ATTENUATION OF IONIC POLLUTANTS IN SELECTED SOUTH AFRICAN SOILS

Mireille KM Mwepu

Thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science (Agriculture)
Department of Soil Science
Stellenbosch University
July 2006

Supervisor: Prof M.V. Fey

UITTREKSEL
DIE VERDUNNING VAN BESOEDELENDE IONIESE STOWWE IN UITGESOEKTE GRONDE VAN SUID-AFRIKA

Twee-derdes van Suid-Afrika is hoofsaaklik van grondwater as bron van drinkwater asook vir ontwikkeling afhanklik. Dit sluit meer as 280 dorpe en nedersettings in. Veral in die semi-ariede dele van Suid-Afrika, is grondwater hulpbronne beperk in terme van beide kwaliteit en kwantiteit (Sililo et al., 2001, p. I). Daarom is dit baie belangrik om grondwater hulpbronne teen besoedeling te beskerm.

Die eerste doelwit van die navorsing was om ondersoek in te stel rakende die verdunningskapasiteit van geselekteerde grondhorisonte wat hooftipes diagnostiese horisonte in die Suid-Afrikaanse grondklassifikasie verteenwoordig. Die voorlopige chemiese verdunning skattings wat deur Sililo et al. (2001, p. 4.6) vermeld is, kon sodoende bevestig word. Die tweede doelwit was om die verdunningskapasiteit van besoedelende stowwe in Suid-Afrikaanse grondhorisonte te skat, sowel as die diagnostiese waarde van belangrike chemiese eienskappe van gronde, om inligting oor te dra aangaande die vervoer-/verdunningspotensiaal van die kontaminante. Die derde doelwit was om vas te stel of dit moontlik is om H_2SO_4 of $Ca(OH)_2$ as suur/basis in te pomp in ‘n bulkhoeveelheid grond om die beweeglikheid van die kontaminante te verlaag.

Die chemiese vaslegging van besoedelende stowwe in ongeveer 170 grondmonsters is getoets. Die grond is gekontamineer deur 500, 1000, 2500, 5000 en 10000 mg/kg Cu, en 100, 250, 500, 1000 en 1500 mg/kg P by te voeg. Die sorpsie isoterme is opgestel en gebruik om die sorpsie kapasiteit by ‘n ewewigskonsentrasie van 1 mg/l Cu of P te bereken. Die vasleggingskapasiteit is statisties geëvalueer om te kyk wat die voorspelbaarheid, gebaseer op grondklassifikasie, is. ‘n Poging om die vasleggingskapasiteit te korreleer met verskeie belangrike grond chemiese eienskappe soos klei-inhoud, ekstraheerbare Fe en Al inhoud, organiese materiaal inhoud, S-waarde (uitruilbare basiese katione) en pH, het nie oortuigende resultate gelewer nie. Die gebruik van die chemiese omhulsel (*envelope*) benadering word dus

geregverdig vir die evaluering van die verhouding tussen sorpsie en grondeienskappe. Kwantielregressies is gebruik om die “chemiese omhulsels” vir Cu en P verdunning te voorspel. Die datastel is eerstens vir elke onafhanklike verandering in stygende orde gerangskik en daarna in klasse van gelyke monstergrootte (bandwydte) gedeel. Die kwantiele van die afhanklike veranderlike vir elke klas is bereken en teenoor die ooreenstemmende gemiddelde van die onafhanklike veranderlike uitgestip. Die chemiese omhulsels van die datastel word verteenwoordig deur die kurwes van die 0.95 en 0.05 kwantiele.

Die bevindings stel voor dat grondklassifikasie slegs ‘n gebrekkige kategorisering van gronde moontlik maak in terme van die verdunning van besoedelende stowwe, en dus die potensiële beskerming van grondwater. Die verdunning van besoedelende stowwe kan tot in ‘n mate voorspel word deur ‘n kombinasie van klassifikasie data en sekere ander belangrike grondinligting, te gebruik. Dit bring mee dat grondkaarte gebruik kan word om voorspellings aangaande die kwesbaarheid van grondwater te maak, maar slegs as die gronde voldoende deur laboratorium ontledings gekarakteriseer is.

Om die sorpsie van kontaminante (koper en fosfaat) in die grond te verhoog, is die inpomp van suur/basis deur H_2SO_4 of $Ca(OH)_2$ in vier gronde uitgeoefen. Die oormaat suur of basis is vervolgens geneutraliseer en die vasleggingskapasiteit vir Cu en P is vasgestel. Suur inpomping het ‘n klein of negatiewe effek op Cu-sorpsie gehad in drie van die vier gronde wat getoets is. Aan die ander kant, het basis inpomping ‘n groot toename in Cu–sorpsie getoon in gronde met ‘n hoë residuele pH-waarde. Die inpomp van suur en basis het P-sorpsie in al vier gronde verhoog. Basis inpomping het die beste resultate in drie van die vier gronde gelewer. Die resultate het nie oortuigend gewys dat die inpomping van beide suur en basis in ‘n grond ‘n sterker effek op Cu en P vaslegging het, as wat ‘n eenvoudige pH wysiging met of suur of basis nie.

DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and has not previously in its entirely or in part been submitted at any university for a degree.

Mireille K.M. Mwepu

ABSTRACT

Two–thirds of South Africa, including more than 280 towns and settlements are largely dependent on groundwater for their drinking water supply and development. However, groundwater resources in South Africa are limited both in terms of quantity and quality, especially in the semi–arid parts of the country (Sililo et al., 2001, p. i). Therefore, the importance of protecting groundwater resources from pollution has been recognized.

The first objective of this research was to investigate the attenuation capacity of a selection of soil horizons and materials representing major types of diagnostic horizons and materials in the South African soil classification in order to validate their chemical attenuation ratings as provisionally specified by Sililo et al. (2001, p. 4.6). The second objective was to assess the pollutant attenuation capacity of South African soil horizons and materials as well as describe the diagnostic value of key chemical properties of soils for conveying information on their contaminant transport/attenuation potential. The third objective was to investigate whether it is possible to apply acid/base priming using H_2SO_4 and $Ca(OH)_2$ to a bulk quantity of soil in order to reduce the mobility of contaminants.

The chemical retention of pollutants in about 170 soil samples was tested. The soil was contaminated by adding 500, 1000, 2500, 5000 and 10000 mg/kg Cu, and 100, 250, 500, 1000 and 1500 mg/kg P. We constructed the sorption isotherms from which the sorption capacity at an equilibrium Cu or P concentration of 1 mg/l could be calculated. The retention capacity was statistically examined to check predictability based on soil classification. An attempt to correlate the retention capacity with several key soil chemical properties such as clay content, extractable Fe and Al content, organic matter content, S value (exchangeable basic cations) and pH did not yield convincing results; thus warranting the use of a chemical envelope approach for the evaluation of the relationship between sorption and soil properties. Quantile regression was used to predict “chemical envelopes” for Cu and P attenuation. The dataset was first sorted in terms of ascending order for each independent variable and divided into classes of equal sample size (bandwidth). The quantiles of the dependent variable for each class were calculated and plotted against the corresponding mean for the independent variable. The curves of 0.95 and 0.05 quantiles represent the chemical envelope for the dataset.

The findings suggest that soil classification allows only an imperfect categorization of soils in terms of pollutant attenuation and thus potential groundwater protection. Pollutant attenuation can be predicted to some degree if we combine data used for classification and some other key soil data. This implies that soil maps can be useful for making predictions about groundwater vulnerability provided the soils have been well characterized by laboratory analyses.

In order to increase the sorption of contaminants (copper and phosphate) to soil, acid/base priming of four soils was performed by adding H_2SO_4 or $Ca(OH)_2$ then neutralizing the excess acid or base and determining the retention capacity for Cu and P. Acid priming had little or negative effect on Cu sorption in three of the four soils tested. On the other hand, base priming showed a large increase in Cu sorption in soils that had high residual pH values. Both acid and base priming enhanced P sorption in all four soils tested, with base priming showing the best results in three of the four soils. The results did not conclusively demonstrate that priming a soil with both acid and base has a stronger effect on Cu and P retention than simple pH modification with either acid or base.

ACKNOWLEDGMENTS

First I would like to thank God for his support that enabled me to complete this endeavour.

I would like to thank my supervisor Professor M.V. Fey, Head of the Soil Science Department, Stellenbosch University, for supervising this thesis; providing insightful comments, academic expertise as well as much needed support and guidance throughout the duration of this endeavour.

My gratitude is extended to the Water Research Commission for funding this project.

I am grateful to the laboratory staff at the Department of Soil Science, Stellenbosch University especially Matt Gordon, Judie Smith and Godfrey Mongwe for their assistance with the lab work.

I wish to thank Professor David Kreamer, Anthony Mills, Ailsa Hardie and Tanya Medinski who have encouraged me with their comments on certain parts of this thesis.

I would like to thank my family, especially my husband, for moral, spiritual and psychological support.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Introduction

Groundwater resources in South Africa are limited both in terms of quantity and quality, especially in the semi–arid parts of the country. More than 280 towns and settlements are largely dependent on groundwater for their drinking water supply and development (Sililo et al., 2001, p. i). The economy of the country is largely driven by mining and agricultural sectors that to a certain extent depend on groundwater, especially agriculture (Table 1.1). Although groundwater contributes only about 15% of the total water consumption, it is estimated that 90% of extracted groundwater in South Africa is used by farmers (Colvin, 2001). Unfortunately, a wide range of pollutants occur in groundwater. These include bacteria and other micro-organisms, organic chemicals as well as ionic pollutants which constitute the focus on this study.

Table 1.1 Groundwater uses in South Africa (Colvin, 2001)

Use	Percentage
Irrigation	78
Domestic	7
Stock	6
Mining	5
Industrial	4

It is important that the quality of groundwater should be monitored and that protection measures put in place to safeguard groundwater from pollution. However, many factors influence groundwater flow and contamination.

In determining the susceptibility (vulnerability) of groundwater to contamination, consideration must be given to factors such as land use and soil variables. The concept of groundwater vulnerability recognizes that differing soil and hydrogeological conditions will give rise to differing vulnerabilities and afford different degrees of protection to the underlying aquifer (Worrall and Kolpin, 2004). Sililo et al., 2001) proposed two criteria as a basis for classifying soil forms in the existing South African soil classification system i.e. hydraulic attenuation (Table 1.2) and chemical attenuation (Table 1.3)

Table 1.2 Hydraulic attenuation: soil contribution to intensity of ground water recharge (Sililo et al., 2001)

Class	Attenuation capacity and pedogenic inference
1	*Maximal hydraulic attenuation*: bare sheet rock; heavy crusting clays; steep slopes; extreme aridity; minimal vegetation cover; shallow dorbank or calcrete horizons
2	Most calcareous and eutrophic clay soils; duplex and margalitic soils; lithocutanic soils with steeper relief
3	*Intermediate*: mostly loamy, thicker eutrophic or mesotrophic soil profiles on gentler relief
4	Dystrophic or mesotrophic loams and ferrallitic clays and loams on gentle relief
5	Minimal hydraulic attenuation: extreme water surplus sustained for significant periods; sandy soil texture; absence of luvic or clay pan features in soil profile+vadose zone; regic sands of humic climates on level topography

Table 1.3 Soil chemical contribution to contaminant attenuation (Sililo et al., 2001)

Class	Attenuation capacity and pedogenic inference
A	**Cationic contaminants (inorganic and polar organic)**
1	*Maximal attenuation*: Thick, clayey profiles especially margalitic soils; strongly calcareous clays; eutrophic peats
2	
3	*Intermediate* all other soils (based on criteria in section 4 and research data
4	
5	*Minimal attenuation*: Dystrophic sands low in humus
B	**Anionic contaminants (inorganic and polar organic)**
1	Maximal attenuation: Deep, dystrophic, ferrallic clays
2	
3	*Intermediate* all other soils (based on criteria in section 4 and research data
4	
5	*Minimal attenuation*: Eutrophic sands
C	**Organic contaminants (non-polar)**
1	Maximal attenuation: Deep humic clays and peats
2	
3	*Intermediate* all other soils (based on criteria in section 4 and research data
4	
5	*Minimal attenuation*: Pure sands low in humus

This study focuses on soils and their role in attenuating contaminants since the soil is often the “first line of defence” against the migration of contaminants to groundwater. An attempt to address this concern calls for an in-depth investigation of related questions which may include the following:

-does the exisiting soil classification allow a useful categorization of soils in terms of pollutant attenuation and potential groundwater protection?

-how is the sorption capacity of soils related to commonly measured properties?

- can acid-base treatment increase significantly the sorption capacity of the soil?

-what are the implications of the above questions on groundwater protection strategies?

This is the procedure used in order to answer these questions: the retention of pollutants was tested in about 170 soil samples representing major kinds of diagnostic horizons and materials in the South African soil classification. The soil was contaminated with an increasing load of copper or phosphate. The retention capacity of different diagnostic horizons/materials was statistically examined to check predictability based on soil classification and then the retention capacity was correlated with several key soil properties such as CEC, pH, organic matter, extractable Fe and Al and clay. The study also proceeded to compare on the one hand copper and zinc sorption, and on the other hand phosphate and sulfate sorption in order to investigate whether or not copper could be a potential representative of metals and if phosphate could be a potential representative of ligands. A study performed by Hardie (2004) on smectitic and kaolinitic soils on acid/base priming using the acid-base pair H_2SO_4-$Ca(OH)_2$ has shown that these chemicals are effective in reducing copper in solution. In this study, however, a highly weathered soil from the Paarl Mountain was used to investigate whether it is possible to apply acid/base priming using H_2SO_4 and $Ca(OH)_2$ to reduce copper and phosphate in solution.

Therefore, the first objective of this research was to investigate the attenuation capacity of a selection of soil horizons and materials representing major types of diagnostic horizons and materials in the South African soil classification in order to establish their chemical attenuation ratings as provisionally specified by Sililo et al. (2001, p. 4.6).

The second objective was that of assessing the pollutant attenuation capacity of South African soil horizons and materials as well describing the diagnostic value of key chemical properties of soils for conveying information on their contaminant transport/attenuation potential. The third objective was to investigate whether it is possible to apply acid/base priming using H_2SO_4 and $Ca(OH)_2$ to a bulk quantity of soil in order to reduce the mobility of contaminants. The acid/base priming consists of treating soils with a harsh acid or base so as to reach an extreme pH, then bringing back the soil's pH to the approximate original value. It was expected that this process would generate new hydrous precipitates which serve to increase the capacity of the soil for contaminant attenuation.

Chapter 1

1. Review of literature on pollutant attenuation

1.1 Introduction

Pollution has become a grave worldwide problem not only from an environmental point of view but also because many pollutants are hazardous to human health (Pakdel et al., 1992, p. 381). The extent of pollutants in the environment represents a major ecological problem. In particular, heavy metals constitute a serious risk not only to plants and animals but also to human lives due to the toxicity and non-biodegradability of these elements (Martin-Garin et al., 2002).

Due to land's high price, polluted soils contaminated with heavy metals are often used for vegetable growing; an increasing amount of these heavy metals in these plants can occur and pose toxicity in plants and significant health risks once entered into the human food chain (Moreno et al., 2005). For example, copper which is a key component of various proteins mainly those involved in both the photosynthetic and respiratory electron transport chains, when in excess it is strongly phytotoxic, altering membrane permeability chromatin structure, protein synthesis, enzyme activities photosynthetic and respiratory processes, and may activate the onset of senescence (Leep, 2005, p. 136). Once in the human food chain, high concentration of copper can cause Wilson's disease: copper accumulated in the liver affects infant growth, evidence of histological damage can be seen in early infancy. Unfortunately, clinical illness is usually not observed before the age of 5 years (Baker, 1995, p.171). However, a contaminated soil can generate apparently normal crops (Kabata-Pendias, 2001, p. 18). Due to health risks involved, the accumulation of heavy metals makes the plant materials less appropriate for human consumption and for use as animal fodder (Moreno et al., 2005).

Pollutants (e.g. metals, organic compounds, anions, acids, alkalis) can have a direct or an indirect effect on aquatic species, such as a reduction in the survival, growth and reproduction of the species and an unacceptable percentage of deformities or visible tumours in organisms (Van Vuren et al., 1994, p. 38).

Excess copper within the organism can react with organics. This may change the nature of the organic itself and detrimentally affect copper's metabolic action. As a teratogenic agent, excess copper can cause disruptions of mitosis and may interfere with transcription. It may interfere as well with energy utilization, cell interactions and growth (Lewis, 1995, p. 32). However, reports of excess copper in drinking water affecting human health are rare. The general effects are a metallic taste, a feeling of nausea and, in extreme cases, vomiting. It has been suggested that Indian childhood cirrhosis may be a consequence of hypersensitivity to excess copper (Lewis, 1995, p. 44).

Large inputs of P from urban wastewater systems, surface runoff, or subsurface groundwater flow may raise the aquatic biomass to undesirable levels by a phenomenon called *eutrophication*. Once eutrophic conditions are established, algal blooms and other ecologically negative effects can occur, including low dissolved oxygen levels, excessive aquatic weed growth, increased sedimentation, and greater turbidity. Decreased oxygenation is the major negative effect of eutrophication since low dissolved oxygen levels seriously limit the growth and diversity of aquatic biota and, under extreme conditions cause fish kills. The increased biomass resulting from eutrophication causes the diminution of oxygen, particularly during microbial decomposition of plant and algal residues. Under the more turbid conditions common to eutrophic lakes, light penetration into lower depths of the water body is decreased, resulting in reduced growth of subsurface plants and benthic (bottom-living) organisms. Additionally, eutrophication can increase economic costs of maintaining surface waters for recreational and navigational purposes. Surface scum of algae, foul odours, insect problems, impeded water flow and boating due to aquatic weeds, shallower lakes that must be dredged to remove sediment, and disappearance of desirable fish communities are among the most frequently undesirable effects of eutrophication (Pierzynski et al., 1994, p. 103-104).

It appears important at this stage of the study to define the terms pollutant and contaminant, which will often be used in the rest of this study. Some researchers use these terms interchangeably as synonyms whilst others distinguish them because of some different layers of meanings that they imply. For example, Yong and Mulligan (2004, p. 9), differentiate between the two terms.

Contaminants are the substances (solutes, chemicals etc.) that are not part of the initial composition of a natural soil material. These are generally introduced in the soil as a result of regional and environmental factors and anthropogenic activities. The term pollutant is used to mean a contaminant that has been identified as a threat to human health and the environment because of its nature – as opposed to its concentration.

The Cobuild Dictionary (1995), however, defines a pollutant as a substance that pollutes the environment especially fumes from vehicles and poisonous chemicals that are produced as waste by industrial processes whilst a contaminant is something that contaminates a substance such as water or food. The South African Oxford Dictionary (2002) defines the term *pollute* as to contaminate (water, air etc.) with harmful or poisonous substances. The same dictionary defines the term *contaminate* as to make impure by exposure to or addition of a poisonous or polluting substance. It can be seen that generically the two terms are used with same meaning. In this study, the two terms will be used with the generic meaning, which stresses their common features.

1.2 Common pollutants

The most common types of pollutants, i.e. contaminants that pose a threat to human health found in contaminated sites fall in two categories: (1) inorganic pollutants (e.g., heavy metals such as lead, copper, cadmium) and (2) organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbons (PHCs), benzene, toluene, ethylbenzene, xylene (BTEX) (Yong and Mulligan, 2004, p. 101). It should be noted however, that this study will focus on inorganic pollutants only.

Some of the principal sources of pollutants in soils are (Alloway, 1995, p. 34):

- Motor vehicles: the use of leaded petrol has been accountable for the global dispersion of Pb aerosols.
- The combustion of fossil fuels: this results in the dispersion of many elements in the air over a large area. The disposal of ash is a potential source of metals.
- Agricultural fertilisers and pesticides: several of these including phosphatic fertilisers, slags from iron manufacture, pesticides and herbicides which have

various combinations of heavy metals, organic substances, either as impurities or active constituents.

- Organic manures: these include pig and poultry manures which may have high concentrations of Cu or As fed to improve food conversion efficiency. Sewage sludges usually contain relatively high concentrations of several metals, particularly those from industrial catchments.
- The disposal of urban and industrial wastes: the deposition of aerosol particles emitted by the incineration of metal-containing materials can lead to soil pollution. The unauthorised dumping or disposal of metal-containing items, ranging from miniature dry-cell batteries (Ni, Cd and Hg) to abandoned cars and car components (e.g. Pb-acid batteries) can also be responsible of small areas of very high metal concentrations in soils. The disposal of some domestic waste by burning on garden bonfires or burial in the garden can result as well in localised anomalously high concentrations of metals, such as Pb, in soils used for growing vegetables.
- Metallurgical industries can contribute to soil pollution in numerous ways: (a) by emissions of fumes and dusts containing metals which are transported in the air and finally deposited onto soils and vegetation; (b) by effluents that may pollute soils when water courses flood, (c) by the creation of waste dumps from which metals may be leached and therefore pollute underlying or soils in close proximity.
- The mining and smelting of non-ferrous metals: they can lead to soil pollution because metals are dispersed in dusts, effluents and seepage water. Although most of this type of pollution has occurred since the Industrial Revolution, mining and smelting of non-ferrous metals date back to Roman times and even earlier in some places.

1.2.1 Inorganic pollutants

There are a number of inorganic pollutants that are important. These include heavy metals, radionuclides and other pollutants such as aluminium, beryllium and fluorine. ‘Heavy metals’ is a general collective term applying to the group of metals and metalloids with an atomic density greater than 6 g/cm. Even though this is only a loosely defined term it is widely recognized and usually applied to the elements such as Cd, Cr, Cu, Hg, Ni, Pb and Zn which are generally associated with pollution and toxicity problems. An alternative name for this group of elements is ‘trace metals’ but it is not as commonly used (Alloway and Ayres, 1993, p. 140-141).

Some of the elements in this group are required by most living organisms in small but critical concentrations for normally healthy growth (referred to as ‘micronutrients’ or ‘essential trace elements) but high concentrations can cause toxicity. Those metals include Cu, Mn, Fe, and Zn for plants and animals, Co, Cr, Se and I for animals and B, Mo for plants. Some other elements are called ‘non-essential elements’ but can also be referred to (incorrectly) as ‘toxic’ elements. These elements include As, Cd, Hg, Pb, Pu, Sb, Tl and U (Alloway and Ayres, 1993, p. 140-141).

Radionuclides are unstable isotopes which undergo radioactive decay. Some can be found naturally in air, rocks, soils and plants at concentrations that give measurable amounts of radiation and some are produced artificially, as in nuclear weapon testing. Radionuclides may include various isotopes of americium (Am), cerium (Ce), Co, cesium (Cs), Fe, I, krypton (Kr), plutonium (Pu), radium (Ra), radon (Rn), ruthenium (Ru), thorium (Th), uranium (U), and Zn which commonly exist in plants and soils at low concentrations and as such would be considered trace elements. Moreover, elements such as barium (Ba), C, H, P, and S that are typically present in high concentrations in soils and plants would not be considered as trace elements and have radioactive isotopes. It has been established that there are three kinds of radiation called alpha, beta and gamma. Each of the three kinds of radiation can be a health hazard. It has been estimated that, on average, 79% of the radiation to which humans are exposed is from natural sources, 19% is from medical applications and the remaining 2% is from consequences of weapons testing, television sets and the nuclear power industry. Although natural sources are prevailing, most of the concern over radiation from radionuclides took place with the development of nuclear weapons, after which increasing amounts of radionuclides were deposited on the Earth’s surface (Wild, 1993, p. 204-206).

1.2.2 Organic pollutants

The chemicals and compounds listed in the Toxicity Characteristics Leaching Procedure (TCLP), a test based on the EPA method 1311 with regulatory levels limit for characterization of a chemical as toxic are examples of organic pollutants. These chemicals include benzene, carbon tetrachloride, chlordane, chlorobenzene, 1,4-dichlorobezene, 1,2-dichloroethane, 1,1 dichloroethylene, 2,4 dinitrotoluene, endrin, heptachlor, hexachlorobenzene, hexachloro-1,3-butadiene, hexachloroethane, lindane, methoxychlor, methyl ethyl ketone, nitrobenzene, pyridine, tetrachloroethylene, toxaphene, trichloroethylene, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, silvex and vinyl chloride (Yong and Mulligan, 2004, p. 11).

Organic contaminants can be classified either as synthetic organic chemicals (e.g. pesticides, solvents and pharmaceuticals) or hydrocarbons (e.g. petroleum). Pesticides can be chemically subdivided to include organohalogen, organophosphorus, organonitrogen, organotin and organosulfur compounds. Pharmaceutical compounds are a class of organic contaminants that is causing growing concern due to their impact on water resources. Hydrocarbons can be divided into two classes, aromatic hydrocarbons, which have a benzene ring, and aliphatic hydrocarbons, which don’t have benzene ring. Hydrocarbons can also be classified to include aromatic hydrocarbons, oxygenated, hydrocarbons and hydrocarbons with specific elements (e.g. with N, P, S, Cl, Br, I, F), and other hydrocarbons. Petroleum hydrocarbons are generally present as a mixture of individual organic compounds and are often classed by their separation in the crude oil refining process into categories such as tars, waxes, bitumen, heavy fuel oil, fuel oil, petrol, kerosene and diesel (Usher et al., 2004, p. 6).

1.3 Soil properties affecting attenuation

Several soil processes play a significant role in regulating the quality of groundwater (Lal and Stewart, 1994). Soil properties that are influencing attenuation in different parts of the profile are possibly organic matter, clay, Fe and Al hydrous oxides and pH (Barry et al., 1995). Metal hydroxides of aluminium, iron and amorphous aluminium silicates as well as organic matter are very important reactive surfaces with respect to metal adsorption in soils (van Riemsdijk and Hiestra 1993, p. 7). Most trace metal cations are adsorbed strongly on minerals and organic matter, or form insoluble precipitates (e.g., oxides, carbonates, sulfides), thus have a low mobility in soil. Anions are also known to be sorbed on oxides and silicate mineral fractions of the soils. However, only certain anions can be bond to soil organic matter (McBride, 1994, p. 135). Since groundwater is generally protected by overlying soils, it is not likely to be severely affected by contaminants; it is likely to be controlled by natural processes (Singh and Steinnes, 1994, p. 258).

1.3.1 Organic matter content

Although soil organic matter composes anywhere from 0.5 to 5% by weight of a typical soil mass, its role in the processes associated with contaminant attenuation cannot be neglected, even at such low proportions (Yong and Mulligan, 2004, p. 39). Organic matter of soils is a mixture of plant and animal products in different stages of decomposition and substances that were chemically and biologically synthesized. This complex material can be divided into humic and non-humic substances (Sparks, 2003, p. 98). The non-humic substances contain unaltered biochemicals such as amino acids, carbohydrates, organic acids, fats and waxes that have not changed from the form in which they were synthesised by living organisms. Humic substances which are the most stable compound in soil are subdivided into the fractions of humic acid, fulvic acid and humin which are similar in structure but differ in their reactions. Soil organic matter, and especially its humified fractions, i.e., humic substances, of which humic acid is a major constituent, exerts an important role in environmental processes (Plaza et al., 2005).

Humic substances are amorphous organic materials that have an array of chemical properties that make them unique from other types of environmental substances. They are considered natural polyelectrolytic organic compounds of complex structure involving a huge number of functional groups such as –OH, -CO, phenol, carboxyl, and quinine (Pandey et al., 2002). Because carboxyl and phenolic groups can deprotonate at pH’s common in many soils, they are the most important contributors to the negative charge of soils (Sparks, 2003, p. 98). Humic substances may react with heavy metal ions, radionuclides, and other environmental pollutants. Even a low concentration of humic substances may considerably affect both free and total metal concentrations in soil (Zhou et al., 2005).

Organic matter is a variable charge substance, i.e. its charge varies with pH. Its surface is positive at low pH and negative at high pH (Barrow, 1999). The role that organic matter plays in soil in the retention of ions is important, even at low organic matter content. Furthermore, it has been estimated that up to 80% of cation exchange capacity (CEC) in soils is due to organic matter (Sparks, 2003, p. 98).

In fact the cation exchange capacity is an important parameter at sites contaminated by heavy metals because the latter will often replace exchangeable ions such as sodium, potassium, calcium and magnesium that are in natural soil (Boulding, 1994, p. 3-68). Some trace anions, such as B, I, and Se can also bound to organic matter (kabata-Pendias, 2001, p. 66). However, most anions adsorb very little in humus and it is safe to say that anion bonding at mineral surfaces account for most of the anion retention in soils (McBride, 1994, p. 135). As the content of organic matter usually decreases with depth in the soil profile, the removal of heavy metal may be attributed to the increasing content of inorganic colloids (Jones and Jarvis, 1981, p. 604).

1.2.2 Type and clay content

The common phyllosilicates in soils may be subdivided into 5 groups: kaolinite, illite, vermiculite, chlorite and smectite. The two major sources of negative charges are isomorphous substitution and dissociation of exposed hydroxyl groups (Tan, 1994, p. 160-162).

The existence of permanent negative sites in certain phyllosilicates accounts for the aptitude of many soils to hold cations against leaching (Dixon, 1998, p. 38-39). The cation exchange capacity (CEC) differs from soil to soil depending on clay content and type of clays. Kaolinite has a 1:1 (silica: alumina layer) structure that has a low CEC and surface area whereas 2:1 clay minerals such as vermiculite and montmorillonite have a high CEC and surface area and other 2:1 clays with non-expanded layers (illite, mica) or filled interlayers (chlorite) have intermediate reactivity.

Many types of clays have actually been shown to have a useful impact on leachates which pass through them due to a process known as attenuation. This process causes significant reductions in the concentration of some components of leachate, and processes such as sorption and ion exchange have been shown to prevent the migration of contaminants through soil. This attenuation effect has been established to be greater with some materials than with others; in particular, smectite has a high cation exchange capacity and has been found efficient to attenuate contaminants (Arch, 1998, p. 219).

The capacity of phyllosilicates to accept and retain inorganic (and some organic) contaminants can be assessed by the determination of their buffering potential. The buffer capacity of a soil determines the potential of a soil for effective interaction with leachate contaminants, and is more appropriate for inorganic soils and inorganic leachates (Yong et al., 1992, p. 158 -159).

1.3.3 Al and Fe Oxide content

Even though the clay minerals might be an important factor influencing the removal of pollutants due to their large surface areas and their predominance in natural soils, the small fraction of metal oxides may as well have a great potential for removing pollutants (Zhuang and Yu, 2002). Al hydroxides, oxyhydroxides, and oxides occur in natural settings. The oxyhydroxides are less frequent than the hydroxides. The most important Fe oxides and oxyhydroxides are akaganeite, ferrihydrite, feroxyhyte, goethite, hematite, lepidocrocite, maghemite and magnetite (Sparks, 2003, p. 59 - 60).

The iron and aluminium oxide minerals are amphoteric; in acid condition they may possess a weak electronegative charge and in alkaline soil, they may develop an electropositive charge. The minerals can have no charge at certain pH values. The pH value at which the mineral has no charge is called the zero point charge (ZPC) (Tan, 1993, p. 153). The chemical nature and high specific surface area of oxides as discrete particles and coatings on other minerals make them efficient sinks for many contaminants including both cations and anions (Trivedi et al., 2001). They can interact with positively charged species like H+, Al^{3+}, Co^{2+}, Zn^{2+}, Pb^{2+}, and Cu^{2+} and with negatively charged species like phosphate, arsenate, sulfate, selenite, borate, bicarbonate and fluoride (Van Riemsdijk and Hiemstra, 1993, p. 7). Soils with high contents of Fe and Al oxides have as well high phosphate sorbing capacities (Barry et al., 1995). The general view being that retention occurs as a result of the exchange between the phosphate and hydroxyl ions associated with the iron and / or aluminium (Morgan, 1997, p. 140). Sorbed PO_4^{3-} can diffuse inside pedogenic oxides and turn out to be less soluble (Leinwer et al., 2002, p. 32).

Marosits et al. (2000) reported the following decreasing sequence of adsorption of metal ions on goethite at different pH values: Cu^{2+}> Pb^{2+}> Zn^{2+} >Co^{2+} >Ni^{2+} >Mn^{2+} (for hematite the order of Pb^{2+} and Cu^{2+} was reversed). It has been found that, the greater the tendency to hydrolyse, the greater the affinity for the surface sites on oxides. In fact, the divalent ions of copper, zinc, cobalt, nickel, cadmium, manganese, and mercury hydrolyse to varying extents. It has been reported a decreasing order of preferential adsorption among the following anions: $SiO_4^{4-} > PO_4^{3-} >> SO_4^{2-} > NO_3^-$ (Tan, 1993, p. 246).

The retention of ions by oxide surfaces has been found to be inversely dependent upon the degree of crystallinity (Harter, 1991, p.76). De la Flor et al. (1995) observed a generalized tendency towards an association of copper with the oxide phase, which are less crystalline. This generalized tendency of copper association towards phases of amorphous or free iron oxyhydroxides confirm the results of several authors. Many studies have shown that poorly ordered iron oxides are more reactive with phosphate than their crystalline counterparts (Bastin et al., 1999).

1.3.4 pH

Sorption is a pH-dependent process which suggests that hydroxy cations (e.g. $HgOH^+$) and other hydroxylated metal species formed by hydrolysis are generally bound much more strongly than the free aquo cations of the metals (e.g. Hg^{2+}), although other researchers reported preferential sorption of Pb^{2+}, as opposed to $PbOH^+$. A possible reason for which the hydroxylated cation is preferentially sorbed that of its hydration sphere is less stable than that of the free cation and so does not hinder surface complexation as much (Jackson, 1998, p. 111-114).

Under acidic conditions, the metals are in the form of free cations, and the fraction sorbed by a mineral colloid is minimal. The minimal sorption may be explained by competition between H^+ ions and metal cations for binding sites, and by an increase in the number of cation-repelling positively charged sites.

With increasing pH, the concentration of hydroxyl metal cations rises at the expense of free cations, and the percentage of the metal sorbed increases at its maximum.

With further increase in pH, uncharged hydroxyl species [e.g. $Hg(OH)_2$] increase, and the percentage of the metal bound to the sorbent levels off; and , with more alkaline conditions, the percentage may decline owing to the formation of an anionic metal species [e.g. $Hg(OH)_3^-$] accompanied by the formation of anion-repelling negative sites on the mineral surface.

However, from the fact that metals are hydrolysed within different pH ranges, it is apparent that in mixed solution of metals the influence of pH may account for preferential binding of some metals with respect to others. And, the relative affinities of metal cations for mineral surfaces at different pH values also depend on the nature of the mineral (Jackson, 1998, p. 111-114).

The sorption of anions is also a function of pH. Generally, this sorption is most efficient under acidic conditions because of the number of positively charged sites, while it is less efficient under alkaline conditions, which promote the formation of negatively charged sites (Jackson, 1998, p. 115). Soil pH, because of its influence on the presence and solubility of calcium, iron, and aluminium affects the reactions of phosphate (Miller and Gardiner, 1998, p. 339). In acidic soils, phosphate is sorbed on the surfaces of insoluble iron and aluminium hydrous oxides. Moreover phosphate can react with soluble iron, and aluminium ions to form insoluble phosphate (Miller and Gardiner, 1998, p. 335). In calcareous soils, phosphate can react with the soluble Ca^{2+} resulting in the formation of dicalcium phosphate dihydrate ($CaHPO_4.2H_2O$). Furthermore, dicalcium phosphate dihydrate may slowly revert to other more stable Ca phosphates such as octacalcium phosphate [$Ca_8H_2(PO4)_6.5H_2O$], and in the long term to apatite [$Ca_{10}(PO_4)_6F_2$] (Pierynski, 1994, p. 121).

However, well-buffered soils can resist pH changes whether acidity or alkalinity is added in one form or another. Some of the most important mechanisms potentially involved in this ability to buffer pH are (McBride, 1994):

- carbonate mineral buffering: free carbonate minerals in soil constitute a reserve of alkalinity that can neutralize soil acidity or alkalinity introduced as pollutants.
- exchangeable base cation buffering: added acid cations (H^+, Al^{3+}) exchange base cations from clay or humus exchange sites, to produce pH buffering.

- buffering by aluminosilicate mineral decomposition: in moderately to strongly acid soils (pH<5.5), variable-charge mineral surfaces and layer silicate edges accept protons to generate anion exchange sites.

1.3.5 Ionic strength

Ionic strength is a measure of the degree of interaction between ions in solution associated to the total electrolyte concentration in solution (Sparks, 2003, p. 124). The macroscopic research of ionic strength effects in the study of ion adsorption to oxides has become a standard method to distinguish between inner sphere and outer sphere adsorption. In inner sphere surface complex, the sorbing ions and the surface functional groups establish covalent bonds, while in an outer sphere surface complex at least one water molecule remains between a surface functional group and the sorbed ion. This method attributes the inner sphere mechanism to a change in the value of ionic strength does not visibly change the adsorption of a certain ion on a certain oxide, and the outer sphere mechanism to an increase in ionic strength resulting in a decrease of ion uptake (Lützenkirchen, 1997).

Many studies have been oriented towards an understanding of the mechanism of Cu sorption onto goethite. Peacock et al. (2000) measured the sorption of Cu on goethite, hematite and ferrihydrite as a function of ionic strength and pH. They obtained EXAFS spectra to determine the mechanism of Cu sorption on goethite at low and high pH. At pH= 4.6, the sorption of Cu was strongly enhanced by increasing the ionic strength from 0.1 to 1.0 M. EXAFS spectra suggested that, at pH= 4.6, Cu sorbs via an outer sphere complex insofar as there is no evidence for any Cu-Fe or Cu-Cu interaction.

In contrast, sorption of Cu at pH= 6.27 showed no strong augmentation with increasing ionic strength and the EXAFS spectra showed strong evidence for an inner sphere complex. Egirani et al. (2005) investigated the dependence of Cu and Zn removal from aqueous solutions by mixed mineral systems of kaolinite, montmorillonite, and goethite of the sorbing ions. Based on the amount of Cu and Zn sorbed on the mixed mineral suspensions at 0.01 and 0.1 M ionic strength and pH 4, it is suggested that Cu and Zn removal from aqueous solution was by both the inner and the outer sphere complexation.

There are strong differences in sorption behaviour between different anions on the sorbent. Weakly sorbing anions are assumed to have outer sphere electrostatic attraction. For instance, sulfate sorption to goethite is ionic strength dependent in sodium chloride media and has been found to be outer sphere. Strongly sorbing anions, such as phosphate and selenite show little dependence of sorption on ionic strength, and are believed to adsorb by an inner sphere ligand exchange mechanism (Collins et al.,1999) .It was demonstrated that for soils, the effects of ionic strength on phosphate adsorption are transient and disappear after long periods of equilibration (Bolan et al., 1989).

