INVESTIGATION OF THE CONTAMINANT ATTENUATION CHARACTERISTICS OF THE SOIL AQUIFER SYSTEM WITH SPECIAL EMPHASIS ON THE VADOSE ZONE.

FINAL REPORT
to the
WATER RESEARCH COMMISSION

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EXECUTIVE SUMMARY

INTRODUCTION

Groundwater contamination can occur as a result of various activities of man. In view of the importance of groundwater as a potential source of water supply, both for domestic and industrial uses, every effort must be made to minimize the deterioration of its quality due to human activities. With increased human settlement and economic development, a number of undesirable waste products are produced and disposed of into the environment. Most of these waste products contain substances which are directly hazardous to human life and will, therefore, render water unusable.

The vulnerability of an aquifer to pollution is directly linked to the hydraulic characteristics of the aquifer overburden and to a significant degree determined by the characteristic of contaminant attenuation. During infiltration through soils and transport in aquifers, many contaminants are naturally attenuated. However, not all subsurface environments are equally effective in this respect. The degree of attenuation will to a certain extent depend on porous media properties. If one knew both the porous media and the contaminant properties, an assessment can be made regarding the extent to which natural attenuation can be depended upon to reduce the concentration of potential contaminants.

In terms of the Receiving Water Quality Objective Approach adopted by the Department of Water Affairs & Forestry, two possible options exist when managing groundwater quality. Either

- ☐ no quality deterioration allowed, or
- ☐ controlled degradation within specified limits

It is noted that it is not always possible to enforce a policy of zero pollution. If the subsurface attenuation characteristics are known, the extent of contamination tolerable in a given situation can be determined. In addition, if one knew the geographical distribution of soils, an assessment can be made with regard to areas with high or low attenuation potential. For planners and policy makers, such information is of crucial importance when linked to vulnerability mapping.

Aims

A project was formulated to investigate the contaminant attenuation capacity of the soil/aquifer system with special emphasis on the vadose zone. The main aim of the project was:

- ☐ to determine the contaminant attenuation capacity characteristics of various soils, aquifers and the subsurface environment as a whole for specific contaminants in order to provide a useful tool for planners, policy makers and pollution control authorities to assess groundwater pollution risks.

In order to achieve this, the following specific objectives were set:

- ☐ To determine the relationship between soil physical and chemical properties (e.g. soil type, soil thickness and other attributes) and its contaminant attenuation capacity;
- ☐ To determine similar relationships for the vadose zone and the aquifer itself;
- ☐ To provide information in the form of GIS based maps and/or expert system based decision aids for the use of planners.

METHODOLOGY

This research was conducted by two research institutions: CSIR and University of Stellenbosch. The project was initially supposed to run for 3 and half years, but was later extended for another year. A summary of the activities conducted to meet the objectives above is given below.

Literature review of contaminant attenuation in the subsurface

A major component of the study related to conducting a literature study on contaminant attenuation processes in soils. The approach involved summarizing the important porous media (soil) properties and the chemical processes that are potentially important in the attenuation of heavy metals and organic compounds in the subsurface. The emphasis was on chemical processes. Biological processes were only dealt with briefly. Transport processes of advection and dispersion were not considered.

Laboratory studies

Laboratory studies were conducted to determine the potential for contaminant attenuation in selected soil materials. Specific objectives included:

☐ development and testing of experimental methods for evaluating contaminant attenuation
☐ comparison of selected soils with regard to their ability to attenuate specific contaminants
☐ assessment of the effect of variation of soil parameters on contaminant attenuation
☐ compilation of a matrix to facilitate comparison of different physical and chemical properties of soil materials and their ability to attenuate different chemicals

Six different soils from the Western Cape were used in the study. For the contaminants: three heavy metals (Pb, Cd, Cr) and three organic compounds (toluene, Phenol, Perchloroethylene) were used.

For the heavy metals, batch studies were conducted to get an indication of their adsorption capacity. Batch studies were also conducted for phenol. For toluene and perchloroethylene, small scale column studies were conducted.

Field studies

Field studies were conducted to examine whether contaminant attenuation processes as indicated by the literature and laboratory studies, could be confirmed at the field scale. To achieve this, the following activities were conducted:

A Infiltration experiments: field infiltration experiments were conducted on top of an unconfined sand aquifer to examine the migration and attenuation of organic contaminants from the surface, through the unsaturated zone to the water table. During the experiments, leachate/runoff mixture containing aliphatic hydrocarbons was irrigated on the site. In addition, four organic compounds: toluene, butyric acid, phenol and aniline were introduced. Two days after the experiment, water samples were collected from both the unsaturated and saturated zone to examine concentration changes of the compounds with depth.

B Sampling of soil and/or water below sites where waste disposal activities have occurred over several years to examine the distribution of contaminants. Sampling was conducted at:

- ☐ industrial liquid waste evaporation pans
- ☐ industrial liquid waste - flood spreading site
- ☐ industrial liquid waste- leaking point source
- ☐ domestic solid waste disposal site

Solute transport modelling

The main aim of the modelling aspect of this project was to develop procedural guidelines for modelling soil pollutant transport in the unsaturated zone. To achieve this, integrated literature, laboratory and computer modelling studies were conducted. The activities conducted included:

- ☐ literature survey to identify factors and processes that influence attenuation capacity
- ☐ comparison of available numerical models to select a suitable one for attenuation studies
- ☐ performing a sensitivity analysis on the selected model
- ☐ validation of the model at both the laboratory and field scales
- ☐ using the model to predict the movement of contaminants leaching through soil at a field site
- ☐ development of software to aid in the modelling process
- ☐ calculation of the attenuation capacity of soil from modelling results

A PhD thesis on this work is available at the University of Stellenbosch.

GIS

The main aim of the GIS component was to develop a methodology for generating regional scale maps of vadose zone attenuation characteristics for use by planners. Specific objectives were:

- ☐ to use available digital data sets to produce soils characteristic maps
- ☐ to produce qualitative attenuation maps for a given group of contaminants

No soils maps exist for the country at the moment and as such land type maps had to be used to derive soils characteristic maps. The latter were then combined with information on contaminant attenuation characteristics to produce qualitative contaminant attenuation maps.

Prototype expert system models

The overall objective of this part of the project was to determine the feasibility of developing a prototype, expert-systems based, decision support software for use when assessing the contaminant attenuation potential of soils.

CONCLUSIONS

Literature review of contaminant attenuation in the subsurface.

- ☐ A number of chemical processes are important in the attenuation of heavy metals in the subsurface. These include complexation, dissolution/precipitation, adsorption, reduction/oxidation and hydrolysis. pH is the 'primary variable' controlling these processes.

- ☐ For organic contaminants, the main factors and processes that may affect their fate in the subsurface are sorption, hydrolysis, oxidation/reduction, volatization and biological degradation. The behaviour of organic molecules in soils is controlled by the chemical properties of the molecules and the surface properties of the particular soil.

- ☐ The porous media (soil) properties that are important in contaminant attenuation include surface area, particle size, structure, mineralogy, organic and mineral coatings. Texture and surface area are closely related so that as particle size decreases, the surface area per unit mass increases. Elements are less mobile in soils that provide a large quantity of sorption sites. Oxides of Fe, Al, and Mn can provide chemisorption sites for cation and anion forms of elements. Layer silicate minerals provide exchange sites for cations, and a few chemisorption sites for both cations and anions. Noncrystalline aluminosilicates possess large quantities of chemisorption sites for both cations and anions. Soil organic matter can act as cation adsorption sites and is also involved in hydrophobic sorption of organic compounds.

- ☐ The literature review revealed that several factors and processes will operate in the soil/aquifer system that will affect contaminant attenuation. These processes and factors will occur simultaneously and in certain cases compete with each other. Ultimately, the fate of a given chemical in the subsurface will, therefore, be determined by its properties and consequent reactivity in a variety of chemical, physical, and biologically mediated processes and the rate of its physical transport. The 'attenuation potential' of a given soil is, therefore, not a fixed parameter but a variable.

Laboratory studies

- ☐ A suitable method was successfully developed for determining contaminant attenuation of heavy metals at the laboratory scale. For organic compounds, establishing a method was more difficult, and although a method was developed, there was insufficient time to validate it.

- ☐ The results of the laboratory studies showed that the attenuation of the anion, Cr, was negligible in comparison to that of the cations, Pb and Cd. It was also found that the calcic and smectitic soils attenuated the two cations best. For Cr, the highest attenuation occurred in the kaolinitic soil.

- ☐ A matrix was compiled from literature to facilitate comparison of different physical and chemical properties of soil materials and their ability to attenuate different chemicals. Adsorption isotherms for Pb and Cd obtained from the literature compare well with isotherms obtained during this study.

Field studies

Infiltration experiment

☐ Results of the organic contaminants added during the infiltration experiment showed possible attenuation. Butyric acid and aniline were not detected in any of the water samples. Phenol was only detected at 1 m and was not detected at depth. Toluene was detected at 4 m and its derivatives at 1 m. On the other hand, aliphatic hydrocarbons were detected at 8 m, two days after the infiltration experiment indicating that the subsurface environment will not be as effective in attenuating all compounds.

Industrial liquid waste evaporation pans - Vissershok

☐ Heavy metals were detected at significant concentrations 1.6 m below the pans. The migration of contaminants to depth may be due to the fact that the attenuation capacity of the clay has been exceeded. Alternatively, the attenuation potential of the clay under the pans is not as high as might have been assumed for this Class 1 site. The uncertainty as to the loading history makes it difficult to speculate as to what the dominant factors were in the migration and attenuation of the metals in this area.

Industrial liquid waste - flood spreading

☐ The metal concentrations in the unsaturated zone and groundwater are low at this site. Most of the metals precipitated at the surface during flood spreading. The low mobility of the metals is attributed to the high buffering capacity of the sands.

Domestic solid waste disposal site

☐ Natural attenuation of organic compounds is evident in the aquifer as shown by the decline of DOC both in time and in space.

Industrial liquid waste

☐ The heavy metal pollution shows a marked decline a few metres from the source, indicating that metals are not very mobile in this area. The low mobility is attributed to the high pH buffering capacity in the aquifer. Natural attenuation of organic compounds is also apparent.

Solute transport modelling

☐ The CHAIN_2D model was selected as a suitable code for simulating the movement of water and solutes in the vadose zone. The model was used in this study without any modifications.

☐ The sensitivity analysis of CHAIN_2D model to changes in input parameters showed that the most important parameters influencing the attenuation of heavy metals in soils were soil moisture retention, saturated hydraulic conductivity, climate, soil bulk density and the adsorption isotherm coefficient.

☐ The CHAIN_2D model was successfully validated on a laboratory scale using data from soil column breakthrough curves. The order of adsorption of the heavy metals considered was as follows : Pb > Cd > Cr. This sequence was found to be valid for both distilled water solutions and the Coastal Park leachate. The Wilmot coefficient of agreement used in the laboratory validation of the model was calculated as d = 0.9959 showing a good agreement between the laboratory data and the CHAIN_2D predictions.

☐ The CHAIN_2D model was also validated on a field scale using soil moisture content data. The validation was not as successful as the laboratory scale validation.

GIS

☐ Using GIS, a methodology has been developed for generating regional/national scale maps of vadose zone attenuation characteristics. It has been demonstrated that land type maps, which are available at a scale of 1:250 000, can be used to derive soils information per land type. The following maps were derived:

→ clay content per land type
→ lime presence per land type
→ Fe content per land type
→ average CEC per land type

☐ The soils information maps when combined with contaminant attenuation characteristics can be used to obtain a qualitative indication of the attenuation potential of a given land type. In this study qualitative attenuation maps were derived by using:

→ clay content and lime to map attenuation potential of cation forming elements
→ Fe content to map attenuation potential of anion forming elements
→ CEC to map attenuation potential of basic organic molecules and organic cations

☐ The qualitative attenuation maps can be used to rapidly assess/identify areas with low or high attenuation potential. When such maps are combined with vulnerability maps, a means is provided for rapidly assessing groundwater pollution risks on a regional scale.

☐ A limitation of using land type maps in attenuation studies stems from the fact that the spatial distribution of the soils is not known within the land type. The results can not, therefore, be used for site specific work.

Prototype expert system models

Two prototype expert systems have been developed to address the feasibility of using expert systems as decision-support tools for vadose-zone contaminant attenuation assessment purposes. ***Additional work is still required on these systems. At present, their use is solely for demonstration purposes only.*** The two systems developed are:

☐ A prototype expert system which uses climatic, topographical, vegetation, and soil-texture and soil-colour data to deduce the presence of important soil characteristics for contaminant-attenuation purposes, for feasibility-level or preliminary site-screening investigations.

☐ A prototype expert system which performs as a relative contaminant-attenuation assessment aid for specific contaminants within three contaminant categories, namely: organic non-polar contaminants, heavy metals and anionic inorganic trace contaminants.

The second prototype expert system, the contaminant attenuation assessment aid, is the most relevant in attenuation studies. The potential uses of this expert system are

☐ to compare the suitability of specific sites for disposal of wastes

☐ to give preliminary indication of contaminants which are likely to be problematic for land users, soils, agriculture or groundwater, based on contaminant toxicity type, soil type, and the resource at risk.

Comment on Preferential flow

In this study, preferential flow was not considered. Homogeneity and uniform wetting fronts during infiltration were assumed. It is noted that if preferential flow occurs, the transport of contaminants to the saturated zone will be at velocities many times those calculated with the convective-dispersive theory. The attenuation or filtering capacity of a soil will be greatly reduced since there will be less time for degradation of chemicals and less surface area for sorption. In situations where preferential flow is significant, natural attenuation will, therefore, play a minor role in reducing the concentration of contaminants.

RECOMMENDATIONS

Recommendations are given in two sections: implementation and further research.

Implementation

GIS vadose zone attenuation maps

The methodology that was developed in this study for generating vadose zone attenuation maps for the Western Cape should be applied to the whole country. This should be possible because land type maps which were used to generate the attenuation maps are available for the whole country at a scale of 1:250 000.

The recommended approach is as follows:

☐ use available land type maps to produce soils characteristics maps per land type.

☐ using soils characteristic maps , produce qualitative contaminant attenuation maps.

The qualitative contaminant attenuation maps can be used for regional planning purposes. They can be used

☐ for land-use planning to give a broad overview of favourable or unfavourable areas for certain human activities.

☐ to indicate potentially suitable areas for further detailed investigation.

☐ in combination with geological and hydrogeological maps to assess aquifer vulnerability to pollution.

Solute transport modelling

The modelling package CHAIN_2D, which is now available at the University of Stellenbosch, can be utilized to model fate and transport of contaminants in the unsaturated zone. Specifically, the model can be used

☐ to investigate the likely variability in contaminant behaviour in a much wider range of conditions than is possible experimentally.

☐ to estimate the contaminant attenuation capacity of the unsaturated zone.

