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PARTITIONING COEFFICIENTS AND SOLUBILITIES OF Cu, Pb AND V IN SELECTED SOUTH AFRICAN SOIL HORIZONS

by

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DECLARATION

I, Michelle Papenfus declare that the thesis, which I hereby submit for the degree MSc Soil Science at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

SIGNATURE: ______________________ **DATE:** ____________________

DEDICATION

This master's thesis is dedicated to my husband, Stefan. I give my deepest expression of love and appreciation for the encouragement that you gave and the sacrifices you made during my post graduate studies. Thank you for the support and company during late nights and weekends of writing.

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ABSTRACT

In the past, contaminated soil as a source for water contamination has been largely neglected from the South African legislation. Inconsistent evaluation and remediation of contaminated sites have resulted in many sources of water contamination not being sufficiently addressed. The Draft National Norms and Standards for the Remediation of Contaminated Land and Soil Quality (GN 233 of 2012) (henceforth Norms and Standards) was published for comments and suggestions in August 2012. A number of uncertainties have been identified that may impact on the successful implementation of the Framework and the Norms and Standards.

Some of the issues are related specifically to the setting of soil screening values (SSV) for protection of water resources. There is no particular method specified to determine the soluble fraction of contaminants in soil. In a phase 1 assessment SSVs are used to judge whether constituents present in the soils are at concentrations high enough to pose a potential risk to the receiving environment. With the determination of the SSV a known water quality standard is converted to a total concentration by making use of a dilution factor and partitioning coefficient (K_d). The proposed K_d values in the Framework are surrounded by uncertainties and information regarding K_d values for South African soils are limited. In addition, the Framework does not take into account the natural background concentration of soils to differentiate between anthropogenic and natural contamination.

Setting appropriate extraction method plays the key role for an objective and standardised initial assessment of soluble concentrations in the soil. Similarly, the selection of appropriate K_d values based on soil properties minimizes the uncertainties during the estimation of SSV. Appropriate screening of contaminated land is imperative to the registration of contaminated land and has significant implications for industry, government and the environment.

The aims of this study were: a) to assess fast and simple analytical methodologies which can be performed by a commercial laboratory to mimic the standard saturated paste extraction method to determine soluble metal concentration in soils, b) to determine K_d values for selected South African soils in 10 soil horizons, and c) to determine baseline concentration ranges for selected soluble contaminants to assist in the setting of appropriate soil screening values for the protection of water resources. The study will test the hypothesis that a 1:2.5 (soil:water ratio) water extraction could better mimic the standard saturated paste extraction than the 1:20 ratio, commonly used in USA. The 1:2.5 ratio can be done by most commercial laboratories and gives a better indication of the pore water quality.

To assess analytical methods, four extraction methods (1:2.5, 1:5, 1:10 and 1:20 soil:water) were tested against the standard saturated paste extraction using three trace metals (Cu, Pb and V). These three metals were selected based on reactivity and environmental abundance. Lead and Cu are B type metals which complex readily with organic material and are generally more environmentally toxic. Anthropogenic activities are increasing enrichment of B type metals in the environment. Vanadate is an A type metal and is redox sensitive. Its association with the Bushveld complex was the reason for its inclusion in this study. The baseline soluble concentrations of Cu, Pb, and V were determined for selected 100 South African soils using the extraction method selected above. The K_d values of Cu, Pb, and V were determined for selected 10 soil horizons (1:1 clay dominated A horizon, Vertic soil dominated by 2:1 clay minerals, Yellow oxidic / Plinthic (Soft plinthic B horizon), low clay red oxidic B horizon, red oxidic B horizon, plinthic B horizon, gleyed horizon (G horizon), melanic A horizon, orthic A horizon with high organic content (OC) and E-horizon) using a batch method. For each constituent three different metal concentrations were added to each of the soil horizons. After extraction the concentration in the solution was used to determine the amount of metal sorbed to the soil.

Considering the standard saturated paste extract as a bench mark, the 1:2.5 soil:water ratio extraction gave more representative soil pore water quality for Cu, Pb and V in the low to medium concentrations. Therefore, the hypothesis was accepted. It was also apparent that the K_d values selected for the Framework are not representative of typical South African soils. The K_d values for Cu range between 12.7 and 19044 L kg^{-1}. These values exceeded the value of 10 L kg^{-1} provided by the Framework in all soils. For V the K_d values (10.5 – 865 L kg^{-1}) in all soils were lower than the value of 1000 L kg^{-1} specified in the Framework. For Pb, the K_d of 100 L kg^{-1} as indicated in the Framework is not representative of soils found in South Africa. For Pb, low clay content, weathered soils have lower K_d values, whereas higher clay content soils have K_d values up to 4 orders of magnitude higher than the K_d in the Framework. Therefore, due to the large variability in K_d values, a single value cannot be used for all soil types.

To conclude, the 1:2.5 soil:water ratio was found to be more representative to the soil pore content especially in the low to medium solute concentrations. The study also showed that a single K_d value cannot be used across soil types. The K_d values currently used in the Framework have low representativity of the South African soils. In the meantime, the K_d values for Cu, Pb, and V generated from this study for selected South African soil horizons could be used by the framework. There is, however, a need to develop local K_d values of contaminants across soil types.

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CHAPTER 1: INTRODUCTION

Heavy metals are naturally occurring elements in the environment that vary in concentration and composition across geographic regions. Globally, it has been a growing concern that the heavy metal contents of soil are increasing as the result of industrial, mining, agricultural and domestic activities. While certain heavy metals are essential for plant growth as micronutrients, they may become toxic at higher concentrations. In addition, as the concentration of toxic metals in the soil increases, the risk of non-localized groundwater pollution from metal leaching increases. The extent of toxicity is dependent on the metal and its chemical form. The total soil metal content alone is not a good measure of risk and not a very useful tool to determine potential risks for soil and water contamination (Sauvé *et al.*, 2000). Metals and metalloids that most likely pose a risk for concern include Hg, Cd, Pb, As, Ni, Cu, Zn, Cr, Mo, Mn, Se, F, and V (Brady & Weil, 2002; Domingo, 1996).

In the past, contaminated soil as a source for water contamination has been largely neglected from the South African legislation. Inconsistent evaluation and remediation of contaminated sites have resulted in many sources of water contamination not being sufficiently addressed. The National Environmental Management: Waste Act, 2008 (Act No. 59 of 2008) (NEMWA) clearly identifies the status and risk of contaminated sites and provides a legislative action plan for remediation activities to be implemented and controlled. The Draft National Framework for the Management of Contaminated Land (henceforth the Framework) (Department of Environmental Affairs, 2010) stipulates national norms and standards for the practical execution of remediation activities in compliance with Section 7 (2) (d) of the NEMWA pertaining to *'the remediation of contaminated land and soil quality'*. The Draft National Norms and Standards for the Remediation of Contaminated Land and Soil Quality (GN 233 of 2012) (henceforth Norms and Standards) was published for comments and suggestions in August 2012.

In NEMWA, the concept of contamination is defined as:
'"contaminated", in relation to Part 8 of Chapter 4 (of the NEMWA document), means the presence in or under any land, site, buildings or structures of a substance or

micro-organism **above the concentration that is normally present** in or under that land, which substance or micro-organism directly or indirectly affects or may affect the quality of soil or the environment adversely;'.

The concept of background concentrations (normally present) of substances that could affect the environment adversely is used to define contaminated land and, by implication, also the risk to the environment. A reference value is thus required in order to determine if a metal concentration found is in fact due to contamination or not. The background concentration was defined by Korte (1999) as: *'the normal chemical composition of an earth material prior to its contamination'*. It is important to note that the background value is a function of a particular material (parent material, soil type, etc.) and location and therefore highly variable. Background concentrations represent an ideal condition that no longer exists in most countries. Baseline concentrations have thus been defined as 95% of the expected range of background concentrations (Herselman, 2007). These values are then used to give an indication of the trace element concentration of an uncontaminated soil (Herselman, 2007). Only when one has an indication of what the natural range of an element in a soil should be can one assess the possibility of the soil being contaminated. Thereafter, guidelines for maximum threshold levels of trace elements in soils can be established. A number of countries have developed such guidelines (Herselman, 2007; E.S. Environmental Protection Agency, 2002).

A conditioning statement regarding the specifics of contamination is further made in the Framework between '*contaminated*' and '*posing a risk to the environment*' in sections such as 38 (1):

'38 (1) On receipt of a site assessment report contemplated in section 37, the Minister or MEC, as the case may be, may, after consultation with the Minister of Water Affairs and Forestry and any other organ of state concerned, decide that (a) the investigation area is contaminated, presents a risk to health or the environment, and must be remediated urgently; (b) the investigation area is contaminated, presents a risk to health or the environment, and must be remediated within a specified period; (c) the investigation area is contaminated and does not present an immediate risk, but that measures are required to address the monitoring and management of that risk; or (d) the investigation area is not contaminated.'

Therefore, the evaluation of contaminated land should consider constituents above normally present concentrations (background concentrations) during the initial investigation to determine whether the land is contaminated or not. Once the presence of contamination on land has been established, further studies are required to determine the potential impact on the soil quality and the risk of the contaminated land to the environment and hence, whether remediation is required. Despite the definitions in the NEMWA mentioned above, the Framework follows a risk based approach in setting soil screening values (SSVs) for total contaminant concentrations in soil without considering background concentrations.

Furthermore, the SSVs are set for total concentrations of contaminants in soil and represent soil values required to achieve South African Water Quality Guideline levels for protection of the aquatic ecosystem and domestic water use. A partitioning coefficient (K_d) is used to calculate the total soil concentration that provides for the water quality target concentration and is therefore one of the most sensitive parameters for the protection of water resources. According to the Framework, the proposed K_d values may be adapted on site specific bases, but will essentially be used as it is during initial investigations. For the protection of our water resources, the appropriateness of the K_d values and derived SSVs should always be considered.

In a phase 1 assessment, SSVs are used to judge whether constituents present in the soils are at concentrations high enough to pose a potential risk to the receiving environment. The SSV is the lowest concentration provided by the pathway-receptor models for the protection of human health and protection of water resources (Department of Environmental Affairs, 2010). Soil screening levels represents a multi-functional soil quality criterion that is conservative under a large number of potential exposure scenarios and is appropriate to assess potential soil contamination when: a) there is potential risk to the groundwater resource; b) there are groundwater users within 1 km of a site; and c) there are surface water bodies that could be impacted by off-site migration of contaminants.

The SSV for the protection of water resources is based on a two phase equilibrium partitioning and dilution model and is calculated as follows:

$$Y = C_w \times K_d \times DAF$$

Where:

Y = total contaminant concentration in soil at equilibrium with pore water at a defined water quality standard (mg kg^{-1})

C_w = water quality standard (aquatic ecosystem/domestic drinking water use guideline) (mg L^{-1})

K_d = partition coefficient (L kg^{-1})

DAF or DF = dilution attenuation factor

A number of uncertainties have been identified that may impact on the successful implementation of the Framework and the Norms and Standards. Some of the issues are related specifically to the setting of SSVs for protection of the water resources. These issues can be summarised as follows: 1) no specific analytical methodologies have been specified for analyses of potentially contaminated soils. This may result in inappropriate methodologies being used and discrepancies between the screening levels set as a consequence of different methods used; 2) uncertainty surrounding the determination of K_d values makes its application in the setting of screening levels open to debate. Information regarding K_d values for South African soils and the determination thereof are limited, resulting in subjective decision making regarding data interpretation; 3) screening values proposed for certain contaminants appear unrealistic considering the natural background soil concentrations for South African soils. Therefore, the appropriateness of screening values should be evaluated against natural concentrations of constituents in South African soils.

Appropriate screening of contaminated land is imperative to the registration of contaminated land and has significant implications for industry, government and the environment. Inappropriate screening during initial investigations will result in some constituents and sites being screened for further detailed assessment and registered as contaminated land when in actual fact it could be naturally occurring soil concentrations. On the other hand, some constituents and sites that pose a potential risk may appear uncontaminated while further investigation is actually warranted. A high degree of uncertainty therefore exists in screening soils for further assessment and registration as contaminated land.

The aim of this study was to address a number of these uncertainties and to assist in setting appropriate norms and standards for the assessment of contaminated land:

1) To assess analytical methodologies for determining the soluble metal concentrations in a soil by means of a laboratory study;
2) To determine K_d values for South African soils and evaluate its use in the setting of appropriate screening values for the protection of the water resources; and
3) Determine baseline concentration ranges for soluble contaminants in South African soils to assist in the setting of appropriate soil screening values for the protection of water resources.

Although saturated paste extract is the standard method to estimate soil pore water quality, the subjective nature of evaluating the point where a soil reaches saturation has led scientists to look for objective methods that could be standardised against the saturated paste extract. This study hypothesised that a 1:2.5 (soil:water ratio) water extraction could better mimic the standard saturated paste extraction than the 1:20 ratio, which is commonly used in USA to determine soluble metal concentration in soils.

Three metal species will be used throughout this study: Cu, Pb and V. Metals were selected based on reactivity and environmental abundance. Lead and Cu are B type metals which complex readily with organic material and are generally more environmentally toxic. Anthropogenic activities are increasing enrichment of B type metals in the environment. Vanadate is an A type metal and is redox sensitive. Its association with the Bushveld complex was the reason behind its inclusion in this study.

To assess the most appropriate soluble extraction method, two contrasting soils will be used (1:1 clay dominated A horizon, Vertic soil dominated by 2:1 clay minerals). The K_d values of the preceding two soils and other eight additional soils will be determined using a batch method. The eight additional soils include: Yellow oxidic / Plinthic (Soft plinthic B horizon), low clay red oxidic B horizon, red oxidic B horizon, plinthic B horizon, gley horizon (G horizon), melanic A horizon, orthic A horizon with high organic content (OC)% and E-horizon. These soil horizons were selected because of their abundance where predominantly South African soil forming factors exist. In addition, these soils lack K_d values for any of the contaminants.

The thesis consists of a literature review (Chapter 2) detailing on the candidate metals (Cu, Pb, and V) background information and reviews methods used to classify contaminated land in selected areas around the globe. Chapter 3 deals with the selection of appropriate soluble extraction method. Chapter 4 investigates the determination of K_d values for Cu, Pb, and V on 10 selected South African soil horizons. Chapter 5 deals with the establishment of soluble baseline concentrations for Cu, Pb and V in selected 100 South African soils. Finally, the findings are summarised in Chapter 6.

CHAPTER 2: LITERATURE REVIEW

For this study Cu, Pb and V were selected as the contaminants of concern. Metals were selected based on reactivity and environmental abundance. Lead and Cu are B type metals which complex readily with organic material and are generally more environmentally toxic. Anthropogenic activities are increasing enrichment of B type metals in the environment. Vanadate is an A type metal and is redox sensitive. Its association with the Bushveld complex resulted in its inclusion in the study. The K_d values supplied in the Department of Environmental Affairs (2010) for these three elements are inconsistent with values obtained from literature. The general chemistry and availability in soils of these three candidate elements are presented in detail in the following section. A brief discussion on the phase one contaminated land regulations of other countries are also given.

2.1 Copper (Cu)

2.1.1 Geochemistry, abundance and occurrence

Copper in its natural state is a reddish solid with a bright metallic luster. It is a good conductor of electricity, malleable and ductile. When mixed with zinc it produces brass and with tin it produces bronze (Barker and Pilbeam, 2007). The abundance of Cu in some environmental compartments is shown in Table 2.1. Soil parent material is thought to be the largest contributor of Cu in soils (Baker and Copper*,* 1995). Other sources of Cu to the soil include metal plating, industrial and domestic wastes, mining and mineral leaching (Sparks, 2003). The most dominant Cu mineral is chalocyrite ($CuFeS_2$ with trace amounts of Co, Ni, Zn, As, Se, Ag, Au, Pt, Pb, V and Cr). Other Cu containing minerals include: bornite (Cu_5FeS_4), chalcocite (Cu_2S) and covellite (CuS), cuprite (Cu_2O), tenarite, (CuO), malachite, ($Cu_2CO_3(OH)_2$) and azurite ($Cu_2(CO_3)_2(OH)_2$ (Kabata-Pendias and Mukherjee, 2007).

Copper has two oxidation states, cuprous (Cu^{1+}) and cupric (Cu^{2+}) ions. The divalent variant is most abundant in nature (Hooda, 2010).

Table 2.1: Abundance of Cu in the environment (adapted from Kabata-Pendias and Mukherjee, 2007)

Environmental compartment	Cu concentration (mg kg^{-1})
Earth's Crust	25 – 27
Igneous Rocks	50
Mafic	10 – 120
Acidic	5 – 30
Sedimentary Rocks	
Argillaceous	40 – 60
Sandstones	5 – 30
Calcareous	2 – 10
Raw Energy Material	
Coal	12 – 280
Fly ash	72
Crude oil	0.2 – 1
Petrol	0.05 – <1
Soils	
Light sandy	1 – 70 (13)[a]
Medium loamy	4 – 100 (23)
Heavy loamy	7 – 140 (24)
Calcareous	7 – 70 (23)
Organic	1 – 115 (16)

[a] Arithmetic means are given in parenthesis

Copper is an essential micronutrient for animals, humans and plants. In animals and humans it is chiefly found in the bloodstream as a cofactor in various enzymes and pigments. In excess amounts it may be poisonous and even fatal to organisms (Spitalny *et al.*, 1984). Extensive Cu toxicity primarily affects the liver. High Cu concentrations can cause increased oxidative damage to lipids, proteins and DNA which can contribute to neurodegenerative disorders (Gaetke and Chow, 2003).

Copper is added to the soil system via agrochemicals, animal feeds, animal manure, sewage sludge and composted forms. Other anthropogenic activities that may lead to the increase of Cu concentration in soil include: metal smelting, mining, industrial (metal plating, steelworks, and refineries) and domestic waste (Flemming and Trevors, 1989).

Generally, the background concentration of Cu in soils ranges from 13 to 24 mg kg^{-1} (Kabata-Pendias and Pendias, 2001). Alloway (1995) estimated an average Cu content in soils of different types as ranging between 20 and 30 mg kg^{-1}. Values below 10 mg kg^{-1} have often been cited and therefore, the global mean range for Cu is estimated at 8 mg kg^{-1}in acid sandy soils to 80 mg kg^{-1} in clay loam soils (Kabata-Pendias and Mukherjee, 2007). In the soil solution, the concentration of Cu has been reported as 0.5 to 135 µg L^{-1}, depending on the extraction method. Copper concentrations in selected regions around the globe and in South Africa are given in Table 2.2.

Table 2.2: Copper concentration (mg kg^{-1}) in selected regions and in South Africa (Herselman, 2007)

Country	**Cu concentration ranges (mg kg^{-1})**
USA[1]	3.8 - 94.9
Australia and New Zealand[2]	1 – 190
Florida[3]	0.22 - 21.9
Belgium[4]	1.7 – 39
South Africa (EPA 3050, total)	2.98 – 117
South Africa (EDTA; bio-available)	0.84 - 10.6

[1] Holmgren *et al.* (1993) – nitric acid digestion, agricultural soils without anthropogenic contamination, 5th and 95th percentile

[2] Summers & Pech (1997) - nitric acid digestion of topsoil samples

[3] Ma *et al.* (1997) – EPA3052 microwave digestion method

[4] Tack *et al.* (1997) - *aqua regia* digestion method

2.1.2 Behaviour in the soil

Copper is one of the least mobile heavy metals in soils and generally accumulates in the upper few centimetres of the soil (Herselman, 2007). Copper is found in soils mostly in the form of Cu^{2+} adsorbed onto clay minerals or co-precipitated on other inorganic and organic soil constituents (Kabata-Pendias and Pendias, 2007). Table 2.3 shows common forms in which Cu exist in the soil and soil solution.

Table 2.3: Forms of Cu in the soil and soil solution (Kabata-Pendias and Mukherjee, 2007)

Soil	Soil Solution
Cu^{2+}	Cu^{2+}
Cu^{+}	$CuOH^{+}$
$Cu(Cl_2)^{-}$	$Cu_2(OH)_2^{2+}$
$CuSO_4$	$Cu(OH)_3^{-}$
$CuCO_3$	$Cu(OH)_4^{2-}$
$CuCl$	$Cu(CO_3)_2^{2-}$

In the soil solution, it predominantly occurs as either aqua cations or complexed ions in soil solution. Chelation and complexation governs the Cu behaviour in soils. It has a tendency to be absorbed by organic compounds, carbonates, clay minerals and oxides of Mn and Fe. The distribution and occurrence of Cu in soil is largely associated with soil texture, pH and soil organic matter. Copper ions are tightly held on organic and inorganic exchange sites. Copper can be substituted isomorphously for Mn, Fe and Mg in several minerals (Kabata-Pendias and Mukherjee, 2007; Barker and Pilbeam, 2007). Similar to most heavy metals, dissolved organic matter has a strong chemical attraction for Cu and tends to fix Cu and hinder its sorption on soils. The largest contributors to for the concentration of adsorbed Cu are Fe and Mn oxides, organic matter, clay content and mineralogy in the soil (Kabata-Pendias and Mukherjee, 2007).

The availability of Cu is largely affected by the soil pH, decreasing 99% for each unit increase in pH. In soil, Cu^{2+} dominates at pH below 7.3 with $CuOH^{+}$ most common at pH above 7.3 (Barker and Pilbeam, 2007). Complexes formed between Cu and surfaces or soluble organic ligands tend to be very strong as it forms inner-sphere complexes and thus it is not very mobile in the soil (Hanrahan, 2009; Herselman, 1998).

2.2 Lead (Pb)

2.2.1 Geochemistry, abundance and occurrence

In its elemental form, Pb is a dense blue-grey metal with a low melting point. Lead metal is very soft and is readily cut and shaped. Lead is used largely for lead-acid batteries also known as the SLI battery. It is also used in alloys, chemicals, cables, lead weights, lead wool, pigments, ceramics, pesticides and plumbing (Kabata-Pendias and Mukherjee, 2007).

Lead has two stable oxidation states, Pb(II) and Pb(IV), with the divalent ion dominant in the environmental chemistry of the element. It is primarily found in its chief ore, galena (PbS). Other common Pb minerals include cerussite ($PbCO_3$), anglesite ($PbSO_4$) and pyromorphite ($Pb_5(PO_4)_3$) which are all mostly insoluble (Hooda, 2010).

The average Pb concentration in uncontaminated soils has been reported as 29 mg kg^{-1} by Ure and Berrow (1982) while Nriagu (1979) reported a mean concentration of 17 mg kg^{-1} for 10 arable Scottish soils derived from parent materials of different geological origin. Lead concentrations found in different environmental sources are shown in Table 2.4. Reaves and Berrow (1984) examined 3944 Scottish soils and found a geometric mean Pb content of all mineral soil samples to be 13 mg kg^{-1} with organic and organomineral soils having an average concentration of 30 mg kg^{-1}. Five hundred soils taken to a depth of 150 mm from randomly selected agricultural field in Europe indicated a distribution of Pb of 10.9-145 mg kg^{-1} (Archer and Hodgson, 1987). Kabata-Pendias and Pendias (2001) calculated the overall mean value of Pb in different soils to be 25 mg kg^{-1}. Studies by Angelone and Bini (1992) estimated unpolluted soil Pb concentration being less than 100 mg kg^{-1}. Lead in the soil solution has been estimated at <1 to 60 µg L^{-1} (Kabata-Pendias and Mukherjee, 2007). Lead concentrations from different regions as well as in South Africa are shown in Table 2.5.

Lead is not considered to be an essential element for humans or animals. It is conceived to be one of the most persistent environmental pollutants that can be harmful to plants, animals and humans. During the 1970s and 1980s, most lead pollution was caused by the emission from leaded fuels. In the 1990s, the use of Pb in fuel was basically eliminated in most countries. It is however still used in a number of African countries (Kabata-Pendias and Mukherjee, 2007).

Table 2.4: Abundance of Pb in the environment (adapted from Kabata-Pendias and Mukherjee, 2007)

Environmental compartment	Pb concentration (mg kg^{-1})
Earth's Crust	15
Igneous Rocks	
Mafic	0.1 – 8.0
Acid	10 – 25
Sedimentary Rocks	
Argillaceous	14 – 40
Sandstones	5 – 10
Calcareous	3 – 10
Raw Energy Material	
Coal, hard	10 – 1900
Fly ash	52
Crude oil	1 – 4
Petrol	2 – 650
Soils	
Light sandy	5 – 40
Medium loamy and silty	10 – 50
Heavy loamy	10 – 90
Calcareous	17 – 63
Organic	2 – 80

Lead pollution quite often has an air-borne origin. It returns to soil, water and plants as dust and can become hazardous, especially to grazing livestock. Lead poisoning in livestock has been well documented (Hooda, 2010). More Pb is consumed by ingestion of soil by animals and children than through the consumption of plant material (Barltrop *et al.*, 1975). A number of ingestion studies have indicated that children who can potentially ingest substantial amounts of soil can also be exposed to Pb toxicity (Calabrese *et al.*, 1997). Lead toxicity in humans most severely affects the nervous and reproductive systems as well as the urinary tract (Papanikolaou *et al.,* 2005). Soil Pb concentrations have increased due to mining, industrial and automotive emissions (Barltrop *et al.*, 1975).

Table 2.5: Lead concentration ranges (mg kg^{-1}) in selected regions and in South Africa (Herselman, 2007)

Country	Pb concentration ranges (mg kg^{-1})
USA[1]	4 - 23
Australia and New Zealand[2]	<2 – 200
Florida[3]	0.69 - 42.0
Belgium[4]	0.0 – 132
South Africa (EPA 3050) total	2.99 - 65.8
South Africa (EDTA) bio-available	0.93 - 11.9

[1] Holmgren *et al.* (1993) – nitric acid digestion, agricultural soils without anthropogenic contamination, 5th and 95th percentile

[2] Summers & Pech (1997) - nitric acid digestion of topsoil samples

[3] Ma *et al.* (1997) – EPA3052 microwave digestion method

[4] Tack *et al.* (1997) - *aqua regia* digestion method

2.2.2 Behaviour in the soil

Lead is considered as one of the least mobile heavy metals in the soil. Background Pb values are relatively low and concentrations are mainly controlled by the composition of the bedrock. Clay layer silicate minerals, Mn oxides, Fe and Al hydroxides and organic matter are some of the most prominent soil components associated with Pb immobilisation. Lead is more soluble in acidic conditions. The solubility can be greatly decreased by liming causing precipitation of Pb as hydroxide, phosphate or carbonate and may also promote the formation of organic Pb complexes. The reason for high concentration of Pb in surface soils can be ascribed to the surficial accumulation of organic matter (Kabata-Pendias and Pendias, 2001).

2.3 Vanadium (V)

2.3.1 Geochemistry, abundance and occurrence

Vanadium is used in the production of steel alloys for tools and for construction purposes and also in numerous other industrial applications. These strong and hard ferrovanadium alloys are used in armour plating for military and other protective vehicles, constructing the frames of high-rise buildings and oil drilling platforms. Other industrial applications include the use of vanadium pentoxide (V_2O_5) in the production of glass and ceramics and as a chemical catalyst (Hooda, 2010).

Vanadate (VO_4^{3-}) ions are similar to phosphate ions and thus are found in rocks with phosphorus-containing minerals. Carbon-rich deposits, for example coal, oil shale, crude oil and tar sands have also been reported to have high vanadium concentrations. In coal, however, it is believed to be associated with inorganic clay minerals (Swaine, 1990). A strong association exists between Si and V and thus most V found in rivers are thought to be as a result of weathering of silicate minerals (Shiller and Mao, 2000). Anthropogenic sources of V include phosphate fertilizers, mining activities and the disposal and discharge of petroleum and coal products (Kabata-Pendias and Pendias, 2001, Soldi *et al.,* 1996).

Vanadium naturally occurs as a trace element in a number of different rock materials. Due to the similarities between V^{3+}, Fe^{3+} and Al^{3+}, it is commonly found in magnetite and bauxite deposits. Vanadium can replace Al in the octahedral sheets of clay minerals (Jakubowska *et al.*, 2007).

The global average distribution of V in soils, range from trace amounts up to 400 mg kg^{-1} (Ure and Berrow, 1982). Extremely high V concentrations have been measured in the area close to a vanadium mine in RSA (Panichev *et al.,* 2006). Vanadium concentrations found in different environmental sources are shown in Table 2.6.

Table 2.6: Abundance of V in the environment (adapted from Kabata-Pendias and Mukherjee, 2007)

Environmental compartment	**V concentration (mg kg^{-1})**
Earth's Crust	53 – 60
Igneous Rocks	
Mafic	40 – 250
Acid	40 – 90
Sedimentary Rocks	
Argillaceous	90 – 130
Sandstones	10 – 60
Calcareous	10 – 45
Raw Energy Material	
Coal, hard	20 – 58
Crude oil	14 – 90
Petrol	50
Soils	
Light sandy	10 – 260
Medium loamy and silty	27 – 110
Heavy loamy	20 – 330
Calcareous	10 – 500
Organic	10 -22

Vanadium can be essential and toxic to humans (Mukherjee *et al.*, 2004). Vanadium is associated in the pathogenesis of some human diseases and also in sustaining normal body functions. Excess V interferes with a number of essential enzymatic systems, while V deficiency can result in a number of physiological malfunctions. Vanadium was implicated as an essential plant nutrient as early as 1953. Toxicity is uncommon in plants as V is believed to precipitate in the roots as insoluble calcium vanadate (Hooda, 2010).

2.3.2 Behaviour in the soil

The behaviour of V in soil is strongly dependent on its oxidation state (+2, +3, +4 and +5). Vanadium is normally evenly distributed along a soil profile and the variation in V content of soil is inherent from the parent material (Kabata-Pendias, 2000). Compared to other trace metals, there is little information regarding the solubility of V.

In aerobic environments and alkaline pH the V(V) species dominate. V(IV) dominates in acidic and slightly reducing conditions. Vanadium in the +3 oxidation state is found only in anaerobic conditions. Vanadium is relatively immobile in soils and therefore has a relatively low environmental risk (Hooda, 2010; Gäbler, *et al.*, 2009). The maximum adsorption of EDTA-extractable V occurs at pH 4 (Gäbler, *et al.,* 2009; Mikkonen and Tummavuori, 1994). The distribution of V is dependent on the land use type: forest, range land, agricultural, industrial or domestic (Soldi *et al.,* 1996).

2.4 Screening of contaminated land

A review of methods for developing ecological soil quality guidelines (US Environmental Protection Agency, 1999) showed that there are three generic methods used to set protective soil concentrations amongst the countries studied, including: a) selecting the lowest reported toxicity value and divide by a safety factor; b) using statistical distribution and select a particular percentile of the value; and c) rank reported soil concentrations from lowest to highest and determine an upper limit that represents a concentration under which no toxic effects are known to occur. Concentrations above this value however, do not always cause toxicity.

The end result of all environmental protection values is to protect whichever media, in a reasonable way. The level of protection, use of assessment factors, background levels, and minimum data requirements are determined by the responsible authorities. There are a number of differences regarding the soil protection guidelines and the methods of determination in different countries, which will be discussed in the following sections.

2.4.1 US ENVIRONMENTAL PROTECTION AGENCY

The US Environmental Protection Agency has developed a tool to standardize and quicken the evaluation and clean-up of contaminated soils where future residential land use is expected. A step-by-step methodology to calculate risk-based, site specific soil screening levels (SSLs) for contaminants in soil is provided. A technical document depicting analysis and modelling approaches is also available (US Environmental Protection Agency, 1994). In the US Environmental Protection Agency guidance, “screening” refers to the procedure of identifying and defining areas, contaminants and conditions at a particular site that do not require further action.

To apply site-specific screening levels, a few easily obtainable soil parameters (water filled soil porosity, bulk density, and soil water partition coefficient) and a measure of the contaminant concentration is required. This methodology was developed to be used during the early stages of a site evaluation where limited information may be available. Therefore, it is based on conservative, simplified assumptions about the release and transport of contaminants in the soil. A linear equilibrium soil / water partition equation is used to estimate contaminant release in soil leachate. A water-balance equation is used to determine a dilution factor which accounts for reduction of the leachate concentration with mixing in an aquifer (Table 2.7).

Soil pH is used to select site specific K_d values to be used in the equation. Usually where contaminant concentrations are equal to or exceed the SSLs, further investigation is initiated. This does not necessarily trigger a clean-up response. If the contaminant concentration is below the SSL value, no further action is required under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) (US Environmental Protection Agency, 1996).

$$Screening\ level\ in\ soil\ (mg/kg) = C_w \left[K_d + \frac{(\theta_w + \theta_a H')}{\rho_b} \right]$$

Table 2.7: Definitions, units and additional information of parameters used to determine site specific SSLs

Parameter	Definition	Units	Default
C_w	Target soil leachate concentration	mg L^{-1}	Nonzero max contaminant level goals, maximum contaminant levels, or health based limits x dilution factor
K_d	Soil-water partition coefficient	L kg^{-1}	Chemical Specific
θ_w	Water filled soil porosity	L_{water} / L_{soil}	0.3
θ_a	Air filled porosity	L_{air} / L_{soil}	n - θ_w
ρ_b	Dry soil bulk density	kg L^{-1}	1.5
n	soil porosity	L_{pore} / L_{soil}	1 - (ρ_b / ρ_s)
ρ_s	Soil particle density	Kg L^{-1}	2.65
H'	Dimensionless Henry's law constant		Chemical specific (Assume 0 for inorganic contaminants except Hg)

2.4.2 Dutch Guidelines

The Netherlands have established methods for developing critical loads of metals in soils. It is defined as the concentration of constituents that can be present without causing harm to terrestrial organisms, taking into account specific soil properties, including pH, organic matter and cation exchange capacity. Soil values for metals which are validated to an extent have been derived. Uncertainty analysis for calculating critical soil loads as well as sensitivity analysis of which parameters contribute the most uncertainty to critical load estimations, have been done by De Vries and Bakker (1998). The European Community have three different methods for deriving soil critical values, including:

Distribution method - To use this method, an adequate number of reported toxicity threshold values (four or more) which represent a wide array of species should be available. An assumption is made that the varying sensitivities of soil organisms follow an expectable statistical distribution with most of the genera having about the same sensitivity. It is normally assumed that the species sensitivities distribution assume a log-normal spread. The 5th percentile of the toxicity threshold values is then estimated and is used as the final criterion value.

Factor method - When less than four data sets (or acute data) regarding the hazard of the chemical of concern to terrestrial organisms are available, the Factor method is used. Acute toxicity data are obtained from short-term eco-toxicological experiments and is normally expressed as an LC_{50} (lethal concentration to 50% of test animals) or a non-lethal response at the 50% level. The lowest available value is used and assessment factors are applied (Table 2.8). The data is further adjusted to standardize pH and organic matter according to algorithms developed from background scenarios of uncontaminated sites.

Table 2.8: Assessment factors for determination of soil quality criteria in Europe

Information available	**Assessment Factor**
Only acute LC_{50} data are available and the data set is small or represents only a few genera (<3)	1000
Only acute LC_{50} data are available, but there is an extensive phylogenetic range represented (≥3)	100
Chronic test data are available but from a limited data set (<4)	10

Equilibrium partitioning method - For this method it is assumed that toxicity to soil organisms is due to the concentration of chemicals in the soil pore water. Allowable concentrations of a certain chemical is set to be the concentration of chemical that move into the pore water combined with the concentration that is sorbed to soil particles. It is proposed that the critical soil values can then be set based on toxicity to standard aquatic organisms such as daphnia and algae and an estimation of the partitioning of the chemical between the solution and solid phase. Reactions are assumed to be reversible and can be described by a linear sorption isotherm. To obtain the critical soil concentration, this linear partition coefficient is multiplied with the aquatic toxicity threshold value.

The method selected for a specific site depends on the amount of toxicity data present. The distribution method is the preferred method to be used, but requires at least four sets of toxicity data. If this data is not available, the factor method is applied. If no data is available for terrestrial organisms, the Equilibrium Partitioning method is used. Irrespective of the method used, a single number is derived that is meant to be protective of all organisms in the native ecosystem (Beroggi *et al*., 1997).

2.4.3 Canada

Contaminated sites are normally evaluated using the Canadian Environmental Quality guidelines (CEQG). The framework is based on common risk assessment methods and has been adopted from other jurisdictions with some modifications. The CEQGs are risk-based numeric guidelines set at levels where the occurrence of unacceptable effects on the environment or human health is expected. It is a multi-tier framework (Figure 2.1) that includes the following options: a) direct application of generic numerical guidelines; b) modification of guidelines based on site-specific conditions; and c) use of site specific risk assessments.

The numeric guidelines are estimates of a chemical concentration associated with low or no effect derived from toxicology information of that chemical and screening-level assessment of environmental fate and transport as well as the intake or exposure rates by potential receptors.

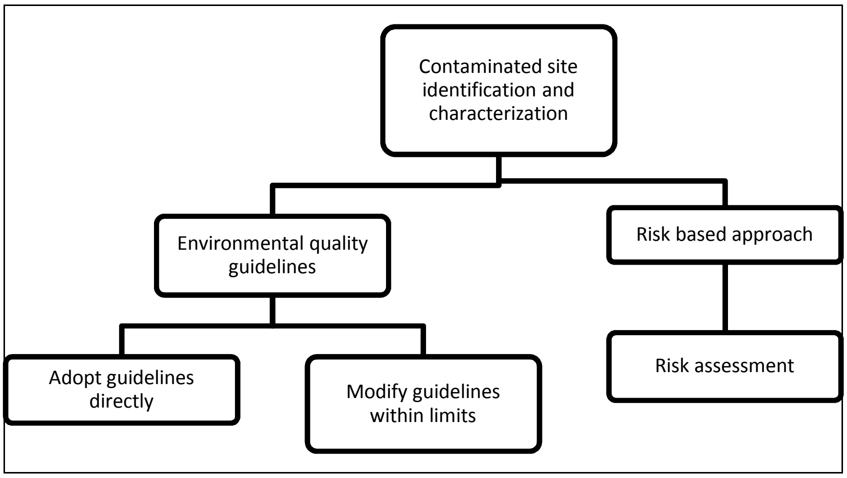

Figure 2.1: Multi-tier framework for contaminated land assessment in Canada

At Tier 1 in the framework, the generic numerical guidelines are directly applied. It is believed that most sites will be addressed using this Tier. The Tier 2 approach allows for consideration of site-specific conditions by modifying the guidelines based on site-specific scenarios. Although the generic guidelines are expected to be protective of most contaminated sites, more sensitive sites where assumptions applied when determining the numerical guidelines do not apply, must be assessed at higher tiers.

To apply the numerical guidelines for a Tier 1 assessment, a soil texture determination is required as the model differentiates between coarse (median particle diameter ≥ 75 μm) and fine (median particle diameter < 75 μm soil textures. The land use should also be known (Environment Canada, 2010).

2.4.4 Australia

A staged approach to site contamination is used and forms the basis for risk assessment of contaminated sites. Conservative assumptions are used in preliminary assessments to identify which issues is the most important regarding risk. This allows for more site-specific risk assessment to focus on these issues.

Measured contaminated values are compared to soil assessment levels (EILs) compiled by the Department of Environment (DoE). These values have been compiled from literature based in Australia and internationally (Table 2.9).

Table 2.9: Soil contamination assessment levels for Australia (adapted from Department of Environment, 2003)

Parameter	EIL (mg/kg)	Health Investigation Levels (mg/kg)					
		A	B	C	D	E	F
As	20	100	-	-	400	200	500
Cd	3	20	-	-	80	40	100
Cr (III)	-	12	-	-	48	24	60
Cr (VI)	-	100	-	-	400	200	500
Co	50	100	-	-	400	200	500
Cu	60	1000	-	-	4000	2000	5000
Pb	300	300	-	-	1200	600	1500
Zn	200	7000	-	-	28000	14000	35000
Ni	60	600	-	-	2400	600	3000
Mn	500	1500	-	-	6000	3000	7500
Hg	1	15	-	-	60	30	75
V	-	-	-	-	-	-	-
A	Standard residential with garden/accessible soil (home grown produce contributing less than 10% of vegetable and fruit intake; no poultry); this category includes children's daycare centres, kindergartens, pre-schools and primary schools.						
B	Residential with substantial vegetable garden (contributing 10% or more of vegetable and fruit intake) and/or poultry providing any egg or poultry meat dietary intake.						
C	Residential with substantial vegetable garden (contributing 10% or more of vegetable and fruit intake); poultry excluded.						
D	Residential with minimal opportunities for soil access: includes dwellings with fully or permanently paved yard space such as high- rise apartments and flats.						
E	Parks, recreational open space and playing fields, includes secondary schools.						
F	Commercial/Industrial, includes premises such as shops and offices as well as factories and industrial sites						

Australia have developed two separate soil values, one for plants and animals that live within a soil and another considering animals that live above ground and have direct soil contact and animals that can be affected by off-site movement of contaminants. The lowest of these values from literature is selected as the Environmental Impact Level (EIL_{soil}) for the soil. Each land use has its own set of values. EIL_{soil} is based on background concentrations or chemical detection limits. The EIL_{soil} values should be below the background or detection concentrations. These values are then used as a screening tool for evaluating if a site may be considered as being contaminated or not. If a contaminant concentration exceed the EIL_{soil} value, further assessment of actual risk through the derivation of site-specific EIL_{soil} may be required. If the site conditions differ from the assumptions implied in the DoE then adjustments in the levels may be required to reflect the specific site situation (Department of Environment (DoE), 2003).

2.4.5 South Africa

A risk based approach based on international best practice is used. It is based on the original US EPA methodologies. Soil screening values (SSVs) are derived from back calculation from a desired concentration in a water body as detailed in the South African Water Quality Guidelines (SAWQG), (Department of Water Affairs and Forestry, 1996). The SSV's are considered to be conservative under a broad range of assumptions and indicates a 'safe' or 'clean' site towards which remediation is aimed.

