical approach. *Water, Air and Soil Pollution,* **85** pp 2413-2418.

Bond, W.J., Stock, W.D., Hoffman, M.T. (1994). Has the Karoo spread? A test for desertification using carbon isotopes from soils. *South African Journal of Science,* **90** pp 391–397.

Boutton, T.W. (1996) Stable carbon isotope ratio of soil organic matter and their use as indicators of vegetation and climate change. In: Boutton, T.W., Yamasaki, S. (Eds), *Mass Spectrometry of Soil*. Marcel Dekker, New York, pp. 47–82.

Boxman, A. W., van Dam, D., van Dyck, H. F. G., Hogervorst, R. F. and Koopmans, C. J. (1995) Ecosystem responses to reduced nitrogen and S inputs into two coniferous forest stands in the Netherlands. *Forest Ecology and Management* ,**71** pp 7–30.

Bragazza, L., Tahvanainen, T., Kutnar, L., *et al.* (2004) Nitrogen concentration and δ15N signature of ambrotropic Sphagnum mosses at different N deposition levels in Europe. *Global Change Biology*, **11** pp 106 – 114.

Brodin, Y.W. and Kuylenstierna, J.C.I. (1992) Acidification and critical loads in Nordic countries: a background. *Ambio* **21**:5 pp 332-338.

Cerri, C.C., Feller, C., Balesdent, J., Victoria, R.L. and Plennecassagne, A. (1985) Application du traqage isotopique naturel en ~3C a l'~tude de la mati~re organique dans les sols. C.R. *Académie des sciences Paris*, **300** pp 423-428.

Clark, A.J. (1979) Emission of S dioxide, nitrogen oxides and particulate matter from Coal burning power stations In Robinson, F.A. (Ed) *Environmental effects of using more coal*, Royal Society of Chemistry, London, pp 50-70.

Clark, F. E., Cole, C. V. and Bowman, R. A. (1980) Nutrient cycling, in Breymeyer, A. J., and Van Dyne, G. M. (Eds) *Grasslands, Systems Analysis and Man,* Cambridge, Cambridge University Press, pp 659-712.

Clark, K.I., Fritz, P. (1997) *Environmental Isotopes in Hydrogeology*. Lewis Publishers, New York, pp 328.

Comfort, S.D., Dick, R.P. and Baham, J. (1992) Modeling soil sulfate sorption characteristics. *Journal of Environmental Quality,* **21** pp 426-432.

Cronan, C. S., and Grigal, D. F. (1995) Use of calcium/aluminium ratios as indicators of stress in forest ecosystems. *Journal of Environmental Quality,* **24** pp 209–226.

Crutzen, P.J. (1972) SST's a threat to the earth's ozone shield. *Ambio,* **3** pp 201-210.

Crutzen, P.J. (1974) Estimation of possible variations in total ozone due to natural causes and human activities. *Ambio,* **3** pp 201-210.

Curtin, D. and Syers, J.K. (1990a) Mechanism of sulfate adsorption by two tropical soils. *Journal of Soil Science,* **41** pp 295-304.

Dalton, H. and Brand-Hardy, R. (2003) Nitrogen: the essential public enemy. *Journal of Applied Ecology,* **40** pp 771-781.

David M. B. and Mitchell M. J. (1987) Transformations of organic and inorganic S: Importance to sulfate flux in an Adirondack forest soil. *Journal of the Air Pollution Control Association,* **37** pp 39-44.

Dawson, T.E., Mambelli1, S., Plamboeck, A.H., Temple, P.A. and Tu, K.P. (2002) Stable isotopes in plant ecology, *Annual. Review of Ecoogical. Systems*, **3** pp 507–59/

Desjardins, T. (1991) Variations de la distribution de la mati~re organique (carbone total et 13C) dans les sols ferrallitiques du Br~sil. Modifications consrcutives/l la d~forestation et la mise en culture en Amazonie orientale. Doctoral thesis, University of Nancy I, pp 144.

Desjardins, T., Andreux', F., Volkoff, B., Cerri, C.C. (1994) Organic carbon and ^{13}C contents in soils and soil size-fractions, and their changes due to deforestation and pasture installation in eastern Amazonia. *Geoderma,* **61**:1 pp 103–118.

Dillon, P. J., Lusis, M., Reid, R. and Yap, D. (1988) Ten-year trends in sulphate, nitrate and hydrogen deposition in central Ontario. *Atmospheric Environment*, **22** pp 901-905.

Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L. and Weathers, K.C. (2001) Acid deposition in the Northeastern United States: sources and inputs, ecosystem effects, and management strategies. *Bioscience,* **51:**3 pp 180-198.

Du Preez, C., Mnkeni, P. and van Huyssteen, C. (2010) Knowledge review on land use and soil organic matter in South Africa. 9th World Congress of Soil Science, Soil Solutions for a Changing World, August 2010, Brisbane, Australia. Published on DVD.

Du Toit, M.C. and du Preez, C.C. (1995) Swawelfraksies, -verhoudings en –verwantskappe in geselekteerde onversteurde en bewerke Suid-Afrikaanse gronde *South African Journal of Plant Soil,* **12**:1 pp 11– 19.

Durka, W.E., Schultze, D.S., Gebauer, G. and Voerkelius, S. (1994) Effects of forest decline on uptake and leaching of deposited nitrate determined from ^{15}N and ^{18}O measurements. *Nature,* **372** pp 765–69.

Dzurec, R.S., Boutton, T.W., Caldwell, M.M., Smith, B.N. (1985) Carbon isotope ratios of soil organic matter and their use in assessing community composition changes in Curlew Valley, Utah. *Oecologia,* **65** pp 17–24.

Eckardt, F.D. and Spiro, B. (1999) The origin of sulfur in gypsum and dissolved sulfate in the Central Namib Desert, Namibia. *Sedimentary Geology,* **123** pp 255–273.

Ek, A.S., Löfgren, S., Bergholm, J. and Qvarfort, U. (2001) Environmental Effects of One Thousand Years of Copper Production at Falun, Central Sweden. *Ambio,* **30**:2 pp 96-103.