☐ to estimate the time it would take a contaminant to migrate from the surface to the water table. Using this approach, sites can be compared or ranked in terms of pollution risk.

Further research

Relationships between porous media characteristics, contaminant types and contaminant attenuation

An integrated literature, laboratory and field studies is recommended. A significant amount of literature still needs to be sourced regarding the relationships between soil characteristics, contaminant properties and contaminant attenuation. For each contaminant, information on the following should be collected:

☐ mechanisms of attenuation
☐ relationships between contaminant attenuation and porous media properties
☐ relationships between contaminant attenuation and contaminant properties
☐ measured adsorption coefficients for a given contaminant and conditions under which the results were obtained, eg pH, organic carbon content, etc.

Verification of these literature based results should be conducted for South African soils at the **laboratory scale**. The laboratory tests should have an added requirement of producing results which can be used for management purposes. For this reason, it is recommended that the selection of soils for laboratory experiments should be conducted in close consultation with the ISCW, who are the suppliers of land type and soil maps.

The following type of experiments are recommended:

Experiments designed to compare and rank soils according to their attenuation potential

☐ Batch experiments to measure the adsorptive capacity of soil materials at different pH values. If enough measurements are conducted, regression equations can be obtained which can be used for ranking.

Experiments designed to predict transport of contaminants in the subsurface

☐ Batch experiments to measure the distribution coefficient (K_d) of a given contaminant

☐ column experiments designed to obtain information on transport of contaminants in porous media.

Field studies should be conducted in areas where (1) pollution incidences have been observed and (2) pollution loading is high but no groundwater pollution has occurred. The idea here is to establish the most important factors at the field scale which can be used as 'predictors' for aquifer pollution risks. These factors may be related to aquifer sensitivity, contaminant attenuation characteristics or pollution loading.

Decision aids

The data/information from above should be captured in a form that can be utilized by practitioners. GIS is best suited for this purpose. Using GIS, contaminant attenuation information can be combined with information on aquifer sensitivity (vulnerability) to determine aquifer pollution risks under different land-use management practises.

The GIS component should also investigate ways of incorporating solute transport modelling - through coupling with mathematical models. There are a spectrum of strategies for linking models to GIS ranging from loose through tight coupling to an embedded system approach in which the GIS and the model are fully-integrated into a single software system.

In applying GIS, the significance of spatial variability must be investigated and users must be cautioned about the limitations. The spatial variability investigation should be conducted in close consultation with the ISCW.

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CHAPTER 1

INTRODUCTION

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1. INTRODUCTION

1.1 Preamble

Water is one of South Africa's most precious natural resources. Unfortunately, the country is not blessed with ample water resources. Approximately two-thirds of the country is semi-arid and water demand is likely to exceed supply in many parts by the year 2010 (DWA&F, 1986). Groundwater resources, although limited in comparison to surface water, will play a major role in meeting this water supply deficit in large parts of the country. It is, therefore, very important that every effort be made to safeguard the existing groundwater resources.

Groundwater contamination can occur as a result of various activities of man. The vulnerability of an aquifer to pollution is directly linked to (Foster, 1987):

(i) inaccessibility of the saturated zone, in a hydraulic sense, to the penetration of mobile contaminants;
(ii) attenuation capacity, as a result of physicochemical retention or reaction of pollutants.

These two components interact primarily with the following respective components of subsurface pollution loading (Foster, 1987):

(iii) the manner of pollutant disposition;
(iv) the physicochemical mobility and persistence of the pollutant.

The degree/extent of interactions between the soil/aquifer characteristics and the pollutants (components (i) - (iv)) will determine the vulnerability of an aquifer to pollution. Defining the extent of such interactions is complex and requires knowledge of a multitude of physical, chemical and sometimes biological parameters for both the porous medium and the pollutant of interest. Before the extent of interactions between the components can be defined, it is important that each component be well understood. The present study focused on the contaminant attenuation characteristics of the subsurface (components (ii) and (iv)). Contaminant attenuation is usually defined as a process by which a decrease in concentration of a given species occurs for some fixed time or distance travelled. A number of physical, chemical and biological processes occur in the subsurface which may work individually or in combination to reduce the concentration of contaminants.

Another WRC project: 'The relationship between the geotechnical and hydrogeological properties of residual soils and rocks in the vadose zone', is currently in progress. One of the main objectives of the project is to identify the hydrogeological properties of soils and rocks in the vadose zone which affect aquifer recharge and contamination. It is envisaged, therefore, that this project will contribute significantly to our understanding of the accessibility of the saturated zone (component (i) above).

The fact that contaminants may be naturally attenuated is an important factor which should be taken into account in groundwater protection strategies. If the latter are not to be unnecessarily restrictive, the extent of contamination tolerable in a given situation must be determined. During infiltration through the unsaturated zone, many contaminants are naturally attenuated, but not all subsurface environments are equally effective in this respect. The degree of attenuation will to a certain extent depend on porous media properties. If one knew the porous media properties, and in addition contaminant properties, an assessment can be made regarding the extent to which natural attenuation can be depended upon to reduce the concentration of potential contaminants.

1.2 Aims

As indicated above, a project was formulated to investigate the contaminant attenuation capacity of the soil/aquifer system with special emphasis on the vadose zone. The main aim of the project was:

- ☐ To determine the contaminant attenuation capacity characteristics of various soils, aquifers and the subsurface environment as a whole for specific contaminants in order to provide a useful tool for planners, policy makers and pollution control authorities to assess groundwater pollution risks.

In order to achieve this, the following specific objectives were set:

- ☐ To determine the relationship between soil physical and chemical properties (e.g. soil type, soil thickness and other attributes) and its contaminant attenuation capacity;
- ☐ To determine similar relationships for the vadose zone and the aquifer itself;
- ☐ To provide information in the form of GIS based maps and/or expert system based decision aids for the use of planners.

The first two objectives relate to determining the relationships between porous media properties, contaminant types and contaminant attenuation. The third objective requires that information/knowledge gained from the latter be provided in a form which can be utilized by managers and practitioners when assessing groundwater pollution risks.

1.3 Approach and report layout

This research was conducted by two research institutions: CSIR and University of Stellenbosch. The project was initially supposed to run for three and half years but was later extended for another year. Figure 1.1 shows the various components of the research and the involvement of each institution. The components are described below.

In order to address the first two objectives above, the questions that had to be answered were:

- ☐ what are the important *porous media properties* relevant to contaminant attenuation?
- ☐ what other *factors and processes* are important in the attenuation of contaminants in the subsurface?

In order to address these questions, integrated literature, laboratory, field and computer modelling studies were conducted.

The main aim of the literature study was to identify the important factors and processes that are potentially important in the attenuation of heavy metals and organic compounds in soils. The laboratory studies focused on obtaining data on the attenuation characteristics of a range of soil types. The literature and laboratory studies are reported in Chapter 2 and Chapter 3 respectively.

Field studies were important in order to verify whether or not contaminant attenuation characteristics, as indicated by the literature and laboratory results, could be confirmed on a field scale. The approach adopted included sampling at a number of sites where waste disposal activities have occurred for a number of years to examine the distribution of contaminants in space and from this, to postulate on the contaminant attenuation processes. In addition, field infiltration experiments were conducted. At the initiation of the project, it was envisaged that sampling would also be conducted at agricultural sites. On the advice of the steering committee, it was decided to exclude this aspect of the study, mainly because of the difficulties encountered in trying to find laboratory facilities where soil organic extraction could be conducted. Results of field studies are reported in Chapter 4.

Computer modelling studies were conducted to identify the important factors and processes that will influence contaminant attenuation in the subsurface. Modelling offers an effective way of making generalised predictions and in addition offers an opportunity to investigate the likely variability in behaviour in a much wider range of conditions than is possible experimentally. Activities conducted here included selection of a suitable model, sensitivity analysis, measurement of parameters influencing solute movement in soils and development of software to aid the modelling process. A PhD thesis (Eigenhuis, 1997) on this work is available at the University of Stellenbosch. A summary of the latter is given in Chapter 5.

The knowledge/information gained from the studies above was then used to address the third objective of the study: development of decision aids. Two decision aids, namely GIS and expert system models, were investigated.

The GIS component was aimed at developing a methodology for generating regional scale maps of vadose zone attenuation characteristics. Specific objectives included:

☐ to produce soils characteristic maps from available data sets.
☐ to produce qualitative attenuation maps for a given group of contaminants.

Work conducted on this aspect of the study is reported in Chapter 6.

The feasibility of developing a prototype, expert systems based decision support software for use when assessing contaminant attenuation potential of soils is reported in Chapter 7.

In Chapter 8, major findings of the research are discussed and conclusions given. Recommendations for further research are given in Chapter 9.

1.4 Comment on preferential flow

In this study, preferential flow was not considered. Homogeneity and uniform wetting fronts during infiltration were assumed. It is noted that if preferential flow occurs, the transport of contaminants to the saturated zone will be at velocities many times those calculated with the convective-dispersive theory. The attenuation or filtering capacity of a soil will be greatly reduced since there will be less time for degradation of chemicals and less surface area for sorption. In situations where preferential flow is significant, natural attenuation will, therefore, play a minor role in reducing the concentration of contaminants.

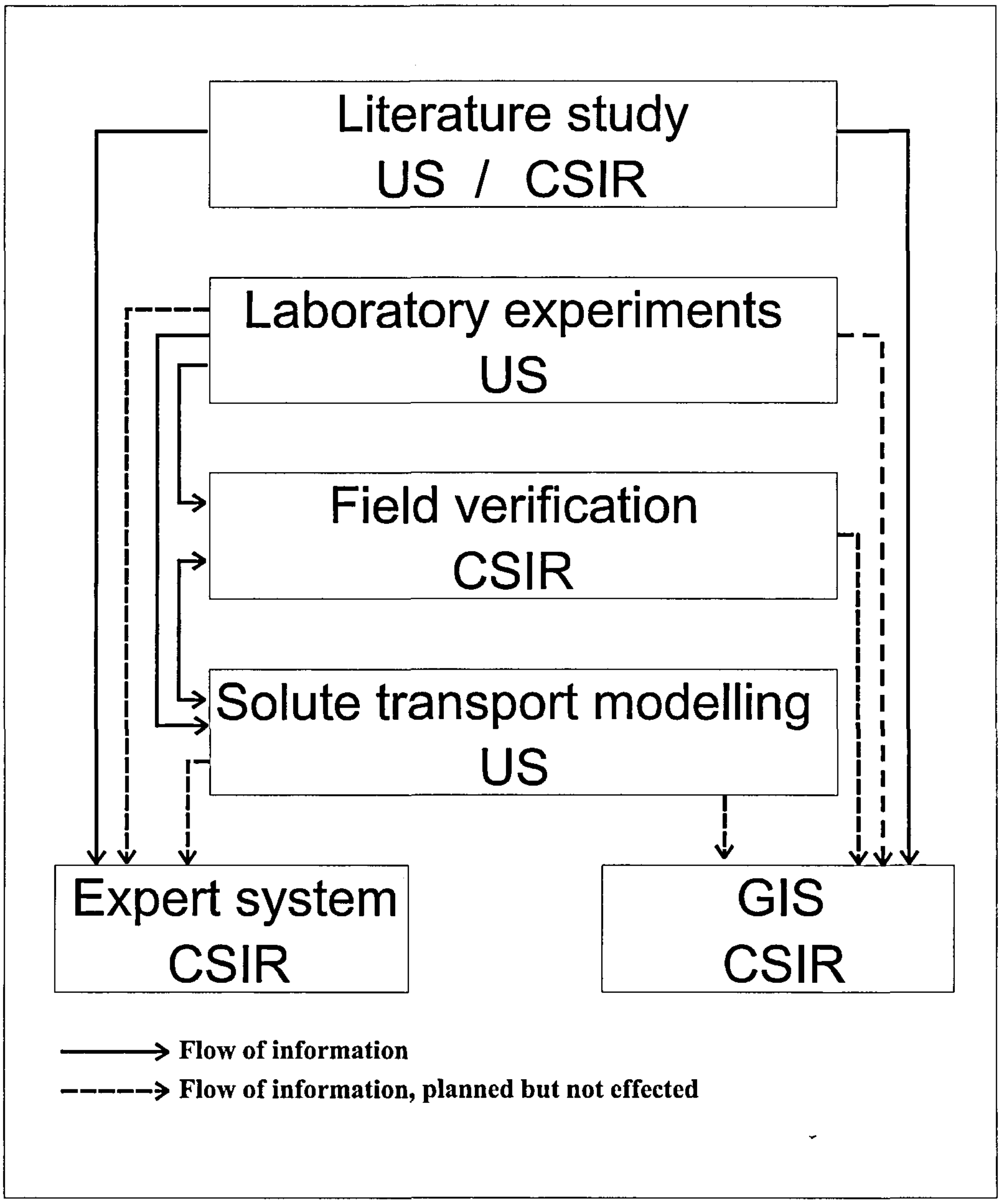

Figure 1.1 : Components of the research and involvement of CSIR and University of Stellenbosch (US)

CHAPTER 2

LITERATURE REVIEW

BY O T N SILILO

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2. LITERATURE REVIEW ON ATTENUATION OF CONTAMINANTS IN THE SUBSURFACE

2.1 Introduction

During contaminant migration through the subsurface, a variety of physical, chemical and biological processes will occur, by which the concentration of various parameters will be reduced. This chapter reviews the literature on contaminant attenuation processes in soils. The emphasis is on chemical processes. Transport processes of advection and dispersion are not discussed. Biological processes are mentioned but only briefly in the section on attenuation of organic contaminants.

In the section that follows, a summary of important porous media (soil) properties relevant to contaminant fate is given. This is then followed by a description of the chemical processes that are potentially important in the attenuation of inorganic and organic compounds in the subsurface.

2.2 Porous media properties

Porous media (soil) properties such as surface area, particle size, structure, mineralogy, organic and mineral coatings affect the capacity for adsorption of solutes. Porous media, such as soils, involve an underlying mineral coupled with adsorbed organic and inorganic species which possess a heterogeneous collection of adsorption sites. The surface charge is generally negative and therefore there is greater adsorption of cationic species than anionic species (Oliver *et al.*, 1996).

The grain size distribution of gravel, sand, silt and clay provides a basis for classifying soil by texture. Texture and surface area are closely related so that as particle size decreases, the surface area per unit mass increases, thereby increasing the capacity for adsorption. In addition, finer-textured soils are generally less permeable and, therefore, will have a longer contact time for sorption of dissolved species, than coarser-textured soils.

The effect of surface area can be seen in the case of negatively charged species, where the most significant factor affecting the mobility of this class of compounds in soils is the oxide surface (Brusseau and Wilson, 1995). For example, in the weathering process, ferric iron precipitates as amorphous material, which has several hundred square metres per gram of available surface. Even though the amount of iron is a fraction of percent by weight in soil, it is often the dominant surface affecting the sorption of metal contaminants because of this extremely high surface area (Brusseau and Wilson, 1995).