The contaminant soil concentration is calculated using the following equation:

$$Y = C_w \times K_d \times DAF$$

Where:

Y = total contaminant concentration in soil at equilibrium with pore water at a defined water quality standard (mg kg^{-1})

C_w = water quality standard (aquatic ecosystem/domestic drinking water use guideline) (mg L^{-1})

K_d = partition coefficient (L kg^{-1})

DAF or DF = dilution attenuation factor

The Y value indicates the concentration that is targeted for by the SAWQG levels for aquatic ecosystem protection and domestic water use. As there are not sufficient information available to determine partition coefficients for specific soil types in South Africa, values were obtained from international literature. A table providing one K_d value for each contaminant at a soil pH of 7 is provided in the Framework.

CHAPTER 3: EVALUATION AND SELECTION OF ANALYTICAL METHODS

3.1 Introduction

The term ‘solubility’ refers to the amount of a substance that can be dissolved in a given amount of solvent. When a measure of a single solute in a soil is required, a water extraction of the soil sample is necessary (Page *et al.*, 1982). The measurement of soluble elements mainly consists of two steps: (1) preparation of a soil-water extract and (2) measurement of the concentration of elements in the extract.

In general, the higher the water content used for the extraction, the easier it is to remove the extract, but the less representative the extract is of the solution in the soil pores (Black, 1965). However, if pore water quality is not the focus of the study but rather changes in chemical content over time, a higher soil:solution extract can be used.

The aim of this phase of the study was to assess and select analytical methodologies based on objective criteria for use in the setting of soluble screening values for the protection of water resources. To achieve this, a comparison of analytical methods was conducted in order to select the most reliable analytical method to predict pore water quality.

Two soils with contrasting clay mineralogy (kaolinitic vs. smectitic dominated) were selected for this experiment. The main purpose was to investigate the various methods that can be used to determine soluble fractions of metals in the soil.

3.2 Methodology

In general, solution to soil ratio greater than that used for saturated paste extracts increases the ease of removing the solution from the soil after equilibration, however, soluble metal levels obtained do not reflect actual concentrations in the pore solution (Black, 1965).

3.2.1 Soil Selection

Two contrasting South African soils with different soil properties and clay mineralogy (kaolinitic and smectitic clays) were selected for the method screening. The soils are termed as ‘Soil 1’ (S1) for the kaolinite clay soil and ‘Soil 2’ (S2) for the smectite clay soil. The chemical and physical characteristic data for the soils used is shown in Appendix A.

3.2.2 Preparation of bulk soil samples

Three known concentrations of lead (Pb), copper (Cu) and vanadium (V) were added to bulk soil samples of 1.5 kg each except for the control, which did not receive any inorganic salt. For Cu a cocktail of metal salts were added ($Cu(NO_3)_2{\cdot}3H_2O$, $CuCl_2{\cdot}2H_2O$ and $CuSO_4{\cdot}5H_2O$) and one salt for Pb, $Pb(NO_3)_2$ and V (NH_4VO_3). All chemicals listed were purchased from Merck and of an analytical grade (EMSURE). Different metal concentrations were added to the soil in order to evaluate extraction methods at different metal concentrations. The complexities of competitive sorption between these cations were beyond the focus of this study. Therefore, the various metal treatments were single metal loading. This was done for each soil, amounting to a total of 24 treatments. The experimental set-up is presented in Figure 3.1.

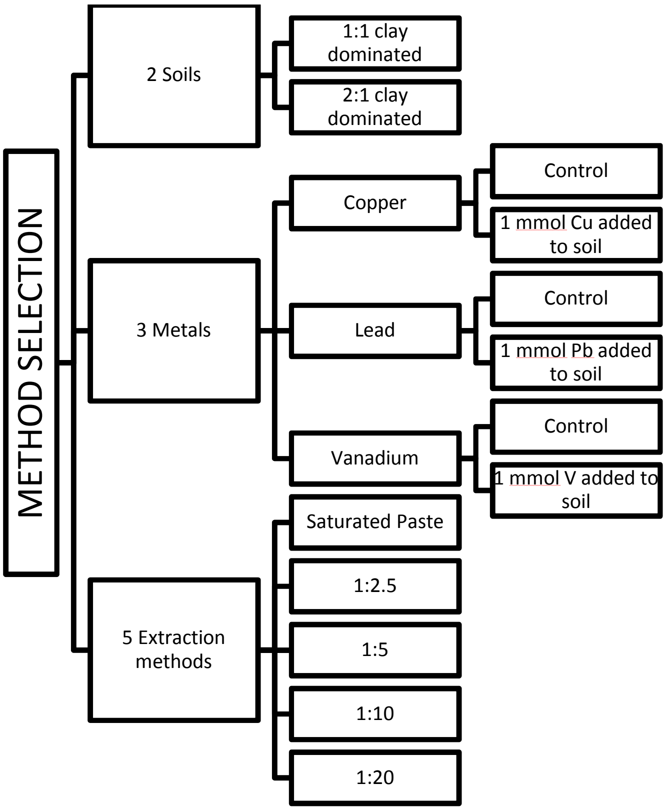

Figure 3.1 Experimental design for method selection

The contaminants were added to the bulk soil samples (1.5 kg) which were weighed into round bottom bowls to enable thorough mixing. The concentrations selected for the study was based on findings from sorption isotherms constructed for each of the metals in each of the soils. The metal solutions were added to the soils for the different treatments (Table 3.1) with enough deionised water added to form a slurry. To ensure adequate mixing, the samples were mixed for 15 minutes using an electric mixer (Figure 3.2). After 24 hours, the contents of the bowls were decanted into a large flat tray. Care was taken to transfer all the soil to the trays. Deionised water was used to rinse and transfer soil remaining in the bowl. The samples were allowed to air dry to simulate a wet and dry cycle. After 4 days, the dry samples were sieved and subjected to saturated paste extracts and the various soil:water ratio extractions to determine water soluble pollutant concentrations.

Table 3.1: Mass concentrations of Cu, Pb and V added to the soil (with molar concentrations in brackets)

Soil	Treatment ID	Cu	Pb	V
		mg kg^{-1} (mmol kg^{-1})		
Soil 1	0	0	0	0
	1	945 (14.9)	3105 (14.9)	3000 (58.9)
	2	4725 (74.4)	15525 (74.9)	7500 (147.2)
	3	9450 (148.7)	31050 (112.4)	11250 (220.8)
Soil 2	0	0	0	0
	1	1890 (29.7)	6210 (30.0)	375 (7.4)
	2	4725 (74.4)	15525 (74.9)	1875 (36.8)
	3	7088 (111.5)	23288 (112.4)	3750 (73.6)

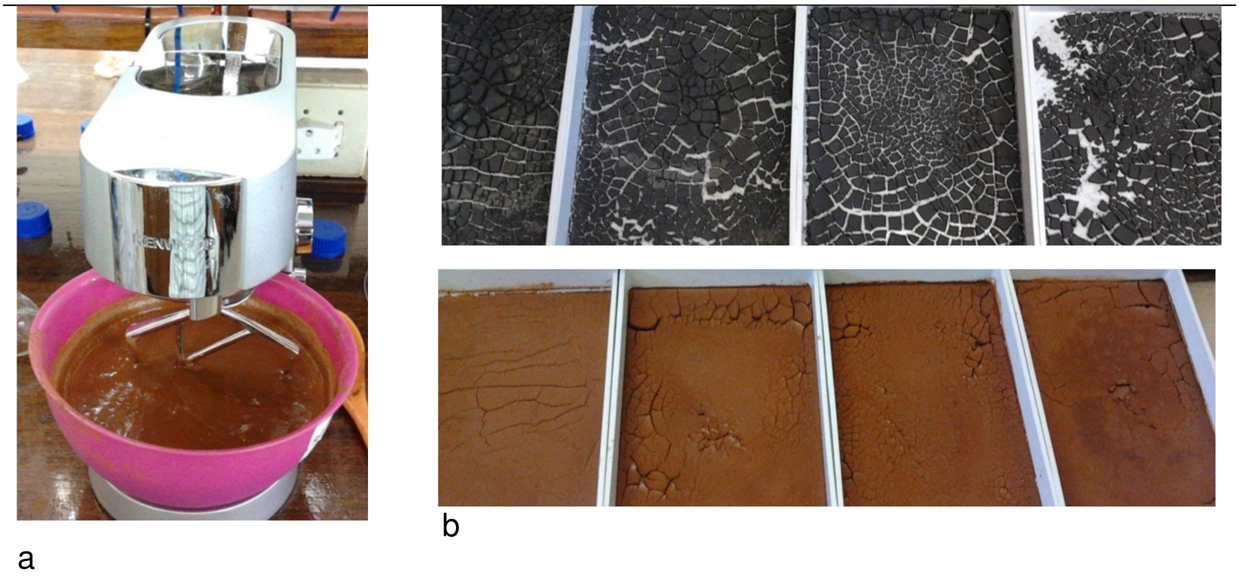

Figure 3.2: Mixing of the slurry with a mixer (a) and air drying (b) to simulate dry and wet cycles

Concentrations of Cu and Pb added to S2 were notably higher compared to S1. This was done because S2 was a smectitic soil with high clay content and displayed a very high affinity for the Cu and Pb resulting in equilibrium Pb and Cu concentrations below detection limit. As a result, the loading rates were increased in order to obtain measurable levels of the constituents. On the other hand, Soil S1 showed a greater affinity for V because S1 was hematitic and kaolinitic soil.

3.2.3 Determining soluble Cu, V and Pb levels of contaminated soils

The following water extraction methods were performed on the contaminated soils to determine soluble metal levels at the various metal loading rates : saturated paste, 1:2.5, 1:5, 1:10 and 1:20 (soil:solution ratios). Each treatment was replicated three times. The methodology followed for each extraction is discussed in the sections that follow.

3.2.3.1 Saturated Paste extract (Rhoades, 1996)

The amount of water required to obtain saturated pastes which have definable characteristics and is reproducible, is about four times the quantity of water held by the soil at permanent wilting point. Therefore, a saturated paste extract takes into account the field water holding capacity of the soil (Black, 1965). The amount of soil to be used for the extraction depends on the number and kind of analysis to be performed on the extract, the analytical methods used and the salt content of the soil. Usually one fourth to one third of the water in a saturated paste can be extracted by vacuum filtration (Page *et al*., 1982).

The methodology followed for saturated paste extraction was as follows: A 300 g air dry soil sample was weighted off into a plastic container (the exact mass of the soil and container was noted).Deionised water was added to the soil while stirring until the soil was saturated. The samples were left overnight for the soil to equilibrate with the solution. Additional deionised water was added the following day to achieve a saturated soil-water paste. The mass of the container with soil and water was recorded. The samples were then filtered under vacuum through Whatman no 42 and the filtrate was collected into a Scott bottle by vacuum (Rhoades, 1996).Finally, the samples were membrane filtered (0.2 µm pore size) to remove most of the suspended colloidal material left after the previous filtration step.

3.2.3.2 Water extracts at various solution to soil ratios

Typically water extracts employ higher water contents than at saturation and also water content of saturated paste extracts. Errors due to hydrolysis, cation exchange, and mineral dissolution are also expected to become larger with increasing extraction ratios (Page *et al*., 1982).

To examine the effect of increasing solution to soil ratios, the following ratios were used: 1:2.5, 1:5, 1:10 and 1:20.

The following basic procedure was used for the 1:2.5 extractions: Fifteen grams of soil was weighed into a 50 ml centrifuge tube. Deionised water was added to the sample (37.5 ml) where after the samples were shaken on a mechanical shaker for 24 hours. After 24 hours the samples were centrifuged at 4000 rpm for 5 minutes. The samples were then filtered through Whatmann 42 filter paper Finally, the samples were membrane filtered (0.2 µm pore size) to remove most of the suspended colloidal material left after the previous filtration step Samples were then analysed for Cu, Pb and V by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) AES. The mass of soil and volume of water used for the soil:solution extractions are indicated in Table 3.2.

Table 3.2: Soil mass to water volumes ratio used for the various water extractions

Soil:solution ratio	Mass of soil added (g)	Volume of water added (ml)
1 : 2.5	15	37.5
1 : 5	6	30
1 : 10	4	40
1 : 20	2	40

3.3 Results and Discussion

3.3.1 Analytical Results

The complete set of analytical results for this investigation is presented in Appendix B. In order to determine which soluble extraction will best predict the pore water concentration of the soil, the ICP results, in mg L^{-1} of metal in solution, was converted to mg kg^{-1} metal extracted from the soil. The data interpretation and evaluation for the different metals will be discussed in the sections that follow. The most reliable method is selected based on the statistical significance of differences in the results and also the closeness of the concentrations to the value obtained from the saturated paste extraction. Statistical analysis was conducted using GenStat® (Payne, *et al.,* 2012) and complete results are shown in Appendix C.

3.3.2 Copper

Figure 3.3 shows the concentrations of Cu extracted from S1 (kaolinite) and S2 (smectite) samples, which were treated with different concentrations of Cu and extracted with different soil to water ratios. All the concentrations were standardised to represent a 1:1 extraction by taking the dilution factors (1:2.5, 1:5, 1:10 and 1:20) into account to represent all the results on a 1 (soil) to 1 (water) ratio basis.

The different treatments are represented by 0, 1, 2 and 3 with the allocation of the numbers representative of a concentration as discussed in section 3.2. In order to conduct comparison of the extracted Cu concentration from the two soil types, the log values of the results were used. Table 3.3 shows the statistical t-groupings for the extracts and different Cu treatments. The smectite dominated soil (S2) showed significantly lower recovery of applied Cu in the extracted solution than the kaolinite dominated soil (S1), indicating that the Cu is more strongly adsorbed by the 2:1 clay minerals than the 1:1 clay minerals of S1.

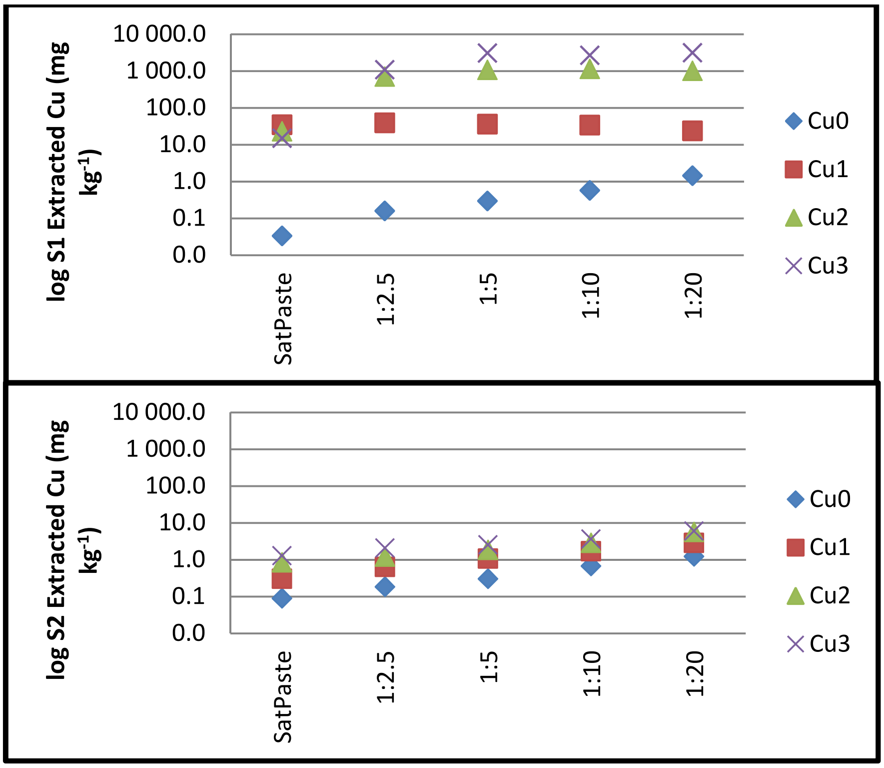

Figure 3.3: Log Cu concentrations extracted from kaolinite (S1) and smectite (S2) with different soluble extraction methods

Table 3.3: Statistical t-groupings of soil water extracts and Cu treatments

Treatments		Saturated Paste	1:2.5	1:5	1:10	1:20
		Mean solution Cu concentration (mg kg^{-1})*				
S1	Cu0	0.03^{a}	0.34^{abc}	0.18^{ab}	0.57^{cb}	0.72^{c}
	Cu1	34.8^{a}	39.5^{a}	36.2^{a}	34.0^{a}	23.6^{a}
	Cu2	23.0^{a}	705^{b}	1059^{d}	1121^{e}	996^{c}
	Cu3	15.1^{a}	1078^{b}	3090^{d}	2669^{c}	3131^{d}
S2	Cu0	0.09^{a}	0.18^{a}	0.31^{b}	0.61^{c}	1.22^{d}
	Cu1	0.30^{a}	0.63^{a}	1.06^{ab}	1.67^{b}	2.81^{b}
	Cu2	0.83^{a}	1.2^{ab}	1.8^{b}	2.9^{c}	5.6^{d}
	Cu3	1.3^{a}	2.1^{b}	2.5^{b}	3.6^{c}	6.0^{d}

*Means with the same letter are not significantly different

Taking the saturated paste extract as a benchmark, the following conclusion can be drawn for the other soil:water ratio extractions: For kaolinitic clay dominated soil

(S1), there was a gradual in the amount of Cu extracted from the soil as the soil:water ratio increased for the CU0 treatment. According to the statistical analysis, the 1:2.5 and 1:5 extracted equivalent concentrations of copper as the saturated paste extract from CU0. In contrast, the amount of Cu extracted from Cu1 treatment did not differ significantly among the different soil:water ratio extractions. It was also interesting to note that the 1:2.5, 1:5 and the 1:10 extraction ratios highly overestimated the soluble Cu content of the soil while the 1:20 ratio slightly underestimated it for treatment CU2. For the highest concentration treatment of Cu3, all soil:water ratio's overestimated the soluble copper content compared to the saturated paste, with the 1:2.5 extraction resulting in the lowest overestimation.

For the smectite clay dominated soil (S2) in the control treatment (Cu0), the 1:2.5 soil:water ratio extracted a statistically similar concentrations of Cu as the saturated paste extract. The other extraction ratios, however, overestimated the Cu concentration of the leachate in treatment Cu0. In the second treatment (Cu1), extraction conducted using the 1:2.5 and 1:5 soil:water ratio was statistically similar compared with the saturated paste, however, the 1:10 and 1:20 ratios overestimated the Cu concentration. In treatment Cu2, similar to the control treatment, the 1:2.5 ratio was the only extraction ratio that extracted a statistically similar copper concentration to the saturated paste. At the highest Cu treatment (Cu3), all soil:water ratio extractions overestimated Cu concentration in the leachate compared with the saturated paste extract.

Generally, an increase in the soil:water ratio during extraction resulted in overestimation of the soluble Cu in the soil. On the other hand, at higher soil Cu concentrations none of the soil:water ratios imitated the bench mark, saturated paste extract.

The statistical analyses (Table 3.3) showed that there were no significant differences between the saturated paste, 1:2.5 and 1:5 extracts for S1 with the Cu0 and Cu1 treatments, while the differences between saturated paste results and all other soil:solution extracts were significant at higher Cu application levels. In S2, however, no significant difference could be established between the saturated paste, 1:2.5 and

1:5 extracts in treatment Cu1. In the control samples only the 1:2.5 extract was statistically similar to the saturated paste extract.. The overestimation of Cu in pore water was less noticeable in S2 and could be attributed to S2 having a higher sorption capacity for Cu due to the dominance of 2:1 clay minerals, while the Cu added to S1 are available for extraction.

3.3.3 Lead

Lead concentrations extracted using different soil:water ratios from S1 and S2, treated with varying concentrations of Pb are presented in Figure 3.4 and the statistical t-groupings are summarised in Table 3.4.

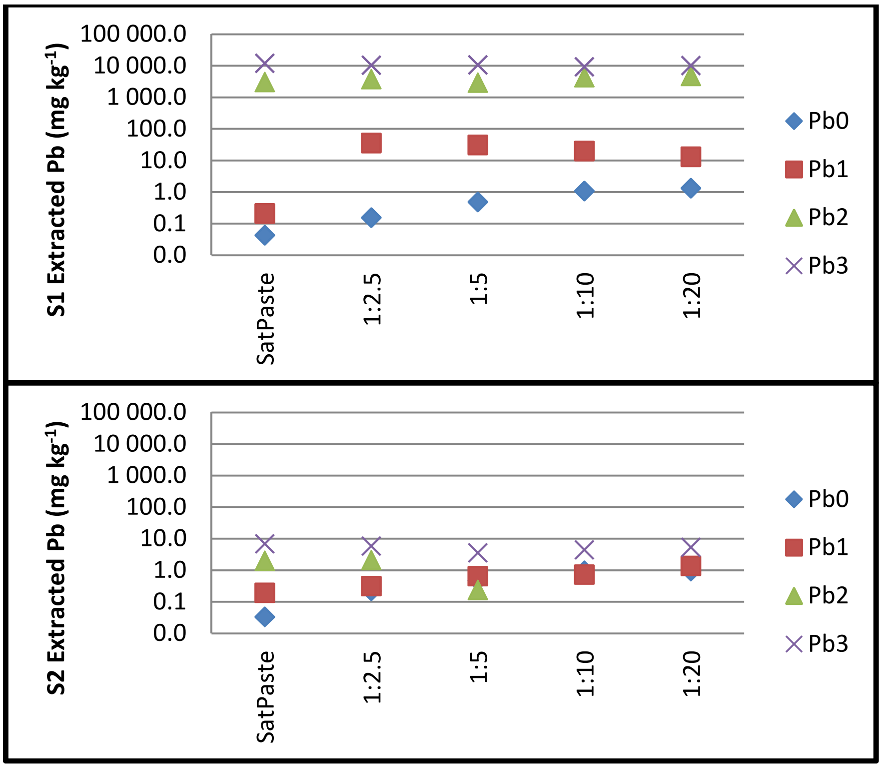

Figure 3.4: Log Pb concentrations extracted from S1 and S2 with different solid:water ratios

In the Kaolinitic clay dominated soil (S1), there was a gradual increase of the extracted Pb as the soil:water ratio increased. The 1:2.5 and 1:5 extracts were statistically similar to the saturated paste extraction for the Pb0 treatment. Similarly, the 1:2.5 ratio for the Pb1 treatment and the 1:2.5 and 1.5 ratios for the Pb2 treatments extracted similar Pb concentrations as the saturated paste extract while higher ratios overestimated the values. It was interesting to note that at the highest concentration treatment (Pb3), almost all soil:water ratios extracted a statistically similar concentration of Pb. Unlike Pb0 and other treatments, the mean soluble Pb concentration of the Pb1 treatment decreased significantly with increase in the volume of water used for extraction.

Table 3.4: Statistical t-groupings of soil water extracts and Pb treatments

Treatments		Saturated Paste	1:2.5	1:5	1:10	1:20
		Mean solution Pb concentration (mg kg^{-1})*				
S1	Pb0	0.043^{a}	0.15^{ab}	0.48^{a}	1.1^{c}	1.2^{c}
	Pb1	36.8^{a}	35.4^{a}	28.8^{b}	20.0^{c}	13.2^{c}
	Pb2	3031^{a}	3690^{ab}	2850^{a}	4288^{b}	4725^{b}
	Pb3	12509^{ab}	10457^{a}	10643^{a}	9147^{b}	10061^{b}
S2	Pb0	0.03^{a}	0.31^{ab}	0.47^{ab}	0.95^{b}	0.93^{b}
	Pb1	0.19^{a}	0.31^{a}	0.83^{a}	0.73^{a}	1.4^{a}
	Pb2	2.0^{a}	0.49^{a}	0.24^{a}	No data	No data
	Pb3	6.9^{a}	5.8^{a}	3.6^{a}	4.4^{a}	5.3^{a}

*Means with the same letter are not significantly different

In the smectite clay dominated soil (S2), the soil:water ratio of 1:2.5 and 1.5 extracted statistically similar soluble Pb as the saturated paste extraction method from the Pb0 and Pb2 treatments. The soluble Pb concentration from treatments Pb1 and Pb3 was, however, similar across the various soil:water ratio extractions. Generally, there was a gradual increase in the amount of Pb extracted from Pb0, which levelled out after the 1:10 soil:water ratio. It was also interesting to note that the concentration of Pb in solution from Pb3 decreased as the soil:water ratio decreased, to such an extent that the 1:10 and 1:20 Pb extracts were below the Pb detection limit.

S1 and S2 had similar Pb concentrations in the control samples (Pb0) and the different extraction methods yielded similar results. The added Pb was better adsorbed by the 2:1 clay minerals of S2 than the 1:1 clay minerals of S1, resulting in lower extractability for S2 as was the case with Cu. For S1 and S2 there was no significant difference between the saturated paste, 1:2.5 and 1:5 extracts of all treatments except for Pb1 of S1.

3.3.4 Vanadium

The analytical data of the V extractions for S1 and S2 for the different extraction methods and application rates is presented graphically in Figure 3.5 and the statistical probability groupings is shown in Table 3.5.

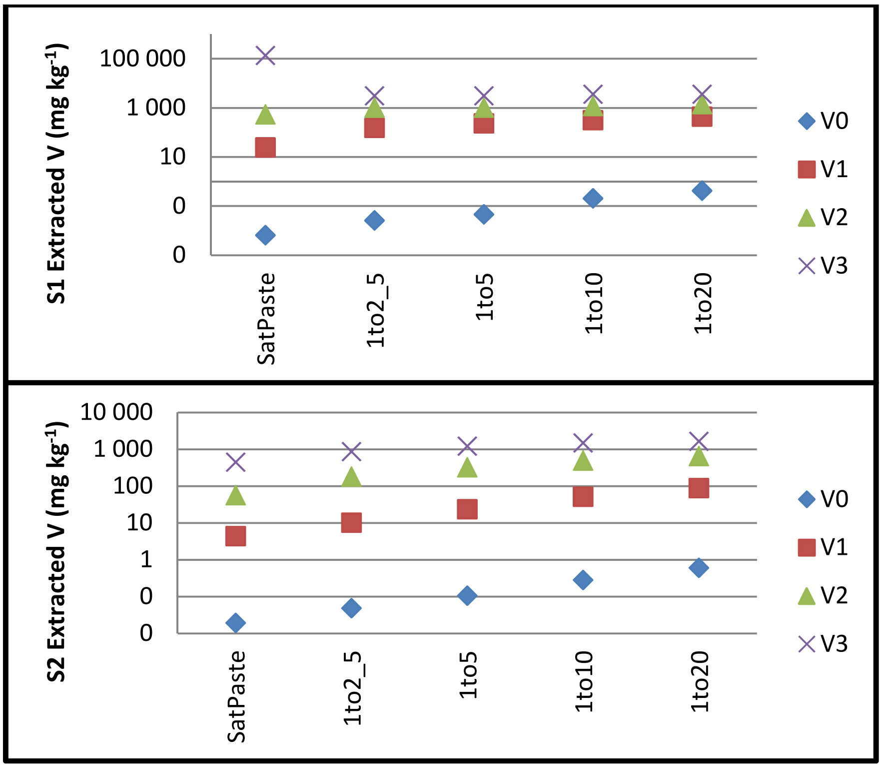

Figure 3.5: Log V concentrations extracted from S1 and S2 with different solid:water ratios

In the kaolinitic clay dominated soil (S1), the application of V to S1 caused dispersion of the clay particles. This resulted in the suspension of colloidal particles, which was challenging to filter out through membrane filtration, and has compromised the analytical results to certain degree. Nonetheless, the results can be summarised as follows: the 1:2.5 and 1:5 ratios extracted statistically similar soluble V concentrations as the saturated paste from the control treatment (V0). Soluble V extractions made by all soil:water extraction ratios from all other treatments were, however, significantly higher than the saturated paste extract. As a result of extensive dispersion, a saturated paste extract value for V3 was not able to be established.

Table 3.5: Statistical t-groupings of soil water extracts and V treatments

Treatments		Saturated Paste	1:2.5	1:5	1:10	1:20
		Mean solution V concentration (mg kg^{-1})*				
S1	V0	0.0064^{a}	0.026^{a}	0.046^{ab}	0.20^{c}	0.42^{d}
	V1	24.5^{a}	392^{b}	229^{c}	598^{d}	429^{e}
	V2	532^{a}	1011^{b}	1012^{b}	1163^{bc}	1178^{c}
	V3	No data	3034^{a}	3068^{b}	3097^{c}	3531^{d}
S2	V0	0.019^{a}	0.048^{ab}	0.10^{ab}	0.28^{b}	0.60^{c}
	V1	4.3^{a}	10.0^{b}	23.3^{c}	50.5^{d}	86.6^{e}
	V2	56.4^{a}	178^{b}	327^{c}	484^{d}	647^{e}
	V3	439^{a}	860^{b}	1214^{c}	1491^{d}	1619^{e}

*Means with the same letter are not significantly different

The response of V solubility to various soil:water ratio extractions at various V concentrations were similar between kaolinite dominated and smectite dominated soils. The 1:2.5 and 1:5 soil:water ratios extracted statistically similar soluble V concentrations as the saturated paste extraction from the V0 treatment. Soluble V extractions from all other V concentration treatments were (V1, V2, and V3), however, significantly higher than the saturated paste extraction. There was a clear general pattern observed for all treatments, where the soluble V concentration increased as the soil: water ratio increased.

Higher V concentrations were extracted from S1 than S2 for all treatments (except V0). The differences, however, were not as large as that observed for Cu and Pb for all treatments. This indicates that the V adsorption by the 2:1 clay minerals in S2 is greater than that of the 1:1 clay minerals in S1. However, to a lesser degree than in the case of Cu and Pb as it would be adsorbed as the vanadate ion which is negatively charged.

The statistical t-grouping results show that the 1:2.5 results of the V0 treatment of both S1 and S2 were not significantly different from the saturated paste results, while the results for all other treatments were significantly different from the saturated paste results. However, even in these cases, the results of the 1:2.5 extract were closest to the saturated paste results.

3.4 Discussion

In this investigation different application rates of Cu, Pb and V were tested on two contrasting soils with different clay mineralogy, Different soil:water ratio extraction were used to determine the soil:solution extract that would best predict the pore water quality. The saturated paste extract is used as the benchmark method for pore water quality determination of soil samples. However, this method is subjective when it comes to quantitative evaluation of the amount of water added to saturate a soil because the visual observation used to evaluate saturation of a soil depends on the experience of the person. Deionised water extracts with a constant/prescribed soil:solution ratio are easier to use on a routine basis.

The soil:solution ratio can have an impact on the chemical composition of a system, which in turn can affect sorption characteristics. In a review by Reitemeir (1945) on the effects of dilution on ionic concentration in soil solutions, an attempt was made to generalize the sorption behaviour. One of the factors influenced by the soil:solution ratio is pH. The pH of a soil suspension in a batch extraction procedure is controlled by three factors: (i) the “natural” pH of the soil and its buffering capacity; (ii) the pH and composition of the liquid phase; and (iii) adsorption reactions that influence the H_3O^+/OH^- concentration in the solution.

For the first two factors Reitemeir found that at ratios of 1:20 and higher, the pH of the solution dominated the pH of the suspensions. However, at lower soil:solution ratios the equilibrium pH of the solution became more like that of the soil. The strength of this tendency is dependent on the pH-buffering capacity of the soil.

Therefore, an extraction performed at a soil:solution ratio lower than the 1:20 ratio for example will produce lower amounts of soluble metal simply due to the pH.

A study by Grover and Hance (1970) found that the dispersion of soil aggregates is influenced when different soil:solution ratios are utilised. They placed 10 g of soil into flasks adding 2.5, 10 and 100 mL of a 0.1 M $CaCl_2$ solution. The dispersion of soil aggregates was greater for the 1:10 than the 1:2.5 ratio. The 1:1 ratio produced intermediate results. This effect could be seen in S1 with the control samples (Figure 3.6). The effect was amplified with the addition of the V treatments.

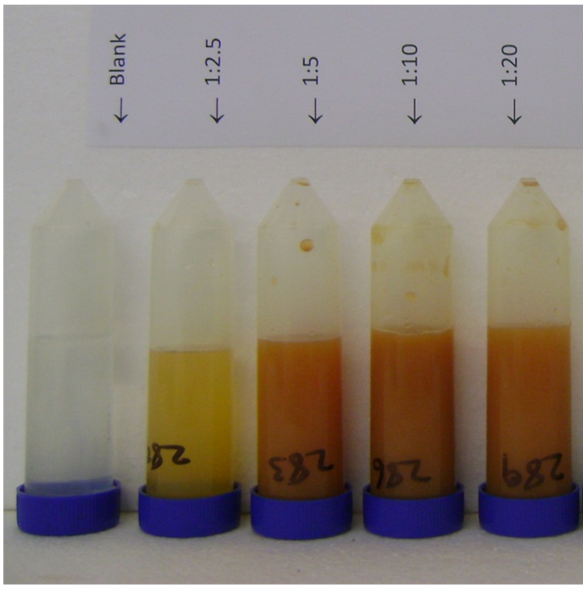

Figure 3.6: Extractions from S1 Control showing increase in colloidal material with increase in soil:water ratio's

The analytical results and statistical analyses of the data showed the permanently charged 2:1 clay minerals had a strong affinity to sorb Cu, Pb and V, resulting in low extractable concentrations. In the case of S1, with predominantly pH dependent charge (1:1 clay minerals), the elements were not strongly adsorbed onto the clay complex and the water extraction methods were able to dissolve more Cu, Pb and V than from S2 (2:1 clay mineral) (Sparks, 2003; Barker and Pilbeam, 2007; Brady and Weill, 2002).

Soluble metal concentration was overestimated with the fixed soil:solution ratio extractions, compared to the saturated paste extract (assumed to be the benchmark for immediately available water quality). This overestimation was more pronounced with higher pollutant concentrations and higher soil:solution ratios.

Most of the soil:solution ratio extracts overestimate the soluble metal concentration of Cu, Pb and V in both soils compared to the saturated paste extract with the 1:2.5 ratio being the closest to the results of the saturated paste extract. In most instances the results for the 1:2.5 extracts were not significantly different from saturated paste results. This was seen for most of the Cu treatments and all the Pb treatments.

For the V treatments, the 1:2.5 extract was only significantly similar to the saturated paste for S2, V0. For S1, none of the 1:2.5 extract results was proven as having no significant difference to values obtained for the saturated paste extract. This overestimation was more pronounced at higher pollutant concentrations and higher soil:solution ratios. The 1:20 extracts, commonly used for analyses of waste samples (Department of Water and Forestry, 1998), specially overestimated pore water quality.

Based on the analytical results and interpretations of this investigation, the 1:2.5 extraction method produced similar values to the saturated paste extract but only at low pollutant concentrations. This method could be used to determine the soluble concentration of soil as an estimate of pore water quality because it is the closest to saturated pastes extract in terms of soil to solution ratio, but more analytically convenient and easy to be done routinely by commercial labs. This is also the standard method used for the determination of soil pH and is therefore considered as an acceptable method for implementation by laboratories. However, this method is not appropriate for polluted sites, as 1:2.5 severely over-estimates metal concentrations compared to saturated paste values.

CHAPTER 4: PARTITIONING COEFFICIENTS OF Cu, Pb AND V FOR SELECTED SOUTH AFRICAN SOILS

4.1 Introduction

4.1.1 Defining K_d

The partitioning coefficient (or K_d) is a factor related to the partitioning of a solute between a solid and aqueous phases (US Environmental Protection Agency, 1999). A single point measurement of K_d is given by the quotient of the concentration of a metal sorbed by the soil and the equilibrium solution concentration:

$$K_d = \frac{C_s}{C_w}$$

Where C_s is the concentration of the sorbed phase and C_w is the concentration in the solute phase.

The units for the K_d depends on the units of the C_s and C_w measurements, and is typically given in mL g^{-1} or L kg^{-1}. Extrapolation of the K_d to other concentrations assumes that the soil has a constant chemical attraction for the solute, i.e. a linear isotherm. Therefore, the solution partitions in the same proportion irrespective of concentration (Papiernik *et al.*, 2002).

The K_d represents the net effect of several soil sorption processes acting upon the contaminant (e.g. ion exchange, complexation, precipitation). This does not necessarily mean that the K_d value for a given chemical in a given soil is constant. Many dynamic soil variables may further affect solid-solution partitioning, e.g. pH, clay content, organic matter content (Brady and Weil, 2002) and the amount of Fe and Mn oxides in the soil. Time is another factor to be considered. Metals become less available over time. Such variables should be taken into account if an appropriate K_d value is to be derived (Ashworth and Shaw, 2006). Another important factor that was not considered in this study is the presence of cations like Ca, Mg, K and Na.

The K_d values of contaminants which are currently used by the South African Framework, are surrounded by uncertainties. Therefore, there is a lack of enough local information regarding K_d values for South African soils. A single value, with an assumed soil pH of 7 derived from international literature for each element, is currently proposed in the Framework for all soil types (Department of Environmental Affairs, 2010). As the K_d is dependent on the metal and soil properties, values reported in literature show high variability that may span over several orders of magnitude. Although a site specific K_d value, determined experimentally will be more accurate and highly recommended in site specific assessments, a conservative approach is followed in the Framework at a screening level to save money and time (Carlon *et al.*, 2004, Covelo *et al.*, 2007).

The aim of this section of the study was to determine K_d values of Cu, Pb, and V for a selection of typically South African soil horizons. By using various diagnostic horizons, it was possible to determine how different ensembles of properties influence K_d values.

4.1.2 Interpreting K_d

A low K_d value indicates a low degree of soil sorption and, potentially, high mobility within the soil profile. On the other hand, a high K_d value indicates a high affinity for the soil solid phase, thus low mobility (Ashworth & Shaw, 2006).

Knowledge of the processes that determine the partitioning of contaminants between the solid and aqueous phases is of fundamental significance in evaluating the risk to groundwater due to contaminants in soil.. The K_d value is an important parameter in chemical models to predict contaminant dynamics in soil systems. Any assessment of the fate, transport and related risks of a contaminant in the geosphere requires a realistic assessment of its K_d value under a range of conditions (Ashworth *et al.*, 2008).

4.1.3 Evaluation of Methods used to Determine the K_d values of pollutants

An ideal approach to determining K_d values experimentally is one in which: a realistic soil water content can be maintained, sufficient time is allowed for time reliant changes in soil variables are permitted to take place, and a representative sample of water can be removed at times without causing major disturbance to the soil-water system.

The most common method used in the determination of the K_d value is the laboratory batch method, other methods include the column (laboratory flow through) method (Papiernik *et al*., 2002), *in-situ* batch method. Look-up tables are also usually used in industry (U.S. Environmental Protection Agency, 1999).

4.1.3.1 Batch Method

For soils, the K_d value of a certain contaminant is most often determined using the batch sorption method in which increasing quantities of the contaminant are added in an excess of solution to a fixed mass of soil. After a period of 'equilibration', the loss of the contaminant from the solution is taken as a measure of soil adsorption (Figure 4.1). It is important to note that at this macroscopic level it is not possible to elucidate the exact mechanisms responsible for the removal of the element from solution.

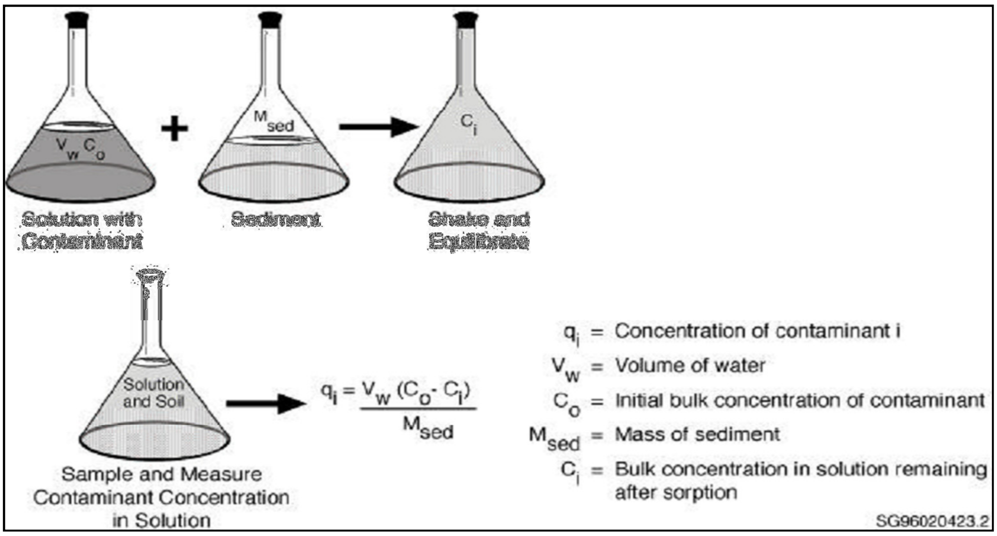

Figure 4.1: Illustration of the batch method to determine K_d (U.S. Environmental Protection Agency, 1999)

The batch method is very popular for determining K_d due to the low equipment, cost and time requirements. However, there are a few disadvantages to this method which include: it provides an estimate of chemical processes occurring at equilibrium which is not always the case in field conditions, better mixing occurs in the batch method than is realistic in nature, and it measures adsorption instead of desorption which usually occurs at a slower rate than adsorption (US Environmental Protection Agency, 1999).