Chubar et al. (2005) studied the effect of ionic strength (with NaCl as background electrolyte) on the sorption of phosphate on oxide of zirconium. Both maximum sorption capacity and affinity constant for phosphate increased with the increase of the ionic strength (electrolyte concentration). In this case, sorption capacity also increased with increasing ionic strength but the affinity constant was almost the same for the experiment without electrolyte NaCl and with 0.01M NaCl. Yet, as the pH was kept stable by adding the solution of HCl, so some Cl ions were already present in the solution, which, the most likely, increased the affinity constant. The background electrolyte dependence may be due to the participation of Cl ions in the adsorption of phosphate ions as intermediate stage. In the first stage of this process, the Cl ions replace the surface OH groups via formation of tetra-centred complex. The next stage $H_2PO_4^-$ replaces the surface Cl ions.

1.4 Mechanism of attenuation

Complexation with organic matter, sorption on oxides and silicate clays and precipitation as carbonate, hydroxide, sulfide or phosphate are the mechanisms responsible for contaminants attenuation in soil (Alvarez- Ayuso and Garcia-Sanchez, 2003). The mechanism of interactions between contaminants and the soil are greatly influenced by the chemistry of the soil constituents, the contaminants, their soil and contaminants respective functional groups as well as the pH of the system (Yong et al., 1992).

1.4.1 Sorption

The term “sorption” is commonly used to describe numerous chemical processes (e.g. adsorption, partitioning, surface precipitation, polymerization, and secondary solid phases) that result in a substance (sorbate) being retained by soil inorganic and organic solid phases (sorbent). This term is often chosen when the mechanism of retention of a sorbate is unidentified as is often the case with P and many organic chemicals. Sorption can happen due to physical processes involving van der Walls forces or electrostatic outer sphere complexes, such as, anion exchange, which is referred to as non-specific adsorption, to chemical processes, for instance, inner-sphere complexes, ligand exchange, and chemisorption, many of which are referred to as specific adsorption (Pierzynski, 2005, p. 83).

Physical adsorption occurs when the contaminants in the soil solution are attracted to the soil constituent surfaces owing to the unsatisfied charge of the soil particles. The ions are primarily held by electrostatic force. It is the bonds’ weak nature that allows the exchange of one cation for another in cation exchange, and one anion for another in anion exchange (Singher and Munns, 1996, p. 68-71).

.

In ion exchange, the ions in solution exchange places with those held on the exchange complex (clays and organic matter of a soil). Small cations tend to be held more tightly and are replaced from the exchange complex less easily than are large cations; highly charged cations tend to be held more strongly than those that are less charged. However, the concentration of the cation in the soil solution influences the exchange. If one cation is in large concentration, it will be preferred in the exchange reaction, regardless of its size or charge. In anion exchange, anions replace other anions that are attracted to positively charged sites on clays and organic matter. Ion charge, size, and concentration also affect anion exchange (Singher and Munns, 1996, p. 68-71).

Chemical adsorption refers to high affinity, specific adsorption, which generally occurs in the inner Helmholtz layer through covalent bonding. It involves the exchange of cations and most anions with surface ligands (Yong et al., 1992, p. 152). In specific cation adsorption, the cations are bound directly to surface OH groups and

O atoms (including O^- formed by dissociation of H^+ from OH), which function as ligands. Surface ligands have a strong preferential affinity for heavy metals with respect to alkali and alkaline-earth metals, forming more stable bonds with some heavy metals than with others due to differences in specific metal properties. These properties are related to the metal's tendency to form covalent bonds with ligands, and to the hydrated cation's distance of closest approach to the mineral surface, which make it more possible for some metals than others to fit into openings in the crystal structures of minerals (Jackson, 1998, p. 105-109). The most important minerals in this regard are non-crystalline aluminosilicates (allophanes), oxides and hydroxides of Fe, Al and Mn, and layer silicate clays (edge sites only) (McBride, 1994, p. 135).

In specific anion adsorption, anions are incorporated into surfaces of minerals that possess hydroxyl groups bound to metal cations, such as Fe or Al oxides, hydroxides, or amorphous minerals. Some ligand exchange can occur at the edges of silicate clays like kaolinite. The anions that contain oxygen are the most prone to ligand exchange. Anions such as $H_2PO_4^-$, HPO_4^{2-}, $H_3SiO_4^-$, and SO_4^- can replace the hydroxyl group (OH) as the ligand bound to the Fe or Al. This form of exchange differs from anion exchange since the anion is held more tightly and the anion loses its hydration water to become part of the mineral structure (Singher and Munns, 1996, p. 71-73).

Adsorption can be defined as the accumulation of a substance or material at an interface between the solid surface and the bathing solution. It can consist of the removal of solute molecules from the solution and of solvent from the solid surface, and the attachment of the solute molecule to the surface. In regard to contaminant-soil interaction, the adsorption reactions are processes by which contaminant solutes in solution are held to the surface of soil particles through mechanisms which try to satisfy the forces of attraction from the soil solids (Yong et al., 1992, p. 149). Adsorption has been acknowledged as one of the important processes determining the fate of trace metal contaminants in soil (Yin, 1996). Adsorption determines as well the quantity of plant nutrients, metals, pesticides, and other organic chemicals retained on soil surfaces and therefore is one of the primary processes that influences transport of nutrients and contaminants in soils (Sparks, 2003, p.134).

An initial adsorption reaction can be followed by a penetration of the adsorbed ions into the interior of the reacting particles. Studies have shown that sorption of nickel, zinc, and cadmium by goethite continued for many weeks. Dissolution studies and detailed modelling have all shown consistence with an initial adsorption reaction followed by a diffusive penetration of the surface. It was also shown that the phenomena differ for different metals. Copper, lead, cadmium, and manganese tend to diffuse via pores. On the other hand, nickel and chromium were little affected by the presence of pores and may diffuse via smaller defects such as crystal vacancies (Barrow, 1999).

The extent of the slow reaction between phosphate and goethite has been shown to be dependent on crystallinity of the goethite. For well crystallised samples, there was no slow reaction but for poorly crystallised samples the reaction continued for weeks. Strong evidence proved that the mechanism was slow penetration of the spaces between the crystal domains. This suggested that the penetrating ions had reached the ends of their pathways. However, in most cases, diffusion appears to be so slow that the depth of penetration is small compared to the size of the reacting particle (Barrow, 1999).

1.4.2 Precipitation

The beginning of precipitation and the end of chemisorption during sorption is not easily recognised by experimentalists since the chemical bonds formed in both processes can be similar (McBride 1994, p. 154). Precipitation is the opposite of dissolution, and in the case of contaminants in the aqueous phase, precipitation occurs when the transfer of solutes from the aqueous to the interface results in accumulation of a new substance in the form of a new soluble solid phase (Yong et al., 1992, p.155). Precipitation of mineral forms is common in soil and can direct the solubility of elements such as Al, Fe, Si, Mn, Ca, and Mg and (perhaps P and S). Most trace metal cations have a low mobility in soils, they adsorb strongly on minerals and organic matter, or form insoluble precipitates (McBride, 1994, p. 155).

However, precipitation of trace metals is likely only when soils become heavily loaded with these metals. Precipitation of these metals as hydroxides and carbonates is prone in alkaline conditions when the ionic activity of heavy metal solutes exceeds their respective solubility products (Yong and Mulligan, 2004, p. 106). Carbonates can be the dominant trace element sink in a particular soil, but the most important mechanisms for regulating the trace element behaviour by carbonates are related to variation of the soil pH. For instance, $CdCO_3$, $Cu_2(OH)_2CO_3$, and $Zn_5(OH)_6(CO_3)_2$ are likely to occur in neutral or alkaline soils polluted with these metals (Kabata-Pendias, 2001, p. 56). In the presence of free calcium carbonate ($CaCO_3$), adsorption of $H_2PO_4^-$/ HPO_4^{2-} on to calcite can also occur by the replacement of water, bicarbonate (HCO_3^-) or OH^- ions present on the calcite particles, and $H_2PO_4^-$ ions in solutions may undergo precipitation reactions (Morgan, 1997, p. 140). The order of solubility of the common phosphate ions is: $H_2PO_4^- > HPO_4^{2-} > PO_4^{3-}$ (Yaron et al., 1996, p. 28), $H_2PO_4^-$ and HPO_4^{2-} ions being predominant in acid and basic soil solutions, respectively (Bohn et al., 1985, p. 305).

The metallic ions (mainly Fe^{2+}, Mn^{2+}, Hg^{2+}, and Cu^{2+}) may form stable sulfides in acidic or neutral reducing environment. Precipitation of metallic ions as sulfides constitutes an important mechanism regulating both S^{2-} and metallic cations concentrations (Kabata-Pendias, 2001, p. 56). In acid soils the phosphate ions can react with soluble iron and aluminium ions to form insoluble phosphates (Miller and Gardiner, 1998, p. 335-336).

As the amount of metal cation or anion sorbed on a surface increases, sorption can proceed from mononuclear adsorption to surface precipitation. There are numerous types of surface precipitates. They can occur via polymeric metal complex that form on mineral surfaces and via the sorption of aqueous polymers. Homogeneous precipitates can form on a surface acting as a nucleation site. When adsorption attains monolayer coverage, sorption continues on the newly created sites, promoting a precipitate on the surface. If the precipitate is derived from both the aqueous solution and dissolution of the mineral, it is called a co-precipitate. The composition of the co-precipitate varies between that of the original solid and a pure precipitate of the sorbing metal. The ionic radius of the sorbing metal and sorbent ions has to be similar for co-precipitates to form (Matthess, 1984, p. 87).

The types of mixed solid commonly formed include phyllosilicates, hydrous oxides and calcite in which isomorphous substitution has occurred. Calcite ($CaCO_3$) is perhaps the most common form of the carbonate minerals found in soil influencing the pH and reactions (Yong and Mulligan, 2004, p. 39). The important feature of co-precipitation processes is that the new solid phase is more stable and insoluble in the final solution than the original solid phase (Matthess, 1984, p. 87). There is no fundamental difference between the sorption and co-precipitation of metals by oxides except that in co-precipitation the sorbed metals are assimilated into the mineral as it precipitates (Jackson, 1998, p. 131). Co-precipitation is essential to many environmental issues such as, acid mine drainage, potential radionuclide migration in fouled waste repositories, metal contaminant transport at industrial and defence sites, and waste-water treatment technology (Zhu, 2004).

There is often a continuum between surface complexation (adsorption) and surface precipitation. At low surface coverage surface complexation (e.g., outer- and inner-sphere adsorption) tends to be dominant. As surface coverage increases, nucleation occurs resulting in the formation of distinct aggregates on the surface. As surface loadings increase further, surface precipitation becomes the dominant mechanism (Sparks, 2003, p. 177).

1.4.3 Complexation

A complex is an ion that forms by combining cations and anions and sometimes molecules with the central cation being a transition metal. The surrounding anions (ligands) include many of the common inorganic species such as Cl^-, F^-, Br^-, SO_4^{2-}, PO_4^{3-} and CO_3^{2-}. Organic molecules can also behave as uncharged ligands. Depending on the nature of the ligand, or the solubility product, complexation processes are called adsorption or precipitation. If the ligand is a hydroxyl group on the surface of soil solid, this process is called adsorption. If the complexation reaction leads to the formation of an insoluble product in the liquid phase, the process is called precipitation (Sililo et al., 1999, p. 23). Organic and inorganic complexing agents may either hinder or promote the sorption of metal cations, depending, respectively, on whether the metal complexes remain in solution or are themselves sorbed by the mineral, and on whether sorbed complexes are tightly or less bound than the free cations.

However, some complexing agents have no effect on metal sorption, at least under certain conditions (e.g. within a particular pH range). The effects of complexing are complicated, because they depend on specific properties of the complexing agents, metals, and sorbents, and on diverse environmental factors, such as the pH and ionic strength of the aqueous phase (Jackson, 1998, p. 116). The kinds of inorganic and organic ligands are important factors in the control of heavy metal retention. The retention study of Cd by kaolinitic clay using two control chloride solutions showed that the formation of complexes changed the amount of Cd sorbed by kaolinite (Yong and Mulligan, 2004, p.131). Many researchers examined sorption of Cd and other hazardous metals in the presence of the anions phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), oxalate ($OOC{=}COO_2^-$),citrate ($HOC(CH_2COO)_2COO_3^-$) and humate. These ligands, with the exception of citrate, have been shown to enhance adsorption of these metals on iron(oxyhydr)oxides (Collins et al., 1999).

However, the complexes between the metal ions and inorganic ligands are much weaker than those produced with organic ligands. For organic ligands, such as amines, phenols, complexation occurs when a central metallic cation is attached to two or more organic groups by coordinate covalent bonds. The attached groups (ligands) alone furnish the electrons for the covalent bond called a coordinate covalent bond.

Ligands can consist of single atoms or molecules in which one of the atoms, termed the ligand atom, contains a pair of unbonded electrons. Ligands possessing more than one ligand atom have the ability to coordinate with more than one site, depending on the number of ligand atoms, and it is called multidentate ligand (Yong et al., 1992, p.153).

The suffix “dentate” can be used to accord with the number of ligand atoms as for instance monodentate for a ligand, which has only one ligand atom, bidentate for the ligand with two ligand atoms. Complexation by coordination with multidentate ligands is called chelation, and the complex formation is commonly known as chelates. Complexes formed with monodentate ligands would be less stable than those formed with multidentate ligands. When there is more than one central (metal) atom in the complex, the complex is called a polynuclear or multinuclear complex (Yong et al., 1992, p. 154).

The metal ions are often coordinated to organic substances, mostly humic and fulvic acids forming olidentate complexes and chelates (Marosits, 2000). Of the micronutrient metals, copper has the greatest affinity for organic matter and some studies have indicated that to half of copper present in soil is organically bound. Cu^{2+} ion is directly bonded to two or more organic functional groups (mainly carboxylic, carbonyl and phenolic), thus it is immobilized in a rigid inner-sphere complex. The ability to form inner-sphere complexes with soil organics at low pH distinguishes copper form other divalent transition metals that are probably bound by outer-sphere complexation with the metal retaining its inner hydratation sphere (McBride, 1981, p. 39). With increasing pH, the stabilities of the complexes are expected to increase because of increased ionisation of the functional groups, and according to Jones and Jarvis (1981), Cu^{2+} will keep stable complexes over a wide range of pH.

2. Development of a soil classification for the retention of ionic pollutants

2.1 Introduction

According to Blum and Laker (2003, p. 43), it can be argued that the importance of soil classification is two fold: on the one hand, it serves as a framework for organising our knowledge of natural systems and on the other hand, it provides means of communication among scientists and between scientists and land users. The link between soil classification and soil chemistry is such that soil chemistry provides the basis for the identification and selection of appropriate diagnostic soil properties and attributes for classification, especially for the development of meaningful class limits (Blum and Laker, 2003, p. 45). However citing Manil (1959), Blum and Laker (2003, p. 46) warn that even the best system of classification will never be able to give all the information necessary for all practical purposes. Moreover, it has been argued that since classification is a basic requirement for all sciences, it needs to be revised periodically as knowledge increases (Blum and Laker, 2003, p. 44).

This section of the study will attempt to provide information so as to enable individuals who are responsible for the care and management of land to make better long-term predictions of how soils will behave and perform when used for specified purposes. The first objective of this section is to outline the basis for the South African soil classification system. The second objective is to test the usefulness of inferred chemical attenuation classes by conducting laboratory sorption tests on a selection of representative South African soils.

In order to achieve the objectives of this research, the chemical retention of pollutants will be tested in about 170 soil samples. The retention capacity of different diagnostic horizons/materials will be statistically examined to check predictability based on soil classification and then the retention capacity will be correlated with several key soil properties such as pH, clay, organic matter, S value and extractable Fe and Al.

It also appeared useful for this study to investigate if copper could be a potential representative of metals and whether phosphate could be a potential representative of ligands. The study will proceed to comparing on the one hand copper and zinc sorption, on the other hand phosphate and sulfate sorption.

2.2 Soil

The Agricultural Research Council's Institute for Soil, Climate and Water (ARC-ISCW) provided soils and accompanying data for more than 170 soil samples representing major kinds of diagnostic horizons and materials in South African soil classification. Some soil properties had already been determined. These included:

- clay (%)
- citrate-bicarbonate-dithionite (CBD) extractable Fe
- citrate-bicarbonate-dithionite (CBD) extractable Al
- C (%)
- S value (sum of exchangeable basic cations – mmol$_c$ kg^{-1})
- pH ($CaCl_2$)

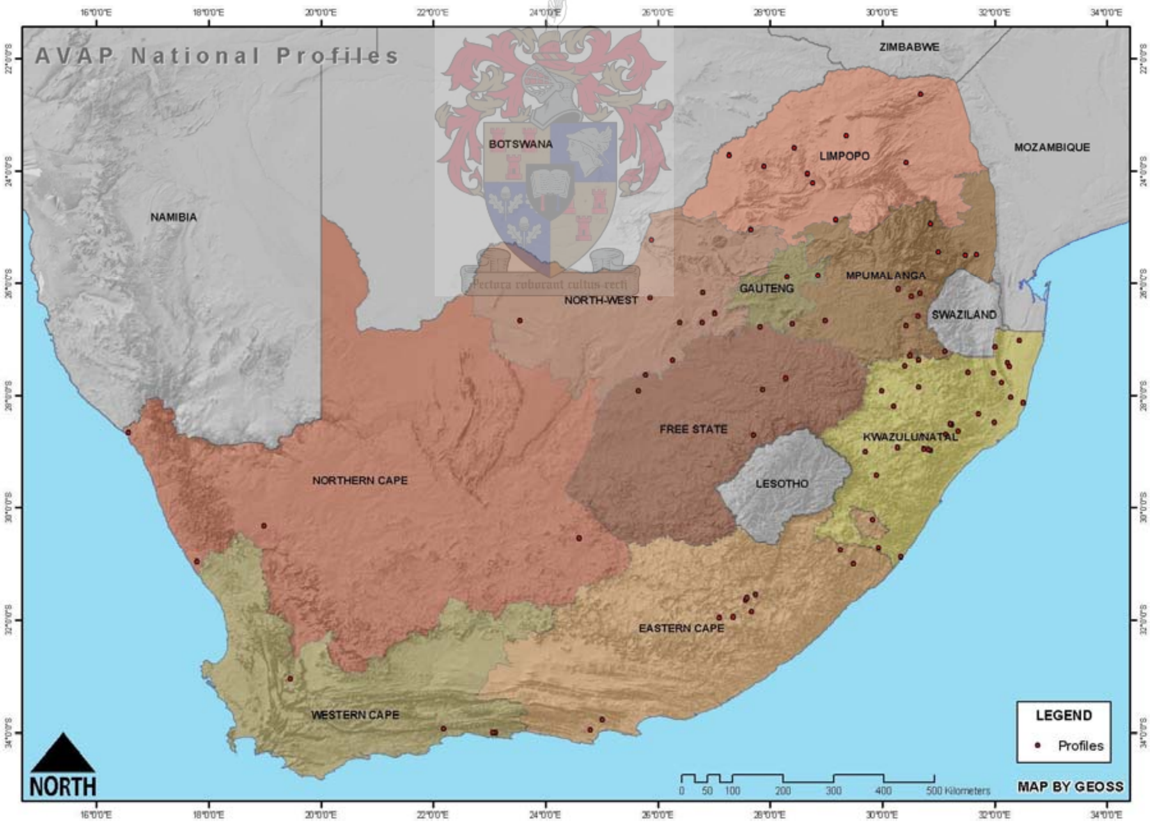


Figure 2.1 Location in South Africa of the modal land type soil profiles used for the sorption studies. A classification summary of these profiles is presented in Table 2.1.

Table 2.1 Inventory of diagnostic horizon samples investigated and the soil forms which they represent (compound with MacVicar et al., 1977)

Diagnostic horizon	Number of samples	Soil forms represented
Humic	9	Ia11, Kp10, Kp11, Kp12, No10, Ia10, Ia12, Av 25, Av33
Melanic	4	Bo20, Bo30, Ik10
Orthic	39	Av22, Av25, Av26, Av27, Av30, Av31, Av32, Av35, Av37, Ct11, Cv13, Cv14, Cv18, Cv20, Cv21, Cv25, Cv26, Cv27, Cv34, Cv42, Cv44, Cv48, Gf11, Gf12, Gf13, Gf20, Gf21, Gf22, Gf23, Gf31, Hu12, Hu20, Hu22, Hu27, Hu28, Sp21
Vertic	5	Ar21, Ar42, Rg20
E horizon	4	Ct11, Ct12, Ct14, Ct23
G horizon	6	Av30, Ch20, Ch21, Rg20
Lithocutanic	10	Ct12, Ct14, Gs10, Gs12, Gs14, Gs16, Ik10, No10, Oa23, Oa46
Neocutanic	6	Ik10, Ik20, Oa23, Oa46
Pedocutanic	4	Bo20, Bo30
Red apedal	26	Gf11, Gf20, Gf21, Gf22, Gf23, Gf31, Hu12, Hu15, Hu16, Hu17, Hu18, Hu22, Hu27, Ia10, Ia12, Kp10, Sp21
Soft plinthic	14	Av15, Av22, Av26, Av27, Av30, Av31, Av35, Av36, Av37, We13
Yellow brown apedal	42	Av15, Av25, Av26, Av27, Av30, Av33, Av35, Av37, Cv13, Cv15, Cv18, Cv20, Cv23, Cv26, Cv27, Cv28, Cv34, Cv37, Cv42, Gf11, Gf12, Gf13, Gf20, Gf21, Gf22, Gf23, Gf31, Kp11, Kp12

2.3 Methods

2.3.1 Chemical attenuation ratings inferred for diagnostic horizons

In this study, the usefulness of inferred attenuation classes was tested by measuring the sorption capacity for metal cations and inorganic anions of more than 170 South

African soil samples from various diagnostic horizons and materials (Appendix 1), representative of some of the commonest soils in South Africa.

2.3.1.1 Copper and zinc sorption

For the Cu and Zn sorption study, 25ml $CuCl_2$ -0.01 M $CaCl_2$ solution or $ZnCl_2$-0.01 M $CaCl_2$ solution was added to 1 g of soil in polyethylene bottles and placed in a shaker for 24 hours. Five different Cu and Zn concentrations were used: 0; 500; 1000; 2500; and 10 000 mg/kg. The Cu and Zn in solution were determined by atomic absorption spectrometry. However, a more limited number of soils were used for the Zn sorption study (approximately 60 samples). The sorption capacity was calculated at an equilibrium solution concentration of 1mg/l as a basis for comparing the sorption capacity of different soils. Figure 2.2 illustrates how sorption is estimated by extrapolation to 1 mg/l Cu in the equilibrium solution. Figure 2.2 represents the fitting of a Freundlich equation in its logarithmic form to the sorption data, as described by McBride (2000). The use of a 1 mg/l concentration as the basis for comparing sorption by different soils is arbitrary but was governed to some extent by convenience, since the log form of the equation would have a zero intercept. The main objective was to obtain a single parameter providing a relative index of the sorption capacity of different soils which means that the value of the equilibrium concentration used for comparison is not critical, provided the fitted equation has the same consistently linear form.

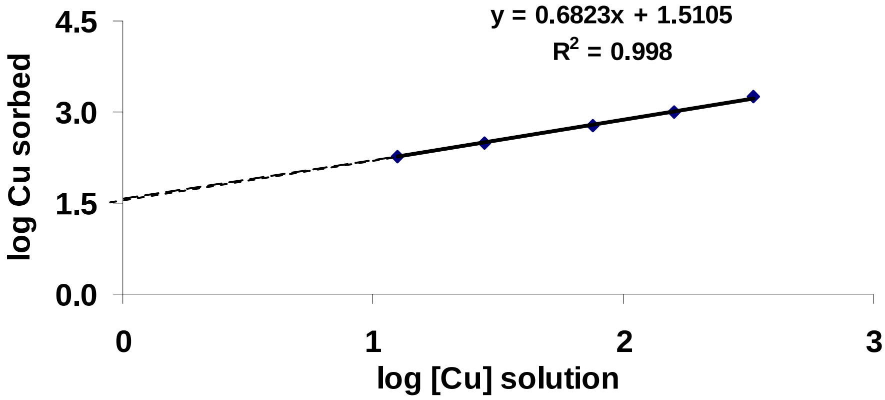


Figure 2.2 Logarithm plot (isotherm) of Cu sorption (mg/kg soil) versus solution Cu concentration (mg/l), demonstrating how sorption is estimated by extrapolation to 1 mg/L Cu in the equilibrium solution

2.3.1.2 Phosphate and sulfate sorption

The P and sulfate sorption capacity were studied by adding 25 ml KH_2PO_4-0.01M $CaCl_2$ or $KHSO_4$-0.01 M $CaCl_2$ solution to 1 g soil in polyethylene bottles. The P concentrations were as follows: 0; 100; 250; 500; 1000; and 1500 mg P/kg, whereas the sulfate concentrations were 0; 150; 300 and 600 mg S/kg. The solutions were shaken for 24 hours. The P content was determined colorimetrically after filtration using the method in Rowell (1993). Up to 5 ml of solution was put into a 100 ml volumetric flask, followed by 8 ml of ascorbic acid solution and 8 ml of ammonium molybdate solution. The solutions were left to rest for 20 minutes before reading absorbance at 880 nm. Sulfate was determined by ion chromatography using a Dionex system with Na carbonate/bicarbonate as the mobile phase. Phosphate and sulfate sorption capacity was calculated at a 1 mg/l equilibrium solution concentration as described for Cu and Zn sorption.

2.3.2 Statistical evaluation

The Statistica software package was used for interpreting Cu and P sorption data. The Cu and P sorption data were statistically related to soil horizons using box & whisker plots. Factor analysis was used to check the relationship between factors that could be closely related to Cu or P sorption.

Additional assessment was made using quantile regression. These data were sorted according to the independent variable and divided into 10 classes, each with a population of about 17. The dataset was sorted in terms of ascending order of each independent variable and divided into 10 classes (bandwidth) of equal sample size. The quantiles of the dependent variable for each class were calculated and plotted against the corresponding mean for the independent variable. The equation which described most fittingly the relationship between the 0.95 quantile of the dependent variable and mean of the independent variable was the one which had the highest r^2 value of those that are amenable to mechanistic interpretation. The curves of 0.95 and 0.05 quantiles represent the chemical envelope for the dataset.

2.4 Results and discussion

2.4.1 Sorption behaviour of some diagnostic horizons

The Cu and P data were related to soil horizons so as to check sorption predictability based on the South African soil classification system. Four diagnostic topsoil horizons and eight diagnostic subsoil horizons as defined by the Soil Classification Working Group (1991) were compared.

Certain expectations of sorption capacity can be made for each of these horizons. Thus among topsoils, the humic A horizon is associated with soils that have undergone moderate to strong weathering. A low pH and low CEC are therefore to be expected, which would imply a low Cu sorption capacity and a high P sorption capacity. Vertic and melanic horizons, on the other hand, are less weathered, less acidic and endowed with clay minerals having a higher CEC than those of than humic horizons. They usually have a low content of free Fe and Al oxides. A low P sorption capacity and a high Cu sorption capacity might therefore be expected. Because orthic topsoils occur over the full range of soil forming conditions encountered in South Africa, they vary widely in terms of texture, organic carbon content and degree of weathering and consequently would be expected to exhibit highly variable sorption of both cations and anions (Soil Classification Working group, 1999).

Among subsoil horizons, red and yellow-brown apedal B horizons occur over the full range of climatic conditions experienced in South Africa. An advanced degree of weathering and a relatively high content of free Al and Fe oxides are usually indicated. High P sorption and low Cu sorption would therefore be expected. By contrast the E horizon is typically light textured and characterized by a depletion of clay, oxides and organic matter and sorption of both cations and anions would be expected to be relatively low. The G horizon is marked by reduction and in some cases removal of Fe, is characterised by higher clay contents than found in E horizons, and might be expected to have a relatively high cation sorption capacity. Accumulation of iron oxides is the predominating feature of the soft plinthic B horizon and a high P sorption capacity would be expected. Although the horizon is usually non-calcareous, lime may be found in the lower parts of the soft plinthic B horizon in the drier parts of regions where this horizon is found. The sorption capacity for cations is therefore likely to be variable. The pedocutanic B horizon is typically clay rich and not strongly weathered and might be expected to have a relatively high sorption capacity for cations but a low capacity for anions. Because lithocutanic and neocutanic B horizons are relatively youthful their sorption capacity for cations and anions is not readily predictable (Soil Classification Working group, 1999).

The sorption data for the diagnostic soil horizons discussed above are presented in Figures 2.3, 2.4 and 2.5. Table 2.2 summarises the number of samples used for collecting the data for each of these horizons.

Table 2.2 Number of samples used for the sorption study for each horizon

Horizon	**Number of samples for copper sorption study**	**Number of samples for phosphate sorption study**
Humic	9	9
Melanic	3	3
Orthic	36	38
Vertic	6	5
Yellow brown	35	42
Soft plinthic	11	14
Red apedal	27	27
E horizon	5	4
G horizon	7	6
Pedocutanic	4	4
Lithocutanic	6	10
Neocutanic	4	6

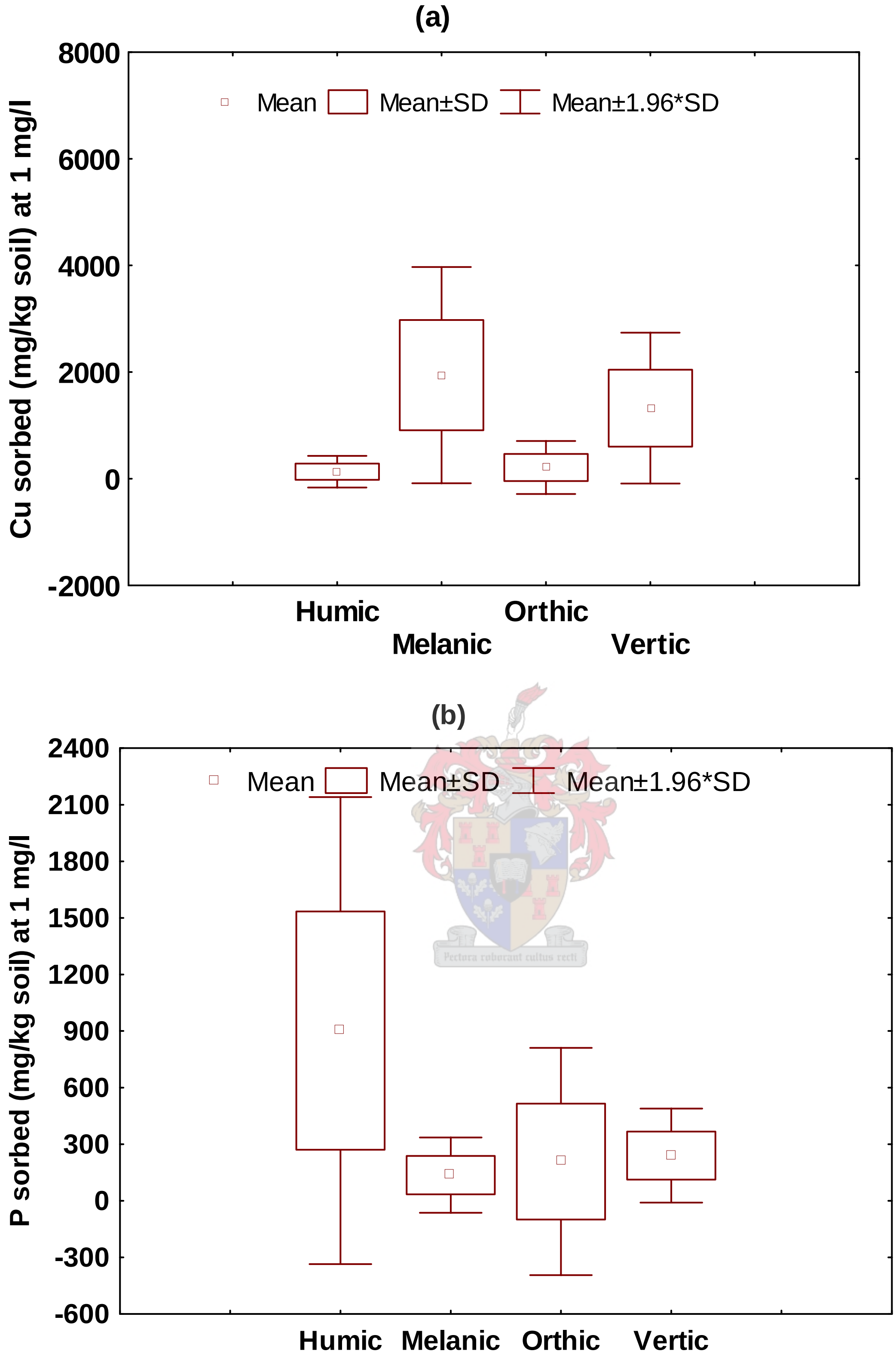


Figure 2.3 Sorption statistics (mean, and standard deviation) for (a) Cu and (b) P in four diagnostic topsoil horizons at 1 mg/l solution concentration

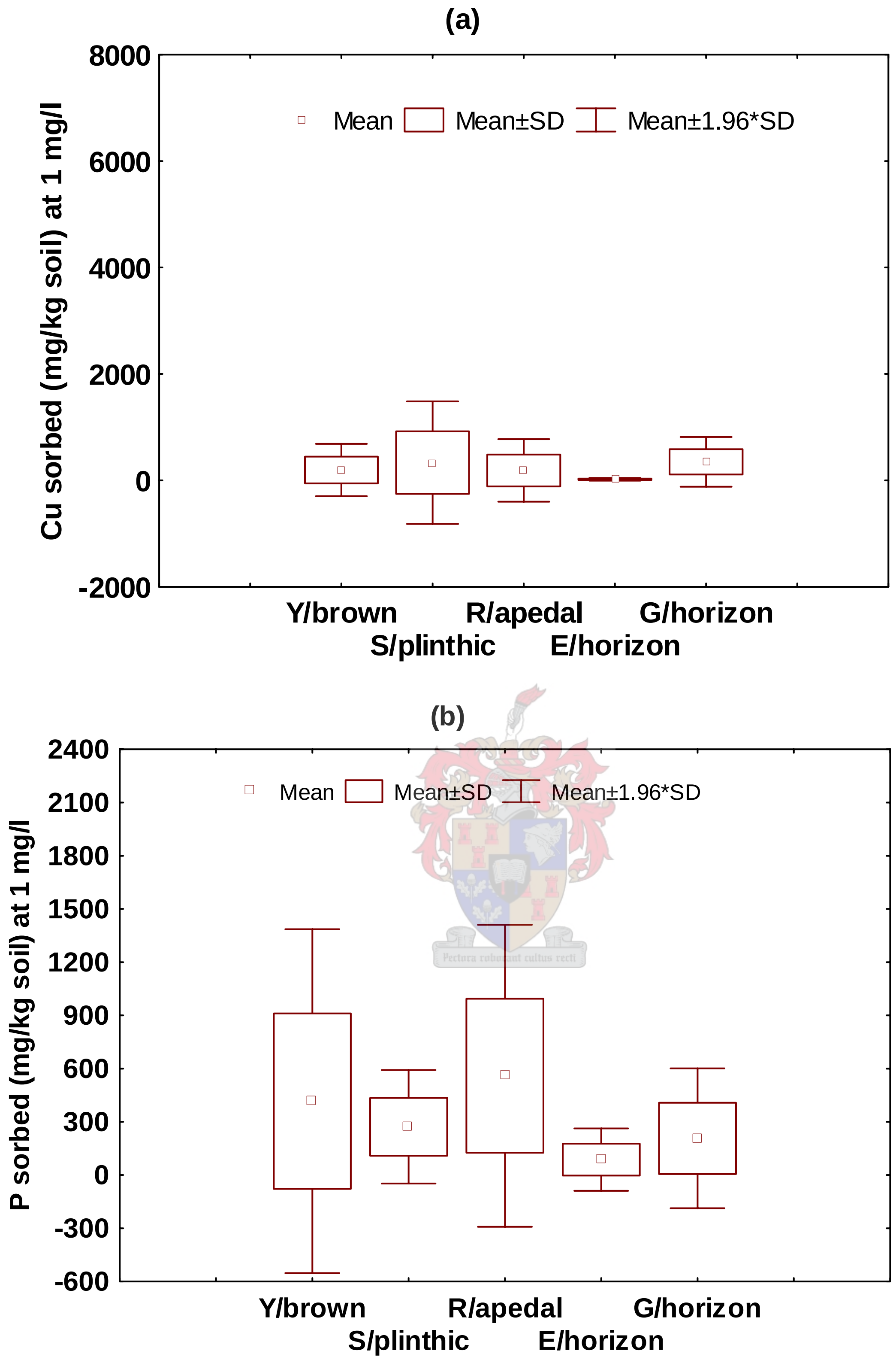


Figure 2.4 Sorption statistics (mean and standard deviation) for (a) Cu and (b) P in five diagnostic subsoil horizons at 1 mg/l solution concentration.