The structure of porous media determines the surface area exposed and will have an effect on water velocity. Structure here refers to the degree of aggregation of the primary soil particles into structural units. The presence of aggregated soil enhances the potential for bypass flow in the macropores between the aggregates, reducing the contact time for sorption.

Other factors that can affect the adsorptive capacity of soils include the mineralogy and presence of inorganic and organic coatings. Solutes are less mobile in soils that provide a large quantity of sorption sites. Oxides of Fe, Al, and Mn can provide chemisorption sites for cation and anion forms of elements. Layer silicate minerals provide exchange sites for cations, and a few chemisorption sites for both cations and anions (McBride, 1994). Non-crystalline alumino-silicates possess large quantities of chemisorption sites for both cations and anions.

The ionic or polar part of soil organic matter provide cation adsorption sites while the non-polar part can be involved in hydrophobic sorption of organic compounds. Organic material in soils is formed from breakdown of plant and animal material or by adsorption of low molecular weight colloids and contains functional groups of carboxylic acids, carbophenolic acid and phenoxy hydroxyl acids (Oliver *et al.* 1996).

2.3 Chemical processes important in inorganic contaminant attenuation

2.3.1 *Introduction*

A number of chemical processes are important in the attenuation of inorganic chemicals in the unsaturated zone. These include complexation, dissolution/precipitation, adsorption, reduction/oxidation and hydrolysis. The importance and role of these processes are discussed below, with special emphasis on heavy metal attenuation.

Before the processes are discussed, the role of pH, which is the 'primary variable' controlling these processes, is described.

2.3.2 *pH*

Soil pH will affect the mobility of some contaminants. For example, with the exception of selenium, chromium, and arsenic at some valence states, the mobility of trace elements and heavy metals increases with decreasing pH (Brusseau and Wilson, 1995). For metal cations, high pH favours sorption and precipitation as oxides, hydroxides and carbonates.

Although pH is regarded as the primary variable, there are instances where well-buffered soils can resist pH changes whether acidity or alkalinity is introduced in one form or another. Some of the most important mechanisms potentially involved in this ability to buffer pH are (McBride, 1994):

- carbonate mineral buffering: Free carbonate minerals in soil, most commonly Ca and Mg carbonates, are a reserve of alkalinity that can neutralize soil acidity or alkalinity introduced as pollutants. The carbonate buffer capacity of many calcareous soils is so large that it would take centuries of acid inputs (natural and anthropogenic) to have an effect on pH.

- exchangeable base cation buffering: added acid cations (H^+, Al^{3+}) exchange base cations from clay or humus exchange sites, to cause pH buffering. For example

$$2H^+ + Ca^{2+}\text{-clay} = 2H^+\text{-clay} + Ca^{2+}$$

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

The role of pH in complexation, dissolution/precipitation, adsorption, reduction/ oxidation and hydrolysis is described below.

2.3.3 *Complexation*

A complex is an ion that forms by combining simpler cations and anions and sometimes molecules. The central cation is usually one of the large number of transition metals making up the 'd block' of the periodic table. The surrounding anions, known as ligands, include many of the common inorganic species found in groundwater e.g. Cl^-, F^-, Br^-, $SO4^{2-}$, $PO4^{3-}$ and $CO3^{2-}$. Organic molecules with free electron lone pairs on the atoms, such as the N atoms in amino acids and S atoms in thiol compounds, can also behave as uncharged ligands.

Most inorganic reactions involving complexes are kinetically fast and can be examined quantitatively using equilibrium concepts. Calculation of the distribution of metals among various complexes involves the solution of a series of mass law equations.

Depending on the nature of the ligand, or the solubility product, complexation processes are classed differently. If the ligand is a hydroxyl group on the surface of a soil solid, the process is termed adsorption. If the complexation reaction leads the formation of an insoluble product in the liquid phase, the process is termed precipitation.

In general, the extent of complex formation depends on (a) concentration of metals and ligands, (b) nature of metals and ligands and (c) pH.

The nature of metals and ligands present in the system is probably best discussed in terms of the Hard and Soft Acid and Base (HASAB) theory. According to this theory, metals and ligands are classified as hard or soft Lewis acids and bases. A Lewis acid is an electron accepting entity while a Lewis base is an electron donating entity. Thus, a metal is viewed as a Lewis acid and a ligand as a Lewis base.

In Table 2.1, the common classification of metals and ligands according to the HASAB concept is given. Soft ligands are easily polarized and therefore readily donate electrons to form covalent bonds with soft metals, which are typically relatively large with low charge. The general rule which may be distilled out of this is that "soft acids (metals) bond preferentially with soft bases and hard acids bond preferentially with hard bases" (McBride, 1994). The effect of pH is illustrated in Figure 2.1 which shows a log C - pH diagram for chromium hydroxide complexes. The plot shows that at pH below 4, Cr^{3+} is the dominant Cr species. As the pH increases, the various hydroxy complexes dominate (Domenico and Schwartz, 1990).

Table 2.1 : Classification of metals and ligands according to the Hard and Soft Acid and Base (HASAB) theory (modified after McBride, 1994).

	Lewis acids (Metals)	**Lewis bases (Ligands)**
Hard	H^+,Li^+,Na^+,K^+,Mg^{2+},Ca^{2+},Sr^{2+},Ti^{3+},Cr^{3+},Mn^{2+},Fe^{3+}, Co^{3+},Al^{3+},Si^{4+}	NH_3, $R\text{-}NH_2$ (amines) H_2O, OH^-, O^{2-}, R-OH CH_3COO^-, CO_3^{2-}, NO_3^-, PO_4^{3-}, SO_4^{2-}, F^-
Borderline	Fe^{2+},Co^{2+},Ni^{2+},Cu^{2+},Zn^{2+},Pb^{2+}	$C_6H_5NH_2$ (aniline & other aromatic amines) C_5H_5N (pyridine), NO_2^-, SO_3^{2-}, Br^-
Soft	Cu^+, Ag^+, Cd^{2+}, Hg^+, Hg^{2+}	CN^-, CO, S^{2-}, R-SH (sulfhydryl), $R\text{-}S^-$

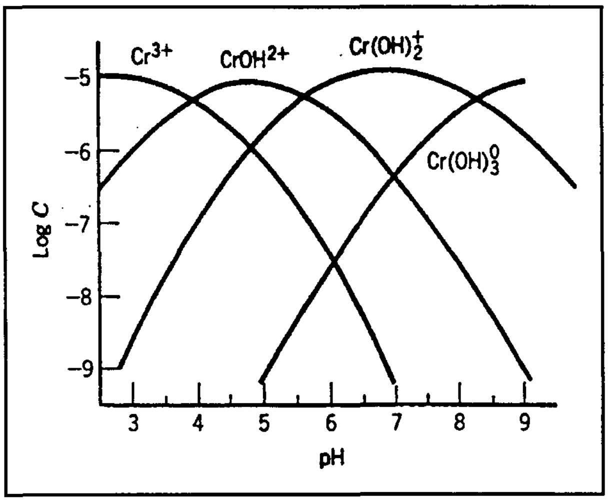

Figure 2.1 : Log C - pH diagram for chromium hydroxide complexes (after Domenico and Schwartz, 1990)

2.3.4 *Precipitation and dissolution*

Certain components of an aqueous system may combine (complex) to form an insoluble product. A solid has the potential to precipitate once its solubility product has been exceeded in a specified system. For a general precipitation reaction forming a solid A_pB_q according to the reaction

$$pA + qB \rightleftharpoons A_pB_q$$

the solubility product, K_{sp}, is defined as

$$K_{sp} = [A]^p[B]^q$$

where [A] and [B] are the free (or uncomplexed) concentrations of components A and B (expressed in moles/l). From this expression, it follows that any competing process taking place in a system which has an effect on [A] and/or [B] will influence the likelihood of a precipitate forming. Thus, it is clear that processes influencing metal complexation will play a role here.

Precipitation is greatly dependent on pH. Most metals will precipitate at high pH levels as hydroxides. However, continued elevation of pH will increase the solubility of metals with amphoteric characteristics as shown in Figure 2.2.

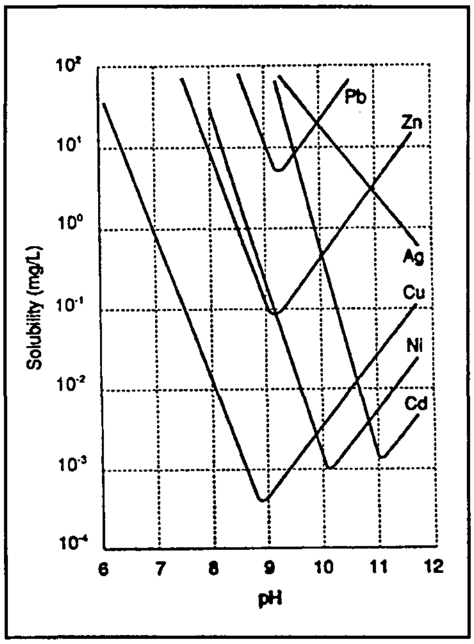

Figure 2.2 : Solubilities of metal hydroxides as a function of pH
(after LaGrega *et al.*, 1994)

2.3.5 *Adsorption processes*

Adsorption is a reversible process involving the attraction of a chemical to the sorbent particle surface and retention on that surface for a time that depends on the affinity of the chemical for the surface.

Mechanisms by which inorganic substances can adsorb onto sorbents were summarized by Oliver *et al.* (1996) as follows:

(i) Physisorption - weak dispersion or dipole interactions, but including stronger hydrogen bonds

eg -OH --- O- or -NH --- N-

(ii) Chemisorption - chemical bond formation (usually covalent), which often occurs as a slow reaction after sorption to the surface

(iii) Ion exchange - cation and anion exchange which includes sorption onto iron and manganese oxyhydroxides

cation exchange - removal and replacement of a surface cation
anion exchange - removal and replacement of surface anion

(iv) Sorption or complexation with organic substances

$$\begin{array}{lcl} SS-OH+L+M^{z+} & = & X-L-M^{(z+1)+}+OH^- \\ SS-L+L & = & SS-L-L \end{array}$$

(v) Incorporation into mineral lattice

$$\begin{array}{llcllcl} X-X & & & & X-X & & \\ X-Ca & +M^{(z+1)} & = & X-M & & + & zCa^{2+} \\ X-X & & & & X-X & & \end{array}$$

where SS = sorbent surface
M = metal or cation
L = organic ligand/matter or organic compound
X = Fe, Al mineral

The adsorption of heavy metals onto soils follows either the linear or the Freundlich adsorption isotherms (see section 2.4.2.2). Heavy metal adsorption will be influenced by particle size, organic matter content, clay content, Fe, Al, Mn oxides and hydroxides of the sorbent. However, there is no strong correlation between adsorption and any single soil property (Oliver *et al.*, 1996). Heavy metal adsorption is generally increased by increasing the pH, which causes a larger net negative surface charge. However increasing the ionic strength causes competition for adsorption sites, thereby decreasing the adsorption (Oliver *et al.*, 1996).

The heavy metals have characteristic adsorption onto oxides where a rapid increase in adsorption occurs over a narrow pH range (Oliver *et al.*, 1996) as shown in Figure 2.3.

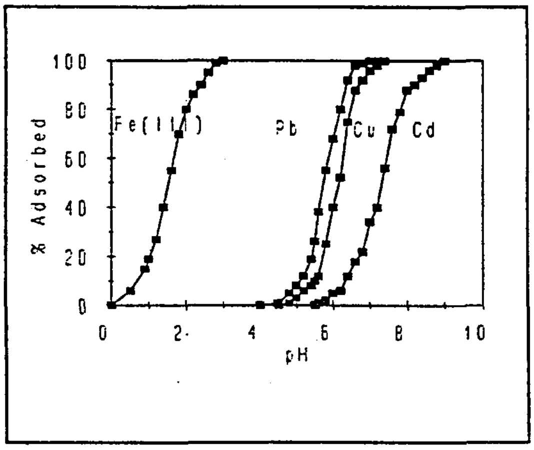

Figure 2.3 : Adsorption of Fe^{3+}, Pb, Cu and Cd on silica at pH ranges (after Oliver *et al.*, 1996)

Generally, the heavy metal divalent cations adsorb in the order Pb >Cu >Cr >Cd >Zn. This order is dependent on the soil/water conditions such as pH and species which can affect the solubility of the heavy metal (Oliver *et al.*, 1996).

2.3.6 *Oxidation-reduction*

Oxidation-reduction (redox) reactions involve the transfer of one or more electrons between chemical species. Factors influencing these reactions are (a) redox potential, (b) pH, (c) temperature and (d) the composition of the system. A change in soil redox state may affect the fate of a metal through (i) a change in pH, (ii) a change in solubility, (iii) changing solution phase ligands and (iv) the dissolution of mineral phases. For a more detailed discussion on the role of redox reactions in aqueous speciation and solubility, reference is made to Hem (1985).

The redox potential in soils is influenced by the soil oxygen content. Waterlogged soils become oxygen deficient because of (i) the low solubility of oxygen in water and (ii) the continued use of oxygen by biological processes occurring in the soil. The influence of pH results from the fact that H$^+$ participates in many redox reactions. However, it should be noted that in certain instances, soil pH is determined by the redox state of the soil system. Thus, it is not always true to view pH as influencing redox reactions. Ligands present in the system will also affect redox reactions.

Redox reactions in soil systems can cause appreciable changes in the distribution of elements in soil systems. This follows directly from the fact that redox processes cause the dissolution of mineral phases which can then lead to the formation of new phases. In addition, the dissolution of a mineral phase will lead to the solubilization of metals which were adsorbed onto the phase. For example, amorphous oxides of manganese and iron are known to adsorb trace metals. Reducing conditions will bring about dissolution of these phases, with the net result that adsorbed metals will be mobilized. Furthermore, the surface properties of the soil system will also change during a redox episode. Freshly precipitated oxides of manganese and iron provide a recently re-oxidized soil with new reactive sites for metal adsorption (McBride, 1994).

In the unsaturated zone, oxidation can produce relatively insoluble oxides that may control the solubility of many metals, such as Cu, Fe, Mn, Hg, Cr, and Ni (Runnells, 1995). If anaerobic conditions develop, mobilization of some of the metals can occur. For example, Runnells (1995) cited a case where rapid infiltration of domestic sewage in Tucson Basin, US, caused a loss of oxidizing conditions in the unsaturated zone and led to increased movement of Cu, Zn, Mn, Ni and Pb through the soil.

Metal fate will also be affected if a solution phase ligand is oxidized or reduced. For instance, in a system containing sulphate, metal-sulphate species will keep the metal in solution. However, the reduction of sulphate to sulphide will facilitate the formation of insoluble metal sulphide complexes which have the potential to immobilize the metal. Conversely, the oxidation of sulphide will lead to the solubilization of metal sulphides under oxidizing conditions.

