Evaluation of partitioning coefficients for South African soils to inform the National Framework for the Management of Contaminated Land with emphasis on the protection of water resources

Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

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 uncertainties and to assist in refining the norms and standards for the assessment of contaminated land.

The objectives of the study were as follows:
1) To assess analytical methodologies for use in the setting of screening values for the protection of water resources through a literature study;
2) To determine K_ds for South African soils and its use in the setting of appropriate screening values for the protection of 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.

This study was conducted in four stages, including an extensive literature review, evaluation and selection of appropriate analytical methods to determine soluble concentrations of constituents in soils and to indicate partitioning coefficients, determination of K_ds of selected metals for a selection of typically SA soils and the determination of baseline concentrations of the soluble fraction of Cu, Pb and V in natural SA soils.

The **comparison of analytical methods** to determine soluble concentrations of elements in soils, in order to select the best analytical method to predict soluble pore water quality, indicated the following:

- Pore water quality is overestimated with the fixed soil:solution ratio extractions, compared with the saturated paste extract (assumed to be the best indicator of pore water quality). This overestimation was more pronounced in highly contaminated soils and higher soil:solution ratios;

- The results of the 1:2.5 water extracts were closest to the results of the saturated paste extract and in most instances the results were not significantly different from saturated paste results.

The **K_d of a soil** represents the net effect of several soil sorption processes acting upon the contaminant under a certain set of conditions. Soil properties such as the pH, clay content, organic carbon content and the amount of Mn and Fe oxides, have an immense influence on the K_d value of a soil. K_ds for Cu, Pb and V for various diagnostic soil horizons were calculated from sorption graphs. In most cases there were contrasting K_d values especially when the cations, Cu and Pb, had high contamination levels, the value for V was low. There is large variation between the K_ds stipulated in the Framework and the values obtained experimentally in this study. The results further 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:

- The Cu K_ds ranged from 12.7 to 19,044 L/kg. Lower K_ds were observed for the 1:1 clay soil, while the red oxidic and plinthic horizons as well as the soils with higer clay content had higher K_d values (vertic, red oxidic with high clay content, melanic and gleyic soils). There was a fair correlation ($r^2 = 0.6$) between Cu K_d, pH and clay content of the soils;
- The K_d values for Pb ranged from 24.8 to as high as 252,294 L/kg. The gley and red oxidic soils with high clay content had higher K_ds than the rest of the soils. The Kd for Pb showed a strong correlation with soil pH ($r^2 = 0.7$);
- The highest K_ds for V determined in this study were 865 L/kg for the 1:1 clay dominated soil, 708 L/kg for the orthic A horizon with high organic C content and 629 L/kg for the plinthic horizon. The K_ds for the rest of the soils varied between 10.5 L/kg and 220 L/kg. The K_d for V showed a strong negative correlation with soil pH ($r^2 = 0.8$) and a positive correlation with the Fe content of the soil ($r^2 = 0.7$).

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 different soil properties. The soluble baseline concentration ranges for Cr, Cu, Ni, V, Co and Pb were <1 mg/l. For Mn the range is wide with a lower limit of 0.189 mg/l and an upper limit of 39.4 mg/l, indicating a significant variability in soluble Mn concentrations between different soils. The correlation between soluble concentrations of selected elements and soil properties could be summarized as follows:

- An increase in soluble Cr and Ni concentrations with an increase in organic carbon and clay content (with a decrease at >40% clay). The soil pH seems to have had little effect on the soluble Cr and Ni in the studied soils;

- Soluble V concentration correlated well with soil pH (R^2=0.7), with the highest solubility at pH <5 and >7.5. The solubility of V decreased when the clay content increase >20%;
- Soil pH had an influence on soluble Cu concentration with a decrease in soluble Cu at pH >6. Correlation with organic C showed an increase in Cu solubility with an increase in organic C content while clay content had no significant effect on Cu solubility (R^2=0.01);
- The soluble Co concentrations showed very strong correlation with organic carbon (R^2=0.8) and soil pH with a significant decrease in Co solubility at pH >6;
- A strong correlation between soluble Mn and soil pH (R^2=0.7) and soluble Mn was higher in soils with lower clay content;
- Pb solubility was high at high organic C, low pH and clay contents. Zn solubility was high at high organic C, low pH, and high clay contents

The **natural partitioning coefficients** give an indication of the 'K_d' of natural soil (no contaminant added) and could be summarised as follows:

- The natural partitioning coefficients for Ni, Cr and Pb increased with an increase in the clay content of the soils;
- The natural partitioning coefficient of Cu and Co did not correlate with the clay content;
- The natural partitioning coefficient of Zn is not influenced by clay content;
- Soil pH does not have significant influence on the natural partitioning coefficients of Ni and Cr (and Pb based on limited data), but the chemical envelope of Cu and Co (and Zn based on limited data) show correlation between soil pH and the natural partitioning coefficient; and
- The natural partitioning coefficients for Cr, Cu and Co were higher at lower organic C contents while there was no correlation between natural partitioning coefficient and organic C content for Ni and Pb.

Following the results obtained from this investigation, **the following is recommended**:

- The 1:2.5 soil:solution ratio extract be used to estimate the pore water quality of soil. This is also the standard method used for the determination of soil pH(H_2O) (a very important parameter that must be consider in any case) and therefore considered as an acceptable method and easily implementable by commercial laboratories;
- Based on the K_ds determined in this study for 10 different diagnostic South African soils horizons, preliminary additional soil screening values could be calculated which is specific for certain soil types. However, the SA baseline concentrations for natural soils were also considered. Based on these calculations, soil types were grouped together

and preliminary risk based soil screening values (RBSSV) were established which can be used during Phase 1 contaminated land assessments;

- During Phase 2 contaminated land assessments, where more information will be available on soil type and properties, the K_ds can be used to further refine the soil screening values for specific soil types/horizons. Vertic soils, red oxidic soils with high clay content, melanic soils and gley soils can have higher soil screening values for Cu and Pb, since these soils have a strong sorption capacity and the risk for groundwater contamination will be less;
- The K_ds determined during this investigation showed a strong correlation with soil pH and therefore, soil pH can be used to refine the Phase 2 soil screening values. Preliminary recommended pH specific SSV (pH-SSV) for Cu, Pb and V were calculated which can be used during Phase 2 contaminated land assessments;
- The potential risk that a contaminant may pose to groundwater can be assessed by determining the soluble fraction of the contaminant in the soil. A 1:2.5 deionised water extract can be conducted on soil samples during the Phase 1 screening level assessment and the results can be compared to the Water Quality Guidelines for the specific contaminant to indicate potential risk for groundwater contamination.

RECOMMENDATIONS FOR FUTURE RESEARCH

However, it must be noted that these ST-SSV1 and pH-SSV1 levels are based on the limited research conducted in this study. Additional research is needed to refine these levels, where:

- More replicates of the current 10 soils are used to refine the K_ds;
- K_ds can be determined for more contaminants in other SA soils; and
- More treatments of ‘contamination’ can be used to refine the K_ds.

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LIST OF ABBREVIATIONS

DAF	Dilution attenuation factor
DEA	Department of Environmental Affairs
DWA	Department of Water Affairs
Kd	Partitioning coefficient
NEMWA	National Environment Management: Waste Act
SSVs	Soil screening levels

1 INTRODUCTION AND OBJECTIVES

1.1 Scope

In the past, contaminated soil as a source for water contamination has been largely ignored in 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 mechanism for remediation activities to be implemented and controlled. The Draft National Framework for the Management of Contaminated Land (Framework) (DEA, May 2010) provides national norms and standards for the practical implementation 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) were published for comment in August 2012.

In NEMWA, the concept of contamination is defined as:

> *"contaminated", in relation to Part 8 of Chapter 4, 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 qualifying statement regarding the specifics of contamination is further made 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 and subsequent studies are required to determine the impact or 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 recourses. According to the Framework, the proposed K_ds in the Framework may be adapted on site specific bases, but will essentially be used as it stands during initial investigations. For the protection of our water resources, the appropriateness of the K_ds and derived SSVs should always be considered.

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_ds makes its application in the setting of screening levels open to debate. Information regarding K_ds 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.

1.2 Objectives

4) To assess analytical methodologies for use in the setting of screening values for the protection of the water resources through a literature study;
5) To determine K_ds for South African soils and its use in the setting of appropriate screening values for the protection of the water resources; and
6) 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.

1.3 Approach

This study was conducted in four stages, including the following:

- An extensive literature review;
- Evaluation and selection of appropriate analytical methods to determine soluble concentrations of constituents in soils and to indicate partitioning coefficients;
- Determination of K_ds of selected metals for a selection of SA soils; and
- Determination of baseline concentrations of the soluble fraction of constituents in natural SA soils.

1.3.1 Literature review

An extensive literature review on national and international analytical methodologies, effect of soil properties on the attenuation capacity of soils, determination of baseline concentrations and partitioning coefficients were conducted. This information was used to select and evaluate analytical methodologies for the determination of partitioning coefficients and baseline concentrations of soluble constituents in natural SA soils.

1.3.2 Evaluation and selection of analytical methods

The total metal concentrations of 10 natural soil samples with different soil properties were determined. These soils were also used for the following:

- Compare and select the most appropriate analytical method to predict soluble pore water quality; and
- Batch studies to evaluate the appropriateness of current K_ds detailed in the Framework. The soils were 'contaminated' with different concentrations of Cu, Pb and V.

The selection of analytical methodology evaluated in this study was conducted by a panel of experts at a workshop to validate the direction of the research.

1.3.3 Determine the partitioning coefficients for a selection of South African soils

K_ds for Cu, Pb and V in a selection of 10 typical SA soil horizons (with different soil properties) were determined to assess the remobilization of constituents in 'contaminated' soils. The results were evaluated to obtain a better understanding of the levels at which soil characteristics affects the solubility of sorbed/precipitated heavy metals phases, therefore contributing to a better understanding and assessment of polluted soils and more appropriate K_ds.

1.3.4 Determine baseline soluble concentrations for a selection of natural soils in SA

The selected analytical method to determine soluble concentrations of constituents in soils were used to determine baseline concentrations of selected elements in natural SA top soils. A total of 100 soils were carefully selected based on existing information contained in the Land Type Survey data and previous research into baseline concentrations of total elements in SA soils. Soils with different soil properties (clay content, pH, base status) were selected. The baseline concentrations can be used during the initial investigations into contaminated land to reference the concept of 'normal' (uncontaminated) soluble concentrations of elements in SA soils with different soil properties.

2 LITERATURE REVIEW

Globally, a growing concern have been that the heavy metal contents of soil are increasing as the result of industrial, mining, agricultural and domestic activities. While certain heavy metals such as zinc are essential for plant growth as micronutrients, it may become toxic at higher concentrations. In addition, as the toxic metals load of the soil increases, the risk of non-localized pollution due to the metals leaching into groundwater increases. Soils can act as a buffer between the source of pollution and water bodies due to its remarkable ability to immobilize metal ions through various kinds of sorption mechanisms. However, it may release sorbed metals if the consistent equilibria are altered by natural or anthropogenic changes in environmental conditions (Covelo *et al*., 2007).

The total soil metal content alone is not a good measure of acute risk and not a very useful tool to determine potential risks for soil and water contamination. Soil solutions are in close contact with the soil solid phase and are consequently much more influenced by mineral equilibrium, cation exchange, sorption reactions as well as complexation by organic matter (Sauvé *et al.*, 2000). Sorption is a major process responsible for the fate of heavy metals in soils, since the freedom of movement of heavy metals is directly related to their partitioning between the soil solid phase and soil solution (K_d value) (Covelo *et al*., 2007). To reduce the uncertainty of the soil K_d value for metals, it is essential to focus on the factors influencing the mobility of these metals in soils and to rank them according to their contribution (Echevarria *et al*., 2001).

2.1 CONCEPTS

2.1.1 Defining K_d

The tendency of a contaminant to seep into the groundwater is determined by its solubility and by the ratio between the concentration of the contaminant sorbed by the soil and the concentration remaining in solution. This ratio is commonly known as the soil partitioning or distribution coefficient (K_d). A higher Kd value indicates stronger attraction to the soil solids and lower susceptibility to leaching. Studies indicate that the K_d for a given constituent may vary widely depending on the nature of the soil in which the constituent occurs. The variation is related mainly to the amount of organic matter in the top soils (Brady *et al*., 2002), but may also be influenced by other soil properties. The K_d is calculated by the equation below and reported as L/kg or mL/g.

$$K_d = \frac{mg\ chemical\ sorbed/kg\ soil}{mg\ chemical/L\ solution}$$

The K_d of a soil 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 and the amount of Fe and Mn oxides in the soil. Such variables should be taken into account if an appropriate K_d value is to be derived (Ashworth & Shaw, 2005).

For particularly poorly sorbed contaminants, an alternate equation should be used, where analytical constraints lead to the measured 'solid-phase' concentration essentially representing both solid and solution phases (i.e. a total concentration). The greater the solution phase concentration in this case, the greater the inaccuracy, and overestimation of the K_d value. The alternative K_d equation (see below) should then first deduct the solution phase concentration from the overall concentration in order to determine the true solid phase concentration. This can be achieved if the volumetric moisture content and dry bulk density of the soil is known.

$$K_d = \frac{S_d}{S_n}$$

$$K_d = \frac{\left((T_\rho) - (\theta S_n)\right)}{\rho/S_n}$$

Where K_d = soil solid-sorption partition coefficient (L/kg);

S_d = solid phase concentration (mg/kg soil);

S_n = solution phase concentration (mg/L);

T = total soil concentration (solid + solution) (mg/kg);

ρ = dry bulk density (kg/L); and

θ = volumetric moisture content (Ashworth & Shaw, 2005).

One of the foremost advantages of using the K_d approach in assessing the solubility of a contaminant is that, for a given soil, it essentially derives a single value which can be used in computer modelling of the environmental behaviour of that contaminant.

2.1.2 Interpreting K_d

A low K_d value indicates a low degree of soil sorption and, potentially, high mobility. On the other hand, a high K_d value indicates a high affinity for the soil solid phase, thus low mobility (Ashworth & Shaw, 2005).

Knowledge of the processes that determine the solid-liquid K_d is of fundamental significance in evaluating the risk of groundwater contamination due to contaminants in soil. The K_d value is an important parameter in mathematical models of contaminant behaviour in soil systems. Any assessment of the fate, transport and related risks of a contaminant in the geosphere involves an accurate quantification of its K_d value under a range of conditions, in order to apply an appropriate value to a given situation (Ashworth *et al*., 2008).

Vidal *et al*. (2009) proposed that, since soils usually contain multi-metal constituents, the K_d of a target metal must be examined in the presence of other competitive metals. Table 1 shows the K_d of Zn, Cu, Pb and Cd in the presence of different concentrations of competing metals.

Table 1: K_ds of target metals in the presence of competing metals (adapted from Vidal *et al*., 2009)

Scenario	Concentration (meq/L)					
	0.1	0.2	0.6	1.0	2.0	10
Zn	41900	16800	6060	3510	1280	84
Zn + Cd (0.2)	9340	6520	2740	1330	410	47
Zn + Cd (10)	130	90	48	39	22	8.4
Zn + Pb (0.2)	17200	6000	3250	2100	606	65
Zn + Pb (10)	39	23	12	7.4	5.8	3.0
Cu	3500	4000	5920	6280	7500	1650
Cu + Cd (0.2)	2205	3600	4700	5450	3260	303
Cu + Cd (10)	3600	2080	990	605	310	31
Cu + Pb (0.2)	5330	3440	5120	5240	3700	473
Cu + Pb (10)	710	550	-	78	42	10
Pb	128000	85000	35400	28000	7300	210
Pb + Cd (0.2)	143000	48200	71400	25500	11690	42
Pb + Cd (10)	19100	6760	2200	1310	3802	25
Cd	2720	1820	643	326	189	11
Cd + Pb (0.2)	1100	1170	400	250	92	11
Cd + Pb (10)	4.5	4.0	3.0	2.7	2.7	2.0

This table indicates that the K_d values decreased significantly from 0.1 to 10 meq/L of initial metal concentration. The Cu was an exception to this, as the K_d did not decrease with an increase in concentration probably due to the ongoing precipitation of Cu minerals along with sorption ruled by surface complexation. Although extremely reliant on the initial concentration, the order in the K_d values for the set of target metals decreased as follows: Pb > Cu > Zn > Cd.