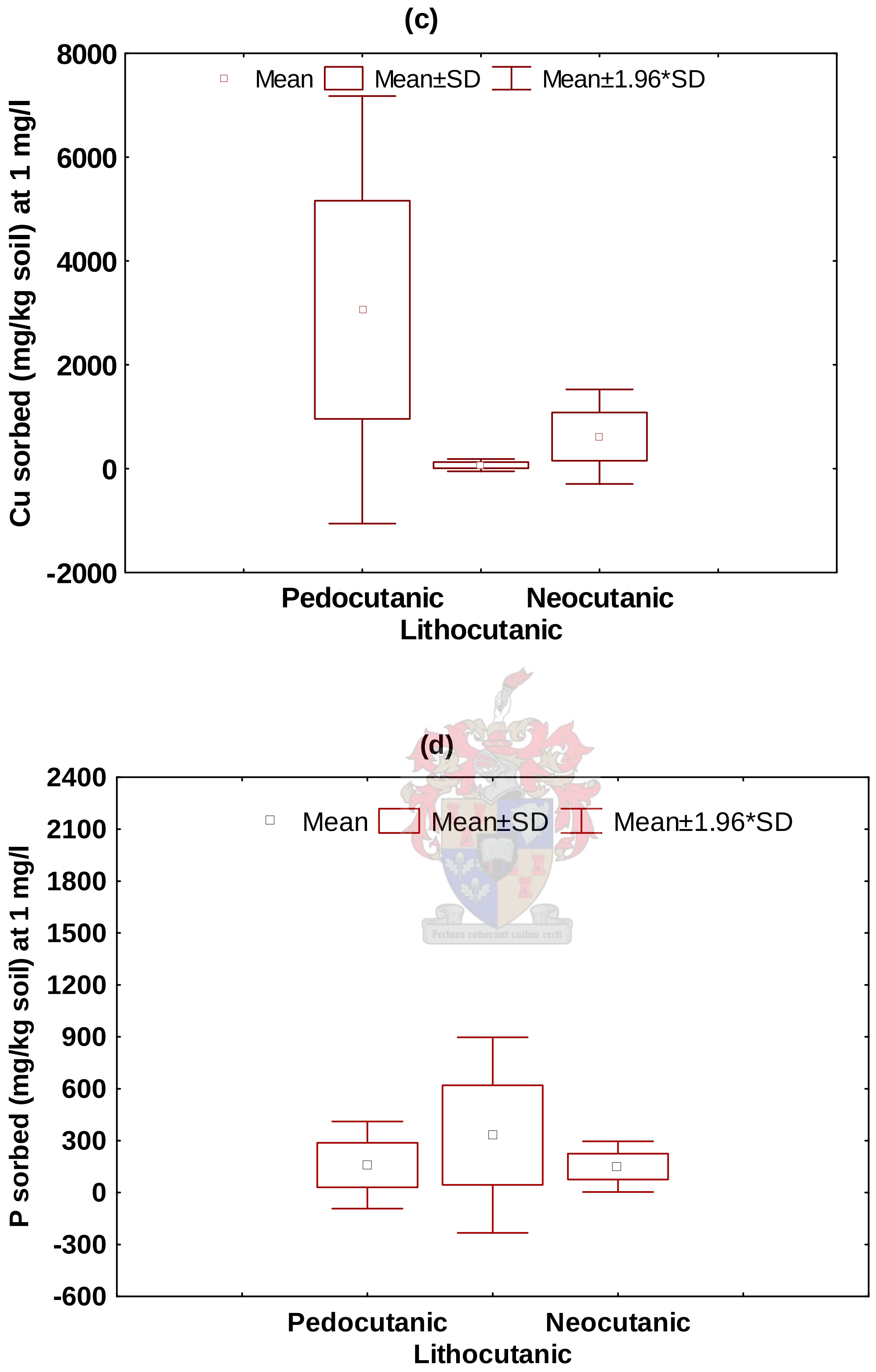


Figure 2.5 Sorption statistics (mean and standard deviation) for (c) Cu and (d) P in three diagnostic subsoil horizons at 1 mg/l solution concentration

The results of the analyses of both the topsoils and subsoils seem to support predictions inferred from the South African soil classification. Results for topsoils have indicated that melanic and vertic horizons have a potential high Cu sorption capacity. This could be due to their relatively high clay content and, especially in the case of the vertic horizon, a high proportion of smectitic clay with a high CEC. These results also indicate that the humic horizon has a potentially high P sorption capacity which is consistent with the strong weathering (and hence high degree of sesquioxide accumulation and kaolinitic clay mineral composition) normally associated with humic soils. On the other hand orthic A horizons show a wider spread of P sorption capacity values than melanic and vertic horizons but Cu sorption behaviour similarly subdued to that of humic horizons (Soil Classification Working Group, 1991).

In accordance with predictions, the results for the subsoils have shown that the E horizon has low sorption capacity for both Cu and P. This can be explained by the fact that E horizon has undergone loss of colloidal matter (iron oxides, silicate clay, organic matter) and generally has a sandy texture. The results have also shown that yellow brown and red apedal B horizons (sesquioxide enriched) have a generally high P sorption capacity while pedocutanic B horizons (typically enriched with silicate clay) have a generally higher Cu sorption capacity than other subsoil materials (Soil Classification Working Group, 1991).

However, these findings demonstrate that while there may be some diagnostic horizons that differ significantly in sorption behaviour from the others, there is no clear distinction among most horizons with respect to either cation or anion sorption. Therefore, no clear basis exists for interpreting pollutant attenuation and hence groundwater vulnerability from soil maps: the range of behaviour for individual forms is generally too large. The results suggest that existing soil maps are unsatisfactory for predicting the contribution of soil to groundwater protection. However, it is possible that the analysis of a few key soil properties, some of which cannot be inferred from the classification, may still allow sorption capacity to be predicted. This possibility is investigated in the next section.

2.4.2 Relationship between ion retention capacity and some key soil properties

Soil properties that are most likely to influence sorption in different parts of the profile are organic matter, Fe and Al hydrous oxides and clay content (Barry et al., 1995). Many studies on heavy metal adsorption by individual components such as organic matter (humic and fulvic acids), silicate minerals (montmorillonite, kaolinite, illite and others) and sesquioxides (iron and aluminium oxides) have indicated relatively strong bonding and high capacities of different materials to adsorb copper (Wu et al., 1999). Additionally, Hooda and Alloway (1998) found that soil pH, organic matter, clay content and CEC were all positively correlated with metal retention by English and Indian soils, while sand content had a negative correlation.

P sorption is associated with the occurrence of reactive surface sites in the mineral soil. The extent to which a soil adsorbs P differs widely between different soils. It tends to be high in soils with a high proportion of small-size particles. The P sorption process is complicated for one main reason. Apparent sorption of P can be thought of as being a combination of several processes, including a fast reversible true sorption process on soil particle surfaces, plus various slower time-dependent processes, some of which lead to deposition of P at a depth below the surface of particles (McGechan and Lewis, 2002).

Lopez-Hernandez and Burnham (1974) used 20 tropical and 20 British acidic soils to examine the behaviour of phosphate using ‘anion exchange capacity’ and phosphate sorption index. These indices were related to soil pH, percent clay, percent carbon, free iron oxides (dithionite-citrate extraction) and extractable aluminium (acidified ammonium acetate). The findings indicated no differences between the British and the tropical soils. Sorption of phosphate was well correlated with extractable aluminium and free iron oxides, the correlation with free iron oxides being the stronger in the freely drained British soils but not in the poorly drained ones. Sorption also correlated well with percent carbon in the poorly drained British soils and in the tropical soils when sorption was estimated using a large phosphate concentration. The relationships with pH and percent clay were not strong. The next sections will deal with the correlations between copper and phosphate sorption of about 170 South African soil samples and some key soil properties such as S value, pH, organic carbon, citrate-bicarobonate-dithionite (CBD) extractable Al and Fe and clay content.

2.4.2.1 Relationship between copper sorption and some key soil properties

The results of the relationship between Cu sorption and some key soil properties are shown in Figures 2.6, 2.7 and 2.8.

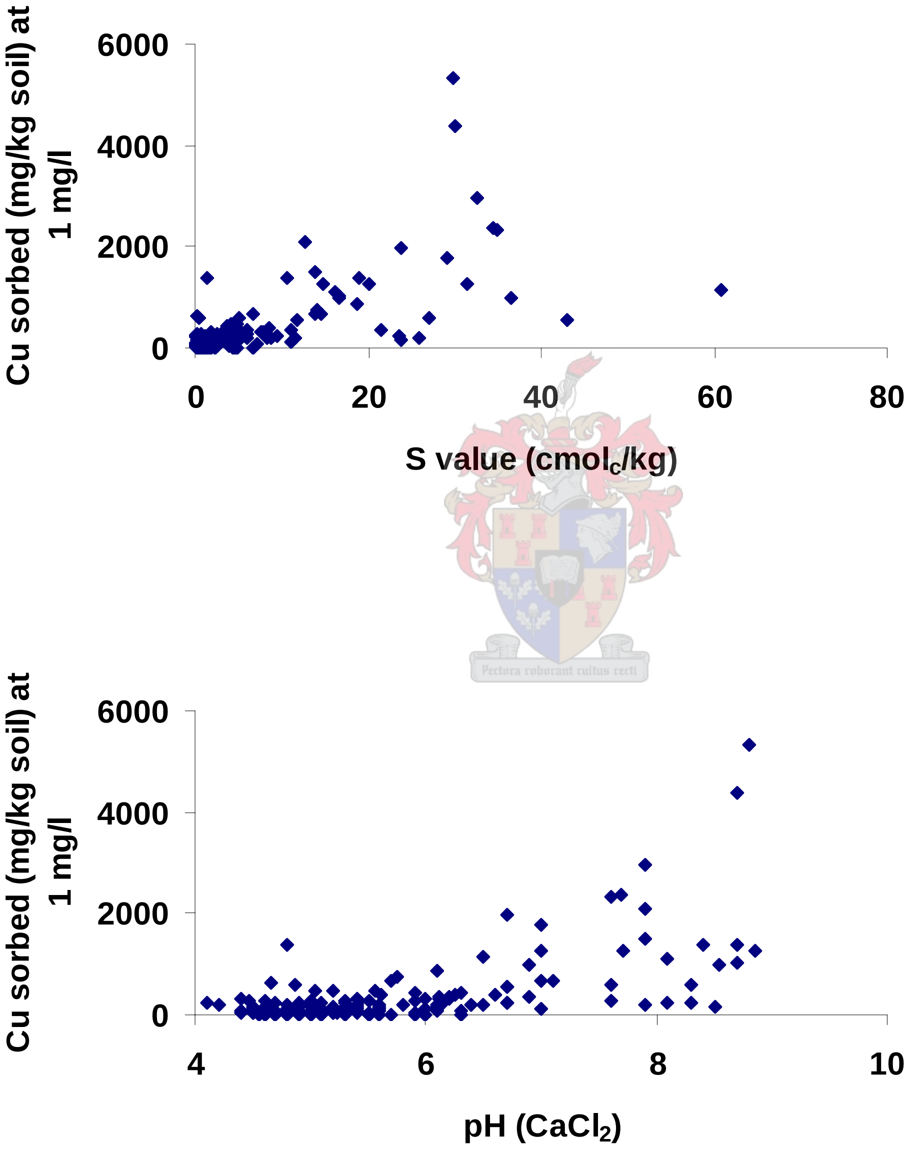
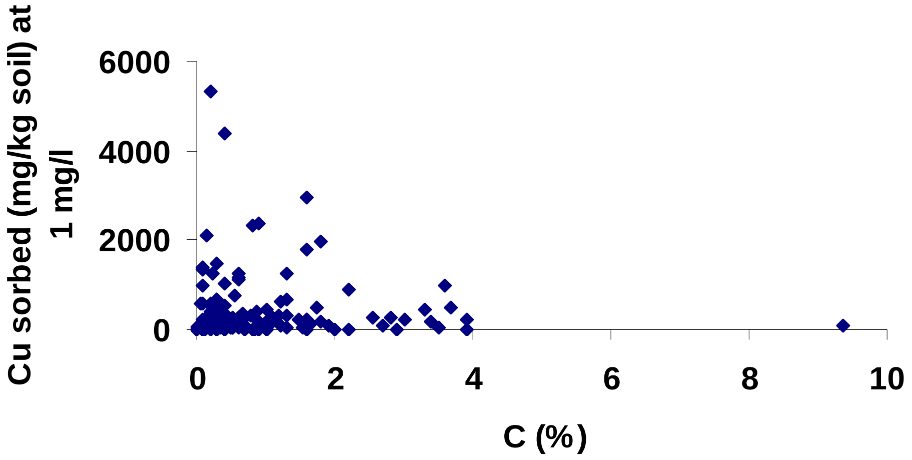


Figure 2.6 Cu sorption at 1 mg/l Cu solution concentration as a function of S value and pH



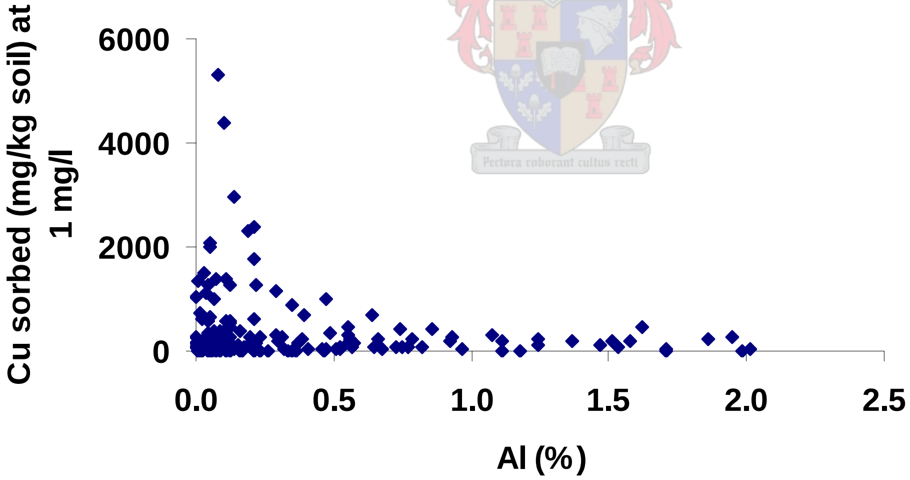


Figure 2.7 Cu sorption at 1 mg/l Cu solution concentration as a function of organic C and CBD-extractable Al content

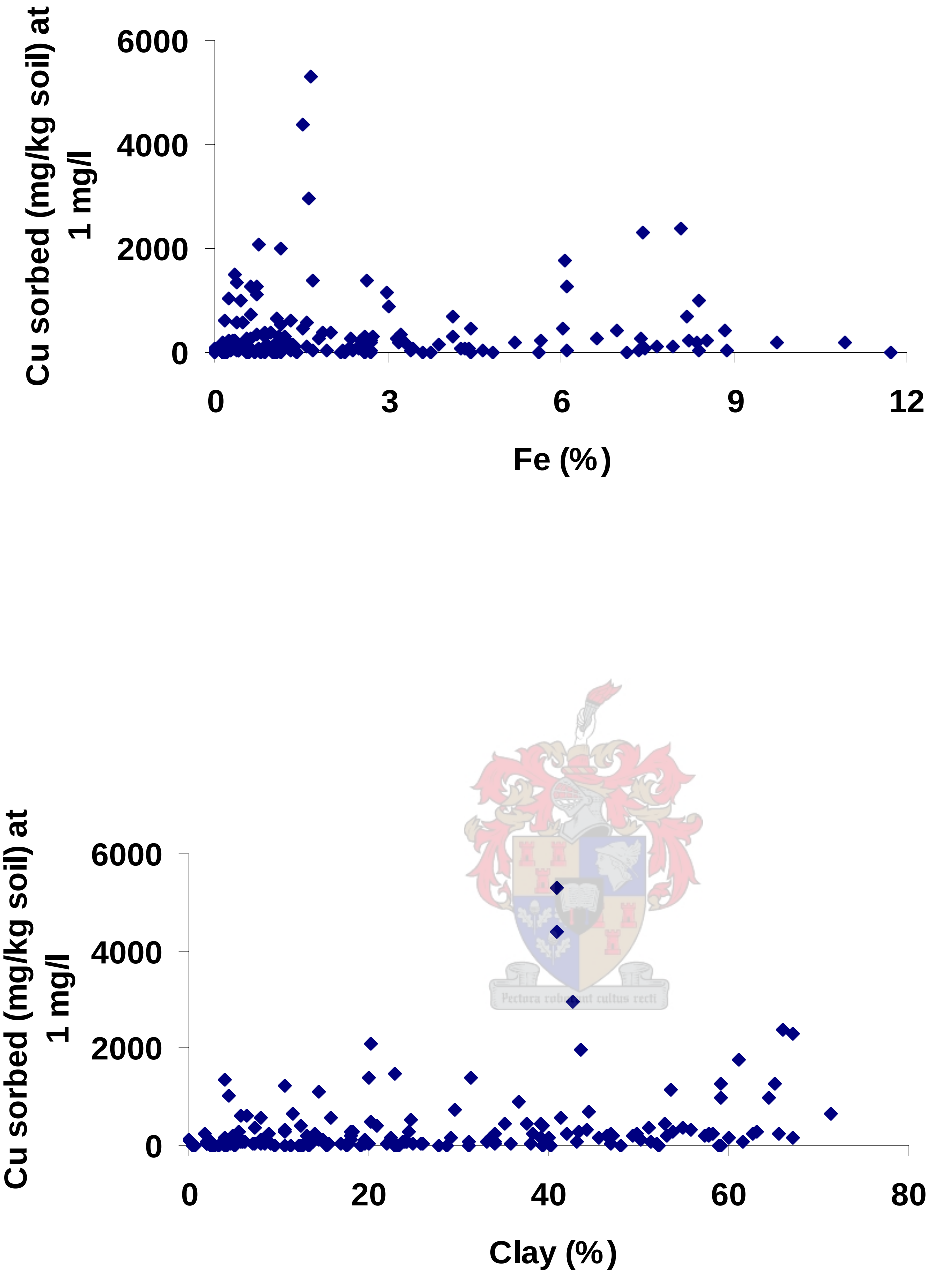


Figure 2.8 Cu sorption at 1 mg/l Cu solution concentration as a function of CBD-extractable Fe content and clay content

These results show that for S value below 10, low Cu sorption can be expected (< 1000 mg/kg soil) while at S value higher than 10, the potential Cu sorption is high (Figure 2.6). Usually, the solid soil phase with a high cation exchange capacity shows a high adsorption of cations (Kabata-Pendias, 2001, p. 45).

In as far as the pH is concerned, this study yielded the following results (Figure 2.6): at pH ($CaCl_2$) < 7, the potential Cu sorption is low (<1000 mg/kg soil), whereas at pH ($CaCl_2$) > 7, the potential Cu sorption is high. Other studies have indicated that with increasing pH, the sorption capacity of soils for metal ions increases, consequently the mobility of the cations is decreased (Marosits et al. 2000; Potgieter et al., 2006). It was also argued that metal adsorption at low pH could be concentrated on permanent charge sites where the protons could exert little competition (Saha et al., 2001).

It is also found that at % carbon below 2, we can have high or low copper sorption, yet above 2 % carbon, copper sorption is consistently low (Figure 2.7). This seems to be a counter intuitive result since other studies have concluded that organic matter was an important soil component when explaining differences in metals' sorption between surface and sub-surface samples of the same soil and that in many cases, an increase in soil organic matter led to increased soil's sorption of these metals (Barry, 1995). However, organic matter can increase solubility of metals by producing ligands that chelate the metals, thereby blocking their sorption and promoting leaching through formation of soluble metal complexes (Madrid and Diaz-Barrientos, 1998). Our results might also be due to the fact that high carbon content is predominantly found in humid soils with high rainfall (Bohn et al., 1985, p. 148). Most soils in areas receiving high rainfall develop acidity because of leaching. Percolating water moves $Al(OH)_2^+$ and H^+ ions through soil. These replace adsorbed basic cations and block the exchange reaction thus lowering the cation exchange capacity i.e. decreasing copper sorption (Miller and Gardiner, 1998, p. 267).

As for Al (CBD) > 0.25, the results show (Figure 2.7) lower Cu sorption (<1000 mg/l soil). Moreover, there seems to be no correlation between copper sorption and Fe (CBD) and % clay (Figure 2.8). This might be explained by the fact that probably iron oxides coated lateral surfaces of layer silicates, blocking access of Cu to potential sorption sites (Wu et al., 1999). These findings might also be explained by other factors, since the sorption behaviour is dependent on one or a combination of soil properties as well as the specific element (Barry et al., 1995).

2.4.2.2 Relationship between phosphate sorption and some key soil properties

The results of the relationship between P sorption and some key soil properties are shown in Figures 2.9, 2.10 and 2.11.

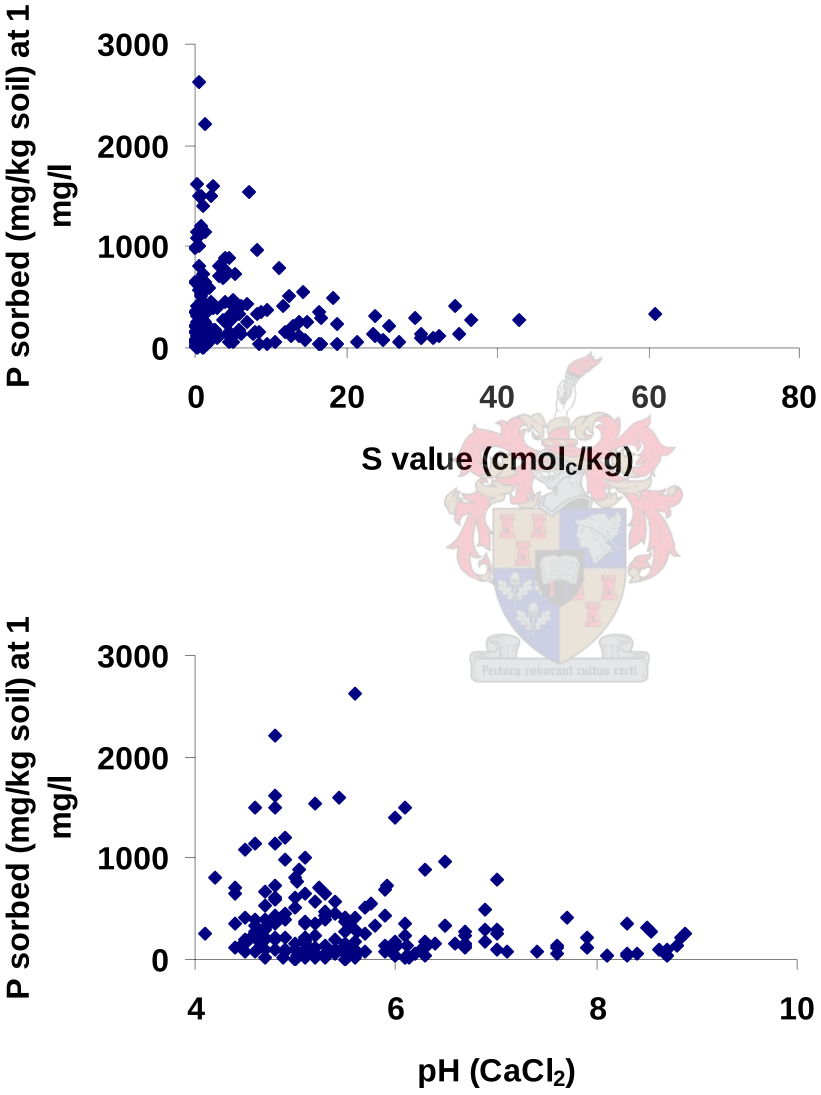


Figure 2.9 P sorption at 1 mg/l P solution concentration as a function of S value and pH

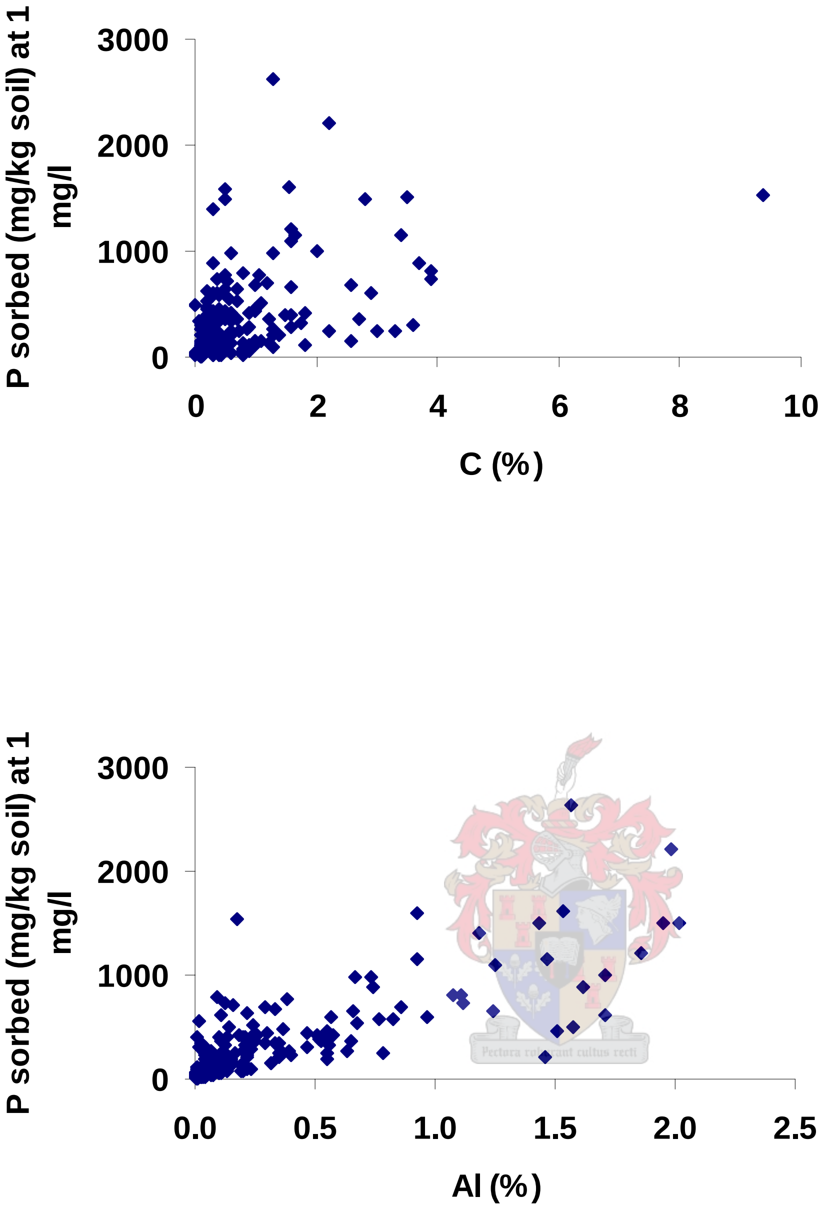


Figure 2.10 P sorption at 1 mg/l P solution concentration as a function of organic C and CBD-extractable Al content

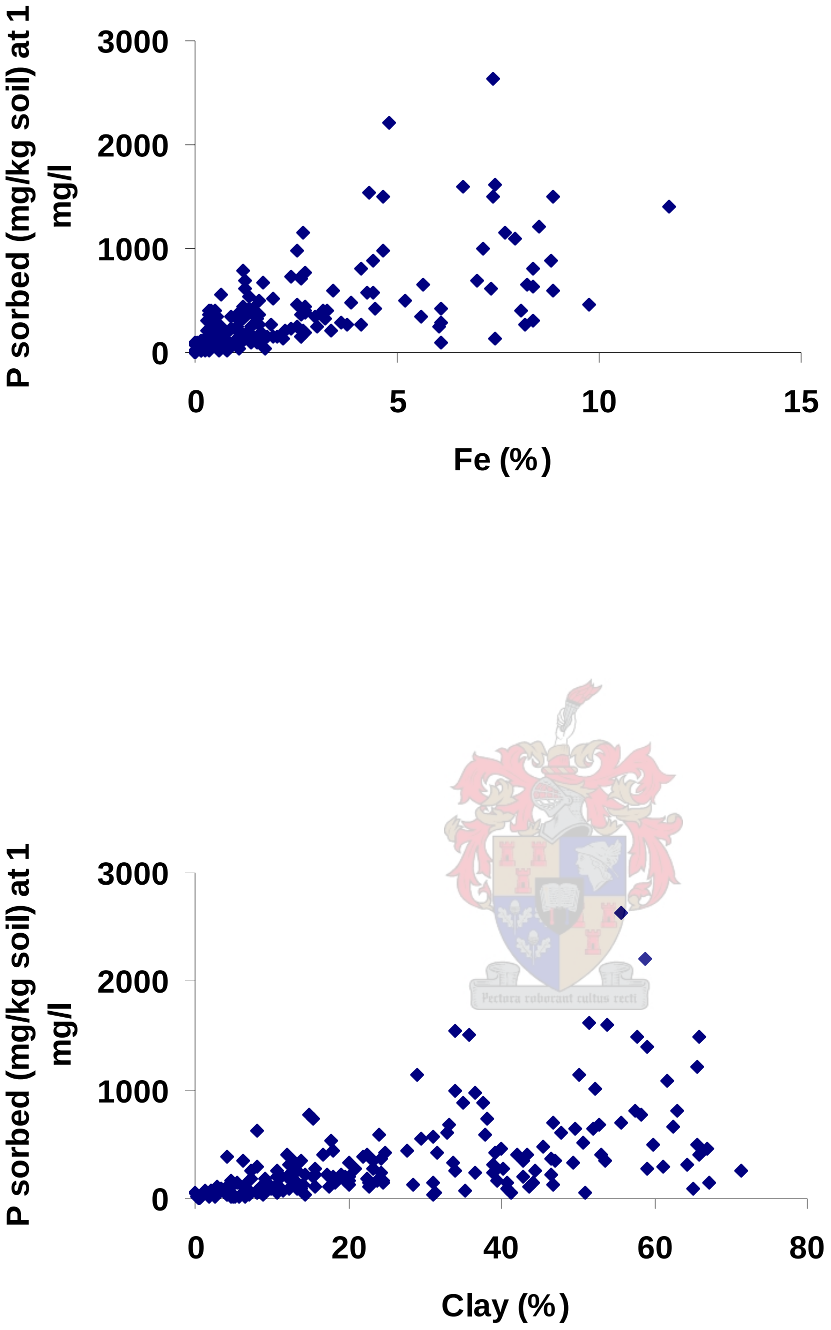


Figure 2.11 P sorption at 1 mg/l P solution concentration as a function of CBD-extractable Fe content and clay content

The analysis shows (Figure 2.9) that for S value < 15, the probability of high P sorption is elevated, whereas at S value > 15, there is low phosphate sorption (< 400 mg/kg).

The results reveal that for pH ($CaCl_2$) below 7, the potential for high P sorption is elevated, while at pH ($CaCl_2$) higher than 7, P sorption is consistently low (<200 mg/kg) (Figure 2.9). Wang and Xing (2004) found that phosphate sorption demonstrated a gradually decreasing trend with increasing pH. Other studies also indicated that adsorption of phosphate onto iron oxides usually decreases with an increase in pH (Bastin et al., 1999). Moreover, Lin et al.(2004) found that increasing pH would lead to a decrease in amount of phosphate sorbed. This is due to the fact that the surface will be more negatively charged at higher solution pH.

Sorption of P may be high irrespective of carbon content (Figure 2.10). There is considerable evidence in the literature to suggest that organic matter may increase phosphate solubility in soil. Three mechanisms have been proposed to explain the influence of soluble organic matter and organic acids on phosphate sorption. First, the organic molecules may specifically sorb to the soil minerals, competing with phosphate for sorption sites. Secondly, the soluble organic matter may complex with surface-bound Al or Fe to form soluble organic-metal compounds and release previously sorbed phosphate. Thirdly, organic matter may be sorbed to soil particles at non-specific sorption sites, which would increase the surface negative charge of the particle. This would reduce the electrostatic attraction of phosphate to soil and keep more phosphate in solution (Erich et al., 2002). The result in this experiment can be explained by the fact that the accumulation of Al and Fe in organic soils increases the capacity of phosphate sorption. It has been shown that the phosphate sorption in Fe-humic substance mixtures was six to seven times larger than amorphous Fe oxide, and they concluded that this might be due to the formation of ternary complexes between the Fe-humic substances and phosphate (Giesler et al., 2005).

The results indicate a potential high P sorption with increasing Al (%), Fe (%) and clay content values (Figures 2.10 and 2.11). The low P sorption at high Al (%), Fe (%) and clay content values could be explained by other factors such as pH, S value and types of clay. Weil and Magdoff (2004, p.22) argue that phosphorus deficiency is commonly associated with acid soils because of the strong sorption or fixation of inorganic phosphorus to iron and aluminium oxide surfaces. It was found that clay minerals generally offer two categories of sorption site, those at the edges of aluminium layers and those on negatively charged surfaces. The broken edges of aluminium layers are variable charge surfaces containing Al (OH) groups which function in the same way as aluminium hydroxide surfaces. There are considerable differences between the various clays in their ability to sorb phosphate (Addiscott and Thomas, 2000). For example, phosphate sorption by smectite is lower by about 2 orders of magnitude than that by kaolinite because of the fewer amounts of reactive sites such as Al-OH (Kasama et al., 2004). It should be noted however, that with high clay content we also have high Al and Fe thus the likelihood of high potential P sorption.

2.4.3 Statistical evaluation

2.4.3.1 Factor analysis

In general, factor analysis is used either to reduce the number of variables or to detect structure in the relationship between variables. The reason for using factor analysis in this study was mainly that of checking the relationship between factors that could be closely related to Cu sorption or P sorption. Figure 2.12 indicates the key properties that are closely related to Cu sorption and P sorption.

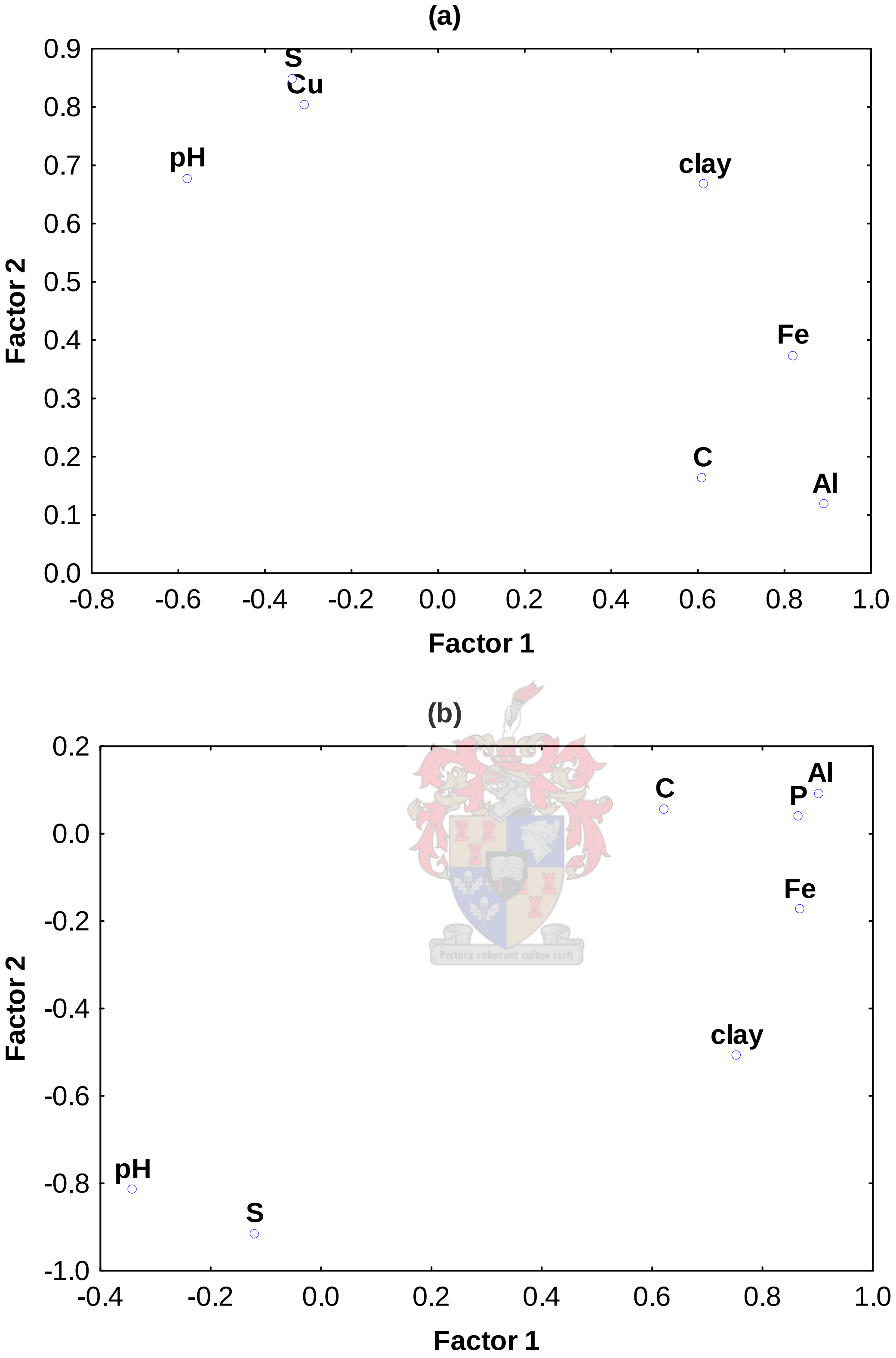


Figure 2.12 Results of factor loading for a) Cu, b) P and some key soil properties

The results show that it is the S value and the pH that are more related to Cu sorption. Considering the relationship between S value and CEC determination, these findings seem to concur with Kabata-Pendias (2001, p. 45) that usually the solid phase with a high CEC shows a high sorption of cations. The role of pH in copper sorption can be attributed to fact that sorption is a pH dependent process. At low pH, one can expect a minimal copper sorption due to competition between H^+ ions and metal cations for binding sites. With increasing pH, the percentage of copper sorbed is expected to increase to its maximum (Jackson, 1998, p. 111-114).

Concerning P sorption, the results show that it is the extractable Al and Fe that are more related to phosphate sorption. This can be confirmed by other findings that soils with high contents of Fe and Al have as well high P sorbing capacities (Barry et al., 1995).

2.4.3.2 Chemical envelopes for copper and phosphate attenuation

The results of factor analysis indicated that some key soil properties are closely related to Cu or P sorption; thus warranting a more detailed assessment. Quantile regression was used to predict chemical envelopes for metal and anionic pollutant attenuation (Beirlant at al., 2004). The way in which this was performed was as follows. The dataset was first sorted in terms of ascending order for each independent variable and divided into 10 classes of equal sample size (bandwidth). However for Cu sorption and clay content the dataset was divided into 6 classes (bandwidth) of equal sample size. The quantiles of the dependent variable for each class were calculated and plotted against the corresponding mean for the independent variable. The equation which described most fittingly the relationship between the 0.95 quantile of the dependent variable and the mean of the independent variable was the one which had the highest r^2 value of those that are amenable to mechanistic interpretation. The curves of 0.95 and 0.05 quantiles represent the chemical envelope for the data set. The quantile regressions are shown in figures 2.13 to 2.18.