2.3.7 *Hydrolysis*

Hydrolysis refers to the breakdown of substances by water and its ionic species H^+ and OH^-. For example,

$$RX + H_2O \rightleftharpoons ROH + HX$$

or:

$$RX + H_2O \rightleftharpoons RH + XOH$$

RX is a dissolved inorganic substance with R representing the main portion of the dissolved molecule and X a replaceable atom or group. The resulting ROH or XOH may be either an aqueous or solid product depending on the solubility of the substance and the pH of the water. Hydrolysis reactions can be considered to be a type of acid-base reaction.

Common examples of hydrolysis in the unsaturated zone involve the precipitation of dissolved ferric (Fe^{3+}) iron, aluminium and manganese by reaction with water to form solid oxyhydroxides plus aqueous H^+. In an aerated environment, the dissolved concentrations of these metals are limited to low values by the processes of hydrolysis and precipitation.

In addition to ferric iron, several toxic metals form highly insoluble hydroxides in the range of pH 6 to 9. These include Cu (above a pH of about 6.5), Cr^{3+} (above a pH of about 6), Ni (above a pH of 9) and Zn (above a pH of about 9) (Runnells, 1995). In some cases coprecipitation of two or more contaminants may occur, e.g. Mo is strongly coprecipitated with iron oxyhydroxide under moderately acidic conditions (Runnells, 1995).

2.3.8 *Summary*

The factors and processes that will affect the fate of inorganic contaminants in the soil include:

- ☐ The characteristics of the contaminant (eg. solubility)
- ☐ The physical and chemical conditions in solution (eg. pH, redox conditions, temperature)
- ☐ The presence of other reactive species (eg. oxygen, oxidising or reducing agents, counter ions)
- ☐ The presence of complexing ligands
- ☐ The nature and surface area of solid particles and adsorbing surfaces

McBride (1994) related the mobility of elements in soil to their characteristics as defined by their ionic radii and valence (Figure 2.4). The valence/radius ratio, or ionic potential, is a key parameter in determining which of the four chemical forms the element takes in water. Figure 2.4 can be used to predict the chemical form for elements, but an assessment of elemental mobility requires knowledge of the soil properties as well. In broad terms, the mobility of the four groups of elements in soil can be classified as shown in Table 2.2.

Table 2.2 : Mobility of elements in soil on the basis of ionic charge and radius

Group	Characteristics	Mobility
1	soluble, weakly hydrating cations	strongly held by clays and humus
2	soluble, strongly hydrating cations	exchangeable and somewhat mobile, excepting strong chemisorbers such as Pb^{2+} and Cu^{2+}
3	easily precipitated amphoteric hydroxides	immobile as insoluble oxides
4	soluble anions	mobile, excepting strong chemisorbers such as phosphate.

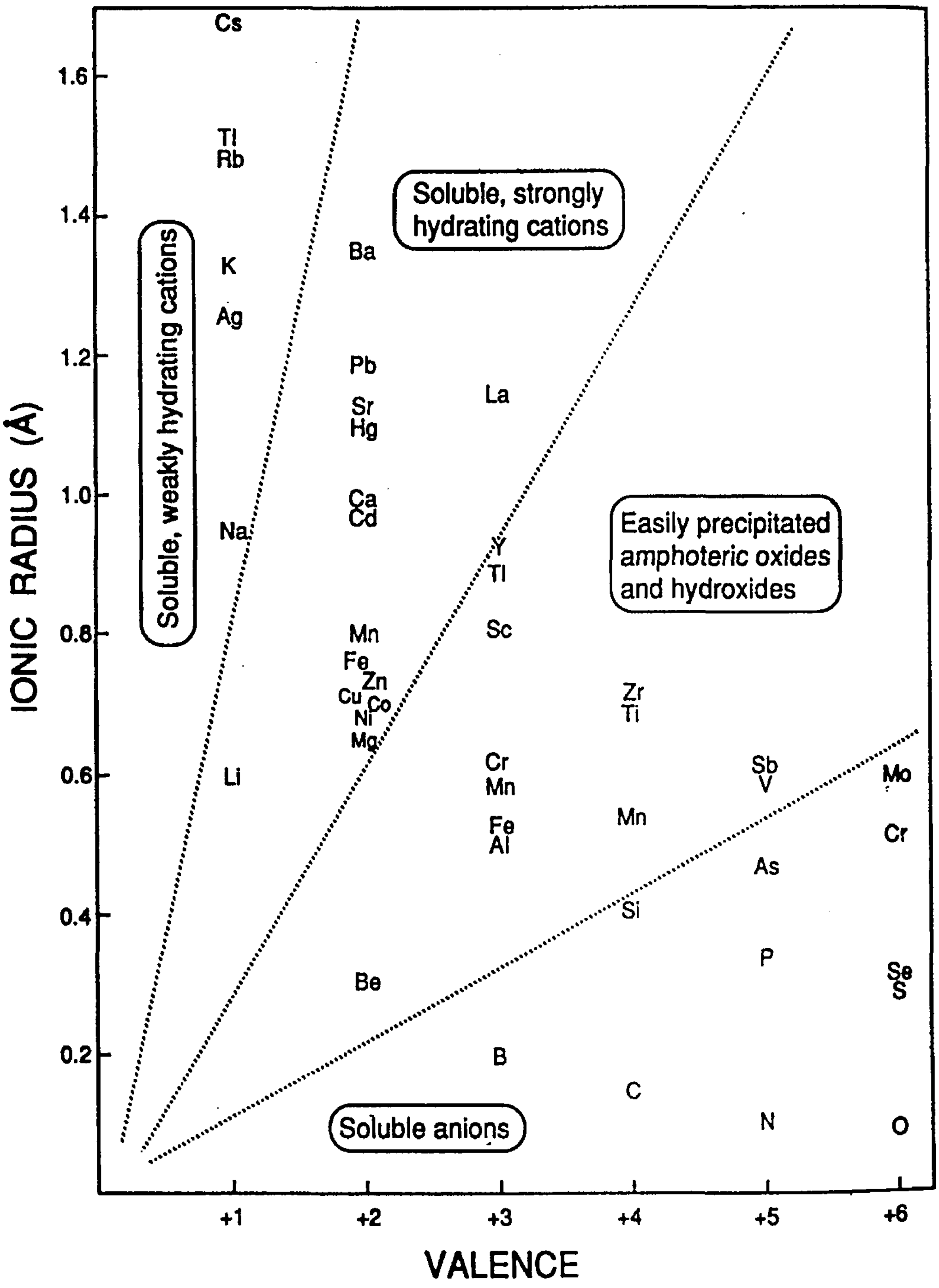

Figure 2.4 : Classification of elements in four groups on the basis of ionic charge (valence) and radius (After McBride, 1994).

The chemical and mineralogical nature of the soil will have an effect on the mobility of several compounds. A soil which has (i) a high level of adsorption surfaces, (ii) pH well buffered in the neutral or higher range and (iii) low dissolved organic carbon will be quite successful in immobilizing metals. A decrease in pH or an increase in strong complexing agents in the solution phase may enhance the mobility of metals. A change in redox condition may or may not enhance the mobility of metals in soil systems.

The factors affecting the mobility of several common inorganic species in the soil/aquifer system are summarised in Appendix 1.

2.4 Attenuation of organic contaminants in the subsurface

2.4.1 *Introduction*

There are several factors and processes that may affect the fate of organic contaminants in the subsurface. These include sorption, hydrolysis, oxidation/reduction, volatization and biological degradation. Sorption and biological transformations are often the dominant reactions governing the fate and transport of organic chemicals in the subsurface (Brusseau, 1995).

The behaviour of organic molecules in soils is mainly controlled by the chemical properties of the molecules and the surface properties of the particular soil. The relevant properties of the organic adsorbate determining its solubility are:

☐ Identity of functional groups attached to the molecule
☐ Acidity or basicity of the functional groups
☐ Molecular size and shape
☐ Polarity and charge of the molecule
☐ Polarizability of the molecule

Water is a polar solvent and smaller polar organic compounds are more soluble in water than large non-polar organic compounds. The polarity and charge can be used to broadly classify organic molecules, as shown in Figure 2.5.

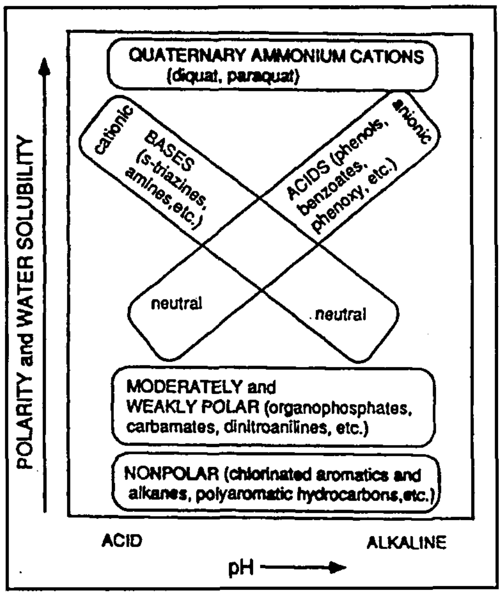

Figure 2.5 : Classification of organic compounds on the basis of their polarity and charge (after McBride, 1994)

In the sections that follow, some important aspects of organic contaminant fate in soils are described, with the main emphasis on sorption (adsorption) reactions. This summary is mainly from McBride (1994).

2.4.2 *Sorption*

2.4.2.1 The nature of physical and chemical adsorption

The mineral and organic surfaces of soils (the adsorbent) may adsorb organic molecules (the adsorbate) weakly or strongly depending on the strength of the adsorbate-adsorbent interaction. Strong interaction is indicative of chemical adsorption, or chemisorption. Weak adsorption on the other hand is characteristic of physical adsorption. Table 2.3 shows the contrasting features of chemisorption and physical adsorption.

Table 2.3 : Characteristics of Physical and Chemical Adsorption (after McBride, 1994)

Property	Physical	Chemical
Heat of adsorption	<10 kcal/mole	> 20 kcal/mole
Temperature range of adsorption	Only below boiling point of adsorbate	Both low and high temperature
Slope of adsorption isotherm	Greater at higher adsorbate concentration	Less at higher adsorbate concentration
Dependence on properties of adsorbent	Relatively little	Great
Dependence on properties of adsorbate	Great	Great
Activation energy for adsorption	Low or none	May be high
Number of layers of adsorbed molecules	Multiple (at most)	Single (at most)

2.4.2.2 Sorption isotherms

Adsorption data are usually represented by an adsorption isotherm, which is a plot of the quantity of adsorbate retained by a solid as a function of the concentration of that adsorbate in the solution phase that is at equilibrium with the solid. Isotherms have no prescribed shape. They can be linear, concave, convex or a complex combination of all these shapes. Experimentally derived isotherms can be fitted to one of several theoretical equations. Two of the most common relationships are the

Freundlich isotherm: $S = KC^n$

and

Langmuir isotherm: $S = Q^o KC / [1 + KC]$

where

K = partition coefficient reflecting extent of sorption
n = exponent, usually ranging between 0.7 and 1.2
S = quantity of mass sorbed on the surface (mg/g)
C = concentration of contaminant in the liquid phase (mg/L)
Q^o = maximum sorptive capacity for the surface (mg/g)

Figure 2.6 shows an example of Langmuir and Freundlich isotherms.

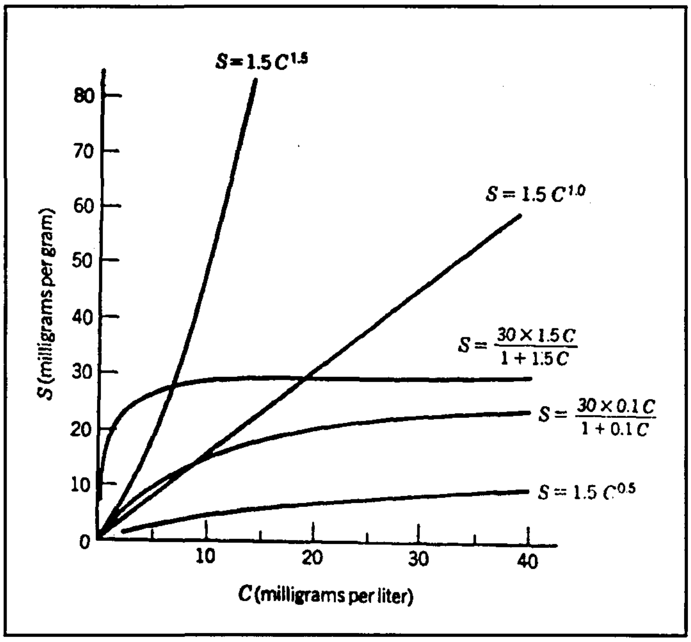

Figure 2.6 : Example of Langmuir and Freundlich Isotherms (after Domenico and Schwartz, 1990)

When n = 1, the Freundlich isotherm becomes linear. The following equation, then relates S to C

$$S = K_d C$$

where K_d is the distribution coefficient (i.e., the slope of the linear sorption isotherm). K_d values provide a simple measure of the distribution of chemicals between aqueous and soil phases. Values range from 10^5 for strongly sorbed chemicals (e.g. DDT and polychlorinated biphenyls) to 1 or less for chemicals that are weakly sorbed and miscible in water (e.g. ethanol, acetone) (Lyman, 1995).

2.4.2.3 Sorption behaviour of ionic organic molecules

Organic Cations

Organic cations are generally very soluble in water because of their ionic nature. The molecules are strongly adsorbed by cation exchange on smectites, and somewhat less strongly adsorbed on vermiculites and kaolinite. Organocations can also adsorb on soil organic matter. The extent to which organic cations are adsorbed by organic matter depends on the cation that initially occupies the exchange sites. The weakly held Na^+ is easily displaced by organocations while Ca^{2+} is less easily exchanged from humic materials.

As the pH is lowered, organocations adsorb to a lesser extent on humus. This is partly because the H^+ ion bonds more strongly with the functional groups in organic matter that generate a negative charge than metal cations, that is,

$$R\text{-}COO^- \text{---} Na^+ + H^+ = R\text{-}COOH + Na^+$$

The potential for leaching and groundwater pollution should be extremely low for organic cations in soils containing layer silicate clays and reasonable levels of organic matter.

Basic molecules

Basic organic molecules become positively charged only when they accept a proton. For any basic molecule B, the protonation reaction can be written:

$$B + H^+ = BH^+$$

where BH^+ is the conjugate acid of B. The dissociation constant of the conjugate acid, Ka, is defined by the equation

$$K_a = (B)(H^+) / (BH^+)$$

This equation shows that, as the solution is made more acidic, a greater fraction of the base is converted to the cationic BH^+ species. As the ratio of BH^+ to B in solution increases, adsorption increases.