For full assessment of metal mobility, the sorption reversibility should be considered. A total K_d that contains the forms of metal irreversibly sorbed at the solid phase can be calculated as a retention factor (R), as the ratio of the K_d values versus extraction yields:

$$R\ (L/kg) = \frac{K_d}{extraction\ yield\ (\%)}$$

Therefore, the higher the K_d and the lower the extraction yield, the higher the retaining capacity of the soil for a given metal, and thus the lower its probable mobility and resulting risk. The retention factor provides an excellent index to estimate the relative mobility of pollutants in a set of soils and to predict situations with theoretically low or high associated risks. The presence of a competitive metal generally decreases the R for any initial target metal concentration. The R value corrects the sequence of mobility reasoned solely on the basis of the K_d. Therefore, the R is proposed as the input parameter to evaluate metal movement in risk assessment exercises, always related to the source term (presence and concentration of the released metals), since predictions based on single metal scenarios may under-predict the risk in several orders of magnitude, especially if the competitive metal has a sorption pattern similar to the target metal. The overestimation in the quantification of the target metal K_d, from data on single scenarios, would eventually lead to underestimating the risk resulting from the contamination event (Vidal *et al.*, 2009).

2.1.3 Defining baseline concentration

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 has a range of values. Background concentrations represent an ideal situation that no longer exists in most countries. Baseline concentrations have thus been defined as 95% of the expected range of background concentrations. 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. Here after guidelines for maximum threshold levels of trace elements in soils can be established. A number of countries have developed such guidelines (Herselman, 2007).

2.2 EVALUATION OF METHODS TO DETERMINE THE ATTENUATION K_d

An ideal approach to determining K_d values experimentally is one in which:

- a realistic soil moisture contents can be maintained;
- 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.

2.2.1 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 1). During interpretation of the results it is important to note that no distinction is made on how the contaminant is associated with the soil.

There are a number of variations for this basic procedure (US EPA, 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:

- It provides an estimate of chemical processes occurring at equilibrium which is not always the case in flow 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.

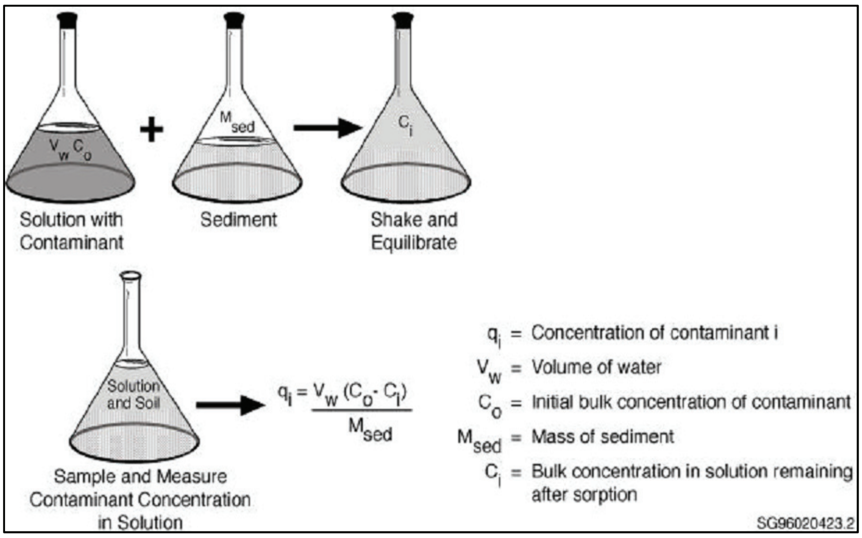


Figure 1: Illustration of the batch method to determine K_d (US EPA, 1999)

2.2.2 Column method

The column method is the second most commonly used method to determine the K_d of a soil (US EPA, 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 & 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 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 EPA, 1999). These methods also allow for conducting studies at realistic soil:solution ratios which can better simulate field conditions (Sparks, 2003).

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. However, column studies are expensive and time consuming to perform.

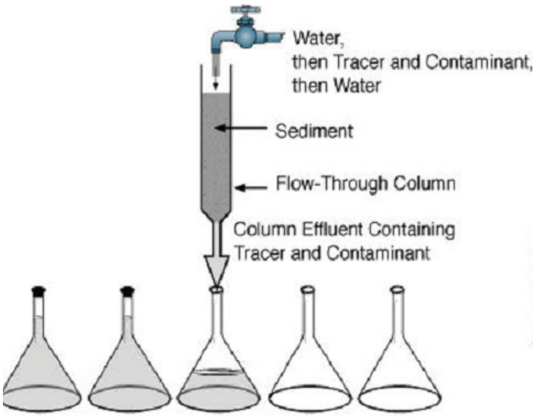


Figure 2: Illustration of a column method for determining the K_d of a soil (US EPA, 1999)

2.2.3 Lookup tables

Another approach that has been evaluated by the US EPA (1999) is the lookup 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 (1999) used 9 categories defined by soil pH and soil texture (MEPAS lookup table). They used the minimum values found in the literature and thus compiled their model based on conservation. 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 arsenic, chromium, molybdenum, neptunium, plutonium, selenium, technetium and uranium. The K_d values of uranium in the 9 MEPAS categories range from 0 to 500 ml/g (Table 2). 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.

Table 2: MEPAS lookup table for uranium (adapted from US EPA, 1999)

pH	**9**			**5-9**			**≤5**		
Fines[1]	**<10**	**10-30**	**>30**	**<10**	**10-30**	**>30**	**<10**	**10-30**	**>30**
U[2]	0	5	50	0	50	500	0	5	50
U(IV)[2]	200	500	1000	100	250	500	20	30	50
U(VI)[3]	0	1	2	1	2	5	2	5	20

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

2 – Reference: Strenge & Peterson (1989)

3 – Authors' opinion based on values reported in Ames & Rai (1978), Ames & McGarrah (1980), Cloninger *et al*. (1980), Cloninger & Cole (1981), Serne & Relyea (1981) and Rai & Zachara (1984)

2.3 EFFECTS OF SOIL PROPERTIES ON THE ATTENUATION CAPACITY OF SOIL

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, clay minerals, and Fe and Mn oxides. Depending on the relative proportions and compositions of these soil constituents, soil texture and CEC (which depends mainly on soil organic matter and clay content in itself), a soil will have more or less capacity to bind a specific heavy metal species.

The different soil properties influencing the attenuation capacity will be discussed in the sections that follow.

2.3.1 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 in increase in pH promotes the sorption of trace elements (Vangheluwe *et al*., 2005). Therefore, soil pH is 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 metals 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 the country'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. According to de Villiers *et al*. (2001) 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 industrial activities of man are the major sources of the dry fallout of oxides of sulphur (S) and nitrogen (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.

2.3.2 Clay content

The soil textural class depend on the percentage of clay, silt and sand in the soil. Clays are soil particles less than 2µm in size, having a higher surface area than other soil particles like sand and silt (Vangheluwe *et al*., 2005). 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 weathering rock 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: montmorrilonite, vermiculite > illite, chlorite > kaolinite (Kabata-Pendias & Pendias, 2001).

2.3.3 Iron and Mn oxides

Hydrous 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 and 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).

Ferric and Mn oxides co-precipitate and adsorb cations including Co, Cr, Mn, Mo, Ni, V and Zn from the soil solution due to a pH dependent charge (negative in alkaline conditions and positive in acid conditions) (Kabata-Pendias & Pendias, 2001). Fe 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).

2.3.4 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. For it to become organic matter, it must be decomposed into humus. Humus is organic material that has been converted by microorganisms to a resistant state of decomposition. Organic matter is stable in the soil. It has been decomposed until it is resistant to further decomposition. Usually, only about 5% of it mineralizes yearly. That rate increases if temperature, oxygen, and moisture conditions become favourable for decomposition (Brady, 1999). 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. Organic matter 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, 1999). Soil organic matter exists 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 (2000) indicated that the majority of dissolved metals in soil were found in metal-organic 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 topsoils 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.

2.4 USE OF K_d IN DIFFERENT COUNTRIES IN SCREENING OF CONTAMINATED LAND

A review of methods for developing ecological soil quality guidelines (EPA, 2000) showed that there are three generic methods used to set protective soil concentrations amongst the countries studied, including:

- Select the lowest reported toxicity value and divide by a safety factor;
- Use statistical distribution and select a particular percentile as the value; and
- 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 authorities responsible. 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 EPA

The US EPA 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 (Technical Background Document for Soil Screening Guidance, 1994). In the US EPA 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 3).

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

Table 3: 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	Nonzero max contaminant level goals, maximum contaminant levels, or health based limits x dilution factor
K_d	Soil-water partition coefficient	L/kg	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	1.5
n	soil porosity	L_{pore} / L_{soil}	1 - (ρ_b / ρ_s)
ρ_s	Soil particle density	Kg / L)	2.65
H'	Dimensionless Henry's law constant		Chemical specific (Assume 0 for inorganic contaminants except Hg)

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 EPA, 1996).

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 & 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 (Figure 3). The 5th percentile of the toxicity threshold values is then estimated and is used as the final criterion value.

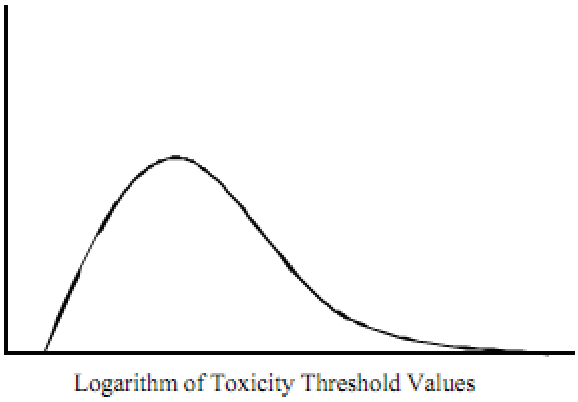


Figure 3: Hypothetical frequency distribution of toxicity threshold (De Vries & Bakker, 1998)

- 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 4). The data is further adjusted to standardize pH and organic matter according to algorithms developed from background scenarios of uncontaminated sites.

Table 4: 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 4) that includes the following options:

- Direct application of generic numerical guidelines
- Modification of guidelines based on site-specific conditions
- Use of site specific risk assessments

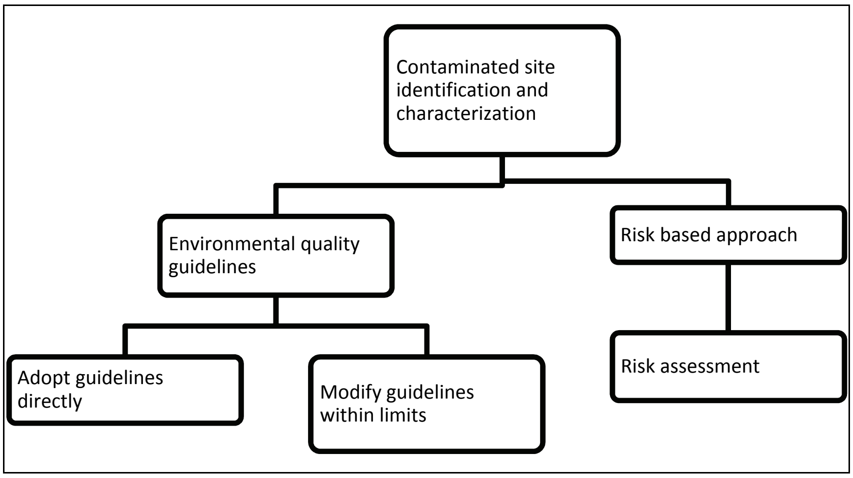


Figure 4: Multi-tier framework for contaminated land assessment in Canada

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.

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 (FFCSA, 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) (Table 5). These values have been compiled from literature based in Australia and internationally.

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 (DoE, 2003).

Table 5: Assessment levels for soils in Australia (adapted from DoE, 2003)

Parameter	**Ecological Investigation Levels1 (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						

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). 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

C_w = water quality standard

K_d = partitioning coefficient of the contaminant

DAF = dilution attenuation factor (assumed to be 20).

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 and presented in Table 6.

Table 6: K_ds detailed in the Framework

Parameter	Kd value (L/kg)	Parameter	Kd value (L/kg)
As	29	Hg	52
Cd	75	Mn	100
Cr(III)	1800000	Ni	65
Cr(VI)	19	Pb	100
Co	100	V	1000
Cu	10	Zn	62

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 is required, a water extraction of the soil sample is necessary (Page *et al*., 1982). The measurement of soluble elements consists mainly 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 *et al*., 1965). However, if pore water quality is not the important issue being studied 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 analytical methodologies for use in the setting of screening values for the protection of the water resources. To achieve this, a comparison of analytical methods was conducted in order to select the best analytical method to predict soluble pore water quality.

3.2 Soil Selection

Two typical South African soils with different soil properties (Table 7) and clay mineralogy (kaolinitic and smectitic clays) were selected for the method screening. Henceforth the soils will be termed ‘Soil 1’ (S1) for the kaolinite clay soil and ‘Soil 2’ (S2) for the smectite clay soil. Figure 5 and Figure 6 show photographic images of the 2 soils and Table 7 contain a summary of soil properties (pH, particle size and organic carbon content).

Figure 5: Soil 1 (1:1 clay)

Figure 6: Soil 2 (2:1 clay)

Table 7: Summary of soil properties for the 2 selected soils

Soil ID	Soil pH(H_2O)	Soil pH(KCl)	Particle size analysis (%)			Organic Carbon (%)
			Sand	Silt	Clay	
Soil 1 (S1)	4.9	4.0	57	11	32	0.63
Soil 2 (S2)	8.1	7.4	28	22	50	1.40

3.3 Experimental design

Bulk soil samples (1.5 kg each) were used for the experiment. Known concentrations of lead (Pb), copper (Cu) and vanadium (V) were added to the soils. The control samples had no chemicals added. The chemicals were added to individual samples as to circumvent the potential effect the metals may have on the sorption of one another. The experimental set up is presented in Figure 7.

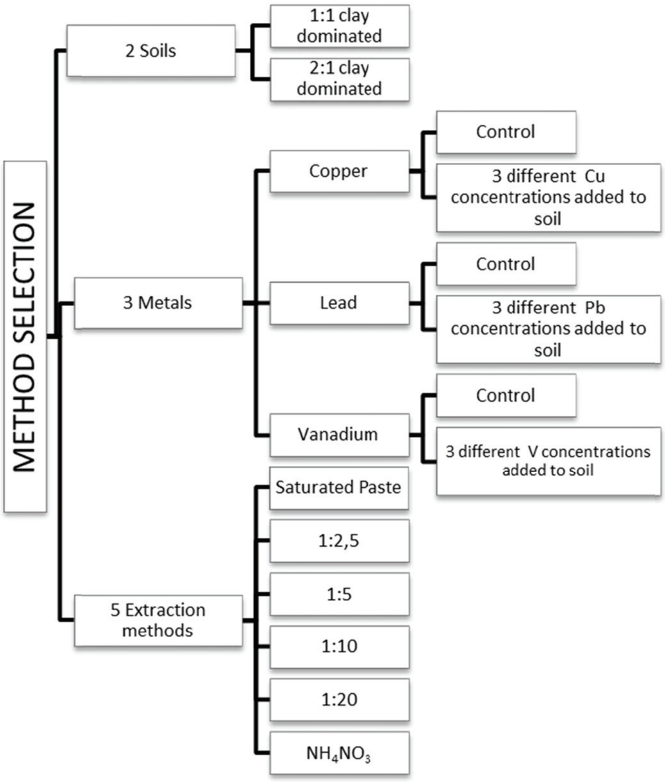


Figure 7: Experimental design

Contaminant application procedure is presented below:

- 1.5 kg soil was weighed into a round bottom bowl with known mass;
- Metals were added to the soil for the different treatments (Table 8) with enough deionized water to form a slurry;
- Samples were then mixed for 15 minutes using an electric mixer to ensure adequate mixing (Figure 8);

- After 24 hours, the contents of the bowls were decanted into a large flat tray, soil remaining in the bowl was rinsed with deionized water;
- Samples were allowed to air dry to simulate a wet & dry cycle (Figure 9);
- After 4 days, the dry samples were sieved and prepared for extraction using the proposed methods.