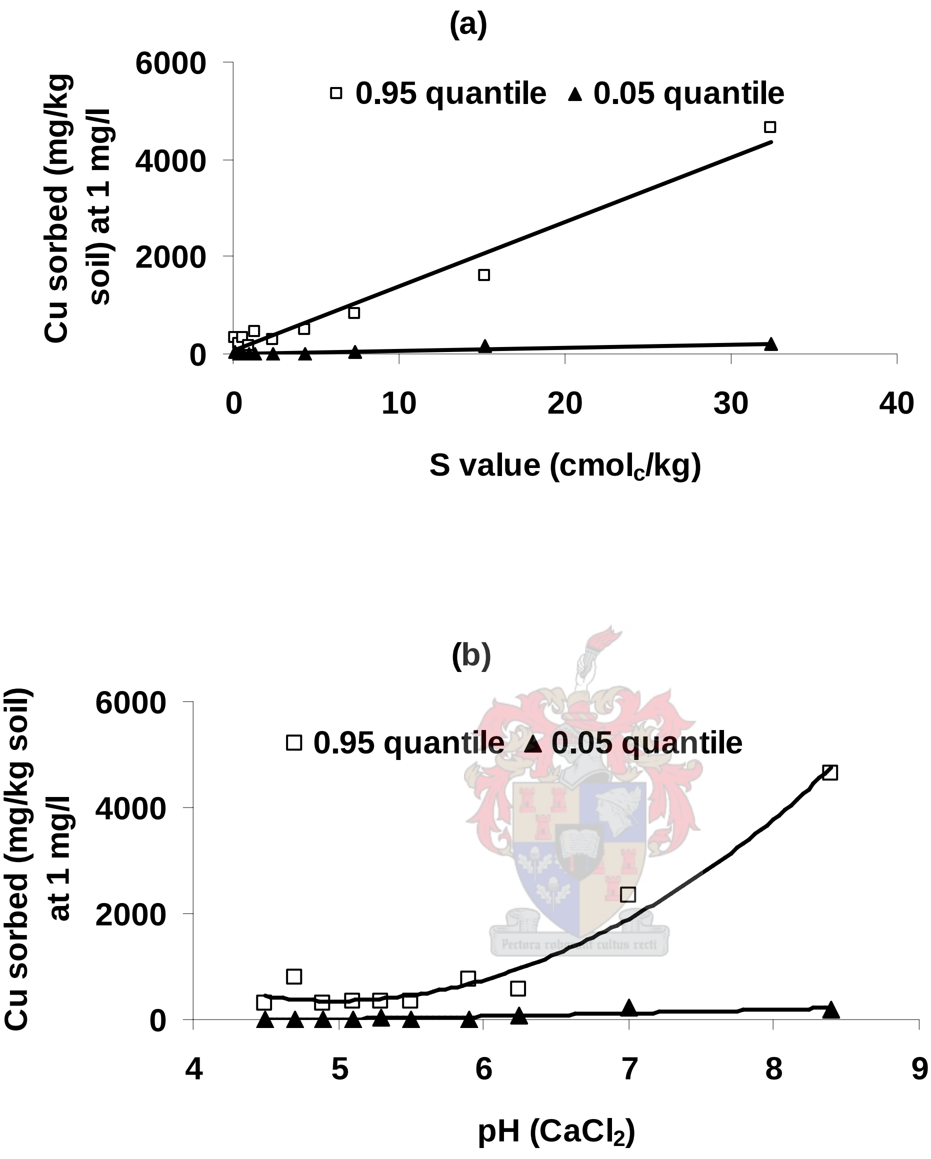
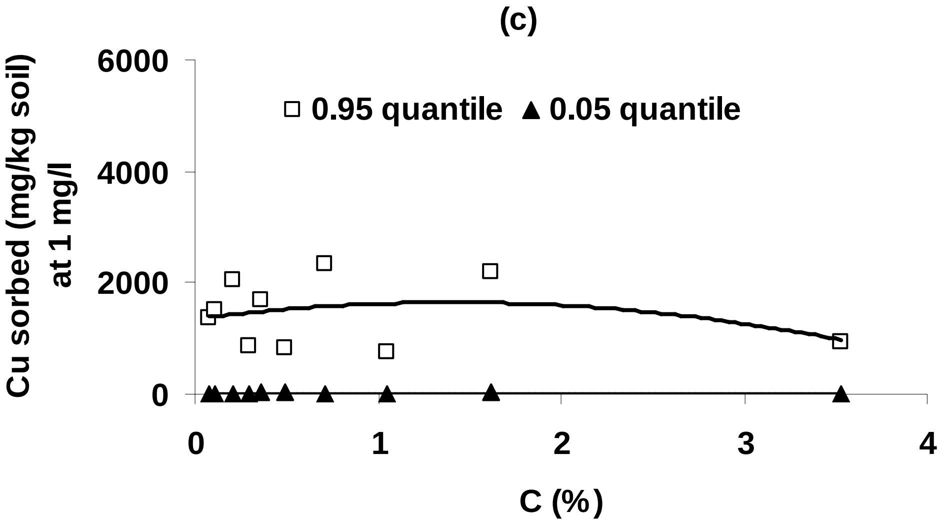


Figure 2.13 Cu sorption data for about 170 soils as a function of (a) S value and (b) pH. Individual data were divided into 10 classes of equal size for the calculation of quantiles. The 0.95 and 0.05 quantile curves represent the chemical envelope of the Cu sorption data across the S value and the pH range



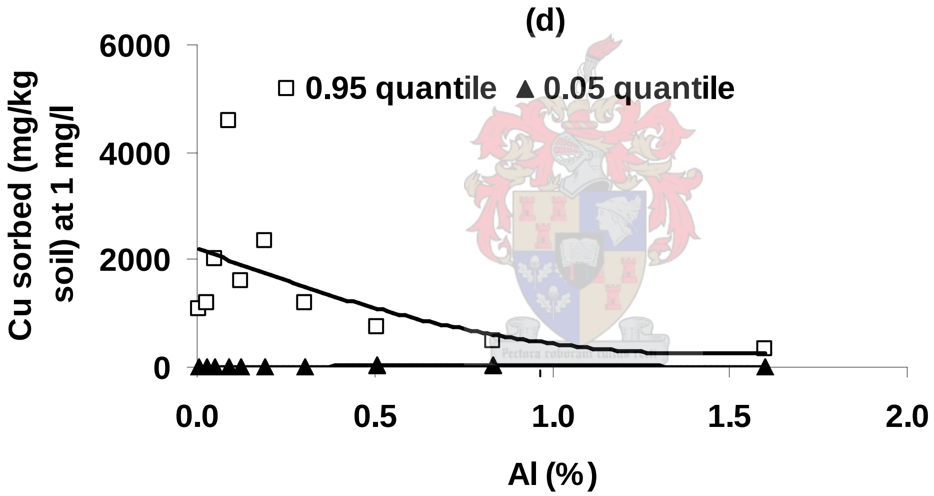


Figure 2.14 Cu sorption data for about 170 soils as a function of (c) organic C content and (d) CBD-extractable Al content. Individual data were divided into 10 classes of equal size for the calculation of quantiles. The 0.95 and 0.05 quantile curves represent the chemical envelope of the Cu sorption data across the organic C content and the CBD-extractable Al content range

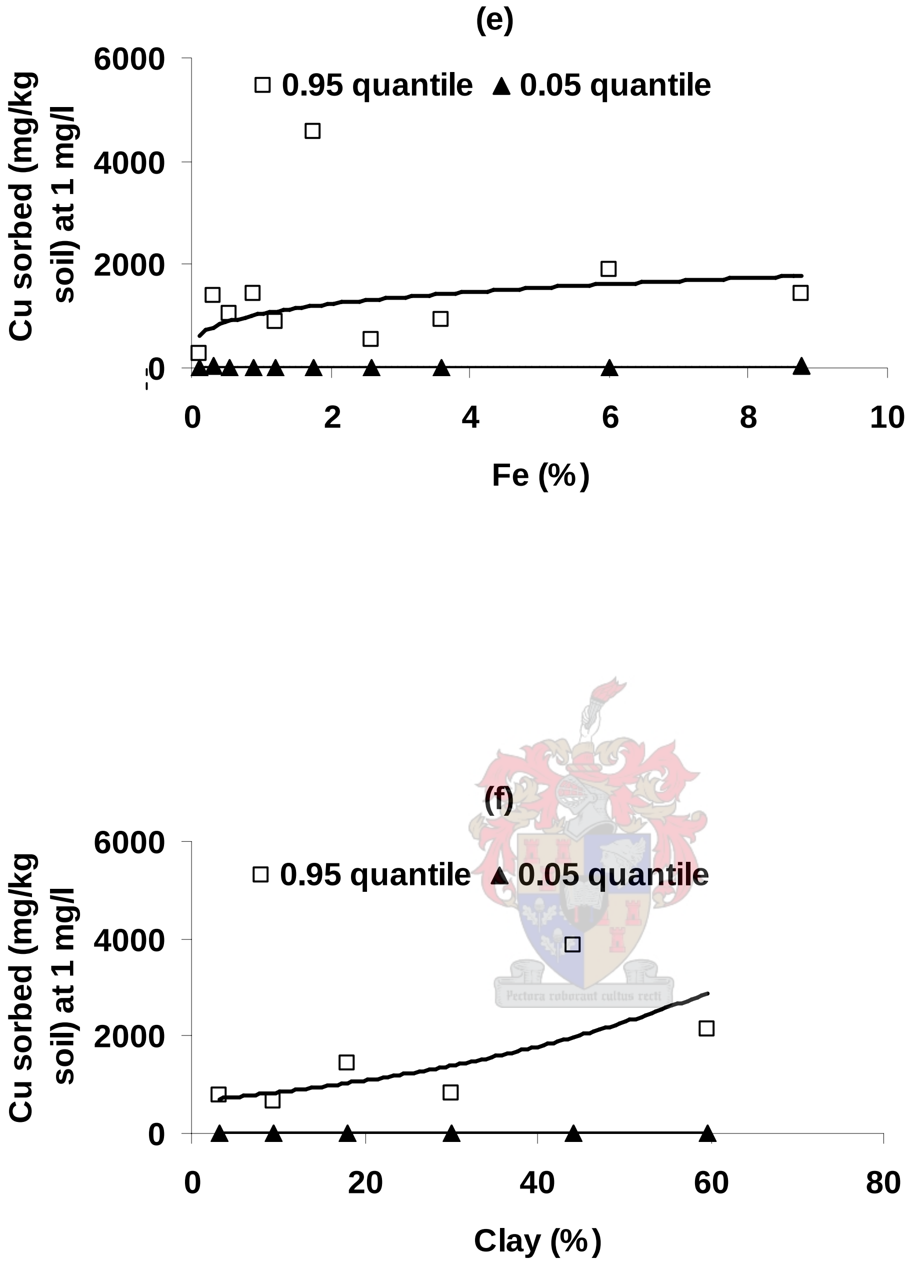
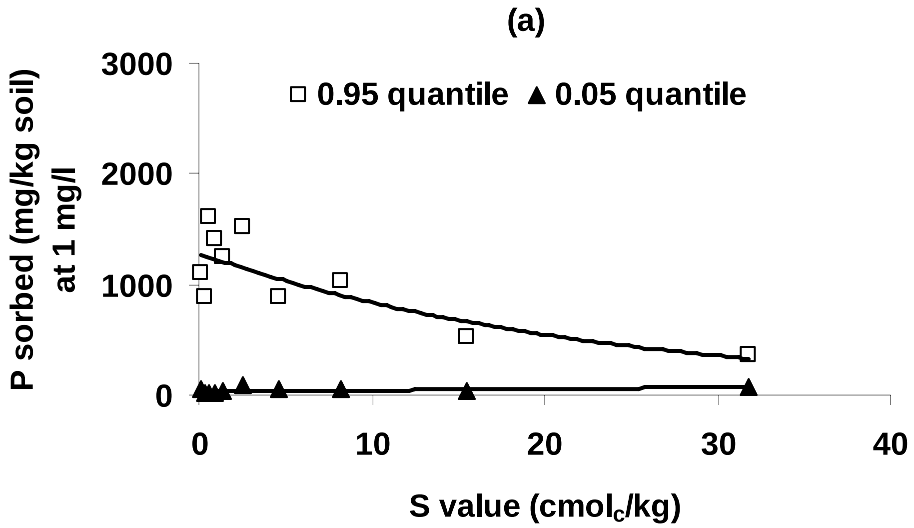


Figure 2.15 Cu sorption data for about 170 soils as a function of (e) CBD-extractable Fe content and (f) clay content. Individual data were divided into 10 classes of equal size for the calculation of quantiles. The 0.95 and 0.05 quantile curves represent the chemical envelope of the Cu sorption data across the CBD-extractable Fe content and the clay content range

The data shows that Cu sorption potential increases with increasing S value (Figure 2.13). In fact, the soil with a high cation exchange capacity (reflected by the S value) shows a high sorption for cations. Whether this increase is realised or not will depend on other factors such as clay content.

The data also indicates that Cu sorption potential increases with increasing pH (Figure 2.13). The acidic condition represents both an environment of strong leaching and one in which Cu would be most mobile. On the other hand the Cu sorption is maximized in alkaline condition which represents a condition of minimum Cu solubility: with increasing pH, Cu is either adsorbed on colloid surfaces or is precipitated as sparingly soluble carbonate (Jackson, 1998, p. 111-114). Whether this maximum potential is realised or not will depend on other factors such as clay content and S value.

The data also shows that Cu sorption potential increases with increasing clay content (Figure 2.15): the higher the clay content, the larger the CEC of the soil (Tan, 1994, p. 164). However, the data does not show any relationship between Cu sorption and other soil properties.



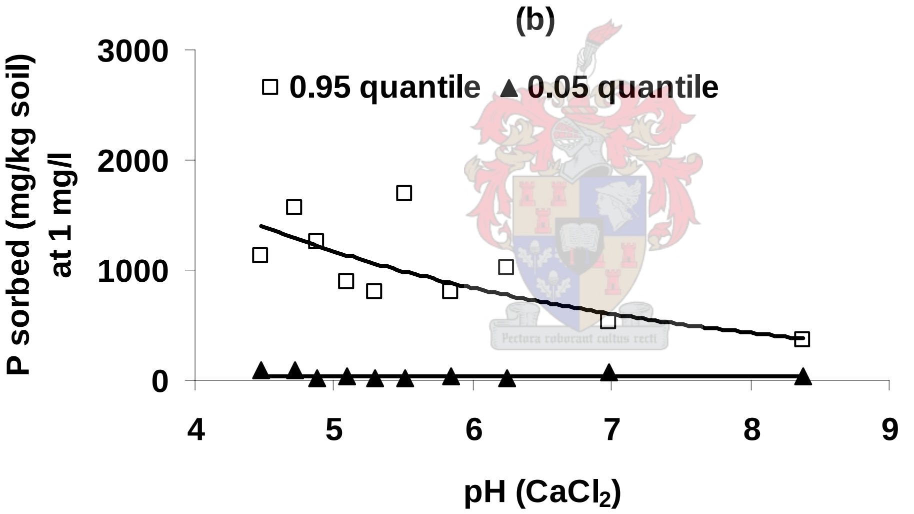


Figure 2.16 P sorption data for about 170 soils as a function of (a) S value and (b) pH. Individual data were divided into 10 classes of equal size for the calculation of quantiles. The 0.95 and 0.05 quantile curves represent the chemical envelope of the P sorption data across the S value and the pH range

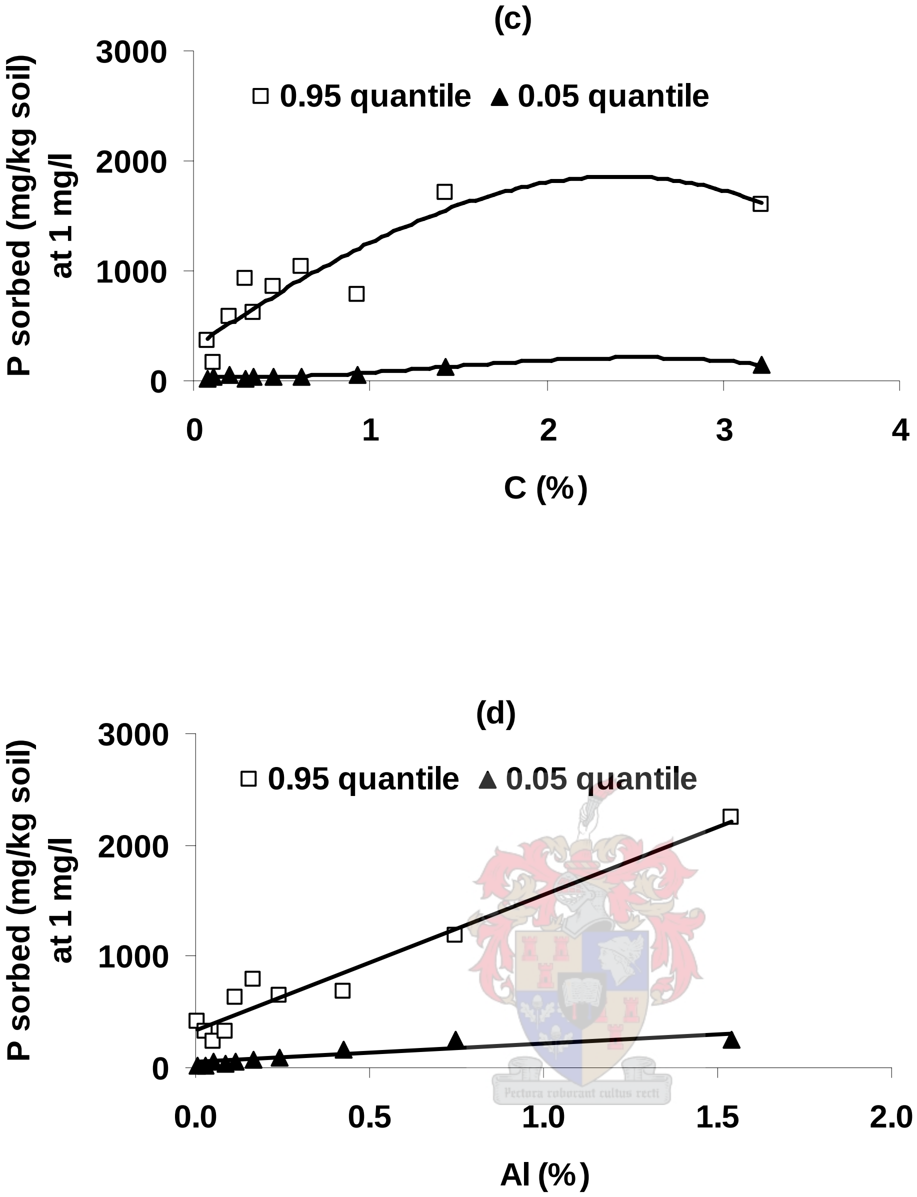


Figure 2.17 P sorption data for about 170 soils as a function of (c) organic C content and (d) CBD-extractable Al content. Individual data were divided into 10 classes of equal size for the calculation quantiles. The 0.95 and 0.05 quantile curves represent the chemical envelope of the P sorption data across the organic C content and the CBD-extractable Al content range

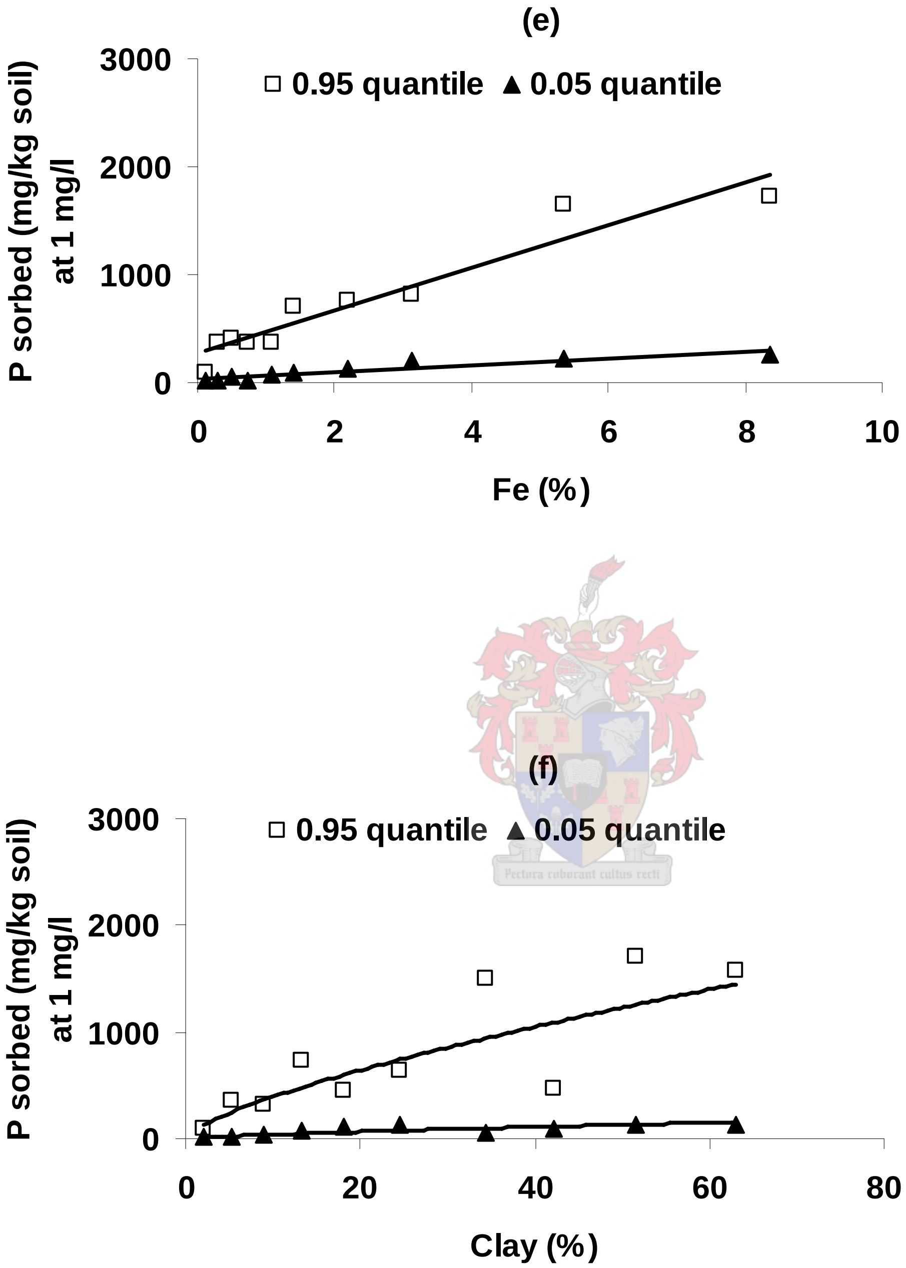


Figure 2.18 P sorption data for about 170 soils as a function of (e) CBD-extractable Fe content and (f) clay content. Individual data were divided into 10 classes of equal size for the calculation of quantiles. The 0.95 and 0.05 quantile curves represent the chemical envelope of the P sorption data across the CBD-extractable Fe content and the clay content range

The data shows that the P sorption decreases with increasing S value (Figure 2.16). The data also indicates that P sorption decreases with increasing pH (Figure 2.16). Sorption of phosphate is efficient under acidic conditions: phosphate is sorbed on the surfaces of insoluble iron and aluminium hydrous oxides, and it can also react with soluble iron, and aluminium ions to form insoluble phosphate. On the other hand, under alkaline conditions, phosphate sorption is less efficient because of the formation of negatively charged sites (Jackson, 1998, p. 115).

Moreover, the data reveals an increase in phosphate sorption for % C below 2.5 (Figure 2.17). In fact, the Fe-humic substance mixtures increase the capacity of phosphate sorption. However, P sorption decreased for % C above 2.5: the organic molecules may specifically sorb to the minerals, competing with phosphate for sorption sites (Erich et al., 2002).

There is a similar trend between phosphate sorption and other soil properties. The phosphate sorption increases with increasing Al (%), Fe (%) and clay (%). The likelihood of the increase seems to be dependent on pH and S value.

It should be noted that, the equations for 0.95 quantile which relate to Cu and P sorption are used to calculate the potential sorption (y) from the value of each variable (x) (Table 2.3). The most restrictive property is given in the last column based on input values in the previous column for the soil in question.

Table 2.3 Equations selected to predict the most restrictive property for copper and phosphate sorption

Factor	**Equation**	**R^2**	**Input values**	**Potential sorption (mg/kg)**	**Sorption limit (mg/kg)**	**Most restrictive property**
		Copper				
Clay	$y = 663e^{0.025x}$	0.59	65.5	3342	174	S value
pH	$y = 393x^2 - 3563x + 8426$	0.97	4.4	354		
S value	$y = 132x + 82$	0.97	0.7	174		
		Phosphate				
Al	$y = 1220x + 333$	0.95	1.86	2603	1209	pH
C	$y = -35x^3 - 97x^2 + 1088x + 299$	0.82	1.6	1645		
Clay	$y = 76x^{0.71}$	0.77	65.5	1489		
Fe	$y = 198x + 267$	0.91	8.52	1955		
pH	$y = 5222e^{-0.33x}$	0.69	4.4	1209		
S value	$y = 1279e^{-0.043x}$	0.80	0.7	1242		

The results for the soil above (Table 2.3) show that the factor limiting Cu sorption the most is S value with high confidence (r^2= 0.97). The clay (%) suggests that potential maximum Cu sorption is about 3340 mg/kg, but this statement can be made with little confidence (r^2= 0.59). On the other hand, the factor limiting P sorption the most is pH ($CaCl_2$), suggesting that potential maximum P sorption is about 1200 mg/kg with high reliability (r^2= 0.69). In all cases the prognosis for P sorption is potentially high. The classification of this soil would therefore be that it presents a high risk for groundwater contamination with Cu. Conversely, it presents a low risk for groundwater contamination with phosphate.

2.4.4 Relationship between copper and zinc sorption

Kabata-Pendias (2001, p. 132) argues that the important factors controlling the mobility of Zn in soil are very similar to those listed for Cu, as both are metals. However, Harter (1991, p. 74) found that Cu and Zn can react either similarly or differently. Figure 3 shows copper sorption plotted against Zn sorption at 1 mg/l sorption concentration.

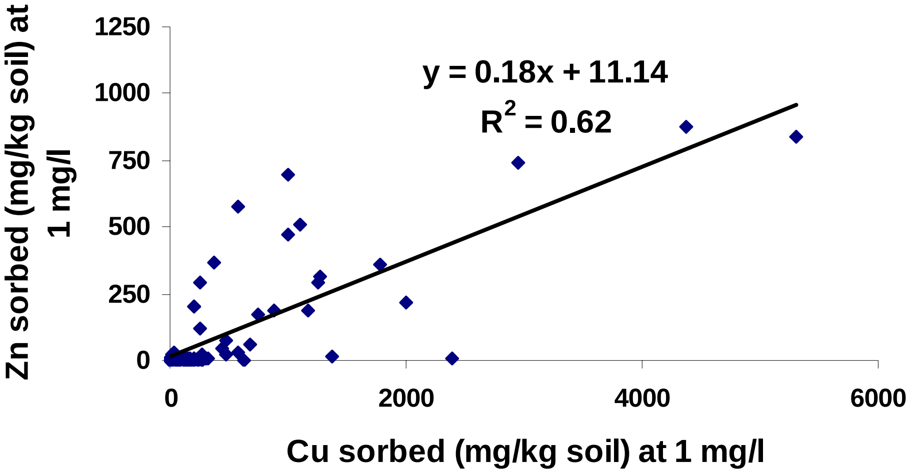


Figure 2.19 Relationship between Cu and Zn sorption at 1 mg/l solution concentration

The results show that the relationship between Cu sorption and Zn sorption at 1 mg/l solution concentration is R^2 =0.62.

Since the ionisation potentials of copper and zinc are quite similar (Cu: 2.71, Zn: 2.70), the different behaviours of the two elements can be attributed to polarisation effects. In fact, Cu^{2+} does not have an unpaired electron in the 3d-orbital and is consequently more strongly polarized than Zn^{2+} (with no unpaired 3d-electrons) and exhibits a greater affinity to anionic sites (Arienzo, 2005, p. 74).

Other similar studies (Eginari et al., 2005; Roberts et al., 2003) provided a different explanation for Cu and Zn behaviours. It has been found that Cu was sorbed by kaolinite and kaolinitic soil clay at solution copper activities lower than that required for oxide/hydroxide precipitation, but Zn was not sorbed at such low activities except if the suspension pH was at/or above neutrality. They interpreted this as an indication that copper is retained on non-specific sites in acid soils and on specific sites in neutral and alkaline soils.

Similarly, it has been indicated that Zinc is probably retained on non-specific exchange complex throughout the pH range of soils, while copper may be precipitated at the higher pH ranges only. Moreover, it was found that Zn unlike copper is one of the most soluble and mobile of the trace metal cations being held in exchangeable forms on clay and organic matter (Álvarez-Ayuso and Gracía-

Sánchez, 2003). Diaz-Barrientas et al. (2003) in their studies, also found that the amounts of Zn retained by unamended and amended (organic amendments) were lower than those of copper, suggesting a higher affinity of the soil for the latter metal. In a nutshell, the difference in Cu and Zn behaviours can be explained by two major factors i.e. the polarisation effects and the pH level.

2.4.5 Relationship between phosphate and sulfate sorption

Phosphate sorption was plotted against sulfate sorption at 1 mg/l solution concentration (Figure 2.20) with the aim of studying their relationship.

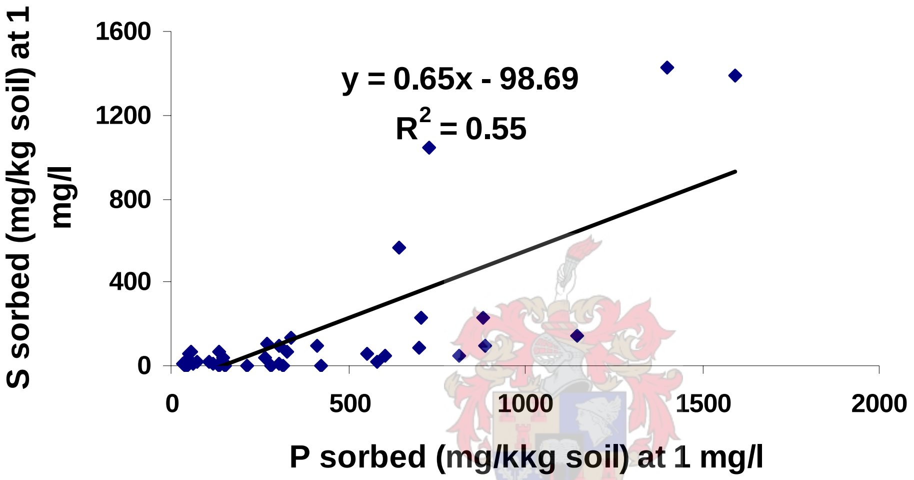


Figure 2.20 Relationship between P and S sorption at 1 mg/l solution concentration

The finding of this study indicates that the relationship between sulfate sorption and phosphate sorption at 1 mg/l solution concentration is R^2= 0 55.

Sulfate (SO_4^{2-}) is believed to have little interaction with the oxyhydroxide surface, but instead occurs as a counter ion in the diffuse layer, while phosphate (PO_4^{3-}) is thought to adsorb by an inner-sphere ligand exchange mechanism (Collins et al., 1999). Furthermore, it has been reported a decreasing order of preferential adsorption among the following anions on soils: SiO_4^{4-}>PO_4^{3-}>SO_4^{2-}>NO_3^-. This lyotropic series shows that $SiO4^{4-}$ and PO_4^{3-} ions are strongly adsorb; SO_4^{2-} and NO_3^- ions are adsorbed in lower concentrations or are often not adsorbed (Tan, 1993, p. 246). Moreover, FTIR data indicated no inner-sphere complexation for sulfate, while it showed monodentate surface coordination for phosphate on goethite (Collins et al., 1999).

2.5 Conclusions

One of the objectives of this research aimed at providing an outline of a basis for the South African soil classification as well as testing the usefulness of inferred chemical attenuation classes by conducting laboratory sorption tests on a selection of representative South African soils. About 170 different soil samples were subjected to an increasing load of metal pollutant (e.g. copper) and anionic pollutants (e.g. phosphate).

The results have demonstrated that there is no clear distinction among most horizons with respect to either cation or anion sorption. The existing classification is unsatisfactory for predicting the contribution of soil to groundwater protection. Furthermore, the findings have indicated that S value and pH are more related to copper sorption. On the other hand, clay, extractable Al and Fe appear to be the most related to phosphate sorption. The relationship between Cu and Zn sorption (R^2= 0.62) and between phosphate and sulfate sorption (R^2= 0.55) might lead to designing a classification which may consider copper as a potential representative of metals and phosphate as a potential representative of ligands.

These results imply that soil classification allows only an imperfect categorization of soils in terms of pollutant attenuation and thus potential groundwater protection. Pollutant attenuation can be predicted to some degree if data used for classification are combined with some other key soil properties. Soil maps can be useful for making predictions about groundwater vulnerability provided the soils have been well characterized by laboratory analysis.

Chapter 3

3. Effect of acid/base priming on sorptive properties of soil

3.1 Introduction

Yong et al. (1992, p. 157) suggest that the migration or transport of leachates containing various types and concentrations of contaminants through soil can lead to eventual groundwater contamination. McGowen and Basta (2001, p. 97) further argue that increased sorption of contaminants to soil colloids can decrease mobile contaminants in solution and reduce metal transport in contaminated soils. Different methods can be used to improve soil sorptive capacity. Acid/base priming consists of treating soils with a harsh acid or base so as to reach an extreme pH, then bringing back the soil pH to its approximate original value. A study by Hardie (2004) on acid/base priming using the acid–base pair HCl and KOH on four contrasting soils showed that new, more receptive surfaces can be generated in soils by partial dissolution of existing crystalline colloids and precipitation of new, amorphous solids with a larger capacity to adsorb ionic and molecular contaminants. Furthermore, her study on acid/base priming of two soils (smectitic and kaolinitic) showed that the acid-base pair H_2SO_4-$Ca(OH)_2$ was as effective as HCl-KOH in enhancing Cu sorption.

In the present study it was decided to focus on acid/base priming using H_2SO_4 and $Ca(OH)_2$ because the two chemicals are of low cost and they generate gypsum which is a non-toxic salt. A moderately acid, sesquioxidic soil was used to investigate whether it is possible to apply such acid/base priming to a bulk quantity of soil in order to reduce the availability of both Cu and P.

3.2 Materials and methods

3.2.1 Soil collection

Soils were collected from a road cut near the base of the main granite outcrop in the Paarl Mountain Nature Reserve on the outskirts of Paarl. The soils contain a relatively high content of organic matter, sesquioxides and clay and were therefore expected to show a relatively large natural buffer capacity. Samples were collected from two different sites, classified and described as follows:

Site 1 Clovelly form (samples PM1A, PM1B)

Road cutting near the top of the mountain; fynbos vegetation; NE facing, 15-20% slope, colluvial midslope.

0-30 cm	Dry, dark yellowish brown (10YR 4/4); gravely loam; weak fine crumb structure; loose; much fine granitic gravel; abundant fine and coarse roots; gradual transition	Orthic A (PM1A)
30-70cm	Dry, dark yellowish brown (10YR 5/8); with strong brown (7.5YR 5/8) mottles; gravelly loam; medium subangular blocky; loose; many medium stone fragment; few fine and coarse roots; gradual smooth transition	Yellow-brown apedal B21 (PM1B)
70-120+ cm	Dry yellowish brown (10YR 5/8) mottles; gravelly loam; medium subangular blocky; hard; many fine-medium stone fragments; fine quartz gravel; organically lined root channels; few fine and coarse roots; grading to granitic saprolite.	B22 (not sampled)

Site 2 Oakleaf form (samples PM2A, PM2B)

Road cutting near to mid-section of mountain; fynbos, grass and wild olive vegetation; N facing, 15-20% slope.

0-30 cm	Dry, yellowish brown (10YR 5/6); gravelly loam; medium-fine subangular blocky; loose; much medium-fine gravel; abundant fine and coarse roots; gradual smooth transition	Orthic A (PM2A)
30-130cm	Dry, yellowish red (5YR 5/8); with few red (2.5YR 4/8) concretions; clay loam; medium-fine subangular blocky; loose to friable; many fine stone fragments; few fine and coarse roots; gradual smooth transition.	Neocutanic B (PM2B)
130 cm+	Dry, strong brown (7.5YR 6/8) with more extensive red (2.5YR 4/8) concretions and reddish and white mottles; clay loam; weak medium subangular blocky; loose and friable; many fine stone fragments; very few coarse roots.	C (not sampled)

3.2.2 Soil analysis

Representative samples of the four soils were air-dried for 3 days, ground to pass a 2-mm sieve and stored in a cool place. The following analyses were performed on the samples: pH, total carbon, saturate paste extract and surface area.

3.2.2.1 pH

The pH in $CaSO_4$, KCl, and H_2O suspensions was measured as follows:

- pH in $CaSO_4$: 10g of gypsum ($CaSO_4.2H_2O$) was mixed with 500ml of distilled water, stirred for one hour then filtered. An amount of 25 ml of the saturated gypsum solution was added to 10 g of soil. Each day, the bottles were shaken three times for

5 minutes by hand i.e. morning, midday and afternoon. After 3 days, the pH was recorded with a pH meter. This pH value was used for determining the target for neutralisation because acid/base priming using H_2SO_4 and $Ca(OH)_2$ generates $CaSO_4$ (see below).

- pH in KCl: 25 ml of 1M KCl was added to 10 g of soil. The pH was measured after three days. The bottles were hand shaken for 5 minutes three times a day.
- pH in H_2O: 25 ml of distilled water was added to 10 g of soil. The solution was kept for three days. The bottles were hand shaken for 5 minutes thrice each day. The pH was measured on the third day.

3.2.2.2 Total C

A 2 g sub-sample of soil was finely ground in a ball mill. A sample was placed in a tin sample cup which was crimped to confine it and placed in a quartz reactor. The dry combustion method was used for C analysis using a Eurovector Elemental Analyser.

3.2.2.3 Effect of pH on copper and phosphate sorption

The effect of pH on Cu and P sorption was initially investigated by potentiometric titration, using HCl or NaOH, of suspensions contain Cu or P. Solutions containing 1000 mg Cu/L and 500 mg P/L were prepared by dissolving 107 mg $CuSO_4.2H_2O$ or 88 mg KH_2PO_4, respectively, in 1L of 1M KCl. An amount of 250 ml of each of these solutions was added to 10 g of untreated soil.

The Cu-treated suspension was titrated with 1M HCl with constant stirring to obtain pH 3.5. After 15 minutes, the supernatant pH was measured and a portion of the suspension (25ml) was kept for analysis after filtration. Then, the suspension was titrated with 1M NaOH to higher pH values in steps of about 1 pH unit. At each step, the reading of the pH was taken after 15 minutes. An aliquot of 25 ml of the solution was kept after filtration for analysis.

The P-treated suspension was titrated with 1M NaOH with constant stirring to achieve a pH of 9.5. After 15 min, the pH was recorded and a portion of the suspension (25ml) was kept for analysis after filtration. Then, the suspension was titrated with 1M HCl to lower pH values in steps of about 1 pH unit. At each step, the pH was read after 15 minutes and 25 ml of the supernatant was kept after filtration for analysis.