The conjugate acid is expected to adsorb strongly on permanent-charge clays, while the base should adsorb weakly by physical forces. McBride (1994) presented isotherms which confirms that adsorption of s-triazines (basic molecule) on Na^+ - montmorillonite, will be greatest at low pH. The optimum pH for maximum adsorption usually occurs near the pK_a of the conjugate acid, where

$$pK_a = \log (BH^+) / (B) + pH$$

Organic matter can also adsorb basic molecules by cation exchange. Adsorption is sensitive to pH, which not only determines the BH^+/B ratio in solution, but also the fraction of carboxylic acid groups that dissociate and thereby become potential adsorption sites for the organic cation. The steps involved in adsorption are:

1 Organic matter dissociation
$R\text{-}COOH = R\text{-}COO^- + H^+$

2 Protonation of the organic base
$B + H^+ = BH^+$

3 Adsorption of the conjugate acid
$R\text{-}COO^- + BH^+ = R\text{-}COO^- \text{---} BH^+$

Because reaction step 1 is favoured at higher pH and step 2 is favoured at lower pH, there exists an intermediate pH at which adsorption attains a maximum. This optimum pH is usually near the pK_a of the conjugate acid. There is, then, the general rule that (McBride, 1994):

> *Optimal adsorption of an organic base on negatively charged soil colloids occurs near the pH numerically equal to the* pK_a *of the organic conjugate acid.*

Acidic molecules

Acidic organic compounds possess acidic functional groups, such as carboxylic or phenolic groups, that dissociate to form anions:

$$\text{R-COOH} = \text{R-COO}^- + H^+$$
$$\phi\text{ - OH} = \phi\text{ - O- } + H^+$$

where R is any organic group and ϕ is the phenyl group. The acid dissociation constant of these acids is defined as it is for the conjugate acid of bases in the previous section. For example, the equation defining the pKa for carboxylic acids is

$$pK_a = pH - \log (\text{R-COO}^-) / (\text{R-COOH})$$

In general, the anionic forms of these acidic molecules adsorb little, if at all, on soil organic matter and layer silicate clays because of electrostatic repulsion between the molecules and the negative charge of these soil particles. Conversely, the neutral form is retained, albeit weakly, by physical adsorption (on organic matter in particular). This class of organics is considered highly mobile and susceptible to leaching in soils. Bonding of these compounds to soil organic matter is weak. As a result, acidic organic compounds do not adsorb on soils (with permanent-charge minerals) to the extent that cationic and basic compounds do.

From the description above, it is reasonable to expect organic acids to desorb readily from soils that are leached by water. This is found to be the case in many soils, with little indication that the organics can be immobilized by adsorption. There is, however, evidence that variable-charge minerals (e.g. oxides and allophones) can strongly retain certain of these molecules by a chemical adsorption (ligand exchange) process. As in the case for organic bases, there is an optimal pH for organic acid adsorption on oxides and other variable-charge minerals, which coincide approximately with the pK_a of the organic acid. A general rule can be stated as follows (McBride, 1994):

> *Optimal adsorption of an organic acid on variable-charge soil colloids occurs near the pH numerically equal to the* pK_a *of the organic compound.*

2.4.2.4 Sorption properties of nonionic and nonpolar organic compounds

As pointed out above, the neutral forms of basic and acidic molecules are adsorbed sparingly by weak physical forces on soil particle surfaces. These molecules have polar functional groups that may allow them to be attracted to surfaces by hydrogen bonding and ion-dipole attraction. These mechanisms are not likely to be effective under moist conditions in soils because the excess water can easily displace physically adsorbed organic molecules from the surfaces. Water molecules have the dual competitive advantage of usually being present greatly in excess of the organic, and having a greater polarity than most organics. Therefore, even organics that can form fairly strong bonds are readily moved through soils by water. This is partly because polar molecules tend to be highly soluble in soil solution.

Bonding of nonionic, nonpolar organic molecules on soil materials is weaker than that of the polar nonionic molecules. Mechanisms such as hydrogen bonding and ion-dipole interaction are not operative for nonpolar molecules. In fact, adsorption of these molecules on wet layer silicate and oxide minerals is often very low, if detectable at all.

Adsorption of non-polars occurs on soil organic matter. For low organic carbon soils ($f_{oc} < 0.001$), physical adsorption dominates. Here the solutes appear to precipitate out of solution due to physical attraction to the soil's surface. Soil surface area is thus a key factor in determining sorption capacity. Soils with a high surface area per unit weight, e.g. clay and silts, adsorb more of a contaminant than those with low surface areas (Lyman, 1995).

For high organic carbon soils ($f_{oc} > 0.001$), chemical adsorption dominates. Here the solutes partition into the organic-water matrix surrounding the soil mineral particles (Lyman, 1995).

The fact that organic molecules have a stronger attraction for soil organic matter than for mineral surfaces is ascribed to the existence of hydrophobic surfaces or phases within the organic matrix. The phenomenon of hydrophobic attraction, defined as the enhanced attraction between the surface and sorbate in a solvent because the solvent-sorbate attractive interaction is weaker than the solvent-solvent attractive interaction, explains the "affinity" of non-polar organic molecules for organic matter. Since water is the solvent in soils, hydrophobic attraction becomes a driving force for sorption if the organic compound has less affinity for water than water has for itself. The disruption of water structure by the hydrophobic surfaces of dissolved non-polar molecules, is energetically unfavourable. Consequently, non-polar organics are forced out of the solution onto weakly hydrating surfaces. Because a large molecule of high molecular weight destabilizes the aqueous solution to a greater extent than a small molecule, large non-polar molecules are "pushed" out of solution onto surfaces more completely than small ones.

The hydrophobic sorption process is often modelled with a linear isotherm. Several studies (e.g., Karickhoff, *et al.*, 1979; Schwarzenbach and Westall, 1981) have shown that K_d is proportional to the weight fraction of organic carbon (f_{oc}) such that

$$K_d \quad = \quad K_{oc} \, f_{oc}$$

where K_{oc} is the partition coefficient of a compound between organic carbon and water, which can be expressed as

$$= \quad \text{(mass of sorbed chemical/mass of organic carbon) / (mass of chemical in solution/volume of solution)}$$

The variable f_{oc} can be determined from field sampling and analyses, and the variable K_{oc} has been tabulated for many chemicals (e.g. LaGrega *et al.*, 1994). When unknown, K_{oc} can be derived by correlation with a property of the chemical's hydrophobic nature. One measure of the latter is the octanol/water partition constant, K_{ow}, a dimensional equilibrium constant that characterizes partitioning of an organic solute between octanol and water.

Several workers have given regression equations that describe the relationship between K_{oc} and K_{ow}. For example, Domenico and Schwartz (1990) cited the following:

Karickhoff *et al.*, 1979 : $\log K_{oc} = -0.21 + \log K_{ow}$
Schwarzenbach and Westall, 1981 : $\log K_{oc} = 0.49 + 0.72 \log K_{ow}$
Hassett *et al.*, 1983 : $\log K_{oc} = 0.088 + 0.909 \log K_{ow}$

2.4.2.5 Summary of the sorption behaviour of organics in solution

On the basis of discussions above, the generalized behaviour of the various classes of organic compounds in soil, is summarized in Table 2.4

Table 2.4 : Sorption Affinity of Organic compounds for Soil Components
(Modified after McBride, 1994)

Molecule Type	Affinity for	Bonding forces
Non-polar or weakly polar	Hydrophobic organic phases in humic acid	Weak physical (van der Waals), hydrophobic attraction
Polar, uncharged	Humic polar groups, coordination sites of multivalent metals on colloids, mineral surface Si - O - Si groups	Dipole-dipole and ion-dipole (fairly strong to rather weak)
Polar, cationic	COO- groups of humic acid, cation exchange sites of clays	Electrostatic (Strong)
Polar, anionic	Surfaces of variable-charge minerals	Metal-ligand coordination bond (Strong)

2.4.3 *Hydrolysis*

Table 2.5 lists the tendency of various functional groups to hydrolyse. The hydrolysis reaction can be catalysed by acid or base. When oxides or silicate clays are present, hydrolysis is often catalysed by surface acidity of either the Lewis or Bronsted type.

The occurrence of hydrolysis may aid in contaminant attenuation. Certain organic compounds may be broken down by hydrolysis into simpler compounds and may then be easily assimilated through other processes.

Hydrolysis half lives can range from a few hours to years or decades. Half life is defined as the time required for 50 % of a chemical to degrade or to be removed from the local environment (Lyman, 1995).

Table 2.5 : Summary of the susceptibility of various functional groups to hydrolysis (Domenico and Schwartz, 1990)

Resistant to hydrolysis	
Alkanes Alkenes Alkynes Benzene Biphenyl Polycyclic aromatic hydrocarbons Halogenated aromatics Halogenated hydrocarbon pesticides (DDT, etc.)	Aromatic nitro compounds Aromatic amines Alcohols Phenols Glycols Ethers Aldehydes Ketones Nitriles Caboxylic acid Sulphonic acid
Susceptible to hydrolysis	
Alkyl halides Amides Cabamates Carboxylic acid esters	Epoxides and lactones Phosphoric acid esters Sulfonic acid esters

2.4.4 *Oxidation - Reduction*

Certain classes of organic compounds, such as phenols and aromatic amines, are subject to degradation by oxidation. Although oxidation can occur in soil solution by reaction with dissolved oxygen, the reaction is often more rapid in the presence of surfaces that serve as oxidizing agents or catalysts. For example, benzidine, an aromatic amine, is adsorbed on smectites as an organic cation, and is subsequently oxidized rapidly by structural iron.

Reducing agents that accumulate in soils under anaerobic conditions, such as Fe^{2+}, sulphide, etc., may react with certain classes of organic chemicals. For example, Fe^{2+} can reduce halogenated aliphatic compounds.

2.4.5 *Volatization*

Volatization is defined as the transfer of a chemical from a liquid or solid phase to a vapour or gas phase. Volatilization is governed by properties of the chemical, the soil and by climatic factors. The chemical properties include vapour pressure, boiling point and solubility of a given compound. The soil properties that will affect volatilization include soil water content, bulk density or porosity, and sorption capacity.

Volatilization provides an attenuation mechanism for those compounds that are resistant to degradation and/or weakly adsorbed, and to those that exhibit low solubilities and high vapour pressures. Volatile organic compounds include hydrocarbons, compounds with simple functional groups such as alcohols, halides, and sulphur-containing compounds, and compounds containing unsaturated functional groups such as aldehydes, ketones and esters.

2.4.6 *Biodegradation*

Biological transformation (biodegradation) results from the enzyme - catalysed transformation of organic compounds by microbes, principally bacteria, fungi, actinomycetes, algae and yeasts. This is one of the most important transformation processes for organic chemicals in soils; but at the same time, because of the numerous environmental variables, it is one of the most difficult to evaluate quantitatively. The rate at which an organic contaminant is degraded in the environment depends on several factors that are directly dependent on contaminant structure (Leahy and Colwell, 1990). These factors include (Miller, 1995):

☐ Genetic potential, or the presence and expression of appropriate degrading genes.

☐ Bioavailability, or the limiting effect of water solubility and sorption on the rate a substrate is taken up by a microbial cell.

☐ Steric effects, or the extent to which substituent groups sterically hinder contact between the active site of the degrading enzyme and the organic molecule.

☐ Electronic effects, or the extent to which substituent groups electronically interfere with the interaction between the active site of the enzyme and the substrate, or alter the energy required to break critical bonds in the molecule.

Biodegradation occurs in situations where the appropriate microbial enzymes are present to catalyse the transformation of the compound of interest. There are two steps in the biodegradative process. The first is the uptake of the substrate by the cell, and the second is the metabolism or degradation of the substrate. In some cases this first step can be the limiting step in biodegradation, e.g., for organic compounds with limited water solubility and for organic compounds that are sorbed onto soils or sediments (Miller, 1995).

Most microorganisms require high water activity (> 0.96) for active metabolism (Miller, 1995), and thus the contact between the degrading organism and an organic compound with low water solubility is limited. A direct consequence of limited contact is a slow rate of uptake (and biodegradation) of the compound (Miller, 1995).

Occurrence and abundance of microorganisms in the environment are determined not only by nutrients but also by various physical and chemical factors. The most important in the vadose zone are: water activity, redox potential (oxygen availability), pH, and for some areas, salinity.

In the presence of oxygen, aerobic microorganisms oxidize organic carbon completely to carbon dioxide using oxygen as the terminal electron acceptor (oxygen is reduced to water) in a series of oxidation-reduction reactions used to produce energy for cell maintenance and growth. In the absence of oxygen, organic material can be mineralized to carbon dioxide by anaerobic respiration.

Certain man-made compounds are resistant to biodegradation. This resistance is mainly due to the presence of chemical substituents such as nitro groups, chlorines and amines, that are attached to the parent compound. Generally, larger molecules are less degradable than smaller ones.

2.5 Implications of the above processes for estimating attenuation potential

The summary provided in this chapter has shown that several factors and processes will operate in the soil/aquifer system that will affect contaminant attenuation. A further complication stems from the fact that these processes and factors will occur simultaneously and in certain cases compete with each other. Ultimately, the fate of a given chemical in the subsurface will, therefore, be determined by its properties and consequent reactivity in a variety of chemical, physical, and biologically mediated processes and the rate of its physical transport. The 'attenuation potential' of a given soil is, therefore, not a fixed parameter but a variable.

In order to accurately predict the attenuation and eventual location of solutes or constituents in the subsurface, a simultaneous consideration of all the important reactions and processes must be conducted. This is complex and can only be accomplished by using sophisticated computer codes. A modelling exercise was carried out in this study (Chapter 5) to help address contaminant attenuation issues.

In order to identify which parameters and processes are important in the attenuation of contaminants in selected South African soils, laboratory studies were conducted and the results are reported in the next chapter. Field studies were also conducted to examine whether some of the contaminant attenuation processes described in this chapter could be confirmed at the field scale.

CHAPTER 3

LABORATORY STUDIES OF CONTAMINANT ATTENUATION IN SELECTED SOILS

BY M C D FERGUSON AND B EIGENHUIS

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3. LABORATORY STUDIES OF CONTAMINANT ATTENUATION IN SELECTED SOILS

3.1 Introduction

The vulnerability of soil and groundwater to contamination depends largely on the mobility of the contaminants in the soil, described by the distribution ratio, rd, between the immobilised concentration and the dissolved concentration (Van der Zee *et al*, 1987). Dissolution of contaminants in soils results in their translocation (Tiller, 1989), and the degree of mobility is governed by the species present in solution. On the other hand, immobilisation of contaminants by soil constituents and the mechanisms involved are specific to the element in question (Linn & Elliott, 1988). The chemistry of the soil is, however, more complex than can be represented simply by precipitation, adsorption or exchange processes (Talibudeen, 1981b). In fact, there is no certainty as to which of the major retention mechanisms participate in any particular reaction, or in which order.