Elliott, E.M., Kendall, C., Burns, D.A., Boyer. E.W., Harlin, K., Wankel, S.D., Butler, T.J. and Carlton, R. (2006) Nitrate Isotopes in precipitation to distinguish NOx sources, atmospheric processes and source areas in the United States. *Eos Transactions, American Geophysical Union*, **87**:36 pp 101 - 117

Emmett, B. A., A. Brittain, S. Hughes, J. Gorres, V. Kennedy, D. Norris, R. Rafarel, B. Reynolds, B. and Stevens, P. A. (1995) Nitrogen additions ($NaNO_3$ and NH_4NO_3) at Aber forest, Wales. I. response of through fall and soil water chemistry. *Forest Ecology and Management*, **71** pp 45–60.

England, G.L. (1979) Keynote Speech In Robinson, F.A (Ed) *Environmental effects of using more coal*, Royal Society of Chemistry, London, pp 7-13.

Eskom, (2006), Annual Report. Available at:

http://www.eskom.co.za/annreport06.

Eskom Environmental Report (2000) Avaliable at
http://www.eskom.co.za/enviroreport01/PDF/index.htm

Evans, R.D. and Belnap, R., (1999) Long-term consequences of disturbance on nitrogen dynamics in an arid ecosystem. *Ecology,* **80** pp 150-160.

Evan, R.D. and Ehleringer, J.R. (1993) A break in the Nitrogen cycle in arid lands? Evidence from $\delta^{15}N$ of soils, *Oecologia,* **94** pp 314-317.

Evans, R.D. (2007) Soil nitrogen isotopic composition In Michener, R. And Lajtha, K. (Eds) *Stable Isotopes in Ecology and Environmental Science*, Blackwell, Singapore pp 83-98S

Eriksson, E. and Rosswall, T. (1976) Man and Biogeochmical cycles: Impacts, problems and research needs In Svensson, B.H. and Soderlund, R. (Eds.) N*itrogen, Phosphorus and Sulphur - Global Cycles*. SCOPE Report 7. Ecological Billiton (Stockholm) **22** pp 11-16.

Fenn, M.E., Baron, J.S., Allen, E.B., Rueth, H.M., Nydick, K.R., Geiser, L., Bowman, W.D., Sickman, J.O., Meixner, T., Johnson, D.W. and Neitlich, P. (2003) Ecological effects of nitrogen deposition in the western United States. *Bioscience,* **53**:4 pp 404-420.

Fey, M.V. and Guy, S.A. (1993) The capacity of soils in the Vaal Dam catchment to retain sulfate from atmospheric deposition. Report to the Water Research Commission by the Department of Agronomy, University of Natal, Pietermaritzburg. WRC Report No 414/1/93.

Fey, M.V. and Netch, A.A. (1996). Chapter 15 - Impacts on the Pedosphere. In: Held, G., Gore, B.J., Surridge, A.D., Tosen, G.R., Turner, C.R. and Walmsley, R.D. (Eds) *Air pollution and its Impacts on the South African Highveld*. Environmental Scientific Association, Cleveland.

Fitzgerald J. W., Strickland T. C. and Swank W. T. (1982) Metabolic fate of inorganic sulfate in soil samples from undisturbed and managed forest ecosystems. *Soil Biological Biochemistry,* **14** pp 529-536.

Flexor, J. M. and Volkoff, B. (1977) Distribution de l'isotope stable I3Cdans la matière organique d'un sol ferrallitique de 'Etat de Bahia (Brésil). *Académie des sciences Paris,* **284** pp 1655-1657.

Freedman, B. and Hutchinson, T.C. (1980) Pollutant inputs from the atmosphere and accumulations in soils and vegetation near a nickel-copper smelter at Sunbury, Ontario, Canada. *Canadian Journal of Botany,* **58** pp 108-132.

Freney, J. R., Melville, G.E. and Williams, C.H. (1971) Organic S fractions labelled by addition of 35S-sulfate to soil. *Soil Biology and Biochemistry,* **3** pp 113-141.

Freyer, H. D., Kobel, K., Delmas, R. J., Kley, D. and Legrand, M. R. (1996) First results of 15N/14Nratios in nitrate from alpine and polar ice cores. *Tellus,* **48** pp 93-105.

Friedland, A.J., Johnson, A.H., Siccama, T.G. and Mader, D.L. (1984) Trace metal profiles in the forest floor of New England. *Soil Science Society of America Journal,* **149** pp 422-425.

Furiness, C., Smith, L., Ran, L. and Cowling, E. (1998) Comparison of emissions of nitrogen and sulfur oxides to deposition of nitrate and sulfate in the USA by state in 1990. *Environmental Pollution,* **102**:1 pp 313-320.

Fustec, E., Mariotti, A., Grillo, X., Sajus, J., (1991) Nitrate removal by denitrification in alluvial groundwater: role of a former channel. *Journal of Hydrology,* **123** pp 337-354.

Galloway, J. N. (1989) Atmospheric acidification: projections for the future. *Ambio,* **18** pp 161-166.

Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C.C., Green, P.A., Holland, E.A., Karl, D.M., Michaels, A.F., Porter, J.H., Townsend, A.R. and Vörösmarty, C.J. (2004) Nitrogen cycles: past, present, and future. *Biogeochemistry,* **70** pp 153-226.

Galpin, J.S. and Turner, C.R. (1999) Trends in rain quality data from the South African interior. *South African Journal of Science,* pp 223-225.

Galy-Lacaux, C., Al Ourabi, H., Galloway, J., Lacaux, J.P., Mphepya, J., Pienaar, K., Pont, V., Sigha, L. and Yoboué, V. (2003) Dry and Wet Atmospheric Nitrogen Deposition in Africa, IGACtivities Newsletter of the International Global Atmospheric Chemistry Project, DEBITS Special Issue no 27, 2003.

Grennfelt, P., and Hultberg, H. (1986) Effects of nitrogen deposition on the acidification of terrestrial and aquatic ecosystems. *Water, Air, and Soil Pollution,* **30** pp 945–963.

Gregorich, E.G., Ellert, B.H., Monreal, C.M. (1995) Turnover of soil organic matter and storage of corn residue carbon estimated from natural 13C abundance. *Canadian Journal of Soil Science,* **75** pp 161–167.

Grey, D. C. and Jensen, M. L. (1972) Bacteriogenic sulfur in air pollution. *Science,* **177** pp 1099-1100.

Groffman, P.M. (2000) Nitrogen in the environment. In Sumner, M.E. (Ed) *Handbook of Soil Science*. CRC Press, New York pp 190 - 200.