3.2.3 Acid/base priming of the soil

The soils were acid/base primed i.e. they were treated with either H_2SO_4 or $Ca(OH)_2$ so as to reach an extreme pH, then brought back to an approximate original pH value. In this study the extreme pH value for base-treated samples was higher than 12 whereas the value for the acid-treated samples was lower than 4. The soils were treated using the following method:

- For the alkaline treatment, 6 g of $Ca(OH)_2$ and 80 ml of distilled water were added to 200 g of soil. The suspension was shaken daily by hand three times, i.e. morning, midday and afternoon for one week at the end of which the suspension pH was recorded.
- For the acid treatment, a similar procedure was followed using 30 ml of 5M H_2SO_4 and 50 ml of water added to 200 g of soil.

The soil suspensions were then allowed to air-dry at room temperature and the treated soil was crushed to pass a 2mm screen for further study.

3.2.3.1 Potentiometric titration

Potentiometric titration was used to estimate the amount of acid or base required to bring the acid- or base-primed soils back to their original pH value. Solid $Ca(OH)_2$ was added to suspensions consisting of 5g sub-samples of the acidified soil in 12.5 ml 1M KCl to achieve the following increments of alkalinity: 0, 162, 324, 486, 648, 810, 972, 1134, 1296 and 1458 mmol OH^-/kg. For the limed samples, 3M H_2SO_4 was added to 5g sub-samples suspended in 12.5 ml 1M KCl to achieve the following increments of acidity: 0, 120, 240, 360, 480, 600, 720, 840, 960 and 1080 mmol H^+/kg. All the above suspensions were shaken simultaneously for 24 hours after which the pH was measured. Titration curves were then plotted and used to estimate the quantities of $Ca(OH)_2$ or H_2SO_4 required to restore the acidified or limed soils to their original pH values (as determined in $CaSO_4$ suspension – section 3.2.2.1). Appropriate quantities of solid $Ca(OH)_2$ or 3M H_2SO_4 were then added to 80 g of the remaining acidified or limed soil together with enough water to ensure a paste with a solid: liquid ratio of 2.5:1. This was thoroughly mixed air-dried gradually over a few days under a fume hood and then ground to pass a 2mm screen.

3.2.3.2 Effect of acid/base priming on Cu sorption

The three soil treatments (acid-primed; based-primed and untreated) were compared in terms of their effects on sorption of Cu. A 25 ml aliquot of $CuCl_2.2H_2O$ – 0,01M $CaCl_2$ solution was added to 1 g of soil in a polyethylene bottle and placed on a shaker for 24 hours. Six different Cu additions were used, equivalent to 0, 500, 1000, 2500, 5000 and 10000 mg/kg. As described in Chapter 2, Cu in solution was determined and sorption at an equilibrium Cu concentration of 1 mg/L was estimated using the isotherm equation.

3.2.3.3 Effect of acid/base priming on P sorption

The P sorption capacity of the acid-primed; based-primed and untreated soils was also studied. An aliquot of 25 ml KH_2PO_4 (0,01M $CaCl_2$) solution was added to 1 g of soil and shaken as described above. The P additions were as follows: 0, 100, 250, 500, 1000 and 1500mg P/kg. As described in Chapter 2, the P content was determined colorimetrically after filtration and sorption at an equilibrium P concentration of 1 mg/L was estimated using the isotherm equation.

3.2.3.4 Surface area

The surface area of untreated and treated topsoil samples was determined using the Brunauer-Emmett-Teller (BET) method of analysis using a Micrometrics Accelerated Surface Area and Porosimetry (ASAP) 2010 system. A 250 mg sample was degassed at 120^oC for 24 hours. and then placed in a N_2 stream and the mass change of the solid due to gas adsorbed was measured relative to the change in partial pressure of N_2.

3.3 Results and discussion

3.3.1 Effect of pH on copper and phosphate sorption

Some characteristics of the soils studied are shown in Table 3.1. The soils are moderately acidic (especially the subsoils) and their sesquioxidic character is confirmed by the markedly higher pH in $CaSO_4$ than in KCl as a result of ligand exchange involving sulfate. The data indicate that organic matter content is high and salinity is negligible. Field estimation suggested that the textural class is close to a clay loam.

Table 3.1 Characteristics of the soils studied

Sample	pH (H_2O)	pH (KCl)	pH ($CaSO_4$)	C (%)
PM1A	5.87	4.56	5.08	2.36
PM1B	5.43	4.24	4.80	1.21
PM2A	6.81	5.86	6.30	2.56
PM2B	5.45	4.48	5.37	1.35

Figure 3.1 shows the effect of pH on Cu and P sorption. The results for the effect of pH on Cu sorption (Figure 3.1a) show a similar trend for both samples. Sorption of Cu increased with increasing pH, from a minimum at pH 3 to a maximum at a pH of about 7.8. Potgieter et al. (2006) observed a similar trend. They found that the sorption of copper by palygorskite increased with increasing pH, from a minimum at pH 3 to a maximum at a pH of about 8.5.

On the other hand, the results for the effect of pH on P sorption (Figure 3.1b) indicated that, for both samples, sorption of P was relatively high over the whole pH range with maximum sorption occurring between pH 4 and 6. Similar results were found by Bolan et al. (1986) who found that maximum sorption of phosphate occurred at about pH 4.

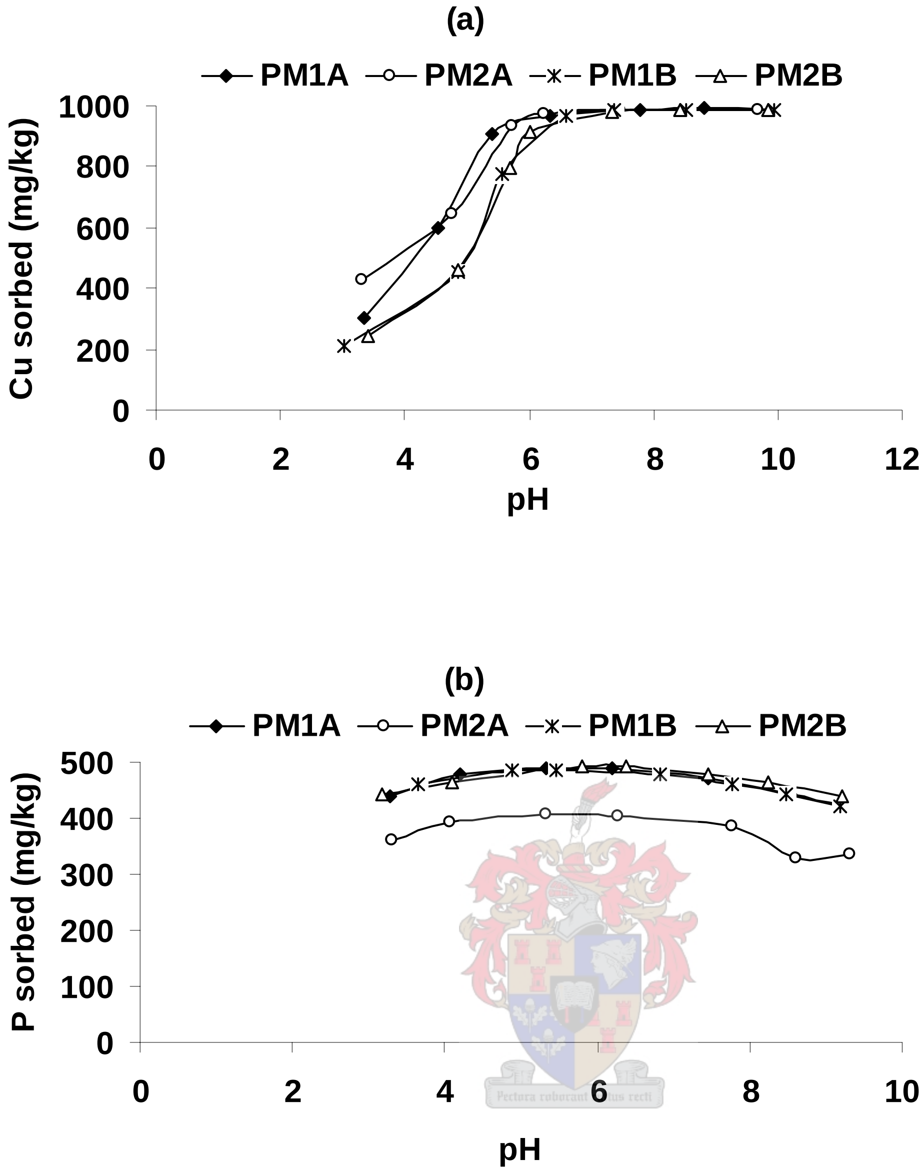


Figure 3.1 Effect of pH on Cu and P sorption for soils (a) treated with 1000 mk/kg Cu and titrated with NaOH after initial pH adjustment with HCl and (b) treated with 500 mg/kg P and titrated with HCl after initial pH adjustment with NaOH (each point represents the solution composition after a 15 minute equilibration)

3.3.2 Acid/base priming of soil

3.3.2.1 Potentiometric titration

Potentiometric titration curves for limed and acidified soils are shown in Figure 3.2. All soils pre-treated with $Ca(OH)_2$ and then titrated with H_2SO_4 showed similar buffering characteristics, with two buffer regions, the first between pH 6.5 and 7, and the second between pH 2.5 and 4 (Fig. 3.2a).

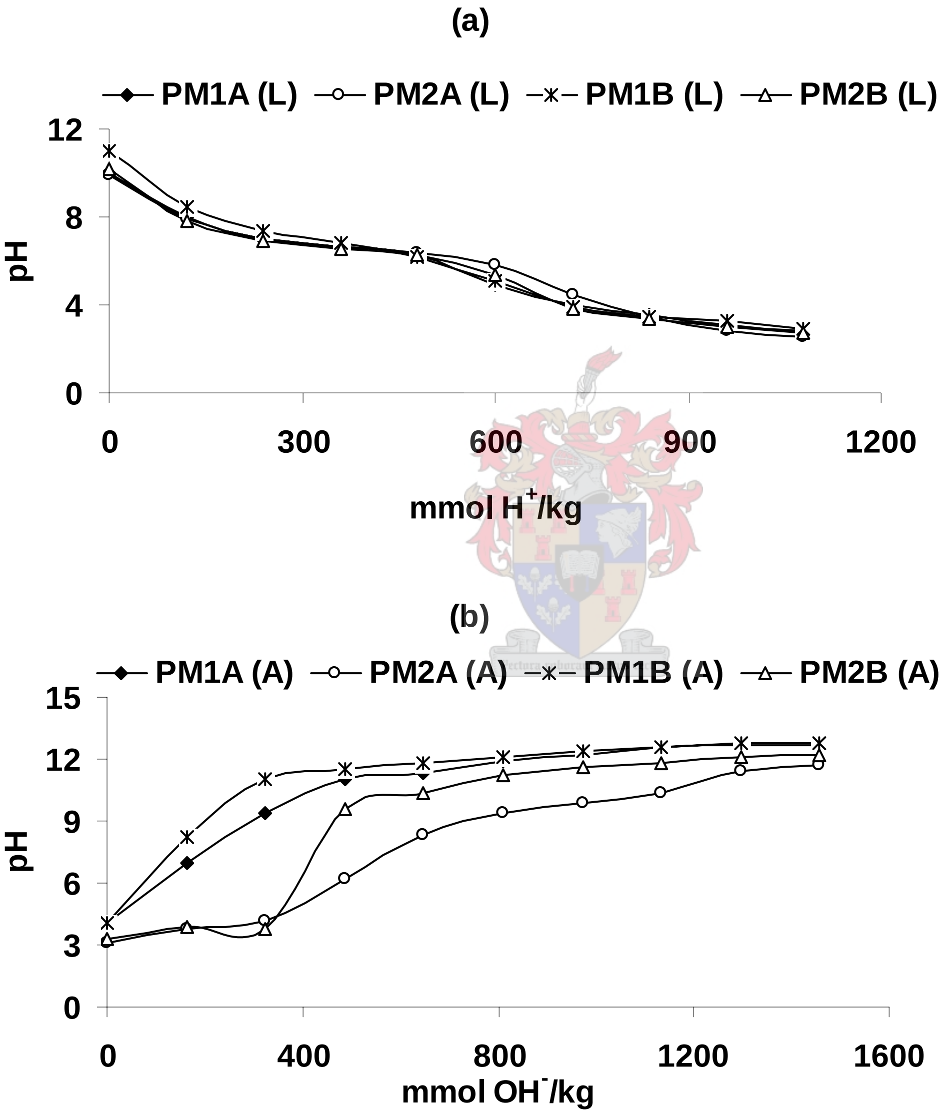


Figure 3.2 Potentiometric titration curve for soils pre-treated by incubation for 1 week with (a) $Ca(OH)_2$ and (b) H_2SO_4 and then titrated with either H_2SO_4 or $Ca(OH)_2$, respectively (each point represents pH after overnight equilibration)

The titration curves for acidified soils, however, showed a difference between the two profiles with PM2A and B horizon soils showing much stronger buffering especially between pH 3.5 and 4, probably as a result of significant Al dissolution during acid incubation. This is confirmed by the pH values following incubation shown in Table 3.2 (treated pH), which are much lower in the acidified PM2 soils than in the PM1 soils.

The amount of acid or base used in neutralising excess acid or base after incubation treatment and the final pH values attained are also shown in Table 3.2. The pH value obtained during acid/ base priming and the amount of acid or base added to 80g of sample for neutralisation are displayed in Table 3.2.

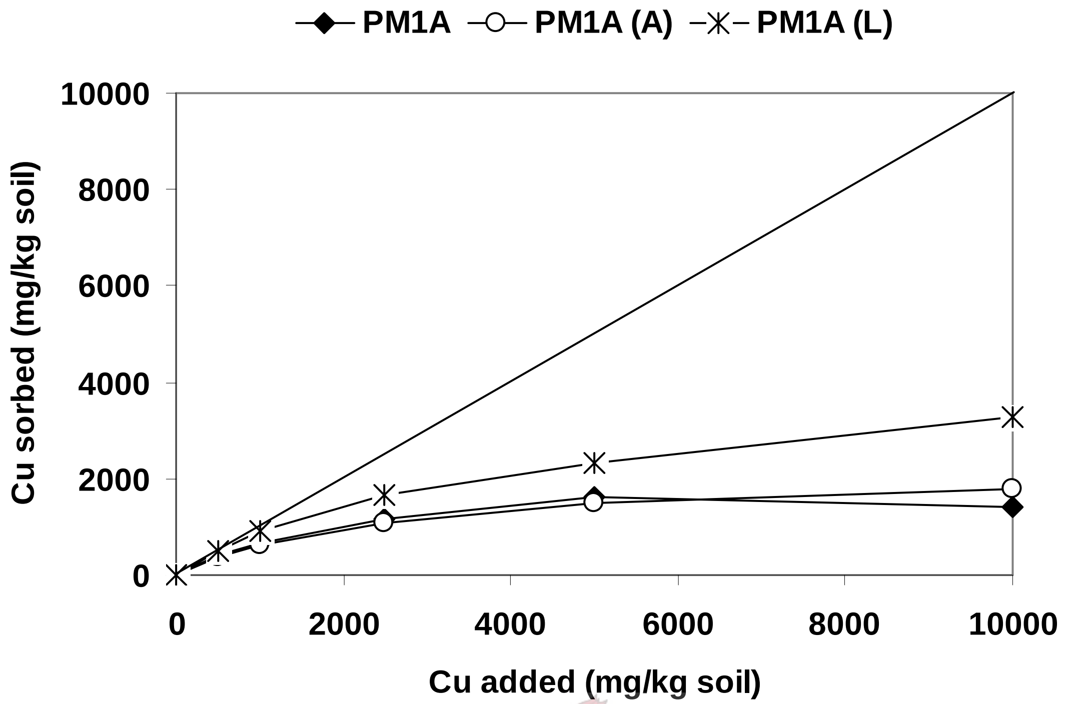
Table 3.2 Summary of acid/base priming results, showing the pH produced by incubation with acid or base and the subsequent amounts of acid or base added to achieve the neutralisation pH

Soil (Treatment)	Treated pH	$Ca(OH)_2$ added (mg)	3 M H_2SO_4 added (ml)	Neutralized pH
PM1A (A)	3.67	80		4.78
PM2A (A)	2.42	1376		4.24
PM1B (A)	3.78	32		5.94
PM2B (A)	2.69	1024		6.26
PM1A (L)	12.53		8.00	5.40
PM2A (L)	12.64		7.84	4.00
PM1B (L)	12.54		9.12	6.37
PM2B (L)	12.50		8.96	4.97

3.3.2.2 Cu sorption

Cu sorption curves for the soil samples in relation to acid and base treatment are shown in Figures 3.3 (topsoils) and 3.4 (subsoils). In all cases the pre-limed soil showed more sorption than the untreated soil whereas in only one case (PM2B) was there a marked increase in Cu sorption as a result of acid pre-treatment. These contradictory results could be explained by the fact that the neutralisation pH achieved following acid or base treatment was never the same, and that differences in sorption may have been more closely related to the final pH than to the pre-treatment itself. This aspect is addressed in a later section.

(a) PM1A



(b) PM2A

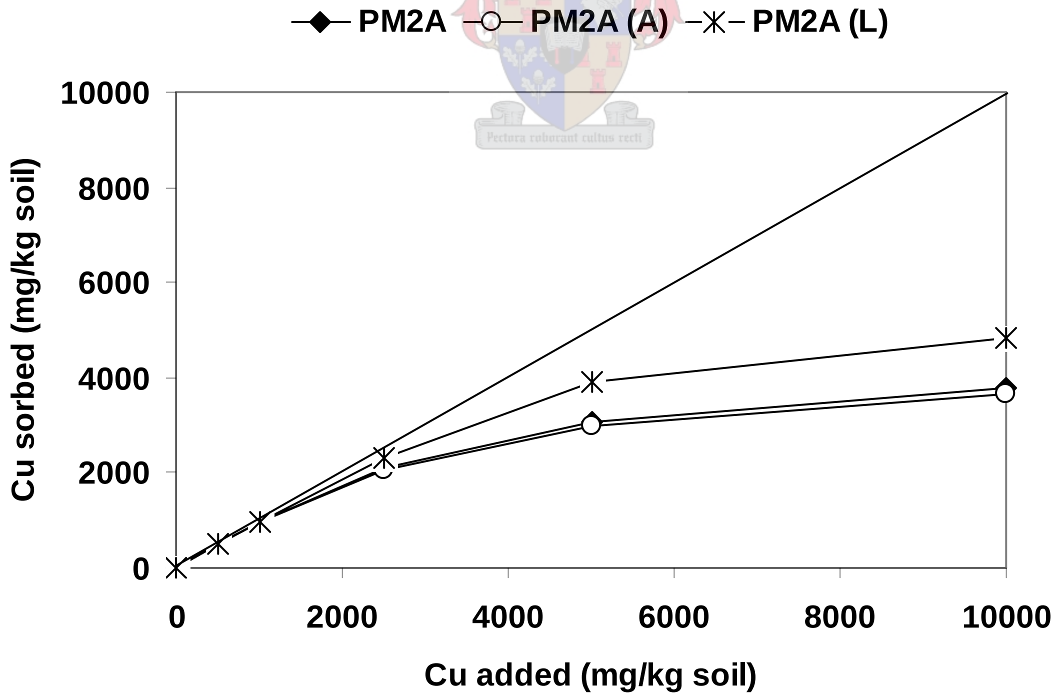
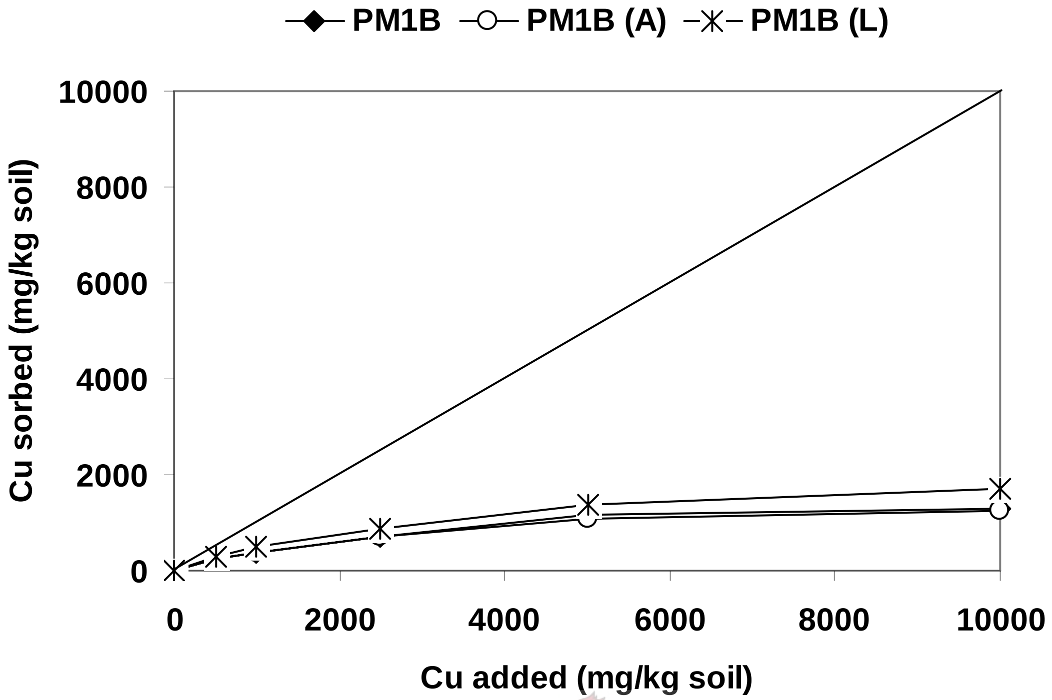


Figure 3.3 Cu sorption relative to the amount of Cu added to acid- (A), base-primed (L) and untreated topsoils: (a) PM1A and (b) PM2A (The plain line represents complete sorption)

(a) PM1B



(b) PM2B

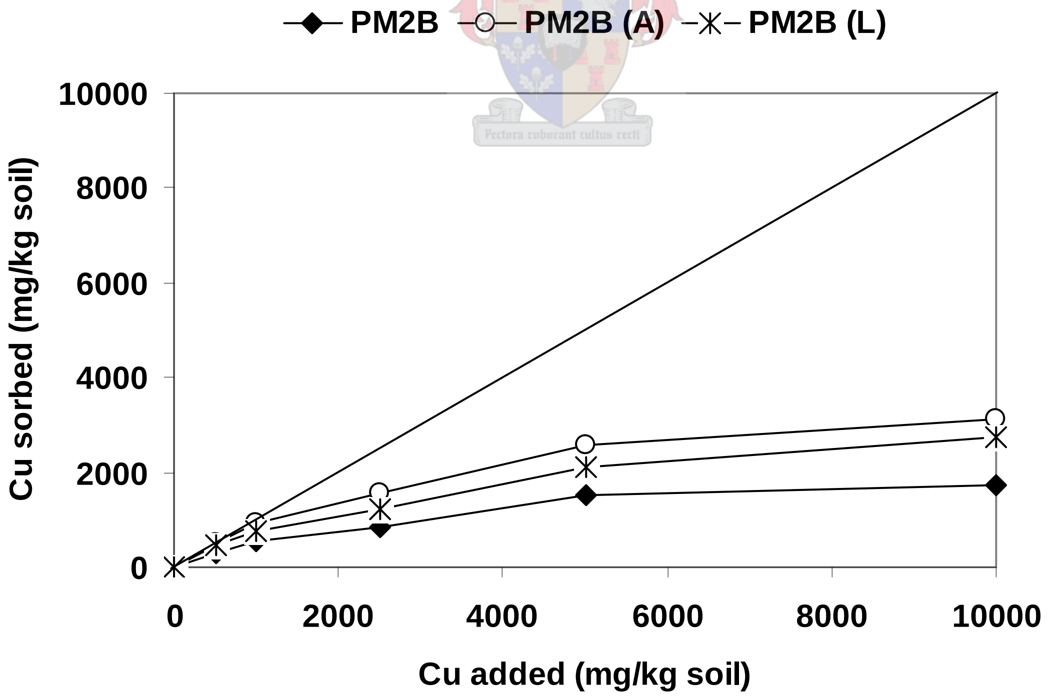


Figure 3.4 Cu sorption relative to the amount of Cu added to acid- (A), base-primed (L) or untreated subsoils: (a) PM1B and (b) PM2B (The plain line represents complete sorption)

Figures 3.3 and 3.4 contain results which are not strictly comparable between soils because sorption is being compared at different equilibrium Cu concentrations. The Cu sorption values at 1 mg/l Cu solution concentration, derived from isotherm equations as described in Chapter 2, are shown in relation to acid and base treatment in Figure 3.5. Here it is clearly evident that base priming consistently enhances Cu sorption whereas acid priming decreases Cu sorption in 3 of the soils and only increases it in the PM2B soil.

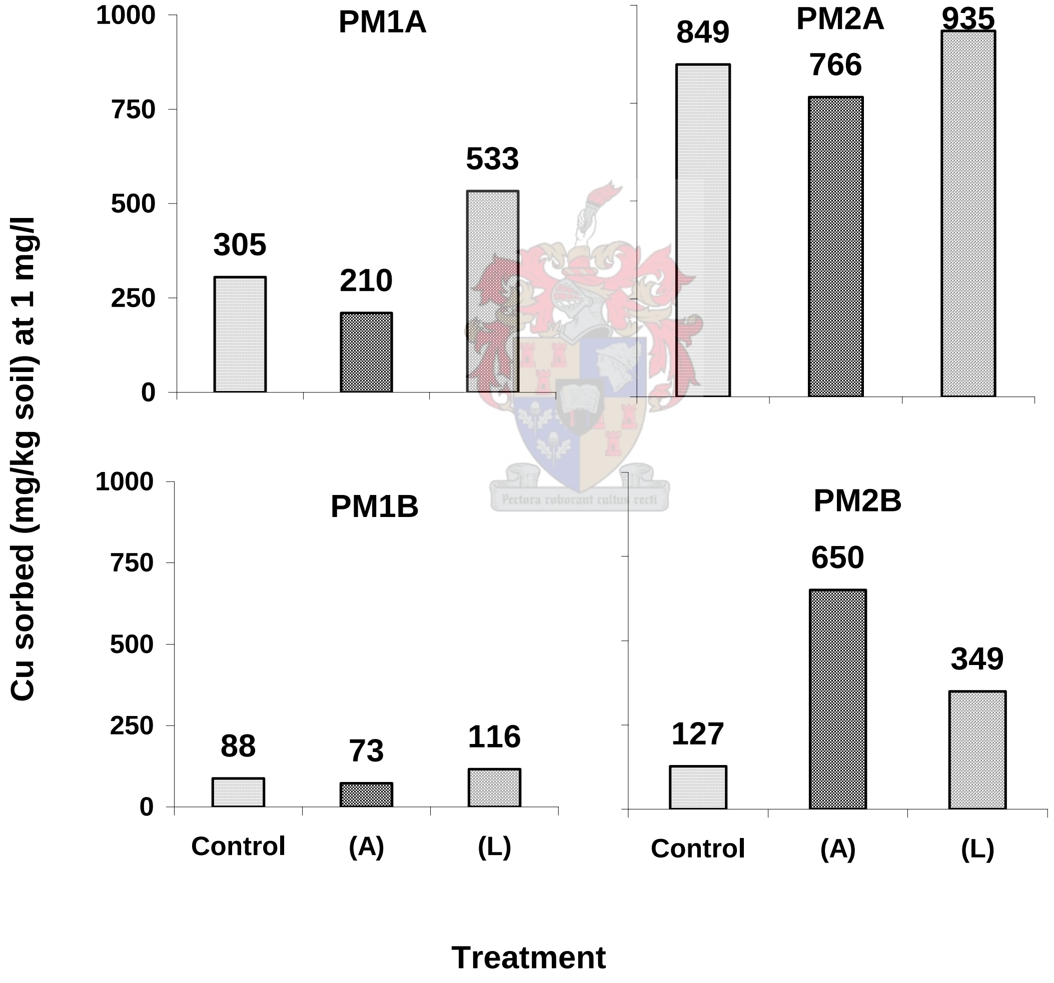


Figure 3.5 Cu sorption at 1 mg/l Cu solution concentration in acid-(A), base-primed (L) and untreated (control) soils

Acid or base priming resulted in increased Cu sorption in some of the soils. Acid priming had a small or negative effect on Cu sorption in all of the soils except PM2B (A). This may be due to the fact that acid treatment could result in the formation of hydroxyaluminium interlaying and coating in 2:1 type silicate clays. It has been reported (Saha et al., 2001) that Cu adsorption is promoted by the presence of hydroxyaluminium polymeric components on Wyoming montmorillonite. Their electron spin resonance data established the existence of chemisorbed Cu on hydroxyaluminium polymeric components of the synthetically interlayered Wyoming montmorillonite; yet, there was also evidence for the existence of mobile aquated copper species, indicating the presence of some electrostatically bound Cu^{2+} (Saha et al., 2001). The high Cu sorption capacity for PM2B (A) could be explained by its high pH (Figure 3.6).

Base priming showed a substantial increase in Cu sorption for soils that had high pH values after neutralisation. Greater negative surface charge associated with the higher pH would be expected to promote cation sorption.

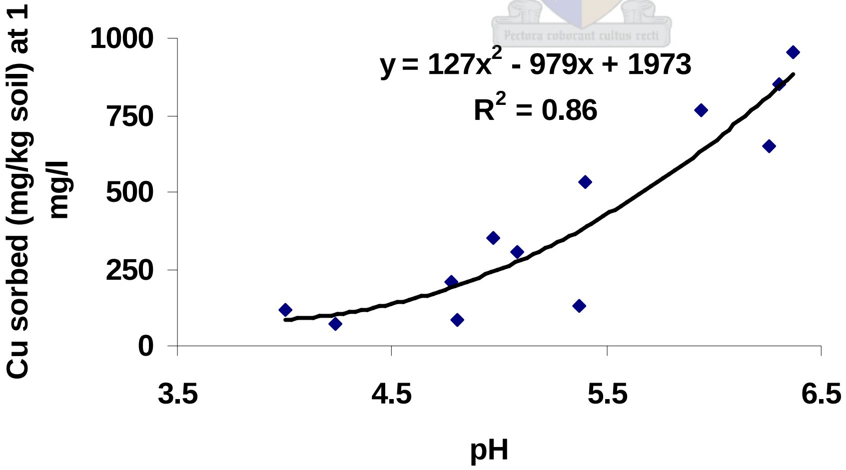
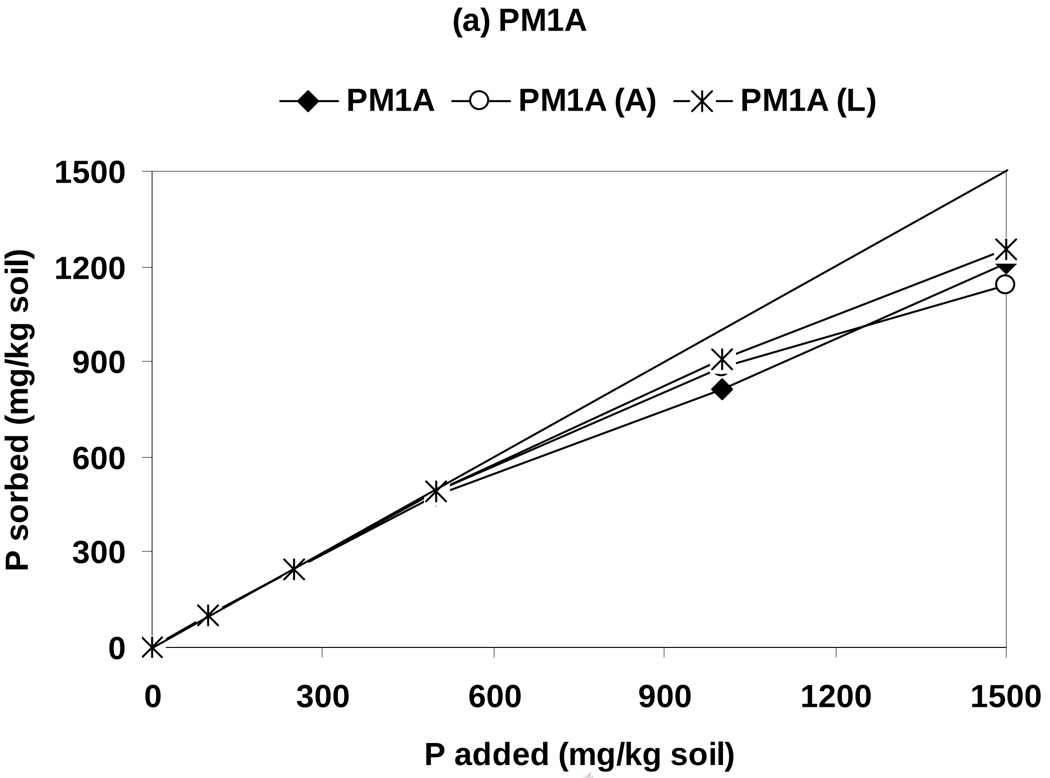


Figure 3.6 Effect of pH in $CaSO_4$ on Cu sorption at 1 mg/l for the unprimed, acid- and- base primed soils

Although the increase in Cu sorption after priming could partly be attributed to the formation of new mineral surfaces (including the formation of gypsum which has been shown by Garrido et al. (2005) to enhance metal attenuation), Figure 3.6 indicates a strong relationship between Cu sorption at 1 mg/l and pH (R^2= 0.86). This suggests that the final pH after neutralisation of base- or acid-primed soils is probably the dominant factor controlling Cu sorption rather than the generation of new, more receptive surfaces by acid or lime treatment.

3.3.2.3. Phosphate sorption

P sorption curves in relation to acid and base treatment are shown in Figures 3.7 (topsoils) and 3.8 (subsoils). In all cases the pre-limed soil showed more sorption than the untreated soil while only in one case (PM2A) was there a marked increase in P sorption as a result of acid pre-treatment. These variable results could be explained by the fact that the neutralisation pH achieved following acid or base treatment was variable, and that differences in sorption may have been more closely related to the final pH than to the pre-treatment itself as discussed for Cu in the previous section.



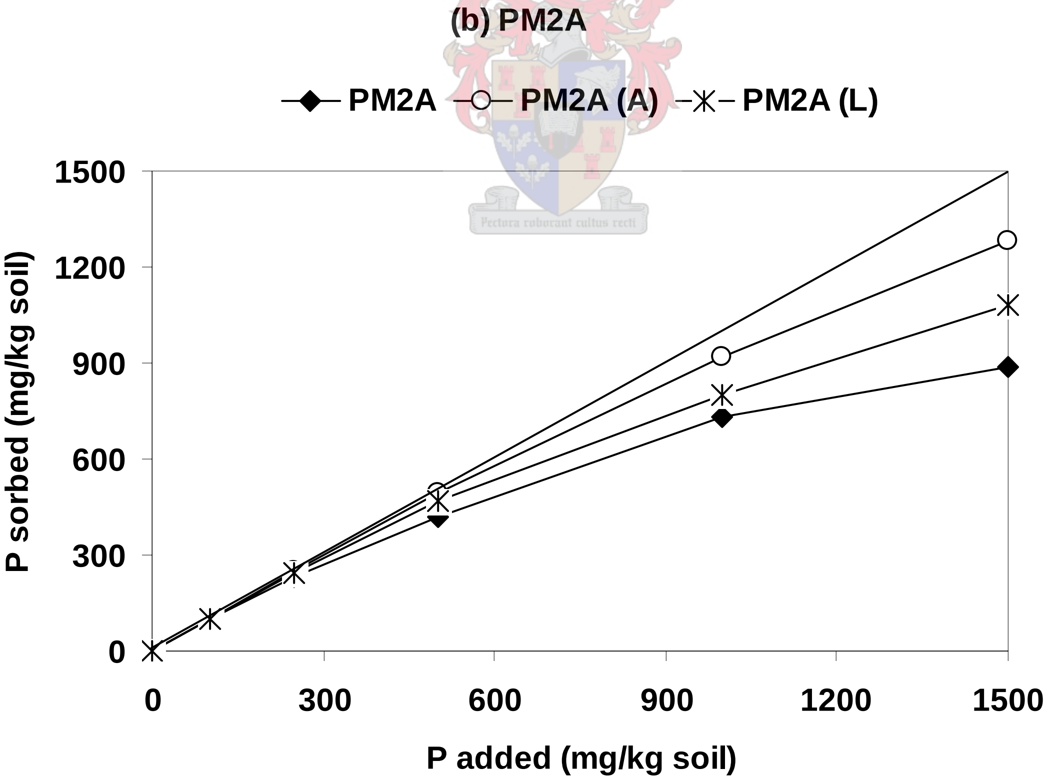
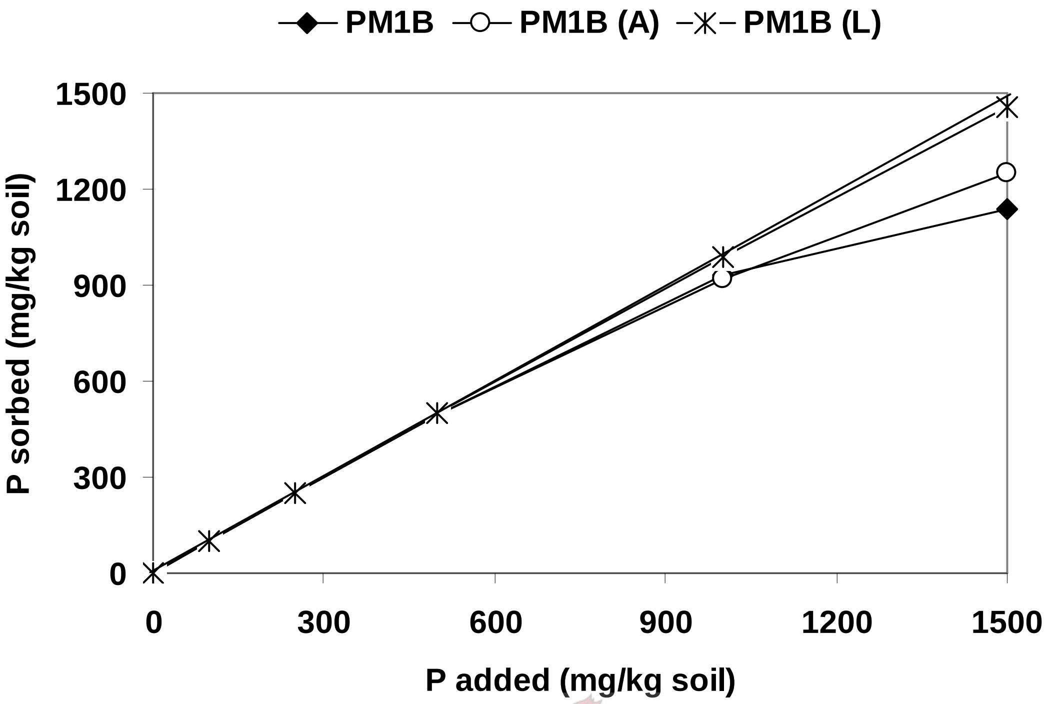


Figure 3.7 P sorption relative to the amount of P added to acid- (A), base-primed (L) or untreated soils: (a) PM1A and (b) PM2A (The plain line represents complete sorption)

(a) PM1B



(b) PM2B

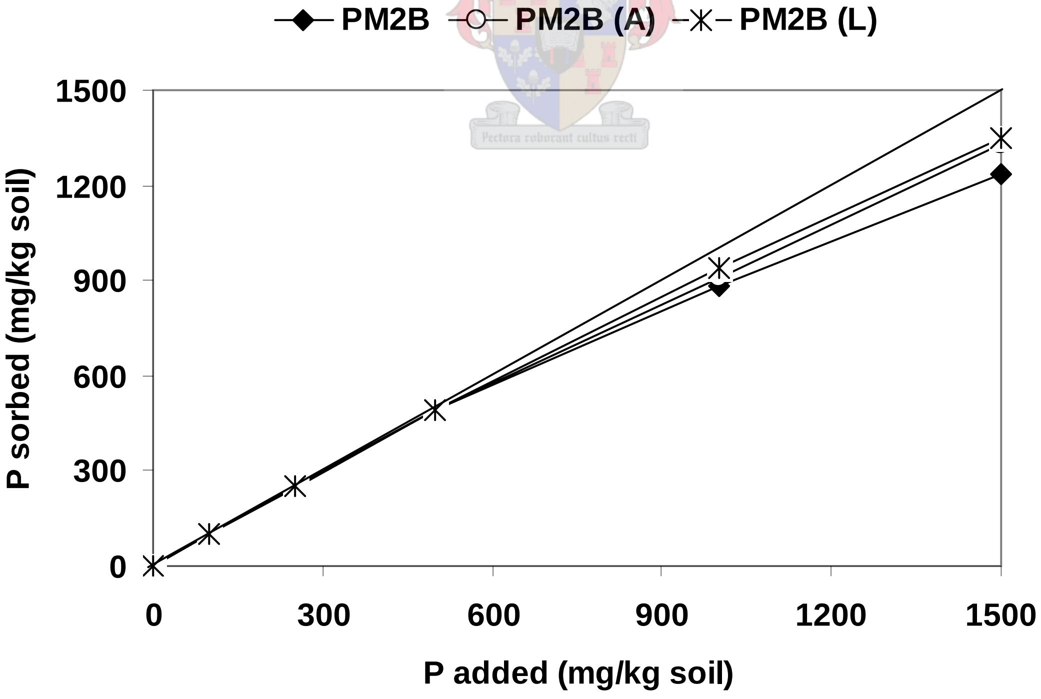


Figure 3.8 P sorption relative to the amount of P added to acid- (A), base-primed (L) or untreated soils: (a) PM1B and (b) PM2B (The plain line represents complete sorption)

As was pointed out in the case of Cu sorption, Figures 3.7 and 3.8 contain results which are not strictly comparable between soils because sorption is being compared at different equilibrium P concentrations. The P sorption values at 1 mg/l P solution concentration, derived from isotherm equations as described in Chapter 2, are shown in relation to acid and base treatment in Figure 3.9, from which it is clearly evident that both acid- and base-priming enhances P sorption in all four soils.