The situation highlights the need for a thorough understanding of chemical speciation, soil properties, and retention mechanisms when studying the behaviour of contaminants in the soil. The best place to start with a study of this nature, is in the laboratory.

3.1.1 *Aims*

The main aim of the laboratory study was to determine the relationship between a soil's physical and chemical properties (e.g. soil type, soil thickness, and other attributes) and its contamination attenuation capacity.

Specific objectives included:

- ➔ Development and testing of experimental methods for determining attenuation standards.
- ➔ Comparison of selected soils, with regard to attenuation of specific contaminants
- ➔ Investigation of the effect of variation of soil parameters on contaminant attenuation.
- ➔ Comparison of contaminant attenuation properties as reported in the literature with results obtained in this study.

3.2 Selection of soils and contaminants

The first task involved identifying suitable soil materials. For logistic reasons, six soil materials were chosen from the Western Cape (Table 3.1). The soils were selected on the basis of texture, pH and cation exchange capacity.

Table 3.1 : Qualitative description of selected soil materials.

		Soil Properties					
Soils		**Soil 1**	**Soil 2**	**Soil 3**	**Soil 4**	**Soil 5**	**Soil 6**
Particle Distribution	Clay	1.4	2.7	0.4	33.9	18.7	24.6
	Silt	0.5	0.8	0.0	33.1	42.2	37.3
	Sand	97.9	96.2	63.4	32.1	34.6	37.4
	Other	0.1	0.4	36.2	0.9	4.5	0.7
pH		4.6	5.8	8.9	4.5	6.7	7.9
CEC	cmol(+)/kg	1.3	1.7	0.4	7.1	26.6	3.1
Colour	Description	V. pale brown	Yellow	White	Red	Black	Grey
	Code	10YR7/3	10YR7/6	10YR8/2	2.5YR4/8	2.5YR2.5/0	10YR6/1
Other		low pH	High [Fe]	calcareous	no swelling	swelling	no swelling

Contaminants were selected on the basis of toxicity, annual production volumes, and extent of perceived threat. The following three heavy metals were selected for investigation:

- → *Lead (Pb)*: because South Africa uses leaded petrol, every exhaust emission constitutes a source of Pb that will eventually impact the soil.
- → *Cadmium (Cd)*: a primary element in the waste generated by electroplating industries; the indiscriminant disposal of batteries is another important source.
- → *Chromium VI (Cr)*: although tanneries claim to dispose of chromium in its immobile Cr III form, the metal quickly becomes mobile as Cr VI, under certain soil conditions; Cr is also present in pigments and corrosives, in significant quantities.

For organic contaminants, the following were selected:

- → *Phenol*: a foundation compound in plastics, resins, pesticides, and medicines.
- → *Toluene*: one of the major constituents of gasoline. Suitable methods are sought for the assessment of both historical and current spills. The BTEX compounds (benzene, toluene, ethylbenzene & xylene) are used as an indication of gasoline contamination.
- → *Perchloroethylene (PCE)*: a solvent widely used for dry-cleaning and degreasing.

3.3 Laboratory experiments

3.3.1 *Heavy Metals*

3.3.1.1 Methods and results

Before laboratory experiments could be conducted, a suitable experimental design for assessing the level of attenuation in the different soil/contaminant combinations, had to be found. Important considerations for method selection were cost, ease of use, duration, and replicability. The following methods were tested:

- Quantity testing (QI)
- Batch studies (BS)
- Column studies: sequential metals extraction (ISCW)
- Column studies: total sorbed metals (EPA)

Batch studies were eventually accepted as the most appropriate for this study. A summary of the other methods is given in Appendix 2. These studies were carried out at room temperature. Five batches were used with individual stock solutions at 1000, 500, 250, 100 and 50 mg/l of each heavy metal. In each case, 30 ml of stock solution was added to 3 g of each of the soil samples (1:10 ratio), in centrifuge tubes, and placed on a rotary shaker for 24 hours. The suspensions were then filtered (Whatman No. 41 filter paper), and the filtrate was analysed with a Varian SpectrAA 250 Plus atomic absorption spectrometer. Three repetitions of each trial were carried out. The mean value of these three results was then plotted against initial solution concentration (Figure 3.1, Figure 3.2 and Figure 3.3).

3.3.1.2 Discussion

The results of the batch studies indicate a correlation between initial concentration of the contaminant solution and the attenuation concentration. One would assume that this relationship must reach a threshold value, beyond which attenuation is unaffected by further increase in concentration of the initial solution. The results for Pb and Cd support this expectation, with the exception of attenuation in Soils 3 and 5. If there is a threshold value for Cr, it is beyond the range of concentrations investigated.

Pb and Cd exhibited similar attenuation tendencies for the soils tested, with Pb attenuation being the higher of the two. The highest attenuation occurred in Soils 3 and 5. The results for Cr (Figure 3.3) are different. The attenuation of Cr is an order of magnitude lower than that of Pb and Cd. Also significant is the fact that with an initial concentration of 250 mg/l, there are negative attenuation values for Cr for all the soils except Soil 4. The latter exhibits significantly higher attenuation for Cr than any of the other soils.

The results indicate, as expected, that attenuation of a specific heavy metal differs from soil to soil. More importantly, it is evident that the heavy metals differ from each other, with respect to attenuation for a specific soil. Pb shows the highest attenuation for all the soils, with the exception of the calcic sand.

When comparing the attenuation potential of the different soil materials, it is important to bear in mind the nature of the heavy metals themselves: Pb and Cd are present in solution as positively charged ions (Pb^{2+} and Cd^{2+}), and Cr is present in anionic (negatively charged) form. The attenuation of Pb and Cd correlates well with CEC. For example, the highest attenuation for Pb and Cd occurs in Soil 5, which has the highest CEC among the soils. Cr is most effectively attenuated by Soil 4, which has a high sesquioxide content. The sandy materials exhibit characteristically low attenuation of the metals, with the exception of the calcareous Soil 3, which has an uncharacteristically high pH as a result of its high lime content.

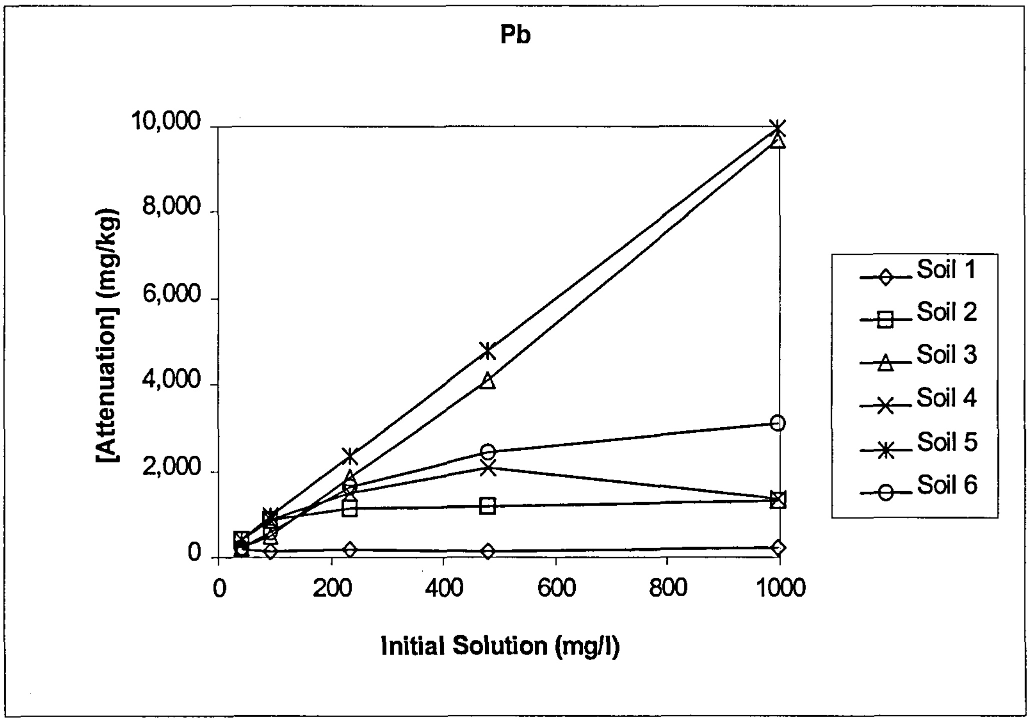


Figure 3.1 : Attenuation of Lead by selected soils.

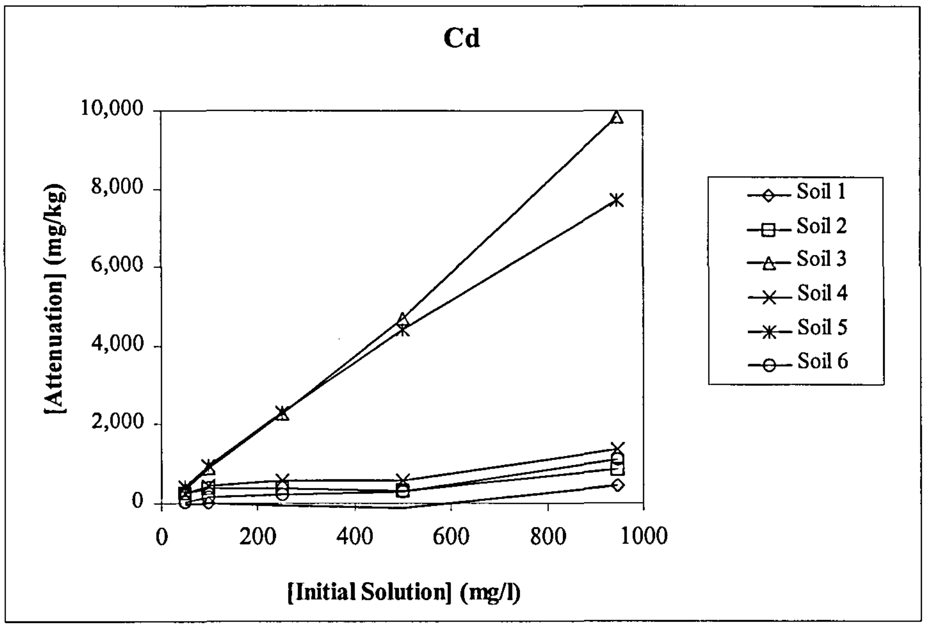


Figure 3.2 : Attenuation of Cadmium by selected soils.

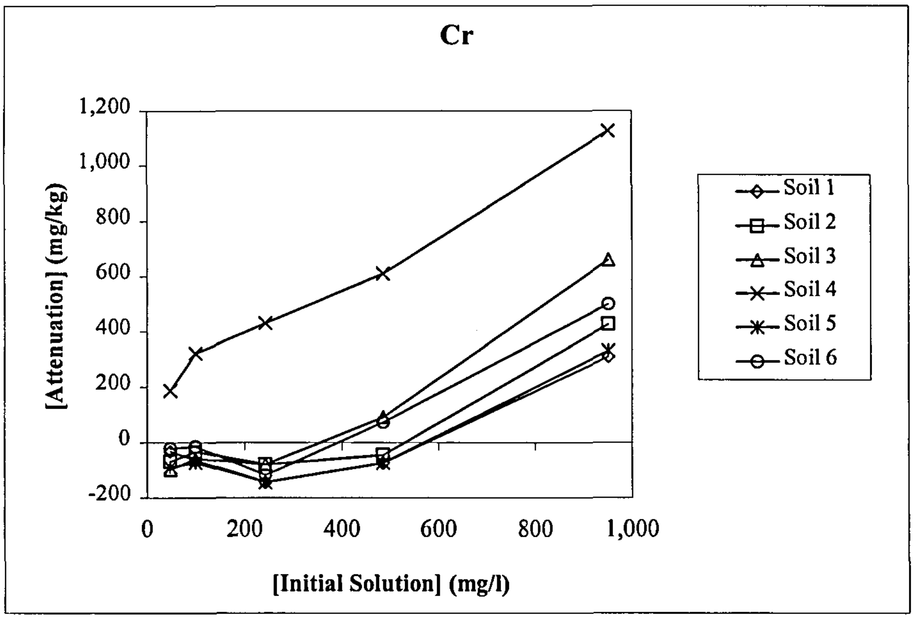


Figure 3.3 : Attenuation of Chromium by selected soils.

3.3.2 *Organic Compounds*

3.3.2.1 Methods and results

Many extraction methods for organic contaminants are subject to one or more of the following drawbacks:

- ➔ time-consuming
- ➔ low yields
- ➔ large amounts of organic solvent required
- ➔ only suitable for a small range of compounds

In light of these problems, a new method has been developed (Figure 3.4). This apparatus is an adaptation of the steam distillation method developed by Seidel & Lindner (1993). Preliminary tests indicate suitability for the full range of selected contaminants, short extraction time, excellent yields, and minimal use of the organic solvent, dichloromethane.

Batch Studies

Phenol is slightly water soluble, and was investigated using batch studies similar to those used for the investigation of the heavy metals. The low solubility of toluene and PCE in water makes it impractical to conduct batch studies with these compounds.

The phenol batch studies were carried out as follows: A stock solution of 200 mg/l phenol in water was made up at room temperature. 10 ml of stock solution was added to 2 g of each of the soil samples (1:5 ratio), in glass centrifuge tubes with PTFE septa, and placed on a rotary shaker for 24 hours. The suspensions were then centrifuged at 3000 rpm for 5 min, and the supernatant was analysed with a gas chromatograph. 1 μl of supernatant was injected on-column, at an injection temperature of 220°C. H_2 was used as carrier gas with an oven temperature of 135°C. Retention time was approximately 8 min. The results are shown in Figure 3.5.

The highest attenuation of phenol occurred in smectitic Soil 5.