4.1.3.2 Column Method

The column method is the second most commonly used method to determine the K_d of a soil (US Environmental Protection Agency, 1999). Soil column trials, whether in the saturated or unsaturated system, have been used for a range of studies including fate and transport modelling columns (Lewis and Sjöstrom, 2010). With the column method, a solution with known concentration of a chemical is introduced into a packed or monolithic (undisturbed) column. The effluent concentration is then monitored over a period of time (Figure 4.2). Column methods allow for the surveillance of contaminant movement in the presence of hydrodynamic effects (e.g., dispersion, colloidal transport, etc.) and chemical occurrences (e.g. multiple species, reversibility, etc.) which can be incorporated into the K_d value (US Environmental Protection Agency, 1999). These methods also allow for conducting studies at realistic soil:solution ratios which can better simulate field conditions (Sparks, 2003).

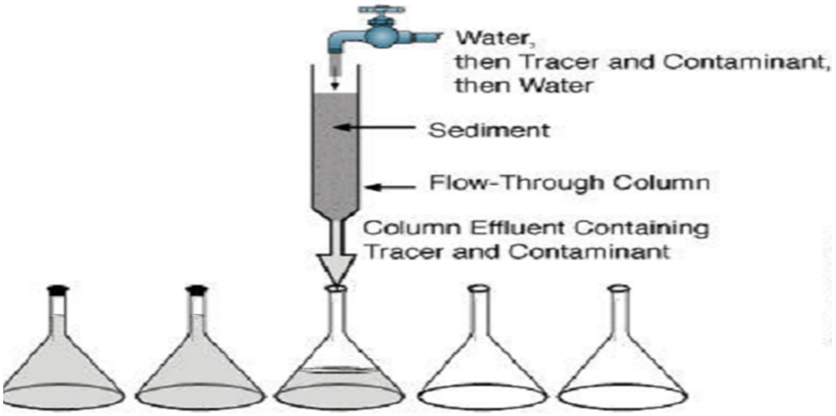

Figure 4.2: Illustration of a column method for determining the K_d of a soil (U.S. Environmental Protection Agency, 1999)

Column methods can measure sorption at field flow rates and non-steady state conditions can be mimicked. Normally flow-through systems are not at equilibrium and the results can therefore not be applied to other flow conditions. The K_d values usually fluctuate with water velocity and column dimensions. Column studies can be more expensive and time consuming to perform.

4.1.3.3 Look-up Tables

Another approach that has been evaluated by the US Environmental Protection Agency (1999) is the look-up table method, where existing data from literature and analytical data is used to set-up a table using different environmental parameters to divide the K_d values into classes. In any K_d look-up table, a small number of ancillary parameters must be selected to define the cells. Strenge and Peterson (1989) used 9 categories defined by soil pH and soil texture (MEPAS look-up table). They used the minimum values found in the literature and thus compiled a conservative model. Soil pH and texture are excellent general categories for a large number of contaminants but may be only of secondary importance to a large number of other contaminants. Redox state is another example of an ancillary parameter that is extremely important relative to affecting the removal from redox sensitive contaminants solution. Some important redox sensitive contaminants include As, Cr, Mo, Se and U. The K_d values of uranium in the 9 MEPAS categories range from 0 to 500 ml g^{-1} (Table 4.1).

Table 4.1: MEPAS look-up table for uranium (adapted from U.S. Environmental Protection Agency, 1999)

pH	9			5-9			≤5		
Fines[1]	<10	10-30	>30	<10	10-30	>30	<10	10-30	>30
U	0	5	50	0	50	500	0	5	50
U(IV)	200	500	1000	100	250	500	20	30	50
U(VI)	0	1	2	1	2	5	2	5	20

[1] Fines (%) = sum of percentages of clay, organic matter, and hydrous-oxide in soil

By including an additional ancillary parameter of oxidation state, appreciably greater accuracy can be assigned to K_d values. Thus, an important point to this discussion is that no single set of ancillary parameters, such as pH and soil texture, is universally appropriate for defining categories in K_d look-up tables for all contaminants. Instead, the ancillary parameters used in look-up tables must be based on the unique chemical properties of each contaminant.

4.1.4 Effects of Soil Properties on K_d values

The vulnerability of soil and groundwater to contamination depends largely on the mobility of the contaminants, described by the distribution ratio between the sorbed and dissolved concentrations. The soil components considered to be responsible for binding metals (especially metal cations) are organic matter, pH, clay minerals, and Fe and Mn oxides. The capacity of a soil to bind specific heavy metal species will depend on the relative proportion and composition of the various soil constituents. The various soil properties influencing the attenuation capacity will be discussed in the sections that follow.

4.1.4.1 Soil pH

The pH of the soil is considered to be the primary soil property that controls every chemical and biological process in the soil environment (Vangheluwe *et al.*, 2005). The pH of the soil applies to the H^+ concentration in solution present in soil pores which is in dynamic equilibrium with the predominantly negatively charged surfaces of the soil particles. The number of negatively charged binding sites for cations is therefore dependant on the soil pH which means an increase in pH promotes the sorption of trace elements (Vangheluwe *et al.*, 2005). Soil pH is therefore considered as a very important soil variable in the attenuation of metals (Sparks, 2003).

Procedures responsible for changes in soil pH cannot be easily separated due to the fact that the pH is a result of the collective activities of soil organisms and abiotic soil chemical processes (Essington, 2004). This parameter has a major influence on a number of soil properties such as the activity of microorganisms, decomposition rate of organic materials and rate of redox reactions (Zeng *et al.*, 2011). Metal speciation, solubility from mineral surfaces, movement and bioavailability is also strongly influenced by soil pH (Zhao *et al.*, 2010).

In a study by Bang and Hesterberg (2004), a decrease in pH revealed an increase in desorption of Cd, Pb and Zn and thus an increase in the mobility and bioavailability of these metals (Wang *et al*., 2006, Du Laing *et al*., 2007). The soil pH can range from pH < 3 in pyritic soils, to pH > 9 in sodium affected or black-alkali soils. Soils with pH values less than 4 and greater than 8.5 is usually considered to be impacted by human activities (Sparks, 2003). In general, heavy metal cations are most mobile under acid conditions and increasing the pH by liming reduces their bioavailability (Kabata-Pendias & Pendias, 2001; Alloway, 1995).

According to Van der Merwe *et al*. (1999), almost 15% of South Africa's arable land is likely to be affected by some degree of subsurface soil acidity and that approximately 60% of the cropland area is moderately to severely acid. The exact extent of human-induced topsoil acidity in South Africa is difficult to ascertain but available information indicates cause for alarm. Natural soil acidification is associated with areas of high rainfall. Within these areas differences may arise due to differences in geology, topographic position and vegetation. The main source of soil acidification on agricultural soils is as a result of the use of NH_4-based fertilizers. The industrial activities of man are the major sources of the dry fallout of oxides of S and N as well as the wet deposition of acids (so-called acid rain) on soil surfaces which causes severe soil acidification. Man is also partly responsible for the increase in carbon dioxide (CO_2) levels in the atmosphere, leading to the deposition of carbonic acid. The worst affected area is the southern Mpumalanga Highveld with its major mining and heavy industries, as well as the biggest concentration of coal-fired power stations in South Africa.

4.1.4.2 Clay Content

Clays are soil particles less than 2 µm in size, having a higher surface area than other soil particles like sand and silt (Vangheluwe *et al*., 2005; Brady & Weil, 2002). These small particles have a permanent charge which is mainly negative but in some instances a positive charge can develop (Coyne & Thompson, 2006). Cations are attracted to the predominantly negative charged surfaces which render them less mobile than in situations where these charges are not available, i.e. where there are less clay particles.

Clay minerals are the products of rock weathering and affect both soil physical and chemical properties. The amount and type of clay minerals present affects soil factors such as the shrink-swell behaviour, plasticity, water holding capacity as well as the exchange capacity of the soil (Brady & Weil, 2002). Clay minerals may contain small amounts of trace elements as structural components, but their sorption capacities to trace elements play a very important role. The cation sorption capacities of different clay minerals vary in the following sequence: montmorilonite, vermiculite > illite, chlorite > kaolinite (Kabata-Pendias & Pendias, 2001).

4.1.4.3 Iron and Mn Oxides

Metal oxides are hydrous and anhydrous oxide, hydroxide and oxyhydroxide minerals of metals such as Fe or Mn. These metal oxides play an important role in the chemistry of soils as they have significant effects on many soil chemical processes such as sorption and redox due to their high specific surface area (Sparks, 2003). They are also referred to as accessory minerals owing to their intimate association with the layer silicates. They occur in the clay size fraction of soils, usually mixed with the clays. Metal oxides are able to mask the surface properties of layer silicates (Essington, 2004). Unlike the layer silicates that have predominantly negative surface charge due to isomorphic substitution, the metal oxides have a pH dependent charge and can consequently develop a negative or positive charge subject to the soil chemical properties (negative charge in alkaline conditions and positive in acid conditions) (Kabata-Pendias & Pendias, 2001).

Iron and Mn oxides co-precipitate and adsorb cations including Co, Cr, Mn, Mo, Ni, V and Zn from the soil solution. Iron and Mn oxides have a much greater adsorption capacity for trace element cations than Al oxides and other clay minerals (Basta *et al*., 2005). Variations in redox conditions affect the quantities of hydrous oxides in the soil as well as the adsorptive capacity of the soil. The onset of reducing conditions result in the dissolution of the oxides and the release of their adsorbed ions (Alloway, 1995).

4.1.4.4 Soil Organic Matter

Soil can be distinguished from regolith or weathered rock by the presence of living organisms and organic debris which is termed organic material. Organic matter is stable in the soil. It has been decomposed until it is resistant to further decomposition. Usually, it is believed that only about 5% of the soil organic matter is mineralized annually (Brady & Weil, 2002). That rate increases if temperature, oxygen, and moisture conditions become favourable for decomposition. Organic substances play an important role in biochemical weathering and geochemical cycling of trace elements (Kabata-Pendias & Pendias, 2001).

Organic matter serves as a reservoir of nutrients, trace elements and water in the soil, aids in reducing compaction and surface crusting, and increases water infiltration into the soil. It has many negative charges due to the dissociation of organic acids, which have a high affinity to adsorb metal cations and reduce its availability (Basta *et al*., 2005; Vangheluwe *et al*., 2005). These elements are gradually released into the soil solution and made available to plants throughout the growing season (Brady & Weil, 2002). They can exist in various forms: discrete particles, coatings on minerals, colloids or solutes (Staunton, 2004). It has a major influence on the buffering capacity, hydrological cycles and the regulation of elemental cycles in the soil (Coyne & Thompson, 2006).

Soil organic matter plays a vital role in metal attenuation. Apart from soil pH, it is viewed as the most important soil factor controlling metal movement. Studies conducted by Sauvé *et al* (2000) indicated that the majority of dissolved metals in soil were found in organo-metallic complexes. Consequently, any factor that has an influence on the organic matter will have an influence on the metal solubility.

According to Barnard (2000), the majority of South African top soils contained less than 0.5% organic matter. It was noted by du Preez *et al*. (2011) that the distribution of organic carbon on the surface layer of South African soils is to a great degree linked to the average rainfall of the country.

4.2 Methodology

The methodology used to determine the K_d values of Cu, Pb, and V for selected South African soil horizons are described in the following section.

4.2.1 Soil selection

The soil selection was based on the South African soil classification system (Soil Classification Working Group, 1991). The GPS coordinates as provided in the Land type survey data base was used to locate the areas in which these soils occur. A hand auger was used to extract the desired soil horizon. The soil samples were air dried and sieved through a 2 mm sieve before treatment applications.

Selected 10 soil horizons were evaluated for logistic reasons. These soil horizons were selected based on the lack of K_d value information for these horizons as well as their abundance where predominantly South African soil forming factors exist. Detailed information about the ten soil horizons and the location where the samples were collected is presented in Table 4.2.

4.2.2 Soil properties

Characterization of the soils used in the K_d trial was done at the Soil Science Laboratory of the Department of Plant Production and Soil Science, University of Pretoria. The soil pH in water, as well as that in 1 *M* KCl was done using a 1:2.5 soil:solution ratio. The organic carbon content was determined using the standard Walkley Black method and the particle size analysis was conducted with the hydrometer technique. The cation exchange capacity (CEC) was determined by extracting with 1 *M* ammonium acetate solution at pH 7. These analytical methods are described in the Handbook of Standard Soil Testing Methods for Analytical Purposes (Non-affiliated Soil Analysis Work Committee, 1990). Exchangeable Fe, Mn and Al was done with the dithionite-citrate-bicarbonate extraction method as described by Mehra & Jackson (1960). Selected properties of the 10 soils used in this investigation are presented in Appedix A.

Table 4. 2: Ten soil horizons selected for K_d determination with the Land type survey reference number (where applicable) and GPS coordinates

Soil Horizon	Land type survey reference number	Latitude	Longitude
1:1 clay dominated A horizon	n/a	NA	NA
Vertic soil dominated by 2:1 clay	n/a	NA	NA
Yellow Oxidic/Plinthic (soft plinthic B horizon)	C2562	-26.24079	28.82683
Low clay Red Oxidic B horizon	C4058	-25.52733	28.47681
Plinthic B horizon	C4097	-26.64243	28.65322
E-horizon	C4107	-26.82118	28.40731
Orthic A horizon with high organic content	C4650	-24.92210	30.85030
Melanic A horizon	C5405	-25.62100	26.61060
Red Oxidic B horizon	C5414	-25.61720	27.03950
Gleyed horizon	C5787	-25.20604	27.35623

4.2.3 K_d determination methodology

The most commonly used procedure for measuring the K_d of a soil and a specific metal is by using a batch method. Soil samples are spiked with a range of known concentrations of a chemical compound in order to obtain a sorption isotherm. The K_d is then represented by the slope of the isotherm. The spiked soil samples are allowed to equilibrate before extraction in order to determine the loss of added compounds from the solution. The loss from solution is calculated by determining the difference between the initial elemental concentration of the solution added and the equilibrium concentration of the metal. (Papiernik *et al.*, 2002). Figure 4.3 shows the experimental design of the trial.

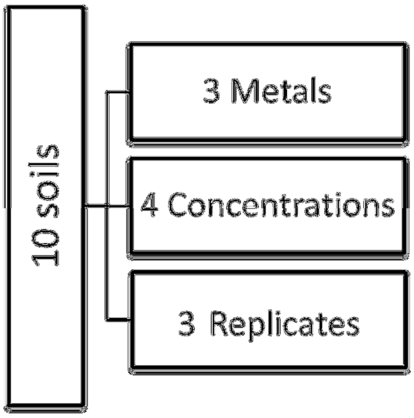

Figure 4.3: Experimental design for the determination of K_d values for the 10 selected soil horizons experimentation

The procedure followed for the determination of K_d is given below:

A mass of 4g soil (sieved and homogenized) was weighed into a 50 ml centrifuge tube. Three replicates for each test was prepared. Various solutions (16 ml) with known Cu, Pb and V concentration were added to the soil samples (Table 4.3). A 0.01 *M* $Mg(NO_3)_2$ solution was used as background electrolyte. In the case of Cu, a cocktail of Cu salts were used: $CuSO_4$, $Cu(NO_3)_2$ and $CuCl_2$. For Pb contamination, a $Pb(NO_3)_2$ chemical agent was added and for V ammonium metavanadate (NH_4VO_3) All chemicals used were of an analytical grade and purchased from Merck. was added to achieve the required V concentrations. The tubes were shaken for 24 hours on a mechanical shaker. After 24 hours, the solid and liquid phases were separated by centrifuging the samples at 4 000 rpm for 30 minutes. The supernatant was then filtered through a 0.2 µm membrane filter. An ICP-OES was used to determine the concentrations of metals extracted. This concentration was then multiplied with the solution volume (L) and divided by the soil mass (kg) then subtracted from the concentration of the metal added to give the concentration sorbed (Papiernik *et al.*, 2002).

Table 4. 3: Four concentration level treatments of Cu, Pb and V added to spike soil samples for batch equilibrium adsorption study

Treatment	Metal added (mg kg^{-1})		
	Cu	Pb	V
0	0	0	0
1	75	651	117
2	159	1692	215
3	189	3118	330

4.3 K_d values of Cu, Pb, and V for typical South African soils

The K_d values of Cu, Pb, and V for selected soil horizons of typical South African soils were determined from a graph of the solution metal concentration plotted against the sorbed metal concentration in the respective soil horizons. The K_d is established by using the slope of the linear graph, which gives a value in L.kg^{-1} (Papiernik *et al.*, 2002). The K_d was then plotted against soil pH, percentage organic carbon (%OC), clay content (clay) and the amount of extractable Al, Fe and Mn. The following sections cover the K_d values determined and the effect of some soil properties on the K_d values of Cu, Pb and V. Detailed analytical results of the K_d investigation are presented in Appendix D.

4.3.1 Copper

The estimated K_d values of Cu for the 10 soil types used in this study, as determined by the slope of the linear regression of the graphs in Figures 4.4 and 4.5, ranged from 12.7 to 19044 L kg^{-1}. It should be noted that the values on the x-axis, the equilibrium Cu, are not all the same. Lower K_d values were observed for the 1:1 clay soil, the red oxidic and plinthic horizons. The red oxidic high clay soil (43.3% clay) (19044 L.kg^{-1}) has a K_d much higher that the red oxidic soil (15.4% clay) with Cu K_d values of 19044 and 14.6 L kg^{-1} respectively. Soils with higher clay and organic carbon contents generally had higher K_d values (vertic, red oxidic with high clay content, melanic and gleyic soils). This difference in the K_d values for different soil horizons indicate the effect of soil properties on the sorption capacity of soils and thus underlines the importance of using appropriate K_d values.

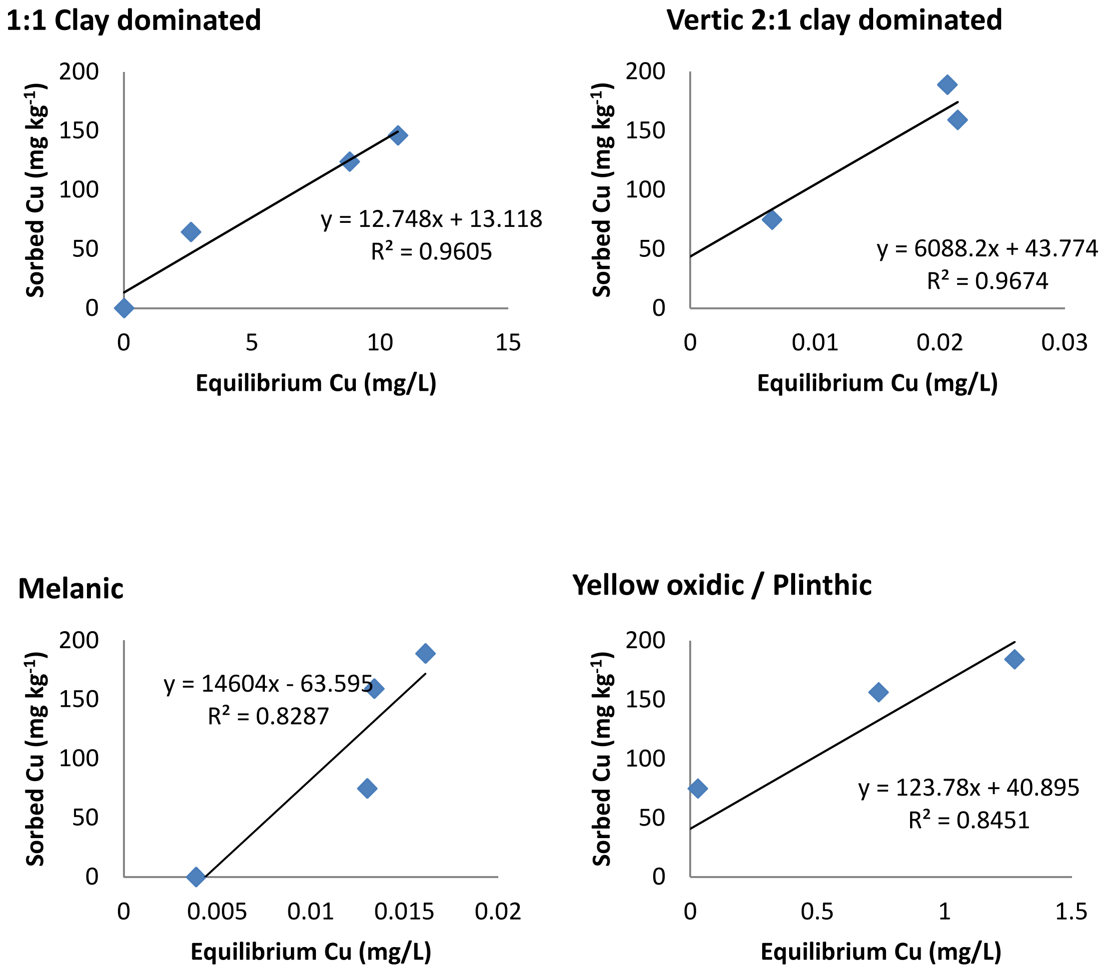

Figure 4.4: Copper sorption graphs for the 1:1 clay dominated, vertic, melanic, yellow oxidic/plinthic.

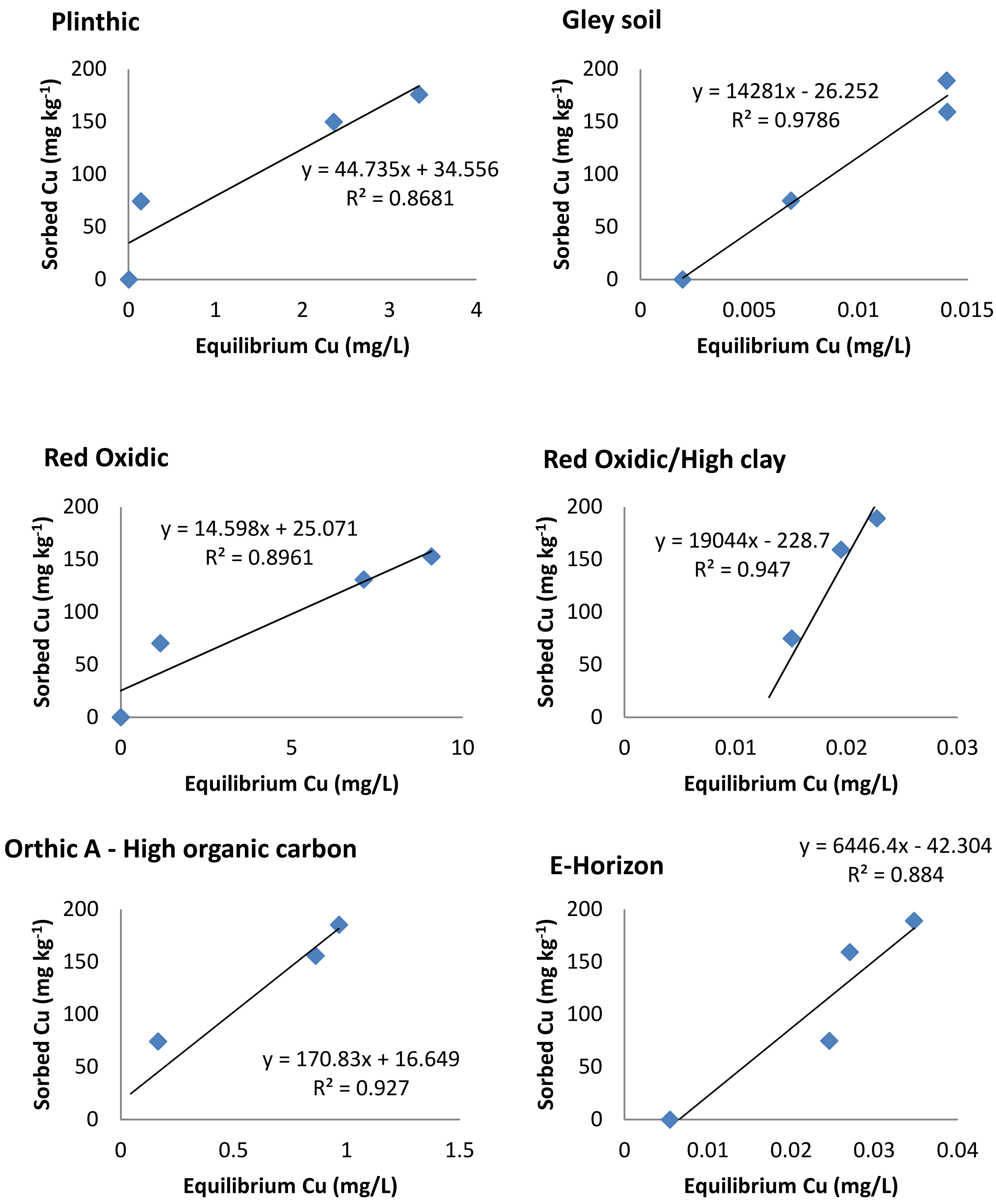

Figure 4.5: Copper sorption graphs for the plinthic, gley soil horizons red oxidic, red oxidic/high clay, orthic A, and E-horizons

4.3.2 Lead

The K_d values for Pb, derived from the slope of the linear regression in Figure 4.6 and Figure 4.7, ranged from 24.8 to as high as 252294 L kg^{-1}. For the vertic and melanic horizons, higher Pb input concentrations were required to determine the K_d value as all the Pb added to the soil was adsorbed. This resulted in equilibrium Pb concentration being below detection. Vertic and melanic soils are known to be highly buffering toward water and chemical substances (Fey, 2010). Therefore, no graphs could be compiled for these 2 soils. For the red oxidic (high clay) soil, extractable concentrations were available only at very high Pb applications of 1692 and 3118 mg l^{-1} solutions.

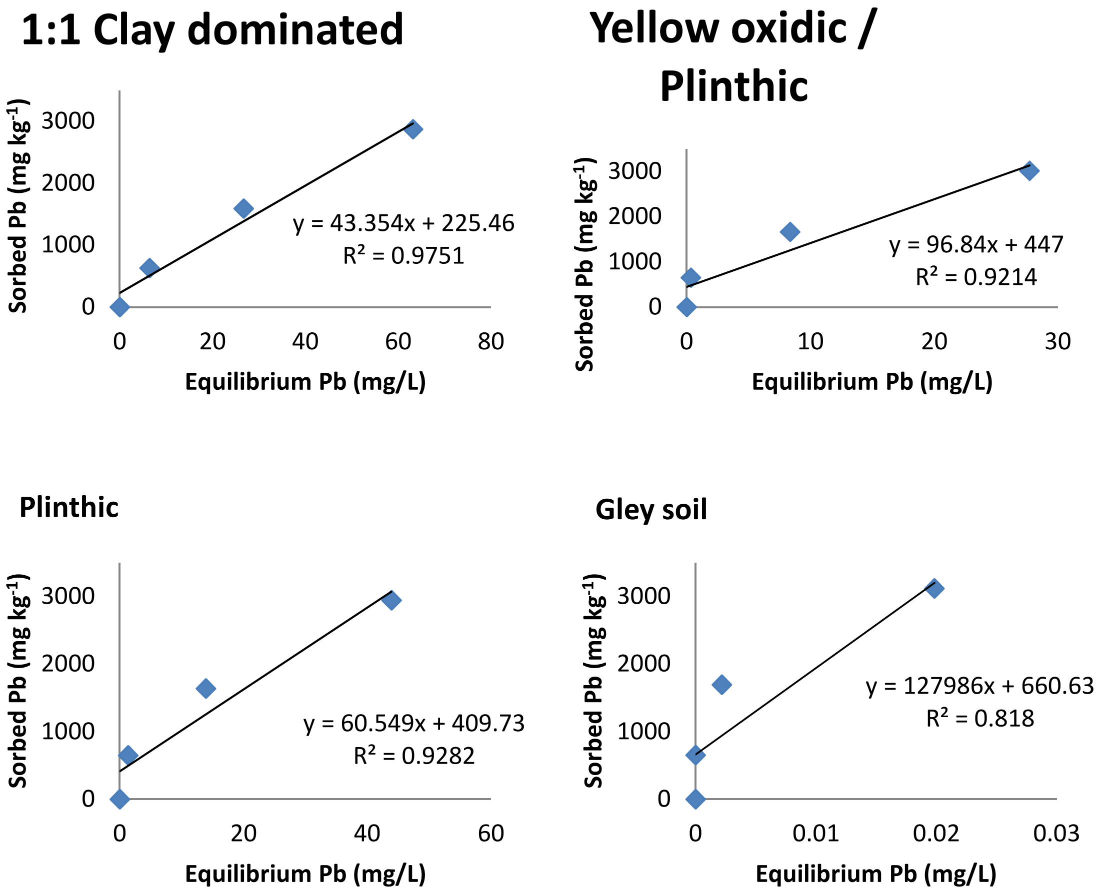

Figure 4.6: Lead sorption graphs for 1:1 clay, yellow oxidic/plinthic soil horizons, plinthic, gleyic soils

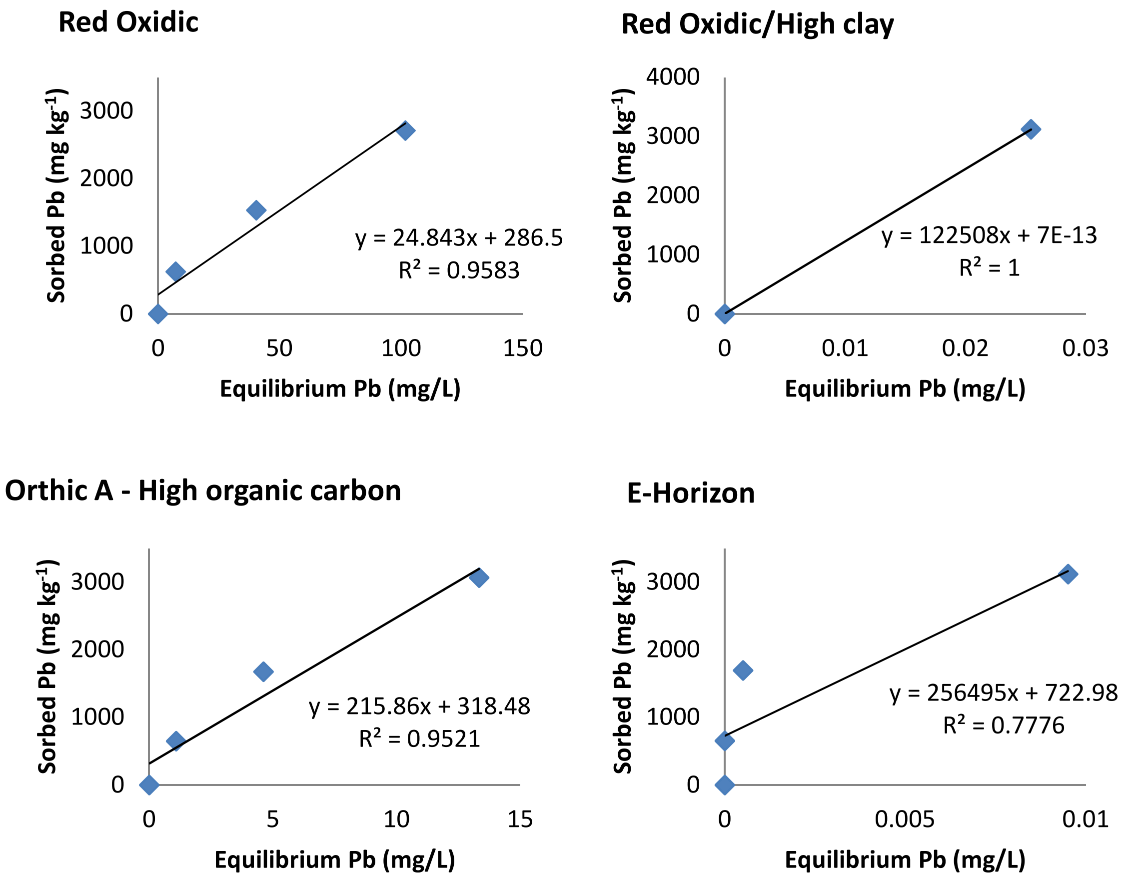

Figure 4.7: Lead sorption graphs for the, red oxidic and red oxidic/high clay soil horizons

4.3.3 Vanadium

The K_d value of V given in the Framework is 1000 L kg^{-1} while the highest K_d values for V in this study was 865 L kg^{-1} for the 1:1 clay dominated soil, 708 L kg^{-1} for the orthic A horizon and 629 L kg^{-1} for the plinthic B horizon (Figure 4.8 and Figure 4.9). The K_d values for the rest of the soils varied between 10.5 L kg^{-1} and 220 L kg^{-1}. This shows that the K_d selected by the Framework appears to be too conservative and may allow contaminted land to be wrongly classified as uncontaminated.

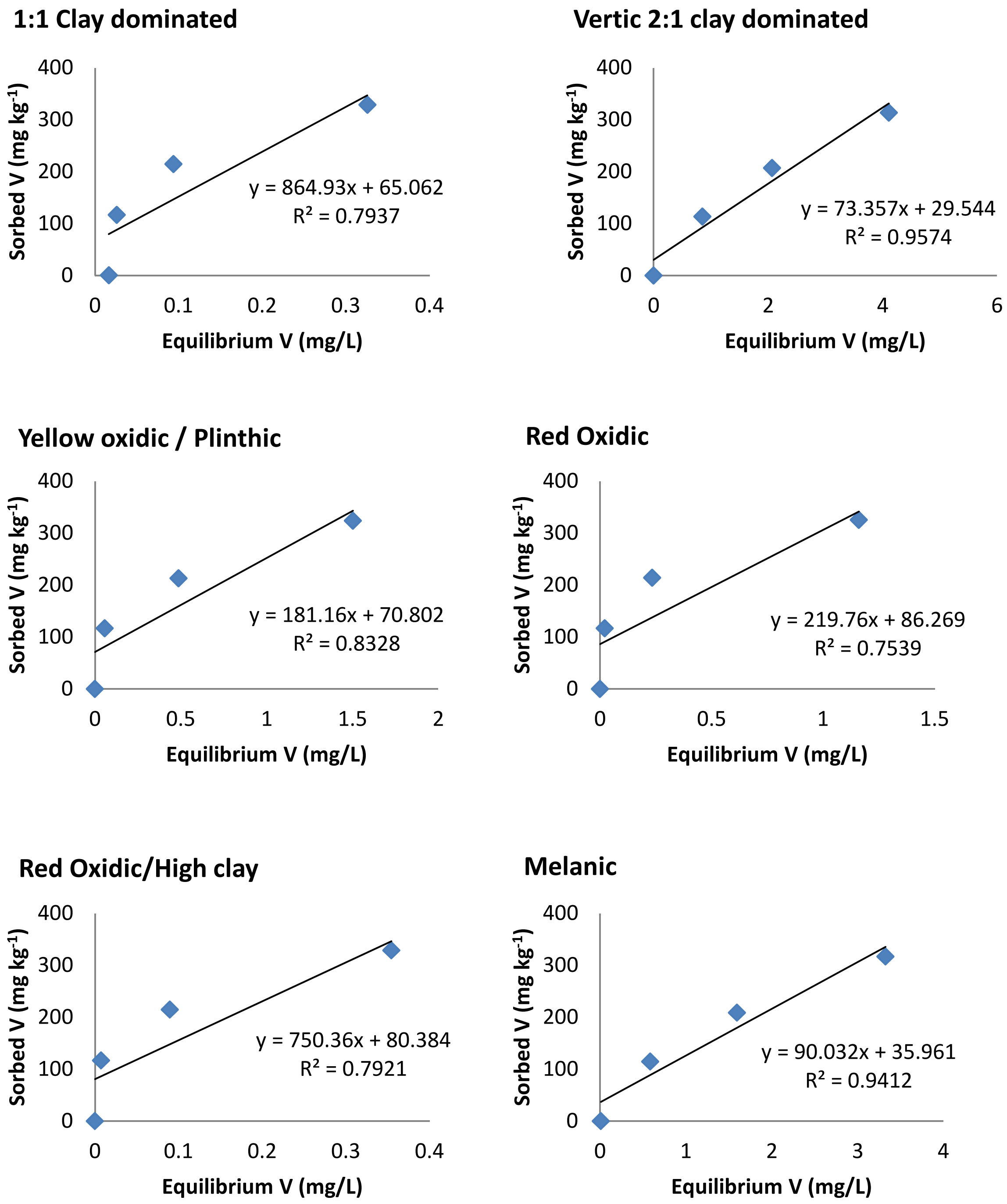

Figure 4.8: Vanadium sorption graphs for the 1:1 clay, vertic, yellow oxidic/plinthic, red oxidic, red oxidic/high clay and melanic soil horizons

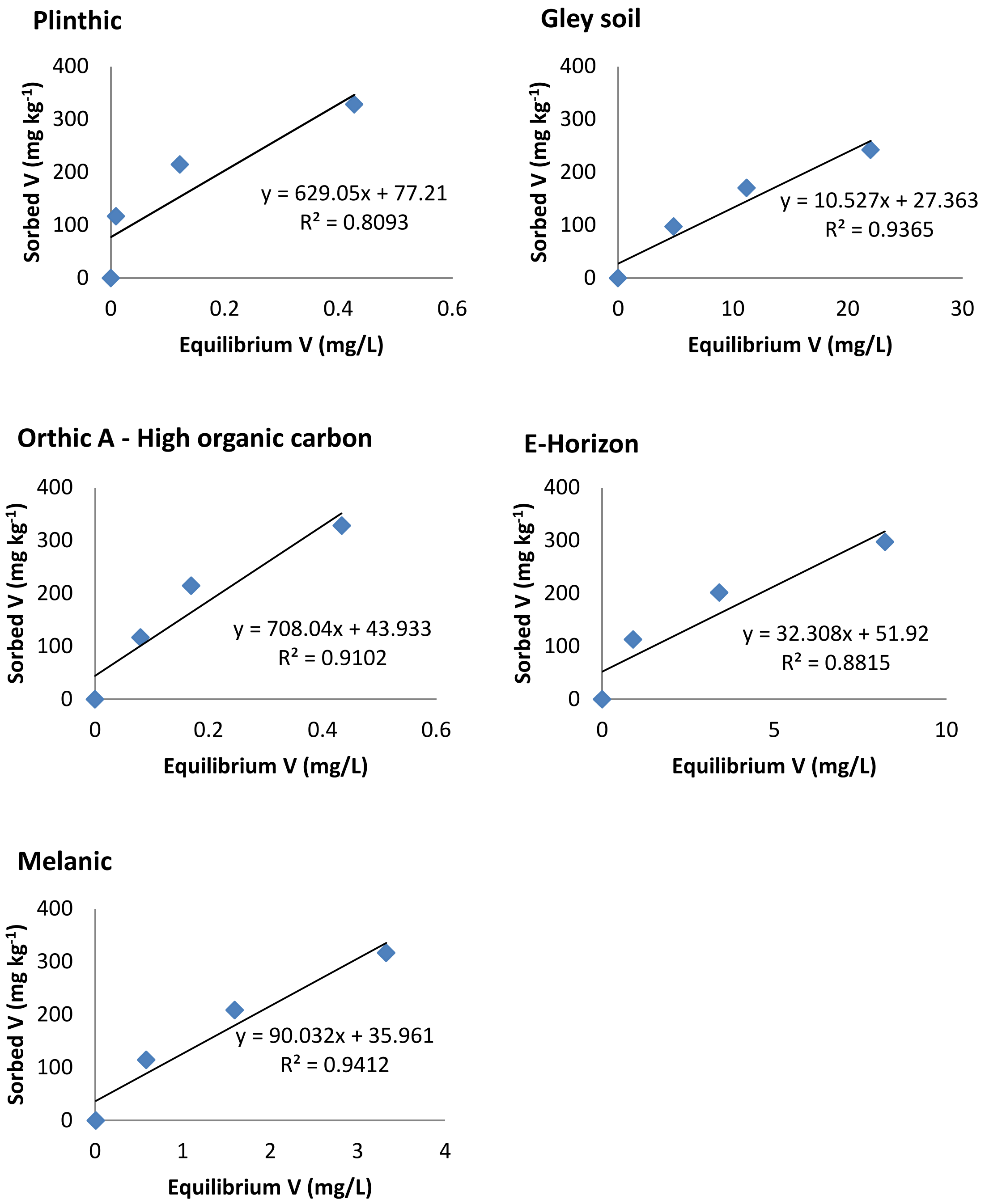

Figure 4.9: Vanadium sorption graphs for the plinthic, gley, orthic A, melanic and E-horizons

4.4 The effect of soil properties on K_d values of Cu, Pb, and V in typical South African Soil Horizons

In this section two distinct statistical methods are applied to assist in the determination of a more appropriate K_d value when very few measured data points are available. The first method is by multiple linear stepwise forward regression to construct an equation for the determination of a soil specific K_d using minimal soil parameters. The second method is by means of a Principal Component Analysis (PCA) where soil horizons are grouped according to the size of the soil properties and K_d value.

4.4.1 Multivariate Linear Regression

Multiple linear regression analysis was used to predict K_d. Forward stepwise regression was used to find the most predictive model. Multiple regression is a flexible tool for the examination of the relationship between a number of independent variables (predictors) and a single dependant variable (criteria) (Aiken *et al*., 2003). Some of the data used in the study were transformed before multiple regression was carried out in order to meet the assumption of normality and homogeneous variances required by the regression method.

A number of studies have been done to attempt to explain the mobility of heavy metals as a function of total metal content, pH, OC, CEC and Fe and Al oxides (John, 1972; Kuo et al., 1985; Bogacz, 1994; He and Singh, 1993; Jopony and Young, 1994; McBride et al., 1997; Sauve´ et al., 1997, 1998).

The method consisted of determining the multiple linear regression model in such a way as to minimize the squared deviations of the observed points from the predicted outcomes. The independent variables are included into the model one by one, with the most significant variables included into the final model. The goodness of fit of the model was evaluated by the adjusted R^2 value and the standard error of the regression was used to provide the dispersion of the observed values around the regression line (Carlon *et al*., 2004). Significance was determined at the 5% level.