Guillet, B., Faivre, P., Mariotti, A., Khobzi, J. (1988) The ^{14}C dates and 13C/12C ratios of soil organic matter as a means of studying the past vegetation in intertropical regions: examples from Columbia, South America. *Palaeogeography, Palaeoclimatology, Palaeoecology***, 65** pp 51–58.

Hackley, K.C. and Anderson, T.F., (1986) Sulphur isotopic variations in low–sulphur coals from the Rocky Mountain region. *Geochimica et Cosmochimica Acta*, **50**, pp 1703–1713.

Hameed, S. and Dignon, J., (1988) Changes in the geographical distributions of global emissions of NO_x and SO_x from fossil-fuel combustion between 1966 and 1980. *Atmospheric Environment,* **22** pp 441-449.

Heaton, T.H.E. (1986) Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. *Chemical Geology,* **59** pp 87 – 102.

Heaton, T. H. E. (1987) 15N/14N ratios of nitrate and NH_4^+ in rain at Pretoria, South Africa. *Atmospheric Environment,* **21** pp 843-852.

Heaton, T.H.E. (1990) 15N/14N ratios of NO_x from vehicle engines and coal-fired power stations. *Tellus,* **42B** pp 304-307.

Henriksen, A., and Brakke, D.F. (1988) Increasing contributions of nitrogen to the acidity of surface waters in Norway. *Water, Air, and Soil Pollution* **42** pp 183–201.

Högberg, P. (1997) Tansley Review No 95: ^{15}N natural abundance in soil-plant systems. *New Phytologist,* **137** pp 179- 203.

Horstmann, U.E., Bester, J. and Bühmann, D. (2001) Pilot study on alteration of coal during storage on mine dumps using S stable isotopes. Council of Geosciences, Project: 6820-0633

Howarth, R.W., Stewart, B.W. and Ivanov, M.V. (1992) *Sulphur Cycling on the Continents*. John Wiley & Sons, New York pp 1 – 6.

Huang, M.Y., Chen, Z.L., Liu, S.R., Wu, Y.X., Xiao, H., Lei, H.C., Bai, C.H. (1995) A study on the formation processes of acid rain in some areas of southwest China. *Scientia Atmospheric Sinica*, **19**:3 pp 359–366.

Hitchcock, D. R. and Black, M. S. (1984) 34S/32S Evidence of biogenic sulfur oxides in a salt marsh atmosphere. *Atmospheric Environment,* **18** pp 1- 17.

Hsieh, Y.P. (1997) Bimodal distribution of soil organic carbon pools and their significance. 7th Annual V.M. Goldschmidt Conference, Tucson, AZ: LPI Contribution 921. Lunar and Planetary Institute, Houston, TX, USA, p. 99.

Inskeep, W.P. (1989) Adsorption of sulfate by kaolinite and amorphous iron oxide in the presence of organic ligands. *Journal of Environmental Quality,* **18** pp 379-385.

Itanna, F. (2005) Sulfur distribution in five Ethiopian Rift Valley soils under humid and semi-arid climate. *Journal of Arid Environments,* **62** pp 597–612.

Jackson, L.L., Gough, L.P. (1988). The use of stable sulfur isotope ratios in air pollution studies: an ecosystem approach in South Florida. In: Rundel, P.W.; Ehleringer, J.R. Nagy, K.A., (Eds) *Stable isotopes in ecological research*. Springe Verlag, New York, pp 471-490.

Janse, M. (2007). An investigation of the effects of fire frequency on soil carbon fractions across a rainfall gradient. Submitted for BSc (Hons) dissertation, University of the Witwatersrand.

Johnson, D.W. and Todd, D.E. (1983) Relationships among iron, aluminium, carbon, and sulfate in a variety of forest soils. *Soil Science Society of America Journal,* **47** pp 792-800.

Johnson, N.C., Wedin, D.A. (1997) Soil carbon, nutrients, and mycorrhizae during conversion of dry tropical forest to grassland. *Ecological Applications*, **7**:1 pp 171–182.

Junk, G. and Svec, H.V. (1958) The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources. *Geochim Cosmochim Acta,* **14** pp 234-243.

Kendall, C. and McDonnell, J.J., (1998) *Isotope tracers in catchment hydrology*, Elsevier, Amsterdam pp 839.

Kendall, C., Elliott, E.M. and Wankel, S.D. (2007) Tracing anthropogenic inputs of Nitrogen to ecosystems In Michener, R. And Lajtha, K. (Eds) *Stable Isotopes in Ecology and Environmental Science*, Blackwell, Singapore pp 375 – 449.

Kennedy, I.R. (1986) *Acid soil and acid rain: the impact on the environment of nitrogen and sulfur cycling*. Research Studies Press, New York.

Kahn, M.E. (2008) Regional growth and exposure to nearby coal fired power plant emissions. *Regional Science and Urban Economics,* **39**: 1 pp 15-22.

Kemp, A.L.W. and Thode, H.G. (1968) The mechanisms of the bacterial reduction of sulfate and of sulfide from isotope fractionations studies. *Geochimica et Cosmochimica Acta,* **32** pp 71-91

Kempster, P.L., Skoroszewski, R.W., Roos, G.N. and Gore, B.J. (1996). Chapter 14 - Impact of Atmospheric Deposition on Water Quality. In: Held, G., Gore, B.J., Surridge, A.D., Tosen, G.R., Turner, C.R. and Walmsley, R.D. (Eds) *Air pollution and its Impacts on the South African Highveld*. Environmental Scientific Association, Cleveland.

Khanna P. K., Prenzel J., Meiwes K. J., Ulrich B. and Matzner E. (1987) Dynamics of sulfate retention by acid forest soils in an acidic deposition environment. *Soil Science Society of America Journal.* **51** pp 446-452.

Khanna, P. K., Weaver, G. T., and Beese, F. (1986) Effect of sulfate on ionic transport and balance in a slightly acidic forest soil. *Soil Science Society of America Journal.* **50** pp 770-776.

Koba, K., Tokuchi, N., Wada, E., Nakajima, T. and Iwat-subo G. (1997). Intermittent denitrification: the application of a 15N natural abundance method to a forested ecosystem. *Geochimica et Cosmochimica Acta* **61** pp 5043–5050.

Koptsik, G. and Mukhina, I. (1995) Effects of acid deposition on acidity and exchangable cations in podzols of the Kola peninsula. *Water, Air and Soil Pollution,* **85** pp 1209-1214.