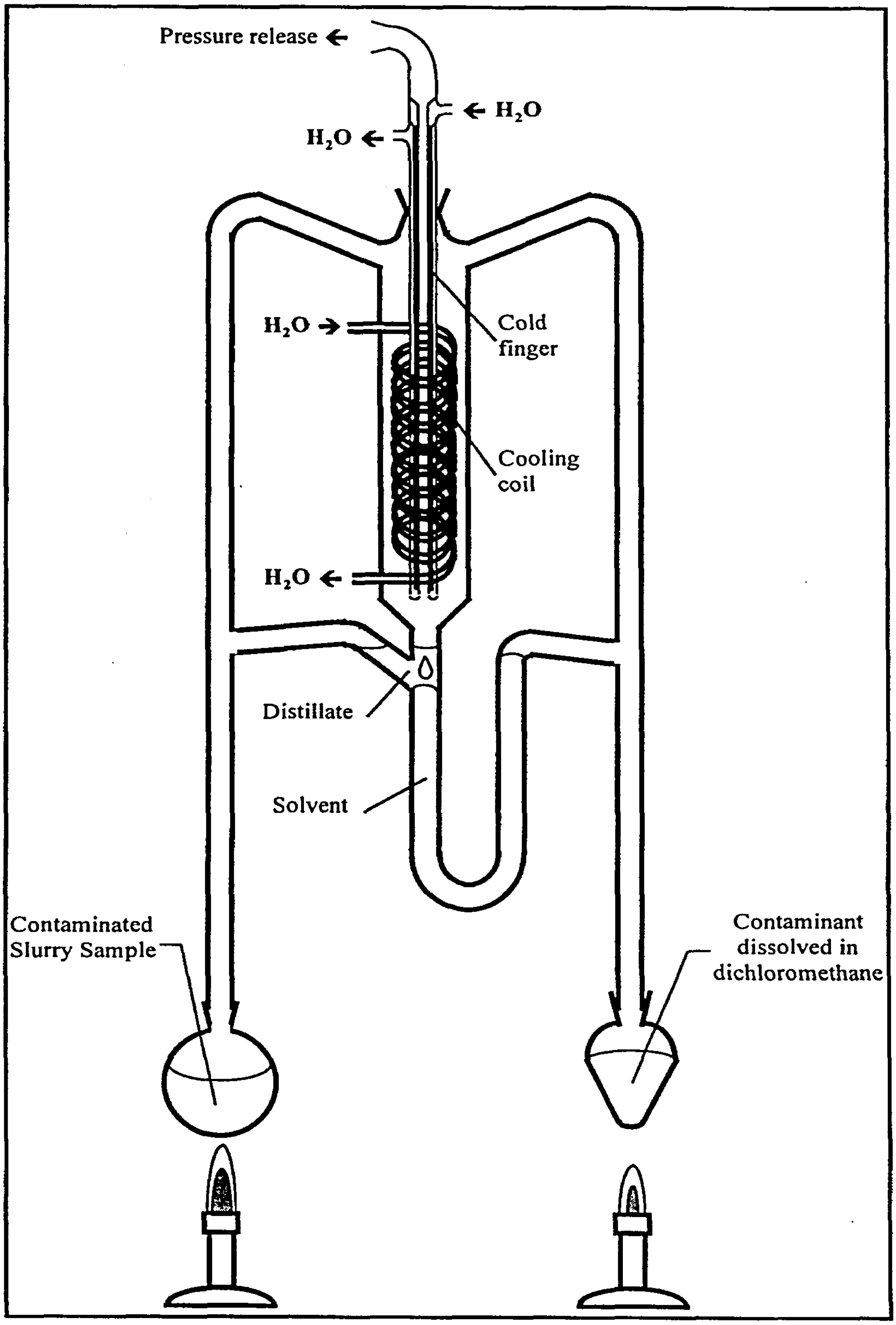


Figure 3.4: Adapted steam distillation apparatus.

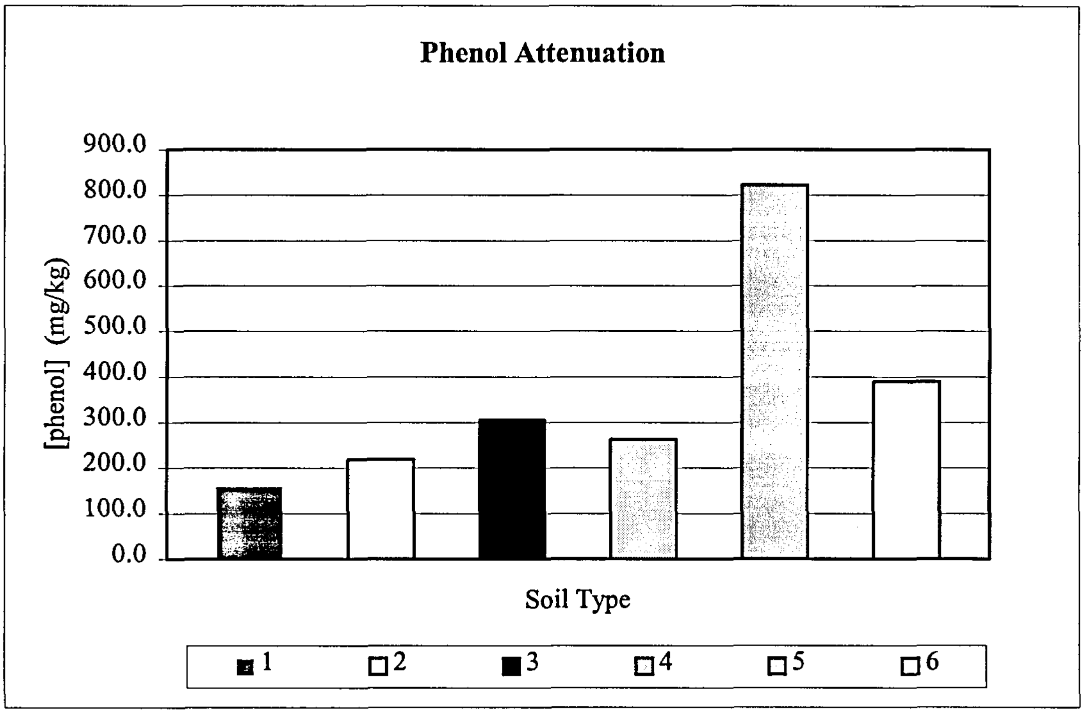


Figure 3.5 : Phenol attenuation following contamination with 200mg/l solution.

Column Studies

Columns studies were conducted for toluene and PCE as follows: small glass columns of 21mm diameter were packed with individual soils to a depth of 38mm, resting on a bed of glass wool, giving a total soil volume of 50cm^3. Sandy soils (Soils 1 to 3) were packed to a bulk density of 1.6g/cm^3, and clayey soils to a bulk density of 1.3g/cm^3. Each of the soil columns was then saturated with the contaminant and allowed to drain. The initial mass retained by the soil was recorded, and then the contaminant was displaced by ponding the column with distilled water. The quantity of chemical displaced was recorded and subtracted from the initial mass retained, to give the residual mass of contaminant in the soil. The results are shown in Figures 3.6 and 3.7.

No analysis was conducted on the contaminated soil, as time constraints did not allow sufficient validation of the newly developed extraction method. In each trial, there was a significant amount of the contaminant retained in the soil pores, which was then mostly displaced when the columns were ponded with water. The highest retention values for toluene were in sandy Soils 2 and 3. Soil 5 had the highest value for residual toluene, however. The difference between initial retention and final attenuation was far greater for the sandy soils (1 to 3), than for the clayey soils (4 to 6).

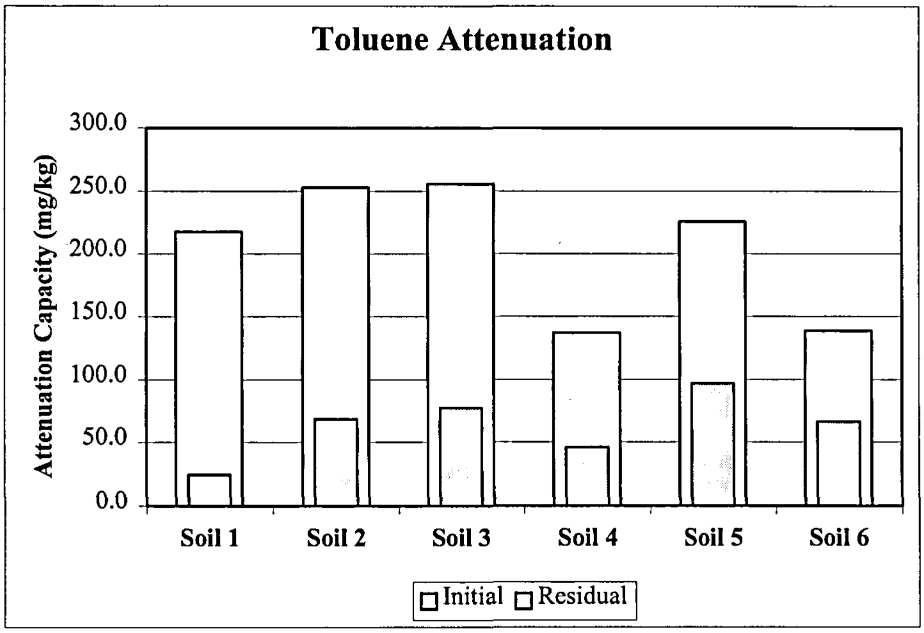


Figure 3.6 :Toluene retention by soil after initial saturation, compared with residual toluene, after displacement and leaching with distilled water.

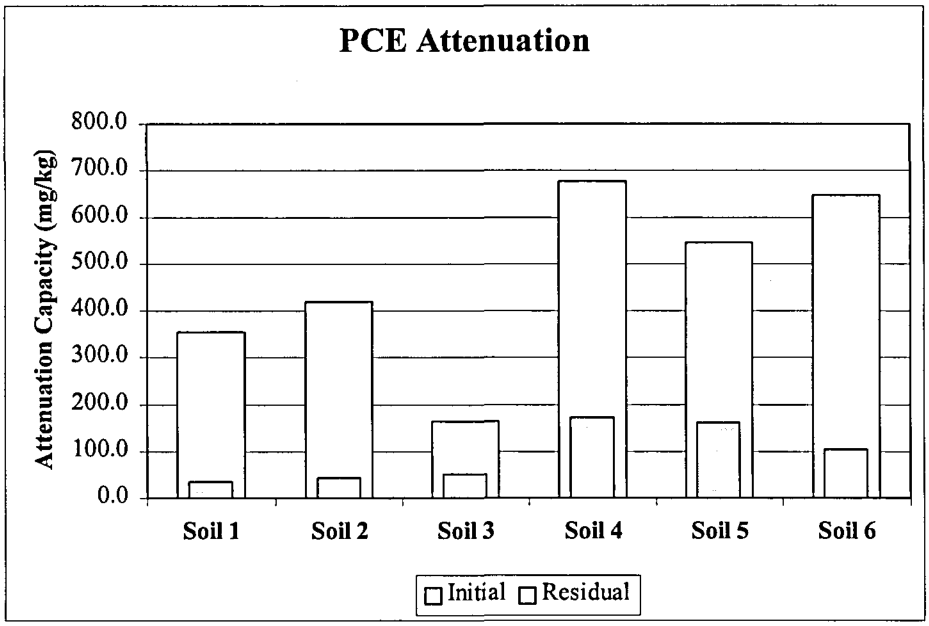
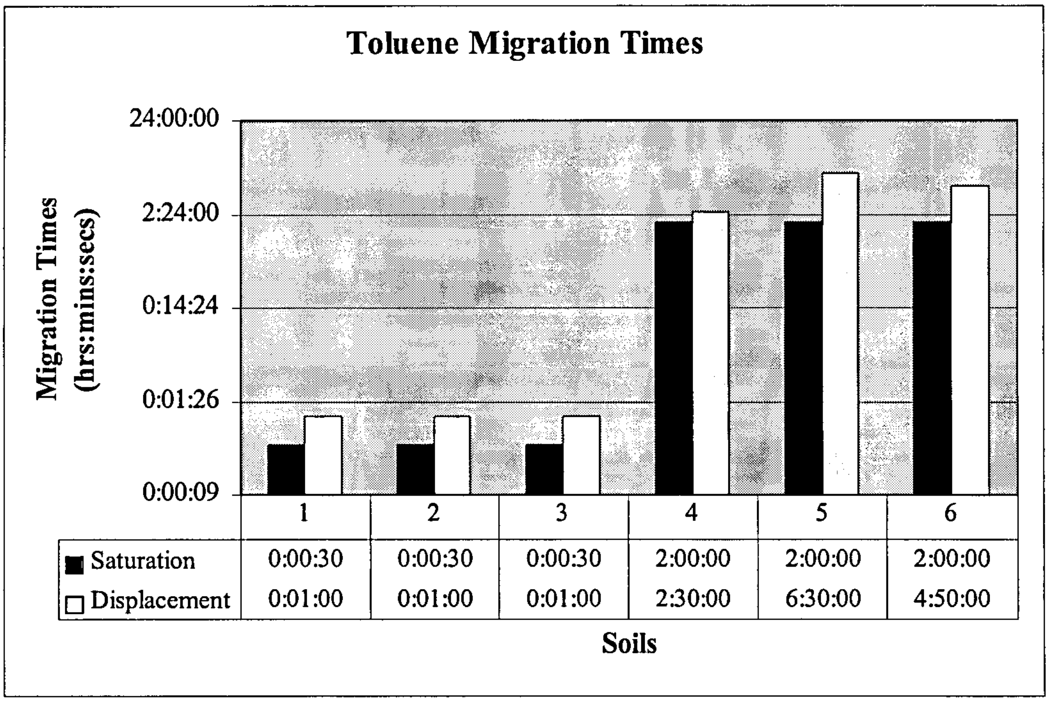


Figure 3.7 : PCE retention by soil after initial saturation, compared with residual PCE, after displacement and leaching with distilled water.

The results for PCE and toluene were different. For PCE, the clayey Soils 4 to 6 showed returned the highest values for both initial and residual retention. In contrast to toluene, the difference between initial and residual retention of PCE was far greater for the clayey soils than the sandy soils. By comparison, residual PCE retention values were much higher than those for toluene, with the exception of Soil 5.