For each metal a stepwise forward regression was performed on the predictors pH(H_20), the square root of OC ($\sqrt{OC}$), the log base e of Fe (InFe) and the Kd value to provide a linear regression model which can give a reliable prediction of the K_d for that metal.

4.4.1.1 Copper

The soil properties which were responsible for approximately 97.9 % of the variation observed in the K_d value of Cu were soil pH, OC, Fe and CEC. The range of data, adjusted R^2, standard error of the regression and model probability is presented in Table 4.4. The resulting linear regression model for the prediction of Cu K_d value is given below.

$$Predicted \ln Cu\ K_d = -26.5 + 4.11pH + 6.38\sqrt{OC} + 2.52lnFe - 0.166CEC$$

Table 4.4: Statistical parameters for the Multivariate Stepwise Regression of Cu K_d values and soil properties

Term in Model	Range	Adjusted R^2 %	Standard Error of regression	Probability of model with each added term
pH	4.8 – 9.4	61.0	1.89	0.005
%OC	0.08 – 5.0	73.3	1.56	0.004
%Fe	0.57 – 13.3	81.2	1.31	0.0004
CEC	7.9 – 44.2	97.9	0.443	<0.001

Soil pH is a master variable determining many chemical reactions (Kabata-Pendias, 2007). Organic carbon is considered to be the most important component responsible for binding Cu in soils. The OC is believed to regulate mobility and bioavailability of Cu in soils (Flemming and Trevors, 1989). Copper sorption onto Fe and Al hydrous oxides and hydrous Mn oxides is significant in soils. Work by Thornton (1979) indicated that Mn oxides showed the highest affinity for Cu with Fe oxides showing the weakest specificity of the three oxides. The CEC is a function of the clay mineralogy of the soil and is thus mainly dependent on the clay content and clay mineralogy.

4.4.1.2 Lead

Approximately 67.4 % of the variation observed in the K_d value of Pb can be explained by the soil pH and CEC. The range of data, adjusted R^2, standard error of the regression and probability is shown in Table 4.5. The resulting linear regression for Pb K_d is given below:

$$Predicted \ln Pb\ K_d = -10.6 + 1.88pH + 0.437CEC$$

The soil properties predicted in the multivariate regression corresponds to work done by Zimdahl and Skogerboe (1977) where pH and CEC were also found to be the most important factors in a multivariate regression constructed to predict the moles of lead per gram of soil at saturation. Clay content, organic matter and Fe and Mn oxides were found to be of secondary significance.

Table 4.5: Statistical parameters for the Multivariate Stepwise Regression of Pb K_d and soil properties

Term in Model	Range	Adjusted R^2 %	Standard Error of regression	Probability
pH	9.4 – 4.8	53.0	2.79	0.025
CEC	7.9 – 44.2	67.4	2.33	0.026

4.4.1.3 Vanadium

Approximately 90.4 % of the variation in the K_d values of V can be explained by the soil pH, clay content and Al. The range of data, adjusted R^2, standard error of the regression and model probability is shown in Table 4.6. The resulting linear regression for predicting the K_d value of V is given below:

$$Predicted\ ln\, V\ K_d = 4.41 - 0.395pH + 0.0675clay + 4.17Al$$

Unlike the other cationic metals such as Cu and Pb, V reacts as an anionic species (Gäbler, *et al.,* 2009). Clay lends a significant contribution to the predicted V K_d value. This was not the case with Cu and Pb. This is due to the fact that V was added to the soil in an anionic form. The CEC was determined and not the AEC. If the AEC was determined it might have been a factor in the regression instead of clay. The same argument applies to Al. Aluminium is a component of clay minerals and is the closest measurement in the data set to link V K_d with mineralogy and AEC.

Table 4.6: Statistical parameters for the Multivariate Stepwise Regression of V K_d and soil properties

Term in Model	Range	Adjusted R^2 %	Standard Error of regression	Probability
pH	9.4 – 4.8	69.0	0.904	0.002
Clay %	3.3 – 47	86.3	0.601	<0.001
Al %	0.06 – 0.87	90.4	0.503	<0.001

4.4.2 Principle Component Analysis

In order to establish which soil horizons are most similar in terms of soil properties and K_d value, PCA was conducted. All statistical analyses were done using the XL*STAT* and GenStat® (Payne, *et al.,* 2012) statistical programs.

Principle component analysis is a multivariate statistical technique. This simplifies the understanding of the data. The objective of the PCA is to transform the set of original correlated variables into a new set of principal soil components, which are linear combinations that explain the greatest amount of observed variability in the data. PCA enables one to reduce the number of soil properties measured in terms of its contribution to the variation in a data set. Essentially, PCA enables one to reduce a large amount of variables to a new set of variables or principle components (Ul-Saufie *et al*., 2013).

Through PCA, the correlation structure of a group of multivariate observations is analysed and the axis along which maximum variability of the data occurs is identified and referred to as the first principal component or PC1. The second principal component or PC2 is the axis along which the 2nd greatest amount of the remaining variability lies.

From the PCA scores generated by this statistical method, a biplot is constructed. A biplot is a two-dimensional graph of the first two principle component scores that account for the most of the variation in the data. Points close together are most similar and points far apart are most dissimilar with respect to some of the soil properties.

Principle component analysis was applied to the soil data in order to identify the main variables that explained the differences in soil horizons. Both the soil property and soil horizon scores are plotted on the biplots for Cu, Pb and V respectively. PC1 which accounts for most of the variation in the data is plotted on the x-axis and PC2 on the y-axis. (Payne *et al.*, 2012).

The correlation between soil horizons are measured in terms of the distance the soil horizon is from a certain soil property on the biplot. By using the biplot soil horizons can be grouped based on associated soil properties.

All data was first checked for normality and transformed where required. The closer to one another they are, the larger the positive correlation between them; when they are opposite to each other the correlation is negative. Detailed Cu, Pb and V PCAs can be found in Appendix E.

4.4.2.1 Copper

A PCA biplot for Cu is presented in Figure 4.10 and scatter plots showing the relationship between Cu and some soil properties are shown in Figure 4.11. Soil forms are indicated on the biplot as points (blue) with the soil properties shown as vectors (red). From the PCA output data the PC1 accounted for 30.9 % of the variation in all the soil property data. PC2 accounted for 24.1 % of the variation. The two-dimensional biplot thus accounted for 55.0 % of the variation.

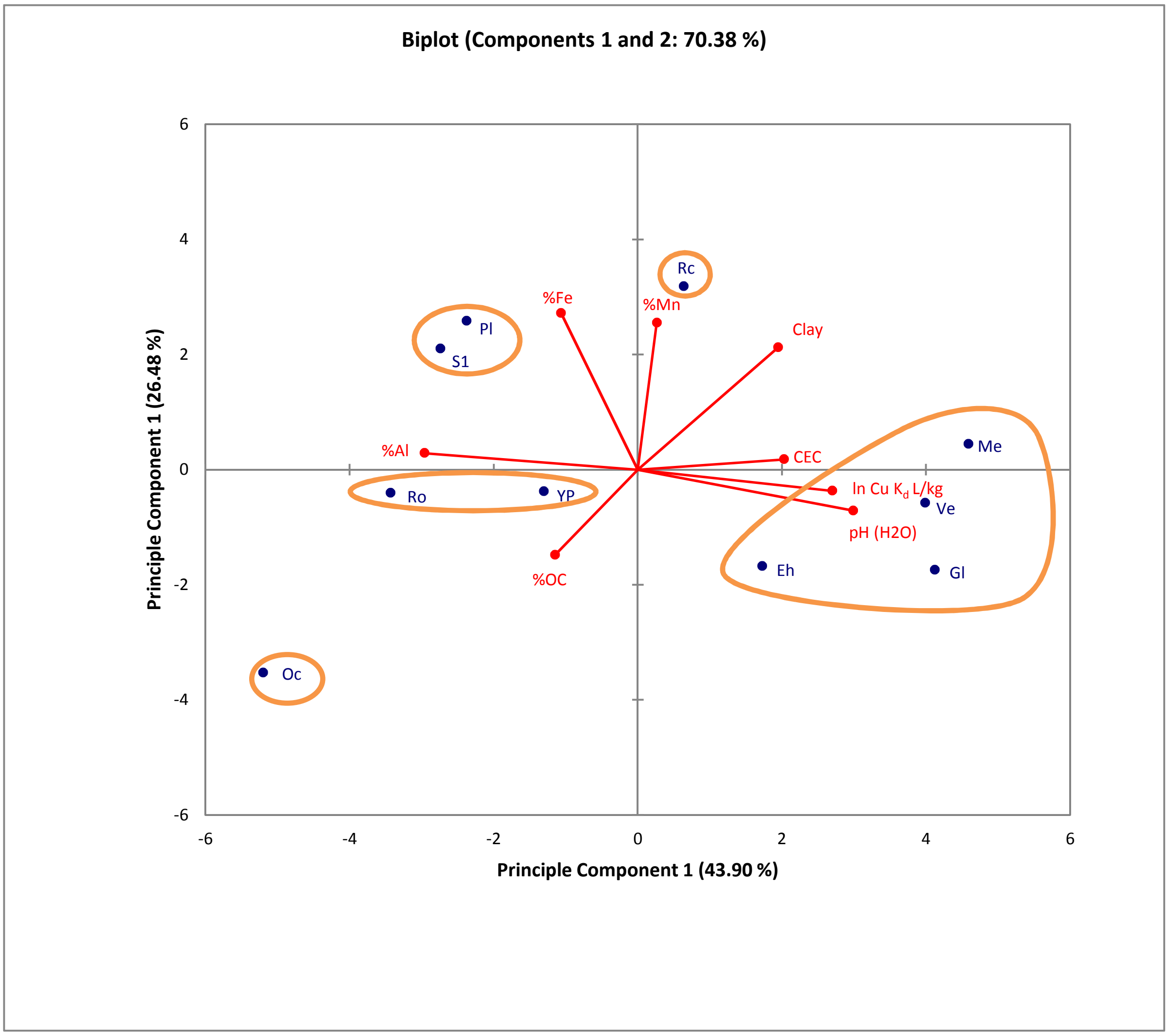

Figure 4.10: Principle Component Analysis for Cu and soil properties. S1 (1:1 clay dominated), Ve (Vertic 1:2 clay dominated), YP (Yellow oxidic/Plinthic, Ro (Red Oxidic), Rc (Red Oxidic/High clay), Me (Melanic), Pl (Plinthic), Gl (Gley), Hu (Orthic A high OC), EH (E-horizon)

Based on the PCA for Cu, five soil horizon groups could be identified as follows: a) S1 (1:1 clay dominated) and Pl (Plinthic) are most similar with the points plotted close together in the left upper quadrant and mostly associated with the soil properties % Fe and % Al; b) Ro (Red oxidic) and YP (Yellow oxidic/Plinthic) are mostly associated with % Al and % OC; c) Oc (Orthic A high OC) is found to be closest to the % OC vector; d) the Eh (E-horizon), Ve (Vertic) and Gl (Gley) horizon is plotted with pH and Cu K_d in the bottom right quadrant. These horizons are thus most similar in terms of their pH and K_d values; e) Melanic (Me) is plotted in the top right quadrant also close associated with pH, Cu K_d, but mostly associated with CEC; and f) Rc (Red oxidic/high clay) is closely associated with the clay content and % Mn.

From the PCA diagram, the following conclusions could be tabulated (Table 4.7):

Table 4.7: Copper K_d value ranges as determined by groupings using the PCA

Soil Profile	Dominant Differentiating Soil Properties	Cu K_d Range L kg^{-1}
S1, Pl	% Fe and % Al	13 – 45
Rc	% Mn	19 044
YP, Ro	% Al, % OC	14.6 – 124
Oc	% OC	171
Ve, Me, Eh, Gl	CEC, pH and Cu K_d	6 090 – 14 607

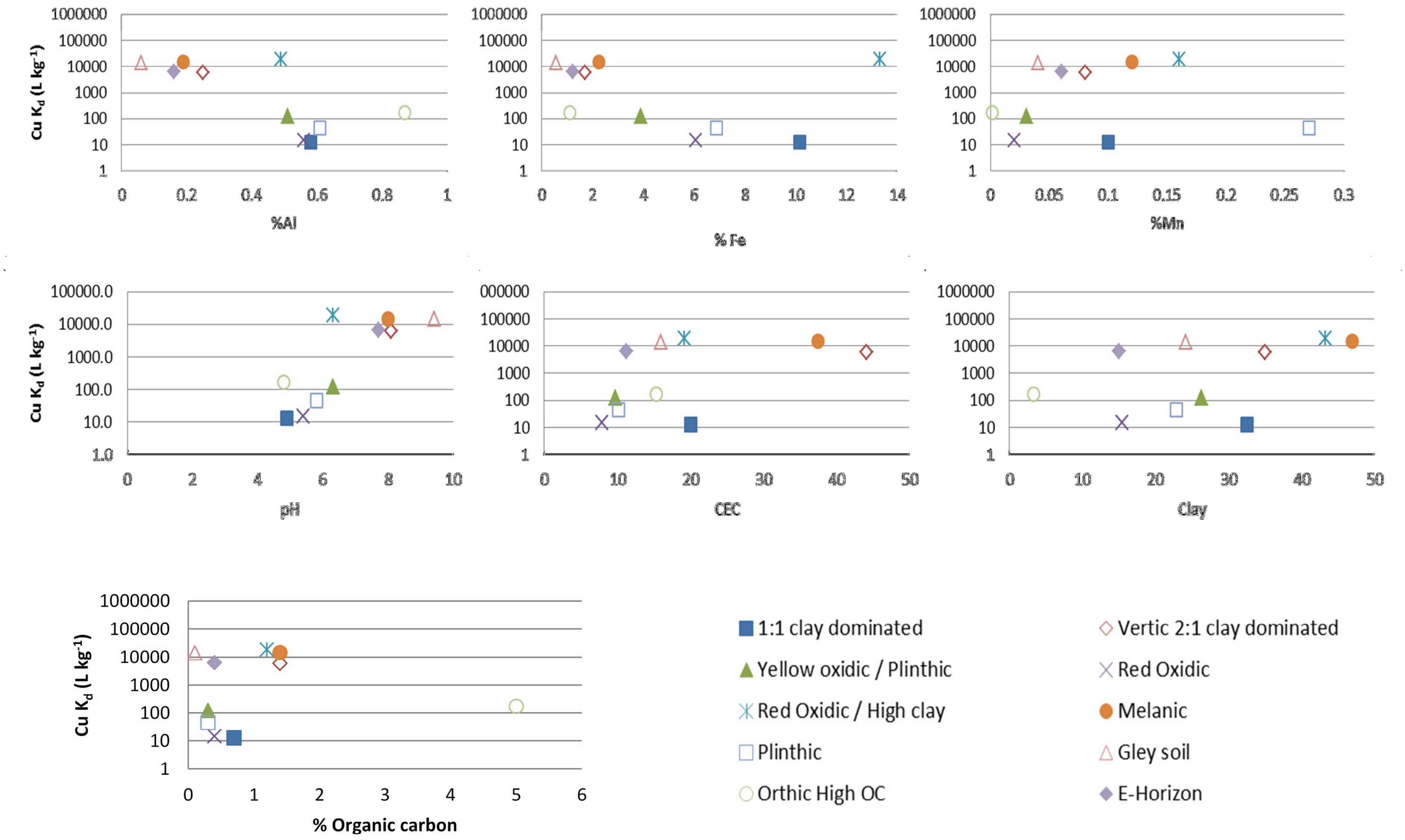

Figure 4.11: Relationship between Cu K_d value and selected soil properties

4.4.2.2 Lead

A principal component analyses biplot for Pb is presented in Figure 4.12. Scatter plots of soil profile specific Pb K_d values compared to some soil properties are shown in Figure 4.13. From the PCA output data the PC1 accounted for 38.5 % of the variation in all the soil property data. PC2 accounted for 32.9 % of the variation.

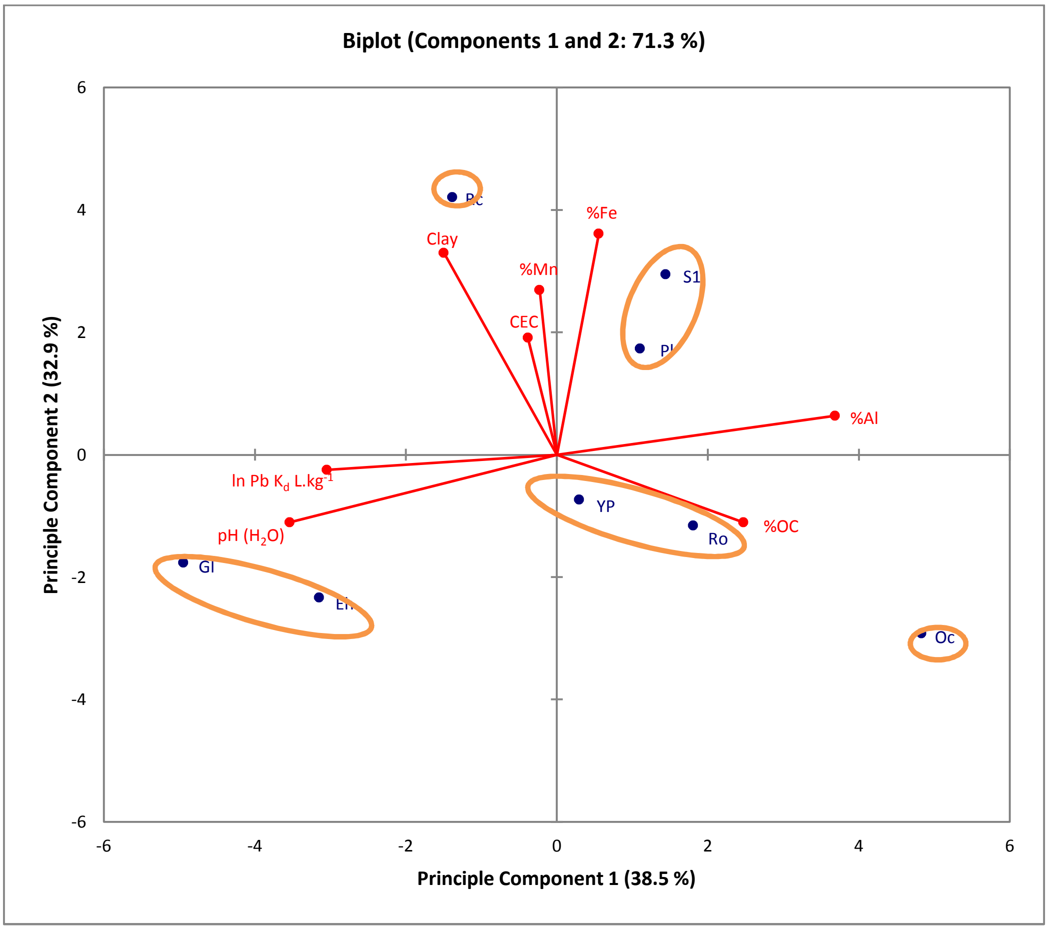

Figure 4.12: Principle Component Analysis for Pb and soil properties. S1 (1:1 clay dominated), Ve (Vertic 1:2 clay dominated), YP (Yellow oxidic/Plinthic, Ro (Red Oxidic), Rc (Red Oxidic/High clay), Me (Melanic), Pl (Plinthic), Gl (Gley), Hu (Orthic A high OC), EH (E-horizon)

The two-dimensional biplot accounted for 71.3 % of the variation. Based on the PCA for Pb, five soil horizon groups could be identified namely: a) S1 and Pl horizons display most similar results with the points plotted close together in the right upper quadrant and mostly associated with the soil property % Fe and % Al; b) Ro and YP are mostly associated with % OC; c) Oc is mostly associated with % OC but situated much further from YP and Ro in the right lower quadrant; d) the Gl and Eh horizons are situated in the lower left quadrant and is mostly associated with pH and Pb K_d;

and e) Rc is closely associated with the clay content, CEC and % Mn. Table 4.8 summarizes the soil profiles and the K_d ranges as determined by the PCA diagram.

Table 4.8: Lead K_d value ranges as determined by associations determined with PCA

Soil Profile	Dominant Differentiating Soil Properties	Pb K_d Range L kg^{-1}
S1, PI	% Fe, % Al	43 – 61
Rc	% Clay, CEC, % Mn	122 508
YP, Ro	% OC	25 – 97
Oc	% OC	216
Eh, GI	pH, In Pb K_d	127 686 – 252 294

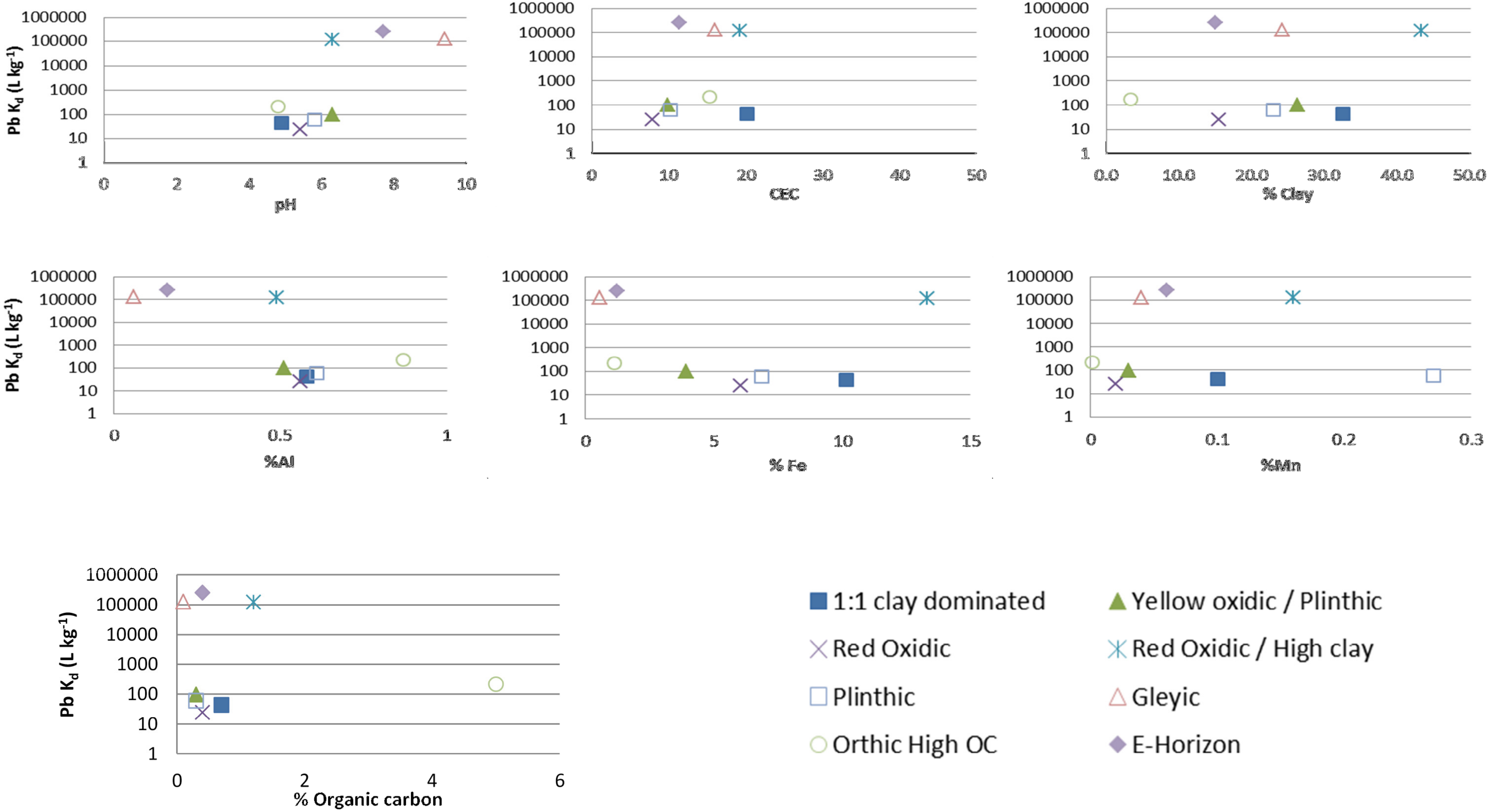

Figure 4.13: Relationship between Pb K_d value and selected soil properties

4.4.2.3 Vanadium

A principal component analyses biplot for V is presented in Figure 4.14. Scatter diagrams of V K_d and some soil properties are shown in Figure 4.15. From the PCA output data the PC1 accounted for 45.1 % of the variation in all the soil property data. PC2 accounted for 28.7 % of the variation. The two-dimensional biplot accounted for 73.8 % of the variation.

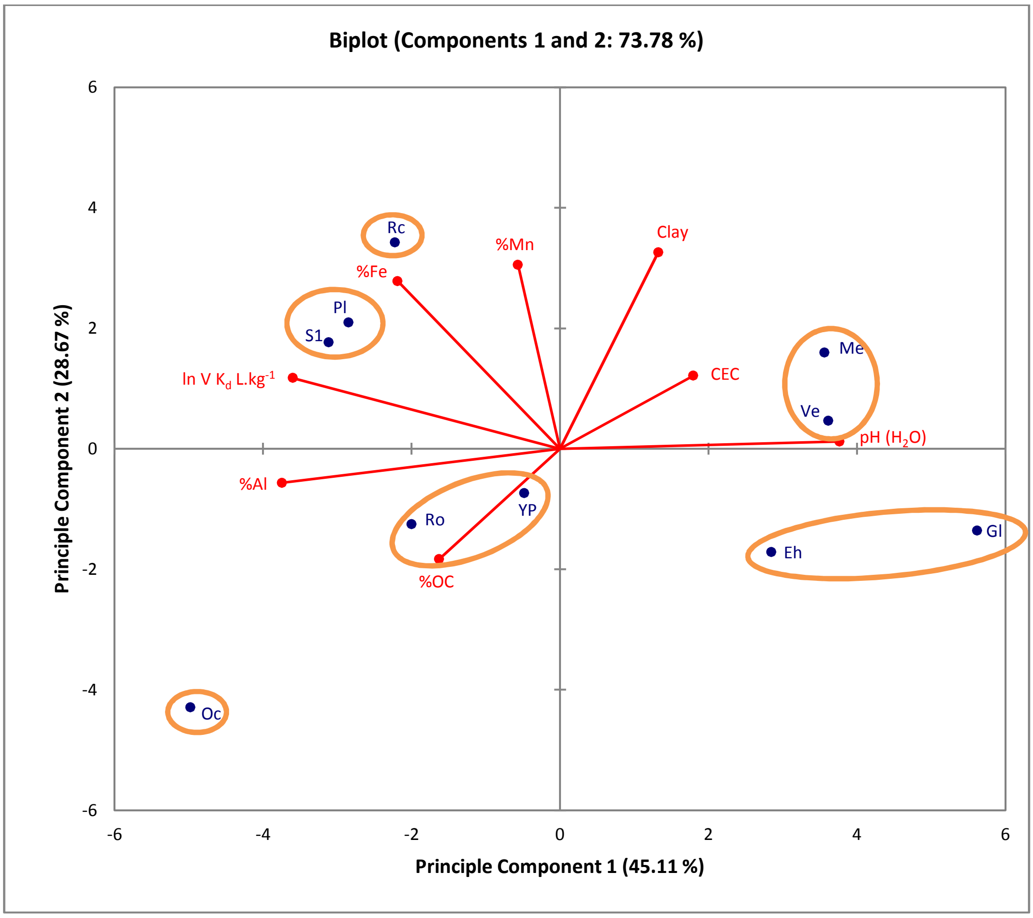

Figure 4.14: Principle Component Analysis for V and soil properties. S1 (1:1 clay dominated), Ve (Vertic 1:2 clay dominated), YP (Yellow oxidic/Plinthic, Ro (Red Oxidic), Rc (Red Oxidic/High clay), Me (Melanic), Pl (Plinthic), Gl (Gley), Hu (Orthic A high OC), Eh (E-horizon)

Based on the PCA for V, six soil horizon groups were identified in the data set. These groups are: a) S1 and Pl horizons display most similar results with the points plotted close together in the left upper quadrant and mostly associated with the soil property % Fe and V K_d. The last two are highly positively correlated; b) horizons Ve and Me are most similar and pH is mostly associated with these two horizons, followed by CEC and % clay; c) Ro and YP are mostly associated with % OC and %

Al; d) the Gl and Eh horizons are situated in the lower right quadrant and is mostly associated with pH; e) Oc is mostly associated with % OC but situated much further from YP and Ro in the left lower quadrant; and f) Rc is closely associated with the % Fe and % Mn.

From the PCA diagram the following summary could be tabulated (Table 4.9):

Table 4.9: Vanadium K_d ranges as determined by associations determined with PCA

Soil Profile	Dominant differentiating soil properties	V K_d Range L kg^{-1}
S1, Pl	% Fe, V K_d	629 – 865
Eh, Gl	pH	11 – 32
YP, Ro	% OC, % Al	181 – 220
Oc	% OC	708
Ve, Me	pH, CEC	73 – 90
Rc	% Fe, % Mn	750

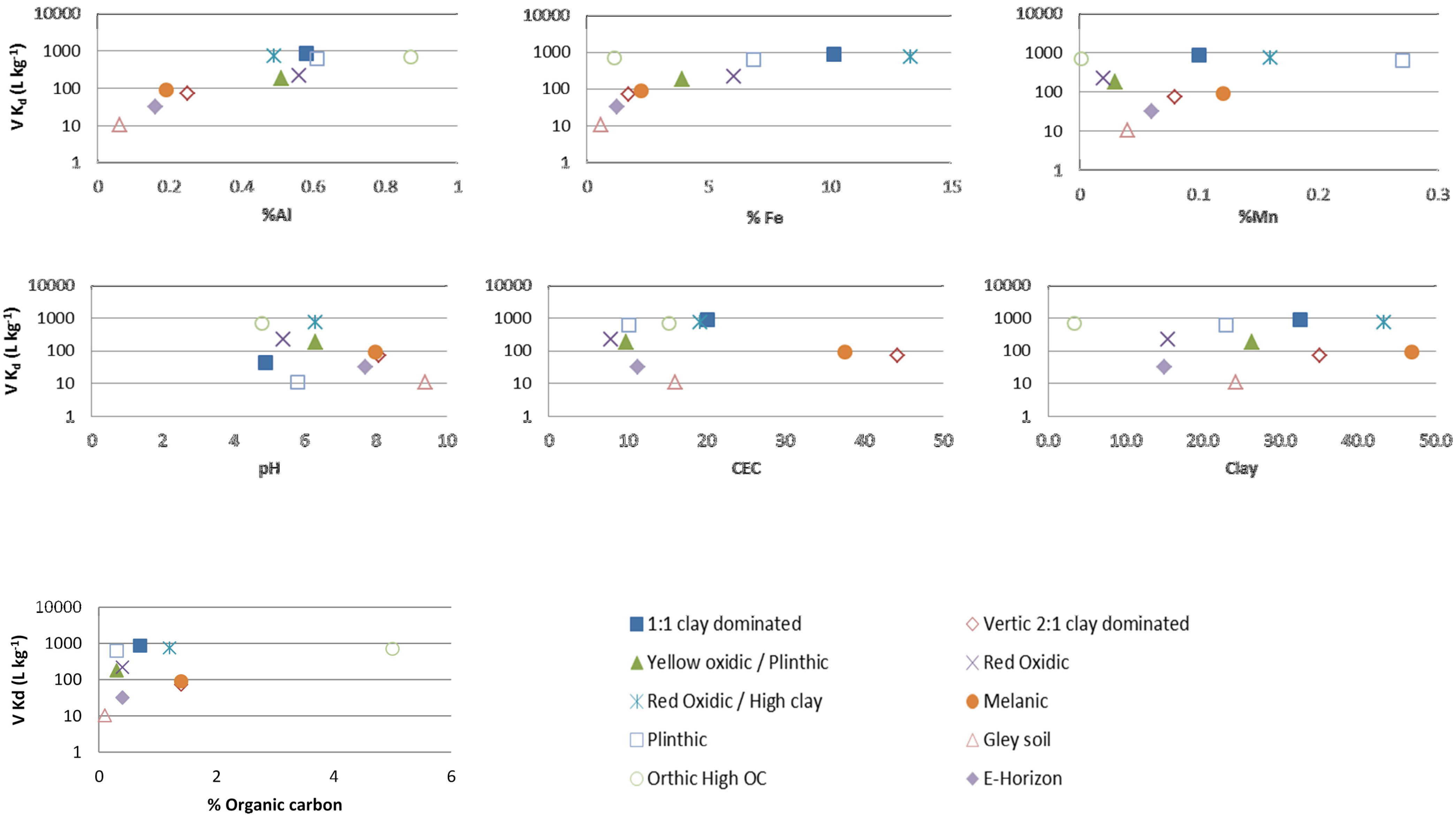

Figure 4.15: Relationship between V K$_d$ value and selected soil properties

4.5 Discussion

4.5.1 Attention coefficient (K_d) values of Cu, Pb, and V for typical South African soils

Table 4.10 summarises the K_d values for Cu, Pb and V for the different soil horizons as calculated from the sorption graphs. In most cases where the K_d was high for the cations, Cu and Pb, it was lower for V.

Table 4.10: Calculated K_d values of Cu, Pb and V for soil horizons derived from batch equilibrium sorption study

Soil Horizon	K_d in L kg^{-1}		
	Cu	Pb	V
1:1 clay dominated	13	43	865
Vertic 1:2 clay dominated	6 090	>252 294	73
Yellow oxidic / Plinthic	124	97	181
Red Oxidic	15	25	220
Red Oxidic / High clay	19 044	122 508	750
Melanic	14 607	>252 294	90
Plinthic	45	61	629
Gley	14 282	127 686	11
Orthic A high OC	171	216	708
E-Horizon	6 448	252 294	32
Coefficient of variation	121%	151%	95%
Framework K_d	10	100	1000

Results from this study indicate that a single K_d for an element/metal cannot be used for all soil types/horizons due to the effect of soil properties on the K_d value. However, additional research is required to determine K_d values of potential contaminants for other South african soil horizons. It is also suggested that more metal treatment levels be used in order to generate K_d values over a larger contamination range with better resolution. Metal sorption isotherms for soils are non-linear and it is reasonable to expect different, and possibly vastly different, K_d values at different contamination levels.

4.5.2 Multivariate Linear Regression

In order to increase the reliability of the K_d selected for a level 1 screening assessment as indicated in the Framework, a site specific K_d can be determined based on a few soil properties. This can greatly improve the accuracy of the SSV determined for the area and at the same time increase the reliability of the screening assessment. A forward stepwise linear regression performed on Cu, Pb and V showed that soil pH, OC and Fe content were the most responsible factors explaining 97.9 % of the variation in the K_d values of Cu. While soil pH and CEC explained 67.4 % of the variation in the K_d values of Pb. On the other hand, the K_d value of V was mainly influenced by soil pH, clay content and % Al. For each of the metals, pH was the dominant factor contributing to the predicted K_d value. Martinez and Motto (2000) found that the solubility of Cu and Pb increased with a decrease in soil pH. It should be noted that a comparatively smaller data set was assessed to provide these outcomes. A more extensive study encompassing larger ranges of soil properties should be conducted to obtain more reliable results. The ranges of soil properties applicable for the regressions are shown in Table 4.11.

$$Predicted \ln Cu\, K_d = -26.5 + 4.11pH + 6.38OC^2 + 2.52lnFe - 0.166CEC$$

$$Predicted \ln Pb\, K_d = -10.6 + 1.88pH + 0.437CEC$$

$$Predicted\ ln\ V\, K_d = 4.41 - 0.395pH + 0.0675clay + 4.17Al$$

Work done by Carlon *et al.* (2004) showed that the pH and the total Pb content of the soil was a significant predictive parameter in all the regression equations tested for Pb. These authors estimated linear regression models for a number of data sets found in literature. In some data sets, OC and CEC were found to contribute significantly to the variation in the K_d values of Pb, but did not feature in others. Unfortunately all total Pb concentrations for the 10 soils used in this study was below the detection limit and thus its effect on the K_d could not be determined for these soils. The discrepancy in the regressions were assumed to be as a results of the effect of pH on the complexation by organic matter and the low variability of the OC content in the data sets (Carlon *et al.*, 2004).

Table 4.11: Soil property restrictions of linear regression models for Cu, Pb and V

Soil Property	Maximum	Minimum	Average
pH (H_2O)	9.4	4.8	6.7
pH (KCl)	7.6	4.0	5.7
%OC	5.0	0.10	1.1
CEC	44	7.9	19
Al	0.87	0.060	0.4
Fe	13	0.57	4.7
Mn	0.27	0.0010	0.1
Sand	87	22	55
Silt	38	3.3	15
Clay	47	3.3	26

Making use of multivariable calculated K_d values allows for considerable reduction of the uncertainty in the accuracy of the contaminant K_d value. Using the K_d linear regression instead of using conservative assumption (i.e. the lowest K_d value as reported in literature) for fate and transport modelling may reduce the risk of over or underestimation by some orders of magnitude. This results in a more accurate prediction of risk and does not decrease the protection level to the receptor (Carlon *et al.*, 2004).

4.5.3 Principle Component Analysis

Principle component analysis was conducted for Cu, Pb and V but the results in terms of soil horizon association were very similar. The Ve and Me horizons were mostly associated with Cu, Pb and V, as was the Gl and Eh, S1 and the plintic and YP and Ro horizons. The Hu and Rc horizons were not closely associated to other horizons. Table 4.12 gives a summary of the K_d values generated for selected South African soil horizons as grouped by the PCA evaluations. These values could be used as preliminary values for screening assessment.

Table 4.12: Attenuation coefficient (K_d) values for Cu, Pb and V divided according to soil horizon associations

Soil Profile	K_d Range (L kg^{-1})		
	Cu	Pb	V
S1 and Pl	13 - 45	43 – 61	629 – 865
YP, Ro	14.6 – 124	25 – 97	181 – 220
EH Gl	6 448 – 14 282	127 686 – 252 294	11 – 32
Ve, Me	6 090 – 14 607	-	73 – 90
Rc	19 044	122 508	750
Oc	171	216	708

CHAPTER 5: BASELINE SOLUBLE CONCENTRATIONS OF Cu, Pb, AND V IN NATURAL SOUTH AFRICAN SOILS

5.1 Introduction

The concentration of trace elements in the topsoil depends on the elemental composition of the parent material and a number of physical and chemical properties that control soil formation. In addition, the enrichment of soil with trace elements also occurs as a result of natural airborne emissions. The emissions may result from a number of natural processes including volcanic eruptions, erosion, surface winds, forest fires and oceans. Human inputs also contribute to the increase of trace metal content in soils. Anthropogenic enrichment of soil with trace metals includes activities such as mining, smelting, power production, pesticides and waste treatment among others. Differentiating between trace element enrichment as a result of human intervention or natural baseline concentration is not an easy task (Nanos and Martín, 2012).

A number of studies have been conducted to establish the baseline concentrations of soils in different regions (Ma *et al*., 1997; Chen *et al*., 1999; Tack *et al*., 1997; Kabata-Pendias & Pendias, 2001). All these studies focused on the total metal concentration as opposed to the soluble concentration. The total concentration provides an estimate of the potential long-term risk of a metal to the environment, whereas the soluble concentration gives a better indication of what the immediate risk to the water resources, plants, animals and humans are (Herselman, 2007). The mobility of a contaminant in a soil can be described as its ability to dissolve into the soil pore water and to be transported through the soil medium. The mobility is therefore described by two processes, the physical-chemically driven desorption process and then the transport process (Carlon *et al*., 2004).

The preferred extraction method, selected from section 4, was used to determine soluble concentrations of Cu, Pb and V in selected SA surface horizons. Additional information on the properties of the other 100 soils used in this study are available in the South African Land Type Memoirs (Land Type Survey Staff, 1972-2001). Some of these properties were used to investigate the effects of soil properties on the solubility of Cu, Pb and V.

The objective of this investigation was to determine soluble baseline concentrations for Cu, Pb and V which can be used during the initial investigations into contaminated land to reference the concept of "normal" (uncontaminated) concentration in SA soils with different soil properties.

5.2 Methodology

5.2.1 Soil selection

Soils used in this study were sourced from the South African Land Type Memoirs (Land Type Survey Staff, 1972-2001) which contains more than 4500 soil samples representing various soil types, terrain units and climate zones. All the soil profiles are recorded in detail in the national inventory of Land Types of the ARC-Institute for Soil Climate and Water in Pretoria. The soil properties documented in this register include clay content, organic carbon content, CEC and pH (H_2O), CBD extractable Fe and the S-value (sum of exchangeable Ca, Mg, Na and K), all analysed by standard methods (Non-affiliated Soil Analysis Work Committee, 1990).

The 100 soils selected for this study were confined to A horizon samples (the first diagnostic horizon). The chosen soils also have baseline total and EDTA extractable trace element concentrations as determined by Herselman (2007). The rationale for the selection of the 100 soils was to obtain soils with a range of soil properties including pH(H_2O), clay content, organic C content, CBD extractable Fe and Al and base status.

5.2.2 Methodology used to determine soluble Cu, Pb and V concentrations

Air-dried samples were gently crushed to pass a 2 mm stainless steel screen prior to analysis. The selected extraction method was 1:2.5 and the procedure was as follows:

Each sample was prepared and analysed in triplicate. A 16 g soil sample was weighted into a 50 ml centrifuge tube. A volume of 40 ml of deionised water was added to the sample and was shaken on a mechanical shaker for 24 hours. The samples were centrifuged at 4000 rpm for 5 minutes. The samples were then filtered through Whatman 42 filter paper and further filtered through a 0.2 µm membrane filter. Samples were analyzed on ICP-OES at the University of Pretoria. Results were standardized to be represented as a one part soil to one part water ratio.