Krammer, M.G, Sollins, P., Sletten, R.S. and Swart, P.K. (2003) N isotope fractionation and measures of organic matter alteration during decoposition. *Ecology,* **84** pp 2021-2025.

Kríbek, B., Majer, V., Veselovský, F. and Nyambe, I. (2010) Discrimination of lithogenic and anthropogenic sources of metals and sulphur in soils of the central-northern part of the Zambian Copperbelt Mining District: A topsoil vs. subsurface soil concept. *Journal of Geochemical Exploration*, **104** pp 69–86.

Krouse, H. R. and Case, J. W. (1981) Sulfur isotope ratios in water, air, soil and vegetation near Teepee Creek gas plant, Alberta. *Water, Air and Soil Pollution,* **15** pp11-28.

Krouse, H.R., Legge, A.H. and Brown, H.M. (1984) Sulfur gas emissions in the boreal forest: The West Whitecourt case study V. Stable sulfur isotopes. *Water, Air and Soil Pollution,* **22** pp 321-347.

Krouse, H. R. (1987) Environmental sulfur isotope studies in Alberta: a review. *Prepared for the Acid Deposition Research Program*, ADPP-B-03-87, Univ. of Calgary, Alberta, Canada.

Krouse, H.R. (1989) Sulfur isotopes studies of the pedosphere and biosphere In Rundel, P.W., Ehleringer, J.A. and Nagy, K.A., (Eds*.) Stable isotopes in Ecological research*, Springer-Verlag, New York, pp 424-444.

Krouse, H.R. and Grinenko, V.A. (1991) *Stable Isotopes. Natural and Anthropogenic Sulfur in the Environment*, SCOPE 43. John Wiley & Sons, UK.

Kuylenstierna, J., Rodhe, H., Cinderby, S. and Hicks, K (2001) Acidification in developing countries: Ecosystem sensitivity and the critical load approach on a global scale. *Ambio,* **30**:1 pp 20 -31.

Land Type Survey Staff, 2002. *Land types of the maps 2728 Frankfort & 2828 Harrismith*. Report number: Memoirs of Agricultural and Natural Resources, South Africa, No. 28, ARC – Institute for Soil Climate & Water, Pretoria, South Africa.

Leck, C. and Rodhe, H. (1989) On the relation between anthropogenic SO_2 emissions and concentration of sulfate in air and precipitation. *Atmospheric Environment,* **23** pp 959-66.

Lehmann, M.F. *et al* (2001) A method for the Extraction of Ammonium from Freshwaters for Nitrogen Isotope Analysis., *Analytical Chemistry*, **73** pp 4717-4721.

Lein, A. Yu. (1968). Mineral composition of sulfur ores in some volcanic deposits of Kamchatka (in Russian). *Tr. Geological Institute Kazan,* **20** pp 80-90

Levy, J. I. and Spengler, J. (2002a) Modeling the benefits of power plant emissions control in Massachusetts. *Journal of the Air & Waste Management Association,* **52** pp 5–18

Levy, J. I., Spengler, J.D., Hlinka, D., Sullivan, D. and Moon, D. (2002b) Using CALPUFF to evaluate the impacts of power plant emissions in Illinois: model sensitivity and implications, *Atmospheric Environment,* **36** pp 1063–1075.

Likens, G. E., Driscoll, C. T. and Buso. D. C. (1996) Long- term effects of acid rain: response and recovery of a forest ecosystem. *Science,* **272** pp 244–246.

Liu, K.K., Su, M.J., Hsueh, C.R., Gong, G.C. (1996) The nitrogen isotopic composition of nitrate in the Kuroshio Water northeast of Taiwan: evidence for nitrogen fixation as a source of isotopically light nitrate. *Marine Chemistry,* **54** pp 273–292.

Lovett, G.M. (1992). Atmospheric Deposition and Canopy Interactions of Nitrogen, Chapter 6 - Nitrogen Chemistry, Deposition, and Cycling in Forests. In: Johnson, D.W. and Lindberg, S.E. (Eds) *Atmospheric Deposition and Forest Nutrient Cycling - A Synthesis of the Integrated Forest Study*. Ecological Studies 91. Springer-Verlag, New York.

Ludlow, M.M., Troughton, J.H., Jones, R.J. (1976) A technique for determining the proportion of C3 and C4 species in plant samples using stable natural isotopes of carbon. *Journal of Agricultural Science*, **87** pp 625–632.

Mach, K., Zak, K. and Jackova, I. (1999) Sulfur speciation and isotope composition in a vertical profile of the main coal seam of the North Bohemian brown coal basin and their palaeographic interpretation. *Bulletin Czech Geological Survey,* **74** pp 51–66.

Mariotti, A., Mariotti, F., Champigny, M. L., Amarger, N. and Moyse, A. (1982) Nitrogen isotope fractionation associated with nitrate reductase activity and uptake of NO_3 by Pearl Millet. *Plant Physiology,* **69** pp 880-884.

Mariotti, A. (1983) Atmospheric nitrogen is a reliable standard for natural 15N abundance measurements. *Nature,* **303** pp 685-687.

Mariotti, A., Peterschmitt, E. (1994) Forest savanna ecotone dynamics in India as revealed by carbon isotope ratios of soil organic matter. *Oecologia,* **97** pp 475–480.

Martin, A., Mariotti, A., Balesdent, J., Lavelle, P., Vuattoux, R. (1990) Estimate of organic matter turnover rate in a savannah soil by 13C natural abundance measurement. *Soil Biology and Biochemistry,* **22** pp 517–523.

Martinelli, L.A., Ometto, J.P., Ishida, F.Y., Domingues, T.F., Nardoto, G.B., Oliveira, R.S. and Ehleringer, J.R. (2007) The Use of Carbon and Nitrogen Stable Isotopes to Track Effects of Land-Use Changes in the Brazilian Amazon Region In Dawson, T. E. and Siegwolf, R. T. W. (Eds) *Stable Isotopes as Indicators of Ecological Change* Elsevier, The Netherlands. pp 301 – 313.

Mayer, B., Fritz, P., Prietzel, J. and Krouse, H. R. (1995) The use of stable sulfur and oxygen isotope ratios for interpreting the mobility of sulfate in aerobic forest soils. *Applied Geochemistry,* **10** pp. 161-173.

Mayer, B. And Krouse, H.R. (2004) Procedures for Sulfur Isotope Abundance Studies. In de Groot P.A. (Ed) *Handbook of Stable Isotopes Analytical Techniques Volume 1*, Elsevier, The Netherlands, pp 538- 600.