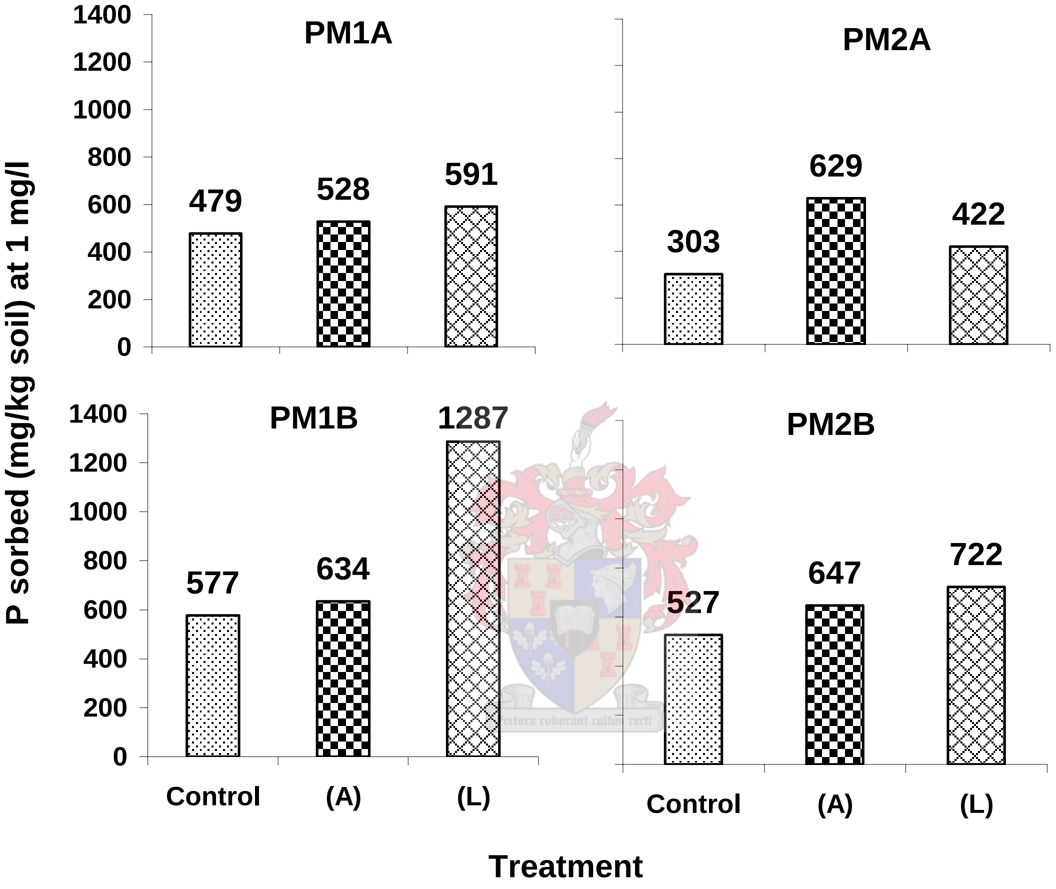


Figure 3.9 P sorption at 1 mg/l P solution concentration in acid- (A), base-primed (L) and untreated (control) soil

Base priming generally showed better results than acid priming except in soil PM2A. Increase in P sorption might be explained by the formation of hydroxyaluminium and hydroxyaluminosilicate during neutralisation following acid and base treatment. The study by Saha et al. (2001) has shown an abrupt modification of phosphate retention properties of montmorillonite and vermiculite as a result of interlaying with hydroxyaluminium and hydroxyaluminosilicate cations. The exception in the case of PM2A (L) may have been due to the effect of neutralisation pH although the influence of pH on P sorption in which sorption shows the expected decrease with increasing pH (Figure 3.10) is not as clear as that which was observed for Cu.

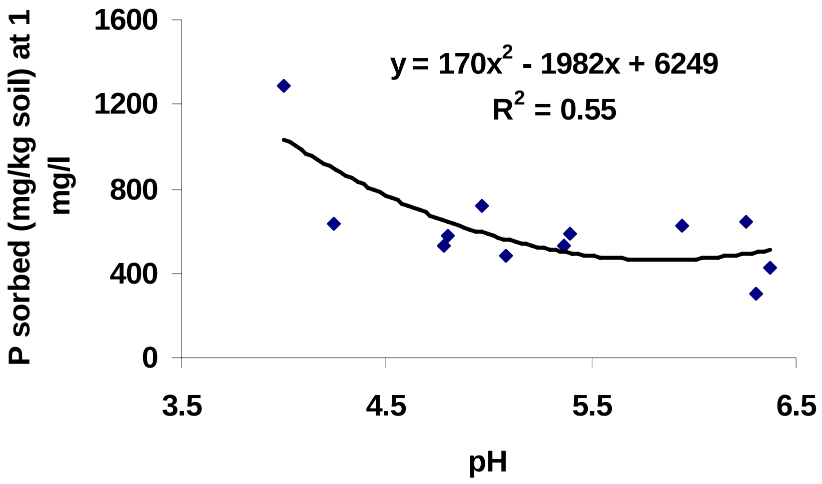


Figure 3.10 Effect of pH in $CaSO_4$ on P sorption at 1 mg/l for the unprimed, acid- and base-primed soils

As was suggested for Cu, the possibility that the formation of gypsum increased the P sorption capacity cannot be ruled out since several studies have alluded to the immobilisation of phosphate by gypsum (Shutt et al., 2004; Bastin et al., 1999; Kordlaghari and Rowell, 2005).

3.3.2.4 BET surface area

The BET surface area of topsoils (untreated and treated) was determined. Table 3.3 shows the results.

Table 3.3 Specific surface area of the PM topsoils (untreated and pretreated with acid (A) or lime (L) then neutralised)

Soil	BET surface area (m^2/g)
PM1A	20.1
PM1A (A)	17.2
PM1A (L)	18.0
PM2A	20.7
PM2A (A)	18.0
PM2A (L)	17.5

The data indicated a decrease in the surface area with respect to acid and base treatment. This decrease in the surface area data could be attributed to the formation of hydroxy-aluminium and hydroxyaluminosilicates, coating existing surfaces and exposing new surfaces to the solution.

Similar results were reported by Saha et al. (2005). They found that hydroxyaluminium- and hydroxyaluminosilicate-interlayered and coated montmorillonite significantly altered the charge and surface properties of montmorillonite. Adsorption of hydroxyaluminium or hydroxyaluminosilicate on montmorillonite reduced total and internal surface areas. Furthermore, a study of the effect of acid and alkaline treatment on surface area showed that the surface area of the soil solid phase decreased in general as a result of acid and alkaline treatments (Jozefaciuk et al., 2002).

3.4 Summary and conclusions

The sorption capacity was studied on the base primed, acid primed and unprimed soil samples using Cu for metal cation and P for ligand. Two low cost chemicals were used for the acid/base priming (i.e. H_2SO_4 and $Ca(OH)_2$). They have an added advantage of generating gypsum which is non toxic salt. The investigation consisted of applying the two chemicals to a bulk quantity of soil in order to reduce the availability of Cu and P. Acid/base priming consisted of treating soils with an acid or a base so as to reach an extreme pH, then bringing it back to an approximate original value.

The effect of pH on Cu and P sorption for the unprimed soil samples was also investigated. The BET specific surface area was determined for the topsoils (untreated and treated) to check if there was any change due to acid or base priming.

The results indicated that the effect of Cu sorption showed a similar trend for both samples. Sorption of Cu increased with increasing pH, from its minimum at pH 3 to its maximum at a pH of about 7.8. On the other hand, the effect of pH on P sorption indicated that for both samples, sorption of P decreased with increasing pH above 4. However, below this pH, sorption of P decreased again.

Acid priming had a small or negative effect on Cu sorption in all of the samples except in one of the subsoils. This might be due the fact that acid treatment could result in the formation of hydroxyaluminium interlaying and coating in silicate clays.

Base priming showed an increase in Cu sorption for samples that had high pH values. The explanation for this could be that the base-primed samples had a greater negative surface charge because of the higher pH, which promotes Cu sorption. The increase in Cu sorption could also be due to the formation of gypsum.

Acid or base priming enhanced P sorption in all the samples, with the base priming showing the best results except for one of the topsoils. The increase in P sorption might be explained by the formation of hydroxy-aluminium and hydroxy-aluminosilicates during acid and base treatments. It should be noted, however, that the increase in P sorption may also be due to the presence of gypsum.

Acid/base priming slightly reduced the external specific surface area of the soils. This implies that the enhanced reactivity from priming is not due to the creation of new surfaces for sorption.

General discussion

This study had three main objectives. The first was to investigate the attenuation capacity of a selection of soil horizons and materials representing major types of diagnostic horizons and materials in the South African soil classification in order to validate their chemical attenuation ratings as provisionally specified by Sillilo et al. (2001, p. 4.6). The second objective was to assess the pollutant attenuation capacity of South African soil horizons and materials and describe the diagnostic value of key chemical properties of soils for conveying information on their contaminant attenuation potential. The third objective was to investigate whether it is possible to apply acid/base priming using H_2SO_4 and $Ca(OH)_2$ to a bulk quantity of soil in order to reduce the availability of contaminants.

The investigation of the attenuation capacity of selected soil horizons did not allow the validation of the chemical attenuation ratings proposed by Sillilo et al. (2001, p. 4.6). On the contrary, the results demonstrated that there is seldom a clear distinction between soil horizons with respect to either cation or anion sorption. The existing soil classification, and soil maps which make use of it, are therefore unsatisfactory for predicting the contribution of soil to groundwater protection.

Our assessment of pollutant attenuation capacity of selected soils and material showed that copper sorption is more related to S value and pH whereas phosphate sorption appears to be most related to clay and extractable Al and Fe content. The relationship, derived using segmented quantile regression to establish a boundary line or chemical envelope equation, is one which predicts the maximum adsorption for any particular value of the determinant variable. Such chemical envelopes could form the basis for developing a systematic classification based on well known soil properties. Thus pollutant attenuation can be predicted to some degree if criteria used for classification are combined with some additional soil properties. This implies that soil maps can be useful for making predictions about groundwater vulnerability provided the soils have been well characterized by laboratory analysis.

Although there was a significant relationship between Cu and Zn sorption (R^2= 0.62) and between P and sulfate sorption (R^2= 0.55), further studies should compare Cu and P to additional metals and ligands, respectively, to ensure that they are indeed representative in reflecting the general capacity of soils to attenuate cationic or anionic pollutants.

Acid/base priming was investigated by applying H_2SO_4 and $Ca(OH)_2$ to bulk quantities of sesquioxidic soil to reduce the availability of Cu and P. Acid/base priming consists of treating soils with a strong acid or base so as to reach an extreme pH, then bringing the soil pH back to its approximate original value. Two chemicals (H_2SO_4 and $Ca(OH)_2$) were used because they are of low cost and have the added benefit of generating gypsum which is a non-toxic salt.

Acid priming had little or negative effect on copper sorption in most of the soils. This might be due to the fact that acid treatment would result in the formation of hydroxyaluminium interlaying and coating in 2:1 type silicate clays. Base priming showed a large increase in Cu sorption but this could have been that base priming increased negative surface charge because the pH after neutralization was generally higher than that of the unprimed soil..

Acid or base priming enhanced P sorption in all the samples, with base priming showing the best results for all but one of the four soils. The increase in P sorption might be explained by formation of hydroxyaluminium and hydroxyaluminosilicate during neutralization following acid or base treatment.. As was the case with Cu, however, the difficulty of achieving the original pH value after neutralization meant that pH dependent surface charge and specific sorption may have been the dominant factor determining cation and anion retention rather than the creation of new solids with fresh surfaces available for sorption. Further work is needed to establish the relative contribution of pH effects vs those of new precipitates in accounting for harsh acid and lime treatment effects on soil decontamination. These findings nevertheless suggest that acid/base priming can be used as a reliable method to reduce the availability of certain contaminants in soils.

One of the limitations of this study was the number of soils available for laboratory analyses. Future research on pollutant attenuation and acid/base priming should include a much bigger number of soils. This will provide the benefit of yielding results that may be generalized more widely using techniques such as quantile regression to establish the limits of soil chemical behaviour.

REFERENCES

Addiscott, T.M. and Thomas, D. 2000. Tillage, mineralization and leaching: phosphate. Soil & Tillage Research 53, 255-273.

Alloway, B.J. 1995. Soil processes and the behaviour of metals. In: Alloway, B.J. (Ed), Heavy metals in soils. John Wiley and Sons, New York, pp.34.

Alloway, B.J. and Ayres, D.C. 1993. Chemical principles of environmental pollution. Chapman and Hall, UK, pp. 140-141.

Álvarez-Ayuzo, E. and García-Sánchez, A. 2003. Palygorskite as a feasible amendment to stabilize heavy metal polluted soils. Environmental Pollution 125, 337-344.

Arch, J. 1998. Clay barriers in landfills. In: Parker, A. and Rae, J.E. (Eds), Environmental interactions of clays. Clays and the environment. Springer, Berlin, pp. 219.

Arienzo,M. 2005. Processes and factors regulating the behaviour and uptake of trace elements in the rhizosphere. In: Shtaneeva,I. (Ed), Trace and ultratrace elements in plants and soil. WIT Press, UK, pp. 74.

Baker, D.E. 1995. Copper. In: Alloway, B.J. (Ed), Heavy metals in soils. John Wiley and Sons, New York, pp.171.

Barrow, N.J. 1999. The four laws of soil chemistry. Aust. J. Soil Res. 37, 787-829.

Barry, G.A.; Chudek, P.J.; Best, E.K. and Moody, P.W. 1995. Estimating sludge application rates to land based on heavy metal and phosphorus sorption characteristics of soil. Water Research 29, 2031-2034.

Bastin, O; Janssens; F; Dufey, J and Peeters, A. 1999. Phosphorus removal by a synthetic iron oxide-gypsum compound. Ecological Engineering 12, 339-351.

Beirlant, J., De Wet, T. and Goegebeur, Y. 2004. Nonparametric estimation of extreme conditional quantiles. Journal of Statistical Computation and Stimulation 74, 567-580.

Blum, W.E.H and Laker, M.C. 2003. Soil classification and soil research. In: Eswaran, H., Rice, T., Ahrens, R. and Stewart, B.A. (Eds), Soil classification. A global desk reference. CRC Press, Boca Raton, pp. 43-46.

Bolan, N.S., Syers, J.K and Tillman, R.W. 1986. Ionic strength effects on surface charge and adsorption of phosphate and sulfate by soils. Journal of Soil Science 37, 379-388.

Bohn, H.L.; Mc Neal, B.L. and O'Connor, G.A. 1985. Soil chemistry. Second edition. John Wiley & Sons.

Boulding, R.J. 1994. Description and sampling of contaminated soils. CRC Press: Florida, pp. 3-68.

Chubar, N.I., Kanibolotskyy, V.A., Strelko, V.V., Gallios, G.G., Samanidou, V.F., Shaposhnikova, T.O., Milgrandt, V.G and Zhuravlev, I.Z. 2005. Adsorption of phosphate ions on novel inorganic ion exchangers. Colloids and Surfaces A: Physicochem. Eng. Aspects 255, 55-63.

Cobuild English Dictionary 1995. Harper Collins Publishers. London.

Collins, C.R., Vala Ragnarsdottir, K. and Sherman, D. M. 1999. Effect of inorganic and organic ligands on the mechanism of cadmium sorption to goethite. Geochimica et Cosmochimica Acta, 63, 2989-3002.

Colvin, C. (2001). Handbook of groundwater quality protection for farmers. Environmentek, CSIR. WRC Report No TT 116/00.

De la flor, M.,Vigil de la Villa, R. and Cala, V. 1995. Copper sorption in clay fractions of alluvial soils. The Science of the Total Environment 172, 245-249.

Díaz-Barrientos et al. 2003. Copper and zinc retention by an organically amended soil. Chemosphere 50, 911-917.

Dixon, J.B. 1998. Role of clay and oxide minerals in soils. In: Parker, A. and Rae, J.E. (Eds), Environmental interactions of clays. Clays and the environment. Springer, Berlin, pp. 38-39.

Egirani, D.E., Baker, A.R. and Andrews, J.E. 2005. Copper and zinc removal from aqueous solution by mixed mineral systems. I. Reactivity and removal kinetics. Journal of Colloid and Interface Science 291, 319-325.

Erish, M.S.; Fitzgerald, C.B. and Porter, G.A. 2002. The effect of organic amendments on phosphorus chemistry in a potato cropping system. Agriculture, Ecosystems and Environment 88, 79-88.

Foth, H.D. 1990. Fundamentals of soil science. 8th edition. Willey: New York.

Garrido, F., Illera, V and Gargía-gonzález, M.T. 2005. Effect of the addition of gypsum- and lime-rich industrial by-products on Cd, Cu and Pb availability and leachability in metal-spiked acid soils. Applied Geochemistry 20, 397-408.

Giesler, R., Andersson, T., Lovgren, L. and Persson, P. 2005. Phosphate sorption in aluminum- and iron-rich humus soils. Soil Science Society of America Journal 69, 1, 77-86.

Hardie, A.G. 2004. Decontamination of soils by activation with acids and bases. Msc. Dissertation. Stellenbosch University.

Harter, R.D. 1991. Micronutrient adsorption – desorption reactions in soils. In Morvedt (Ed). Micronutrients in agriculture. Second edition. Soil Science Society of America. USA, pp. 74-76.

Hooda, P.S. and Alloway, B.J. 1998. Cadmium and lead sorption behavior of selected English and Indian soils. Geoderma 84, 121-134.

Jackson, T.A. 1998. The biogeochemical and ecological significance of interactions between colloidal minerals and trace elements. In: Parker, A. and Rae, J.E. (Eds), Environmental interactions of clays. Clays and the environment. Springer, Berlin.

Jones, L.H.P and Jarvis, S.C.1981. The fate of heavy metals.In Greenland, D.J and Hayes, M.H.B (Eds). The chemistry of soil processes. John Wiley & Sons, New York, pp. 604.

Jozefaciuk, G., Muranyi, A., Alekseeva, T. 2002. Effect of extreme acid and alkali treatment on soil variable charge. Geoderma 109, 225-243.

Kabata – Pendias, A. 2001. Trace elements in soils and plants. 3rd edition. CRC Press LLC. Florida.

Kordlaghari, M.P and Rowell, D.L. 2005. The role of gypsum in the reactions of phosphate with soils. Geoderma 132, 105-115.

Kasama, T., Watanabe, Y., Yamada, H. and Murakami, T. 2004. Sorption of phosphates on Al-pillared smectites and mica at acidic to neutral pH. Applied Clay Science 25, 167-177.

Lal, R. and Stewart, B.A. 1994. Soil processes and water quality. Lewis Publishers, Boca Raton.

Leep, N.W. 2005. Copper. In; Shtangeeva, I. (Ed), Trace and ultratrace elements in plants and soil. WIT Press, UK, pp. 136.

Leinwer, P.; Turner, B.L. and Meissner, R.2002. Phosphorus.In Haygarth, P.M. and Jarvis, S.C (eds). Agriculture, hydrology and water quality. CABI. London, pp. 32.

Lewis, A.G. 1995. Copper in water and aquatic environments. International Copper Association, LTD, New York, pp. 32, 44.

Lin, S., Kao, H., Cheng, C. and Juang, R. 2004. An EXFAS study of the structures of copper and phosphate sorbed onto goethite. Colloids and surfaces A: Physicochemistry Engineering Aspects 234, 71-75.

Lopez-Hernandez, I.D. and Burnham, C.P. 1974. The covariance of phosphate sorption with other soil properties in some british and tropical soils. Journal of Soil Science 25, 196-206.

Lützenkirchen, J. 1997. Ionic strength effects on cation sorption to oxides: Macroscopic observations and their significance in microscopic interpretation. Journal of colloid and interface science 195, 149-155.

MacVicar, C.N., De Villiers, J.M., Loxton, R.F., Verster, E., Lambrechts, J.J.N., Merryweather, F.R., Le Roux, J., Van Rooyen, T.H. and Harmse, H.J. von M. 1977. Soil Classification : A Binominal System for South Africa. Department of Agricultural Technical. Pretoria.

Madrid, L. and Díaz-Barrientos, E. 1998. Release of metals from homogeneous soil columns by wastewater from an agricultural industry. Environmental Pollution 101 (1), 43-48

Marosits, E.; Polyák, K. and Hlavay, J. 2000. Investigation on the chemical bonding of copper ions on different soil samples. Microchemical Journal 67 (1 -3), 219 – 226.

Martin-Garin, A., Gaudet, J.P., Charlet, L. and Vitart, X. 2002. A dynamic study of the sorption and the transport processes of cadmium in calcareous sandy soils. Waste Management 22, 201-207.

Matthess, G. 1984. Unsaturated zone pollution by heavy metals. In: Yaron, B., Dagan, G. and Golshmid, J. (Eds), Pollutants in porous media. The unsatured zone between soil surface and groundwater. Spring-Verlag, Berlin, pp. 87.

McBride, M.B. 1981. Forms and distribution of copper in solid and solution phases of soil. In: Loeragan, J.F.;Robson, A.D. and Graham, R.D. (Eds), Copper in soils and plants. Academic Press. New York, pp. 39.

McBride, M.B. 1994. Environmental Chemistry of soils. Oxford University Press. New York.

McBride, M.B. 2000. Chemisorption and Precipitation Reactions. In: Sumner, M.E. (Ed), Handbook of Soil Science. CRC Press. Boca Raton, pp. B-279.

McGechan, M.B. and Lewis, D.R. 2002. Sorption of phosphorus by soil, Part 1: Principles, Equations and Models. Biosystems Engineering 82 (1), 1-24.

McGowen, S.L. and Basta, N.T. 2001. Heavy metal solubility and transport in soil contaminated by mining and smelting. In Selim, H.M and Sparks, D.L. (eds). eavy metals release in soils. CRC Press: Boca Raton. Florida, pp. 97.

Miller, R.W. and Gardiner, D. 1998. Soils in our environment. 8th edition. Prentice Hall: Saddle River, NJ.

Moreno, D.A., Villora, G., Soriano, M.T, Castilla, N., and Romero, L. 2005. Sulfur, chromium, and selenium accumulated in Chinese cabbage under direct covers. Journal of Environmental Management 74, 89-96.

Morgan, M.A. 1997. The behaviour of soil and fertilizer phosphorus. In: Tunney, H., Carton, O.T., Brookes, P.C. and Johnston, A.E. (Eds), Phosphorus loss from soil to water. CBInternational, UK, pp. 140.

Pakdel, H.; Couture, G.; ROY, C.; Masson, A.; Locat, j.; Gelins, P. and Lesage, S. 1992. Developing Methods for the Analysis of Toxic chemicals in soil and groundwater: The case of Ville Mercier, Quebec,Canada. In: Lesage,S. and Jackson, R.E (Eds). Groundwater contamination and Analysis at hazardous waste sites. Marcel Dekker, New York, pp. 381.

Pandey, A.K., Pandey, S.D. and Misra, V. 2002. Removal of toxic metals from leachates from hazardous solid wastes and reduction of toxicity to microtox by the use of calcium alginate beads containing humic acid. Ecotoxicology and Environmental Safety 52, 92-96.

Peacock, C.L.;Sherman, D.M.; Todd, E. and Heasman, D.M. 2000. Mechanism of Cu sorption onto iron oxides: Results from sorption Isotherms and Spectroscopy. Journal of conference Abstracts, 5 (2), 774. Cambridge Publications.

Pierzynski, G.M., Sims, J.T. and Vance, G.F. 1994. Soils and environmental quality. Lewis Publishers, Boca Raton, pp. 121.

Pierzynski, G.M., Sims, J.T. and Vance, G.F. 2005. Soils and environmental quality. Third edition. CRC Press. Boca Raton, pp. 83.

Plaza, C., D'Orazio, V. and Senesi, N. 2005. Copper (II) complexation of humic acids from the first generation of EUROSOILS by total luminescence spectroscopy. Geoderma 125, 177-186.

Potgieter, J.H., Potgieter-Vermaak, S.S. and Kalibantonga, P.D. 2006. Heavy metals removal from solution by palygorskite clay. Minerals Engineering 19 (5), 463-470.

Roberts, D.R., Ford, R.G. and Sparks, D.L. 2003. Kinetics and mechanisms of Zn complexation on metal oxides using EXAFS spectroscopy. Journal of Colloidal and Interface Science 263, 364-376.

Rowell, D.L. 1993. Soil science: methods and applications. Longman Publishers, USA.

Saha, U.K., Taniguchi, S. and Sakurai, K. 2001. Adsorption behavior of cadmium, zinc, and lead on hydroxyaluminum- and hydroxyaluminosilicate-montmorillonite complexes. Soil Science Society of America Journal 65, 694-703.

Saha, U.K., Liu, C., Kozak, L.M. and Huang, P.M. 2005. Kinetics of selenite desorption by phosphate from hydroxyaluminum- and hydroxyaluminosilicate-montmorillonite complexes. Geoderma 124, 105-119.

Schutt, C. and Noll, MR (2004). Influence of solution composition on phosphate sorption on gypsum. Geological Society of America Journal 36, 25-30.

Sililo, O.T.N., Conrad, J., Murphy, K.O.H., Tredoux, G., Eigenhuis, B., Ferguson, M.C.D. and Moolman, J.H. 1999. Investigation of the contaminant attenuation characteristics of the soil aquifer system with special emphasis on the vadose zone. Water Resarch Commission. Report No 572/1/99, pp. 23.

Sililo, OTN; Saayman, Ic. and Fey, M.V. 2001. Groundwater vulnerability to pollution in urban catchments. WRC Report No 1008/1/01. Water Research Commission.

Singh, B.R. and Steinnes, E. 1994. Soil and water contamination by heavy metals. In: Lal, R. and Stewart, B.A. 1994. Soil processes and water quality. Lewis Publishers, Boca Raton, pp. 258.

Singher, M.J. and Munns, D.N. 1996. Soils, an introduction. 3rd edition. Prentice Hall, USA, pp. 68-73.

Soil Classification Working Group. 1991. Soil classification: a taxonomic system for South Africa. Department of Agricultural Development, South Africa.

South African Concise Oxford Dictionary 2002. Oxford University Press Southern Africa. Cape Town.

Sparks, D.L. 2003. Environmental soil chemistry. Second Edition. Elsevier Science. USA.

Stevenson, F.J. and Fitch, A. 1981. Reactions with organic matter. In: Lonergan, J.F. and Robson (Eds), Copper in soils and Plants. Academic Press, Sydney, pp. 70.

Tan, K.H. 1993. Principles of soil chemistry. Second edition. Marcel Dekker. New York.

Tan, K.H. 1994. Environmental soil science. Marcel Bekker, inc. New York, pp. 160-167.

Trivedi, P., Axe, L. and Dyer, J. 2001. Adsortion of metal ions onto goethite: single-adsorbate and competitive systems. Colloids and Surfaces A: Physiochemical and Engineering Aspects 191, 107-121.

Usher, B.H., Pretorius, J.A., Dennis, I., Jovanovic, N., Clarke, S., Cave, L., Titus, R. and Xu, Y. 2004. Identification and prioritization of groundwater contaminants and sources in South Africa's urban catchments. WRC Report No 1326/1/04, pp. 6.

Van Riemsdijk, W.H. and Hiemstra, T. 1993. Adsorption to heterogeneous surfaces. In: Allen, H.E., Perdue, E.M. and Brown, D.S (Eds), Metals in groundwater. Lewis Publishers. USA, pp. 7.

Van Vuren, L.H.J., Du Preez, H.H. and Deacon, A.R. 1994. Effect of pollution on the physiology of fish in the olifants river (eastern Transvaal). Water Research Commission. Report No 350/1/94, pp. 38.

Wang, K. and Xing, B. 2004. Mutual effects of cadmium and phosphate on their adsorption and desorption by goethite. Environmental Pollution 127, 13-20.

Weil, R.R. and Magdoff, F. 2004. Soil organic matter in sustainable agriculture. CRC Press. USA, pp. 22.

Wild, A. 1993. Soils and the environment: an introduction. Cambridge University Press, Cambridge, pp. 204-206.

Worrall, F. and Kolpin, D.W. 2004. Aquifer vulnerability to pesticide pollution-combining soil, land use and aquifer properties with molecular descriptors. Journal of Hydrology 293, 191-204.

Wu, J., Laird, D.A. and Thompson, M.L. 1999. Sorption and desorption of copper on soil clay components. Journal of environmental quality. Madison 28 (1), 334 – 335.

Yaron, B.; Calvet, R. and Prost, R. 1996. Soil pollution processes and dynamics. Springer, Berlin, pp. 28.

Yin, Y., Allen, H.E., Li, Y., Huang, C.P. and Sanders, P.F. 1996. Adsorption of mercury (II) by soil: Effects of pH, chloride, and organic matter. Journal of Environmental Quality 25, 837-844.

Yong, R.N. and Mulligan, C.N. 2004. Natural attenuation of contaminants in soils. Lewis Publishers, New York.

Yong, R.N.; Mohamed, A.M.O. and Warkentin, BP. 1992. Principles of contaminant transport in soils. Elsevier: London.

Zhou, P., Yan, H. and Gu, B., 2005. Competitive complexation of metal ions with humic substances. Chemosphere 58, 1327-1337.

Zhu, C. 2004. Coprecipitation in the barite isostructural family: 2. Numerical simulations of reactions and mass transport. Geochimica et Cosmochimica Acta 68 (16), 3339-3349.

Zhuang, J. and Yu, G. 2002. Effects of surface coatings on electrochemical properties and contaminant sorption of clay minerals. Chemosphere 49, 619-62.