5.3 Statistical Analyses

5.3.1 Soluble baseline concentrations

From the soluble metal data collected, the baseline concentration range was calculated using the quotient (lower baseline) and product (upper baseline) of the geometric mean and the square of the geometric standard deviation (Chen *et al*., 2001). Data below the instrument detection limit as suggested by Gilbert (1987) was also used. The baseline concentrations give a better estimate of the actual range compared to the observed data as it is calculated using the geometric mean and standard deviation which is less constrained by the distorting effect of outlier values. The upper baseline limit was set at the 97.5th percentile in order to minimize the effect of contamination. This will provide an upper limit that more closely reflects the natural concentrations. The lower limit was set at the 2.5th percentile. This allows for the opportunity to minimize any disturbances near the lower level of the instrument detection (Herselman, 2007).

5.3.2 Correlation coefficients

Firstly linear regressions were performed on the data to reveal possible trends or relationships between the trace element concentration and soil properties. When plotted the data produces a largely scattered distribution. In order to interpret the data quantile regression was applied (Koenker and Bassett, 1978; Koenker and Hallock, 2001; Cade and Noon, 2003; Herselman, 2007). For this study segmented quantile regression was used. It involves dividing the data into equal subsets defined according to the conditioning covariate.

5.3.3 Chemical envelopes

Segmented quantile regression was used to present the data. This involves the segmentation of a data set into equal subsets defined by a specific conditioning covariate (soil property of interest) (Koenker and Hallock, 2001). The data set is initially sorted in terms of increasing soluble concentration with respect to each of the determinant variables, in this case % OC, pH and clay content. The sorted data is then divided into 10 classes or segments of equal size.

For each segment, the 0.025 and 0.975 quantiles were calculated for the dependent variable (soluble metal concentration) and the corresponding median was calculated for the determinant variable (soil property). The 0.975 quantile was selected to exclude extreme outlier values in the data set and to coincide with the upper limit of the baseline concentration. The metal quantile values were plotted against the median of the soil properties in each class.

Regression equations were fitted to the data plots and an appropriate equation was selected based on goodness of fit (R^2 value). The line formed by the 0.975 quantile represents a boundary enclosing all observations excluding extreme outliers. It discloses information about the limits of association of the dependent variable for any specific value of the determinant. In other words it indicates what the expected maximum soluble metal concentration will be at a particular soil pH or clay content. This boundary line is referred to as a chemical envelope (Herselman, 2007).

5.3.4 Multivariate regression method

The K_d and soluble metal contents were correlated to the soil properties by a stepwise forward regression analysis which is based on the linear least square method. The method consisted of determining the linear regression in such a way as to minimize the squared deviations of the observed points from the predicted outcomes. The independent variables are included into the model one by one, with the most significant variables included into the final model (Carlon *et al.*, 2004).

5.4 Results

The complete set of analytical results for this investigation is included in Appendix F. In the sections that follow interpretations of the analytical data will be presented.

5.4.1 Baseline soluble concentrations

Table 5.1 shows the general statistics of the sample population as well as the soluble baseline concentration range calculated as discussed in the previous section. It should be noted that for Cu and V, all samples extracted had concentrations above the instrument detection limit, for soluble Pb concentrations on the other hand only 22 samples were detectable. The soluble baseline for Cu, Pb and V were found to be 0.005-0.2, 0.001-0.15 and 0.03-0.1 mg kg^{-1}, respectively.

Table 5.1: General statistics and baseline soluble concentrations for selected elements (mg L^{-1})

Statistical Parameter	Cu	Pb	V
		mg kg^{-1}	
Minimum	0.001	0.001	0.03
Maximum	8.87	0.17	0.32
Average	0.13	0.03	0.06
Geometric mean	0.033	0.016	0.053
Geometric standard deviation	2.48	3.09	1.38
Baseline range	0.005-0.2	0.001-0.15	0.03-0.1
Number of samples above detection limits	100	22	100

5.4.2 Chemical envelopes

The correlation scatter diagrams and chemical envelopes of Cu and V for selected soil properties (organic C, pH(H_2O) and clay content) are presented in Figure 5.1. Due to the limited number of soil samples with detectable soluble Pb, no chemical envelopes could be established for Pb. Scatter diagrams of soluble Pb for different soil properties were therefore constructed as shown in Figure 5.2.

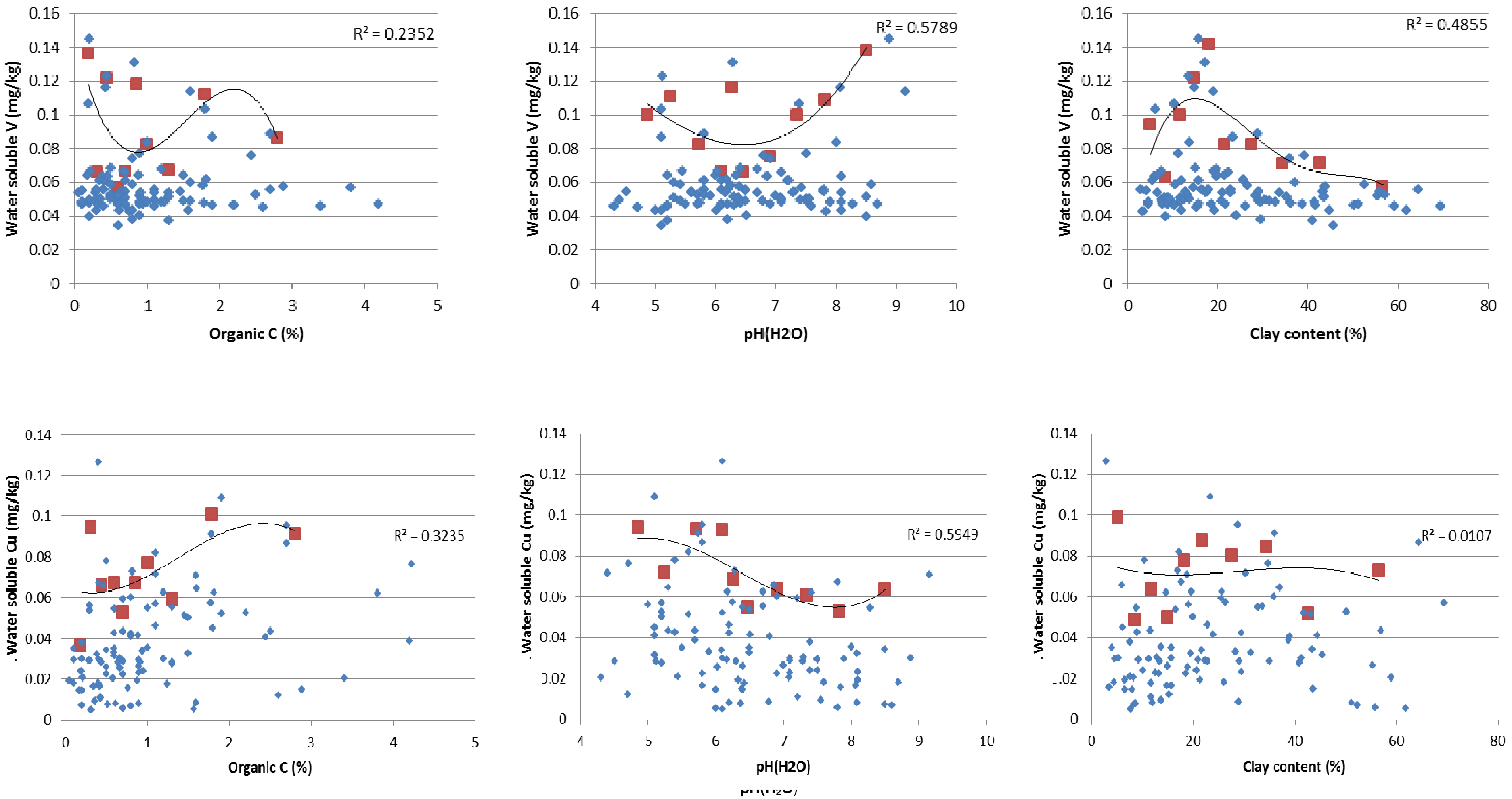

Figure 5.1: Scatter diagrams and chemical envelopes of water soluble Cu and V, with all the soluble data points shown as the blue dots, the red showing the 10 classes which subsequently represent the chemical envelope indicated by the trend line on the graph

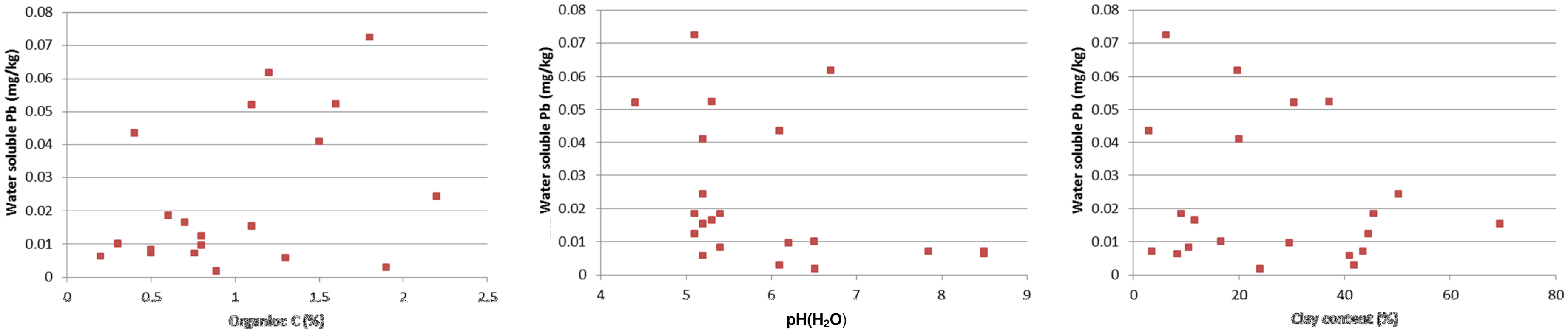

Figure 5.2: Scatter diagrams of water soluble Pb

From the graph of pH and Cu concentration it can be deduced that Cu solubility is influenced to a lesser extent by soil pH than by organic C and clay content. Soluble Cu concentration decreased as the soil pH exceeded 6 (Martinez and Motto, 2000).

The scatter diagrams show that most of the soil samples had higher V solubility at low organic C and clay contents with a weak correlation. The chemical envelope for soluble V and clay content indicates that generally solubility of V decrease where the soils clay content is >20%.

The scatter plot for Pb and pH indicates higher soluble Pb at lower pH ranges in the soil. Soils with lower clay contents had higher soluble Pb concentrations. Soluble Pb was higher at higher organic C contents.

5.5 Discussion

The effect of soil pH on soluble Cu concentration was vivid. Soil pH negatively influenced the solubility of Cu at pH > 6. This is in agreement with the general literature as reported by Barker and Pilbeam (2007). Copper solubility increased as soil organic C content increased while clay content had no significant effect on Cu solubility (R^2=0.01). It was also apparent that Pb solubility was higher at lower soil pH values, which is also in line with the existing literature (Kabata-Pendias and Pendias, 2001). Soils with lower clay content were observed having higher soluble Pb concentrations. This is most probably due to the fact that clay layer silicate minerals, Mn oxides, Fe and Al hydroxides are some of the most prominent soil components associated with Pb immobilisation. Soluble Pb also increased at higher organic C contents.

Soluble V concentration correlates well with soil pH (R^2=0.7), with the greatest solubility at pH < 5 and > 7.5. Work done by Peacock and Sherman (2004) suggested that there is an adsorption plateau with little variation in V adsorption for pH ranges of 3 - 6 with lower adsorption occurring below and above the specified pH range. Smith (1973) reported that V becomes insoluble in pH ranges of 1.5 - 3.5.

The objective of determining soluble baseline concentrations for selected trace elements in South African soils was to reference the concept of 'normal' (uncontaminated) soluble concentrations in SA soils with varying soil properties. The soluble baseline concentration ranges for Cu, Pb and V were all less than 1 mg kg^{-1}.

CHAPTER 6: CONCLUSION

Results from this study showed that the 1:2.5 soil:water ratio extraction method gave the closest representation to the standard saturated paste extract at low to medium soluble metal (Cu, Pb, and V) concentrations. At higher soluble metal concentrations, however, the 1:2.5 extraction ratio gave higher values compared with the saturated paste extract.

The study conducted on the K_d values for Cu, Pb and V indicated that a significant range of values exist for soils with different properties, especially in the case of Cu and Pb. For Cu the K_d values ranged from 12.7 to 19044 L kg^{-1}. The K_d values for Pb ranged from 24.8 to as high as 252294 L kg^{-1}. The K_d values for V showed relatively narrow ranges (10.5 to 865 L kg^{-1}). The results from this study clearly indicate that a single value per metal cannot be employed to represent the array of soil types in South Africa. Using the screening criteria as it is currently specified will have far reaching negative implications to the environment.

Before one can justify the anthropogenic origin of metal constituents the background soil concentration should be examined. The objective of determining soluble baseline concentrations for selected trace elements in South African soils was to assist in the differentiation of elevated metals concentrations as a result of anthropogenic sources and naturally elevated concentrations. The consequence for excluding baseline criteria from contaminated land screenings may result in inappropriate screening where naturally high metal containing soils are shown to be contaminated when in actual fact it is naturally occurring concentrations. The soluble baseline concentration ranges of 100 South African soils for Cu (0.005 – 0.2), Pb (0.001 – 0.15) and V (0.03 – 0.1) were all less than 1 mg kg^{-1}.

Suggested future research:

1. The kd values of other contaminants across a range of soil types need to be established,
2. The study needs to be refined by including more solute concentrations in order to establish more points that could help to generate better regression curves.

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APPENDIX A: CHEMICAL AND PHYSICAL CHARACTERISATION DATA FOR SOILS USED IN METHOD SELECTION AND K_d DETERMINATION

Soil type	**pH H_2O**	**pH KCl**	**Organic C %**	**CEC**	**CBD**			**Particle size**		
					Al	**Fe**	**Mn**	**Sand**	**Silt**	**Clay**
Unit	-	-	%	cmol(+)/kg	%	%	%	%	%	%
1:1 clay dominated	4.9	4.0	0.7	20.1	0.58	10.2	0.1	56.7	10.8	32.5
Vertic 2:1 clay dominated	8.1	7.4	1.4	44.2	0.25	1.71	0.08	22.2	38.3	35.0
Yellow oxidic / Plinthic	6.3	5.3	0.3	9.8	0.51	3.91	0.03	60.7	13.8	26.3
Red Oxidic	5.4	4.4	0.4	7.9	0.56	6.06	0.02	77.7	6.3	15.4
Red Oxidic / High clay	6.3	5.3	1.2	19.2	0.49	13.3	0.16	30.1	23.3	43.3
Melanic	8	6.9	1.4	37.5	0.19	2.24	0.12	22.2	25.6	46.9
Plinthic	5.8	4.9	0.3	10.2	0.61	6.87	0.27	59.0	13.8	22.9
Gleyic	9.4	7.6	0.1	16	0.06	0.57	0.04	65.8	7.5	24.2
Orthic high OC	4.8	4.1	5	15.3	0.87	1.11	0.001	86.6	3.3	3.3
E-Horizon	7.7	6.8	0.4	11.3	0.16	1.22	0.06	72.5	7.5	15.0

APPENDIX B: METHOD SELECTION DATA

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S1	Cu0	1to10	1	0.0557	S1	Cu0	SatPaste	1	0.0944	S1	Cu1	1to2_5	1	16.15	S2	Cu1	1to5	1	0.2113	S2	Cu2	1to10	1	0.3093	S1	Cu3	1to5	1	615.0
S1	Cu0	1to10	2	0.0600	S1	Cu0	SatPaste	2	0.0571	S1	Cu1	1to2_5	2	15.72	S2	Cu1	1to5	2	0.2077	S2	Cu2	1to10	2	0.3181	S1	Cu3	1to5	2	621.0
S1	Cu0	1to10	3	0.0560	S1	Cu0	SatPaste	3	0.0850	S1	Cu1	1to2_5	3	15.52	S2	Cu1	1to5	3	0.2139	S2	Cu2	1to10	3	0.2281	S1	Cu3	1to5	3	618.0
S1	Cu0	1to2_5	1	0.4582	S1	Cu0	SatPaste	1	0.1122	S1	Cu1	1to20	1	1.264	S2	Cu1	NH4NO3	1	9.8560	S2	Cu2	1to2_5	1	0.4942	S1	Cu3	NH4NO3	1	282.9
S1	Cu0	1to2_5	2	0.1114	S1	Cu0	SatPaste	2	0.0874	S1	Cu1	1to20	2	1.155	S2	Cu1	NH4NO3	2	9.9750	S2	Cu2	1to2_5	2	0.4613	S1	Cu3	NH4NO3	2	228.8
S1	Cu0	1to2_5	3	0.0454	S1	Cu0	SatPaste	3	0.0850	S1	Cu1	1to20	3	1.122	S2	Cu1	NH4NO3	3	7.9850	S2	Cu2	1to2_5	3	0.4959	S1	Cu3	NH4NO3	3	241.4
S1	Cu0	1to2_5	1	0.0619	S2	Cu0	1to10	1	0.0803	S1	Cu1	1to5	1	5.904	S2	Cu1	SatPaste	1	0.3521	S2	Cu2	1to20	1	0.2994	S1	Cu3	SatPaste	1	41.96
S1	Cu0	1to2_5	2	0.0703	S2	Cu0	1to10	2	0.0604	S1	Cu1	1to5	2	7.828	S2	Cu1	SatPaste	2	0.3998	S2	Cu2	1to20	2	0.2756	S1	Cu3	SatPaste	2	41.14
S1	Cu0	1to2_5	3	0.0598	S2	Cu0	1to10	3	0.0614	S1	Cu1	1to5	3	8.012	S2	Cu1	SatPaste	3	0.3472	S2	Cu2	1to20	3	0.2639	S1	Cu3	SatPaste	3	40.73
S1	Cu0	1to20	1	0.0007	S2	Cu0	1to2_5	1	0.0887	S1	Cu1	NH4NO3	1	79.00	S1	Cu2	1to10	1	111.4	S2	Cu2	1to5	1	0.3552	S2	Cu3	1to10	1	0.3365
S1	Cu0	1to20	2	0.0004	S2	Cu0	1to2_5	2	0.0685	S1	Cu1	NH4NO3	1	71.36	S1	Cu2	1to10	2	114.5	S2	Cu2	1to5	2	0.3644	S2	Cu3	1to10	2	0.3318
S1	Cu0	1to20	3	0.0020	S2	Cu0	1to2_5	3	0.0641	S1	Cu1	NH4NO3	2	62.74	S1	Cu2	1to10	3	110.6	S2	Cu2	1to5	3	0.3789	S2	Cu3	1to10	3	0.4114
S1	Cu0	1to20	1	0.0686	S2	Cu0	1to20	1	0.0577	S1	Cu1	NH4NO3	2	61.78	S1	Cu2	1to2_5	1	292.4	S2	Cu2	NH4NO3	1	26.02	S2	Cu3	1to2_5	1	1.154
S1	Cu0	1to20	2	0.0746	S2	Cu0	1to20	2	0.0685	S1	Cu1	NH4NO3	3	63.45	S1	Cu2	1to2_5	2	282.7	S2	Cu2	NH4NO3	2	26.77	S2	Cu3	1to2_5	2	0.6755
S1	Cu0	1to20	3	0.0710	S2	Cu0	1to20	3	0.0576	S1	Cu1	NH4NO3	3	61.59	S1	Cu2	1to2_5	3	271.2	S2	Cu2	NH4NO3	3	26.27	S2	Cu3	1to2_5	3	0.6434
S1	Cu0	1to5	1	0.0152	S2	Cu0	1to5	1	0.0594	S1	Cu1	SatPaste	1	93.55	S1	Cu2	1to20	1	50.26	S2	Cu2	SatPaste	1	1.109	S2	Cu3	1to20	1	0.2956
S1	Cu0	1to5	2	0.0110	S2	Cu0	1to5	2	0.0590	S1	Cu1	SatPaste	2	98.64	S1	Cu2	1to20	2	48.48	S2	Cu2	SatPaste	2	1.075	S2	Cu3	1to20	2	0.2880
S1	Cu0	1to5	3	0.0104	S2	Cu0	1to5	3	0.0631	S1	Cu1	SatPaste	3	97.68	S1	Cu2	1to20	3	50.64	S2	Cu2	SatPaste	3	1.165	S2	Cu3	1to20	3	0.3151
S1	Cu0	1to5	1	0.0601	S2	Cu0	NH4NO3	1	0.0916	S2	Cu1	1to10	1	0.1648	S1	Cu2	1to5	1	214.3	S1	Cu3	1to10	1	283.2	S2	Cu3	1to5	1	0.5710
S1	Cu0	1to5	2	0.0599	S2	Cu0	NH4NO3	2	0.1010	S2	Cu1	1to10	2	0.1677	S1	Cu2	1to5	2	205.7	S1	Cu3	1to10	2	273.7	S2	Cu3	1to5	2	0.4392
S1	Cu0	1to5	3	0.0578	S2	Cu0	NH4NO3	3	0.0979	S2	Cu1	1to10	3	0.1690	S1	Cu2	1to5	3	215.4	S1	Cu3	1to10	3	243.9	S2	Cu3	1to5	3	0.5098
S1	Cu0	NH4NO3	1	0.0304	S2	Cu0	SatPaste	1	0.1314	S2	Cu1	1to2_5	1	0.2619	S1	Cu2	NH4NO3	1	573.4	S1	Cu3	1to2_5	1	432.5	S2	Cu3	NH4NO3	1	49.97
S1	Cu0	NH4NO3	2	0.0412	S2	Cu0	SatPaste	2	0.1068	S2	Cu1	1to2_5	2	0.2264	S1	Cu2	NH4NO3	2	573.4	S1	Cu3	1to2_5	2	430.5	S2	Cu3	NH4NO3	2	49.91
S1	Cu0	NH4NO3	3	0.0259	S2	Cu0	SatPaste	3	0.0954	S2	Cu1	1to2_5	3	0.2691	S1	Cu2	NH4NO3	3	556.4	S1	Cu3	1to2_5	3	431.7	S2	Cu3	NH4NO3	3	49.69
S1	Cu0	NH4NO3	1	0.1533	S1	Cu1	1to10	1	3.396	S2	Cu1	1to20	1	0.1374	S1	Cu2	SatPaste	1	63.18	S1	Cu3	1to20	1	158.0	S2	Cu3	SatPaste	1	1.765
S1	Cu0	NH4NO3	2	0.1541	S1	Cu1	1to10	2	3.323	S2	Cu1	1to20	2	0.1452	S1	Cu2	SatPaste	2	63.36	S1	Cu3	1to20	2	155.5	S2	Cu3	SatPaste	2	1.716
S1	Cu0	NH4NO3	3	0.1514	S1	Cu1	1to10	3	3.502	S2	Cu1	1to20	3	0.1395	S1	Cu2	SatPaste	3	68.55	S1	Cu3	1to20	3	156.3	S2	Cu3	SatPaste	3	1.776

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S1	Pb0	1to10	1	*	S1	Pb1	1to5	1	5.740	S1	Pb2	SatPaste	1	9192.8	S2	Pb0	1to20	1	0.0469	S2	Pb1	SatPaste	1	0.5406	S2	Pb3	1to20	1	0.3147
S1	Pb0	1to10	2	0.1115	S1	Pb1	1to5	2	6.890	S1	Pb2	SatPaste	2	8499.8	S2	Pb0	1to20	2	0.0864	S2	Pb1	SatPaste	2	0.1562	S2	Pb3	1to20	2	0.2636
S1	Pb0	1to10	3	0.1034	S1	Pb1	1to5	3	5.765	S1	Pb2	SatPaste	3	7863.8	S2	Pb0	1to20	3	0.0059	S2	Pb1	SatPaste	3	0.0541	S2	Pb3	1to20	3	0.2113
S1	Pb0	1to2_5	1	0.0954	S1	Pb1	NH4NO3	1	278.0	S1	Pb3	1to10	1	987	S2	Pb0	1to5	1	0.1284	S2	Pb2	1to10	1	*	S2	Pb3	1to5	1	0.7358
S1	Pb0	1to2_5	2	0.0353	S1	Pb1	NH4NO3	2	277.6	S1	Pb3	1to10	2	718.5	S2	Pb0	1to5	2	0.0722	S2	Pb2	1to10	2	*	S2	Pb3	1to5	2	0.7209
S1	Pb0	1to2_5	3	0.0541	S1	Pb1	NH4NO3	3	282.4	S1	Pb3	1to10	3	1039	S2	Pb0	1to5	3	0.0805	S2	Pb2	1to10	3	*	S2	Pb3	1to5	3	0.6863
S1	Pb0	1to20	1	0.0846	S1	Pb1	SatPaste	1	0.5415	S1	Pb3	1to2_5	1	4220	S2	Pb0	NH4NO3	1	0.0794	S2	Pb2	1to2_5	1	2.068	S2	Pb3	NH4NO3	1	34.98
S1	Pb0	1to20	2	0.0575	S1	Pb1	SatPaste	2	0.5042	S1	Pb3	1to2_5	2	4240	S2	Pb0	NH4NO3	2	*	S2	Pb2	1to2_5	2	0.1913	S2	Pb3	NH4NO3	2	34.51
S1	Pb0	1to20	3	0.0571	S1	Pb1	SatPaste	3	0.2516	S1	Pb3	1to2_5	3	4088	S2	Pb0	NH4NO3	3	0.1073	S2	Pb2	1to2_5	3	0.1995	S2	Pb3	NH4NO3	3	37.05
S1	Pb0	1to5	1	0.0934	S1	Pb1	SatPaste	1	146.6	S1	Pb3	1to20	1	513.5	S2	Pb0	SatPaste	1	*	S2	Pb2	1to20	1	*	S2	Pb3	SatPaste	1	14.24
S1	Pb0	1to5	2	0.0892	S1	Pb1	SatPaste	2	172.8	S1	Pb3	1to20	2	521.0	S2	Pb0	SatPaste	2	0.0670	S2	Pb2	1to20	2	*	S2	Pb3	SatPaste	2	10.72
S1	Pb0	1to5	3	0.1067	S1	Pb1	SatPaste	3	195.5	S1	Pb3	1to20	3	474.7	S2	Pb0	SatPaste	3	0.0183	S2	Pb2	1to20	3	*	S2	Pb3	SatPaste	3	4.009
S1	Pb0	NH4NO3	1	0.1609	S1	Pb2	1to10	1	440.8	S1	Pb3	1to5	1	2156	S2	Pb1	1to10	1	0.0463	S2	Pb2	1to5	1	0.0473	S1	V0	1to10	1	0.0245
S1	Pb0	NH4NO3	2	0.1567	S1	Pb2	1to10	2	420.7	S1	Pb3	1to5	2	2108	S2	Pb1	1to10	2	0.0835	S2	Pb2	1to5	2	*	S1	V0	1to10	2	0.0139
S1	Pb0	NH4NO3	3	0.1083	S1	Pb2	1to10	3	424.9	S1	Pb3	1to5	3	2123	S2	Pb1	1to10	3	0.0892	S2	Pb2	1to5	3	*	S1	V0	1to10	3	0.0228
S1	Pb0	SatPaste	1	0.0884	S1	Pb2	1to2_5	1	1549	S1	Pb3	NH4NO3	1	5125	S2	Pb1	1to2_5	1	0.0759	S2	Pb2	NH4NO3	1	16.03	S1	V0	1to2_5	1	0.0129
S1	Pb0	SatPaste	2	0.1754	S1	Pb2	1to2_5	2	1405	S1	Pb3	NH4NO3	2	4887	S2	Pb1	1to2_5	2	0.1214	S2	Pb2	NH4NO3	2	18.44	S1	V0	1to2_5	2	0.0094
S1	Pb0	SatPaste	3	*	S1	Pb2	1to2_5	3	1475	S1	Pb3	NH4NO3	3	4939	S2	Pb1	1to2_5	3	0.1736	S2	Pb2	NH4NO3	3	17.26	S1	V0	1to2_5	3	0.0086
S1	Pb1	1to10	1	1.696	S1	Pb2	1to20	1	247.4	S1	Pb3	SatPaste	1	30550	S2	Pb1	1to20	1	0.0784	S2	Pb2	SatPaste	1	4.458	S1	V0	1to20	1	0.0158
S1	Pb1	1to10	2	2.270	S1	Pb2	1to20	2	233.6	S1	Pb3	SatPaste	2	34790	S2	Pb1	1to20	2	0.1084	S2	Pb2	SatPaste	2	2.698	S1	V0	1to20	2	0.0230
S1	Pb1	1to10	3	2.023	S1	Pb2	1to20	3	227.8	S1	Pb3	SatPaste	3	34520	S2	Pb1	1to20	3	0.0153	S2	Pb2	SatPaste	3	1.070	S1	V0	1to20	3	0.0245
S1	Pb1	1to2_5	1	16.51	S1	Pb2	1to5	1	213.8	S2	Pb0	1to10	1	0.1374	S2	Pb1	1to5	1	0.1632	S2	Pb3	1to10	1	0.4651	S1	V0	1to5	1	0.0075
S1	Pb1	1to2_5	2	12.32	S1	Pb2	1to5	2	769.0	S2	Pb0	1to10	2	0.0829	S2	Pb1	1to5	2	0.0531	S2	Pb3	1to10	2	0.4183	S1	V0	1to5	2	0.0106
S1	Pb1	1to2_5	3	13.64	S1	Pb2	1to5	3	727.0	S2	Pb0	1to10	3	0.0638	S2	Pb1	1to5	3	0.1697	S2	Pb3	1to10	3	0.4263	S1	V0	1to5	3	0.0096
S1	Pb1	1to20	1	0.7288	S1	Pb2	NH4NO3	1	2192	S2	Pb0	1to2_5	1	0.1259	S2	Pb1	NH4NO3	1	3.504	S2	Pb3	1to2_5	1	4.110	S1	V0	NH4NO3	1	0.0441
S1	Pb1	1to20	2	0.6405	S1	Pb2	NH4NO3	2	2261	S2	Pb0	1to2_5	2	0.1225	S2	Pb1	NH4NO3	2	4.567	S2	Pb3	1to2_5	2	1.535	S1	V0	NH4NO3	2	0.0387
S1	Pb1	1to20	3	0.6070	S1	Pb2	NH4NO3	3	2260	S2	Pb0	1to2_5	3	0.0165	S2	Pb1	NH4NO3	3	4.652	S2	Pb3	1to2_5	3	1.250	S1	V0	NH4NO3	3	0.0589

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S1	V0	SatPaste	1	0.0156	S1	V2	1to20	1	59.48	S1	V3	SatPaste	1	*	S2	V1	1to20	1	4.364	S2	V2	SatPaste	1	77.22
S1	V0	SatPaste	2	0.0226	S1	V2	1to20	2	93.92	S1	V3	SatPaste	2	*	S2	V1	1to20	2	4.340	S2	V2	SatPaste	2	72.88
S1	V0	SatPaste	3	0.0189	S1	V2	1to20	3	58.36	S1	V3	SatPaste	3	*	S2	V1	1to20	3	4.282	S2	V2	SatPaste	3	71.72
S1	V1	1to10	1	31.86	S1	V2	1to5	1	195.5	S2	V0	1to10	1	0.0311	S2	V1	1to5	1	4.461	S2	V3	1to10	1	148.9
S1	V1	1to10	2	33.91	S1	V2	1to5	2	200.2	S2	V0	1to10	2	0.0253	S2	V1	1to5	2	4.707	S2	V3	1to10	2	149.2
S1	V1	1to10	3	28.88	S1	V2	1to5	3	211.8	S2	V0	1to10	3	0.0267	S2	V1	1to5	3	4.834	S2	V3	1to10	3	140.7
S1	V1	1to2_5	1	60.97	S1	V2	NH4NO3	1	119.9	S2	V0	1to2_5	1	0.0189	S2	V1	NH4NO3	1	0.8012	S2	V3	1to2_5	1	345.6
S1	V1	1to2_5	2	69.63	S1	V2	NH4NO3	2	122.7	S2	V0	1to2_5	2	0.0177	S2	V1	NH4NO3	2	0.8072	S2	V3	1to2_5	2	331.0
S1	V1	1to2_5	3	52.84	S1	V2	NH4NO3	3	87.51	S2	V0	1to2_5	3	0.0211	S2	V1	NH4NO3	3	0.8203	S2	V3	1to2_5	3	356.0
S1	V1	1to20	1	20.62	S1	V2	SatPaste	1	2158	S2	V0	1to20	1	0.0480	S2	V1	SatPaste	1	5.477	S2	V3	1to20	1	84.30
S1	V1	1to20	2	21.43	S1	V2	SatPaste	2	1834	S2	V0	1to20	2	0.0192	S2	V1	SatPaste	2	5.550	S2	V3	1to20	2	78.34
S1	V1	1to20	3	22.30	S1	V2	SatPaste	3	1950	S2	V0	1to20	3	0.0225	S2	V1	SatPaste	3	5.653	S2	V3	1to20	3	80.18
S1	V1	1to5	1	47.22	S1	V3	1to10	1	308.4	S2	V0	1to5	1	0.0236	S2	V2	1to10	1	48.72	S2	V3	1to5	1	242.6
S1	V1	1to5	2	47.92	S1	V3	1to10	2	311.0	S2	V0	1to5	2	0.0179	S2	V2	1to10	2	48.58	S2	V3	1to5	2	235.0
S1	V1	1to5	3	42.40	S1	V3	1to10	3	433.0	S2	V0	1to5	3	0.0210	S2	V2	1to10	3	47.86	S2	V3	1to5	3	243.0
S1	V1	NH4NO3	1	13.76	S1	V3	1to2_5	1	1254	S2	V0	NH4NO3	1	0.0129	S2	V2	1to2_5	1	68.44	S2	V3	NH4NO3	1	74.77
S1	V1	NH4NO3	2	11.27	S1	V3	1to2_5	2	1224	S2	V0	NH4NO3	2	0.0144	S2	V2	1to2_5	2	72.90	S2	V3	NH4NO3	2	75.83
S1	V1	NH4NO3	3	14.81	S1	V3	1to2_5	3	1163	S2	V0	NH4NO3	3	0.0124	S2	V2	1to2_5	3	71.90	S2	V3	NH4NO3	3	72.47
S1	V1	SatPaste	1	84.73	S1	V3	1to20	1	187.4	S2	V0	SatPaste	1	0.0198	S2	V2	1to20	1	33.02	S2	V3	SatPaste	1	548.2
S1	V1	SatPaste	2	88.29	S1	V3	1to20	2	165.6	S2	V0	SatPaste	2	0.0256	S2	V2	1to20	2	31.76	S2	V3	SatPaste	2	574.4
S1	V1	SatPaste	3	86.29	S1	V3	1to20	3	176.6	S2	V0	SatPaste	3	0.0271	S2	V2	1to20	3	32.36	S2	V3	SatPaste	3	589.7
S1	V2	1to10	1	126.9	S1	V3	1to5	1	643.2	S2	V1	1to10	1	5.055	S2	V2	1to5	1	65.20					
S1	V2	1to10	2	111.7	S1	V3	1to5	2	605.8	S2	V1	1to10	2	4.997	S2	V2	1to5	2	65.40					
S1	V2	1to10	3	110.4	S1	V3	1to5	3	592.2	S2	V1	1to10	3	5.100	S2	V2	1to5	3	61.40					
S1	V2	1to2_5	1	360.4	S1	V3	NH4NO3	1	753.5	S2	V1	1to2_5	1	4.288	S2	V2	NH4NO3	1	10.34					
S1	V2	1to2_5	2	406.6	S1	V3	NH4NO3	2	760.7	S2	V1	1to2_5	2	4.082	S2	V2	NH4NO3	2	9.549					
S1	V2	1to2_5	3	446.2	S1	V3	NH4NO3	3	761.5	S2	V1	1to2_5	3	3.579	S2	V2	NH4NO3	3	9.784					

* no data

APPENDIX C: STATISTICS FOR METHOD SELECTION

Exp1_Cu_Upconc.rtf

============================== file name is Exp1_Cu_Upconc.gen

EXP 1: METHOD SCREENING 2011/2012: Soils S1 & S2 Up concentrated Cu

Identifier	Minimum	Mean	Maximum	Values	Missing	
UpConc_Cu	0.03000	344.3	3159	144	0	Skew

========== GLM analysis of Up concentrated Cu for soil S1 ========

Regression analysis

Response variate: UpConc_Cu
Distribution: Gamma
Link function: Log
Fitted terms: Constant, Contaminant

Summary of analysis

Source	d.f.	deviance	mean deviance	deviance ratio	approx F pr.
Regression	3	306.48	102.158	93.12	<.001
Residual	68	74.60	1.097		
Total	71	381.08	5.367		

Coefficient of variation is estimated to be 1.05 from the residual deviance.

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_Cu

Contaminant	Prediction	s.e.
Cu0	0.5	0.1
Cu1	56.5	14.0
Cu2	887.3	219.0
Cu3	1768.7	436.6

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
Cu0                  *
Cu1              0.000            *
Cu2              0.000        0.000            *
Cu3              0.000        0.000        0.052            *
                   Cu0          Cu1          Cu2          Cu3
```

Regression analysis

```
Response variate: UpConc_Cu
    Distribution: Gamma
   Link function: Log
    Fitted terms: Constant, Contaminant, Method
```

Summary of analysis

```
                                          mean   deviance   approx
Source          d.f.     deviance     deviance      ratio    F pr.
Regression         8       339.36      42.4197      64.06    <.001
Residual          63        41.72       0.6622
Total             71       381.08       5.3673

Change            -5       -32.88       6.5764       9.93    <.001
```

Coefficient of variation is estimated to be 0.814 from the residual deviance.

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable, adjusted with respect to some factors as specified below.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The predictions have been standardized by averaging over the levels of some factors:

```
         Factor    Weighting policyStatus of weights
    Contaminant    Marginal weightsConstant over levels of other factors
```

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_Cu

```
              Prediction          s.e.
      Method
    SatPaste        76.3          19.4
      1to2_5       365.2          92.8
        1to5       678.5         172.4
       1to10       750.7         190.8
       1to20      1084.0         275.5
      NH4NO3       756.3         192.2
```

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
SatPaste          *
  1to2_5      0.000          *
    1to5      0.000      0.067          *
   1to10      0.000      0.034      0.761          *
   1to20      0.000      0.002      0.163      0.273          *
  NH4NO3      0.000      0.032      0.745      0.981      0.283
           SatPaste     1to2_5       1to5      1to10      1to20
```

Regression analysis

```
Response variate: UpConc_Cu
    Distribution: Gamma
   Link function: Log
    Fitted terms: Constant + Contaminant + Method + Contaminant.Method
```

Summary of analysis

```
                                         mean  deviance  approx
Source       d.f.    deviance        deviance     ratio   F pr.
Regression     23    380.8293       16.557797   3213.72   <.001
Residual       48      0.2473        0.005152
Total          71    381.0766        5.367277

Change        -15    -41.4719        2.764792    536.62   <.001
```

Coefficient of variation is estimated to be 0.0718 from the residual deviance.