Maynard, D. G., Stewart, J. W. B. and Bettany, J. R. (1984) Sulfur cycling in grassland and parkland soils. *Biogeochemistry,* **1**, pp 97-111.

Mitchell, M.J., Krouse, H.R., Mayer, B., Stam, A.C. and Zhang, Y. (1998) Chapter 15: Use of stable isotopes in evaluating sulfur biogeochemistry of forest ecosystems In Kendall, C and McDonnell, J.J. (Eds) *Isotope tracers in catchment hydrology*. Elsevier, NY.

McNulty, S. G., and Aber, J. D. (1993) Effects of chronic nitrogen additions on nitrogen cycling in a high-elevation spruce–fir stand. *Canadian Journal of Forest Research,* **23**: pp 1252–1263.

McPherson, G.R., Boutton, T.W., Midwood, A.J. (1993) Stable carbon isotope analysis of soil organic matter illustrates vegetation change at the grassland/woodland boundary in southeastern Arizona, USA. *Oecologia,* **93** pp 95–101.

Möller, D. (1984) On the global natural sulphur emission. *Annospheric Enviroment* **18:**I. pp. 29-39.

Mook, W.G. (2000) Natural isotopes of elements other than H, C and O. In Mook, W.G. (Ed) *Volume 1. Introduction: Theory methods review*. UNESCO/IAEA series on environmental isotopes in hydrological cycle principles and applications.

Moore, H. (1977) The isotopic composition of ammonia, nitrogen oxide and nitrate in the atmosphere. *Atmospheric Environment,* **11** pp 1239-1243.

Mphepya J.N. and Held G. (1999) Dry deposition of sulphur on the Mpumalanga Highveld, 1996-1998, National Association for Clean Air Conference, Cape Town, 6 - 8 October 1999.

Mphepya, J.N., Pienaar, J.J., Galy-lacaux, C., Held, G and Turner, C.R. (2004) Precipitation Chemistry in Semi-Arid Areas of Southern Africa: A Case Study of a Rural and an Industrial Site. *Journal of Atmospheric Chemistry,* **47:**1 pp 1 – 24.

Mpumalanga DACE (2003) Mpumalanga State of the Environment Report. Nelspruit, Mpumalanga Department of Agriculture, Conservation and Environment.

Mylona, S. N. (1989) Detection of sulphur emission reductions in Europe during the period 1979-1986. *EMEP MSC-W Report* 1/89, Norwegian Meteorological Institute, Oslo, pp 149.

Nadelhoffer, K.L. and Fry, B. (1988). Controls on natural nitrogen-15 and carbon-13 abundances in forest soil organic matter. *Soil Science Society of America Journal,* **52** pp 1633–1640.

Nadelhoffer, K.J. and Fry, B. (1994) Nitrogen isotope studies in forest ecosystems. In: K. Lajtha, R.H. Michener (Eds) *Stable Isotopes in Ecology and Environmental Science*. Blackwell Wissenschafts-Verlag GmbH pp 22–44.

Newman L, Krouse, H.R. and Grinenko, V.A. (1991) Sulfur isotope variations in the atmosphere. In: Krouse, H.R. and Grinenko, V.A (Eds) SCOPE 43: Stable Isotopes: Natural and Anthropogenic Sulfur in the Environment, J. Wiley & Sons, Chichester, pp 133-176.

Neill, C., Steudler, P.A., Moraes, J.F.L., Piccolo, M.C., Melillo, J.M., Cerri, C.C. (1997) Soil organic matter stocks following forest clearing for pasture in the southwestern Brazilian Amazon. *Ecological Appications,* **7** pp 1216-1225.

Ndala, S.M., Scholes, M.C., and Fey, M.V. (2006) Soil properties and processes driving the leaching of nitrate in the forested catchments of the eastern escarpment of South Africa. *Forest Ecology and Management,* **236**:2-3, pp142- 152.

Nielson H. (1974) Isotopic composition of the major contributors to atmospheric sulfur. *Tellus,* **26** pp 211–221.

Nixon, S. W., Ammerman J. W., Atkinson, L. P., Berounsky V. M., Billen, G., Boicourt, W. C., Boyton, W. R., Church, T. M., Ditoro, D. M., Elmgren, R., Garber, J. H., Giblin, A. E., Jahnke, R. A., Owens, N. P. J., Pilson, M. E. Q. and. Seitzinger, S. P. (1996) The fate of nitrogen and phosphorus at the land–sea margin of the North Atlantic Ocean. *Biogeochemistry* **35** pp 141-180.

Norman, A.L., Giesemann, A., Krouse, H.R. Jäger, H.J. (2002) Sulfur isotope fractionation during sulfur mineralization: results of an incubation–extraction experiment with a Black Forest soil.*Soil Biology and Biochemistry,* **34**:10 pp 1425–1438.

Novak, M., Bottrell, S.H., Fottovai, D., Buzek ,F., Groscheova, H. and ZZik, K. (1996) Sulfur isotope signals in forest soils of Central Europe along an air pollution gradient. *Environment, Science and Technology,* **30** pp 3473-3476.

Novak, M, Kirchner, J.W., Groscheovai, H., Havel, M., Cerny, J., Krejie, R. and Buzek, F. (2000) Sulfur isotope dynamics in two Central European watersheds affected by high atmospheric deposition of SOx. *Geochim. Cosmochim. Acta,* **64** pp 367-383.

Novak, S.M., Portal, J.-M., Schiavon, M. (2001) Effects of soil type upon metolachlor losses in subsurface drainage. *Chemosphere,* **42** pp 235–244.

Nriagu, J. O., Coker, R. D and Barrie, L. A. (1991) Origin of sulfur in Canadian Arctic haze from isotope measurements. *Nature,* **349** pp 142-145.

Nordstrom, D. K. (1982) The effect of sulfate on aluminium concentrations in natural waters: some stability relations in the system AI203-SO3-H20 at 298 K. *Geochimisty. Cosmochimesty. Acta,* 46 pp 681-692.

Oades, J.M. (1988) The retention of organic matter in Soils *Biogeochemistry,* **62** pp. 35-70.

O'Brien, B.J., Stout, J.D. (1978) Movement and turnover of soil organic matter as indicated by carbon isotope measurements. *Soil Biology and Biochemistry,* **10 pp** 309–317.