Table 8: Concentrations of Cu, Pb and V added to the soil

Soil	Treatment ID	Cu	Pb	V
		mg/kg added to soil		
Soil 1	0	0	0	0
	1	945	3105	3000
	2	4725	15525	7500
	3	9450	31050	11250
Soil 2	0	0	0	0
	1	1890	6210	375
	2	4725	15525	1875
	3	7088	23288	3750


Figure 8: Soil mixing


Figure 9: Drying of soils in trays

3.4 Analytical methods

The following water extraction methods were evaluated: saturated paste, 1:2.5, 1:5, 1:10 and 1:20 (soil:solution ratios) and a NH_4NO_3 extract. The methodology followed for each extraction is discussed in the sections that follow.

3.4.1 Saturated Paste extract (SSSA, 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 *et al*., 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 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);
- Deionized water was added to the soil whilst stirring until the soil was nearly saturated;
- Samples were left overnight to allow for readily soluble metals to dissolve and react with the soil;
- Additional deionized water was added to achieve a uniform saturated soil-water paste;
- The mass of the container with soil and water was recorded;
- Samples were then filtered under vacuum through (Whatman no 42) filtrate was collected into a Scott bottle by vacuum (SSSA, 1996); and
- Afterwards the samples where membrane filtered (0.2 µm pore size) to remove most of the colloidal material from the samples.

3.4.2 Soil:solution extracts (1:2.5, 1:5, 1:10 and 1:20)

Soil:solution extracts is often made at water contents higher than that found under normal soil conditions. The soil:solution ratio is standardized to obtain results that can be applied and interpreted realistically. These extraction ratios are easier to duplicate, but are not so well related to field soil:water conditions. Errors due to hydrolysis, cation exchange, and mineral dissolution also become larger with these extraction ratios (Page *et al*., 1982).

To examine the effect of different soil water ratios, different ratios were selected and performed on the same soil. The selected soil:solution ratios were: 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;
- Deionized water was added to the sample (37.5 ml) ;
- The samples were shaken on a mechanical shaker for 24 hours;
- After 24 hours the samples were centrifuged at 4000 rpm for 5 minutes;
- Samples were then filtered through Whatmann 42 filter paper; and

- Afterwards the samples where Membrane filtered (0.2 µm pore size) to remove most of the colloidal material from the samples.

The mass of soil and volume of water used for the soil:solution extractions are indicated in Table 9.

Table 9: Soil mass and water volumes used for soil:solution 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

3.4.3 NH_4NO_3 extract (DIN 19730, 1997)

The German DIN 19730 (1997) describes a method for the extraction of readily available trace elements from soil by shaking the soil with a 1 *M* NH_4NO_3 solution.

The pH-values in 1 *M* NH_4NO_3 soil extracts were about 0.5-1 units lower than in water soil extracts. Soil extraction with 1 *M* NH_4NO_3 is performed at a pH value comparable to the soil solution. The extraction of metals with this method is mainly caused due to the exchange of cations held by negative charged surfaces by NH_4. However, the dissociation of NH_4^+ and subsequent formation of soluble ammine complexes results in an overestimation of readily soluble metals with this method.

The methodology followed for this extraction was as follows:

- Fifteen grams of soil was weighed into a 50 ml centrifuge tube;
- To the sample, 37.5 ml of 1 *M* NH_4NO_3 solution was added;
- Samples were shaken for 2 hours at 180 rpm;
- After 2 hours the samples were centrifuged for 5 minutes at 4000 rpm;
- Samples were filtered through Whatman No. 42 filter paper; and
- Afterwards the samples where Membrane filtered (0.2 µm pore size) to remove most of the colloidal material from the samples.

3.4.4 Detection limits

The detection limits for the different extracts were determined, based on 6 x standard deviation. These detection limits are presented in Table 10.

Table 10: Flocculent method detection limits (mg/L)

Method	Cu	Pb	V
Soil:solution extracts	0.03	1.6	0.09
Saturated paste	0.03	0.39	0.14
NH_4NO_3	0.09	0.8	0.16

3.5 Analytical Results

The complete set of analytical results of this investigation is presented in Appendix A. In order to determine which soluble extraction will best predict the pore water concentration of the soil, the ICP results, in mg/l of metal in solution, was converted to mg/kg metal extracted from the soil. The data interpretation and evaluation for the different metals will be discussed in the sections that follow.

3.5.1 Copper

Figure 10 show the concentrations of Cu extracted from S1 and S2 samples with different soluble extracts after treatment. The different treatments are represented by 0, 1, 2 and 3 with 0 being the control.

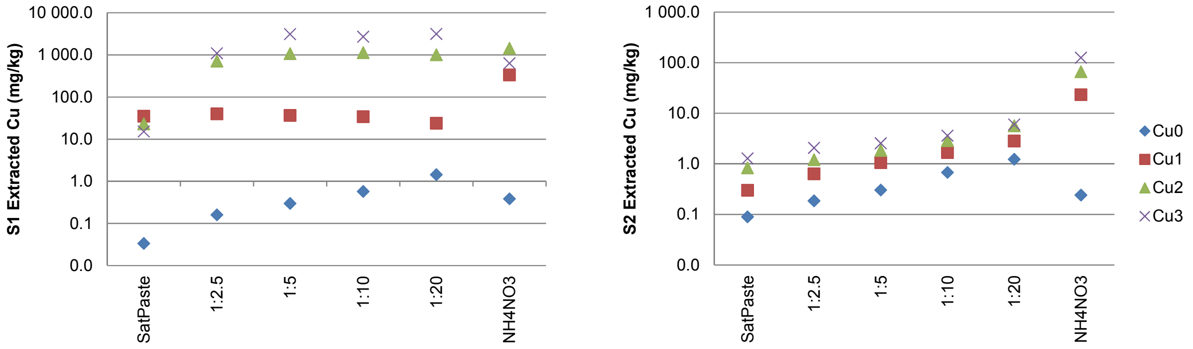


Figure 10: Cu concentrations extracted from S1 and S2 with different soluble extracts

The analytical results show that S2 had significant lower recovery of applied Cu than S1, indicating that the Cu is more strongly adsorbed by the 2:1 clay minerals than the 1:1 clay minerals of S1.

Assuming that the saturated paste extract would be the best prediction of pore water quality, these results show that all the other soluble extracts will overestimate the pore water quality of the soil, except Cu1 in the 1:20 extract. This overestimation was more pronounced in both soils for soluble extracts with higher soil:solution ratios (for S1 Cu0 the 1:20 extract overestimated pore water quality by 4000% and for S2 by 1200%) and in samples receiving higher Cu treatments (especially S1 Cu2 and Cu3 with 2000% to 20000% overestimation).

The statistical analyses (Table 11) showed that there were no significant difference between the saturated paste, 1:2.5 and 1:5 extracts for S1 and S2 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. 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.

Table 11: Statistical t-groupings of extracts and Cu treatments

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

*Means with the same letter is not significantly different

3.5.2 Lead

The Pb concentrations extracted from S1 and S2 with different extractants after treatment are presented in Figure 11. These results show the following:

- 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;
- For S1 the prediction of pore water quality was grossly overestimated by the higher soil:solution extracts, especially in the Pb0 (200-3000%) and Pb1 (6000-16000%) treatments, while all the extractions showed similar results at higher treatments (Pb2 and Pb3); and

- In the case of S2, the pore water quality was also overestimated by the higher soil:solution extracts in Pb0 (500-1700%) and Pb1 (60-600%) as expected, but at the higher treatments (Pb2 and Pb3), the 1:5, 1:10 and 1:20 extracts yielded lower results than the saturated paste and 1:2.5 extracts.

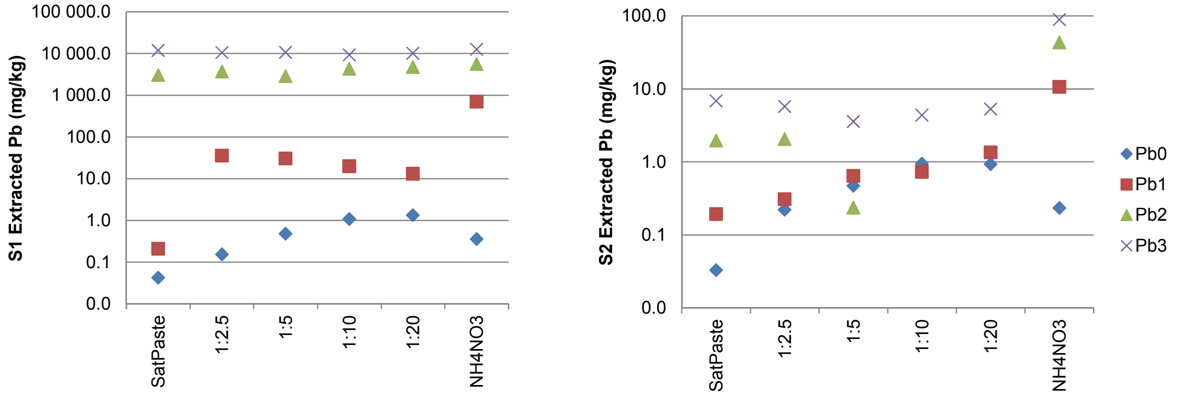


Figure 11: Pb concentrations extracted from S1 and S2 with different extracts

The statistical t-groupings for the Pb treatments and extracts are presented in Table 12. 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. In the case of S2 the 1:10 and 1:20 extracts were also not significantly different from the saturate paste extract.

Table 12: Statistical t-groupings of extracts and Pb treatments

Treatments	1:20	1:10	1:5	1:2.5	Saturated Paste
	Mean Pb concentration (mg/kg)*				
S1					
Pb0	1.3^{a}	1.1^{a}	0.48^{d}	0.04^{d}	0.15^{cd}
Pb1	13.1^{a}	20.0^{a}	30.7^{b}	59.3^{c}	35.4^{c}
Pb2	4725^{a}	4287^{a}	2849^{b}	3030^{b}	3690^{ab}
Pb3	10061^{a}	9146^{a}	10642^{b}	11819^{ba}	10456^{b}
S2					
Pb0	0.95^{a}	0.93^{a}	0.47^{ab}	0.03^{b}	0.22^{ab}
Pb1	1.35^{a}	0.73^{a}	0.64^{a}	0.19^{a}	0.31^{a}
Pb2	No data	No data	0.24^{a}	2.0^{a}	2.0^{a}
Pb3	5.26^{a}	4.4^{a}	3.6^{a}	6.8^{a}	5.7^{a}

*Means with the same letter is not significantly different

3.5.3 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 12.

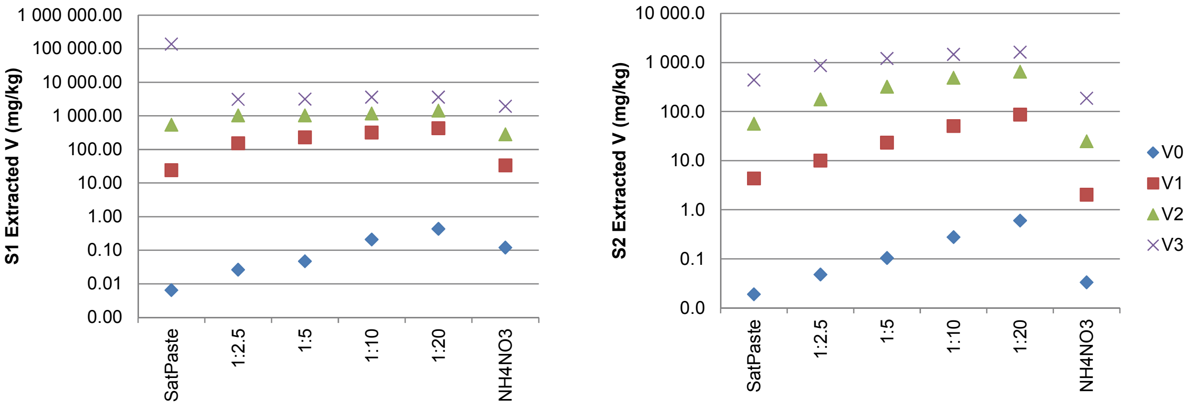


Figure 12: V concentrations extracted from S1 and S2 after treatment

Although higher V concentrations were extracted from S1 than S2 for all treatments (except V0), the differences were not as distinctive as with the Cu and Pb treatments. This indicates that the V adsorption by the 2:1 clay minerals in S2 is still better than that of the 1:1 clay minerals in S1, although to a lesser degree than in the case of Cu and Pb.

The prediction of pore water quality in both S1 and S2 without the application of V, is overestimated by the higher soil:solution extracts (150% with 1:2.5 extract and 3000% with 1:10 and 1:20 extracts) and increase with an increase in soil:solution ratio. The same phenomenon was observed for the treated samples in both soils, except for S1 V3. It should be noted that the application of vanadium to S1 caused dispersion of the clay particles and the sample contained colloidal particles that could not be removed by filtration, causing the analytical results to be unreliable.

The statistical t-grouping results (Table 13) 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.

Table 13: Statistical t-groupings of extracts and V treatments

Treatments	1:20	1:10	1:5	1:2.5	Saturated Paste
	Mean V concentration (mg/kg)*				
S1					
V0	0.42^{a}	0.20^{b}	0.04617^{cd}	0.02575^{d}	0.00639^{d}
V1	429^{a}	316^{b}	229.24^{c}	152.87^{d}	23.98^{e}
V2	1411^{a}	1163^{ab}	1012^{b}	1011^{b}	532^{c}
V3	1618^{a}	1462^{b}	1201^{c}	860^{d}	439^{e}
S2					
V0	0.60^{a}	0.28^{b}	0.10^{bc}	0.05^{bc}	0.02^{c}
V1	86.7^{a}	50.5^{b}	23.3^{c}	10.0^{d}	4.3^{e}
V2	647^{a}	484^{b}	320^{c}	178^{d}	53.4^{e}
V3	3531^{a}	3508^{a}	3069	3034^{a}	No data

*Means with the same letter is not significantly different

3.6 Selection of most appropriate soluble method

The saturated paste extract is considered to be the best indication/estimation of the pore water quality of a soil sample. However, this is not a standard method used by laboratories since the amount of water required for the extract is not a constant but depend on the water holding capacity of the soil. Deionised water extracts with a constant/prescribed soil:solution ratio is easier to use on a routine basis. This investigation with different application rates of Cu, Pb and V on two soils with different clay minerals, followed by extractions with different soil:solution ratios, were conducted to determine the soil:solution extract which would best predict the pore water quality.

The analytical results and statistical analyses of the data showed the following:

- The soil:solution extracts overestimate the pore water quality of Cu, Pb and V in both soils compared to the saturated paste extract;
- This overestimation was more pronounced at higher treatments and higher soil:solution ratios;
- The results of the saturated paste and 1:2.5 extracts did not differ significantly; and
- The 1:20 extracts, commonly used for analyses of waste samples, specially overestimated pore water quality as did the NH_4NO_3 extract.