Accumulated analysis of deviance

```
                                                        mean  deviance  approx
Change                     d.f.      deviance       deviance     ratio   F pr.
+ Contaminant                 3    306.475233     102.158411  19828.05   <.001
+ Method                      5     32.882223       6.576445   1276.43   <.001
+ Contaminant.Method         15     41.471878       2.764792    536.62   <.001
Residual                     48      0.247306       0.005152

Total                        71    381.076640       5.367277
```

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_Cu

Method	SatPaste		1to2_5	
	Prediction	s.e.	Prediction	s.e.
Contaminant				
Cu0	0.0	0.00	0.2	0.01
Cu1	34.8	1.44	39.5	1.64
Cu2	23.0	0.95	705.2	29.22
Cu3	15.1	0.63	1078.9	44.71

Method	1to5		1to10	
	Prediction	s.e.	Prediction	s.e.
Contaminant				
Cu0	0.3	0.01	0.6	0.02
Cu1	36.2	1.50	34.1	1.41
Cu2	1058.8	43.88	1121.3	46.47
Cu3	3089.8	128.05	2669.3	110.62

Method	1to20		NH4NO3	
	Prediction	s.e.	Prediction	s.e.
Contaminant				
Cu0	1.4	0.06	0.4	0.02
Cu1	23.6	0.98	171.0	7.09
Cu2	996.0	41.27	1419.3	58.82
Cu3	3131.3	129.77	627.6	26.01

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

C1-M1	*				
C1-M2	0.000	*			
C1-M3	0.000	0.000	*		
C1-M4	0.000	0.000	0.000	*	
C1-M5	0.000	0.000	0.000	0.000	*
C1-M6	0.000	0.000	0.000	0.000	0.000

C2-M1	0.000	0.000	0.000	0.000	0.000
C2-M2	0.000	0.000	0.000	0.000	0.000
C2-M3	0.000	0.000	0.000	0.000	0.000
C2-M4	0.000	0.000	0.000	0.000	0.000
C2-M5	0.000	0.000	0.000	0.000	0.000
C2-M6	0.000	0.000	0.000	0.000	0.000
C3-M1	0.000	0.000	0.000	0.000	0.000
C3-M2	0.000	0.000	0.000	0.000	0.000
C3-M3	0.000	0.000	0.000	0.000	0.000
C3-M4	0.000	0.000	0.000	0.000	0.000
C3-M5	0.000	0.000	0.000	0.000	0.000
C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.000	0.000
C4-M2	0.000	0.000	0.000	0.000	0.000
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C1-M1	C1-M2	C1-M3	C1-M4	C1-M5

C1-M6	*				
C2-M1	0.000	*			
C2-M2	0.000	0.037	*		
C2-M3	0.000	0.504	0.149	*	
C2-M4	0.000	0.706	0.015	0.297	*
C2-M5	0.000	0.000	0.000	0.000	0.000
C2-M6	0.000	0.000	0.000	0.000	0.000
C3-M1	0.000	0.000	0.000	0.000	0.000
C3-M2	0.000	0.000	0.000	0.000	0.000
C3-M3	0.000	0.000	0.000	0.000	0.000
C3-M4	0.000	0.000	0.000	0.000	0.000
C3-M5	0.000	0.000	0.000	0.000	0.000
C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.000	0.000
C4-M2	0.000	0.000	0.000	0.000	0.000
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C1-M6	C2-M1	C2-M2	C2-M3	C2-M4

C2-M5	*				
C2-M6	0.000	*			
C3-M1	0.659	0.000	*		
C3-M2	0.000	0.000	0.000	*	
C3-M3	0.000	0.000	0.000	0.000	*
C3-M4	0.000	0.000	0.000	0.000	0.333
C3-M5	0.000	0.000	0.000	0.000	0.302
C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.000	0.000
C4-M2	0.000	0.000	0.000	0.000	0.750
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.052	0.000
	C2-M5	C2-M6	C3-M1	C3-M2	C3-M3

C3-M4	*				
C3-M5	0.049	*			
C3-M6	0.000	0.000	*		
C4-M1	0.000	0.000	0.000	*	
C4-M2	0.514	0.179	0.000	0.000	*
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C3-M4	C3-M5	C3-M6	C4-M1	C4-M2

C4-M3	*			
C4-M4	0.016	*		
C4-M5	0.821	0.009	*	
C4-M6	0.000	0.000	0.000	*
	C4-M3	C4-M4	C4-M5	C4-M6

Soil	Contaminant	Method	Rep	UpConc_Cu	FITTED	RESIDUAL
S1	Cu0	1to10	1	0.5600	0.5733	-0.3999
S1	Cu0	1to10	2	0.6000	0.5733	0.7816
S1	Cu0	1to10	3	0.5600	0.5733	-0.3999
S1	Cu1	1to10	1	33.9600	34.0700	-0.0551
S1	Cu1	1to10	2	33.2300	34.0700	-0.4242
S1	Cu1	1to10	3	35.0200	34.0700	0.4714
S1	Cu2	1to10	1	1113.6400	1121.3067	-0.1169
S1	Cu2	1to10	2	1144.6400	1121.3067	0.3526
S1	Cu2	1to10	3	1105.6400	1121.3067	-0.2395
S1	Cu3	1to10	1	2832.1400	2669.3067	1.0204
S1	Cu3	1to10	2	2737.1400	2669.3067	0.4300
S1	Cu3	1to10	3	2438.6400	2669.3067	-1.5192
S1	Cu0	1to2_5	1	0.1500	0.1600	-1.0895
S1	Cu0	1to2_5	2	0.1800	0.1600	2.0499
S1	Cu0	1to2_5	3	0.1500	0.1600	-1.0895
S1	Cu1	1to2_5	1	40.3800	39.4933	0.3802
S1	Cu1	1to2_5	2	39.3000	39.4933	-0.0837
S1	Cu1	1to2_5	3	38.8000	39.4933	-0.3013
S1	Cu2	1to2_5	1	730.9100	705.1600	0.6156
S1	Cu2	1to2_5	2	706.6600	705.1600	0.0363
S1	Cu2	1to2_5	3	677.9100	705.1600	-0.6681
S1	Cu3	1to2_5	1	1081.2900	1078.9133	0.0376
S1	Cu3	1to2_5	2	1076.1600	1078.9133	-0.0436
S1	Cu3	1to2_5	3	1079.2900	1078.9133	0.0060
S1	Cu0	1to20	1	1.3700	1.4267	-0.6869
S1	Cu0	1to20	2	1.4900	1.4267	0.7465
S1	Cu0	1to20	3	1.4200	1.4267	-0.0799
S1	Cu1	1to20	1	25.2800	23.6067	1.1820
S1	Cu1	1to20	2	23.1000	23.6067	-0.3689
S1	Cu1	1to20	3	22.4400	23.6067	-0.8576
S1	Cu2	1to20	1	1005.2900	995.9567	0.1594
S1	Cu2	1to20	2	969.6900	995.9567	-0.4540
S1	Cu2	1to20	3	1012.8900	995.9567	0.2885
S1	Cu3	1to20	1	3159.2900	3131.2900	0.1521
S1	Cu3	1to20	2	3109.2900	3131.2900	-0.1202
S1	Cu3	1to20	3	3125.2900	3131.2900	-0.0327
S1	Cu0	1to5	1	0.3000	0.2967	0.1910
S1	Cu0	1to5	2	0.3000	0.2967	0.1910
S1	Cu0	1to5	3	0.2900	0.2967	-0.3863

S1	Cu1	1to5	1	29.5200	36.2400	-3.3838
S1	Cu1	1to5	2	39.1400	36.2400	1.3306
S1	Cu1	1to5	3	40.0600	36.2400	1.7390
S1	Cu2	1to5	1	1071.3200	1058.8200	0.2006
S1	Cu2	1to5	2	1028.3200	1058.8200	-0.4963
S1	Cu2	1to5	3	1076.8200	1058.8200	0.2884
S1	Cu3	1to5	1	3074.8200	3089.8200	-0.0830
S1	Cu3	1to5	2	3104.8200	3089.8200	0.0827
S1	Cu3	1to5	3	3089.8200	3089.8200	0.0000
S1	Cu0	NH4NO3	1	0.3800	0.3833	-0.1488
S1	Cu0	NH4NO3	2	0.3900	0.3833	0.2950
S1	Cu0	NH4NO3	3	0.3800	0.3833	-0.1488
S1	Cu1	NH4NO3	1	197.5000	170.9933	2.5195
S1	Cu1	NH4NO3	2	156.8500	170.9933	-1.4522
S1	Cu1	NH4NO3	3	158.6300	170.9933	-1.2647
S1	Cu2	NH4NO3	1	1433.4900	1419.3233	0.1697
S1	Cu2	NH4NO3	2	1433.4900	1419.3233	0.1697
S1	Cu2	NH4NO3	3	1390.9900	1419.3233	-0.3429
S1	Cu3	NH4NO3	1	707.2400	627.5733	2.0806
S1	Cu3	NH4NO3	2	571.9900	627.5733	-1.5583
S1	Cu3	NH4NO3	3	603.4900	627.5733	-0.6634
S1	Cu0	SatPaste	1	0.0400	0.0333	3.2084
S1	Cu0	SatPaste	2	0.0300	0.0333	-1.7667
S1	Cu0	SatPaste	3	0.0300	0.0333	-1.7667
S1	Cu1	SatPaste	1	33.8900	34.8367	-0.4679
S1	Cu1	SatPaste	2	35.5400	34.8367	0.3422
S1	Cu1	SatPaste	3	35.0800	34.8367	0.1189
S1	Cu2	SatPaste	1	21.9800	23.0000	-0.7682
S1	Cu2	SatPaste	2	22.4900	23.0000	-0.3812
S1	Cu2	SatPaste	3	24.5300	23.0000	1.1108
S1	Cu3	SatPaste	1	16.0500	15.0833	1.0710
S1	Cu3	SatPaste	2	14.1300	15.0833	-1.1020
S1	Cu3	SatPaste	3	15.0700	15.0833	-0.0151

```
========== GLM analysis of        Up concentrated Cu        for soil        S2    ========
```

Regression analysis

```
          Response variate: UpConc_Cu
              Distribution: Gamma
             Link function: Log
              Fitted terms: Constant, Contaminant
```

Summary of analysis

```
                                                      mean    deviance   approx
Source              d.f.         deviance         deviance       ratio    F pr.
Regression             3            103.0           34.330       15.14    <.001
Residual              68            154.2            2.267
Total                 71            257.1            3.622
```

Coefficient of variation is estimated to be 1.51 from the residual deviance.

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_Cu

```
                      Prediction           s.e.
   Contaminant
           Cu0              0.45          0.161
           Cu1              4.94          1.754
           Cu2             13.04          4.626
           Cu3             23.36          8.291
```

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
           Cu0             *
           Cu1         0.000            *
           Cu2         0.000        0.057            *
           Cu3         0.000        0.003        0.249            *
```

Cu0 Cu1 Cu2 Cu3

Regression analysis

Response variate: UpConc_Cu
Distribution: Gamma
Link function: Log
Fitted terms: Constant, Contaminant, Method

Summary of analysis

Source	d.f.	deviance	mean deviance	deviance ratio	approx F pr.
Regression	8	238.76	29.8449	102.25	<.001
Residual	63	18.39	0.2919		
Total	71	257.15	3.6218		
Change	-5	-135.77	27.1537	93.03	<.001

Coefficient of variation is estimated to be 0.540 from the residual deviance.

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable, adjusted with respect to some factors as specified below.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The predictions have been standardized by averaging over the levels of some factors:

Factor	Weighting policy	Status of weights
Contaminant	Marginal weights	Constant over levels of other factors

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_Cu

Method	Prediction	s.e.
SatPaste	0.583	0.094
1to2_5	1.024	0.166
1to5	1.558	0.252
1to10	2.665	0.431
1to20	4.767	0.771
NH4NO3	38.931	6.294

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
SatPaste          *
  1to2_5      0.013          *
    1to5      0.000      0.062          *
   1to10      0.000      0.000      0.018          *
   1to20      0.000      0.000      0.000      0.011          *
  NH4NO3      0.000      0.000      0.000      0.000      0.000
           SatPaste     1to2_5       1to5      1to10      1to20
```

Regression analysis

```
Response variate: UpConc_Cu
    Distribution: Gamma
   Link function: Log
    Fitted terms: Constant + Contaminant + Method + Contaminant.Method
```

Summary of analysis

```
                                          mean   deviance   approx
Source        d.f.      deviance      deviance      ratio    F pr.
Regression      23      256.5033      11.15232     830.94    <.001
Residual        48        0.6442       0.01342
Total           71      257.1475       3.62180

Change         -15      -17.7438       1.18292      88.14    <.001
```

Coefficient of variation is estimated to be 0.116 from the residual deviance.

Accumulated analysis of deviance

```
                                                    mean   deviance   approx
Change                     d.f.     deviance    deviance      ratio    F pr.
+ Contaminant                 3    102.99082    34.33027    2557.90    <.001
+ Method                      5    135.76864    27.15373    2023.19    <.001
+ Contaminant.Method         15     17.74383     1.18292      88.14    <.001
Residual                     48      0.64422     0.01342

Total                        71    257.14751     3.62180
```

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_Cu

```
      Method      SatPaste                 1to2_5
                Prediction      s.e.    Prediction      s.e.
 Contaminant
         Cu0          0.09    0.0062          0.18    0.0123
         Cu1          0.30    0.0201          0.63    0.0421
         Cu2          0.83    0.0555          1.21    0.0809
         Cu3          1.27    0.0847          2.06    0.1380

      Method          1to5                   1to10
                Prediction      s.e.    Prediction      s.e.
 Contaminant
         Cu0          0.31    0.0205          0.67    0.0448
         Cu1          1.06    0.0707          1.67    0.1119
         Cu2          1.83    0.1224          2.85    0.1906
         Cu3          2.53    0.1694          3.60    0.2406

      Method         1to20                  NH4NO3
                Prediction      s.e.    Prediction      s.e.
 Contaminant
         Cu0          1.22    0.0818          0.24    0.0161
         Cu1          2.81    0.1882         23.18    1.5504
         Cu2          5.59    0.3741         65.90    4.4076
         Cu3          5.99    0.4006        124.66    8.3378
```

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
   C1-M1           *
   C1-M2       0.000           *
   C1-M3       0.000       0.000           *
   C1-M4       0.000       0.000       0.000           *
   C1-M5       0.000       0.000       0.000       0.000           *
   C1-M6       0.000       0.006       0.013       0.000       0.000
   C2-M1       0.000       0.000       0.817       0.000       0.000
   C2-M2       0.000       0.000       0.000       0.518       0.000
   C2-M3       0.000       0.000       0.000       0.000       0.128
   C2-M4       0.000       0.000       0.000       0.000       0.002
   C2-M5       0.000       0.000       0.000       0.000       0.000
   C2-M6       0.000       0.000       0.000       0.000       0.000
   C3-M1       0.000       0.000       0.000       0.028       0.000
   C3-M2       0.000       0.000       0.000       0.000       0.908
   C3-M3       0.000       0.000       0.000       0.000       0.000
   C3-M4       0.000       0.000       0.000       0.000       0.000
   C3-M5       0.000       0.000       0.000       0.000       0.000
```

C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.000	0.714
C4-M2	0.000	0.000	0.000	0.000	0.000
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C1-M1	C1-M2	C1-M3	C1-M4	C1-M5

C1-M6	*				
C2-M1	0.022	*			
C2-M2	0.000	0.000	*		
C2-M3	0.000	0.000	0.000	*	
C2-M4	0.000	0.000	0.000	0.000	*
C2-M5	0.000	0.000	0.000	0.000	0.000
C2-M6	0.000	0.000	0.000	0.000	0.000
C3-M1	0.000	0.000	0.005	0.014	0.000
C3-M2	0.000	0.000	0.000	0.158	0.001
C3-M3	0.000	0.000	0.000	0.000	0.349
C3-M4	0.000	0.000	0.000	0.000	0.000
C3-M5	0.000	0.000	0.000	0.000	0.000
C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.061	0.005
C4-M2	0.000	0.000	0.000	0.000	0.032
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C1-M6	C2-M1	C2-M2	C2-M3	C2-M4

C2-M5	*				
C2-M6	0.000	*			
C3-M1	0.000	0.000	*		
C3-M2	0.000	0.000	0.000	*	
C3-M3	0.000	0.000	0.000	0.000	*
C3-M4	0.891	0.000	0.000	0.000	0.000
C3-M5	0.000	0.000	0.000	0.000	0.000
C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.631	0.000
C4-M2	0.002	0.000	0.000	0.000	0.211
C4-M3	0.273	0.000	0.000	0.000	0.001
C4-M4	0.012	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C2-M5	C2-M6	C3-M1	C3-M2	C3-M3

C3-M4	*				
C3-M5	0.000	*			
C3-M6	0.000	0.000	*		
C4-M1	0.000	0.000	0.000	*	
C4-M2	0.001	0.000	0.000	0.000	*
C4-M3	0.219	0.000	0.000	0.000	0.035
C4-M4	0.018	0.000	0.000	0.000	0.000
C4-M5	0.000	0.472	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C3-M4	C3-M5	C3-M6	C4-M1	C4-M2

C4-M3	*			
C4-M4	0.001	*		
C4-M5	0.000	0.000	*	
C4-M6	0.000	0.000	0.000	*
	C4-M3	C4-M4	C4-M5	C4-M6

Soil	Contaminant	Method	Rep	UpConc_Cu	FITTED	RESIDUAL
S2	Cu0	1to10	1	0.8000	0.6700	1.9318
S2	Cu0	1to10	2	0.6000	0.6700	-1.1455
S2	Cu0	1to10	3	0.6100	0.6700	-0.9766
S2	Cu1	1to10	1	1.6500	1.6733	-0.1481
S2	Cu1	1to10	2	1.6800	1.6733	0.0421
S2	Cu1	1to10	3	1.6900	1.6733	0.1049
S2	Cu2	1to10	1	3.0900	2.8500	0.8664
S2	Cu2	1to10	2	3.1800	2.8500	1.1798
S2	Cu2	1to10	3	2.2800	2.8500	-2.2745
S2	Cu3	1to10	1	3.3600	3.5967	-0.7115
S2	Cu3	1to10	2	3.3200	3.5967	-0.8351
S2	Cu3	1to10	3	4.1100	3.5967	1.4425
S2	Cu0	1to2_5	1	0.2200	0.1833	1.9879
S2	Cu0	1to2_5	2	0.1700	0.1833	-0.7883
S2	Cu0	1to2_5	3	0.1600	0.1833	-1.4072
S2	Cu1	1to2_5	1	0.6500	0.6300	0.3321
S2	Cu1	1to2_5	2	0.5700	0.6300	-1.0407
S2	Cu1	1to2_5	3	0.6700	0.6300	0.6575
S2	Cu2	1to2_5	1	1.2400	1.2100	0.2600
S2	Cu2	1to2_5	2	1.1500	1.2100	-0.5331
S2	Cu2	1to2_5	3	1.2400	1.2100	0.2600
S2	Cu3	1to2_5	1	2.8900	2.0633	3.7738
S2	Cu3	1to2_5	2	1.6900	2.0633	-2.0422
S2	Cu3	1to2_5	3	1.6100	2.0633	-2.5186
S2	Cu0	1to20	1	1.1500	1.2233	-0.6469
S2	Cu0	1to20	2	1.3700	1.2233	1.2201
S2	Cu0	1to20	3	1.1500	1.2233	-0.6469
S2	Cu1	1to20	1	2.7500	2.8133	-0.2398
S2	Cu1	1to20	2	2.9000	2.8133	0.3224
S2	Cu1	1to20	3	2.7900	2.8133	-0.0879
S2	Cu2	1to20	1	5.9900	5.5933	0.7327
S2	Cu2	1to20	2	5.5100	5.5933	-0.1583
S2	Cu2	1to20	3	5.2800	5.5933	-0.6037
S2	Cu3	1to20	1	5.9100	5.9900	-0.1418
S2	Cu3	1to20	2	5.7600	5.9900	-0.4112
S2	Cu3	1to20	3	6.3000	5.9900	0.5380
S2	Cu0	1to5	1	0.3000	0.3067	-0.2315
S2	Cu0	1to5	2	0.3000	0.3067	-0.2315
S2	Cu0	1to5	3	0.3200	0.3067	0.4531
S2	Cu1	1to5	1	1.0600	1.0567	0.0333
S2	Cu1	1to5	2	1.0400	1.0567	-0.1676
S2	Cu1	1to5	3	1.0700	1.0567	0.1328
S2	Cu2	1to5	1	1.7800	1.8300	-0.2915
S2	Cu2	1to5	2	1.8200	1.8300	-0.0579
S2	Cu2	1to5	3	1.8900	1.8300	0.3429
S2	Cu3	1to5	1	2.8500	2.5333	1.2701
S2	Cu3	1to5	2	2.2000	2.5333	-1.4572
S2	Cu3	1to5	3	2.5500	2.5333	0.0694
S2	Cu0	NH4NO3	1	0.2300	0.2400	-0.4468
S2	Cu0	NH4NO3	2	0.2500	0.2400	0.4345
S2	Cu0	NH4NO3	3	0.2400	0.2400	0.0000

```
S2      Cu1   NH4NO3     1    24.6400    23.1800    0.6524
S2      Cu1   NH4NO3     2    24.9400    23.1800    0.7832
S2      Cu1   NH4NO3     3    19.9600    23.1800   -1.5427
S2      Cu2   NH4NO3     1    65.0600    65.8967   -0.1348
S2      Cu2   NH4NO3     2    66.9400    65.8967    0.1665
S2      Cu2   NH4NO3     3    65.6900    65.8967   -0.0332
S2      Cu3   NH4NO3     1   124.9400   124.6567    0.0240
S2      Cu3   NH4NO3     2   124.7900   124.6567    0.0113
S2      Cu3   NH4NO3     3   124.2400   124.6567   -0.0354
S2      Cu0   SatPaste   1     0.1100     0.0933    1.7859
S2      Cu0   SatPaste   2     0.0900     0.0933   -0.3822
S2      Cu0   SatPaste   3     0.0800     0.0933   -1.5888
S2      Cu1   SatPaste   1     0.2900     0.3000   -0.3564
S2      Cu1   SatPaste   2     0.3300     0.3000    1.0239
S2      Cu1   SatPaste   3     0.2800     0.3000   -0.7211
S2      Cu2   SatPaste   1     0.8200     0.8300   -0.1279
S2      Cu2   SatPaste   2     0.7700     0.8300   -0.7835
S2      Cu2   SatPaste   3     0.9000     0.8300    0.8677
S2      Cu3   SatPaste   1     1.3500     1.2667    0.6808
S2      Cu3   SatPaste   2     1.1800     1.2667   -0.7405
S2      Cu3   SatPaste   3     1.2700     1.2667    0.0278
```

Exp1_Pb_Upconc.rtf

```
          ============================== file name is Exp1_Pb_Upconc.gen
```

EXP 1: METHOD SCREENING 2011/2012: Soils S1 & S2 Up concentrated Pb

```
   Identifier    Minimum        Mean    Maximum      Values     Missing
   UpConc_Pb     0.01420        2040      12812         144          12   Skew


========== GLM analysis of      Up concentrated Pb      for soil      S1    ========
```

Regression analysis

```
  Response variate: UpConc_Pb
      Distribution: Gamma
     Link function: Log
     Fitted terms: Constant, Contaminant
```

Summary of analysis

```
                                             mean    deviance   approx
Source            d.f.      deviance     deviance       ratio    F pr.
Regression           3        364.02      121.341       89.99    <.001
Residual            66         89.00        1.348
Total               69        453.02        6.565
```

Coefficient of variation is estimated to be 1.16 from the residual deviance.

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_Pb

```
                  Prediction        s.e.
   Contaminant
           Pb0             1           0
           Pb1           133          36
           Pb2          4029        1103
           Pb3         10764        2946
```

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
           Pb0             *
           Pb1         0.000            *
           Pb2         0.000        0.000            *
           Pb3         0.000        0.000        0.013            *
                         Pb0          Pb1          Pb2          Pb3
```

Regression analysis

```
    Response variate: UpConc_Pb
        Distribution: Gamma
       Link function: Log
        Fitted terms: Constant, Contaminant, Method
```

Summary of analysis

```
                                               mean   deviance   approx
Source           d.f.     deviance         deviance      ratio    F pr.
Regression          8       389.83           48.729      47.04    <.001
Residual           61        63.19            1.036
Total              69       453.02            6.565

Change             -5       -25.81            5.161       4.98    <.001
```

Coefficient of variation is estimated to be 1.02 from the residual deviance.

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable, adjusted with respect to some factors as specified below.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The predictions have been standardized by averaging over the levels of some factors:

```
                 Factor     Weighting policyStatus of weights
            Contaminant     Marginal weightsConstant over levels of other factors
```

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_Pb

```
                  Prediction           s.e.
      Method
    SatPaste            2022            681
      1to2_5            2990            983
        1to5            3329           1094
       1to10            4118           1387
       1to20            5018           1650
      NH4NO3           19798           6509
```

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
    SatPaste             *
      1to2_5         0.361            *
        1to5         0.246        0.797            *
       1to10         0.106        0.455        0.618            *
       1to20         0.037        0.218        0.327        0.644            *
      NH4NO3         0.000        0.000        0.000        0.000        0.002
                  SatPaste       1to2_5         1to5        1to10        1to20
```

Regression analysis

```
    Response variate: UpConc_Pb
        Distribution: Gamma
       Link function: Log
        Fitted terms: Constant + Contaminant + Method + Contaminant.Method
```

Summary of analysis

```
                                             mean     deviance    approx
Source             d.f.     deviance     deviance        ratio     F pr.
Regression           23      450.671     19.59441       384.07     <.001
```

```
Residual          46          2.347        0.05102
Total             69        453.018        6.56548

Change           -15        -60.843        4.05618       79.51     <.001
```

Coefficient of variation is estimated to be 0.226 from the residual deviance.

Accumulated analysis of deviance

```
                                                       mean    deviance     approx
Change                      d.f.       deviance    deviance       ratio      F pr.
+ Contaminant                  3      364.02276   121.34092     2378.41      <.001
+ Method                       5       25.80595     5.16119      101.16      <.001
+ Contaminant.Method          15       60.84274     4.05618       79.51      <.001
Residual                      46        2.34681     0.05102

Total                         69      453.01827     6.56548
```

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_Pb

Method	SatPaste		1to2_5	
	Prediction	s.e.	Prediction	s.e.
Contaminant				
Pb0	0	0.0	0	0.0
Pb1	0	0.0	35	4.6
Pb2	3031	395.2	3690	481.2
Pb3	11819	1541.3	10457	1363.6

Method	1to5		1to10	
	Prediction	s.e.	Prediction	s.e.
Contaminant				
Pb0	0	0.1	1	0.2
Pb1	31	4.0	20	2.6
Pb2	2850	371.6	4288	559.2
Pb3	10643	1387.9	9147	1192.8

Method	1to20		NH4NO3	
	Prediction	s.e.	Prediction	s.e.
Contaminant				
Pb0	1	0.2	0	0.0
Pb1	13	1.7	698	91.1
Pb2	4725	616.2	5593	729.4
Pb3	10061	1312.0	12459	1624.8

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

C1-M1	*				
C1-M2	0.000	*			
C1-M3	0.000	0.000	*		
C1-M4	0.000	0.000	0.000	*	
C1-M5	0.000	0.000	0.000	0.310	*
C1-M6	0.000	0.000	0.103	0.000	0.000

C2-M1	0.000	0.100	0.000	0.000	0.000
C2-M2	0.000	0.000	0.000	0.000	0.000
C2-M3	0.000	0.000	0.000	0.000	0.000
C2-M4	0.000	0.000	0.000	0.000	0.000
C2-M5	0.000	0.000	0.000	0.000	0.000
C2-M6	0.000	0.000	0.000	0.000	0.000
C3-M1	0.000	0.000	0.000	0.000	0.000
C3-M2	0.000	0.000	0.000	0.000	0.000
C3-M3	0.000	0.000	0.000	0.000	0.000
C3-M4	0.000	0.000	0.000	0.000	0.000
C3-M5	0.000	0.000	0.000	0.000	0.000
C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.000	0.000
C4-M2	0.000	0.000	0.000	0.000	0.000
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C1-M1	C1-M2	C1-M3	C1-M4	C1-M5

C1-M6	*				
C2-M1	0.007	*			
C2-M2	0.000	0.000	*		
C2-M3	0.000	0.000	0.440	*	
C2-M4	0.000	0.000	0.003	0.024	*
C2-M5	0.000	0.000	0.000	0.000	0.029
C2-M6	0.000	0.000	0.000	0.000	0.000
C3-M1	0.000	0.000	0.000	0.000	0.000
C3-M2	0.000	0.000	0.000	0.000	0.000
C3-M3	0.000	0.000	0.000	0.000	0.000
C3-M4	0.000	0.000	0.000	0.000	0.000
C3-M5	0.000	0.000	0.000	0.000	0.000
C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.000	0.000
C4-M2	0.000	0.000	0.000	0.000	0.000
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C1-M6	C2-M1	C2-M2	C2-M3	C2-M4

C2-M5	*				
C2-M6	0.000	*			
C3-M1	0.000	0.000	*		
C3-M2	0.000	0.000	0.291	*	
C3-M3	0.000	0.000	0.740	0.168	*
C3-M4	0.000	0.000	0.066	0.420	0.032
C3-M5	0.000	0.000	0.020	0.186	0.009
C3-M6	0.000	0.000	0.002	0.029	0.001
C4-M1	0.000	0.000	0.000	0.000	0.000
C4-M2	0.000	0.000	0.000	0.000	0.000
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C2-M5	C2-M6	C3-M1	C3-M2	C3-M3

C3-M4	*				
C3-M5	0.601	*			
C3-M6	0.156	0.365	*		
C4-M1	0.000	0.000	0.000	*	
C4-M2	0.000	0.000	0.001	0.510	*
C4-M3	0.000	0.000	0.001	0.572	0.924
C4-M4	0.000	0.001	0.011	0.171	0.472
C4-M5	0.000	0.000	0.003	0.387	0.835
C4-M6	0.000	0.000	0.000	0.776	0.347
	C3-M4	C3-M5	C3-M6	C4-M1	C4-M2

C4-M3	*			
C4-M4	0.416	*		
C4-M5	0.762	0.608	*	
C4-M6	0.397	0.101	0.252	*
	C4-M3	C4-M4	C4-M5	C4-M6

Soil	Contaminant	Method	Rep	UpConc_Pb	FITTED	RESIDUAL
S1	Pb0	1to10	1	*	1.0745	*
S1	Pb0	1to10	2	1.1150	1.0745	0.2331
S1	Pb0	1to10	3	1.0340	1.0745	-0.2390
S1	Pb0	1to2_5	1	0.2385	0.1540	2.5581
S1	Pb0	1to2_5	2	0.0882	0.1540	-2.7631
S1	Pb0	1to2_5	3	0.1353	0.1540	-0.6891
S1	Pb0	1to20	1	1.6920	1.3280	1.3687
S1	Pb0	1to20	2	1.1500	1.3280	-0.7621
S1	Pb0	1to20	3	1.1420	1.3280	-0.7981
S1	Pb0	1to5	1	0.4670	0.4822	-0.1724
S1	Pb0	1to5	2	0.4460	0.4822	-0.4174
S1	Pb0	1to5	3	0.5335	0.4822	0.5580
S1	Pb0	NH4NO3	1	0.4022	0.3549	0.6933
S1	Pb0	NH4NO3	2	0.3917	0.3549	0.5444
S1	Pb0	NH4NO3	3	0.2707	0.3549	-1.4044
S1	Pb0	SatPaste	1	0.0286	0.0427	-2.3446
S1	Pb0	SatPaste	2	0.0568	0.0427	1.8706
S1	Pb0	SatPaste	3	*	0.0427	*
S1	Pb1	1to10	1	16.9600	19.9633	-0.8607
S1	Pb1	1to10	2	22.7000	19.9633	0.7118
S1	Pb1	1to10	3	20.2300	19.9633	0.0721
S1	Pb1	1to2_5	1	41.2750	35.3917	0.8558
S1	Pb1	1to2_5	2	30.8000	35.3917	-0.7364
S1	Pb1	1to2_5	3	34.1000	35.3917	-0.2004
S1	Pb1	1to20	1	14.5760	13.1753	0.5572
S1	Pb1	1to20	2	12.8100	13.1753	-0.1518
S1	Pb1	1to20	3	12.1400	13.1753	-0.4378
S1	Pb1	1to5	1	28.7000	30.6583	-0.3540
S1	Pb1	1to5	2	34.4500	30.6583	0.6448
S1	Pb1	1to5	3	28.8250	30.6583	-0.3309
S1	Pb1	NH4NO3	1	694.8750	698.2083	-0.0259
S1	Pb1	NH4NO3	2	693.8750	698.2083	-0.0337
S1	Pb1	NH4NO3	3	705.8750	698.2083	0.0593
S1	Pb1	SatPaste	1	0.2550	0.2100	1.0892
S1	Pb1	SatPaste	2	0.2470	0.2100	0.9058
S1	Pb1	SatPaste	3	0.1279	0.2100	-2.4842
S1	Pb2	1to10	1	4407.5000	4287.8333	0.1499
S1	Pb2	1to10	2	4207.0000	4287.8333	-0.1029
S1	Pb2	1to10	3	4249.0000	4287.8333	-0.0493

S1	Pb2	1to2_5	1	3871.2500	3690.0000	0.2621
S1	Pb2	1to2_5	2	3512.5000	3690.0000	-0.2651
S1	Pb2	1to2_5	3	3686.2500	3690.0000	-0.0055
S1	Pb2	1to20	1	4948.0000	4725.3333	0.2516
S1	Pb2	1to20	2	4672.0000	4725.3333	-0.0614
S1	Pb2	1to20	3	4556.0000	4725.3333	-0.1967
S1	Pb2	1to5	1	1069.0000	2849.6667	-4.5729
S1	Pb2	1to5	2	3845.0000	2849.6667	1.7097
S1	Pb2	1to5	3	3635.0000	2849.6667	1.3756
S1	Pb2	NH4NO3	1	5480.0000	5593.3333	-0.1106
S1	Pb2	NH4NO3	2	5651.2500	5593.3333	0.0560
S1	Pb2	NH4NO3	3	5648.7500	5593.3333	0.0535
S1	Pb2	SatPaste	1	3128.3008	3030.6296	0.1729
S1	Pb2	SatPaste	2	3082.3012	3030.6296	0.0919
S1	Pb2	SatPaste	3	2881.2866	3030.6296	-0.2717
S1	Pb3	1to10	1	9865.0000	9146.6667	0.4152
S1	Pb3	1to10	2	7185.0000	9146.6667	-1.2583
S1	Pb3	1to10	3	10390.0000	9146.6667	0.7061
S1	Pb3	1to2_5	1	10550.0000	10456.6667	0.0483
S1	Pb3	1to2_5	2	10600.0000	10456.6667	0.0740
S1	Pb3	1to2_5	3	10220.0000	10456.6667	-0.1237
S1	Pb3	1to20	1	10270.0000	10061.0000	0.1119
S1	Pb3	1to20	2	10420.0000	10061.0000	0.1912
S1	Pb3	1to20	3	9493.0000	10061.0000	-0.3121
S1	Pb3	1to5	1	10777.5000	10642.5000	0.0685
S1	Pb3	1to5	2	10537.5000	10642.5000	-0.0537
S1	Pb3	1to5	3	10612.5000	10642.5000	-0.0153
S1	Pb3	NH4NO3	1	12812.5000	12459.1667	0.1523
S1	Pb3	NH4NO3	2	12217.5000	12459.1667	-0.1059
S1	Pb3	NH4NO3	3	12347.5000	12459.1667	-0.0487
S1	Pb3	SatPaste	1	10439.8759	11819.1884	-0.6592
S1	Pb3	SatPaste	2	12461.6969	11819.1884	0.2896
S1	Pb3	SatPaste	3	12555.9923	11819.1884	0.3312

```
========== GLM analysis of        Up concentrated Pb        for soil        S2    ========
```

Regression analysis

```
      Response variate: UpConc_Pb
          Distribution: Gamma
         Link function: Log
          Fitted terms: Constant, Contaminant
```

Summary of analysis

```
                                                   mean   deviance   approx
Source           d.f.        deviance          deviance      ratio    F pr.
Regression          3            99.3            33.099      15.70    <.001
Residual           58           122.3             2.108
Total              61           221.6             3.632
```

Coefficient of variation is estimated to be 1.45 from the residual deviance.

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_Pb

```
                 Prediction          s.e.
   Contaminant
           Pb0        0.514         0.187
           Pb1        2.304         0.789
           Pb2       14.159         6.501
           Pb3       19.097         6.535
```

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
           Pb0             *
           Pb1         0.004             *
           Pb2         0.000         0.002             *
           Pb3         0.000         0.000         0.603             *
```

Pb0	Pb1	Pb2	Pb3

Regression analysis

Response variate: UpConc_Pb
Distribution: Gamma
Link function: Log
Fitted terms: Constant, Contaminant, Method

Summary of analysis

Source	d.f.	deviance	mean deviance	deviance ratio	approx F pr.
Regression	8	178.96	22.3694	27.83	<.001
Residual	53	42.61	0.8039		
Total	61	221.56	3.6322		
Change	-5	-79.66	15.9319	19.82	<.001

Coefficient of variation is estimated to be 0.897 from the residual deviance.

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable, adjusted with respect to some factors as specified below.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The predictions have been standardized by averaging over the levels of some factors:

Factor	Weighting policy	Status of weights
Contaminant	Marginal weights	Constant over levels of other factors

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_Pb

	Prediction	s.e.
Method		
SatPaste	1.496	0.436
1to2_5	1.720	0.487
1to5	2.184	0.670
1to10	3.664	1.195
1to20	4.616	1.505
NH4NO3	32.680	9.525

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
   SatPaste         *
     1to2_5     0.711          *
       1to5     0.344      0.540          *
      1to10     0.035      0.067      0.216          *
      1to20     0.009      0.018      0.076      0.587          *
     NH4NO3     0.000      0.000      0.000      0.000      0.000
             SatPaste     1to2_5       1to5      1to10      1to20
```

Message: term Contaminant.Method cannot be fully included in the model because 2 parameters are aliased with terms already in the model.

(Contaminant Pb2 .Method 1to10) = 0

(Contaminant Pb2 .Method 1to20) = 0

Regression analysis

```
Response variate: UpConc_Pb
    Distribution: Gamma
   Link function: Log
    Fitted terms: Constant + Contaminant + Method + Contaminant.Method
```

Summary of analysis

```
                                      mean   deviance   approx
Source        d.f.    deviance    deviance      ratio    F pr.
Regression      21      203.17      9.6748      21.04    <.001
Residual        40       18.39      0.4598
Total           61      221.56      3.6322

Change         -13      -24.22      1.8627       4.05    <.001
```

Coefficient of variation is estimated to be 0.678 from the residual deviance.

Accumulated analysis of deviance

```
                                                     mean   deviance    approx
Change                      d.f.     deviance    deviance      ratio     F pr.
+ Contaminant                  3      99.2958     33.0986      71.98     <.001
+ Method                       5      79.6593     15.9319      34.65     <.001
+ Contaminant.Method          13      24.2151      1.8627       4.05     <.001
Residual                      40      18.3927      0.4598

Total                         61     221.5629      3.6322
```

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_Pb

Method	SatPaste		1to2_5	
	Prediction	s.e.	Prediction	s.e.
Contaminant				
Pb0	0.033	0.016	0.221	0.086
Pb1	0.192	0.075	0.309	0.121
Pb2	1.961	0.768	2.049	0.802
Pb3	6.849	2.681	5.746	2.249

Method	1to5		1to10	
	Prediction	s.e.	Prediction	s.e.
Contaminant				
Pb0	0.468	0.183	0.947	0.371
Pb1	0.643	0.252	0.730	0.286
Pb2	0.236	0.160	*	*
Pb3	3.572	1.398	4.366	1.709

Method	1to20		NH4NO3	
	Prediction	s.e.	Prediction	s.e.
Contaminant				
Pb0	0.928	0.363	0.233	0.112
Pb1	1.347	0.527	10.603	4.151
Pb2	*	*	43.108	16.877
Pb3	5.264	2.061	88.783	34.759

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

C1-M1	*				
C1-M2	0.004	*			
C1-M3	0.000	0.182	*		
C1-M4	0.000	0.012	0.211	*	
C1-M5	0.000	0.013	0.224	0.970	*
C1-M6	0.006	0.928	0.267	0.029	0.031
C2-M1	0.007	0.805	0.116	0.006	0.007

C2-M2	0.001	0.547	0.457	0.050	0.054
C2-M3	0.000	0.060	0.570	0.489	0.512
C2-M4	0.000	0.037	0.428	0.641	0.667
C2-M5	0.000	0.002	0.064	0.528	0.505
C2-M6	0.000	0.000	0.000	0.000	0.000
C3-M1	0.000	0.000	0.013	0.196	0.184
C3-M2	0.000	0.000	0.011	0.171	0.160
C3-M3	0.023	0.930	0.388	0.084	0.088
C3-M4	*	*	*	*	*
C3-M5	*	*	*	*	*
C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.001	0.001
C4-M2	0.000	0.000	0.000	0.002	0.002
C4-M3	0.000	0.000	0.001	0.021	0.019
C4-M4	0.000	0.000	0.000	0.009	0.008
C4-M5	0.000	0.000	0.000	0.004	0.003
C4-M6	0.000	0.000	0.000	0.000	0.000
	C1-M1	C1-M2	C1-M3	C1-M4	C1-M5

C1-M6	*				
C2-M1	0.757	*			
C2-M2	0.652	0.397	*		
C2-M3	0.109	0.035	0.193	*	
C2-M4	0.073	0.021	0.128	0.820	*
C2-M5	0.007	0.001	0.011	0.189	0.275
C2-M6	0.000	0.000	0.000	0.000	0.000
C3-M1	0.001	0.000	0.002	0.051	0.082
C3-M2	0.001	0.000	0.001	0.043	0.070
C3-M3	0.985	0.793	0.734	0.209	0.158
C3-M4	*	*	*	*	*
C3-M5	*	*	*	*	*
C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.000	0.000
C4-M2	0.000	0.000	0.000	0.000	0.001
C4-M3	0.000	0.000	0.000	0.004	0.007
C4-M4	0.000	0.000	0.000	0.001	0.002
C4-M5	0.000	0.000	0.000	0.000	0.001
C4-M6	0.000	0.000	0.000	0.000	0.000
	C1-M6	C2-M1	C2-M2	C2-M3	C2-M4

C2-M5	*				
C2-M6	0.001	*			
C3-M1	0.502	0.004	*		
C3-M2	0.453	0.005	0.936	*	
C3-M3	0.032	0.000	0.010	0.009	*
C3-M4	*	*	*	*	*
C3-M5	*	*	*	*	*
C3-M6	0.000	0.015	0.000	0.000	0.000
C4-M1	0.005	0.435	0.029	0.035	0.000
C4-M2	0.012	0.275	0.059	0.070	0.000
C4-M3	0.086	0.056	0.285	0.322	0.001
C4-M4	0.040	0.117	0.156	0.179	0.001
C4-M5	0.018	0.213	0.082	0.096	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C2-M5	C2-M6	C3-M1	C3-M2	C3-M3

```
C3-M4           *
C3-M5           *           *
C3-M6           *           *           *
C4-M1           *           *       0.002           *
C4-M2           *           *       0.001       0.753           *
C4-M3           *           *       0.000       0.247       0.396
C4-M4           *           *       0.000       0.421       0.622
C4-M5           *           *       0.000       0.637       0.875
C4-M6           *           *       0.199       0.000       0.000
            C3-M4       C3-M5       C3-M6       C4-M1       C4-M2


C4-M3           *
C4-M4       0.719           *
C4-M5       0.488       0.737           *
C4-M6       0.000       0.000       0.000           *
            C4-M3       C4-M4       C4-M5       C4-M6