Odum, E. P. (1971) *Fundamentals of Ecology,* 3rd ed., Saunders Comp. Philadelphia, London, Toronto, pp 1-574.

Olivier, J.G.J., Bouwman, A.F., Van der Hoek, K.W. and Berdowski, J.J.M. (1998) Global air emission inventories for anthropogenic sources of NOx, NH_3 and N_2O in 1990. *Environmental Pollution,* **102**:1 pp 135-148.

Panettiere, P., Cortecci, G., Dinelli, E., Bencini, A., Guidi, M. (2000) Chemistry and sulphur isotopic composition of precipitation at Bologna, Italy. *Applied Geochemistry,* **15** pp 1455–1467.

Pankina, R.G., Mekhtiyeva, V.L., and Maximov, S.P. (1983) Formation of H_2S and CO_2 in oils of Astrakhan deposit (by isotopic data) (in Russian). *Geol. Nefti i gaza,* **4** pp 45-51.

Pearson, J., Wells, D.M., Seller, K.J. et al., (2000) Traffic exposure increases natural ^{15}N and heavy metal concentrations in mosses, *New Phytologist,* **147**:2 pp 317 – 326.

Penner, J. E., Andreae, M. O., Annegarn, H., Barrie, L. A., Fe- ichter, J., Hegg, D. A., Jayaraman, A., Leaitch, W. R., Murphy, D., Nganga, J., and Pitari, G. (2001) Aerosols, their direct and indirect effects, In Houghton, J. T., Ding, Y., Griggset, J., et al. (Eds) *Climate change 2001: The third assessment report to the intergovernmental panel on climate change*. Cambridge University Press, Cambridge, United Kingdom, and New York, USA.

Price, F.T and Shieh, Y.N. (1979) The distribution and isotopic composition of sulphur in coals from the Illinois Basin. *Economic Geology*., **74**, pp 1445–1461.

Pichlmayer, F., Schoner, W., Stichler, P.S.W. and Wagenbache, D. (1998) Stable Isotope analysis for characterization of pollutants at high level Alpine sites. *Atmospheric Environment,* **32:**23 pp 4075- 4085.

Prenzel, J. and Meiwes, K.J. (1994) Sulfate sorption in soils under acid deposition: modelling field data from forest liming. *Journal of Environmental Quality,* **23** pp 1212-1217.

Puiga, R., Vila, A.A. and Solerb, A. (2008) Sulphur isotopes as tracers of the influence of a coal-fired power plant on a Scots pine forest in Catalonia (NE Spain). *Atmospheric Environment,* **42** pp 733–745.

Querol, X., Alastuey, A., Chaves, A., Spiro, B., Plana, F. and Lopez Soler, A. (2000) Sources of natural and anthropogenic sulphur around the Teruel power station, NE Spain. Inferences from sulphur isotope geochemistry. *Atmospheric Environment,* **34** pp 333–345.

Rees, C.E. (1970). The sulfur-isotope balance of the ocean, an improved model. Earth Planet. *Science. Letters*, **7** pp 366-370.

Reid, J.L., (2007). Investigating the long-term effects of air pollution on soil properties in the vicinity of the Arnot Power Station. Master of Science thesis, University of the Witwatersrand.

Reimer, T.O., (1986). Isotopic constraints on the derivation of sulphate in gypsum in inland salt pans of southern Africa. Abstr. Geocongress '86, Geological Society of South Africa, Johannesburg, pp 1049–1052.

Reuss, J.O and Johnson, D.W., (1986). *Acid deposition and the acidification of soils and waters*. Springer-Verlag, New York

Rhode, H.P., Grennfelt, J. Wisniewski, C. Agren, G. Bengtsson, K. Johansson, P. Kauppi, K. V., L. Rasmussen, B. Rasseland, L. Scholte and Sellden, G. (1995). 'Acid Reign '95? - Conference Summary Statement. *Water, Air and Soil Pollution,* **85:**1 pp 1-14.

Rigby, D. and Batts, B.D. (1985). The isotopic composition of nitrogen in Australian coals and oil shales, *Chemistry. Geology Isotopes. Geosciences*, **58** pp 273-282.

Richter, D.D., Ralston, C.W. and Harms, W.R. (1983) Chemical composition and spatial variation of bulk precipitation at a coastal plain watershed in South Carolina. *Water Resources Research* **19**:1 pp 134-140.

Richter, D.D. Markewitz D. (2001) Understanding Soil Change: *Soil Sustainability over Millennia, Centuries, and Decades* Cambirige University Press, New York pp. 182–205

Roscoe, R., Buurman, P., Velthorst, E. (1999) Soil aggregate disruption by ultrasonic energy in SOM fractionation: carbon, nitrogen, and d13C distribution in particle-size fractions. *European Journal of Soil Science,* Submitted for publication..

Rosswall, T. (1981) The Biogeochemical Nitrogen Cycle In Likens,G.E. (Eds) *Some Perspectives of the Major Biogeochemical Cycles*. SCOPE 17 pp 25 – 49.

Runde,l P.W., Ehleringer, J.R., Nagy, K.A. (1989) Stable Isotopes in Ecological Research. *Ecological Studies*, **68**. Springer-Verlag, Heidelberg: pp 525.

Rutherford, M. C. and Westfall, R. H. (1986) Biomes of Southern Africa - an Objective Categorisation. *Memoirs of the Botanical Survey of South Africa.* Botanical Research Institute, Department of Agricultural and Water Supply. Pretoria. **54**:1-98.

Sabine, C.L., Heimann, M, Artaxo, P., Bakker, D.C.E., Chen, C.A., Field, C.B., Gruber, N, Le Quere, C., Prinn, R.G., Richey., J.E., Lankoa, P.R., Sathaye, J.A. and Valenti, R. (2004) Current status and passed trends In: the Global Carbon cycle In Field, C.B. and Raupach, M.R. (Eds) *The Global Carbon Cycle: Integrating humans, climate and the natural world*, Island Press, Washington pp 17-44.

Saggar, S., Bettany, J.R., and Stewart, J.W.B. (1981) Sulphur transformations in relation to carbon and nitrogen in incubated soils. *Soil Biology and Biochemistry* ,**13** pp 499-511.