Based on the analytical results and interpretations of this investigation, the 1:2.5 extraction method was selected as the most appropriate method. 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(H_2O) and is therefore considered as an acceptable method for implementation by laboratories.

4 PARTITIONING COEFFICIENTS FOR SELECTED SA SOILS

The K_d of soils, a parameter used in setting screening values, is surrounded by uncertainties. There is lack of enough local information regarding K_ds for South African soils. A single value, with an assumed soil pH of 7 derived from international literature for each element, is used in the Framework for all soil types. However, the K_d of a soil is affected by factors such as soil organic matter, soil texture, and soil pH among others.

The aim of this part of the study was to determine K_ds for a selection of typically South African soil horizons. By using different soil types and horizons, the discrepancies in the K_d values could be assessed and better estimations of the K_d values for contaminated soils could be derived.

4.1 Materials and methods

4.1.1 Selected soils

The soil selection was based on the South African soil classification system. The ten soil horizons chosen included the following:

- 1:1 clay dominated (used in experiment 1);
- Vertic soil dominated by 2:1 clay minerals (used in experiment 1);
- Yellow oxidic / Plinthic (Soft plinthic B horizon);
- Red Oxidic
- Red Oxidic / High clay;
- Plinthic soil;
- Gley soil (G horizon);
- Melanic soil;
- Orthic A horizon with high OC%; and
- E horizon.

4.1.2 Soil properties

Characterization of the soil 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 KCl was done with a 1:2.5 (soil:water) extract. The organic carbon content was determined using the standard Walkley Black method and the particle size analysis was conducted with the hydrometer technique. The CEC were 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 CBD method as described by Mehra & Jackson (1961). The soil properties of the 10 soils used for this investigation are presented in Table 14.

Table 14: Soil properties of the 10 soils used for K_d experiment

Soil type	pH (H_2O)	pH (KCl)	Organic C %	CEC cmol(+)/ kg	CBD			Particle size		
					Al	Fe	Mn	Sand	Silt	Clay
					%			%		
1:1 clay dominated	4.9	4	0.7	20.1	0.58	10.18	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	13.32	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	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

4.1.3 K_d methodology

The most common procedure for measuring the K_d of a soil is by using a batch method. Soil samples are spiked with known concentrations of a chemical compound. The mixtures were 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 concentration with which the soil was spiked and the concentration extracted from the soil sample (SSSA, 2002). Figure 13 shows the experimental design of the trial.

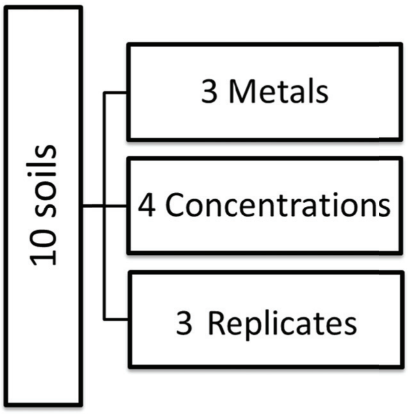


Figure 13: Experimental design for K_d experiment

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

- 4 g soil (sieved and homogenized) was weighed into a 50 ml centrifuge tube;
- 16 ml of the Cu, Pb and V spiked aqueous solution, containing 0.01 M $Mg(NO_3)_2$, was added to the soil. In order to spike the soils with 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 prepared and for V, (NH_4VO_3) ammonium metavanadate was added to achieve the required V concentrations.
- Table 15 show the concentrations of Cu, Pb and V added to contaminate the soils in mg/kg.
- 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 is then filtered through a 0.2 µm membrane filter; and
- An ICP-OES was used to determine the concentrations of metals extracted. This concentration was then subtracted from the concentration of the metal added to give the concentration sorbed (SSSA, 2002).

Table 15: Concentrations of Cu, Pb and V added to soil samples for different treatments

Treatment	**Metal added (mg/kg)**		
	Cu	**Pb**	**V**
0	Control	Control	Control
1	75	651	117
2	159	1692	215
3	189	3118	330

4.2 Results and discussion

The equilibrium metal concentration was plotted against the sorbed metal concentration in the respective soil horizon. The K_d is established by using the slope of the graph, which gives a value in $L.kg^{-1}$. The K_d was then plotted against, soil pH, percentage organic carbon, clay content and the amount of Fe oxides.

The detailed analytical results of the Kd investigation are presented in Appendix B.

4.2.1 Copper

The initial Cu content of soil is mainly governed by the parent material and the governing soil forming processes. The clay content also contributes significantly to the baseline Cu content of a soil. Surface soils have a high affinity to accumulate Cu. Cu ions are quite immobile and are held tightly onto organic and inorganic exchange sites. Regardless of the high immobility, Cu is still abundant as free and complexed aqueous ions in most soils. The solubility of Cu species decreases at pH 7 to 8. Cu sorption has been found to be higher for soils with Fe and Mn oxides, amorphous Fe and Al hydroxides and clays (imogolite, montmorillonite, vermiculite). The adsorption of Cu onto mineral surfaces, are dependent on the surface charge of the minerals. The surface charge in turn is dependent on the soil pH, thus the soil pH has a large influence on the adsorption capacity of Cu.

The estimated K_d's for Cu in the 10 soils used for this study, as determined by the slope of the linear regression of the graphs in Figure 14, ranged from 12.7 to 19,044 L/kg. Lower K_ds were observed for the 1:1 clay soil, the red oxidic and plinthic horizons while the soils with higer clay content and organic C content 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 the soil. Compared to the K_d value suggested for Cu in the Framework (10 L/kg), most of the soil horizons have much higher K_d values which will result in inappropriate screening of the soil during contaminated land assessments.

The graphs in Figure 15 show the correlation between the Cu K_d and selected properties of the studied soil horizons and Table 16 show the correlation coefficients of these graphs. The graphs show that the soils with the highest K_ds (red oxidic high clay, gley soil, E-horizon, melanic soil and vertic soil) have a wide range of CECs (10-45 cmol(+)/kg) and clay contents, their pH values ranged from 6-10 and their organic C was lower than 1.5%. The soils with lower K_ds (yellow oxidic, plinthic, red oxidic and 1:1 clay dominated soil) had CECs < 20 cmol(+)/kg and organic C < 1% while their pH was between 5 and 6.5.

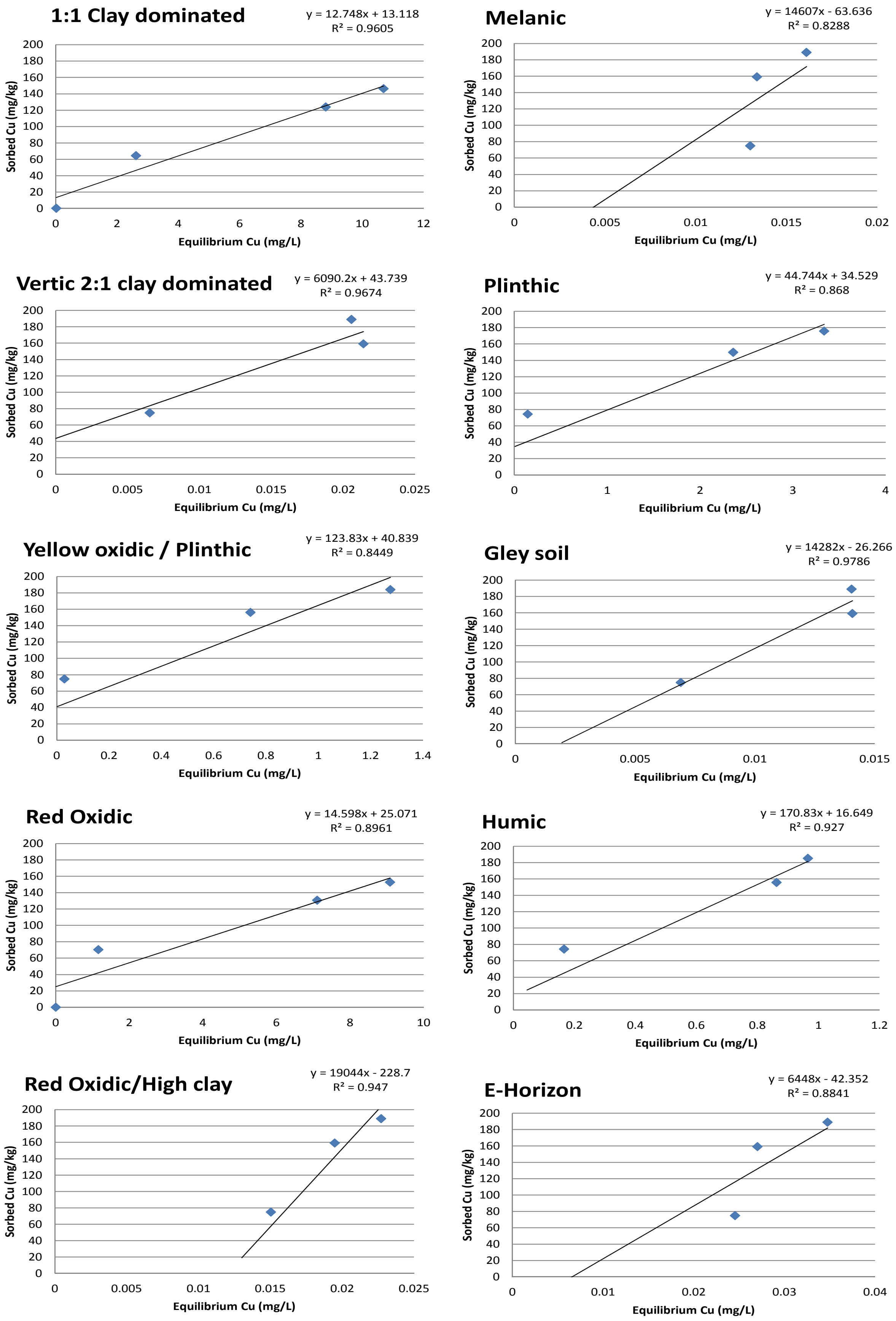


Figure 14: Cu sorption graphs for different soil horizons

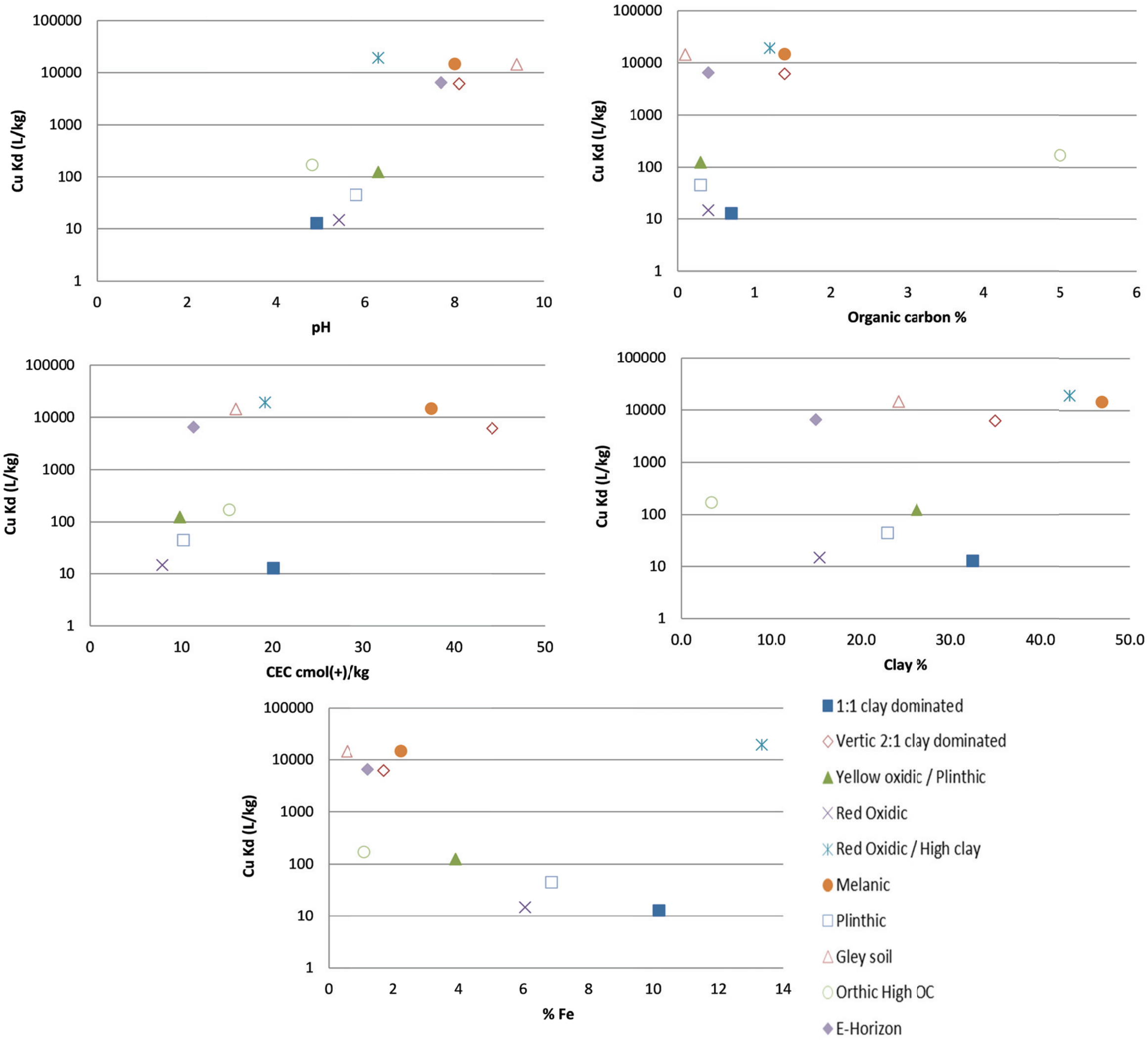


Figure 15: Correlation between Cu Kd and soil properties

Table 16: Correlation coefficients of Kds and soil properties

Metal	**pH**	**OC**	**CEC**	**Fe**	**Clay**
Cu	0.6	(-)0.1	0.4	0.1	0.6
Pb	0.7	(-)0.3	0.1	(-)0.2	0.1
V	(-)0.8	0.4	(-)0.2	0.7	(-)0.03

The Cu K_d of the soils (Table 16) showed a strong correlation with pH and clay content (r^2 = 0.6). It appears that soils with pH <6 and a clay content < 35% will have lower K_ds than soils with pH >6 and clay content > 35%. This hypothesis will have to be verified by more detailed investigations including more samples with these soil properties.

4.2.2 Lead

Pb 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 minerals, Mn oxides, Fe and Al hydroxides and organic matter are some of the most prominent soil components associated with Pb content. 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, 2000).

The K_d values for Pb, derived from the slope of the linear regression in Figure 16, ranged from 24.8 to as high as 252,294 L/kg. The K_d value for Pb suggested by the Framework is 100 L/kg and cannot even be considered as an average when looking at the results from this investigation. For the vertic and melanic horizons, higher Pb input concentrations are required to determine the K_d value as all the Pb added to the soil was adsorbed and thus no extracted concentration was available. Therefore, no graphs could be compiled for these 2 soils. In the red oxidic (high clay) soil, only in the highest concentration of Pb added a small amount of chemical could be extracted. Therefore, higher concentration Pb treatments will have to be applied in order to obtain a more accurate K_d value.