Soil  Contaminant        Method      Rep  UpConc_Pb     FITTED   RESIDUAL
 S2          Pb0          1to10        1     1.3740     0.9470     0.7166
 S2          Pb0          1to10        2     0.8290     0.9470    -0.2351
 S2          Pb0          1to10        3     0.6380     0.9470    -0.6693
 S2          Pb0         1to2_5        1     0.3147     0.2208     0.6810
 S2          Pb0         1to2_5        2     0.3063     0.2208     0.6254
 S2          Pb0         1to2_5        3     0.0413     0.2208    -2.3746
 S2          Pb0          1to20        1     0.9380     0.9280     0.0194
 S2          Pb0          1to20        2     1.7280     0.9280     1.2523
 S2          Pb0          1to20        3     0.1180     0.9280    -2.7858
 S2          Pb0           1to5        1     0.6420     0.4685     0.6005
 S2          Pb0           1to5        2     0.3610     0.4685    -0.4512
 S2          Pb0           1to5        3     0.4025     0.4685    -0.2675
 S2          Pb0         NH4NO3        1     0.1985     0.2334    -0.3287
 S2          Pb0         NH4NO3        2          *     0.2334          *
 S2          Pb0         NH4NO3        3     0.2682     0.2334     0.2974
 S2          Pb0       SatPaste        1          *     0.0330          *
 S2          Pb0       SatPaste        2     0.0518     0.0330     1.0162
 S2          Pb0       SatPaste        3     0.0142     0.0330    -1.5421
 S2          Pb1          1to10        1     0.4630     0.7300    -0.7644
 S2          Pb1          1to10        2     0.8350     0.7300     0.2483
 S2          Pb1          1to10        3     0.8920     0.7300     0.3745
 S2          Pb1         1to2_5        1     0.1898     0.3091    -0.8150
 S2          Pb1         1to2_5        2     0.3035     0.3091    -0.0328
 S2          Pb1         1to2_5        3     0.4340     0.3091     0.6498
 S2          Pb1          1to20        1     1.5680     1.3473     0.2810
 S2          Pb1          1to20        2     2.1680     1.3473     0.9330
 S2          Pb1          1to20        3     0.3060     1.3473    -2.1514
 S2          Pb1           1to5        1     0.8160     0.6433     0.4471
 S2          Pb1           1to5        2     0.2655     0.6433    -1.3938
 S2          Pb1           1to5        3     0.8485     0.6433     0.5241
 S2          Pb1         NH4NO3        1     8.7600    10.6025    -0.3342
 S2          Pb1         NH4NO3        2    11.4175    10.6025     0.1354
 S2          Pb1         NH4NO3        3    11.6300    10.6025     0.1697
 S2          Pb1       SatPaste        1     0.4161     0.1924     1.5974
 S2          Pb1       SatPaste        2     0.1192     0.1924    -0.8010
 S2          Pb1       SatPaste        3     0.0420     0.1924    -2.1980
 S2          Pb2          1to10        1          *    56.2757          *
 S2          Pb2          1to10        2          *    56.2757          *
```

```
S2    Pb2    1to10      3          *    56.2757          *
S2    Pb2    1to2_5     1     5.1700     2.0490     1.9747
S2    Pb2    1to2_5     2     0.4783     2.0490    -2.1192
S2    Pb2    1to2_5     3     0.4988     2.0490    -2.0695
S2    Pb2    1to20      1          *    55.1467          *
S2    Pb2    1to20      2          *    55.1467          *
S2    Pb2    1to20      3          *    55.1467          *
S2    Pb2    1to5       1     0.2365     0.2365          *
S2    Pb2    1to5       2          *     0.2365          *
S2    Pb2    1to5       3          *     0.2365          *
S2    Pb2    NH4NO3     1    40.0750    43.1083    -0.1302
S2    Pb2    NH4NO3     2    46.1000    43.1083     0.1226
S2    Pb2    NH4NO3     3    43.1500    43.1083     0.0017
S2    Pb2    SatPaste   1     3.2363     1.9605     0.9877
S2    Pb2    SatPaste   2     1.8759     1.9605    -0.0791
S2    Pb2    SatPaste   3     0.7694     1.9605    -1.4624
S2    Pb3    1to10      1     4.6510     4.3657     0.1156
S2    Pb3    1to10      2     4.1830     4.3657    -0.0767
S2    Pb3    1to10      3     4.2630     4.3657    -0.0428
S2    Pb3    1to2_5     1    10.2750     5.7458     1.1622
S2    Pb3    1to2_5     2     3.8375     5.7458    -0.6831
S2    Pb3    1to2_5     3     3.1250     5.7458    -0.9988
S2    Pb3    1to20      1     6.2940     5.2640     0.3327
S2    Pb3    1to20      2     5.2720     5.2640     0.0027
S2    Pb3    1to20      3     4.2260     5.2640    -0.3827
S2    Pb3    1to5       1     3.6790     3.5717     0.0537
S2    Pb3    1to5       2     3.6045     3.5717     0.0166
S2    Pb3    1to5       3     3.4315     3.5717    -0.0718
S2    Pb3    NH4NO3     1    87.4500    88.7833    -0.0273
S2    Pb3    NH4NO3     2    86.2750    88.7833    -0.0515
S2    Pb3    NH4NO3     3    92.6250    88.7833     0.0771
S2    Pb3    SatPaste   1    10.1433     6.8490     0.7589
S2    Pb3    SatPaste   2     7.7581     6.8490     0.2299
S2    Pb3    SatPaste   3     2.6456     6.8490    -1.4838
```

Exp1_V_Upconc.rtf

```
                ============================== file name is Exp1_V_Upconc.gen
```

EXP 1: METHOD SCREENING 2011/2012: Soils S1 & S2 Up concentrated V

NOTE: Included V3 SatPaste Rep 3

```
Identifier    Minimum      Mean    Maximum    Values    Missing
 UpConc_V    0.005032     620.4       4330       144          2   Skew
```

```
========== GLM analysis of      Up concentrated V      for soil      S1     ========
```

Regression analysis

```
Response variate: UpConc_V
    Distribution: Gamma
   Link function: Log
    Fitted terms: Constant, Contaminant
```

Summary of analysis

```
                                                   mean    deviance    approx
Source               d.f.         deviance     deviance       ratio     F pr.
Regression              3           338.97     112.9897      141.04     <.001
Residual               66            52.87       0.8011
Total                  69           391.84       5.6789
```

Coefficient of variation is estimated to be 0.895 from the residual deviance.

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_V

```
                Prediction          s.e.
   Contaminant
            V0         0.1           0.0
            V1       197.3          41.6
            V2       900.9         190.1
            V3      2835.1         634.4
```

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
            V0             *
            V1         0.000             *
            V2         0.000         0.000             *
            V3         0.000         0.000         0.000             *
                          V0            V1            V2            V3
```

Regression analysis

```
      Response variate: UpConc_V
          Distribution: Gamma
         Link function: Log
          Fitted terms: Constant, Contaminant, Method
```

Summary of analysis

```
                                          mean     deviance    approx
Source          d.f.       deviance    deviance       ratio     F pr.
Regression         8         368.88     46.1104      122.51    <.001
Residual          61          22.96      0.3764
Total             69         391.84      5.6789

Change            -5         -29.91      5.9828       15.90    <.001
```

Coefficient of variation is estimated to be 0.614 from the residual deviance.

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable, adjusted with respect to some factors as specified below.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The predictions have been standardized by averaging over the levels of some factors:

```
          Factor    Weighting policyStatus of weights
     Contaminant    Marginal weightsConstant over levels of other factors
```

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_V

```
              Prediction          s.e.
     Method
   SatPaste          205          45.0
    1to2_5           759         147.2
      1to5           918         177.9
     1to10          1464         283.8
     1to20          2169         420.4
    NH4NO3           535         103.8
```

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
   SatPaste             *
    1to2_5          0.000             *
      1to5          0.000         0.452             *
     1to10          0.000         0.011         0.067             *
     1to20          0.000         0.000         0.001         0.122             *
    NH4NO3          0.001         0.168         0.035         0.000         0.000
                 SatPaste        1to2_5          1to5         1to10         1to20
```

Regression analysis

```
Response variate: UpConc_V
    Distribution: Gamma
   Link function: Log
    Fitted terms: Constant + Contaminant + Method + Contaminant.Method
```

Summary of analysis

```
                                         mean   deviance   approx
Source          d.f.     deviance    deviance      ratio    F pr.
Regression        23      390.647    16.98463     653.11    <.001
Residual          46        1.196     0.02601
Total             69      391.843     5.67888

Change           -15      -21.764     1.45091      55.79    <.001
```

Coefficient of variation is estimated to be 0.161 from the residual deviance.

Accumulated analysis of deviance

```
                                                    mean   deviance    approx
Change                      d.f.     deviance   deviance      ratio     F pr.
+ Contaminant                  3    338.96916  112.98972    4344.79     <.001
+ Method                       5     29.91380    5.98276     230.05     <.001
+ Contaminant.Method          15     21.76364    1.45091      55.79     <.001
Residual                      46      1.19627    0.02601

Total                         69    391.84287    5.67888
```

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_V

```
      Method     SatPaste                  1to2_5
               Prediction        s.e.  Prediction        s.e.
 Contaminant
          V0          0.0        0.00         0.0        0.00
          V1         24.0        2.23       152.9       14.23
          V2        532.0       49.53      1010.9       94.12
          V3        247.1       39.85      3034.2      282.50


      Method         1to5                    1to10
               Prediction        s.e.  Prediction        s.e.
 Contaminant
          V0          0.0        0.00         0.2        0.02
          V1        229.2       21.34       315.5       29.38
          V2       1012.3       94.25      1163.3      108.31
          V3       3068.5      285.69      3507.6      326.58


      Method        1to20                  NH4NO3
               Prediction        s.e.  Prediction        s.e.
 Contaminant
          V0          0.4        0.04         0.1        0.01
          V1        429.0       39.94        33.2        3.09
          V2       1411.8      131.44       275.1       25.61
          V3       3531.2      328.78      1896.5      176.58
```

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
  C1-M1          *
  C1-M2      0.000          *
  C1-M3      0.000      0.000          *
  C1-M4      0.000      0.000      0.000          *
  C1-M5      0.000      0.000      0.000      0.000          *
  C1-M6      0.000      0.000      0.000      0.000      0.000
```

	C1-M1	C1-M2	C1-M3	C1-M4	C1-M5
C2-M1	0.000	0.000	0.000	0.000	0.000
C2-M2	0.000	0.000	0.000	0.000	0.000
C2-M3	0.000	0.000	0.000	0.000	0.000
C2-M4	0.000	0.000	0.000	0.000	0.000
C2-M5	0.000	0.000	0.000	0.000	0.000
C2-M6	0.000	0.000	0.000	0.000	0.000
C3-M1	0.000	0.000	0.000	0.000	0.000
C3-M2	0.000	0.000	0.000	0.000	0.000
C3-M3	0.000	0.000	0.000	0.000	0.000
C3-M4	0.000	0.000	0.000	0.000	0.000
C3-M5	0.000	0.000	0.000	0.000	0.000
C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.000	0.000
C4-M2	0.000	0.000	0.000	0.000	0.000
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000

	C1-M6	C2-M1	C2-M2	C2-M3	C2-M4
C1-M6	*				
C2-M1	0.000	*			
C2-M2	0.000	0.000	*		
C2-M3	0.000	0.000	0.004	*	
C2-M4	0.000	0.000	0.000	0.019	*
C2-M5	0.000	0.000	0.000	0.000	0.024
C2-M6	0.000	0.017	0.000	0.000	0.000
C3-M1	0.000	0.000	0.000	0.000	0.000
C3-M2	0.000	0.000	0.000	0.000	0.000
C3-M3	0.000	0.000	0.000	0.000	0.000
C3-M4	0.000	0.000	0.000	0.000	0.000
C3-M5	0.000	0.000	0.000	0.000	0.000
C3-M6	0.000	0.000	0.000	0.173	0.304
C4-M1	0.000	0.000	0.013	0.688	0.196
C4-M2	0.000	0.000	0.000	0.000	0.000
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000

	C2-M5	C2-M6	C3-M1	C3-M2	C3-M3
C2-M5	*				
C2-M6	0.000	*			
C3-M1	0.109	0.000	*		
C3-M2	0.000	0.000	0.000	*	
C3-M3	0.000	0.000	0.000	0.988	*
C3-M4	0.000	0.000	0.000	0.292	0.297
C3-M5	0.000	0.000	0.000	0.015	0.015
C3-M6	0.002	0.000	0.000	0.000	0.000
C4-M1	0.005	0.000	0.000	0.000	0.000
C4-M2	0.000	0.000	0.000	0.000	0.000
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000

C3-M4	*				
C3-M5	0.148	*			
C3-M6	0.000	0.000	*		
C4-M1	0.000	0.000	0.567	*	
C4-M2	0.000	0.000	0.000	0.000	*
C4-M3	0.000	0.000	0.000	0.000	0.932
C4-M4	0.000	0.000	0.000	0.000	0.277
C4-M5	0.000	0.000	0.000	0.000	0.255
C4-M6	0.001	0.030	0.000	0.000	0.001
	C3-M4	C3-M5	C3-M6	C4-M1	C4-M2

C4-M3	*			
C4-M4	0.315	*		
C4-M5	0.292	0.959	*	
C4-M6	0.001	0.000	0.000	*
	C4-M3	C4-M4	C4-M5	C4-M6

Soil	Contaminant	Method	Rep	UpConc_V	FITTED	RESIDUAL
S1	V0	1to10	1	0.2450	0.2040	1.4347
S1	V0	1to10	2	0.1390	0.2040	-2.7387
S1	V0	1to10	3	0.2280	0.2040	0.8607
S1	V0	1to2_5	1	0.0323	0.0257	1.7760
S1	V0	1to2_5	2	0.0235	0.0257	-0.6840
S1	V0	1to2_5	3	0.0215	0.0257	-1.3300
S1	V0	1to20	1	0.3160	0.4220	-2.0959
S1	V0	1to20	2	0.4600	0.4220	0.6644
S1	V0	1to20	3	0.4900	0.4220	1.1636
S1	V0	1to5	1	0.0375	0.0462	-1.5262
S1	V0	1to5	2	0.0530	0.0462	1.0730
S1	V0	1to5	3	0.0480	0.0462	0.2977
S1	V0	NH4NO3	1	0.1103	0.1181	-0.5154
S1	V0	NH4NO3	2	0.0968	0.1181	-1.4647
S1	V0	NH4NO3	3	0.1472	0.1181	1.7405
S1	V0	SatPaste	1	0.0050	0.0064	-1.7497
S1	V0	SatPaste	2	0.0076	0.0064	1.3648
S1	V0	SatPaste	3	0.0065	0.0064	0.1689
S1	V1	1to10	1	318.6111	315.5111	0.0744
S1	V1	1to10	2	339.1111	315.5111	0.5545
S1	V1	1to10	3	288.8111	315.5111	-0.6618
S1	V1	1to2_5	1	152.4278	152.8694	-0.0220
S1	V1	1to2_5	2	174.0778	152.8694	1.0085
S1	V1	1to2_5	3	132.1028	152.8694	-1.0825
S1	V1	1to20	1	412.4000	429.0000	-0.2978
S1	V1	1to20	2	428.6000	429.0000	-0.0071
S1	V1	1to20	3	446.0000	429.0000	0.2971
S1	V1	1to5	1	236.1055	229.2389	0.2253
S1	V1	1to5	2	239.6055	229.2389	0.3384
S1	V1	1to5	3	212.0055	229.2389	-0.5859
S1	V1	NH4NO3	1	34.4000	33.2000	0.2713
S1	V1	NH4NO3	2	28.1750	33.2000	-1.2132
S1	V1	NH4NO3	3	37.0250	33.2000	0.8435
S1	V1	SatPaste	1	23.0409	23.9849	-0.3029
S1	V1	SatPaste	2	24.4534	23.9849	0.1474
S1	V1	SatPaste	3	24.4603	23.9849	0.1496
S1	V2	1to10	1	1268.6111	1163.2778	0.6680
S1	V2	1to10	2	1117.0111	1163.2778	-0.3062
S1	V2	1to10	3	1104.2111	1163.2778	-0.3924

S1	V2	1to2_5	1	900.9028	1010.9028	-0.8584
S1	V2	1to2_5	2	1016.4028	1010.9028	0.0412
S1	V2	1to2_5	3	1115.4028	1010.9028	0.7596
S1	V2	1to20	1	1189.6222	1411.7555	-1.2641
S1	V2	1to20	2	1878.4222	1411.7555	2.2774
S1	V2	1to20	3	1167.2222	1411.7555	-1.4002
S1	V2	1to5	1	977.4055	1012.3389	-0.2652
S1	V2	1to5	2	1000.8056	1012.3389	-0.0869
S1	V2	1to5	3	1058.8056	1012.3389	0.3434
S1	V2	NH4NO3	1	299.8645	275.1145	0.6638
S1	V2	NH4NO3	2	306.7145	275.1145	0.8410
S1	V2	NH4NO3	3	218.7645	275.1145	-1.6766
S1	V2	SatPaste	1	679.7442	531.9784	1.9408
S1	V2	SatPaste	2	422.1831	531.9784	-1.6905
S1	V2	SatPaste	3	494.0079	531.9784	-0.5555
S1	V3	1to10	1	3083.6111	3507.6111	-0.9579
S1	V3	1to10	2	3109.6111	3507.6111	-0.8967
S1	V3	1to10	3	4329.6111	3507.6111	1.6571
S1	V3	1to2_5	1	3135.9028	3034.2361	0.2517
S1	V3	1to2_5	2	3060.4028	3034.2361	0.0653
S1	V3	1to2_5	3	2906.4028	3034.2361	-0.3246
S1	V3	1to20	1	3748.8222	3531.2222	0.4587
S1	V3	1to20	2	3312.0222	3531.2222	-0.4816
S1	V3	1to20	3	3532.8222	3531.2222	0.0034
S1	V3	1to5	1	3215.8056	3068.4722	0.3590
S1	V3	1to5	2	3028.8056	3068.4722	-0.0986
S1	V3	1to5	3	2960.8056	3068.4722	-0.2697
S1	V3	NH4NO3	1	1883.8645	1896.5312	-0.0508
S1	V3	NH4NO3	2	1901.8645	1896.5312	0.0213
S1	V3	NH4NO3	3	1903.8645	1896.5312	0.0293
S1	V3	SatPaste	1	*	247.1274	*
S1	V3	SatPaste	2	*	247.1274	*
S1	**V3**	**SatPaste**	**3**	**247.1274**	**247.1274**	*****

========== GLM analysis of Up concentrated V for soil S2 ========

Regression analysis

```
    Response variate: UpConc_V
        Distribution: Gamma
       Link function: Log
        Fitted terms: Constant, Contaminant
```

Summary of analysis

```
                                                 mean   deviance   approx
Source            d.f.      deviance         deviance      ratio    F pr.
Regression           3        319.41          106.470      92.52    <.001
Residual            68         78.25            1.151
Total               71        397.66            5.601
```

Coefficient of variation is estimated to be 1.07 from the residual deviance.

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_V

```
                  Prediction          s.e.
   Contaminant
            V0           0.2          0.05
            V1          29.5          7.45
            V2         285.1         72.07
            V3         961.3        243.05
```

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
            V0            *
            V1        0.000            *
            V2        0.000        0.000            *
            V3        0.000        0.000        0.001            *
```

V0 V1 V2 V3

Regression analysis

Response variate: UpConc_V
Distribution: Gamma
Link function: Log
Fitted terms: Constant, Contaminant, Method

Summary of analysis

Source	d.f.	deviance	mean deviance	deviance ratio	approx F pr.
Regression	8	389.223	48.6529	363.36	<.001
Residual	63	8.436	0.1339		
Total	71	397.659	5.6008		
Change	-5	-69.814	13.9628	104.28	<.001

Coefficient of variation is estimated to be 0.366 from the residual deviance.

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable, adjusted with respect to some factors as specified below.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The predictions have been standardized by averaging over the levels of some factors:
Factor Weighting policyStatus of weights
Contaminant Marginal weightsConstant over levels of other factors

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_V

	Prediction	s.e.
Method		
SatPaste	85.2	10.25
1to2_5	205.4	24.68
1to5	377.7	45.40
1to10	687.6	82.64
1to20	1124.5	135.16
NH4NO3	53.7	6.45

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
 SatPaste          *
   1to2_5      0.000          *
     1to5      0.000      0.000          *
    1to10      0.000      0.000      0.000          *
    1to20      0.000      0.000      0.000      0.002          *
   NH4NO3      0.003      0.000      0.000      0.000      0.000
            SatPaste     1to2_5       1to5      1to10      1to20
```

Regression analysis

```
Response variate: UpConc_V
    Distribution: Gamma
   Link function: Log
    Fitted terms: Constant + Contaminant + Method + Contaminant.Method
```

Summary of analysis

```
                                         mean   deviance  approx
Source         d.f.    deviance      deviance      ratio   F pr.
Regression       23    396.9596      17.25912    1184.44   <.001
Residual         48      0.6994       0.01457
Total            71    397.6591       5.60083

Change          -15     -7.7362       0.51574      35.39   <.001
```

Coefficient of variation is estimated to be 0.121 from the residual deviance.

Accumulated analysis of deviance

```
                                                 mean     deviance     approx
Change                d.f.    deviance       deviance        ratio      F pr.
+ Contaminant           3    319.40934      106.46978      7306.72      <.001
+ Method                5     69.81414       13.96283       958.23      <.001
+ Contaminant.Method   15      7.73616        0.51574        35.39      <.001
Residual               48      0.69943        0.01457

Total                               71      397.65908      5.60083
```

Predictions from regression model

These predictions are estimated mean values, formed on the scale of the response variable.

The predictions have been formed only for those combinations of factor levels for which means can be estimated without involving aliased parameters.

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: UpConc_V

```
          Method      SatPaste                   1to2_5
                    Prediction        s.e.   Prediction        s.e.
    Contaminant
             V0            0.0        0.00          0.0        0.00
             V1            4.3        0.30         10.0        0.69
             V2           56.4        3.93        177.7       12.38
             V3          438.9       30.59        860.4       59.96

          Method          1to5                     1to10
                    Prediction        s.e.   Prediction        s.e.
    Contaminant
             V0            0.1        0.01          0.3        0.02
             V1           23.3        1.63         50.5        3.52
             V2          320.0       22.30        483.9       33.72
             V3         1200.8       83.69       1462.9      101.95

          Method         1to20                    NH4NO3
                    Prediction        s.e.   Prediction        s.e.
    Contaminant
             V0            0.6        0.04          0.0        0.00
             V1           86.6        6.03          2.0        0.14
             V2          647.6       45.13         24.7        1.72
             V3         1618.8      112.82        185.9       12.95
```

Message: s.e's, variances and lsd's are approximate, since the model is not linear.

Message: s.e's are based on the residual deviance.

Pairwise differences

t probabilities of pairwise differences

```
         C1-M1           *
         C1-M2       0.000           *
         C1-M3       0.000       0.000           *
         C1-M4       0.000       0.000       0.000           *
         C1-M5       0.000       0.000       0.000       0.000           *
         C1-M6       0.000       0.000       0.000       0.000       0.000
         C2-M1       0.000       0.000       0.000       0.000       0.000
         C2-M2       0.000       0.000       0.000       0.000       0.000
         C2-M3       0.000       0.000       0.000       0.000       0.000
         C2-M4       0.000       0.000       0.000       0.000       0.000
         C2-M5       0.000       0.000       0.000       0.000       0.000
         C2-M6       0.000       0.000       0.000       0.000       0.000
         C3-M1       0.000       0.000       0.000       0.000       0.000
         C3-M2       0.000       0.000       0.000       0.000       0.000
         C3-M3       0.000       0.000       0.000       0.000       0.000
         C3-M4       0.000       0.000       0.000       0.000       0.000
```

C3-M5	0.000	0.000	0.000	0.000	0.000
C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.000	0.000
C4-M2	0.000	0.000	0.000	0.000	0.000
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C1-M1	C1-M2	C1-M3	C1-M4	C1-M5

C1-M6	*				
C2-M1	0.000	*			
C2-M2	0.000	0.000	*		
C2-M3	0.000	0.000	0.000	*	
C2-M4	0.000	0.000	0.000	0.000	*
C2-M5	0.000	0.000	0.000	0.000	0.000
C2-M6	0.000	0.000	0.000	0.000	0.000
C3-M1	0.000	0.000	0.000	0.000	0.267
C3-M2	0.000	0.000	0.000	0.000	0.000
C3-M3	0.000	0.000	0.000	0.000	0.000
C3-M4	0.000	0.000	0.000	0.000	0.000
C3-M5	0.000	0.000	0.000	0.000	0.000
C3-M6	0.000	0.000	0.000	0.561	0.000
C4-M1	0.000	0.000	0.000	0.000	0.000
C4-M2	0.000	0.000	0.000	0.000	0.000
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C1-M6	C2-M1	C2-M2	C2-M3	C2-M4

C2-M5	*				
C2-M6	0.000	*			
C3-M1	0.000	0.000	*		
C3-M2	0.000	0.000	0.000	*	
C3-M3	0.000	0.000	0.000	0.000	*
C3-M4	0.000	0.000	0.000	0.000	0.000
C3-M5	0.000	0.000	0.000	0.000	0.000
C3-M6	0.000	0.000	0.000	0.000	0.000
C4-M1	0.000	0.000	0.000	0.000	0.002
C4-M2	0.000	0.000	0.000	0.000	0.000
C4-M3	0.000	0.000	0.000	0.000	0.000
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.650	0.000
	C2-M5	C2-M6	C3-M1	C3-M2	C3-M3

C3-M4	*				
C3-M5	0.005	*			
C3-M6	0.000	0.000	*		
C4-M1	0.327	0.000	0.000	*	
C4-M2	0.000	0.006	0.000	0.000	*
C4-M3	0.000	0.000	0.000	0.000	0.001
C4-M4	0.000	0.000	0.000	0.000	0.000
C4-M5	0.000	0.000	0.000	0.000	0.000
C4-M6	0.000	0.000	0.000	0.000	0.000
	C3-M4	C3-M5	C3-M6	C4-M1	C4-M2

C4-M3	*			
C4-M4	0.051	*		
C4-M5	0.004	0.309	*	
C4-M6	0.000	0.000	0.000	*
	C4-M3	C4-M4	C4-M5	C4-M6

Soil	Contaminant	Method	Rep	UpConc_V	FITTED	RESIDUAL
S2	V0	1to10	1	0.3110	0.2770	1.1978
S2	V0	1to10	2	0.2530	0.2770	-0.9058
S2	V0	1to10	3	0.2670	0.2770	-0.3708
S2	V0	1to2_5	1	0.0473	0.0481	-0.1769
S2	V0	1to2_5	2	0.0442	0.0481	-0.8314
S2	V0	1to2_5	3	0.0527	0.0481	0.9545
S2	**V0**	**1to20**	**1**	**0.9600**	**0.5980**	**5.2133**
S2	V0	1to20	2	0.3840	0.5980	-4.1855
S2	V0	1to20	3	0.4500	0.5980	-2.7545
S2	V0	1to5	1	0.1180	0.1042	1.2920
S2	V0	1to5	2	0.0895	0.1042	-1.5017
S2	V0	1to5	3	0.1050	0.1042	0.0810
S2	V0	NH4NO3	1	0.0323	0.0331	-0.2577
S2	V0	NH4NO3	2	0.0360	0.0331	0.8695
S2	V0	NH4NO3	3	0.0310	0.0331	-0.6528
S2	V0	SatPaste	1	0.0156	0.0189	-1.8926
S2	V0	SatPaste	2	0.0198	0.0189	0.4882
S2	V0	SatPaste	3	0.0213	0.0189	1.2305
S2	V1	1to10	1	50.5500	50.5067	0.0087
S2	V1	1to10	2	49.9700	50.5067	-0.1082
S2	V1	1to10	3	51.0000	50.5067	0.0988
S2	V1	1to2_5	1	10.7200	9.9575	0.7579
S2	V1	1to2_5	2	10.2050	9.9575	0.2501
S2	V1	1to2_5	3	8.9475	9.9575	-1.0661
S2	V1	1to20	1	87.2800	86.5733	0.0826
S2	V1	1to20	2	86.8000	86.5733	0.0265
S2	V1	1to20	3	85.6400	86.5733	-0.1098
S2	V1	1to5	1	22.3050	23.3367	-0.4553
S2	V1	1to5	2	23.5350	23.3367	0.0860
S2	V1	1to5	3	24.1700	23.3367	0.3581
S2	V1	NH4NO3	1	2.0030	2.0239	-0.1052
S2	V1	NH4NO3	2	2.0180	2.0239	-0.0297
S2	V1	NH4NO3	3	2.0507	2.0239	0.1339
S2	V1	SatPaste	1	4.2244	4.3099	-0.2026
S2	V1	SatPaste	2	4.3640	4.3099	0.1268
S2	V1	SatPaste	3	4.3413	4.3099	0.0738
S2	V2	1to10	1	487.2111	483.8778	0.0697
S2	V2	1to10	2	485.8111	483.8778	0.0405
S2	V2	1to10	3	478.6111	483.8778	-0.1108
S2	V2	1to2_5	1	171.1028	177.7028	-0.3816
S2	V2	1to2_5	2	182.2528	177.7028	0.2576
S2	V2	1to2_5	3	179.7528	177.7028	0.1166
S2	V2	1to20	1	660.4222	647.6222	0.1992
S2	V2	1to20	2	635.2222	647.6222	-0.1955
S2	V2	1to20	3	647.2222	647.6222	-0.0063
S2	V2	1to5	1	326.0056	320.0055	0.1891
S2	V2	1to5	2	327.0056	320.0055	0.2203
S2	V2	1to5	3	307.0056	320.0055	-0.4179
S2	V2	NH4NO3	1	25.8395	24.7237	0.4512
S2	V2	NH4NO3	2	23.8720	24.7237	-0.3536

S2	V2	NH4NO3	3	24.4595	24.7237	-0.1088
S2	V2	SatPaste	1	59.0617	56.4136	0.4690
S2	V2	SatPaste	2	56.5244	56.4136	0.0199
S2	V2	SatPaste	3	53.6548	56.4136	-0.5045
S2	V3	1to10	1	1489.2111	1462.8778	0.1816
S2	V3	1to10	2	1492.0111	1462.8778	0.2007
S2	V3	1to10	3	1407.4111	1462.8778	-0.3897
S2	V3	1to2_5	1	863.9028	860.4028	0.0412
S2	V3	1to2_5	2	827.4028	860.4028	-0.3942
S2	V3	1to2_5	3	889.9028	860.4028	0.3440
S2	V3	1to20	1	1686.0222	1618.8222	0.4155
S2	V3	1to20	2	1566.8222	1618.8222	-0.3295
S2	V3	1to20	3	1603.6222	1618.8222	-0.0956
S2	V3	1to5	1	1212.8056	1200.8055	0.1011
S2	V3	1to5	2	1174.8056	1200.8055	-0.2213
S2	V3	1to5	3	1214.8056	1200.8055	0.1178
S2	V3	NH4NO3	1	186.9145	185.8812	0.0563
S2	V3	NH4NO3	2	189.5645	185.8812	0.1997
S2	V3	NH4NO3	3	181.1645	185.8812	-0.2597
S2	V3	SatPaste	1	414.8550	438.8608	-0.5654
S2	V3	SatPaste	2	441.7276	438.8608	0.0661
S2	V3	SatPaste	3	459.9999	438.8608	0.4811

APPENDIX D: K_d DATA

S1	R1	Cu0	0.04451	S3	R3	Cu1	0.04121	S5	R2	Cu3	0.02061	S8	R1	Cu1	0.005710	S10	R3	Cu2	0.02911	S3	R2	Pb0	bdl	S5	R1	Pb2	bdl	S7	R3	Pb3	41.12
S1	R2	Cu0	0.008212	S3	R1	Cu2	0.7035	S5	R3	Cu3	0.02491	S8	R2	Cu1	0.007610	S10	R1	Cu3	0.03641	S3	R3	Pb0	bdl	S5	R2	Pb2	bdl	S8	R1	Pb0	bdl
S1	R3	Cu0	0.003512	S3	R2	Cu2	0.8064	S6	R1	Cu0	0.006612	S8	R3	Cu1	0.007410	S10	R2	Cu3	0.02971	S3	R1	Pb1	0.1578	S5	R3	Pb2	bdl	S8	R2	Pb0	bdl
S1	R1	Cu1	2.680	S3	R3	Cu2	0.7125	S6	R2	Cu0	0.002712	S8	R1	Cu2	0.01221	S10	R3	Cu3	0.03821	S3	R2	Pb1	0.3856	S5	R1	Pb3	0.01172	S8	R3	Pb0	bdl
S1	R2	Cu1	2.665	S3	R1	Cu3	1.306	S6	R3	Cu0	0.002312	S8	R2	Cu2	0.01411	S1	R1	Pb0	bdl	S3	R3	Pb1	0.5112	S5	R2	Pb3	0.02302	S8	R1	Pb1	bdl
S1	R3	Cu1	2.518	S3	R2	Cu3	1.460	S6	R1	Cu1	0.01071	S8	R3	Cu2	0.01591	S1	R2	Pb0	bdl	S3	R1	Pb2	7.791	S5	R3	Pb3	0.04162	S8	R2	Pb1	bdl
S1	R1	Cu2	7.968	S3	R3	Cu3	1.062	S6	R2	Cu1	0.01731	S8	R1	Cu3	0.01371	S1	R3	Pb0	bdl	S3	R2	Pb2	8.696	S6	R1	Pb0	bdl	S8	R3	Pb1	bdl
S1	R2	Cu2	8.151	S4	R1	Cu0	0.02051	S6	R3	Cu1	0.01101	S8	R2	Cu3	0.01491	S1	R1	Pb1	7.327	S3	R3	Pb2	8.601	S6	R2	Pb0	bdl	S8	R1	Pb2	0.0006162
S1	R3	Cu2	10.31	S4	R2	Cu0	bdl	S6	R1	Cu2	0.01221	S8	R3	Cu3	0.01351	S1	R2	Pb1	5.976	S3	R1	Pb3	30.16	S6	R3	Pb0	bdl	S8	R2	Pb2	0.005916
S1	R1	Cu3	10.75	S4	R3	Cu0	bdl	S6	R2	Cu2	0.01801	S9	R1	Cu0	0.1157	S1	R3	Pb1	6.025	S3	R2	Pb3	26.10	S6	R1	Pb1	bdl	S8	R3	Pb2	bdl
S1	R2	Cu3	10.65	S4	R1	Cu1	1.167	S6	R3	Cu2	0.009912	S9	R2	Cu0	0.01230	S1	R1	Pb2	25.86	S3	R3	Pb3	26.88	S6	R2	Pb1	bdl	S8	R1	Pb3	bdl
S1	R3	Cu3	10.69	S4	R2	Cu1	1.196	S6	R1	Cu3	0.01681	S9	R3	Cu0	0.005500	S1	R2	Pb2	26.82	S4	R1	Pb0	bdl	S6	R3	Pb1	bdl	S8	R2	Pb3	0.03232
S2	R1	Cu0	-0.007688	S4	R3	Cu1	1.113	S6	R2	Cu3	0.01471	S9	R1	Cu1	0.1796	S1	R3	Pb2	27.38	S4	R2	Pb0	bdl	S6	R1	Pb2	bdl	S8	R3	Pb3	0.02722
S2	R2	Cu0	-0.007288	S4	R1	Cu2	6.914	S6	R3	Cu3	0.01681	S9	R2	Cu1	0.1740	S1	R1	Pb3	66.10	S4	R3	Pb0	bdl	S6	R2	Pb2	bdl	S9	R1	Pb0	bdl
S2	R3	Cu0	-0.008488	S4	R2	Cu2	7.517	S7	R1	Cu0	0.001310	S9	R3	Cu1	0.1449	S1	R2	Pb3	61.77	S4	R1	Pb1	6.562	S6	R3	Pb2	bdl	S9	R2	Pb0	0.01722
S2	R1	Cu1	0.006312	S4	R3	Cu2	6.896	S7	R2	Cu0	0.009410	S9	R1	Cu2	0.6992	S1	R3	Pb3	61.60	S4	R2	Pb1	7.565	S6	R1	Pb3	bdl	S9	R3	Pb0	bdl
S2	R2	Cu1	0.009012	S4	R1	Cu3	9.306	S7	R3	Cu0	0.009210	S9	R2	Cu2	0.9367	S2	R1	Pb0	bdl	S4	R3	Pb1	7.719	S6	R2	Pb3	bdl	S9	R1	Pb1	0.9382
S2	R3	Cu1	0.004312	S4	R2	Cu3	9.080	S7	R1	Cu1	0.0783	S9	R3	Cu2	0.9531	S2	R2	Pb0	bdl	S4	R1	Pb2	40.82	S6	R3	Pb3	bdl	S9	R2	Pb1	1.175
S2	R1	Cu2	0.02171	S4	R3	Cu3	8.884	S7	R2	Cu1	0.2340	S9	R1	Cu3	0.8891	S2	R3	Pb0	bdl	S4	R2	Pb2	39.90	S7	R1	Pb0	bdl	S9	R3	Pb1	1.154
S2	R2	Cu2	0.02351	S5	R1	Cu0	0.01301	S7	R3	Cu1	0.1198	S9	R2	Cu3	0.9781	S2	R1	Pb1	bdl	S4	R3	Pb2	40.78	S7	R2	Pb0	bdl	S9	R1	Pb2	4.813
S2	R3	Cu2	0.01901	S5	R2	Cu0	0.01321	S7	R1	Cu2	2.379	S9	R3	Cu3	1.030	S2	R2	Pb1	bdl	S4	R1	Pb3	100.5	S7	R3	Pb0	bdl	S9	R2	Pb2	4.499
S2	R1	Cu3	0.02271	S5	R3	Cu0	0.01281	S7	R2	Cu2	*	S10	R1	Cu0	0.01031	S2	R3	Pb1	bdl	S4	R2	Pb3	103.8	S7	R1	Pb1	0.6521	S9	R3	Pb2	4.543
S2	R2	Cu3	0.01661	S5	R1	Cu1	0.01471	S7	R3	Cu2	2.337	S10	R2	Cu0	0.003810	S2	R1	Pb2	bdl	S4	R3	Pb3	101.3	S7	R2	Pb1	1.314	S9	R1	Pb3	12.93
S2	R3	Cu3	0.02241	S5	R2	Cu1	0.01561	S7	R1	Cu3	3.454	S10	R3	Cu0	0.002210	S2	R2	Pb2	bdl	S5	R1	Pb0	bdl	S7	R3	Pb1	2.125	S9	R2	Pb3	13.86
S3	R1	Cu0	bdl	S5	R3	Cu1	0.01481	S7	R2	Cu3	3.261	S10	R1	Cu1	0.03151	S2	R3	Pb2	bdl	S5	R2	Pb0	bdl	S7	R1	Pb2	14.50	S9	R3	Pb3	13.20
S3	R2	Cu0	bdl	S5	R1	Cu2	0.01841	S7	R3	Cu3	3.302	S10	R2	Cu1	0.02091	S2	R1	Pb3	bdl	S5	R3	Pb0	bdl	S7	R2	Pb2	14.35	S10	R1	Pb0	bdl
S3	R3	Cu0	bdl	S5	R2	Cu2	0.01951	S8	R1	Cu0	0.002910	S10	R3	Cu1	0.02131	S2	R2	Pb3	bdl	S5	R1	Pb1	bdl	S7	R3	Pb2	12.96	S10	R2	Pb0	bdl
S3	R1	Cu1	0.01221	S5	R3	Cu2	0.02051	S8	R2	Cu0	0.001810	S10	R1	Cu2	0.02561	S2	R3	Pb3	bdl	S5	R2	Pb1	bdl	S7	R1	Pb3	45.41	S10	R3	Pb0	bdl
S3	R2	Cu1	0.03491	S5	R1	Cu3	0.02261	S8	R3	Cu0	0.001110	S10	R2	Cu2	0.02641	S3	R1	Pb0	bdl	S5	R3	Pb1	bdl	S7	R2	Pb3	45.20	S10	R1	Pb1	bdl

S10	R2	Pb1	bdl
S10	R3	Pb1	bdl
S10	R1	Pb2	0.001516
S10	R2	Pb2	bdl
S10	R3	Pb2	bdl
S10	R1	Pb3	0.005416
S10	R2	Pb3	0.02312
S10	R3	Pb3	bdl
S1	R1	V0	0.01475
S1	R2	V0	0.01655
S1	R3	V0	0.01855
S1	R1	V1	0.02365
S1	R2	V1	0.02705
S1	R3	V1	0.02755
S1	R1	V2	0.08765
S1	R2	V2	0.1008
S1	R3	V2	0.09305
S1	R1	V3	0.3186
S1	R2	V3	0.3239
S1	R3	V3	0.3343
S2	R1	V0	bdl
S2	R2	V0	bdl
S2	R3	V0	bdl
S2	R1	V1	0.8420
S2	R2	V1	0.8567
S2	R3	V1	0.8591
S2	R1	V2	2.141
S2	R2	V2	2.005
S2	R3	V2	2.050
S2	R1	V3	3.947
S2	R2	V3	4.160
S2	R3	V3	4.217
S3	R1	V0	bdl
S3	R2	V0	bdl
S3	R3	V0	bdl
S3	R1	V1	0.01735
S3	R2	V1	0.07435
S3	R3	V1	0.07665
S3	R1	V2	0.4581
S3	R2	V2	0.4930
S3	R3	V2	0.5074
S3	R1	V3	1.522
S3	R2	V3	1.424
S3	R3	V3	1.559
S4	R1	V0	bdl
S4	R2	V0	bdl
S4	R3	V0	bdl
S4	R1	V1	0.01665
S4	R2	V1	0.02475
S4	R3	V1	0.02245
S4	R1	V2	0.2089
S4	R2	V2	0.2460
S4	R3	V2	0.2455
S4	R1	V3	1.144
S4	R2	V3	1.244
S4	R3	V3	1.092
S5	R1	V0	bdl
S5	R2	V0	bdl
S5	R3	V0	bdl
S5	R1	V1	0.005872
S5	R2	V1	0.008272
S5	R3	V1	0.007372
S5	R1	V2	0.08167
S5	R2	V2	0.09267
S5	R3	V2	0.09427
S5	R1	V3	0.3384
S5	R2	V3	0.3619
S5	R3	V3	0.3625
S6	R1	V0	bdl
S6	R2	V0	0.02571
S6	R3	V0	bdl
S6	R1	V1	0.5584
S6	R2	V1	0.5959
S6	R3	V1	0.5926
S6	R1	V2	1.5943
S6	R2	V2	1.6093
S6	R3	V2	1.5773
S6	R1	V3	3.3303
S6	R2	V3	3.3003
S6	R3	V3	3.3403
S7	R1	V0	bdl
S7	R2	V0	bdl
S7	R3	V0	bdl
S7	R1	V1	0.003672
S7	R2	V1	0.007672
S7	R3	V1	0.01487
S7	R1	V2	0.1030
S7	R2	V2	0.1255
S7	R3	V2	0.1342
S7	R1	V3	0.4903
S7	R2	V3	0.4175
S7	R3	V3	0.3758
S8	R1	V0	bdl
S8	R2	V0	0.001272
S8	R3	V0	0.0002717
S8	R1	V1	4.4871
S8	R2	V1	4.8531
S8	R3	V1	5.1421
S8	R1	V2	10.01
S8	R2	V2	11.58
S8	R3	V2	11.96
S8	R1	V3	21.55
S8	R2	V3	22.22
S8	R3	V3	22.26
S9	R1	V0	bdl
S9	R2	V0	bdl
S9	R3	V0	bdl
S9	R1	V1	0.06817
S9	R2	V1	0.08137
S9	R3	V1	0.09007
S9	R1	V2	0.1649
S9	R2	V2	0.1748
S9	R3	V2	0.1673
S9	R1	V3	0.4664
S9	R2	V3	0.5063
S9	R3	V3	0.3285
S10	R1	V0	bdl
S10	R2	V0	bdl
S10	R3	V0	bdl
S10	R1	V1	0.8610
S10	R2	V1	0.9483
S10	R3	V1	0.8848
S10	R1	V2	3.367
S10	R2	V2	3.211
S10	R3	V2	3.615
S10	R1	V3	8.517
S10	R2	V3	8.595
S10	R3	V3	7.517

APPENDIX E: PRINCIPLE COMPONENT ANALYSIS

Exp2_Cu_Kd_PCA_CEC.rtf

```
============================== file name is Exp2_Kd_Soil.gen
                        EXPERIMENT 2: Kd Soil Properties: Cu Kd
```

Singular values

```
      1          6.539
      2          4.713
      3          3.786
      4          2.202
      5          2.102
      6          0.872
      7          0.702
      8          0.370
      9          0.212
     10          0.000
```

Coordinates for the individuals

```
 lnCu_Kd_L_kg     1
      pH_H20      2
         %OC      3
     CBD_Al%      4
     CBD_Fe%      5
     CBD_Mn%      6
        Sand      7
        Silt      8
        Clay      9
         CEC     10

                    1          2          3          4          5
      1       -1.1813    -1.8675     0.1563    -0.7363    -0.3579
      2        3.0591     0.4694    -1.2130    -0.2242    -0.6655
      3       -0.8536     0.0721     0.5383    -0.6808    -0.4102
      4       -2.3091    -0.0248     0.6270    -0.6679    -0.6017
      5        1.4044    -2.2957    -0.1121    -0.3476     1.5212
      6        3.2954     0.2123    -1.0306     0.2572    -0.4078
      7       -0.9049    -1.8724     0.7136     1.7029    -0.4431
      8        0.9519     2.1612     1.6549    -0.0179     0.4969
      9       -3.3724     1.3962    -2.5304     0.3182     0.5226
     10       -0.0894     1.7490     1.1961     0.3963     0.3455
```

Coordinates for the variables

	1	2	3	4	5
1	2.010	1.262	-0.111	0.595	4.017
2	1.964	1.930	1.396	0.625	0.503
3	-0.756	0.733	-3.951	0.710	2.091
4	-1.962	-1.545	-2.034	0.239	0.087
5	-0.229	-3.277	0.553	-1.636	2.219
6	0.755	-2.521	0.663	4.785	0.032
7	-2.348	1.196	0.941	0.358	0.432
8	2.258	-0.636	-1.589	0.081	-1.712
9	1.909	-2.066	0.409	-2.087	0.628
10	2.075	0.259	-2.340	-0.369	-1.516

Note: variable coordinates scaling factor = 5.613

Correlations

USCORE[1]	**0.7805**	**0.7627**	-0.2936	**-0.7618**	-0.0891	0.2933
USCORE[2]	0.3532	0.5402	0.2053	-0.4323	**-0.9172**	**-0.7057**
	1	2	3	4	5	6

USCORE[1]	**-0.9119**	**0.8768**	**0.7413**	**0.8056**
USCORE[2]	0.3347	-0.1781	-0.5782	0.0726
	7	8	9	10

Number of observations: 10

Exp2_Pb_Kd_PCA_CEC.rtf

```
============================== file name is Exp2_Kd_Soil.gen
                    EXPERIMENT 2: Kd Soil Properties: Pb Kd
```

Message: Data contain missing values. Procedure MULTMISSING is used to estimate missing values.