Appendix 1. Supplementary data from chapter 2

Table A1.1 Soil series (MacVicar et al., 1977) and profile and lab. Numbers of soils selected to represent diagnostic horizons. The corresponding soil family (Soil Classification Working Group, 1991) is indicated where possible in the final column

Soil series	National profile	Lab number	Diagnostic horizon	Corresponding form and family (blue book)
Ar 21	4197	C 1770	Vertic A	Ar 2200 (Diepsloot)
Ar 21	4197	C 1771	Vertic A	Ar 2200 (Diepsloot)
Ar 21	4197	C 1772	Vertic A	Ar 2200 (Diepsloot)
Ar 21	4197	C 1773	Not Specified	Ar 2200 (Diepsloot)
Av 25	4409	C 5269	Yellow-brown Apedal	Av 2100 (Avondale)
Av 26	140	C 3672	Orthic A	Av 2100 (Avondale)
Av 31	1784	C 4342	Orthic A	Av 3100 (Kameelbos)
Av 32	286	C 6768	Orthic A	Av 3100 (Kameelbos)
Av 32	286	C 6769	Yellow-brown	Av 3100 (Kameelbos)
Av 32	286	C 6770	Yellow-brown	Av 3100 (Kameelbos)
Av 33	4443	C 2368	Orthic A	Av 3100 (Kameelbos)
Av 33	4443	C 2370	Yellow-brown Apedal	Av 3100 (Kameelbos)
Av 36	1705	C 4556	Soft Plinthic	Av 3100 (Kameelbos)
Bo 20	8255	C 4282	Melanic A	Bo 2120 (Rustig)/2220 (Bulhoef)
Bo 20	8255	C 4283	Pedocutanic	Bo 2120 (Rustig)/2220 (Bulhoef)
Bo 20	8255	C 4284	Pedocutanic	Bo 2120 (Rustig)/2220 (Bulhoef)
Bo 20	8255	C 4285	Pedocutanic	Bo 2120 (Rustig)/2220 (Bulhoef)
Bo 30	4192	C 5105	Melanic A	Bo 2110 (Golela)/2210(Rockvale)
Bo 30	B21	C 5106	Pedocutanic	Bo 2110 (Golela)/2210(Rockvale)
Ch 11	4017	C 4302	Organic O	Any family (Champagne form)
Ct 11	2357	C 3817	E - horizon	Family not determined (Constantia form)
Ct 12	2085	C 6954	E - horizon	Family not determined (Constantia form)
Ct 13	4557	C 7966	E-horizon	Family not determined (Constantia form)
Ct 23	2058	C 6819	E - horizon	Family not determined (Constantia form)
Cv 16	4115	C 4891	Orthic A	Cv 1100 (Twyfelaar)
Cv 16	4115	C 4892	Yellow-brown Apedal	Cv 1100 (Twyfelaar)
Cv 16	4115	C 4893	E - horizon	Cv 1100 (Twyfelaar)
Du 10	2657	C 2403	Stratified Alluvium	Dundee form
Du 10	2657	C 2404	Stratified Alluvium	Dundee form
Du 10	4117	C 1629	Stratified Alluvium	Dundee form
Du 10	4117	C 1630	Stratified Alluvium	Dundee form
Du 10	4021	C 3971	Stratified Alluvium	Dundee form
Fw 12	2651	C 3789	Regic Sand	Any family (Fernwood form)
Fw 12	2651	C 3790	Regic Sand	Any family (Fernwood form)
Gf 22	4126	C 2456	Red Apedal	Gf 2100 (Maritzdrif)
Gs 10	2346	C 5150	Lithocutanic	Gs 2111 (Overberg)/2121 (Botrivier)
Gs 12	964	C 6932	Lithocutanic	Gs 2111 (Overberg)/2121 (Botrivier)
Gs 14	18	C 4002	Lithocutanic	Gs 2111 (Overberg)/2121 (Botrivier)
Gs 16	4211	C 4816	Lithocutanic	Gs 2111 (Overberg)/2121 (Botrivier)
Gs 17	4656	C 4629	Lithocutanic	Gs 2111 (Overberg)/2121 (Botrivier)
Hu 15	1761	C 4373	Red Apedal	Hu 1100 (Lillieburn)
Hu 15	1761	C 4374	Red Apedal	Hu 1100 (Lillieburn)
Hu 16	1770	C 4387	Red Apedal	Hu 1100 (Lillieburn)

Table A1.1 Continued

Soil series	National profile	Lab number	Diagnostic horizon	Corresponding form and family (blue book)
Hu 16	B22	C 4388	Red Apedal	Hu 1100 (Lillieburn)
Ia 11	4054	C 6485	Humic A	Ia 1200 (Highlands)/2200 (Glenariff)
Ik 10	1863	C 7527	Neocutanic	Ik 1100 (Oatlands)/2100 (Headford)
Ik 10	2943	C 5199	Neocutanic	Ik 1100 (Oatlands)/2100 (Headford)
Ik 10	14600	D 5684	Melanic A	Ik 1100 (Oatlands)/2100 (Headford)
Ik 11	12077	D 1662	Neocutanic	Ik 1100 (Oatlands)/2100 (Headford)
Ik 20	1863	C 7528	Neocutanic	Ik 1200 (Shingwedzi)/2200 (Sterfontein)
Ik 21	12224	D 1858	Melanic A	Ik 1200 (Shingwedzi)/2200 (Sterfontein)
Ik 21	12224	D 1859	Neocutanic	Ik 1200 (Shingwedzi)/2200 (Sterfontein)
Kp 10	4060	C 5950	Humic A	Kp 1100 (Fordoun)/2100 (Stonyhill)
Kp 11	4056	C 5961	Humic A	Kp 1200 (Dargle)/2200 (Nungwane)
Kp 11	4056	C 5962	Humic A	Kp 1200 (Dargle)/2200 (Nungwane)
Kp 12	4062	C 6597	Humic A	Kp 1200 (Dargle)/2200 (Nungwane)
No 10	4334	C 4122	Lithocutanic	No 1100 (Boston)/2100 (Deepdene)
No 10	4090	C 6023	Lithocutanic	No 1100 (Boston)/2100 (Deepdene)
No 10	11692	D 893	Lithocutanic	No 1100 (Boston)
No11	11694	D 897	Lithocutanic	No 2100 (Deepdene)
Oa 23	10933	D 396	Neocutanic	Oa 2110 (Cooper)/2210 (Gannage)
Oa 23	10933	D 397	Neocutanic	Oa 2110 (Cooper)/2210 (Gannage)
Oa 46	10837	D 388	Neocutanic	Augrabies form
Rg 20	8227	C 4389	G - horizon	Rg 2000 (Rietkuil)
Rg 20	8227	C 4390	G - horizon	Rg 2000 (Rietkuil)
Rg 20	12678	C 2298	G - horizon	Rg 2000 (Rietkuil)
Rg 20	12692	C 2338	Vertic A	Rg 2000 (Rietkuil)
Rg 20	12813	C 2561	G - horizon	Rg 2000 (Rietkuil)
Sp 21	4277	C 3625	E - horizon	Vilafontes form
Sp 21	4277	C 3626	Red Apedal	Vilafontes form
Ss 24	8243	C 1529	Prismacutanic	Ss 2100 (Hermon)
Ss 24	8243	C 1528	Prismacutanic	Ss 2100 (Hermon)
Ss 25	2670	C 3433	Prismacutanic	Ss 2100 (Hermon)
Ss 26	8260	C 4318	Prismacutanic	Ss 2100 (Hermon)
We 13	118	C 2775	Soft Plinthic	We 2000 (Mareetsane)
We 13	134	C 3667	Soft Plinthic	We 2000 (Mareetsane)
We 13	130	C 3689	Soft Plinthic	We 2000 (Mareetsane)
We 13	130	C 3690	Soft Plinthic	We 2000 (Mareetsane)
Hu17	6363	C 1344	Red apedal B	Hu 1200 (Kelvin)
Gf12	6365	C 1364	Orthic A	Gf 1100 (Woodstock)
Gf12	6365	C 1365	Yellow brown	Gf 1100 (Woodstock)
Hu28	8238	C 1525	Orthic A	Hu 2200 (Suurbekom)
Hu28	8238	C 1526	Red apedal	Hu 2200 (Suurbekom)
Cv23	8246	C 1539	Orthic A	Cv 2100 (Buckland)
Cv23	8246	C 1540	Yellow brown	Cv 2100 (Buckland)
Cv23	8246	C 1541	Yellow brown	Cv 2100 (Buckland)
Gf21	4168	C 1658	Orthic A	Gf 2100 (Maritzdrif)
Gf21	4168	C 1659	Yellow brown B	Gf 2100 (Maritzdrif)
Gf21	4168	C 1660	Red apedal B	Gf 2100 (Maritzdrif)
Gf13	6381	C 1661	Orthic A	Gf 1200 (Deelspruit)
Gf13	6381	C 1662	Yellow brown	Gf 1200 (Deelspruit)
Gf13	6381	C 1663	Red apedal	Gf 1200 (Deelspruit)
Gf11	6379	C 1671	Orthic A	Gf 1100 (Woodstock)
Gf11	6379	C 1672	Yellow Brown B	Gf 1100 (Woodstock)

Table A1.1 Continued

Soil series	National profile	Lab number	Diagnostic horizon	Corresponding form and family (blue book)
Gf11	6379	C 1673	Red apedal	Gf 1100 (Woodstock)
Hu22	428	C 2194	Orthic A	Hu 2100 (Hayfield)
Hu22	428	C 2195	Red apedal	Hu 2100 (Hayfield)
Av15	461	C 2288	Orthic A	Av 1100 (Blackmoor)
Av15	461	C 2288	Yellow brown	Av 1100 (Blackmoor)
Av15	461	C 2289	Soft plinthic B	Av 1100 (Blackmoor)
Cv34	8341	C 2310	Orthic A	Cv 3100 (Setlagole)
Cv34	8341	C 2311	Yellow brown B	Cv 3100 (Setlagole)
Hu18	4125	C 2451	Orthic A	Hu 1200 (Kelvin)
Hu18	4125	C 2452	Red apedal	Hu 1200 (Kelvin)
Hu18	4125	C 2453	Red apedal	Hu 1200 (Kelvin)
Gf22	4126	C 2454	Orthic A	Gf 2100 (Maritzdrif)
Gf22	4126	C 2455	Yellow brown	Gf 2100 (Maritzdrif)
Cv13	4145	C 2493	Orthic A	Cv 1100 (Twyfelaar)
Cv13	4145	C 2494	Yellow brown	Cv 1100 (Twyfelaar)
Cv13	4145	C 2495	Yellow brown	Cv 1100 (Twyfelaar)
Cv13	4145	C 2496	C	Cv 1100 (Twyfelaar)
Ct14	2359	C 3541	E horizon	Family not determined (Constantia form)
Ct14	2359	C 3542	Lithocutanic	Family not determined (Constantia form)
Ct14	2359	C 3543	Lithocutanic	Family not determined (Constantia form)
Ct14	2359	C 3544	C	Family not determined (Constantia form)
Gf20	2349	C 3554	Orthic A	Gf 2100 (Maritzdrif)
Gf20	2349	C 3555	Yellow brown B	Gf 2100 (Maritzdrif)
Gf20	2349	C 3556	Red apedal B	Gf 2100 (Maritzdrif)
Sp21	4277	C 3624	Orthic A	Vilafontes form
Sp21	4277	C 3627	C1	Vilafontes form
Sp21	4277	C 3628	C2	Vilafontes form
Av26	140	C 3673	Yellow brown	Av 2100 (Avondale)
Av26	140	C 3674	Soft plinthic	Av 2100 (Avondale)
Ik10	1731	C 3714	Melanic A	Ik 1100 (Oatlands)/2100 (Headford)
Ik10	1731	C 3715	Neocutanic B	Ik 1100 (Oatlands)/2100 (Headford)
Ik10	1731	C 3716	Neocutanic B	Ik 1100 (Oatlands)/2100 (Headford)
Ct11	2357	C 3816	Orthic A	Family not determined (Constantia form)
Ct11	2357	C 3819	C	Family not determined (Constantia form)
Cv14	4	C 3984	Orthic A	Cv 1100 (Twyfelaar)
Cv14	4	C 3985	Yellow brown	Cv 1100 (Twyfelaar)
Av37	1805	C 4087	Orthic A	3200 (Mafikeng)
Av37	1805	C 4088	Yellow brown	3200 (Mafikeng)
Av37	1805	C 4089	Yellow brown	3200 (Mafikeng)
Av37	1805	C 4090	Soft plinthic B	3200 (Mafikeng)
Hu27	1808	C 4094	Orthic A	Hu 2200 (Suurbekom)
Hu27	1808	C 4095	Red apedal B	Hu 2200 (Suurbekom)
Hu27	1808	C 4096	Red apedal	Hu 2200 (Suurbekom)
Av30	8339	C 4144	Orthic A	Av 3100 (Kameelbos)
Av30	4007	C 4245	Yellow brown	Av 3100 (Kameelbos)
Cv27	1764	C 4205	Orthic A	Cv 2200 (Leiden)
Cv27	1764	C 4206	Yellow brown	Cv 2200 (Leiden)
Av31	1784	C 4344	Soft plinthic B	Av 3100 (Kameelbos)
Cv26	1767	C 4375	Orthic A	Cv 2100 (Buckland)
Cv26	1767	C 4376	Yellow brown	Cv 2100 (Buckland)
Cv26	1767	C 4377	Yellow brown	Cv 2100 (Buckland)

Table A1.1 Continued

Soil series	National profile	Lab number	Diagnostic horizon	Corresponding form and family (blue book)
Cv20	2674	C 4415	Orthic A	Cv 2100 (Buckland)
Cv20	2674	C 4416	Yellow brown	Cv 2100 (Buckland)
Av30	8359	C 4553	Soft plinthic B	Av 3100 (Kameelbos)
Av30	8359	C 4554	G-horizon	Av 3100 (Kameelbos)
Av36		C 4555	Soft plinthic	Av 3100 (Kameelbos)
Cv41	206	C 4704	AB	1100/2100 Ag
Cv42	2220	C 4926	Orthic A	1100/2100 Ag
Cv42	2220	C 4927	Yellow brown B	1100/2100 Ag
Hu20	6279	C 5055	Orthic A	Hu 2100 (Hayfield)
Hu20	6279	C 5056	Red apedal	Hu 2100 (Hayfield)
Hu20	6279	C 5057	Red apedal	Hu 2100 (Hayfield)
Cv37	6292	C 5078	Orthic A	Cv 3200 (Mooilaagte)
Cv37	6292	C 5079	Yellow brown	Cv 3200 (Mooilaagte)
Cv37	6292	C 5080	Yellow brown B	Cv 3200 (Mooilaagte)
Bo30	4192	C 5107	Unspecified	Bo 2110 (Golela)/2210(Rockvale)
Av25	4409	C 5267	Orthic A	Av 2100 (Avondale)
Av25	4409	C 5268	Yellow brown B	Av 2100 (Avondale)
Ch20	4136	C 5278	G horizon	Any family (Champagne form)
Av22	206	C 5794	Orthic A	Av 2100 (Avondale)
Av22	206	C 5796	Soft plinthic B	Av 2100 (Avondale)
Av27	4027	C 5832	Orthic A	Av 2200 (Vryheid)
Av27	4027	C 5833	Yellow brown	Av 2200 (Vryheid)
Av27	4027	C 5834	Soft plinthic	Av 2200 (Vryheid)
No10	4077	C 5907	Humic A	No 1100 (Boston)/2100 (Deepdene)
No10	4077	C 5908	Humic A	No 1100 (Boston)/2100 (Deepdene)
Kp10	4060	C 5952	Red apedal B	Kp 1100 (Fordoun)/2100 (Stonyhill)
Ia10	4057	C 5956	Humic A	Ia 1100 (Himeville)/2100 (Mayfield)
Ia10		C 5957	Red apedal	Ia 1100 (Himeville)/2100 (Mayfield)
Ia10	4057	C 5958	Red apedal	Ia 1100 (Himeville)/2100 (Mayfield)
Kp11	4056	C 5963	Yellow Brown	Kp 1200 (Dargle)/2200 (Nungwane)
Cv48	2263	C 5993	Orthic A	1100/2100 Ag
Cv48	2263	C 5994	Yellow brown B	1100/2100 Ag
Cv21	2015	C 6387	Orthic A	Cv 2100 (Buckland)
Cv21	2015	C 6388	Yellow brown	Cv 2100 (Buckland)
Kp12	4062	C 6599	Yellow brown	Kp 1200 (Dargle)/2200 (Nungwane)
Kp12	4062	C 6600	Red apedal	Kp 1200 (Dargle)/2200 (Nungwane)
Cv18	4063	C 6601	Orthic A	Cv 1200 (Brereton)
Cv18	4063	C 6602	Yellow brown	Cv 1200 (Brereton)
Cv18	4063	C 6603	Yellow brown	Cv 1200 (Brereton)
Hu21	285	C 6675	Orthic A	Hu 2100 (Hayfield)
Hu21	285	C 6676	Red apedal	Hu 2100 (Hayfield)
Hu13	326	C 6744	Orthic A	Hu 1100 (Lillieburn)
Hu13	326	C 6745	Red apedal	Hu 1100 (Lillieburn)
Ct12	2085	C 6955	Lithocutanic	Family not determined (Constantia form)
Ct12	2085	C 6956	Lithocutanic	Family not determined (Constantia form)
Cv15	1318	C 7292	Yellow brown	Cv 1100 (Twyfelaar)
Cv15	1318	C 7293	Yellow brown	Cv 1100 (Twyfelaar)
Cv15	1318	C 7294	Yellow brown	Cv 1100 (Twyfelaar)
Cv25	1311	C 7309	Orthic A	Cv 2100 (Buckland)
Cv25	1311	C 7310	Yellow brown	Cv 2100 (Buckland)
Cv25	1311	C 7311	Yellow brown B	Cv 2100 (Buckland)

Table A1.1 Continued

Soil series	National profile	Lab number	Diagnostic horizon	Corresponding form and family (blue book)
Av35	1848	C 7415	Orthic A	Av 3100 (Kameelbos)
Av35	1848	C 7416	Yellow brown	Av 3100 (Kameelbos)
Av35	1848	C 7417	Soft plinthic B	Av 3100 (Kameelbos)
Cv44	1830	C 7743	Orthic A	1100/2100 Ag
Ch21	4562	C 7985	Organic O	Any family (Champagne form)
Ch21	4562	C 7986	G horizon	Any family (Champagne form)
Ia12	4760	C 8402	Humic A	Ia 1200 (Highlands)/2200 (Glenariff)
Ia12	4760	C 8404	Red apedal	Ia 1200 (Highlands)/2200 (Glenariff)
Hu12	10668	D 255	Orthic A	Hu 1100 (Lillieburn)
Hu12	10668	D 256	Red apedal B	Hu 1100 (Lillieburn)
Hu12	10668	D 257	4957 Red apedal	Hu 1100 (Lillieburn)
Cv28	12075	D 1657	Yellow brown	Cv 2200 (Leiden)
Gf23	12268	D 1773	Orthic A	Gf 2200 (Braeside)
Gf23	12268	D 1774	Yellow brown	Gf 2200 (Braeside)
Gf23	12268	D 1775	Red apedal B	Gf 2200 (Braeside)
Gf31	12039	D 1837	Orthic A	Gf 2100 (Maritzdrif)
Gf31	12039	D 1838	Yellow brown B	Gf 2100 (Maritzdrif)
Gf31	12039	D 1839	Red apedal B	Gf 2100 (Maritzdrif)
Ar42	13794	D 3967	Vertic A	Ar 3200 (Deercroft)
Ar42	13794	D 3968	Vertic A	Ar 3200 (Deercroft)
No11	13874	D 4138	Humic A	No 1200 (Overwood)/2200 (Peakvale)
No11	13874	D 4139	B	No 1200 (Overwood)/2200 (Peakvale)
Av13	13876	D 4142	Orthic A	Av 1100 (Blackmoor)
Av13	13876	D 4143	Yellow brown B	Av 1100 (Blackmoor)
Ma11	13882	D 4154	Humic A	Ma 2100 (Lambasi)/2200 (Ntsubane)
Ma12	14028	D 4414	Humic A	Ma 2100 (Lambasi)/2200 (Ntsubane)
Ma12	14028	D 4415	Yellow brown	Ma 2100 (Lambasi)/2200 (Ntsubane)
Hu48	14089	D 4646	Orthic A	1200/2200 Ag
Hu48	14089	D 4647	Red apedal	1200/2200 Ag
Ar10	14492	D 5542	Vertic A	Ar 1100 Lonehill
Cv11	14791	D 5894	Orthic A	Cv 1100 (Twyfelaar)
Av23	14831	D 5974	Orthic A	Av 2100 (Avondale)

Table A1.2 Continued

Soil series	National profile	Lab number	Diagnostic horizon	Cu sorbed (mg/kg soil)	pH $(CaCl_2)$	S value $(cmol_c/kg)$	Clay	Fe	Al	C
								(%)		
Ar 21	4197	C 1770	Vertic A	1786	6.50	29.1	61.1	6.08	0.21	1.60
		C 1771	Vertic A	1257	6.50	31.5	65.0	6.09	0.22	1.30
		C 1772	Vertic A	2384	7.20	34.4	65.9	8.08	0.21	0.90
		C 1773	Not Specified	2316	7.10	34.8	67.1	7.42	0.19	0.80
Av 25	4409	C 5269	Yellow-brown Apedal	16	4.10	1.4	13.4	1.05	0.16	0.10
Av 26	140	C 3672	Orthic A	112	5.10	2.8	13.3	1.00	0.11	0.50
Av 33	4443	C 2368	Orthic A	117	4.90	1.9	0.1	0.60	0.10	0.90
		C 2370	Yellow-brown Apedal	34	5.40	1.2	7.0	0.42	0.06	0.10
Av 36	1705	C 4556	Soft Plinthic	2084	7.40	12.8	20.2	0.78	0.05	0.15
Bo 20	8255	C 4282	Melanic A	2952	7.40	32.5	42.6	1.63	0.14	1.60
		C 4283	Pedocutanic	4380	8.20	30.0	40.9	1.51	0.10	0.40
		C 4284	Pedocutanic	5313	8.30	29.9	40.9	1.66	0.08	0.20
		C 4285	Pedocutanic	1381	8.20	18.9	31.4	1.71	0.07	0.10
Bo 30	4192	C 5105	Melanic A	885	5.60	18.7	36.7	3.00	0.35	2.20
		C 5106	Pedocutanic	1163	6.00	60.8	53.6	2.98	0.29	0.60
Ch 11	4017	C 4302	Organic O	22	4.40	2.4	16.8	0.39	0.01	1.60
		C 3817	E horizon	14	4.80	0.3	0.7	0.15	0.01	0.10
Ct 12	2085	C 6954	E horizon	22	4.60	0.5	1.9	0.01	0.01	0.40
Ct 23	2058	C 6819	E horizon	4	4.60	0.6	12.2	0.68	0.21	0.30
Cv 16	4115	C 4891	Orthic A	76	4.30	0.2	33.7	2.31	0.75	1.90
		C 4892	Yellow-brown Apedal	61	4.40	<0.1	34.0	2.51	0.73	1.30
		C 4893	E horizon	32	4.40	<0.1	26.1	2.23	0.47	0.60
Du 10	4021	C 3971	Stratified Alluvium	359	6.40	5.9	7.4	0.73	0.04	0.40
Fw 12	2651	C 3789	Regic Sand	13	4.50	0.3	0.5	0.01	0.00	0.10
		C 3790	Regic Sand	65	5.10	0.1	0.3	0.01	0.00	0.00
Gs 17	4656	C 4629	Lithocutanic	28	4.40	2.6	25.8	1.71	0.46	0.20
Hu 15	1761	C 4373	Red Apedal	11	4.20	0.3	11.3	1.14	0.05	0.10
		C 4374	Red Apedal	11	4.20	0.3	12.4	1.08	0.04	0.10
Hu 16	1770	C 4387	Red Apedal	29	4.40	0.6	19.6	3.39	0.14	0.10
		C 4388	Red Apedal	1379	4.30	1.3	20.1	2.65	0.11	0.10
Ia 11	4054	C 6485	Humic A	239	3.60	0.7	34.1	2.53	0.79	3.00
Ik 10	1863	C 7527	Neocutanic	200	5.90	2.7	13.1	0.52	0.04	1.00
		C 5199	Neocutanic	359	5.61	11.2	54.8	3.23	0.49	0.66
Kp 10	4060	C 5950	Humic A	5	4.30	1.1	15.3	2.60	1.11	3.90
Kp 11	4056	C 5961	Humic A	29	4.30	2.1	35.8	4.64	2.02	3.50
		C 5962	Humic A	14	4.30	1.4	58.8	4.82	1.99	2.20
Kp 12	4062	C 6597	Humic A	20	4.30	1.6	47.9	7.35	1.71	2.90
No 1100	11692	D 893	Lithocutanic	26	4.80	2.3	24.9	6.10	0.51	0.50
No 2100	11694	D 897	Lithocutanic	42	4.20	0.9	17.7	1.33	0.68	0.70
Oa 23	10933	D 396	Neocutanic	1253	8.35	14.8	10.6	0.61	0.04	0.24
Rg 20	8227	C 4389	G horizon	171	8.00	23.7	39.0	0.29	0.02	0.30
		C 4390	G horizon	368	5.70	21.5	51.1	0.87	0.10	0.20

Table A1.2 Continued

Soil series	National profile	Lab number	Diagnostic horizon	Cu sorbed (mg/kg soil)	pH ($CaCl_2$)	S value cmol$_c$/kg	Clay	Fe	Al	C
								(%)		
Rg 20	12678	C 2298	G horizon	579	7.10	27.1	41.3	0.38	0.11	0.10
Rg 20	12692	C 2338	Vertic A	248	6.20	23.6	46.8	0.36	0.06	0.60
Rg 20	12813	C 2561	G horizon	200	7.40	25.8	46.5	0.32	0.06	0.30
Sp 21	4277	C 3625	E horizon	34	4.50	0.1	4.0	0.72	0.08	0.14
		C 3626	Red Apedal	40	4.30	1.9	38.0	8.88	0.97	0.37
Ss 24	8243	C 1529	Prismacutanic	1482	7.40	13.8	22.8	0.34	0.03	0.30
Ss 25	2670	C 3433	Prismacutanic	687	6.50	13.9	44.4	4.12	0.64	0.30
Ss 26	8260	C 4318	Prismacutanic	544	6.20	11.8	24.6	1.13	0.12	0.40
We 13	118	C 2775	Soft Plinthic	185	6.00	8.3	33.6	1.19	0.21	0.40
We 13	134	C 3667	Soft Plinthic	200	5.10	11.6	53.2	3.29	0.20	0.60
We 13	130	C 3689	Soft Plinthic	191	5.60	8.8	47.1	1.06	0.11	0.50
Hu17	4829	C 1344	Red apedal B	246	4.80	0.1	49.7	5.65	0.66	0.70
Gf12	4831	C 1365	Yellow brown	72	4.30	0.1	43.0	2.64	0.65	1.22
Hu28	4832	C 1525	Orthic A	1003	6.40	16.6	64.4	8.39	0.47	3.60
Hu28	4833	C 1526	Red apedal	675	5.20	6.8	71.3	8.19	0.39	1.30
Cv23	4834	C 1539	Orthic A	80	4.20	1.3	6.0	0.42	0.03	0.30
Cv23	4835	C 1540	Yellow brown	31	4.20	0.9	8.0	0.52	0.03	0.20
Cv23	4836	C 1541	Yellow brown	57	4.00	1.9	9.2	0.57	0.04	0.20
Gf21	4837	C 1658	Orthic A	467	4.70	4.2	39.0	6.03	0.55	3.30
Gf21	4838	C 1659	Yellow brown B	442	5.40	3.6	52.9	6.97	0.86	1.00
Gf21	4839	C 1660	Red apedal B	434	5.80	4.1	35.0	8.83	0.74	0.30
Gf13	4840	C 1661	Orthic A	264	4.10	0.6	57.8	7.38	1.95	2.80
Gf13	4841	C 1662	Yellow brown	65	4.30	0.2	51.4	7.44	1.53	1.55
Gf13	4842	C 1663	Red apedal	126	4.30	0.2	50.2	7.66	1.47	1.65
Gf11	4843	C 1671	Orthic A	303	4.90	1.9	18.0	2.74	0.55	1.30
Gf11	4844	C 1672	Yellow Brown	46	4.60	0.8	22.0	2.72	0.52	0.52
Gf11	4845	C 1673	Red apedal	62	4.90	0.4	31.0	4.28	0.77	0.25
Hu22	4846	C 2194	Orthic A	165	5.60	0.6	5.1	0.33	0.02	0.30
Hu22	4847	C 2195	Red apedal B	57	4.90	0.4	3.5	0.29	0.05	0.10
Av15	4848	C 2288	Orthic A	134	4.80	0.2	8.0	0.37	0.04	0.30
Av15	4849	C 2289	Yellow brown	62	4.70	0.1	8.5	0.34	0.04	0.10
Av15	4850	C 2288	Soft plinthic B	234	6.20	1.3	14.1	0.23	0.08	0.10
Cv34	4852	C 2311	Yellow brown	285	7.10	3.2	10.6	0.61	0.05	0.20
Hu18	4853	C 2451	Orthic A	235	4.60	1.2	62.6	8.23	1.24	1.60
Hu18	4854	C 2452	Red apedal	179	4.90	0.7	67.0	9.76	1.51	1.00
Hu18	4855	C 2453	Red apedal	7	5.50	1.0	59.1	11.73	1.18	0.30
Gf22	4856	C 2454	Orthic A	5	4.60	0.6	52.2	7.14	1.71	2.00
Ct14	4864	C 3543	Lithocutanic	187	4.30	1.4	18.0	1.18	0.30	0.30
Gf20	4866	C 3554	Orthic A	6	4.60	0.4	12.7	0.87	0.34	0.70
Gf20	4867	C 3555	Yellow brown	136	4.60	1.1	14.5	0.89	0.22	0.20
Gf20	4868	C 3556	Red apedal B	10	4.40	2.2	27.8	2.70	0.46	0.20
Sp21	4869	C 3624	Orthic A	2	4.60	1.1	10.6	1.41	0.23	0.84
Sp21	4870	C 3627	C1	19	4.10	1.0	23.3	3.76	0.36	0.13
Sp21	4871	C 3628	C2	3	4.10	1.2	23.2	5.61	0.35	0.08
Av26	4872	C 3673	Yellow brown	121	5.50	2.7	19.5	1.22	0.13	0.20
Av26	4873	C 3674	Soft plinthic	172	4.80	5.1	45.5	3.87	0.37	0.20
Ik10	4874	C 3714	Melanic A	1992	6.20	23.9	43.6	1.14	0.05	1.80

Table A1.2 Continued

Soil series	**National profile**	**Lab number**	**Diagnostic horizon**	**Cu sorbed (mg/kg soil)**	**pH ($CaCl_2$)**	**S value cmol$_c$/kg**	**Clay**	**Fe**	**Al**	**C**
									(%)	
Ik10	4875	C 3715	Neocutanic B	657	6.60	14.6	11.5	1.07	0.05	0.30
Ik10	4877	C 3716	Orthic A	3	4.20	0.9	2.5	0.80	0.02	0.80
Ct11	4878	C 3816	C	6	5.20	0.4	3.3	0.16	0.07	0.10
Ct11	4881	C 3819	Orthic A	12	5.50	1.8	17.6	1.00	0.11	0.90
Hu27	4885	C 4094	Orthic A	4	5.00	4.5	31.1	2.61	0.16	1.00
Hu27	4886	C 4095	Red apedal B	6	5.00	4.9	40.2	3.62	0.23	0.90
Hu27	4887	C 4096	Red apedal	8	5.40	6.8	39.3	4.44	0.26	1.00
Av30	4888	C 4144	Orthic A	10	5.50	0.5	2.7	0.14	0.02	0.12
Cv27	4890	C 4205	Orthic A 4	9	5.00	4.5	28.6	2.18	0.12	1.00
Cv27	4891	C 4206	Yellow brown	287	5.00	5.1	43.4	3.16	0.23	0.60
Av31	4892	C 4344	Soft plinthic B	11	4.50	0.8	9.5	0.56	0.06	0.10
Cv26	4893	C 4375	Orthic A	142	4.40	1.1	13.5	1.08	0.12	0.40
Cv26	4894	C 4376	Yellow brown	107	4.60	1.6	18.0	1.61	0.15	0.30
Cv26	4895	C 4377	Yellow brown	98	4.60	1.4	23.8	1.38	0.12	0.20
Cv20	4896	C 4415	Orthic A	51	4.70	0.5	1.9	0.19	0.05	0.10
Cv20	4897	C 4416	Yellow brown	41	4.70	0.3	4.6	0.40	0.13	0.10
Av30	4898	C 4553	Soft plinthic B	19	5.80	1.3	2.8	0.15	0.01	0.10
Av30	4899	C 4554	G-horizon	68	5.80	1.5	6.2	0.20	0.01	0.10
Cv41	4901	C 4704	AB	1030	8.20	16.6	4.5	0.26	0.00	0.40
Cv42	4902	C 4926	Orthic A	254	7.80	9.6	1.8	0.56	0.00	0.30
Cv42	4903	C 4927	Yellow brown B	1364	7.90	10.7	4.1	0.37	0.01	0.10
Hu20	4904	C 5055	Orthic A	5	5.00	0.8	4.0	0.15	0.01	0.10
Hu20	4905	C 5056	Red apedal	3	5.10	0.8	4.2	0.13	0.01	0.00
Hu20	4906	C 5057	Red apedal	3	5.50	0.8	5.0	0.21	0.01	0.00
Cv37	4907	C 5078	Orthic A	13	5.40	4.7	22.8	0.60	0.09	0.30
Cv37	4908	C 5079	Yellow brown	310	5.50	7.9	44.3	2.60	0.09	0.30
Cv37	4909	C 5080	Yellow brown	397	6.10	8.6	39.4	2.01	0.16	0.20
Bo30	4910	C 5107	Unspecified	558	6.20	43.0	15.8	1.59	0.12	0.20
Av25	4911	C 5267	Orthic A	76	4.10	1.5	2.1	0.51	0.14	0.30
Av25	4912	C 5268	Yellow brown	72	4.00	1.7	13.8	0.75	0.19	0.30
Ch20	4913	C 5278	G horizon	318	3.90	3.2	55.8	1.23	0.29	1.20
Av22	4914	C 5794	Orthic A	148	5.10	1.0	4.1	0.20	0.00	0.30
Av22	4915	C 5796	Soft plinthic B	67	5.60	0.3	2.5	0.30	0.00	0.10
Av27	4916	C 5832	Orthic A	285	4.80	6.0	24.5	1.79	0.31	1.10
Av27	4917	C 5833	Yellow brown	161	4.90	4.0	40.1	2.54	0.55	0.40
Av27	4918	C 5834	Soft plinthic	210	5.30	5.9	49.4	3.20	0.56	0.30
No10	4919	C 5907	Humic A	85	3.90	0.2	24.3	1.30	0.52	2.70
No10	4920	C 5908	Humic A	161	4.00	0.3	22.4	1.34	0.57	1.80
Kp10	4921	C 5952	Red apedal B	96	4.70	0.5	24.0	4.39	0.82	0.40
Ia10	4922	C 5956	Humic A	176	4.10	1.2	29.0	2.69	0.93	3.40
Ia10	4923	C 5957	Red apedal	122	6.50	11.0	14.9	1.21	0.09	0.50
Ia10	4924	C 5958	Red apedal	89	4.30	0.6	33.0	3.42	0.57	0.30
Kp11	4925	C 5963	Yellow Brown	173	4.50	0.8	59.9	5.19	1.58	1.10
Cv48	4926	C 5993	Orthic A	1100	7.60	16.3	14.4	0.74	0.03	0.60
Cv21	4928	C 6387	Orthic A	139	4.70	<0.1	4.9	0.23	0.03	0.43
Cv21	4929	C 6388	Yellow brown	63	4.90	<0.1	5.7	0.30	0.02	0.36
Kp12	4930	C 6599	Yellow brown	227	4.40	0.7	65.5	8.52	1.86	1.60
Kp12	4931	C 6600	Red apedal	201	4.50	0.4	57.8	10.91	1.36	0.90

Table A1.2 Continued

Soil series	National profile	Lab number	Diagnostic horizon	Cu sorbed (mg/kg soil)	pH ($CaCl_2$)	S value $cmol_c/kg$	Clay	Fe	Al	C
									(%)	
Cv18	4932	C 6601	Orthic A	206	3.70	0.4	57.4	8.37	1.11	3.90
Cv18	4933	C 6602	Yellow brown	101	4.00	0.2	61.6	7.94	1.25	1.60
Cv18	4934	C 6603	Yellow brown	46	3.90	0.2	52.0	8.38	0.21	0.50
Ct12	4939	C 6955	Lithocutanic	67	4.50	0.6	3.8	0.03	0.07	0.40
Ct12	4940	C 6956	Lithocutanic	58	5.00	0.4	2.1	0.01	0.02	0.10
Cv15	4941	C 7292	Yellow brown	31	4.00	0.1	20.0	1.95	0.32	0.51
Cv15	4942	C 7293	Yellow brown	19	4.05	0.3	19.0	2.24	0.35	0.41
Cv15	4943	C 7294	Yellow brown	30	4.10	0.1	15.6	2.38	0.40	0.32
Cv25	4944	C 7309	Orthic A	201	5.64	1.1	4.8	0.15	0.02	0.13
Cv25	4945	C 7310	Yellow brown	601	4.37	0.4	5.7	0.17	0.02	0.07
Av35	4947	C 7415	Orthic A	312	5.70	4.4	10.7	0.86	0.06	0.36
Av35	4948	C 7416	Yellow brown	393	5.75	4.8	12.4	0.98	0.09	0.34
Av35	4949	C 7417	Soft plinthic B	306	5.61	7.7	18.3	1.12	0.10	0.32
Cv44	4950	C 7743	Orthic A	246	7.60	8.4	8.9	0.32	0.03	0.60
Ch21	4951	C 7985	Organic O	75	4.70	7.2	34.0	4.32	0.17	9.36
Ch21	4952	C 7986	G horizon	741	5.26	14.2	29.6	0.62	0.02	0.55
Ia12	4953	C 8402	Humic A	471	4.54	4.4	37.6	4.43	1.62	3.68
Ia12	4954	C 8404	Red apedal	274	4.93	2.5	53.8	6.63	0.93	0.51
Hu12	4955	D 255	Orthic A	277	3.97	0.2	5.6	1.23	0.20	2.56
Hu12	4956	D 256	Red apedal B	625	4.16	0.2	6.5	1.31	0.21	1.22
Hu12	4957	D 257	Red apedal	50	4.12	0.2	7.4	1.39	0.21	0.72
Cv28	4958	D 1657	Yellow brown	292	4.50	3.1	63.0	4.12	1.08	0.78
Gf23	4959	D 1773	Orthic A	234	4.20	2.9	42.1	2.70	0.56	1.48
Gf23	4960	D 1774	Yellow brown	238	4.52	4.1	58.3	2.71	0.38	1.06
Gf23	4961	D 1775	Red apedal B	55	4.73	4.0	46.9	2.60	0.16	0.53
Gf31	4962	D 1837	Orthic A	474	5.06	4.8	20.2	1.51	0.12	1.75
Gf31	4963	D 1838	Yellow brown	397	5.11	3.7	20.9	1.89	0.07	0.86
Gf31	4964	D 1839	Red apedal B	267	5.41	5.3	38.3	2.36	0.13	0.37
Ar42	4965	D 3967	Vertic A	1273	7.21	20.1	59.1	0.75	0.12	0.62
Ar42	4966	D 3968	Vertic A	1001	8.04	36.5	59.1	0.44	0.06	0.10

Table A1.2 Amount of Cu sorbed at 1 mg/l Cu solution concentration by a selection of South African soils in relation to their texture and chemical properties

Soil series	**National profile**	**Lab number**	**Diagnostic horizon**	**Cu sorbed (mg/kg soil)**	**pH (CaCl$_2$)**	**S value (cmol$_c$/kg)**	**Clay**	**Fe**	**Al**	**C**
							(%)			
Ar 21	4197	C 1770	Vertic A	1786	6.50	29.1	61.1	6.08	0.21	1.60
		C 1771	Vertic A	1257	6.50	31.5	65.0	6.09	0.22	1.30
		C 1772	Vertic A	2384	7.20	34.4	65.9	8.08	0.21	0.90
		C 1773	Not Specified	2316	7.10	34.8	67.1	7.42	0.19	0.80
Av 25	4409	C 5269	Yellow-brown Apedal	16	4.10	1.4	13.4	1.05	0.16	0.10
Av 26	140	C 3672	Orthic A	112	5.10	2.8	13.3	1.00	0.11	0.50
Av 33	4443	C 2368	Orthic A	117	4.90	1.9	0.1	0.60	0.10	0.90
		C 2370	Yellow-brown Apedal	34	5.40	1.2	7.0	0.42	0.06	0.10
Av 36	1705	C 4556	Soft Plinthic	2084	7.40	12.8	20.2	0.78	0.05	0.15
Bo 20	8255	C 4282	Melanic A	2952	7.40	32.5	42.6	1.63	0.14	1.60
		C 4283	Pedocutanic	4380	8.20	30.0	40.9	1.51	0.10	0.40
		C 4284	Pedocutanic	5313	8.30	29.9	40.9	1.66	0.08	0.20
		C 4285	Pedocutanic	1381	8.20	18.9	31.4	1.71	0.07	0.10
Bo 30	4192	C 5105	Melanic A	885	5.60	18.7	36.7	3.00	0.35	2.20
		C 5106	Pedocutanic	1163	6.00	60.8	53.6	2.98	0.29	0.60
Ch 11	4017	C 4302	Organic O	22	4.40	2.4	16.8	0.39	0.01	1.60
		C 3817	E horizon	14	4.80	0.3	0.7	0.15	0.01	0.10
Ct 12	2085	C 6954	E horizon	22	4.60	0.5	1.9	0.01	0.01	0.40
Ct 23	2058	C 6819	E horizon	4	4.60	0.6	12.2	0.68	0.21	0.30
Cv 16	4115	C 4891	Orthic A	76	4.30	0.2	33.7	2.31	0.75	1.90
		C 4892	Yellow-brown Apedal	61	4.40	<0.1	34.0	2.51	0.73	1.30
		C 4893	E horizon	32	4.40	<0.1	26.1	2.23	0.47	0.60
Du 10	4021	C 3971	Stratified Alluvium	359	6.40	5.9	7.4	0.73	0.04	0.40
Fw 12	2651	C 3789	Regic Sand	13	4.50	0.3	0.5	0.01	0.00	0.10
		C 3790	Regic Sand	65	5.10	0.1	0.3	0.01	0.00	0.00
Gs 17	4656	C 4629	Lithocutanic	28	4.40	2.6	25.8	1.71	0.46	0.20
Hu 15	1761	C 4373	Red Apedal	11	4.20	0.3	11.3	1.14	0.05	0.10
		C 4374	Red Apedal	11	4.20	0.3	12.4	1.08	0.04	0.10
Hu 16	1770	C 4387	Red Apedal	29	4.40	0.6	19.6	3.39	0.14	0.10
		C 4388	Red Apedal	1379	4.30	1.3	20.1	2.65	0.11	0.10
Ia 11	4054	C 6485	Humic A	239	3.60	0.7	34.1	2.53	0.79	3.00
Ik 10	1863	C 7527	Neocutanic	200	5.90	2.7	13.1	0.52	0.04	1.00
		C 5199	Neocutanic	359	5.61	11.2	54.8	3.23	0.49	0.66
Kp 10	4060	C 5950	Humic A	5	4.30	1.1	15.3	2.60	1.11	3.90
Kp 11	4056	C 5961	Humic A	29	4.30	2.1	35.8	4.64	2.02	3.50
		C 5962	Humic A	14	4.30	1.4	58.8	4.82	1.99	2.20
Kp 12	4062	C 6597	Humic A	20	4.30	1.6	47.9	7.35	1.71	2.90
No 1100	11692	D 893	Lithocutanic	26	4.80	2.3	24.9	6.10	0.51	0.50
No 2100	11694	D 897	Lithocutanic	42	4.20	0.9	17.7	1.33	0.68	0.70
Oa 23	10933	D 396	Neocutanic	1253	8.35	14.8	10.6	0.61	0.04	0.24
Rg 20	8227	C 4389	G horizon	171	8.00	23.7	39.0	0.29	0.02	0.30
		C 4390	G horizon	368	5.70	21.5	51.1	0.87	0.10	0.20