Figure 17 show the correlation graphs between K_ds derived for Pb during this investigation and selected soil properties of the 10 soil horizons. Altin *et al*. (1999) established that hydrogen competes with heavy metal cations for sorption at low pH values (2.5-3) and that the percentage of metal removal declines. At pH levels between 3 and 6 the amount of sorption mainly depends on the ion size of the metal. For pH values above 6, precipitation becomes dominant, especially in the case of Pb ions. This is prominent from the graph of Pb and pH ($r^2 = 0.7$, Table 16) where soils with higher pH had higher K_ds than soils with pH <6. From the rest of the correlation graphs in Figure 17 it appears that the soils are divided into two distinct groups with low and high K_d values but that the CEC, organic C and clay contents of these soils are in similar ranges. It indicates that pH is the determining factor in the Pb K_d of soils.

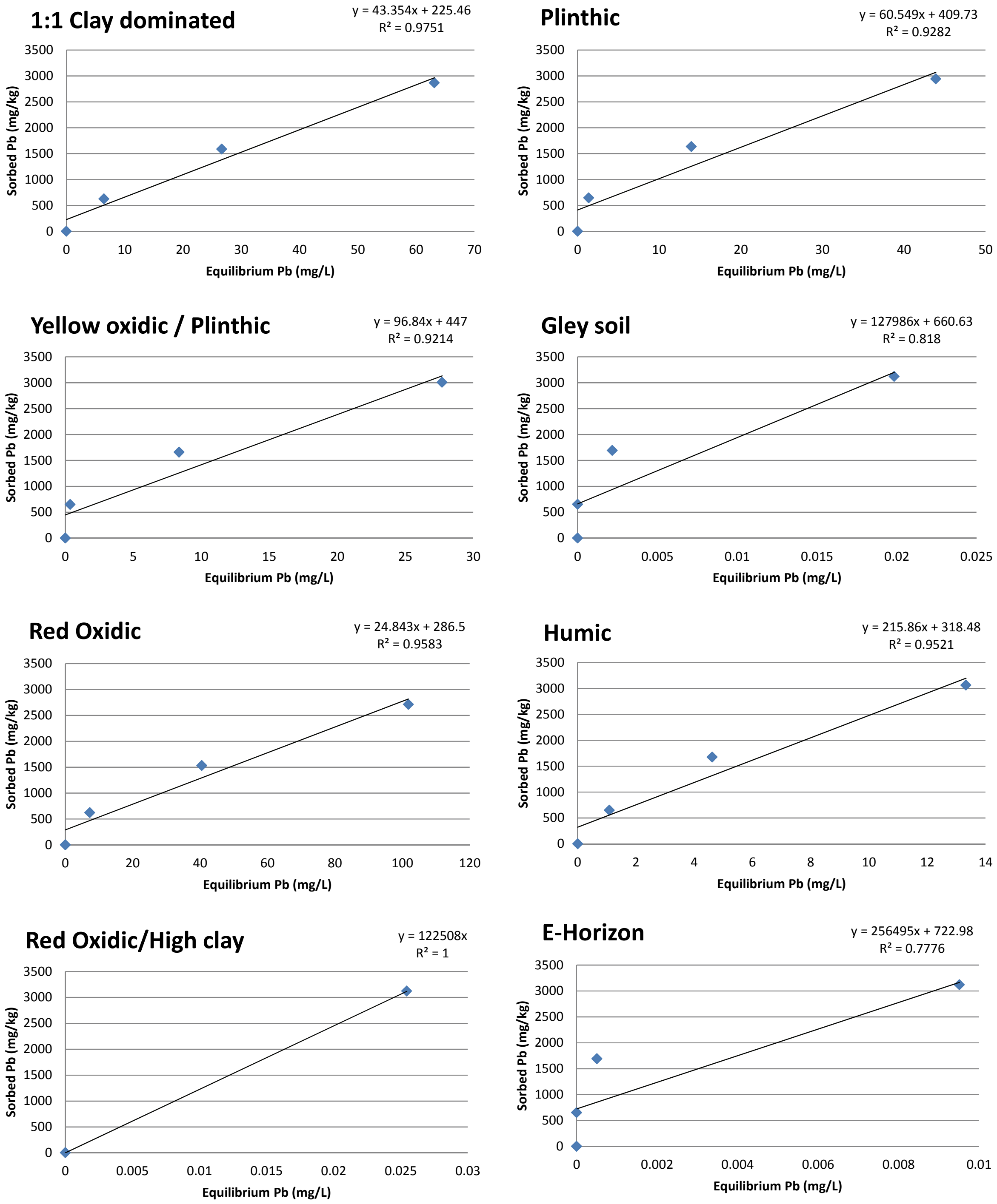


Figure 16: Pb sorption graphs for different soil horizons

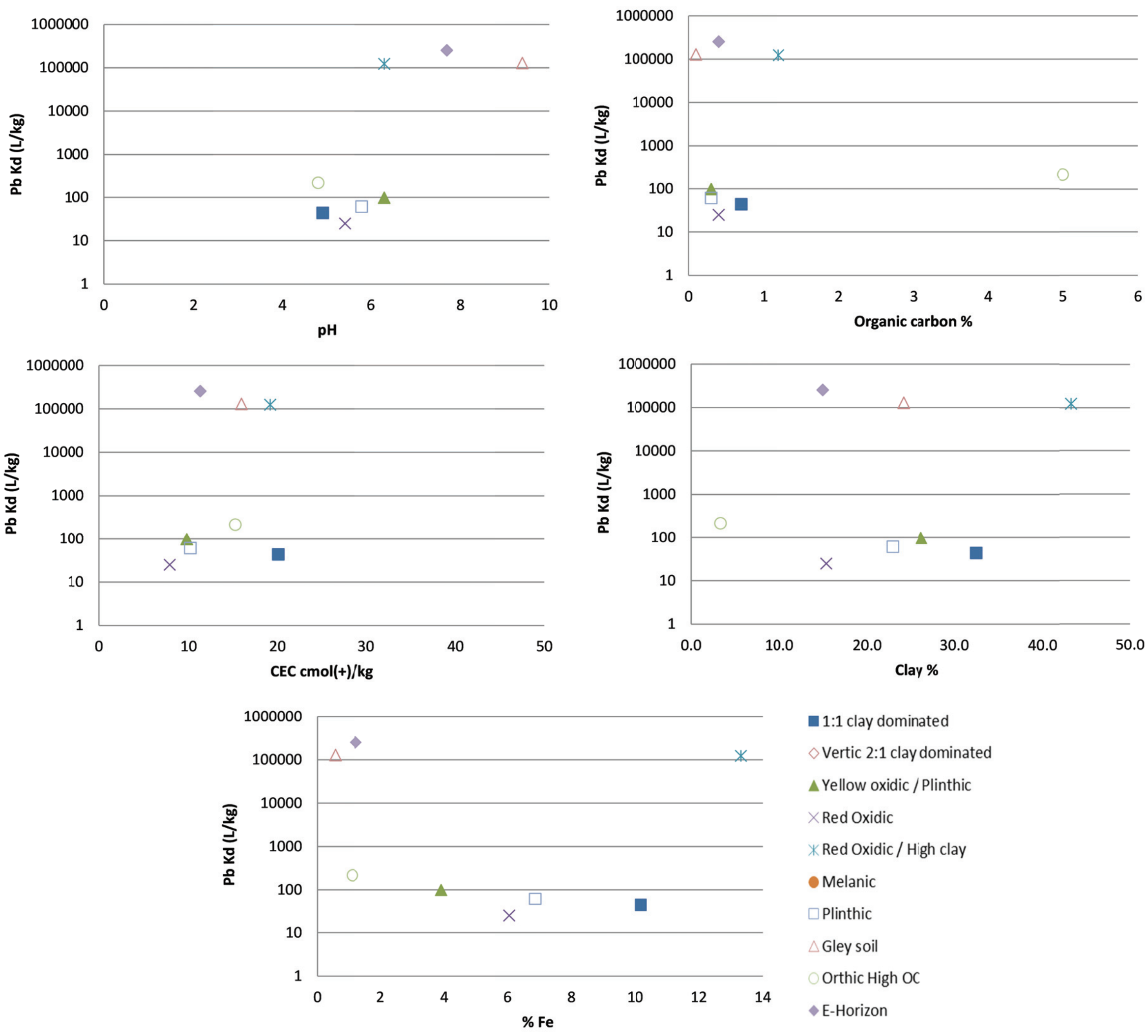


Figure 17: Correlation graphs of Pb K_d and soil properties

4.2.3 Vanadium

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.

The K_d value given in the Framework is 1,000 L/kg while the highest K_ds for V in this study was 865 L/kg for the 1:1 clay dominated soil, 708 L/kg for the orthic A horizon and 629 L/kg for the plinthic horizon (Figure 18). The K_ds for the rest of the soils varied between 10.5 L/kg and 220 L/kg. This shows that the K_d selected by the Framework may be too conservative and may allow contaminted land to be wrongly classified as uncontaminated.

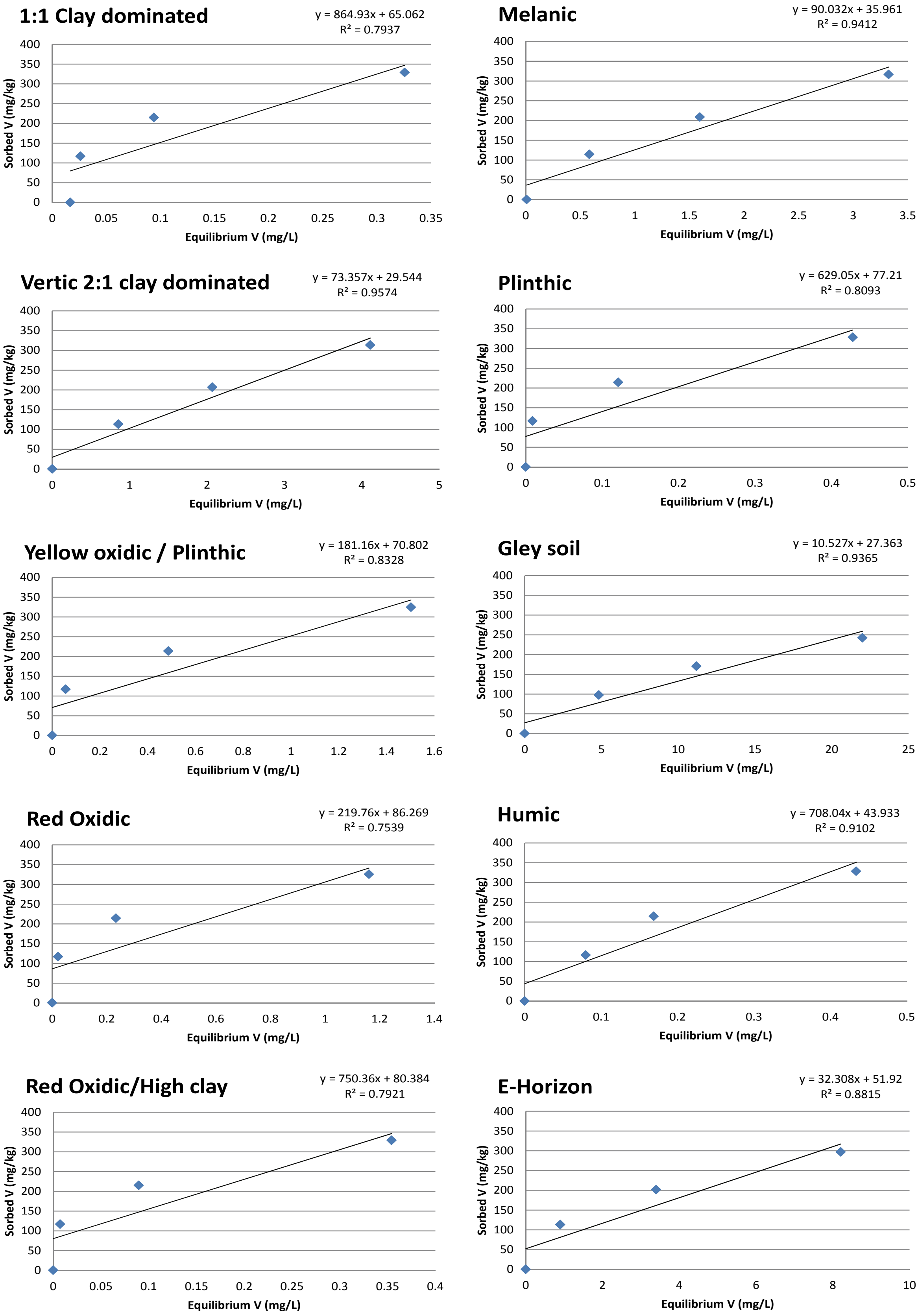


Figure 18: Vanadium sorption graphs for different soil horizons

Figure 19 show the correlation graphs between K_ds of the different soil horizons and selected soil properties. Compared to the cations, Cu and Pb, the K_d for V decreased with an increase in pH ($r^2 = 0.8$, Table 16), especially at pH > 6. There were no correlation between the K_ds of the different soils and CEC, clay content and organic C content. Figure 19 and Table 16 show a strong correlation between the V K_d and Fe content of the soil (higher K_d with higher Fe content).

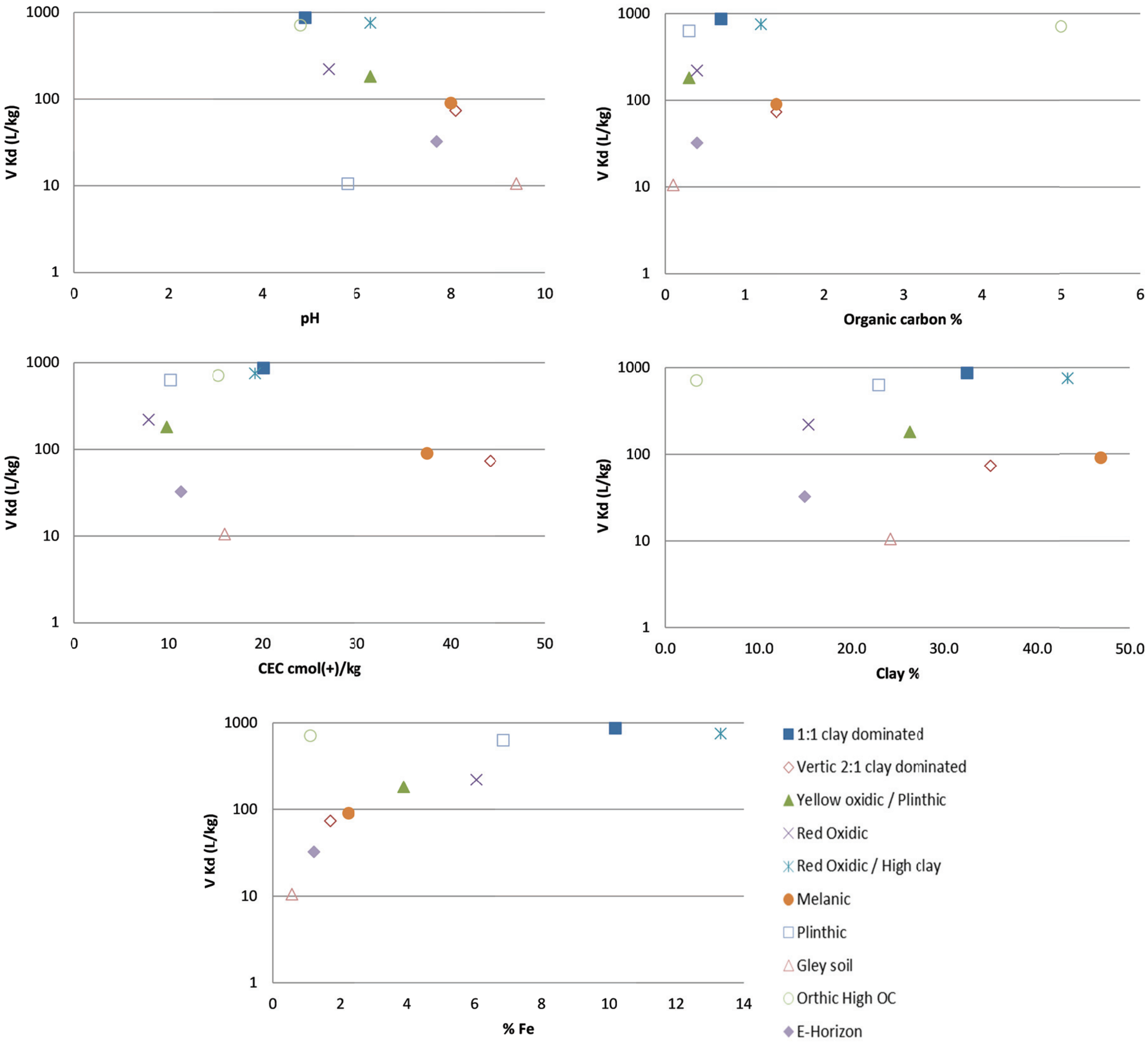


Figure 19: Correlation between V K_d and soil properties

4.3 Summary

Table 17 summarises the K_ds for Cu, Pb and V for the different soil horizons as calculated from the sorption graphs. In most cases where the K_d is high for the cations it is lower for V. This table shows the large variation between the K_ds stipulated in the Framework and the values obtained experimentally.