Sala, O.E., I.F.S. Chapin II, J.J. Armesto, E. Berlow, J. Bloomfield, R. Dirzo, E. Huber-Sanwald, L.F. Huenneke, R.B. Jackson, Ann. Kinzig, R. Leemans, D.M. Lodge, H.A. Mooney, M. Oesterheld, N.L. Poff, M.T. Sykes, B.H. Walker, M. Walker, D.H. Wall Global biodiversity scenarios for the year 2100. *Science,* **287** pp. 1770–1774.

Savoie, D.L., Prospero, J.M. (1989) Comparison of oceanic and continental sources of non-sea-salt sulfate over the Pacific Ocean. *Nature,* **339** pp 685–687.

SAWB (1986) *Climate of South Africa. Climate statistics up to 1984*, WB 40, South African Weather Bureau, Department of Environment Affairs, Pretoria, pp 136.

Schaaf, W., Weisdorfer, M. and Huettl, R.F. (1995) Soil solution chemistry and element budgets of three scots pine ecosystems along a deposition gradient in north- eastern Germany. *Water, Air and Soil Pollution,* **85** pp 1197-1202.

Schimel, D.S. (1995) Terrestrial ecosystems and the carbon cycle. *Global Change Biology,* **1** pp 77–91.

Schimel, J.P. and Bennett, J. (2004) Nitrogen minerlization: Challenges of a changing paradigm, *Ecology,* **85** pp 591- 602.

Scholes, M.C., Olbrich, K.A. and van Rensburg, E. (1996) Chapter 13 - The Environmental Impact of Atmospheric Pollution in the Industrial Highveld and Adjacent Regions: Crops, Indigenous Vegetation and Commercial Forestry. In: Held, G., Gore, B.J., Surridge, A.D., Tosen, G.R., Turner, C.R. and Walmsley, R.D. (Eds) *Air pollution and its Impacts on the South African Highveld*. Environmental Scientific Association, Cleveland.

Schulze, E. D. (1989) Air pollution and forest decline in a spruce (*Picea abies*) forest. *Science,* **244** pp 776–783.

Scorgie, Y and Thomas, R (2006) Eskom Mpumalanga Highveld Cumulative Scenario Planning Study: Air Pollution Compliance Assessment and Health Risk Analysis of Cumulative Operations of Current, RTS and Proposaed Eskom Power Station Located within the

Mpumalanga and Gauteng Provinces, Confidential Report No. APP/06/ESKOM-05 Rev 1.0, Airshed Planning Professionals, on behalf of Eskom Holdings Limited, Midrand.

Silva, S.R. *et al* (2000) A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios, *Journal of Hydrology*, **228** pp 22-36.

Silvertsen, B., Matale, C. and Pereira, L.M.R. (1995) Sulphur emissions and transfrontier air pollution in Southern Africa. Southern African Development Community, Environmental and Land Management Sector, Report Series 34, South Africa.

Singh, B.R. (1984) Sulfate adsorption by acid forest soils: 1. Sulfate adsorption isotherms and comparison of different adsorption equations in describing sulfate adsorption. *Soil Science,* **138** pp 189-197.

Singh, B.R. and Johnson, D.W. (1986) Sulfate content and adsorption in soils of two forest watersheds in southern Norway. *Water, Air and Soil Pollution,* **31** pp 847-856.

Singh, J., Agrawal, M. and Narayan, D. (1995) Changes in soil characteristics around coal-fired power plants. *Environment International,* **21**:1 pp 93-102.

Slanina, S. and Davis, W. (2008) Impact and abatement of acid deposition and eutrophication. In Cutler, J. (Ed) Encyclopaedia of the Earth, Environmental Information Coalition, National Council for Science and the Environment Washington, D.C.

Smith, B., (1989). Production and deposition of Airborne Pollution In Mallanby, K. (Ed) *Air pollution, acid rain and the environment*, Watt Committee Report Number 18, Elsevier Applied Science Publishers, London.

Smith, J. W. and Batts, B. D. (1974) The distribution and isotopic composition of sulfur in coal. *Geochim. Cosmochim. Acta,*, **38** pp 121-133.

Smith, J.W., Gould, K.W. and Rigby, D. (1982) The stable isotope geochemistry of Australian coals. *Organic. Geochemist*, **3**, pp 111–131.

Sparks, D.L. (2000) Bioavailability of soil potassium. In: Sumner, M.E. (ed) *Handbook of Soil Science*. CRC Press, New York, pp 38-53.

Sperry, L.J., Belnap, J. and Evans, R.D. (2006) *Bromus Tectorum* invasion alters nitrogen dynamics in an undisturbed arid grassland ecosystem. *Ecology,,* **87**:3, pp. 603–615.

Spiker, E.C., Pierce, B.S., Bates, A.L. and Stanton, R.W. (1994) Isotopic evidence for the source of sulphur in the Upper Freeport coal bed (west–central Pennsylvania, U.S.A.). *Chemical Geology*., **114**, pp 115–130.

Sposito, G. (1989). *The chemistry of soils*. Oxford University Press, London.

Stevens, C.J. Dise, N.B. Mountford, O., Gowing, D.J. (2004) Impact of nitrogen deposition on the species richness of grasslands *Science,* **303** pp. 1876–1879

Stevenson, F.J. (1994) *Humus Chemistry*, Wiley, New York.

Steuter, A.A., Jasch, B., Ihnen, J., Tieszen, L.L. (1990) Woodland/grassland boundary changes in the Middle Niobrara Valley of Nebraska identified by y13C values of soil organic matter. *The American Midland Naturalist Journal,* **124** pp 301–308.

Stoddard, J. L. (1994) Long-term changes in watershed retention of nitrogen: its causes and aquatic consequences. In Baker, L. A. (Ed) *Environmental chemistry of lakes and reservoirs*. American Chemical Society, Washington, D.C., USA pp 23–284.

Sullivan, T.J., Fernandez, I.J., Herlihy, A.T., Driscoll, C.T., McDonnell, T.C., Nowicki, N.A., Snyder, K.U. and Sutherland, J.W. (2006) Acid-base characteristics of soils in the Adirondack mountains, New York. *Soil Science Society of America Journal,* **70**:1 pp 141-152.

Sweeney, R.E., Liu, K.K. and Kaplan, I.R. (1978) Oceanic nitrogen isotopes and their uses in deter mining the source of sedimentary nitrogen. In: Stable Isotopes in the Earth Sciences. DSIR (New Zealand Dep. Sci. Ind. Res.), Wellington, Bull, No. **220**, pp. 9-26.