Table A1.3 Amount of P sorbed at 1 mg/l P solution concentration by a selection of South African soils in relation to their texture and chemical properties

Soil series	Lab number	National profile	Diagnostic horizon	P sorbed (mg/kg soil)	pH ($CaCl_2$)	S value (cmolc/kg)	Clay	Fe	Al	C
							(%)			
Ar 21	4197	C 1770	Vertic A	291	6.50	29.1	61.1	6.08	0.21	1.60
Ar 21	4197	C 1771	Vertic A	93	6.50	31.5	65.0	6.09	0.22	1.30
Ar 21	4197	C 1772	Vertic A	410	7.20	34.4	65.9	8.08	0.21	0.90
Ar 21	4197	C 1773	Not Specified	140	7.10	34.8	67.1	7.42	0.19	0.80
Av 25	4409	C 5269	Yellow-brown Apedal	256	4.10	1.4	13.4	1.05	0.16	0.10
Av 26	140	C 3672	Orthic A	90	5.10	2.8	13.3	1.00	0.11	0.50
Av 31	1784	C 4342	Orthic A	100	4.20	0.9	3.3	0.17	0.02	0.30
Av 33	4443	C 2368	Orthic A	64	4.90	1.9	0.1	0.60	0.10	0.90
Av 33	4443	C 2370	Yellow-brown Apedal	79	5.40	1.2	7.0	0.42	0.06	0.10
Av 36	1705	C 4556	Soft Plinthic	124	7.40	12.8	20.2	0.78	0.05	0.15
Bo 20	8255	C 4283	Pedocutanic	99	8.20	30.0	40.9	1.51	0.10	0.40
Bo 20	8255	C 4284	Pedocutanic	148	8.30	29.9	40.9	1.66	0.08	0.20
Bo 20	8255	C 4285	Pedocutanic	48	8.20	18.9	31.4	1.71	0.07	0.10
Bo 30	4192	C 5105	Melanic A	245	5.60	18.7	36.7	3.00	0.35	2.20
Bo 30	4192	C 5106	Pedocutanic	342	6.00	60.8	53.6	2.98	0.29	0.60
Ch 11	4017	C 4302	Organic O	404	4.40	2.4	16.8	0.39	0.01	1.60
Ct 11	2357	C 3817	E - horizon	17	4.80	0.3	0.7	0.15	0.01	0.10
Ct 12	2085	C 6954	E - horizon	17	4.60	0.5	1.9	0.01	0.01	0.40
Ct 23	2058	C 6819	E - horizon	205	4.60	0.6	12.2	0.68	0.21	0.30
Cv 16	4115	C 4892	Yellow-brown Apedal	990	4.40	0.0	34.0	2.51	0.73	1.30
Du 10	2657	C 2403	Stratified Alluvium	211	4.60	13.0	42.8	1.07	1.46	1.40
Du 10	4117	C 1629	Stratified Alluvium	395	4.80	0.4	4.1	0.37	0.10	0.30
Du 10	4117	C 1630	Stratified Alluvium	358	4.70	0.3	6.3	0.33	0.21	0.30
Du 10	4021	C 3971	Stratified Alluvium	184	6.40	5.9	7.4	0.73	0.04	0.40
Fw 12	2651	C 3789	Regic Sand	8	4.50	0.3	0.5	0.01	0.00	0.10
Fw 12	2651	C 3790	Regic Sand	15	5.10	0.1	0.3	0.01	0.00	0.00
Gf 22	4126	C 2456	Red Apedal	1500	5.60	0.8	65.9	8.84	1.43	0.50
Gs 10	2346	C 5150	Lithocutanic	10	5.00	1.1	6.5	0.60	0.04	0.30
Gs 12	964	C 6932	Lithocutanic	170	5.10	2.3	4.8	0.45	0.05	0.40
Gs 14	18	C 4002	Lithocutanic	201	4.60	1.8	15.4	1.09	0.15	0.60
Gs 16	4211	C 4816	Lithocutanic	973	6.00	8.2	36.5	4.65	0.67	0.60
Hu 15	1761	C 4373	Red Apedal	201	4.20	0.3	11.3	1.14	0.05	0.10
Hu 15	1761	C 4374	Red Apedal	307	4.20	0.3	12.4	1.08	0.04	0.10
Hu 16	1770	C 4387	Red Apedal	211	4.40	0.6	19.6	3.39	0.14	0.10
Hu 16	1770	C 4388	Red Apedal	211	4.30	1.3	20.1	2.65	0.11	0.10
Ia 11	4054	C 6485	Humic A	255	3.60	0.7	34.1	2.53	0.79	3.00
Ik 10	1863	C 7527	Neocutanic	159	5.90	2.7	13.1	0.52	0.04	1.00
Ik 10	2943	C 5199	Melanic A	43	5.61	16.3	31.2	1.11	0.07	0.75
Kp 10	4060	C 5950	Humic A	736	4.30	1.1	15.3	2.60	1.11	3.90
Kp 11	4056	C 5961	Humic A	1501	4.30	2.1	35.8	4.64	2.02	3.50
Kp 11	4056	C 5962	Humic A	2212	4.30	1.4	58.8	4.82	1.99	2.20
Kp 12	4062	C 6597	Humic A	613	4.30	1.6	47.9	7.35	1.71	2.90
No 10	4334	C 4122	Lithocutanic	427	4.80	2.3	24.9	6.10	0.51	0.50
No 10	4090	C 6023	Lithocutanic	531	4.20	0.9	17.7	1.33	0.68	0.70
Oa 23	10933	D 396	Neocutanic	254	8.38	14.8	10.6	0.61	0.04	0.24
Oa 23	10933	D 397	Neocutanic	223	8.35	<0.1	17.2	0.70	0.04	0.29
Oa 46	10837	D 388	Neocutanic	102	8.13	29.8	15.7	0.82	0.05	0.47
Rg 20	8227	C 4389	G - horizon	316	8.00	23.7	39.0	0.29	0.02	0.30
Rg 20	8227	C 4390	G - horizon	55	5.70	21.5	51.1	0.87	0.10	0.20

Table A1.3 Continued

Soil series	Lab number	National profile	Diagnostic horizon	P sorbed (mg/kg soil)	pH ($CaCl_2$)	S value (cmolc/kg)	Clay	Fe	Al	C
								(%)		
Rg 20	C 2298	12678	G - horizon	58	7.10	27.1	41.3	0.38	0.11	0.10
Rg 20	C 2338	12692	Vertic A	135	6.20	23.6	46.8	0.36	0.06	0.60
Rg 20	C 2561	12813	G - horizon	212	7.40	25.8	46.5	0.32	0.06	0.30
Sp 21	C 3626	4277	Red Apedal	595	4.30	1.9	38.0	8.88	0.97	0.37
Ss 24	C 1529	8243	Prismacutanic	246	6.20	13.6	24.4	0.40	0.04	0.60
Ss 24	C 1528	8243	Prismacutanic	112	7.40	13.8	22.8	0.34	0.03	0.30
Ss 25	C 3433	2670	Prismacutanic	261	6.50	13.9	44.4	4.12	0.64	0.30
Ss 26	C 4318	8260	Prismacutanic	157	6.20	11.8	24.6	1.13	0.12	0.40
We 13	C 2775	118	Soft Plinthic	336	6.00	8.3	33.6	1.19	0.21	0.40
We 13	C 3667	134	Soft Plinthic	406	5.10	11.6	53.2	3.29	0.20	0.60
We 13	C 3689	130	Soft Plinthic	359	5.60	8.8	47.1	1.06	0.11	0.50
We 13	C 3690	130	Soft Plinthic	492	6.40	18.4	65.7	1.60	0.14	0.00
Hu17	C 1344	6363	Red apedal B	645	4.80	0.1	49.7	5.65	0.66	0.70
Gf12	C 1364	6365	Orthic A	680	4.20	0.5	33.3	1.66	0.33	2.59
Gf12	C 1365	6365	Yellow brown	358	4.30	0.1	43.0	2.64	0.65	1.22
Hu28	C 1525	8238	Orthic A	305	6.40	16.6	64.4	8.39	0.47	3.60
Hu28	C 1526	8238	Red apedal	265	5.20	6.8	71.3	8.19	0.39	1.30
Cv23	C 1540	8246	Yellow brown	286	4.20	0.9	8.0	0.52	0.03	0.20
Cv23	C 1541	8246	Yellow brown	192	4.00	1.9	9.2	0.57	0.04	0.20
Gf21	C 1658	4168	Orthic A	242	4.70	4.2	39.0	6.03	0.55	3.30
Gf21	C 1659	4168	Yellow brown B	683	5.40	3.6	52.9	6.97	0.86	1.00
Gf21	C 1660	4168	Red apedal B	884	5.80	4.1	35.0	8.83	0.74	0.30
Gf13	C 1661	6381	Orthic A	1490	4.10	0.6	57.8	7.38	1.95	2.80
Gf13	C 1662	6381	Yellow brown	1613	4.30	0.2	51.4	7.44	1.53	1.55
Gf13	C 1663	6381	Red apedal	1147	4.30	0.2	50.2	7.66	1.47	1.65
Gf11	C 1671	6379	Orthic A	200	4.90	1.9	18.0	2.74	0.55	1.30
Gf11	C 1672	6379	Yellow Brown B	383	4.60	0.8	22.0	2.72	0.52	0.52
Gf11	C 1673	6379	Red apedal	573	4.90	0.4	31.0	4.28	0.77	0.25
Hu22	C 2194	428	Orthic A	25	5.60	0.6	5.1	0.33	0.02	0.30
Hu22	C 2195	428	Red apedal B	94	4.90	0.4	3.5	0.29	0.05	0.10
Av15	C 2288	461	Orthic A	59	4.80	0.2	8.0	0.37	0.04	0.30
Av15	C 2288	461	Yellow brown	58	4.70	0.1	8.5	0.34	0.04	0.10
Av15	C 2289	461	Soft plinthic B	136	6.20	1.3	14.1	0.23	0.08	0.10
Cv34	C 2310	8341	Orthic A	64	7.80	5.0	8.0	0.48	0.04	0.20
Cv34	C 2311	8341	Yellow brown B	128	7.10	3.2	10.6	0.61	0.05	0.20
Hu18	C 2451	4125	Orthic A	658	4.60	1.2	62.6	8.23	1.24	1.60
Hu18	C 2452	4125	Red apedal	461	4.90	0.7	67.0	9.76	1.51	1.00
Hu18	C 2453	4125	Red apedal	1403	5.50	1.0	59.1	11.73	1.18	0.30
Gf22	C 2454	4126	Orthic A	1007	4.60	0.6	52.2	7.14	1.71	2.00
Gf22	C 2455	4126	Yellow brown	2628	5.10	0.6	55.7	7.37	1.57	1.30
Cv13	C 2493	4145	Orthic A	98	4.30	0.2	6.6	0.00	0.01	0.30
Cv13	C 2494	4145	Yellow brown	212	4.20	0.2	10.7	0.57	0.10	0.30
Cv13	C 2495	4145	Yellow brown	196	4.30	0.2	12.0	0.66	0.11	0.20
Cv13	C 2496	4145	C	620	4.50	0.5	8.0	1.22	0.11	0.20
Ct14	C 3541	2359	E horizon	111	3.90	0.8	8.5	0.32	0.14	1.00
Ct14	C 3542	2359	Lithocutanic	400	4.10	0.8	12.0	0.51	0.14	0.20
Ct14	C 3543	2359	Lithocutanic	443	4.30	1.4	18.0	1.18	0.30	0.30
Ct14	C 3544	2359	C	77	4.40	0.1	8.0	0.43	0.09	0.10
Gf20	C 3554	2349	Orthic A	350	4.60	0.4	12.7	0.87	0.34	0.70
Gf20	C 3555	2349	Yellow brown B	227	4.60	1.1	14.5	0.89	0.22	0.20

Table A1.3 Continued

Soil series	Lab number	National profile	Diagnostic horizon	P sorbed (mg/kg soil)	pH ($CaCl_2$)	S value (cmolc/kg)	Clay	Fe	Al	C
								(%)		
Gf20	C 3556	2349	Red apedal B	450	4.40	2.2	27.8	2.70	0.46	0.20
Sp21	C 3624	4277	Orthic A	94	4.60	1.1	10.6	1.41	0.23	0.84
Sp21	C 3627	4277	C1	273	4.10	1.0	23.3	3.76	0.36	0.13
Sp21	C 3628	4277	C2	341	4.10	1.2	23.2	5.61	0.35	0.08
Av26	C 3673	140	Yellow brown	170	5.50	2.7	19.5	1.22	0.13	0.20
Av26	C 3674	140	Soft plinthic	477	4.80	5.1	45.5	3.87	0.37	0.20
Ik10	C 3714	1731	Melanic A	119	6.20	23.9	43.6	1.14	0.05	1.80
Ik10	C 3715	1731	Neocutanic B	83	6.60	14.6	11.5	1.07	0.05	0.30
Ik10	C 3716	1731	Neocutanic B	80	6.90	24.9	35.3	0.79	0.12	0.40
Ik10	C 3816	2357	Orthic A	12	4.20	0.9	2.5	0.80	0.02	0.80
Ct11	C 3819	2357	C	88	5.20	0.4	3.3	0.16	0.07	0.10
Cv14	C 3984	4	Orthic A	83	4.90	1.2	10.0	1.10	0.20	0.80
Av37	C 3819	2357	Orthic A	118	5.50	32.3	17.6	1.00	0.11	0.90
Av37	C 4088	1805	Yellow brown	415	5.00	6.1	31.6	1.45	0.18	0.60
Av37	C 4089	1805	Yellow brown	374	5.00	9.5	46.6	1.60	0.25	0.50
Av37	C 4090	1805	Soft plinthic B	519	5.20	12.4	50.7	1.91	0.24	0.20
Hu27	C 4094	1808	Orthic A	151	5.00	4.5	31.1	2.61	0.16	1.00
Hu27	C 4095	1808	Red apedal B	281	5.00	4.9	40.2	3.62	0.23	0.90
Hu27	C 4096	1808	Red apedal	426	5.40	6.8	39.3	4.44	0.26	1.00
Av30	C 4144	8339	Orthic A	42	5.50	0.5	2.7	0.14	0.02	0.12
Av30	C 4245	4007	Yellow brown	65	4.90	0.0	1.3	0.12	0.02	0.10
Cv27	C 4205	1764	Orthic A	136	5.00	4.5	28.6	2.18	0.12	1.00
Cv27	C 4206	1764	Yellow brown	407	5.00	5.1	43.4	3.16	0.23	0.60
Av31	C 4344	1784	Soft plinthic B	155	4.50	0.8	9.5	0.56	0.06	0.10
Cv26	C 4375	1767	Orthic A	107	4.40	1.1	13.5	1.08	0.12	0.40
Cv26	C 4376	1767	Yellow brown	186	4.60	1.6	18.0	1.61	0.15	0.30
Cv26	C 4377	1767	Yellow brown	164	4.60	1.4	23.8	1.38	0.12	0.20
Cv20	C 4415	2674	Orthic A	47	4.70	0.5	1.9	0.19	0.05	0.10
Cv20	C 4416	2674	Yellow brown	115	4.70	0.3	4.6	0.40	0.13	0.10
Av30	C 4553	8339	Soft plinthic B	113	5.80	1.3	2.8	0.15	0.01	0.10
Av30	C 4554	8339	G-horizon	48	5.80	1.5	6.2	0.20	0.01	0.10
Av36	C 4555	1705	Soft plinthic	184	5.80	5.7	22.5	0.80	0.12	0.21
Cv41	C 4704	216	AB	31	8.20	16.6	4.5	0.26	0.00	0.40
Cv42	C 4926	2220	Orthic A	49	7.80	9.6	1.8	0.56	0.00	0.30
Cv42	C 4927	2220	Yellow brown B	60	7.90	10.7	4.1	0.37	0.01	0.10
Hu20	C 5055	6279	Orthic A	54	5.00	0.8	4.0	0.15	0.01	0.10
Hu20	C 5056	6279	Red apedal	37	5.10	0.8	4.2	0.13	0.01	0.00
Hu20	C 5057	6279	Red apedal	40	5.50	0.8	5.0	0.21	0.01	0.00
Cv37	C 5078	6292	Orthic A	143	5.40	4.7	22.8	0.60	0.09	0.30
Cv37	C 5079	6292	Yellow brown	153	5.50	7.9	44.3	2.60	0.09	0.30
Cv37	C 5080	6292	Yellow brown B	160	6.10	8.6	39.4	2.01	0.16	0.20
Bo30	C 5107	4192	Unspecified	278	6.20	43.0	15.8	1.59	0.12	0.20
Av25	C 5267	4409	Orthic A	76	4.10	1.5	2.1	0.51	0.14	0.30
Av25	C 5268	4409	Yellow brown B	85	4.00	1.7	13.8	0.75	0.19	0.30
Ch20	C 5278	4136	G horizon	701	3.90	3.2	55.8	1.23	0.29	1.20
Av22	C 5794	206	Orthic A	33	5.10	1.0	4.1	0.20	0.00	0.30
Av22	C 5796	206	Soft plinthic B	29	5.60	0.3	2.5	0.30	0.00	0.10
Av27	C 5832	4027	Orthic A	144	4.80	6.0	24.5	1.79	0.31	1.10
Av27	C 5833	4027	Yellow brown	458	4.90	4.0	40.1	2.54	0.55	0.40
Av27	C 5834	4027	Soft plinthic	332	5.30	5.9	49.4	3.20	0.56	0.30

Table A1.3 Continued

Soil class	Lab number	National profile	Horizon	P sorbed (mg/kg soil)	pH (CaCl$_2$)	S value (cmolc/kg)	Clay	Fe	Al	C
								(%)		
No10	C 5907	4077	Humic A	364	3.90	0.2	24.3	1.30	0.52	2.70
No10	C 5908	4077	Humic A	414	4.00	0.3	22.4	1.34	0.57	1.80
Kp10	C 5952	4060	Red apedal B	581	4.70	0.5	24.0	4.39	0.82	0.40
Ia10	C 5956	4057	Humic A	1146	4.10	1.2	29.0	2.69	0.93	3.40
Ia10	C 5957		Red apedal	782	6.50	11.0	14.9	1.21	0.09	0.50
Ia10	C 5958	4057	Red apedal	605	4.30	0.6	33.0	3.42	0.57	0.30
Kp11	C 5963	4056	Yellow Brown	504	4.50	0.8	59.9	5.19	1.58	1.10
Cv48	C 5993	2263	Orthic A	34	7.60	16.3	14.4	0.74	0.03	0.60
Cv48	C 5994	2263	Yellow brown B	354	7.80	16.3	13.8	0.55	0.03	0.50
Cv21	C 6387	2015	Orthic A	15	4.70	<0.1	4.9	0.23	0.03	0.43
Kp12	C 6599	4062	Yellow brown	1208	4.40	0.7	65.5	8.52	1.86	1.60
Cv18	C 6601	4063	Orthic A	811	3.70	0.4	57.4	8.37	1.11	3.90
Cv18	C 6602	4063	Yellow brown	1091	4.00	0.2	61.6	7.94	1.25	1.60
Cv18	C 6603	4063	Yellow brown	644	3.90	0.2	52.0	8.38	0.21	0.50
Ct12	C 6955	2085	Lithocutanic	96	4.50	0.6	3.8	0.03	0.07	0.40
Ct12	C 6956	2085	Lithocutanic	73	5.00	0.4	2.1	0.01	0.02	0.10
Cv15	C 7292	1318	Yellow brown	163	4.00	0.1	20.0	1.95	0.32	0.51
Cv15	C 7293	1318	Yellow brown	217	4.05	0.3	19.0	2.24	0.35	0.41
Cv15	C 7294	1318	Yellow brown	225	4.10	0.1	15.6	2.38	0.40	0.32
Cv25	C 7309	1311	Orthic A	19	5.64	1.1	4.8	0.15	0.02	0.13
Cv25	C 7310	1311	Yellow brown	12	4.37	0.4	5.7	0.17	0.02	0.07
Cv25	C 7311	1311	Yellow brown B	45	4.52	0.3	7.0	0.19	0.01	0.06
Av35	C 7415	1848	Orthic A	52	5.70	4.4	10.7	0.86	0.06	0.36
Av35	C 7416	1848	Yellow brown	97	5.75	4.8	12.4	0.98	0.09	0.34
Av35	C 7417	1848	Soft plinthic B	146	5.61	7.7	18.3	1.12	0.10	0.32
Cv44	C 7743	1830	Orthic A	43	7.60	8.4	8.9	0.32	0.03	0.60
Ch21	C 7985	4562	Organic O	1537	4.70	7.2	34.0	4.32	0.17	9.36
Ch21	C 7986	4562	G horizon	553	5.26	14.2	29.6	0.62	0.02	0.55
Ia12	C 8402	4760	Humic A	880	4.54	4.4	37.6	4.43	1.62	3.68
Ia12	C 8404	4760	Red apedal	1593	4.93	2.5	53.8	6.63	0.93	0.51
Hu12	D 255	10668	Orthic A	149	3.97	0.2	5.6	1.23	0.20	2.56
Hu12	D 256	10668	Red apedal B	135	4.16	0.2	6.5	1.31	0.21	1.22
Hu12	D 257	10668	Red apedal	250	4.12	0.2	7.4	1.39	0.21	0.72
Cv28	D 1657	12075	Yellow brown	801	4.50	3.1	63.0	4.12	1.08	0.78
Gf23	D 1773	12268	Orthic A	400	4.20	2.9	42.1	2.70	0.56	1.48
Gf23	D 1774	12268	Yellow brown	776	4.52	4.1	58.3	2.71	0.38	1.06
Gf23	D 1775	12268	Red apedal B	708	4.73	4.0	46.9	2.60	0.16	0.53
Gf31	D 1837	12039	Orthic A	329	5.06	4.8	20.2	1.51	0.12	1.75
Gf31	D 1838	12039	Yellow brown B	268	5.11	3.7	20.9	1.89	0.07	0.86
Gf31	D 1839	12039	Red apedal B	729	5.41	5.3	38.3	2.36	0.13	0.37
Ar42	D 3968	13794	Vertic A	268	8.04	36.5	59.1	0.44	0.06	0.10

Table A1.4 Continued

Soil series	Lab number	National profile	Diagnostic horizon	Zn sorbed	Cu sorbed
				(mg/kg soil)	
Ik10	C 3716	1731	Orthic A	3	3
Ct11	C 3819	2357	Orthic A	12	12
Hu27	C 4094	1808	Orthic A	4	4
Hu27	C 4095	1808	Red apedal B	6	6
Hu27	C 4096	1808	Red apedal	8	8
Av30	C 4144	8339	Orthic A	5	10
Cv27	C 4205	1764	Orthic A	9	9
Cv26	C 4375	1767	Orthic A	7	142
Cv20	C 4415	2674	Orthic A	3	51
Av30	C 4554	8339	G-horizon	10	68
Cv42	C 4926	2220	Orthic A	291	254
Hu20	C 5055	6279	Orthic A	5	5
Hu20	C 5056	6279	Red apedal	3	3
Hu20	C 5057	6279	Red apedal	3	3
Cv37	C 5078	6292	Orthic A	14	13
Av25	C 5267	4409	Orthic A	2	76
Ch20	C 5278	4136	G horizon	10	318
Av22	C 5794	206	Orthic A	3	148
Av27	C 5832	4027	Orthic A	11	285
No10	C 5907	4077	Humic A	3	85
No10	C 5908	4077	Humic A	5	161
Kp10	C 5952	4060	Red apedal B	5	96
Ia10	C 5956	4057	Humic A	7	176
Ia10	C 5957	4923	Red apedal	7	122
Ia10	C 5958	4057	Red apedal	8	89
Cv48	C 5993	2263	Orthic A	508	1100
Cv21	C 6387	2015	Orthic A	3	139
Kp12	C 6600	4062	Red apedal	11	201
Cv18	C 6601	4063	Orthic A	6	206
Cv25	C 7309	1311	Orthic A	3	201
Av35	C 7415	1848	Orthic A	6	312
Cv44	C 7743	1830	Orthic A	3	246
Ch21	C 7986	4562	G horizon	169	741
Ia12	C 8402	4760	Humic A	19	471
Ia12	C 8404	4760	Red apedal	7	274
Hu12	D 255	10668	Orthic A	1	277
Hu12	D 256	10668	Red apedal B	0	625
Hu12	D 257	10668	Red apedal	1	50
Gf23	D 1773	12268	Orthic A	7	234
Gf23	D 1775	12268	Red apedal B	14	55
Gf31	D 1837	12039	Orthic A	77	474
Gf31	D 1839	12039	Red apedal B	20	267
Ar42	D 3967	13794	Vertic A	315	1273
Ar42	D 3968	13794	Vertic A	700	1001

Table A1.4 Comparison between the amount of zinc sorbed and the amount of copper sorbed at 1 mg/l solution concentration in selected South African soils

Soil class	Lab number	National profile	Horizon	Zn sorbed	Cu sorbed
				(mg/kg soil)	
Ar 21	C 1770	4197	Vertic A	356	1786
Ar 21	C 1771	4197	Vertic A	293	1257
Ar 21	C 1772	4197	Vertic A	9	2384
Av 26	C 3672	140	Orthic A	6	112
Av 33	C 2368	4443	Orthic A	2	117
Bo 20	C 4282	8255	Melanic A	743	2952
Bo 20	C 4283	8255	Pedocutanic	873	4380
Bo 20	C 4284	8255	Pedocutanic	837	5313
Bo 30	C 5105	4192	Melanic A	189	885
Bo 30	C 5106	4192	Pedocutanic	187	1163
Ct 11	C 3817	2357	E - horizon	2	14
Ct 12	C 6954	2085	E - horizon	2	22
Ct 23	C 6819	2058	E - horizon	4	4
Cv 16	C 4891	4115	Orthic A	5	76
Fw 12	C 3789	2651	Regic Sand	2	65
Hu 15	C 4373	1761	Red Apedal	1	11
Hu 15	C 4374	1761	Red Apedal	12	11
Hu 16	C 4387	1770	Red Apedal	17	1379
Ia 11	C 6485	4054	Humic A	4	239
Kp 10	C 5950	4060	Humic A	5	5
Kp 11	C 5961	4056	Humic A	29	29
Kp 11	C 5962	4056	Humic A	14	14
Kp 12	C 6597	4062	Humic A	20	20
Rg 20	C 4389	8227	G - horizon	368	368
Rg 20	C 2298	12678	G - horizon	579	579
Rg 20	C 2338	12692	Vertic A	120	248
Rg 20	C 2561	12813	G - horizon	200	200
Hu17	C 1344	6363	Red apedal B	9	246
Hu28	C 1525	8238	Orthic A	472	1003
Hu28	C 1526	8238	Red apedal	60	675
Cv23	C 1539	8246	Orthic A	4	80
Gf21	C 1658	4168	Orthic A	26	467
Gf21	C 1660	4168	Red apedal B	47	434
Gf13	C 1661	6381	Orthic A	10	264
Gf13	C 1663	6381	Red apedal	8	126
Gf11	C 1671	6379	Orthic A	6	303
Gf11	C 1673	6379	Red apedal	1	62
Hu22	C 2194	428	Orthic A	3	165
Hu22	C 2195	428	Red apedal B	2	57
Cv34	C 2310	8341	Orthic A	30	575
Hu18	C 2452	4125	Red apedal	1	179
Hu18	C 2453	4125	Red apedal	7	7
Gf22	C 2454	4126	Orthic A	5	5
Gf20	C 3554	2349	Orthic A	3	6
Gf20	C 3556	2349	Red apedal B	10	10
Sp21	C 3624	4277	Orthic A	2	2
Sp21	C 3627	4277	C1	3	19
Sp21	C 3628	4277	C2	3	3
Ik10	C 3714	1731	Melanic A	215	1992

Table A1.5 Comparison between the amount of sulfate sorbed and the amount of P sorbed at 1 mg/l solution concentration in selected South African soils

Soil class	Lab number	National profile	Horizon	S sorbed	P sorbed
				(mg/kg soil)	
Hu28	C 1525	8238	Orthic A	11	305
Hu28	C 1526	8238	Red apedal	35	265
Gf21	C 1660	4168	Red apedal B	91	884
Hu22	C 2194	428	Orthic A	6	25
Cv34	C 2310	8341	Orthic A	11	64
Sp21	C 3627	4277	C1	101	273
Sp21	C 3628	4277	C2	136	341
Ct11	C 3819	2357	Orthic A	13	118
Hu27	C 4094	1808	Orthic A	2	151
Hu27	C 4095	1808	Red apedal B	3	281
Hu27	C 4096	1808	Red apedal	0	426
Cv26	C 4375	1767	Orthic A	19	107
Cv20	C 4415	2674	Orthic A	3	47
Av30	C 4554	8339	G-horizon	7	48
Hu20	C 5056	6279	Red apedal	4	37
Hu20	C 5057	6279	Red apedal	7	40
Cv37	C 5078	6292	Orthic A	19	143
Av25	C 5267	4409	Orthic A	16	76
Ch20	C 5278	4136	G horizon	90	701
Av22	C 5794	206	Orthic A	8	33
Av27	C 5832	4027	Orthic A	17	144
No10	C 5908	4077	Humic A	91	414
Kp10	C 5952	4060	Red apedal B	18	581
Ia10	C 5956	4057	Humic A	144	1146
Ia10	C 5958	4057	Red apedal	52	605
Cv48	C 5993	2263	Orthic A	9	34
Cv18	C 6601	4063	Orthic A	47	811
Av35	C 7415	1848	Orthic A	57	52
Cv44	C 7743	1830	Orthic A	4	43
Ch21	C 7986	4562	G horizon	56	553
Ia12	C 8402	4760	Humic A	227	880
Ia12	C 8404	4760	Red apedal	1394	1593
Hu12	D 255	10668	Orthic A	38	149
Hu12	D 256	10668	Red apedal B	2	135
Gf23	D 1775	12268	Red apedal B	228	708
Gf31	D 1837	12039	Orthic A	72	329
Gf31	D 1839	12039	Red apedal B	1045	729

APPENDIX 2- Supplementary data from chapter 3

Table A2.1 Equilibrium Cu concentration in relation to solution pH after addition of 1000 mg Cu/kg to four soils. The soils were treated with 1 M HCl and titrated with 1 M NaOH

Soil	pH	Concentration (mg/l)
PM1A		
	3.36	27.97
	4.54	16.02
	5.4	3.68
	6.33	1.19
	7.78	0.51
	8.82	0.39
	9.95	0.54
PM2A		
	3.3	22.91
	4.76	14.15
	5.73	2.66
	6.24	0.94
	7.46	0.51
	8.48	0.44
	9.68	0.55
PM1B		
	3.03	31.47
	4.86	21.97
	5.55	8.97
	6.61	1.25
	7.36	0.57
	8.52	0.4
	9.95	0.65
PM2B		
	3.41	30.32
	4.85	21.67
	5.68	8.05
	6.03	3.37
	7.35	0.69
	8.43	0.43
	9.84	0.44

Table A2.2 Equilibrium P concentration in relation to solution pH after addition of 500 mg P/kg to four soils. The soils were treated with 1 M NaOH and titrated with 1 M HCl

P treatment (mg/kg soil)	**pH**	**P sorbed (mg/kg)**
PM1A		
500	3.29	439
500	4.19	479
500	5.32	488
500	6.19	488
500	7.45	471
500	8.53	442
500	9.19	424
PM2A		
500	3.32	362
500	4.07	393
500	5.32	407
500	6.26	405
500	7.76	387
500	8.6	328
500	9.31	335
PM1B		
500	3.64	460
500	4.89	485
500	5.45	487
500	6.83	477
500	7.76	461
500	8.49	442
500	9.19	422
PM2B		
500	3.17	445
500	4.1	465
500	5.81	493
500	6.39	493
500	7.46	479
500	8.24	464
500	9.21	439

APPENDIX 3- Methods and data reliability

A3.1 Quantile regression

In search for the best fit, we tried different quantile regressions; however 0.95 quantile provided the best R^2 for all the data. The figure hereunder shows the chemical envelope for Cu sorption as a function of S value.

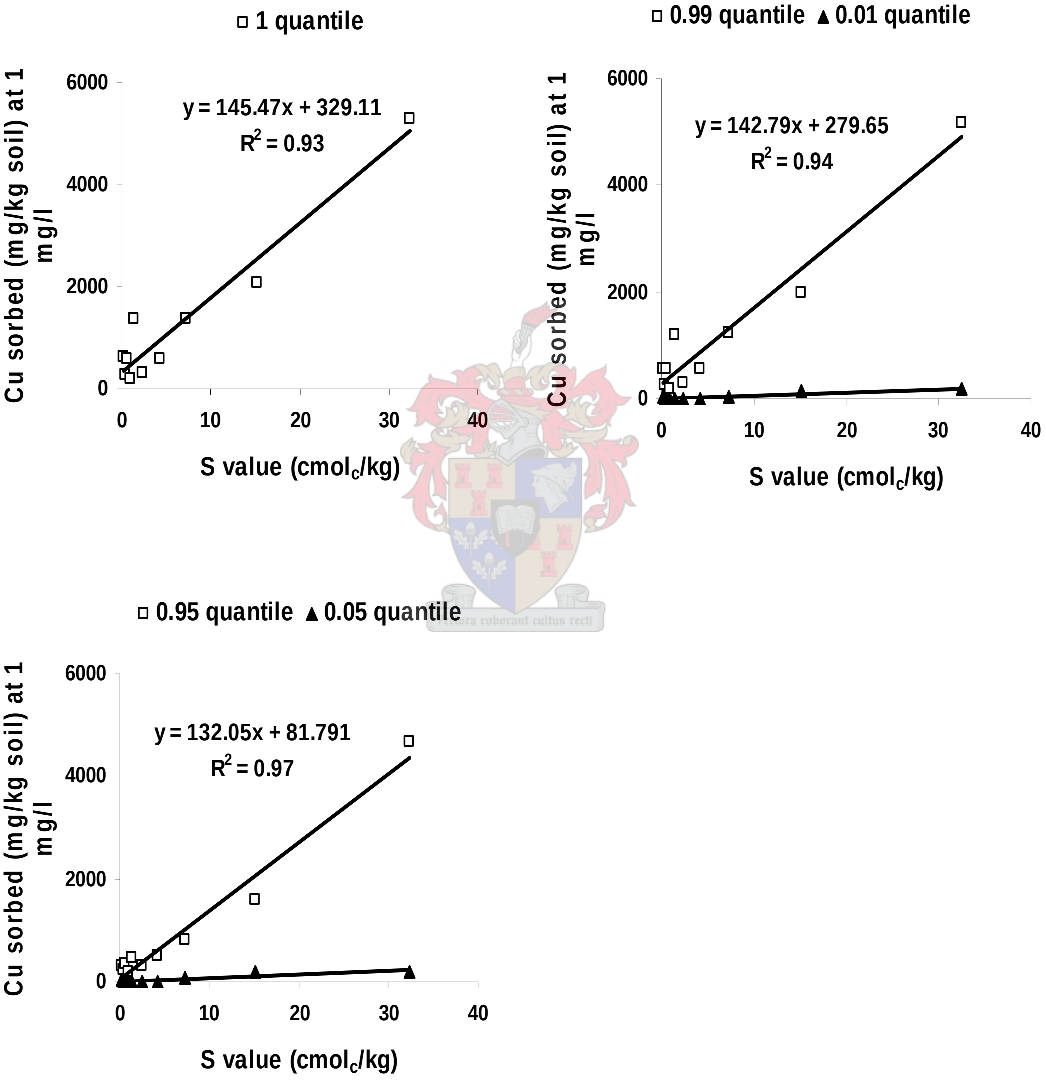


Figure A3.1 Cu sorption data for about 170 soils as a function of S value. Individual data were divided into 10 classes of equal size for the calculation of quantiles. The curves represent the chemical envelope of the Cu sorption data across the S value range

A3.2 Logarithm approach

The sorption capacity of different soils was determined at 1 mg/l solution concentration by plotting log pollutant sorbed versus log pollutant in the solution. Table A3.1 shows the reliability for the Paarl mountain data.

Table A3.1 Equations derived from logarithm plot (isotherm) of pollutant sorption (mg/kg soil) versus logarithm of pollutant concentration in the solution (mg/l)

Pollutant	**Sample**	**Equation**	**R^2**
Copper			
	PM1A	$y = 0.3x + 2.48$	0.91
	PM1A (A)	$y = 0.38x + 2.32$	0.99
	PM1A (L)	$y = 0.32x + 2.72$	0.99
	PM2A	$y = 0.29x + 2.93$	0.99
	PM2A (A)	$y = 0.3x + 2.88$	0.99
	PM2A (L)	$y = 0.34x + 2.98$	0.96
	PM1B	$y = 0.48x + 1.94$	0.97
	PM1B (A)	$y = 0.51x + 1.86$	0.98
	PM1B (L)	$y = 0.48x + 2.07$	0.99
	PM2B	$y = 0.47x + 2.1$	0.97
	PM2B (A)	$y = 0.28x + 2.81$	0.99
	PM2B (L)	$y = 0.36x + 2.54$	0.99
Phosphate			
	PM1A	$y = 0.34x + 2.68$	0.99
	PM1A (A)	$y = 0.34x + 2.72$	0.97
	PM1A (L)	$y = 0.36x + 2.77$	0.97
	PM2A	$y = 0.33x + 2.48$	0.99
	PM2A (A)	$y = 0.37x + 2.8$	0.96
	PM2A (L)	$y = 0.33x + 2.62$	0.99
	PM1B	$y = 0.34x + 2.76$	0.94
	PM1B (A)	$y = 0.34x + 2.8$	0.92
	PM1B (L)	$y = 0.54x + 3.11$	0.85
	PM2B	$y = 0.4x + 2.72$	0.91
	PM2B (A)	$y = 0.36x + 2.81$	0.94
	PM2B (L)	$y = 0.35x + 2.86$	0.90