Table 17: Calculated K_d values of Cu, Pb and V for different soil horizons

Soil Horizon	Kd L/kg		
	Cu	**Pb**	**V**
1:1 clay dominated	13	43	865
Vertic 1:2 clay dominated	6090	>252294	73
Yellow oxidic / Plinthic	124	97	181
Red Oxidic	15	25	220
Red Oxidic / High clay	19044	122508	750
Melanic	14607	>252294	90
Plinthic	45	61	629
Gley	14282	127686	11
Orthic A high OC	171	216	708
E-Horizon	6448	252294	32
Coefficient of variation	121%	151%	95%
Framework K_d	**10**	**100**	**1000**

5 BASELINE SOLUBLE CONCENTRATIONS OF SELECTED ELEMENTS IN NATURAL SOUTH AFRICAN SOILS

5.1 Introduction

Soils are the primary source of trace elements in the food-chain. Therefore, trace element problems (both deficiencies and toxicities) are commonly associated with soil properties such as pH, clay content, cation exchange capacity (CEC), organic matter content and Fe content (Basta *et al*., 2005; Kabata-Pendias & Pendias, 2001). Some of these properties can be linked to the soil parent material. More siliceous parent material will result in sandier soils with lower fertility, while mafic rocks will release the greatest quantity of basic cations (Ca, Mg, K and Na) and therefore influence soil fertility, have a higher clay content and influence other soil properties (e.g. Fe content) at least to some extent. It is difficult to make reliable statements about trace element levels based only on parent material but most trace elements show an increasing or decreasing trend with increasing mafic character of the parent material. In general, ultramafic igneous rocks contain higher Cr, Ni and Co concentrations whereas mafic rocks contain higher Cu, Pb and Zn concentrations than other parent materials (Gray & Murphy, 2000).

Several studies have been conducted on trace element baseline concentrations in various countries and on the influence of soil properties on the trace element contents of soils (Ma *et al*., 1997; Burt *et al*., 2003; Chen *et al*., 1999; Tack *et al*., 1997; Kabata-Pendias & Pendias, 2001). However, all these studies focussed on total concentrations of trace elements and not soluble concentrations. Total trace element concentrations gives an indication of potential long-term risk to the environment and not the immediate risk to water resources, plants, animals and humans which depend on the availability/solubility of the trace element.

The objective of this investigation is to determine soluble baseline concentrations for selected trace elements 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 Materials and Methods

5.2.1 Soil selection

The South African Land Type Memoirs (Land Type Survey Staff, 1986) contains in access of 4500 soil samples representing various soil patterns, terrain units and climate zones. All the soil profiles are documented 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 inventory 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 selected soils for this study was confined to A-horizon samples (the first diagnostic horizon). The selected 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 variety of soil properties including pH(H2O), clay content, organic C content, CBD extractable Fe and Al and base status (Table 18).

Table 18: Soil properties of 100 selected soils

Soil properties	pH <5.5	pH 5.5- 6.5	pH 6.5-7.8	pH 7.8-8.5	pH > 8.5
	Property range				
Clay (%)	6.2-69	2.9-64.5	4.1-55.4	3.5-56	4.5-52
Organic C (%)	0.2-4.22	0.17-4.2	0.1-3.81	0.05-1	0.1-1.6
CBD Fe (%)	0.09-9.8	0.12-9	0.3-5.3	0.04-1.9	0.09-0.8
CBD Al (%)	0.01-1.5	0.01-0.85	0.02-0.2	0-0.4	0.02-0.14
Base status (cmol/kg clay)	0.34-65.8	8.9-96.8	21.7-95.4	30.4-114.4	48.8-214.66
Number of samples	20	35	28	11	6

5.2.2 Analytical method

Air-dried samples were gently crushed to pass a 2 mm stainless steel screen prior to analysis. The selected soluble method was 1:2.5 (see 3.6) and the procedure was as follows:

- Weigh 16 g soil into a 50 ml centrifuge tube;
- Add 40 ml of deionized water to the sample;
- Shake the sample on a mechanical shaker for 24 hours;
- Centrifuge samples at 4000 rpm for 5 minutes;
- Filter samples through Whatman 42 filter paper; and
- Filter sample through 0.2 µm membrane filter.

Analyses of Cd, Co, Cr, Cu, Pb, Ni and Zn were conducted with an ICP-OES at the University of Pretoria.

5.2.3 Statistical analyses

Soluble baseline concentrations

The baseline concentration range was calculated using the quotient and product of the geometric mean and the square of the geometric standard deviation, as recommended by

Chen *et al*. (1999; 2001), including data below the instrument detection limit as suggested by Gilbert (1987). The baseline concentration range is a better reflection of variation than the range actually observed because it is freer of the distorting effect of outlier (anomalous) values. The upper limit of the baseline concentration range was set at the 97.5th percentile value of the population in order to minimize the influence of contamination (i.e. to more closely reflect natural concentrations). The lower limit was set at the 2.5th percentile value in order to minimize problems that might be associated with analytical uncertainty near the lower limit of detection.

Correlation coefficients

Simple regression was first performed on the dataset as a formality in order to reveal possible relationships between trace element levels and soil properties. In general such relationships can be expected to be weak because when one soil property appears to be conducive to a high extractability of a particular trace element (e.g. low pH) there may be other factors which limit the concentration to low levels (e.g. high clay content). When plotted graphically, relationships of this kind tend to produce a scattered distribution, the meaning of which may be interpreted using a relatively recently developed (or at least only recently applied in the natural sciences) statistical technique known as quantile regression (Koenker and Bassett, 1978; Koenker and Hallock, 2001; Cade and Noon, 2003).

Chemical envelopes

In the present case, segmented quantile regression was employed. This consisted of segmenting the sample into equal subsets defined according to the conditioning covariate (Koenker and Hallock, 2001). The data set was first sorted with respect to each of the determinant variables (organic C, pH and clay content) and then divided into 10 classes (segments) of equal size (n=10). Within each class, the 0.025 and 0.975 quantiles were calculated for the dependent variable (trace metal concentration) and the corresponding 0.50 quantile (i.e. the median) was calculated for the determinant variable (soil property). Values of the 0.975 quantile for the dependent variable were plotted against the corresponding 0.50 quantile for the independent variable in each class. The 0.975 quantile was employed as a way of excluding extreme outlier values from the analysis and because it coincides with the upper limit of the baseline concentration.

Regression equations were fitted to the plots and a combination of goodness of fit and explicability (i.e. being amenable to soil chemical interpretation) was employed as a basis for selecting the most appropriate equation. The line delineated by the 0.975 quantile represents a boundary enclosing all observations except extreme outliers and reveals information about the limits of expression of the dependent variable for any particular value of the determinant (e.g. it can tell us what the expected maximum extractable metal concentration will be at a particular soil pH or clay content). The boundary line is referred to specifically as a chemical envelope.

Natural partitioning coefficient

Since the total trace element concentrations for most trace elements are available, the natural partitioning coefficients for the 100 natural soils could be calculated with the following formula:

$$Natural\ partitioning\ coefficient = \frac{Total\ mg/kg\ -\ Soluble\ mg/L}{Soluble\ \ mg/L}$$

These values were then related to different soils properties to determine the effect of pH(H_2O) and clay content on the natural partitioning coefficient.

5.3 Results and Discussion

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

5.3.1 Baseline soluble concentrations

Table 19 show the general statistics of the sample population as well as the soluble baseline concentration range. It should be noted that only 16 of the 100 samples had water soluble Zn concentrations higher than the detection limit while only 22 samples had detectable soluble Pb concentrations.

Table 19: General statistics and baseline soluble concentrations for selected elements (mg/l)

	Cr	Cu	Mn	Ni	Zn	V	Co	Pb
Number of samples above detection limits	100	100	100	100	16	100	100	22
	mg/l							
Minimum	0.02	0.001	0.05	0.01	0.001	0.03	0.01	0.001
Maximum	0.41	8.87	63.51	0.42	0.22	0.32	0.73	0.17
Average	0.09	0.13	5.69	0.05	0.08	0.06	0.07	0.03
Geometric mean	0.077	0.033	2.729	0.044	0.057	0.053	0.038	0.016
Geometric st deviation	1.692	2.481	3.799	1.827	7.811	1.377	2.597	3.094
Baseline range	0.03-0.22	0.005-0.2	0.2-39.4	0.013-0.15	0.001-3.5	0.03-0.1	0.006-0.26	0.001-0.15

The soluble baseline concentration ranges for all these elements, except Mn and Zn, were <1 mg/l. For Mn the range is wide with a lower limit of 0.189 mg/l and an upper limit of 39.4 mg/l, indicating a significant variability in soluble Mn concentrations between different soils.

5.3.2 Chemical envelopes

The correlation scatter diagrams and chemical envelopes of Ni, Cr, V, Cu, Co and Mn for different soil properties (organic C, pH(H_2O) and clay content) is presented in Figure 20 and Figure 21.

Cr and Ni show very similar chemical envelopes for organic carbon and clay contents, indicating an increase in soluble Cr and Ni concentrations with an increase in organic carbon content. There is also an increase in soluble Cr and Ni with an increase in clay content, reaching a plateau at 25% clay and a decrease in soluble Cr and Ni at >40% clay. The soil pH(H_2O) seems to have had little effect on the soluble Cr and Ni in the studied soils.

Soluble V concentration correlates well with soil pH (R^2=0.7), with the highest solubility at pH <5 and >7.5. The scatter diagrams show that some of the soil samples had higher V solubility at low organic C and clay contents. The chemical envelope for soluble V and clay content show that solubility decrease at >20% clay.

Soil pH has an influence on soluble Cu concentration with a decrease in soluble Cu at pH >6. Correlation with organic C show an increase in Cu solubility with an increase in organic C content while clay content had no significant effect on Cu solubility (R^2=0.01).

The soluble Co concentrations showed very strong correlation with organic carbon (R^2=0.8) with an increase in solubility as the organic carbon increases. The correlation with clay content was not as good, but solubility still showed an increase with an increase in clay content. However, this could be due to the outlier samples. If these two samples are ignored, the chemical envelope show a decrease in Co solubility with an increase in clay content, which is expected. There is a significant decrease in Co solubility at pH >6.

The soluble Mn showed similar chemical envelope patterns as Co, but with stronger correlation between soluble Mn and soil pH (R^2=0.7). The low soluble Mn concentrations at low pH could be due to the distrophic nature of soils with low pH values. The soluble Mn was higher in soils with lower clay content, except for the 2 outlier soils. Multiple factors can influence the solubility of Mn, including organic complexes and variable Eh-pH conditions.

Even small changes in the Eh-pH conditions can have a significant influence on Mn content of the soil solution. The mobility of Mn is especially effected by soil pH (Kabata-Pendias & Pendias, 2001).

Due to the limited number of soil samples with detectable soluble Pb and Zn, no chemical envelopes could be calculated for these elements. Figure 22 show the scatter diagrams of soluble Pb and Zn for different soil properties. These graphs indicate higher soluble Pb and Zn at lower pH ranges in the soil. Soils with lower clay contents had higher soluble Pb concentrations while the soluble Zn was higher at high clay contents. There was no correlation between organic C and soluble Zn while soluble Pb was higher at higher organic C contents.

5.3.3 Natural partitioning coefficients

The natural partitioning coefficients give an indication of the "K_d" of natural soil where no contaminant was added to the soil. The ranges of natural partitioning coefficients for the different elements (min and max) are indicated in Table 20. The data show the large variability of the natural partitioning coefficient for different soil samples for the same element.

Table 20: Natural partitioning coefficients for different elements (L/kg)

	Natural partitioning coefficient					
	Co	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Min	8	49	33	15	118	106
Max	1475	21083	26971	7667	9868	125799

Figure 23 and Figure 24 show the scatter plots and chemical envelopes of the natural partitioning coefficients of the different elements for different soil properties. These graphs show that the natural partitioning coefficients for Ni and Cr increased with an increase in the clay content of the soils, while the natural partitioning coefficient of Cu and Co did not correlate with the clay content. The limited data on soluble Pb and Zn could bias the interpretation of the data, but it seems as if the natural partitioning coefficient of Pb increased with an increase in clay content while that of Zn is not influenced by clay content.

Soil pH does not have a significant influence on the natural partitioning coefficients of Ni and Cr (and Pb), but the chemical envelope of Cu and Co (and Zn) show a correlation between soil pH and the natural portioning coefficient.

The natural partitioning coefficients of Cr, Cu and Co was higher at lower organic C contents, with correlation coefficients of 0.4-0.6. Ni and Pb showed no correlation between natural partitioning coefficients and organic C content.