Singular values

```
 1      6.716
 2      4.676
 3      3.860
 4      2.207
 5      1.340
 6      0.923
 7      0.695
 8      0.340
 9      0.070
10      0.000
```

Coordinates for the individuals

```
               1          2          3          4          5
 1       -1.0335    -1.7427     0.0022    -0.6738    -0.0637
 2        3.3788     0.6764    -0.9998    -0.1763    -0.2938
 3       -0.9515     0.0372     0.5765    -0.6370    -0.5047
 4       -2.1912     0.0624     0.5249    -0.5578    -0.5463
 5        1.0324    -2.5464    -0.2562    -0.5373     0.7524
 6        3.7177     0.4317    -0.9265     0.3090    -0.2260
 7       -0.9073    -1.8661     0.5356     1.7550    -0.1771
 8        0.5506     1.8445     1.8980    -0.0899     0.6094
 9       -3.2875     1.5582    -2.6221     0.2330     0.3507
10       -0.3084     1.5448     1.2673     0.3752     0.0991
```

Coordinates for the variables

```
               1          2          3          4          5
 1         2.287      0.991     -0.900      0.394      0.487
 2         1.788      1.774      1.799      0.496      2.513
 3        -0.623      0.933     -3.846      0.373      3.331
 4        -1.796     -1.386     -2.361      0.231     -1.205
 5        -0.274     -3.357      0.143     -1.787      1.946
 6         0.711     -2.559      0.428      4.708      0.762
 7        -2.308      1.115      0.741      0.372      0.351
 8         2.281     -0.467     -1.316      0.191     -2.344
 9         1.798     -2.115      0.441     -2.161      1.123
10         2.123      0.469     -1.950     -0.314     -0.738
```

Note: variable coordinates scaling factor = 5.558

Correlations

USCORE[1]	**0.7198**	**0.6784**	**-0.6238**	**-0.7280**	0.3249	0.3986
USCORE[2]	0.2725	0.4719	0.2479	-0.3506	**-0.9493**	**-0.7492**
	1	2	3	4	5	6

USCORE[1]	**-0.8047**	0.7008	**0.7684**	0.4236
USCORE[2]	0.7539	**-0.7727**	-0.7490	-0.1886
	7	8	9	10

Number of observations: 8

Exp2_V_Kd_PCA_CEC.rtf

============================== file name is Exp2_Kd_Soil.gen

EXPERIMENT 2: Kd Soil Properties: V Kd

Singular values

1	6.269
2	5.284
3	3.867
4	2.202
5	1.340
6	0.748
7	0.700
8	0.340
9	0.111
10	0.000

Coordinates for the individuals

	1	2	3	4	5
1	-1.0525	1.7052	0.5168	0.6638	-0.0823
2	3.0345	-0.0398	-1.4327	0.1225	-0.2580
3	-0.6223	-0.3561	0.5051	0.6240	-0.4735
4	-1.8943	-0.5064	0.6620	0.5784	-0.5808
5	0.5322	3.0333	0.3588	0.5532	0.7301
6	3.1266	0.2874	-1.1883	-0.3150	-0.2445
7	-0.8494	1.6062	1.1061	-1.7565	-0.1612
8	1.2378	-2.7308	1.2210	0.1047	0.6408
9	-3.5631	-0.8627	-2.6292	-0.2515	0.3527
10	0.0505	-2.1363	0.8802	-0.3234	0.0767

Coordinates for the variables

	1	2	3	4	5

1	-1.466	2.956	-0.835	0.224	0.420
2	2.387	-1.774	0.661	-0.522	3.104
3	-1.103	-0.002	-4.220	-0.536	3.661
4	-2.421	1.549	-1.429	-0.335	-1.470
5	-0.520	3.043	1.650	2.020	1.797
6	0.708	2.359	1.433	-5.234	0.829
7	-2.541	-1.612	0.861	-0.295	0.339
8	2.488	1.140	-1.719	-0.360	-2.517
9	2.035	2.158	0.867	2.320	1.292
10	2.310	0.390	-2.760	0.152	-0.637

Note: variable coordinates scaling factor = 6.15

Correlations

USCORE[1]	-0.4980	**0.8111**	-0.3749	**-0.8226**	-0.1765	0.2407
USCORE[2]	**0.8466**	-0.5082	-0.0005	0.4438	**0.8715**	**0.6758**
	1	2	3	4	5	6

USCORE[1]	**-0.8634**	**0.8456**	**0.6917**	**0.7848**
USCORE[2]	-0.4616	0.3266	0.6180	0.1118
	7	8	9	10

Number of observations: 10

APPENDIX F: BASELINE DATA

[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
C1732	1	R 1	0.0344	0.0716	0.041	0.0424	0.1393	6.881	0.0855	0.068	C3768	18	R 1	0.0042	0.008	0.0155	0.0107	0.0308	2.961	0	0.0351	C4880	35	R 1	0.1563	0.0621
	1	R 2	0.0316	0.0661	0.0325	0.0402	0.126	8.032	0.0659	0.1434		18	R 2	0.0036	0.0082	0.0149	0.0116	0.027	2.653	0.003	0.013		35	R 2	0.171	0.0598
	1	R 3	0.0285	0.0668	0.033	0.0317	0.1234	6.363	0.0469	0.0063		*18*	*R 3*	0.0054	0.0084	0.0144	0.0108	0.0289	2.785	0.0039	0.0119		35	R 3	0.1823	0.0597
C1794	2	R 1	0.0195	0.0228	0.0211	0.035	0.1373	4.611	0.0023	bdl	C3938	19	R 1	0.011	0.0256	0.019	0.0231	0.0452	1.605	0.0079	bdl	C4989	36	R 1	0.0402	0.056
	2	R 2	0.0173	0.0218	0.0207	0.0342	0.1394	4.541	0.0068	bdl		19	R 2	0.0114	0.0266	0.019	0.0213	0.0434	1.527	0.0138	bdl		36	R 2	0.0415	0.0536
	2	R 3	0.0185	0.0213	0.0247	0.0349	0.1315	4.447	bdl	0.0124		19	R 3	0.0126	0.0266	0.0178	0.0188	0.0449	1.591	0.0076	bdl		36	R 3	0.0404	0.0668
C2188	3	R 1	0.0195	0.0219	0.0228	0.0181	0.0395	3.71	0.0017	bdl	C4018	20	R 1	0.0081	0.0275	0.0195	0.0164	0.0041	0.2497	0.0089	bdl	C5020	37	R 1	0.0241	0.0505
	3	R 2	0.0195	0.0217	0.0206	0.024	0.0344	3.692	0.0046	bdl		20	R 2	0.0096	0.0283	0.0191	0.0163	0.006	0.2369	0.0008	bdl		37	R 2	0.0266	0.0511
	3	R 3	0.0213	0.0207	0.0235	0.0224	0.0367	3.752	0.0059	bdl		20	R 3	0.01	0.0285	0.02	0.0185	0.0049	0.2206	0.0124	bdl		37	R 3	0.0236	0.0492
C2224	4	R 1	0.0089	0.0212	0.0231	0.0224	0.0517	2.89	0.0038	0.1183	C4046	21	R 1	0.0128	0.0216	0.0185	0.0309	0.006	1.318	bdl	bdl	C5095	38	R 1	0.0219	0.0232
	4	R 2	0.0104	0.0216	0.0212	0.0195	0.0439	2.731	bdl	0.0333		21	R 2	0.0136	0.0216	0.02	0.0198	0.0081	1.363	0.0011	bdl		38	R 2	0.0257	0.0355
	4	R 3	0.0097	0.0218	0.0214	0.02	0.0442	2.786	bdl	0.0023		21	R 3	0.0123	0.0215	0.0196	0.0153	0.0069	1.449	bdl	bdl		38	R 3	0.021	0.0267
C2242	5	R 1	0.0221	0.0229	0.0222	0.0223	0.027	2.757	bdl	bdl	C4070	22	R 1	0.013	0.0219	0.0209	0.0141	0.0585	4.729	bdl	0.0817	C5172	39	R 1	0.0147	0.0258
	5	R 2	0.0233	0.022	0.0216	0.0244	0.0289	2.997	bdl	bdl		22	R 2	0.0083	0.0227	0.0198	0.0126	0.0453	4.022	bdl	0.0403		39	R 2	0.028	0.0455
	5	R 3	0.028	0.0233	0.0207	0.0196	0.0326	3.423	bdl	bdl		22	R 3	0.0113	0.0213	0.0218	0.0132	0.0511	4.3	bdl	0.0678		39	R 3	0.015	0.0241
C2402	6	R 1	0.0144	0.0232	0.0227	0.0708	0.0065	0.8292	0.0178	0.0111	C4193	23	R 1	0.0106	0.0239	0.0214	0.0146	0.0079	0.2891	bdl	bdl	C5297	40	R 1	0.0142	0.0242
	6	R 2	0.0191	0.0308	0.0213	0.0388	0.0069	0.9387	0.0154	bdl		23	R 2	0.0135	0.0235	0.0215	0.0136	0.0077	0.2482	bdl	bdl		40	R 2	0.0109	0.0243
	6	R 3	0.0148	0.028	0.023	0.0419	0.009	1.145	0.0188	bdl		23	R 3	0.0122	0.0243	0.0233	0.0141	0.0077	0.2467	0.0004	bdl		40	R 3	0.0165	0.0229
C2614	7	R 1	0.0244	0.0524	0.024	0.0332	0.0218	3.024	0.0149	bdl	C4330	24	R 1	0.0188	0.0546	0.0193	0.0149	0.0222	2.747	0.0022	bdl	C5380	41	R 1	0.02	0.0243
	7	R 2	0.0264	0.0529	0.0267	0.0191	0.0266	3.432	bdl	bdl		24	R 2	0.0175	0.0532	0.0203	0.012	0.0261	2.823	0.0015	bdl		41	R 2	0.0161	0.0238
	7	R 3	0.0224	0.0455	0.0225	0.0191	0.0253	3.235	bdl	bdl		24	R 3	0.0197	0.0546	0.0195	0.0124	0.0228	2.724	bdl	bdl		41	R 3	0.0208	0.0244
C2804	8	R 1	0.0175	0.0229	0.0218	0.0126	0.0119	0.8917	bdl	bdl	C4347	25	R 1	0.0239	0.0236	0.0222	0.0172	0.0276	6.066	0.0032	bdl	C5405	42	R 1	0.0347	0.0617
	8	R 2	0.0153	0.0215	0.0191	0.011	0.0097	0.8191	bdl	bdl		25	R 2	0.0211	0.0245	0.022	0.022	0.0297	6.069	bdl	bdl		42	R 2	0.0384	0.0616
	8	R 3	0.0152	0.0208	0.019	0.0115	0.0082	0.7208	bdl	bdl		25	R 3	0.0199	0.0244	0.0226	0.0163	0.0294	5.907	bdl	bdl		42	R 3	0.0362	0.0623
C2914	9	R 1	0.0085	0.0204	0.0206	0.0076	0.0033	0.2035	0.0029	bdl	C4402	26	R 1	0.0212	0.0678	0.0274	0.0441	0.0183	1.67	0.0223	bdl	C5407	43	R 1	0.0221	0.024
	9	R 2	0.0093	0.0219	0.0227	0.0076	0.0042	0.1484	bdl	bdl		26	R 2	0.0195	0.0673	0.0278	0.0188	0.0204	1.795	0.0306	bdl		43	R 2	0.0206	0.0245
	9	R 3	0.0085	0.0204	0.0216	0.0079	0.0043	0.1304	bdl	bdl		26	R 3	0.0211	0.0668	0.0263	0.0121	0.0208	1.825	0.0213	bdl		43	R 3	0.0199	0.0241
C3138	10	R 1	0.0146	0.032	0.02	0.0352	0.0288	1.383	0.0247	0.097	C4525	27	R 1	0.0103	0.0326	0.0433	0.0273	0.005	0.1827	0.0349	0.0067	C5414	44	R 1	0.0253	0.0554
	10	R 2	0.0106	0.0314	0.0195	0.0264	0.0256	1.231	0.0174	0.0511		27	R 2	0.0136	0.0322	0.0408	0.0151	0.0047	0.115	0.0279	bdl		44	R 2	0.0241	0.0554
	10	R 3	0.0105	0.0316	0.0201	0.0242	0.024	1.124	0.0204	0.0409		27	R 3	0.0074	0.0333	0.0398	0.0118	0.0043	0.0989	0.0241	bdl		44	R 3	0.0261	0.0567
C3163	11	R 1	0.0087	0.0231	0.0197	0.0397	0.0808	6.233	0.0067	bdl	C4612	28	R 1	0.0085	0.0219	0.0196	0.0066	0.0054	0.2806	0.0025	bdl	C5422	45	R 1	0.0374	0.0583
	11	R 2	0.0083	0.0233	0.0202	0.0164	0.0867	6.336	0.0079	bdl		28	R 2	0.009	0.0228	0.0182	0.0054	0.0053	0.3555	bdl	bdl		45	R 2	0.0384	0.0552
	11	*R 3*	0.001	0.006	0.015	0.012	0.078	6.244	0.004	0.019		28	R 3	0.0097	0.0228	0.0193	0.0056	0.0068	0.3687	0.0057	bdl		45	R 3	0.0389	0.0581
C3171	12	R 1	0.0662	0.0164	0.0236	0.0198	0.0505	4.584	0	0.0008	C4637	29	R 1	0.0286	0.0551	0.0231	0.0026	0.0057	0.2561	0.0007	bdl	C5522	46	R 1	0.0342	0.0517
	12	R 2	0.0642	0.0165	0.0156	0.0197	0.0483	3.908	0.0013	0.0027		29	R 2	0.0244	0.0557	0.0232	0.003	0.005	0.2586	bdl	bdl		46	R 2	0.0119	0.0436
	12	R 3	0.0774	0.0142	0.0167	0.0231	0.0548	4.317	0.0021	0.0011		29	R 3	0.0243	0.0555	0.0239	0.0027	0.0048	0.2525	bdl	bdl		46	R 3	0.0233	0.0527
C3181	13	R 1	0.0121	0.0077	0.0145	0.0172	0.0226	2.088	0.003	0	C4671	30	R 1	0.0273	0.0569	0.0211	0.011	0.0105	1.579	bdl	bdl	C5570	47	R 1	0.0233	0.0536
	13	R 2	0.0085	0.0096	0.0148	0.0182	0.0277	2.345	0.0086	0.0007		30	R 2	0.0278	0.056	0.0204	0.0105	0.0119	1.508	bdl	bdl		47	R 2	0.0231	0.0529
	13	R 3	0.0117	0.0088	0.0165	0.0155	0.0254	2.274	0	0.0015		30	R 3	0.0353	0.057	0.021	0.01	0.0143	2.087	bdl	bdl		47	R 3	0.0242	0.0535
C3188	14	R 1	0.0037	0.0106	0.0142	0.0127	0.0177	0.5639	0.0028	0.0357	C4674	31	R 1	0.0216	0.026	0.0227	0.0403	0.0077	1.071	bdl	bdl	C5754	48	R 1	0.0152	0.06
	14	R 2	0.0012	0.0087	0.0131	0.013	0.0075	0.3962	0.0119	0.0133		31	R 2	0.0195	0.0254	0.0225	0.0227	0.0088	1.287	bdl	bdl		48	R 2	0.0154	0.0608
	14	R 3	0.0026	0.01	0.0142	0.0123	0.0086	0.4164	0.0076	0.0113		31	R 3	0.0192	0.0251	0.0214	0.0177	0.0083	1.332	0.0022	bdl		48	R 3	0.0175	0.0587
C3287	*15*	*R 1*	0.0074	0.0093	0.0215	0.017	0.0045	0.7427	0.0042	0	C4681	32	R 1	0.0071	0.0241	0.0195	0.0071	0.0035	0.4137	bdl	bdl	C5938	49	R 1	0.0225	0.0327
	15	R 2	0.0062	0.0092	0.0189	0.0122	0.0067	1.217	0	0		32	R 2	0.0085	0.0238	0.0186	0.0073	0.0048	0.338	bdl	bdl		49	R 2	0.0221	0.0244
	15	R 3	0.0074	0.01	0.021	0.0118	0.0041	1.009	0.0043	0		32	R 3	0.0069	0.0224	0.0183	0.0071	0.004	0.3338	bdl	bdl		49	R 3	0.0237	0.0255
C3560	16	R 1	0.0281	0.0289	0.0264	0.0191	0.0226	1.346	0.0174	0.0148	C4811	33	R 1	0.0096	0.0226	0.0174	0.0226	0.0173	0.39	0.0056	bdl	C5959	50	R 1	0.0099	0.0245
	16	R 2	0.0246	0.0302	0.0272	0.0233	0.022	1.285	0.015	0.0131		33	R 2	0.0098	0.0233	0.0167	0.0158	0.0151	0.31	0.0034	bdl		50	R 2	0.0107	0.025
	16	R 3	0.0289	0.0278	0.0237	0.0179	0.0238	1.313	0.0168	0.0176		33	R 3	0.0101	0.023	0.0177	0.0108	0.0156	0.2927	0.0058	bdl		50	R 3	0.0119	0.0239
C3735	17	R 1	0.0058	0.0109	0.0161	0.0035	0.009	2.326	0.0032	0	C4863	34	R 1	0.0209	0.0264	0.0243	0.0138	0.0208	1.322	0.004	bdl	C5990	51	R 1	0.021	0.0537
	17	R 2	0.0085	0.0112	0.0157	0.0031	0.0104	2.439	0.0028	0.0001		34	R 2	0.0187	0.0261	0.0246	0.0103	0.022	1.496	bdl	bdl		51	R 2	0.0219	0.0554
	17	R 3	0.0103	0.0089	0.0158	0.0022	0.0089	2.452	0.0014	0.0006		34	R 3	0.0189	0.0271	0.0248	0.0117	0.0236	1.5	0.0054	bdl		51	R 3	0.0203	0.0552

C4880	0.02	0.01	0.0588	4.975	bdl	bdl	C5996	52	R 1	0.0168	0.057	0.033	0.0177	0.0215	1.49	0.0044	bdl	C7516	69	R 1	0.0218	0.026	0	0	0.0165	0.4606
	0.02	0.01	0.072	5.033	bdl	bdl		52	R 2	0.0168	0.057	0.034	0.0141	0.0157	1.511	bdl	bdl		69	R 2	0.0275	0.041	0	0	0.0146	0.3714
	0.02	0.01	0.0714	5.351	0.0011	bdl		52	R 3	0.0195	0.055	0.034	0.011	0.0164	1.458	bdl	bdl		69	R 3	0.029	0.044	0	0	0.0138	0.3269
C4989	0.04	0.07	0.3025	26.27	bdl	0.0315	C6011	53	R 1	0.013	0.033	0.02	0.0195	0.0155	0.457	0.0063	bdl	C7521	70	R 1	0.0478	0.044	0	0	0.0375	3.328
	0.03	0.03	0.2873	24.32	0.0022	0.0299		53	R 2	0.0107	0.032	0.02	0.0182	0.0199	0.3644	0.008	bdl		70	R 2	0.0764	0.122	0	0	0.0499	3.663
	0.04	0.03	0.2918	25.62	0.0117	0.0364		53	R 3	0.0111	0.035	0.021	0.0143	0.0146	0.2259	0.0054	bdl		70	R 3	0.0384	0.025	0	0	0.035	3.214
C5020	0.03	0.03	0.0141	0.3481	0.0209	0.0027	C6021	54	R 1	0.0089	0.028	0.018	0.006	0.0066	0.1094	bdl	bdl	C7656	71	R 1	0.0299	0.061	0	0	0.0965	11.96
	0.02	0.02	0.0159	0.2693	0.0181	bdl		54	R 2	0.0085	0.028	0.018	0.0052	0.0048	0.1186	0.001	bdl		71	R 2	0.0296	0.062	0	0	0.1098	11.85
	0.02	0.02	0.0131	0.2253	0.0238	bdl		54	R 3	0.0091	0.028	0.018	0.0032	0.0065	0.0907	bdl	bdl		71	R 3	0.0273	0.061	0	0	0.115	12.17
C5095	0.02	0.01	0.0292	4.296	0.0035	bdl	C6164	55	R 1	0.0093	0.024	0.021	0.0074	0.0174	2.676	0.0047	bdl	C7663	72	R 1	0.0148	0.056	0	0	0.0304	3.568
	0.03	0.01	0.0372	5.044	bdl	bdl		55	R 2	0.0094	0.022	0.018	0.0003	0.0033	0.0364	bdl	bdl		72	R 2	0.0211	0.057	0	0	0.0396	3.962
	0.03	0.01	0.0335	4.729	bdl	bdl		55	R 3	0.0133	0.085	0.017	10.64	0.0037	0.0469	0.0072	0.0594		72	R 3	0.019	0.057	0	0	0.0321	3.858
C5172	0.02	0.01	0.0456	4.617	bdl	bdl	C6259	56	R 1	0.0151	0.06	0.02	0.0104	0.0186	3.315	bdl	bdl	C7689	73	R 1	0.0677	0.169	0	0	0.0741	4.008
	0.03	0.01	0.0393	3.588	bdl	bdl		56	R 2	0.0113	0.058	0.019	0.0098	0.0174	2.852	bdl	bdl		73	R 2	0.0606	0.162	0	0	0.0613	3.753
	0.02	0.01	0.0623	5.942	0.0025	bdl		56	R 3	0.0156	0.058	0.019	0.0065	0.0166	3.104	bdl	bdl		73	R 3	0.0589	0.158	0	0	0.0595	3.668
C5297	0.02	0.01	0.0308	4.727	bdl	bdl	C6406	57	R 1	0.0083	0.023	0.019	0.008	0.0054	0.3309	bdl	bdl	C7704	74	R 1	0.0135	0.023	0	0	0.0133	0.6955
	0.02	0.01	0.0201	4.011	0.0004	bdl		57	R 2	0.0112	0.053	0.02	0.0182	0.0319	2.436	bdl	bdl		74	R 2	0.013	0.023	0	0	0.0123	0.6372
	0.02	0.02	0.0241	4.544	0.0065	bdl		57	R 3	0.0073	0.023	0.018	0.0095	0.0084	0.367	bdl	bdl		74	R 3	0.0136	0.022	0	0	0.0165	0.8672
C5380	0.02	0.04	0.0093	0.3195	0.0031	bdl	C6456	58	R 1	0.014	0.035	0.02	0.0185	0.0351	2.441	0.003	bdl	C7721	75	R 1	0.0514	0.115	0	0	0.0186	0.4369
	0.02	0.01	0.0073	0.236	bdl	bdl		58	R 2	0.0045	0.026	0.018	0.0156	0.0212	0.7651	bdl	0.0016		75	R 2	0.0135	0.03	0	0	0.0076	0.1964
	0.02	0.01	0.0077	0.2902	0.0022	bdl		58	R 3	0.0119	0.031	0.025	0.0182	0.0377	2.421	bdl	bdl		75	R 3	0.019	0.036	0	0	0.009	0.2753
C5405	0.02	0.01	0.0346	2.624	0.003	bdl	C6466	59	R 1	0.0116	0.025	0.018	0.012	0.0203	0.7426	0.0056	bdl	C7743	76	R 1	0.0162	0.021	0	0	0.0046	0.1061
	0.02	0.01	0.0309	2.519	bdl	bdl		59	R 2	0.0104	0.023	0.018	0.0018	0.0044	0.5278	bdl	bdl		76	R 2	0.0195	0.021	0	0	0.0042	0.1647
	0.02	0.01	0.041	2.747	bdl	bdl		59	R 3	0.0076	0.026	0.018	0.0107	0.0171	0.722	0.0042	bdl		76	R 3	0.015	0.022	0	0	0.0043	0.105
C5407	0.02	0.01	0.0611	8.044	bdl	bdl	C6506	60	R 1	0.0173	0.023	0.018	0.0015	0.0036	0.5246	bdl	bdl	C7756	77	R 1	0.0185	0.023	0	0	0.0064	0.5829
	0.02	0.01	0.0611	8.822	0.0023	bdl		60	R 2	0.0067	0.022	0.02	0.0181	0.007	0.4314	0.0024	bdl		77	R 2	0.02	0.023	0	0	0.0074	0.605
	0.02	0.01	0.0601	8.021	0.0018	bdl		60	R 3	0.0138	0.022	0.017	0.0023	0.0029	0.5295	bdl	bdl		77	R 3	0.0227	0.027	0	0	0.0117	0.8917
C5414	0.02	0	0.0201	1.353	bdl	bdl	C6863	61	R 1	0.0367	0.035	0.021	0.0493	0.0954	4.382	0.0039	bdl	C7761	78	R 1	0.0264	0.042	0	0	0.0085	0.5003
	0.02	0	0.0133	1.047	bdl	bdl		61	R 2	0.0351	0.044	0.021	0.0277	0.0913	4.298	bdl	bdl		78	R 2	0.0331	0.052	0	0	0.0117	0.564
	0.02	0	0.0172	1.191	bdl	bdl		61	R 3	0.0413	0.054	0.022	0.0215	0.0886	4.21	0.0067	bdl		78	R 3	0.0361	0.057	0	0	0.0125	0.575
C5422	0.02	0	0.0279	2.758	0.0019	bdl	C6944	62	R 1	0.0184	0.034	0.038	0.0148	0.026	0.7697	bdl	bdl	C8289	79	R 1	0.0231	0.034	0	0	0.0127	0.8456
	0.02	0	0.0227	2.542	bdl	bdl		62	R 2	0.0178	0.031	0.032	0.0118	0.012	0.5449	bdl	bdl		79	R 2	0.0187	0.025	0	0	0.0097	0.7992
	0.02	0	0.0321	2.698	0.0008	bdl		62	R 3	0.0125	0.025	0.023	0.009	0.0109	0.6157	bdl	bdl		79	R 3	0.0133	0.022	0	0	0.0042	0.292
C5522	0.02	0.02	0.0113	1.457	bdl	bdl	C7282	63	R 1	0.0159	0.028	0.024	0.0046	0.0062	0.3186	bdl	bdl	C8297	80	R 1	0.0169	0.022	0	0	0.0087	1.153
	0.02	0.01	0.0076	1.189	bdl	bdl		63	R 2	0.0188	0.031	0.025	0.0058	0.0106	0.473	bdl	bdl		80	R 2	0.0138	0.024	0	0	0.0077	1.098
	0.02	0.01	0.0112	1.44	0.0086	bdl		63	R 3	0.0206	0.035	0.029	0.0071	0.0084	0.4433	bdl	bdl		80	R 3	0.0153	0.024	0	0	0.0095	1.108
C5570	0.03	0.01	0.0156	2.185	bdl	bdl	C7304	64	R 1	0.0188	0.022	0.02	0.0098	0.0152	1.409	bdl	bdl	C8364	81	R 1	0.0129	0.052	0	0	0.0847	14.52
	0.03	0.01	0.0169	2.395	bdl	bdl		64	R 2	0.0218	0.022	0.021	0.0081	0.0173	1.386	bdl	bdl		81	R 2	0.0088	0.053	0	0	0.086	14.57
	0.03	0.01	0.0138	2.259	bdl	bdl		64	R 3	0.0158	0.022	0.02	0.0094	0.012	1.204	bdl	bdl		81	R 3	0.0152	0.052	0	0	0.0711	12.94
C5754	0.02	0.01	0.0076	0.6712	0.0014	bdl	C7404	65	R 1	0.0165	0.022	0.019	0.0093	0.0129	1.799	bdl	bdl	C8449	82	R 1	0.0169	0.054	0	0	0.0288	2.964
	0.02	0.01	0.0061	0.5663	bdl	bdl		65	R 2	0.0195	0.033	0.019	0.0103	0.0177	2.141	0.0007	bdl		82	R 2	0.0194	0.057	0	0	0.0231	3.079
	0.02	0.01	0.0068	0.6822	bdl	bdl		65	R 3	0.0199	0.023	0.02	0.0093	0.014	1.908	bdl	bdl		82	R 3	0.0158	0.056	0	0	0.0228	3.146
C5938	0.03	0.04	0.2144	4.279	0	0.0213	C7407	66	R 1	0.058	0.024	0.045	0.0435	0.01	0.037	bdl	bdl	C8533	83	R 1	0.0374	0.084	0	0	0.0306	3.208
	0.02	0.03	0.2342	4.701	0.0075	0.0174		66	R 2	0.0543	0.025	0.044	0.0189	0.0098	0.0465	0.0027	bdl		83	R 2	0.0306	0.069	0	0	0.0301	3.027
	0.02	0.03	0.2442	4.829	0.0024	0.0301		66	R 3	0.0647	0.026	0.048	0.0228	0.0099	0.0518	0.0015	bdl		83	R 3	0.0165	0.025	0	0	0.0207	2.762
C5959	0.02	0.02	0.0225	1.254	bdl	bdl	C7410	67	R 1	0.0242	0.039	0.024	0.0095	0.0076	0.6049	bdl	bdl	C8651	84	R 1	0.0272	0.061	0	0	0.0139	1.334
	0.02	0.02	0.0237	1.16	bdl	bdl		67	R 2	0.0183	0.022	0.018	0.0079	0.0084	0.6911	bdl	bdl		84	R 2	0.0242	0.062	0	0	0.0168	1.377
	0.02	0.02	0.0226	1.16	bdl	bdl		67	R 3	0.0168	0.022	0.019	0.0073	0.0101	0.7697	bdl	bdl		84	R 3	0.0254	0.061	0	0	0.0129	1.195
C5990	0.03	0.04	0.0145	2.347	bdl	bdl	C7443	68	R 1	0.0071	0.022	0.018	0.0023	0.0187	1.299	bdl	bdl	C8664	85	R 1	0.0216	0.061	0	0	0.0246	3.156
	0.03	0.02	0.0164	2.639	bdl	bdl		68	R 2	0.0081	0.022	0.018	0.0021	0.0219	1.331	bdl	bdl		85	R 2	0.0201	0.06	0	0	0.0251	3.422
	0.03	0.02	0.0187	2.7	bdl	bdl		68	R 3	0.009	0.022	0.017	0.002	0.0237	1.368	bdl	bdl		85	R 3	0.0202	0.06	0	0	0.0253	3.692

[redacted]	[redacted]	[redacted]
C7516	0	bdl
	bdl	bdl
	bdl	bdl
C7521	bdl	bdl
	bdl	bdl
	0	bdl
C7656	0	bdl
	0	bdl
	bdl	bdl
C7663	bdl	bdl
	bdl	bdl
	bdl	bdl
C7689	bdl	0.11
	bdl	0.08
	bdl	0.07
C7704	0	bdl
	bdl	bdl
	bdl	bdl
C7721	bdl	bdl
	0	bdl
	bdl	bdl
C7743	bdl	bdl
	bdl	bdl
	0	bdl
C7756	0	bdl
	bdl	bdl
	bdl	bdl
C7761	bdl	bdl
	bdl	bdl
	bdl	bdl
C8289	bdl	bdl
	0	bdl
	0.01	bdl
C8297	0	bdl
	bdl	bdl
	bdl	bdl
C8364	bdl	bdl
	0	bdl
	bdl	bdl
C8449	bdl	bdl
	bdl	bdl
	bdl	bdl
C8533	bdl	0.01
	bdl	0
	bdl	bdl
C8651	0	bdl
	0.01	bdl
	bdl	bdl
C8664	0	bdl
	0	bdl
	bdl	bdl

[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
C8701	86	R 1	0.0131	0.0215	0.0195	0.0456	0.0074	0.422	bdl	bdl
	86	R 2	0.0185	0.0317	0.0261	0.0182	0.0105	0.638	bdl	bdl
	86	R 3	0.0209	0.0381	0.0307	0.0151	0.0103	0.552	bdl	bdl
C8741	87	R 1	0.0155	0.0215	0.0189	0.0153	0.0155	2.468	bdl	bdl
	87	R 2	0.0144	0.0216	0.0189	0.0134	0.0197	2.625	bdl	bdl
	87	R 3	0.02	0.0411	0.0184	0.012	0.027	3.41	0.006	bdl
C8954	88	R 1	0.0154	0.0235	0.0478	0.0085	0.0129	0.293	bdl	bdl
	88	R 2	0.0164	0.0515	0.0447	0.006	0.0097	0.3	bdl	bdl
	88	R 3	0.0139	0.0324	0.0467	0.0055	0.0088	0.236	bdl	bdl
C8992	89	R 1	0.0107	0.0205	0.0581	0.0116	0.0052	0.052	0.000	bdl
	89	R 2	0.0115	0.0219	0.0597	0.0133	0.006	0.05	bdl	bdl
	89	R 3	0.0091	0.0224	0.0563	0.0113	0.0046	0.048	bdl	bdl
C9002	90	R 1	0.0184	0.0411	0.0393	0.0082	0.0123	0.942	bdl	bdl
	90	R 2	0.0163	0.0216	0.0195	0.0072	0.012	1.061	bdl	bdl
	90	R 3	0.0143	0.0205	0.0185	0.0076	0.0117	1.112	bdl	bdl
C9005	91	R 1	0.0162	0.0546	0.0221	0.0538	0.0075	0.643	bdl	bdl
	91	R 2	0.0177	0.0539	0.024	0.0127	0.0081	0.76	bdl	bdl
	91	R 3	0.0195	0.0539	0.0219	0.0079	0.0074	0.765	bdl	bdl
C9477	92	R 1	0.0126	0.0207	0.0198	0.0073	0.0106	1.21	bdl	bdl
	92	R 2	0.0149	0.0203	0.0192	0.0075	0.0138	1.352	bdl	bdl
	92	R 3	0.0124	0.0209	0.0191	0.0065	0.0131	1.282	0.005	bdl
C9481	93	R 1	0.0107	0.0283	0.0256	0.004	0.0067	0.501	bdl	bdl
	93	R 2	0.0109	0.021	0.0182	0.0028	0.0068	0.531	0.000	bdl
	93	R 3	0.009	0.0199	0.0175	0.0024	0.0069	0.511	bdl	bdl
C9483	94	R 1	0.0196	0.0398	0.0312	0.0065	0.0061	0.212	bdl	bdl
	94	R 2	0.0105	0.0214	0.0214	0.0034	0.0027	0.043	bdl	bdl
	94	R 3	0.0122	0.0219	0.0206	0.0034	0.0035	0.042	bdl	bdl
C9493	95	R 1	0.0079	0.0218	0.0168	0.0026	0.0036	0.019	bdl	bdl
	95	R 2	0.0086	0.0212	0.017	0.0036	0.0018	0.022	0.001	bdl
	95	R 3	0.0072	0.0203	0.0182	0.0037	0.002	0.022	bdl	bdl
C9552	96	R 1	0.0106	0.0243	0.0198	0.0526	0.0291	1.21	bdl	bdl
	96	R 2	0.0121	0.0232	0.0195	0.0325	0.0322	1.348	0.001	bdl
	96	R 3	0.0125	0.0226	0.0181	0.0243	0.0319	1.395	bdl	bdl
C9949	97	R 1	0.0122	0.021	0.0204	0.0048	0.0047	0.166	bdl	bdl
	97	R 2	0.0066	0.0198	0.0202	0.0031	0.0039	0.088	bdl	bdl
	97	R 3	0.0081	0.0204	0.0197	0.0035	0.0021	0.139	bdl	bdl
D204	98	R 1	0.0145	0.0334	0.0273	0.0082	0.0073	0.556	bdl	bdl
	98	R 2	0.0115	0.023	0.0204	0.0069	0.0079	0.673	bdl	bdl
	98	R 3	0.0167	0.0395	0.0325	0.0097	0.009	0.649	bdl	bdl
D263	99	R 1	0.0156	0.0091	0.0177	0.0066	0.0142	0.185	0.003	0.0012
	99	R 2	0.0156	0.0089	0.0168	0.0072	0.005	0.033	0.002	0.00000
	99	R 3	0.0154	0.0092	0.0168	0.005	0.0055	0.064	0.003	0.00000
D351	100	R 1	0.0474	0.0206	0.0171	0.0056	0.0073	0.15	0.000	0.0515
	100	R 2	0.0373	0.0204	0.0155	0.019	0.0076	0.127	0.000	0.0407
	100	R 3	0.076	0.023	0.0157	0.025	0.0068	0.139	0.002	0.1275