Szynkiewicz A., Modelska, M., Jędrysek, M.O and Mastalerz, M. (2008) The effect of acid rain and altitude on concentration, $\delta^{34}S$, and $\delta^{18}O$ of sulfate in the water from Sudety Mountains, Poland, *Chemical Geology,* **249** pp 36–51.

Tabatabai, M.A. (2005) Chapter 3: Chemistry of sulfur in soils. In of Tabatabai, M.A. and Sparks, D.L (Eds) Chemical processes in soils. SSSA, WI.

Teece, M.A and Fogel, M.L (2004) Chapter 9: Preparation of Ecological and biochemical samples for isotope analysis In de Groot (Ed) *Handbook of Stable Isotopes Analytical Techniques Volume 1*, Elsevier, The Netherlands, pp 177- 202.

Terblanche, P. (1996) Impacts of Removing Air Pollution: Health Aspects, Report compiled on behalf of Department of Minerals and Energy, Report No. ES 9411, May 1996.

Trouve, C., Mariotti, A., Schwartz, D., Guillet, B. (1994) Soil organic carbon dynamics under Eucalyptus and Pinus planted on savannas in the Congo. *Soil Biol. Biochem.* **26**:2, pp 287–295.

Tyson, P.D., Kruger, F.J. and Louw, C.W. (1988) Atmospheric pollution and its implications in the Eastern Transvaal Highveld. CSIR, Pretoria. South African National Scientific Programmes Report No. 150. England, G., (1979). Keynote speech In Robinson, F.A., *Environmental effects of utilising more coal*, The Royal Society of Chemistry, London.

Ulrich, B. (1983) Soil acidity and its relations to acid deposition In B. Ulrich and J. Pankrath (Eds) *Effects of accumulation of air pollutanta in forest ecosystems*. D Reidel Publishing Company, Göttingen, pp 127 – 146.

Van Stempvoort. R. (1989) The use of stable isotope techniques to investigate the sulfur cycle in upland forests of central and southern Ontario. Ph.D. thesis, University of Waterloo, Waterloo. Ontario, Canada.

Van Stempvoort, D.R., Reardon E.J. and Fritz, P. (1990) Fractionation of sulfur and oxygen isotopes in sulfate by soil sorption. *Geochimisty. Cosmochimistry. Acta,* **54** pp 2817-2826

Van Tienhoven, A.M., Olbrich, K.A., Skoroszewski, R., Taljaard, J. and Zunckel, M. (1995) Application of the critical loads approach in South Africa. *Water Air Soil Pollution,* **85** pp 2577-2582.

Van Tienhoven, A.M., (1997). Assessment of long-term pollution impacts on soil properties in the vicinity of the Arnot power station on the South African Highveld. Department of Geological Sciences, University of Cape Town. **MSc**.

Van Tienhoven, A.M. and Scholes, M.C. (2003) Air pollution impacts on vegetation in South Africa. In: Emberson, L., Ashmore, M. and Murray, F. (Eds) *Air pollution reviews volume 4. Air pollution impacts on crops and forests: a global assessment*. Imperial College Press, London.

Vitorello, V.A., Cerri, C.C., Andreux, F.G., Feller, C. and Victoria, R. (1989) Organic matter and natural carbon-I 3 distribution in forested and cultivated oxisols. *Soil Science Society of America Journal,* **53** pp 773-778.

Vitoria, L., Otero, N., Soler, A and canals, A. (2004) Fertlizer characterization: Isotopic data (N, S, O, C and Sr). *Environmental Science and Technology,* **38** pp 3254 – 3262.

Vitousek, P.M., et al. (1997) Human alteration of the global nitrogen cycle: sources and consequences. *Ecological Applications,* **7**:3 pp. 737–750.

Volkoff, B., Cerri, C.C. (1987) Carbon isotopic fractionation in subtropical Brazilian grassland soils: comparison with tropical forest soils. *Plant Soil,* **102** pp 27–31.

Wadleigh, M.A., Schwarcz, H.P. and Kramer, J.R.,(1994) Sulfur isotope tests of seasalt correction factors in precipitation: Nova Scotia, Canada. *Water, Air, and Soil Pollution,* **77** pp 1-16.

Wang, J., Solomon, D., Lehmann, J., Zhang, X. and Amelung, D. (2006) Soil organic sulfur forms and dynamics in the Great Plains of North America as influenced by long-term cultivation and climate. *Geoderma,* **133** pp 160–172.

Webb, A.H. and Hunter, G.C., (1998). Power-station contributions to local concentrations of NO_2 at ground level. *Environmental Pollution* **102**:1 pp 283-288.

Wedin, D.A., Tieszen, L.L., Dewey, B., Pastor, J. (1995) Carbon isotope dynamics during grass decomposition and soil organic matter formation. *Ecology,* **76** pp 1383–1392.

Whelpdale, D.M. (1992) An Overview of the Atmospheric Sulphur Cycle In. Howarth, R.W., Stewart, J.W.B. and Ivanov, M.V. (Eds) SCOPE 48: *Sulfur cycling on the continents* Chapter 2 pp 6 – 20.

Winner, W.E. and Atkinson, C.J. (1986) Absorption of air pollutants by plants and consequences for growth. *Trends in ecology and evolution,* **1** pp 15 -18.

Winner, W.E., Berg, V.S. and Langston-Unkefer, P.J. (1989) The Use of stable sulfur and nitrogen isotopes in studies of plant responses to air pollution In Rundel, P.W., Ehleringer, J.A. and Nagy, K.A. (Eds) *Stable isotopes in Ecological research*, Springer-Verlag, New York, pp 454-470.

Witzell, J. Shevtsova, A. (2004) Nitrogen-induced changes in phenolics of Vaccinium myrtillus – implications for the interaction with a parasitic fungus *Journal of Chemical Ecology,* **30** pp. 1919–1938.

Wlotzka F. (1972) Nitrogen isotopes in Nature. In.Wedepohl, K.H. (Eds*) Handbook Of Geochemistry* 2-l Springer, Berlin. pp. 7-B. l-7-B-9.

Xiao, H,Y. And Liu, C.Q. (2002) Sources of Nitrogen and Sulfur in wet deposition at Guiyang, southwest China, *Atmospheric Environment* **36** pp 5121–5130.

Zhang, G.Y., Zhang, X.N. and Yu, T.R. (1987) Adsorption of sulfate and fluoride by variable charge soils. *Journal of Soil Science,* **38** pp 29-38.