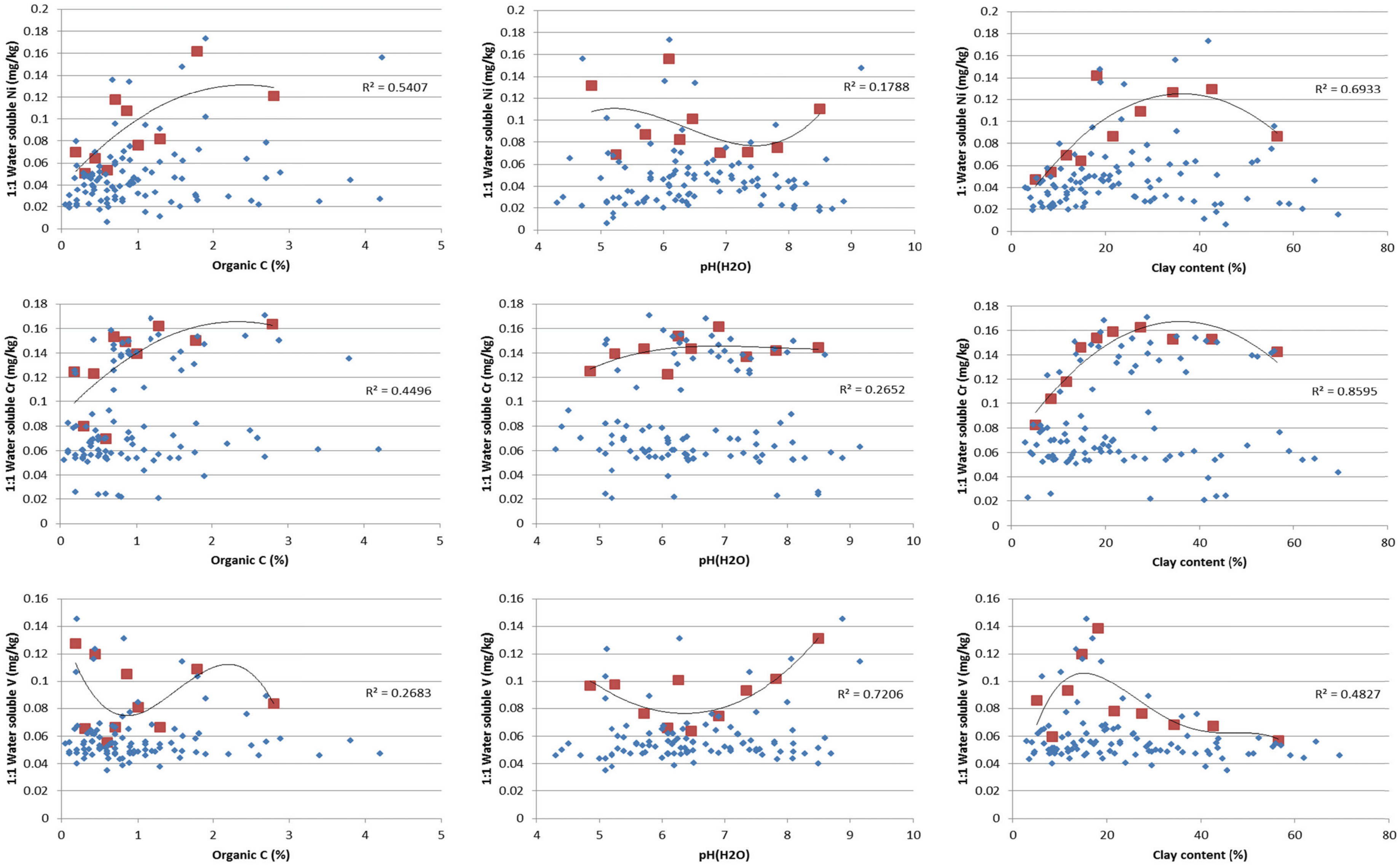


Figure 20: Scatter diagrams and chemical envelopes of water soluble Ni, Cr and V

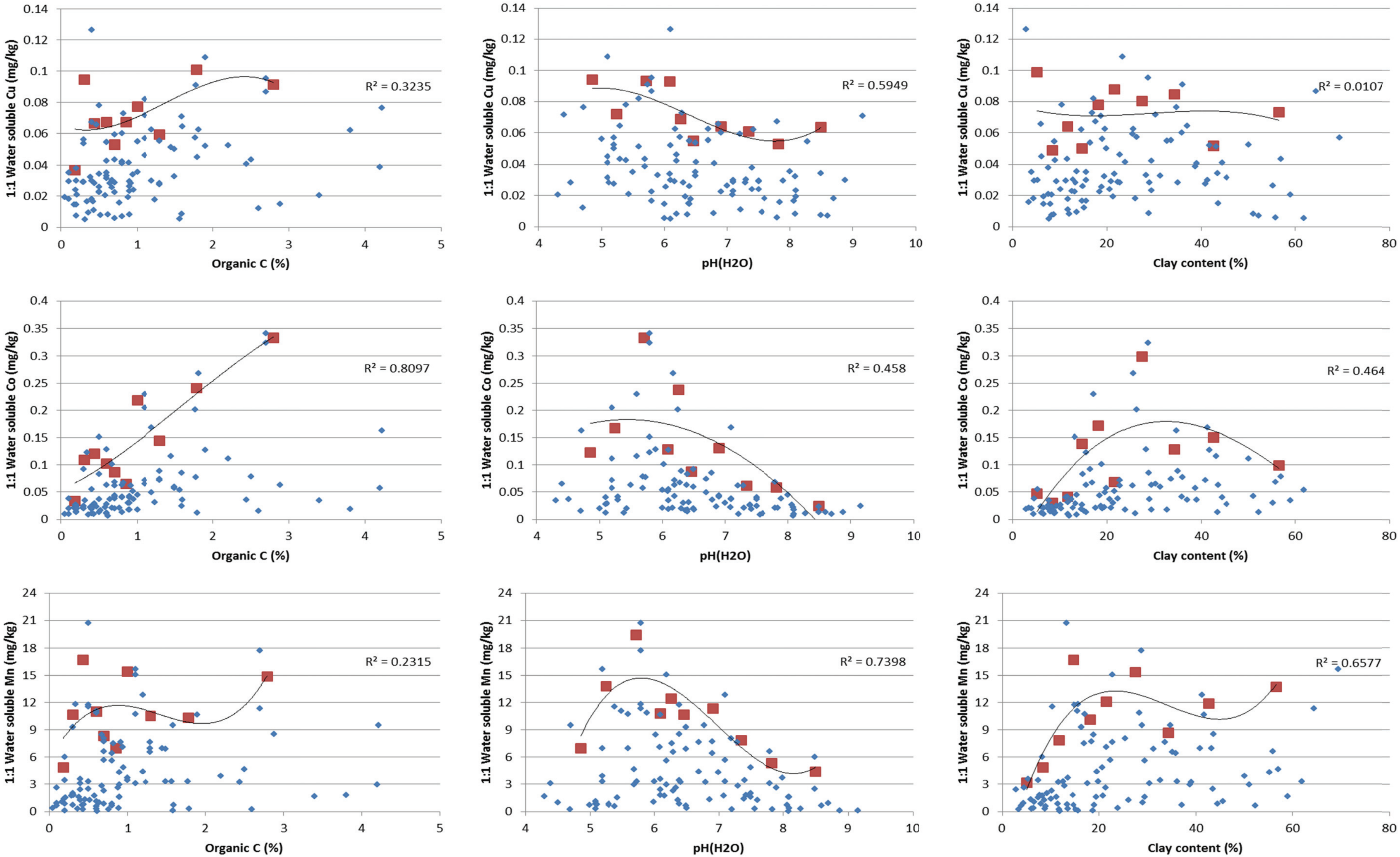


Figure 21: Scatter diagrams and chemical envelopes of water soluble Cu, Co and Mn

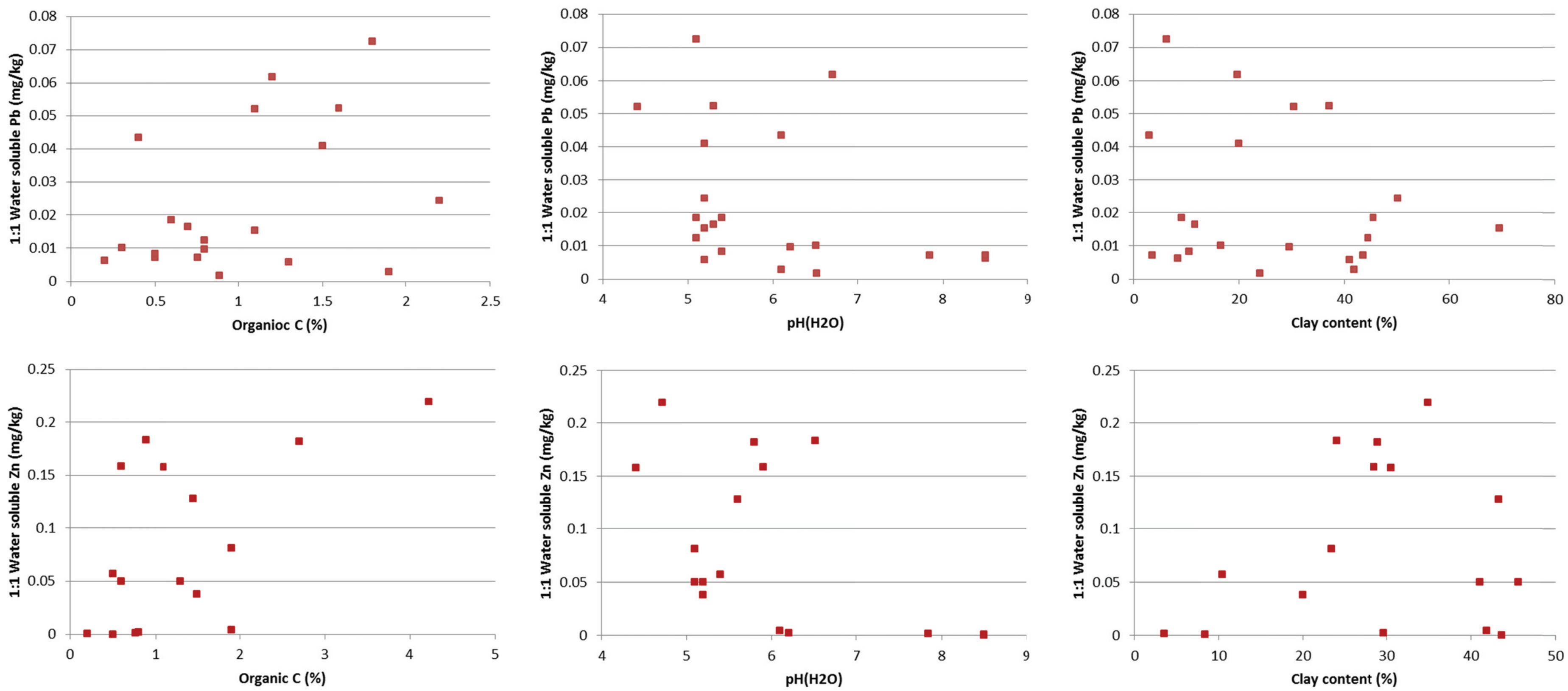


Figure 22: Scatter diagrams of water soluble Pb and Zn

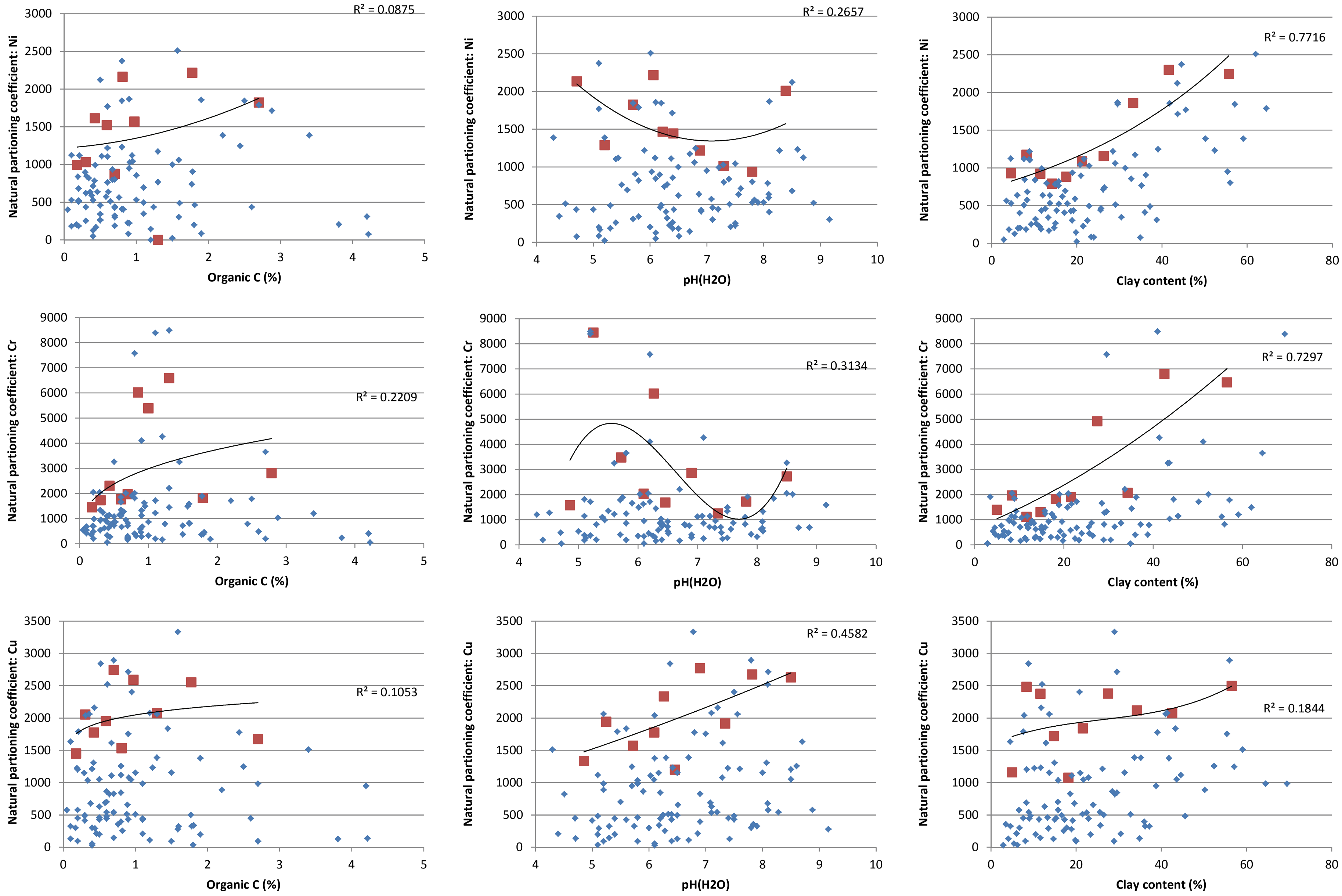
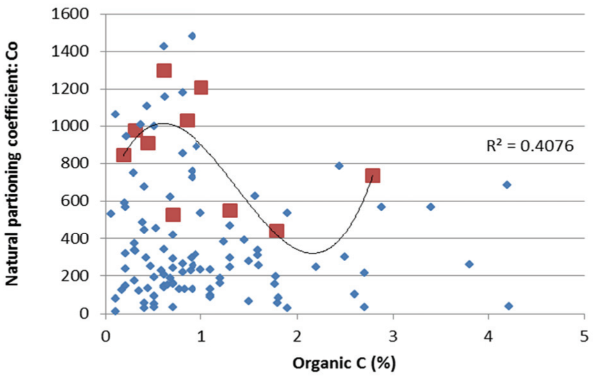
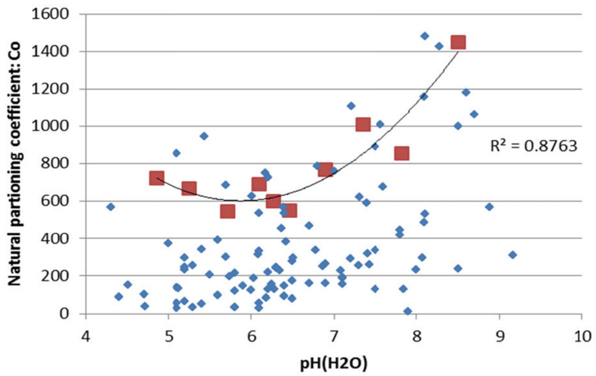
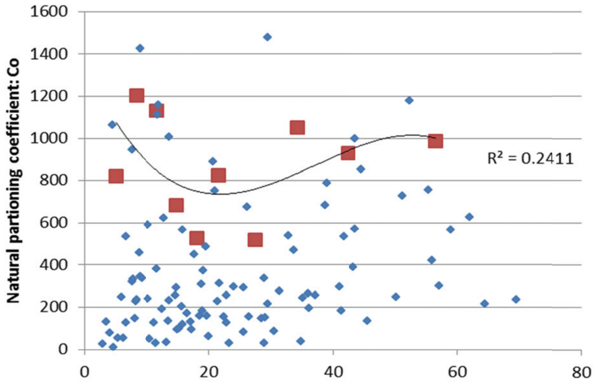
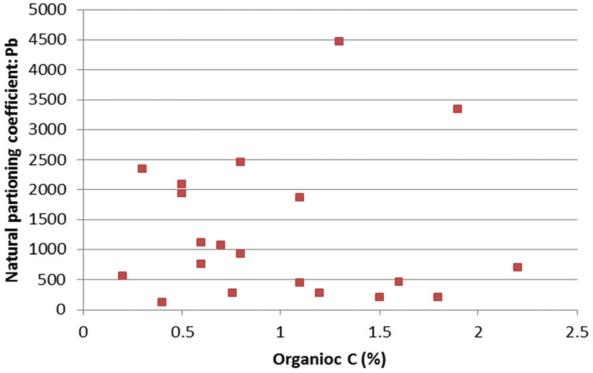


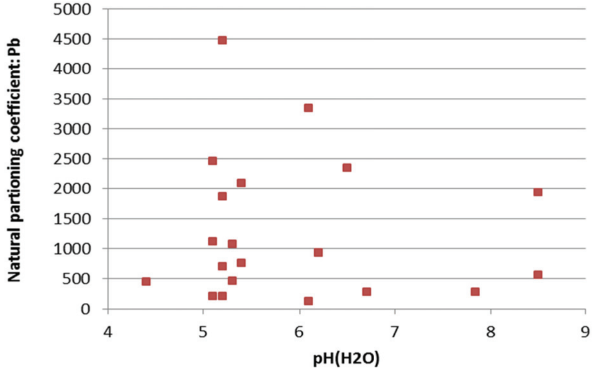
Figure 23: Scatter diagrams and chemical envelopes of natural partitioning coefficients of Ni, Cr and Cu

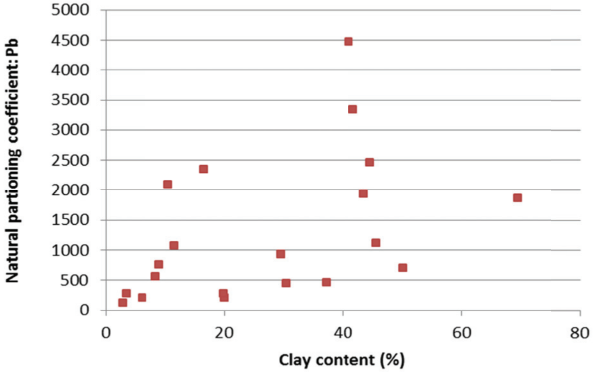

Natural partioning coefficient: Co
1600
1400
1200
1000
800
600
400
200
0
0
1
2
3
4
5
Organic C (%)
R² = 0.4076

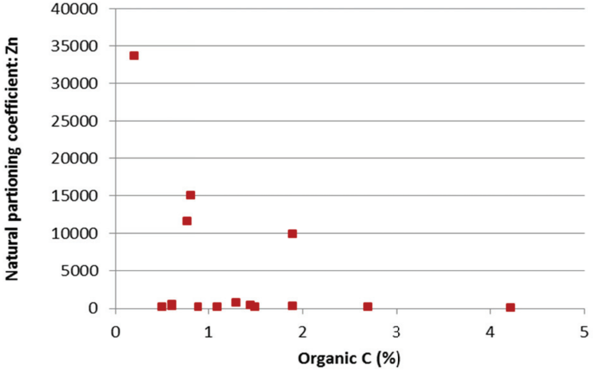

Natural partioning coefficient: Co
1600
1400
1200
1000
800
600
400
200
0
4
5
6
7
8
9
10
pH(H2O)
R² = 0.8763

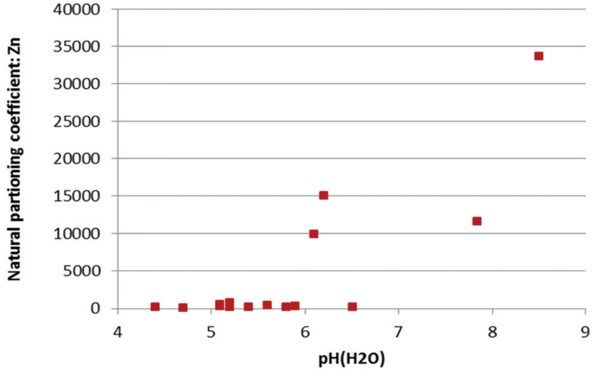

Natural partioning coefficient: Co
1600
1400
1200
1000
800
600
400
200
0
0
20
40
60
80
R² = 0.2411

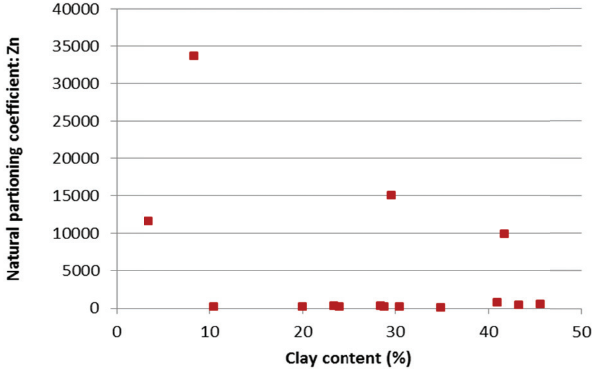

Natural partioning coefficient: Pb
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
0.5
1
1.5
2
2.5
Organioc C (%)


Natural partioning coefficient: Pb
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
4
5
6
7
8
9
pH(H2O)


Natural partioning coefficient: Pb
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
20
40
60
80
Clay content (%)


Natural partioning coefficient: Zn
40000
35000
30000
25000
20000
15000
10000
5000
0
0
1
2
3
4
5
Organic C (%)


Natural partioning coefficient: Zn
40000
35000
30000
25000
20000
15000
10000
5000
0
4
5
6
7
8
9
pH(H2O)


Natural partioning coefficient: Zn
40000
35000
30000
25000
20000
15000
10000
5000
0
0
10
20
30
40
50
Clay content (%)

6 CONCLUSIONS

The results obtained from this investigation achieved the following:

- Selection of the most appropriate soil:solution extract ratio to determine the soluble fraction of contaminants in soil to estimate pore water quality;
- Determination of K_ds for Cu, Pb and V of 10 different diagnostic South African soils horizons, representing a variety of soil properties, which can be used to refine SSV1 levels;
- Baseline concentration ranges for soluble elements (Cr, Cu, Mn, Ni, Zn, V, Co and Pb) in natural, uncontaminated South African soils which could be used during initial site assessments; and
- Natural partitioning coefficients for selected metals in natural South African topsoils which indicate the fraction of the element that is mobile and pose a risk to groundwater resources.

6.1 Determination of appropriate soluble extraction method

The comparison of analytical methods to determine soluble concentrations of elements in soils, in order to select the best analytical method to predict soluble pore water quality, indicated the following:

- The 2:1 clay minerals had a strong affinity to adsorb Cu, Pb and V, resulting in low extractable concentrations. In the case of S1 (1:1 clay minerals), the elements were not strongly adsorbed onto the clay complex and the water extract methods could extract the Cu, Pb and V;
- Pore water quality is overestimated with the fixed soil:solution ratio extractions, compared to the saturated paste extract (assumed to be the best indicator of pore water quality). This overestimation was more pronounced with higher treatments (more 'contamination') and higher soil:solution ratios;
- The results of the 1:2.5 water extracts were closest to the results of the saturated paste extract. In most instances the results were not significantly different from saturated paste results.

Based on the analytical results and interpretations of this study, the 1:2.5 extraction method was selected as the most appropriate method to determine the soluble concentration of soil as an estimate of pore water quality, because it is the closest to saturated pastes extracts in terms of soil to solution ratio, but more analytically convenient and easy to be done routinely by commercial labs.

6.2 Determination of K_d values for typical SA soils

The K_d of a soil represents the net effect of several soil sorption processes acting upon the contaminant. Soil properties such as the pH, clay content, organic carbon content and the amount of Mn and Fe oxides, have an immense influence on the K_d value of a soil. Soil properties should be considered when deciding on a quantitative contaminant K_d value to use for a specific site.

K_ds for Cu, Pb and V for the different soil horizons was calculated from the sorption graphs. In most cases where the K_d was high for the cations (Cu and Pb) it was low for V. There is a large variation between the K_ds stipulated in the Framework and the values obtained experimentally in this study:

- The K_d values for Cu ranged from 12.7 to 19,044 L/kg. Lower K_ds were observed for the 1:1 clay soil, the red oxidic and plinthic horizons while the soils with higer clay content had higher K_d values (vertic, red oxidic with high clay content, melanic and gleyic soils). There were a good correlation (r^2 = 0.6) between Cu K_d and the pH and clay content of the soils;
- The K_d values for Pb ranged from 24.8 to as high as 252,294 L/kg. The gley soil and the red oxidic soil with high clay content had higher K_ds than the rest of the soils. The Kd for Pb showed a strong correlation with soil pH (r^2 = 0.7);
- The highest K_ds for V determined in this study were 865 L/kg for the 1:1 clay dominated soil, 708 L/kg for the orthic A horizon with high organic C content and 629 L/kg for the plinthic horizon. The K_ds for the rest of the soils varied between 10.5 L/kg and 220 L/kg. the V Kd showed a strong negative correlation with soil pH (r^2 = 0.8) and a positive correlation with the Fe content of the soil (r^2 – 0.7).

The 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. However, additional research is required to determine K_ds for other SA soils and more potential contaminants. It is also suggested that more ‘contamination’ treatments be used in order to generate Kd values over a larger contamination range. Metal sorption isotherms by soils are non-linear and it is reasonable to expect different, and possibly vastly different, Kd values at different contamination levels.

6.3 Soluble baseline concentrations for 100 top soils

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 different soil properties. The soluble baseline concentration ranges for Cr, Cu, Ni, V, Co and Pb were <1 mg/l. For Mn the range is wide with a lower limit of 0.189 mg/l and an upper limit of 39.4 mg/l, indicating a significant variability in soluble Mn concentrations between different soils.

The correlation between soluble metal ions and soil properties for selected metals and soils could be summarised as follows:

- An increase in soluble Cr and Ni concentrations with an increase in organic carbon and clay content (with a decrease at >40% clay). The soil pH(H_2O) seems to have had little effect on the soluble Cr and Ni in the studied soils;
- Soluble V concentration correlated well with soil pH (R^2=0.7), with the highest solubility at pH <5 and >7.5. The solubility of V decreased when the clay content increase >20%;
- Soil pH had an influence on soluble Cu concentration with a decrease in soluble Cu at pH >6. Cu solubility increased with an increase in organic C content while clay content had no significant effect on Cu solubility (R^2=0.01);
- The soluble Co concentrations showed very strong correlation with organic carbon (R^2=0.8) and soil pH with a significant decrease in Co solubility at pH >6;
- A strong correlation between soluble Mn and soil pH (R^2=0.7) and soluble Mn was higher in soils with lower clay content;
- The available results indicated higher soluble Pb and Zn at lower pH ranges in the soil. Soils with lower clay contents had higher soluble Pb concentrations while the soluble Zn was higher at high clay contents. There was no correlation between organic C and soluble Zn while soluble Pb was higher at higher organic C contents.

6.4 Natural partitioning coefficients

The natural partitioning coefficients give an indication of the 'K_d' of natural soil (no contaminant added). The results showed that:

- The natural partitioning coefficients for Ni and Cr increased with an increase in the clay content of the soils;
- The natural partitioning coefficient of Cu and Co did not correlate with the clay content;
- The natural partitioning coefficient of Pb increased with an increase in clay content while that of Zn is not influenced by clay content;
- Soil pH does not have a significant influence on the natural partitioning coefficients of Ni and Cr (and Pb), but the chemical envelope of Cu and Co (and Zn) show a correlation between soil pH and the natural portioning coefficient; and

- The natural partitioning coefficients of Cr, Cu and Co were higher at lower organic C contents while Ni and Pb showed no correlation between natural partitioning coefficients and organic C content.

7 RECOMMENDATIONS

7.1 Soluble extraction method

It is recommended that the 1:2.5 soil:solution ratio extract be used to estimate the pore water quality of soil. This is also the standard method used for the determination of soil pH(H_2O) and is therefore considered an easily implementable method for routine analysis in commercial laboratories. However, overestimation of metal solubility should be kept in mind when interpreting results especially for higher contamination loads in soils.

7.2 Risk Based Soil Screening Value (RBSSV)

Based on the K_ds determined in this study for 10 different diagnostic South African soils horizons, preliminary additional soil screening values could be calculated which is specific for certain soil types. However, the SA baseline concentrations for natural soils were also considered. Based on these calculations, soil types were grouped together and preliminary risk based soil screening values (RBSSV) were established which are presented in Table 21 together with the current SSV1 of the Draft National Norms and Standards for the Remediation of Contaminated Land and Soil Quality (GN 233 of 2012). These RBSSV levels are lower than the calculated risk based values as calculated using the K_ds and can be used in the Phase 1 contaminated land assessment if the soil was classified during sampling During a Phase 1 assessment, to determine sites for further Phase 2 detailed assessments, soils with concentrations above South African baseline concentrations should also be included due to the uncertainty associated with a high level Phase 1 risk assessment. These soils would probably be contaminated although not necessarily holding any risk.

Table 21: Recommended Risk Based Soil Screening Value (RBSSV)

Soil Horizon	Risk Based Soil Screening Value (RBSSV)		
	Cu	Pb	V
1:1 clay dominated	110	20	360
Red Oxidic			200
Plinthic			360
Yellow oxidic / Plinthic			200
Orthic A high OC			360
Vertic 2:1 clay dominated		65	100
Red Oxidic / High clay			360
Melanic			100
Gley			20
SA Baseline	**117**	**66**	**360**
Framework SSV1	**16**	**20**	**150**

7.3 K_ds for Phase 2 contaminated land assessments

During Phase 2 contaminated land assessments, where more information will be available on soil type and properties, the K_ds determined during this study can be used to further refine the soil screening values for specific soil types/horizons. Vertic soils, red oxidic soils with high clay content, melanic soils and gley soils could potentially have higher site specific soil screening values for Cu and Pb than the Phase 1 screening values, since these soils have a strong sorption capacity and the risk for groundwater contamination will be less. The recommended K_ds for use in site specific Phase 2 risk assessments are presented in Table 22.

Table 22: Recommended Phase 2 K_ds

Soil Horizon	Phase 2 K_ds		
	Cu	Pb	V
1:1 clay dominated	10	40	800
Red Oxidic		20	200
Plinthic	40	60	600
Yellow oxidic / Plinthic	100	90	180
Orthic A high OC		200	700
Vertic 2:1 clay dominated	5000	10000	70
Red Oxidic / High clay			750
Melanic			90
Gley			10
Framework K_d	**10**	**100**	**1000**

The K_ds determined during this investigation showed a strong correlation with soil pH and therefore, soil pH can also be used to refine the Phase 2 soil screening values. The determination of soil pH is an easy method which is routinely done on soil samples submitted for analyses. Table 23 show the preliminary recommended pH specific SSV (pH-SSV) for Cu, Pb and V which can be used during Phase 2 contaminated land assessments.

Table 23: Recommended pH specific SSV

	Cu		Pb		V	
pH	**<6**	**>6**	**<6**	**>6**	**<7.5**	**>7.5**
K_d	10-50	100-1000	100-1000	1000-5000	100-500	10-100
pH-SSV	200-1000	1000-10000	20-200	2000-10000	200-1000	20-200

However, it must be noted that these are only preliminary refined K_ds and additional soil screening values which are based on the limited research conducted in this study. Additional research is required to refine and confirm these levels and establish baseline ranges, where:

- More replicates of the current 10 soils are used to refine the K_ds;
- K_ds can be determined for more contaminants and more soils can be considered; and
- More treatments of 'contamination' can be used to refine the K_ds.

7.4 Evaluation of risk to the environment

The potential risk that a contaminant may pose to groundwater can be assessed by determining the soluble fraction of the contaminant in the soil. It is recommended that a 1:2.5 deionised water extract be conducted on soil samples during the Phase 1 screening level assessment. The results can be compared to the Water Quality Guidelines for the specific contaminant to indicate potential risk for groundwater contamination.

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