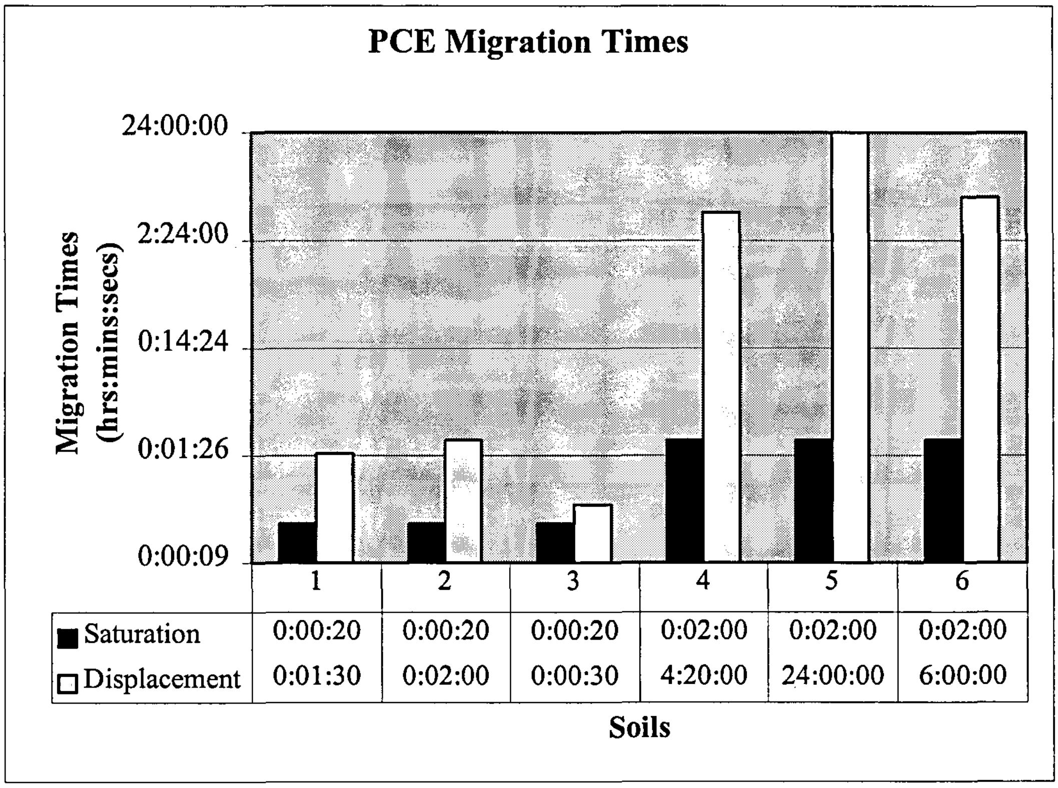
The migration times for the contaminants have been plotted against a logarithmic scale, to allow comparison between the almost instantaneous migration through the sands, and the very slow migration through the clays (Figures 3.8 and 3.9). Migration times for toluene differed greatly for the sandy soils (30 seconds) and the clayey soils (2 hours).

Saturation of the soil with PCE was immediate in the sandy soils (30 seconds) and almost as fast in the clayey soils (2 minutes). Displacement of the PCE was again slower than saturation in the sandy soils (up to 2 minutes). There were, however, significant differences in duration for the clayey soils. In particular, the ponded distilled water took 24 hours to replace the PCE in the clayey Soil 5.



	1	2	3	4	5	6
■ Saturation	0:00:30	0:00:30	0:00:30	2:00:00	2:00:00	2:00:00
□ Displacement	0:01:00	0:01:00	0:01:00	2:30:00	6:30:00	4:50:00

Figure 3.8 : Times recorded for saturation of soil columns with toluene, and displacement of toluene by ponding column with distilled water.



	1	2	3	4	5	6
■ Saturation	0:00:20	0:00:20	0:00:20	0:02:00	0:02:00	0:02:00
□ Displacement	0:01:30	0:02:00	0:00:30	4:20:00	24:00:00	6:00:00

Figure 3.9: Times recorded for saturation of soil columns with PCE, and displacement of PCE by ponding column with distilled water.

3.4 Compilation of Matrix

One of the goals of the study was to produce a matrix table, which would facilitate comparison of different chemical and physical properties of soil materials, as well as their ability to attenuate different chemicals. When the prediction of contaminant movement using a computer model like CHAIN_2D is considered, physical and chemical properties need to be numerically described. Attenuation influencing soil properties such as pH, CEC and OC are not always used as input for a computer model, but are determined by most soil laboratories and the data are available in most of the known soil databases. Particle size distribution (PSD) of a soil of interest is also determined as a standard procedure, while clay type or information about the soil mineralogy is readily available. PSD is of importance since it is used to estimate saturated hydraulic conductivity and soil water retention. The problem with current databases is that they do not contain information on the attenuation of specific chemical contaminants.

Fuller (1978) examined the effect of soil properties/factors on the contaminant attenuation of trace elements. The research made great strides in a area of soil science where little was known and substantiated the importance of some factors previously suspected of affecting attenuation in soils. However, insufficient data were available to clearly assess the importance of all of the studied factors.

Therefore, three groups of attenuation influencing factors were presented in summary as a basis for further discussion. These were :

- **Most important factors in retention.**
    - ➜ Clay content
    - ➜ Free iron oxide content
    - ➜ Soil lime (pH effect), and
    - ➜ Solution flux through soil.
- **Least important factors in retention.**
    - ➜ Sand
    - ➜ Clay mineral type
    - ➜ Cation exchange capacity (CEC)
    - ➜ Soil pH (anion-forming elements).
- **Factors not fully assessed in Fuller's study**
    - ➜ TDS (total dissolved solids or soluble salts)
    - ➜ Hydrous oxides (primarily Mn and Al)
    - ➜ Specific ion effect and ion interaction effects
    - ➜ Biological activity in mineralization and immobilization
    - ➜ Reaction of organic constituents both in soil and in leachate (TOC)
    - ➜ Precipitation
    - ➜ Ion exchange reaction
    - ➜ Pore size distribution, surface reaction, physico-chemical adsorption and temperature.

Matrix tables were prepared for Pb, Cd and Cr using limited data from literature (Tables 3.2 to 3.4), while no information was gathered on the organic contaminants of interest due to the limitation on the available time. In compiling the matrix, the following information (where available) was collected :

- Soil Type (Kaolinite, Illite, Montmorillonite, Al oxides (amorphous), Mn oxides, Fe oxides (amorphous), Goethite, Calcareous, etc)
- pH [-]
- Clay %
- Sand %

- Free iron oxide content %
- Adsorption Isotherm [equation, where ***C*** is concentration]
- Contaminant concentration (***S***), [mg/kg]
- Initial concentration (***C***), [g/cm3]
- Mobility [***Pre***cipitation, ***Ads***orption, etc..]
- Experiment type (ET), (***B***atch or ***C***olumn)
- Solution flux through the soil (***F***), [cm/min]
- Adsorption Isotherm Source (AIS), (***D***erived or published by ***A***uthor)
- Reference

Adsorption isotherms were included in the matrix tables with the initial concentration used in experiments presented in literature where possible. In the case where no isotherms were found, mathematical regression were used to determined this information from column breakthrough curves and batch test results where possible. Since the mobility of contaminants can only be partially described by adsorption isotherms, it was necessary to include a column in the table describing other possible processes influencing the mobility of the contaminant.

Experimental data obtained during this project were compiled in the format mentioned above, using the same procedures in deriving the information with the experimental data shown in Tables 3.5 to 3.7. Table 3.2 shows literature data for Pb attenuation in different soils with a single linear adsorption isotherm for the Swartklip sand studied in this project, as well as Pb attenuation values published by Zimdahl *et. al.* (1977). In general, Pb is more mobile (less attenuation) at lower values of pH, while precipitation normally starts occurring at pH values higher than 8.4. When the adsorption isotherms for Swartklip sand listed in Tables 3.2 and 3.5 are compared, it is clear that these isotherms are not similar. This unsimilarity is attributed to the difference in the experimental determination of these isotherms (batch vs column studies), or possible nonlinear adsorption at initial concentrations higher than 2400 mg/l. All the Cd adsorption isotherms derived from literature data (Table 3.3) are linear, as well as isotherms derived from experimental data (Table 3.6). Again in general, the attenuation of Cd increased with an increase in pH values. Furthermore, the adsorption isotherm for acidic sand from Vissershok (Table 3.6) compares excellent with the adsorption isotherm for the Wingst soil from Germany (Table 3.3), having similar pH values and percentages of sand. The adsorption isotherms derived for Swartklip sand from batch (Table 3.6) and column (Table 3.3) study results are also similar. For all the soils in Tables 3.3 and 3.6, adsorption was considered to be the primary influence of the mobility of Cd in the selected soils.

Finally, nonlinear Cr adsorption isotherms were found in literature (Table 3.4). The adsorption isotherms derived from experimental data for the studied South African soils were linear for certain ranges of initial concentration (Table 3.7). In some instances no adsorption took place at all, thereby indicating high mobility of Cr in a specific soil (e.g. Swartklip sand in Table 3.4). No general Cr attenuation trend could be observed from the data listed in Tables 3.4 and 3.7 and further study is recommended.

Table 3.2 : Literature data on adsorption and mobility of Pb in soils.

Soil Type	pH [-]	Clay [%]	Sand [%]	Fe oxides [%]	Isotherm	S [mg/kg]	Initial Conc Range [mg/l]	Mobility	ExpType	F [cm/min]	AIS	Ref
Swartklip Calcic Sand	8.1	0.2	96.4	***	3.24C	7776	2400	Ads	C	2.159	A	Eigenhuis 1997
Lakeland	7.4	13	86	***	***	3108	860	Ads	B	***	A	Zimdahl *et al.*, 1977
***	7.1	21	67	***	***	9324	860	Ads	B	***	A	Zimdahl *et al.*, 1977
Ascalon	6.4	25	51	***	***	7459	860	Ads	B	***	A	Zimdahl *et al.*, 1977
San Luis	8.2	13	67	***	***	10774	860	Ads	B	***	A	Zimdahl *et al.*, 1977
Cecil	5.4	51	28	***	***	6216	860	Ads	B	***	A	Zimdahl *et al.*, 1977
***	8.1	27	56	***	***	17404	860	Ads	B	***	A	Zimdahl *et al.*, 1977
***	8	38	46	***	***	10774	860	Ads	B	***	A	Zimdahl *et al.*, 1977
Troy	4.1	34	34	***	***	6423	860	Ads	B	***	A	Zimdahl *et al.*, 1977
Weld	6.8	54	18	***	***	13260	860	Ads	B	***	A	Zimdahl *et al.*, 1977

Table 3.3 : Literature data on adsorption and mobility of Cd in soils.

Soil Type	pH [-]	Clay [%]	Sand [%]	Fe oxides [%]	Isotherm	S [mg/kg]	Initial Conc [mg/l]	Mobility	ET	F [cm/min]	AIS	Ref
Swartklip Calcic Sand	8.1	0.2	96.4	***	10.44C	2610	250	Ads	C	2.159	A	Eigenhuis 1997
Wingst Germany Al-OH	4.3	1.3	96	***	0.2262C	226	0 - 1000	Ads	B	***	D	Schulte *et.al.* 1994
Reyersh Germany Al-OH	4.3	7.5	58.1	***	2.1905C	2200	0 - 1000	Ads	B	***	D	Schulte *et.al.* 1994
Erhorn Germany Al-OH	4.4	7.6	79.2	***	1.784C	1780	0 - 1000	Ads	B	***	D	Schulte *et.al.* 1994
Hils Germany Al-OH	4.3	16.1	19.9	***	3.3543C	3354	0 - 1000	Ads	B	***	D	Schulte *et.al.* 1994
Solling I Germany Al-OH	4.4	20.7	31.3	***	2.513C	2510	0 - 1000	Ads	B	***	D	Schulte *et.al.* 1994
Det Yitsak Israel Carbonate	7.4	1.8	96.8	***	5.3C	5252	0-1000	Ads	B	***	D	Schulte *et.al.* 1994

Table 3.4 : Literature data on adsorption and mobility of Cr in soils.

Soil Type	pH [-]	Clay [%]	Sand [%]	Fe oxides [%]	Isotherm	S [mg/kg]	Initial Conc [mg/l]	Mobility	ET	F [cm/min]	AIS	Ref
Swartklip Calcic Sand	8.1	0.2	96.4	***	0C	0	1506	Y	C	0.92	A	Eigenhuis 1997
Oliver	6.4	6	5	0.44	$1.616C^{0.8}$	46.22	0 -100	Ads	C	0	A	Selim *et al.* (1989)
Cecile	5.1	51	30	10.2	$2.614C^{0.513}$	27.75	0 - 100	Ads	C	0	A	Selim *et al.* (1989)
Windsor	5.4	3	77	2.2	$15.29C^{0.418}$	104.8	0 - 100	Ads	C	0	A	Selim *et al.* (1989)

Table 3.5 : Experimental data on adsorption and mobility of Pb in soils.

Soil Type	pH [-]	Clay [%]	Sand [%]	Fe oxides [%]	Isotherm	S [mg/kg]	Initial Conc Range [mg/l]	Mobility	ExpType	F [cm/min]	AIS	Ref
VissershokAcidic Sand	4.6	1.4	97.9	***	$233C^0$	233	50 - 1000	Yes	B	***	D	Exp Data
VissershokFerric Sand	5.8	2.7	96.2	***	$1306C^0$	1306	200 - 1000	Yes	B	***	D	Exp Data
Swartklip Calcic Sand	8.9	0.4	63.4	***	9.674C	9674	50 - 1000	Ads	B	***	D	Exp Data
HelshoogteKaolinite	4.5	33.9	32.1	***	$1E\text{-}6C^3\text{-}0.007C^2 + 7.3076C$	1333	0 -1000	Ads	B	***	D	Exp Data
MalmesburySmectite	6.7	18.7	34.6	***	9.94C	9944	0 - 1000	Ads	B	***	D	Exp Data
Vissershok Saprolite	7.9	24.6	37.4	***	1065LnC - 4165.5	3100	0 - 1000	Ads	B	***	D	Exp Data

Table 3.6 : Experimental data on adsorption and mobility of Cd in soils.

Soil Type	pH [-]	Clay [%]	Sand [%]	Fe oxides [%]	Isotherm	S [mg/kg]	Initial Conc [mg/l]	Mobility	ET	F [cm/min]	AIS	Ref
VissershokAcidic Sand	4.6	1.4	97.9	***	0.223C	446	0 - 945	Ads	B	***	D	Exp Data
VissershokFerric Sand	5.8	2.7	96.2	***	0.67C	846	0 - 945	Ads	B	***	D	Exp Data
Swartklip Calcic Sand	8.9	0.4	63.4	***	10.42C	9855	0 - 945	Ads	B	***	D	Exp Data
HelshoogteKaolinite	4.5	33.9	32.1	***	1.38C	1360	0 - 945	Ads	B	***	D	Exp Data
MalmesburySmectite	6.7	18.7	34.6	***	8.0C	7700	0 - 945	Ads	B	***	D	Exp Data
Vissershok Saprolite	7.9	24.6	37.4	***	0.945C	1130	0 - 945	Ads	B	***	D	Exp Data

Table 3.7 : Experimental data on adsorption and mobility of Cr in soils.

Soil Type	pH [-]	Clay [%]	Sand [%]	Fe oxides [%]	Isotherm	S [mg/kg]	Initial Conc [mg/l]	Mobility	ET	F [cm/min]	AIS	Ref
VissershokAcidic Sand	4.6	1.4	97.9	***	0.833C - 472.5	310	567 - 950	Ads	B	***	D	Exp Data
VissershokFerric Sand	5.8	2.7	96.2	***	0.475C - 5.7	426	50 - 950	Ads	B	***	D	Exp Data
Swartklip Calcic Sand	8.9	0.4	63.4	***	1.21C - 462.7	660	380 - 950	Ads	B	***	D	Exp Data
HelshoogteKaolinite	4.5	33.9	32.1	***	1.392C	1126	50 - 950	Ads	B	***	D	Exp Data
MalmesburySmectite	6.7	18.7	34.6	***	0.976C - 564.11	330	580 - 950	Ads	B	***	D	Exp Data
Vissershok Saprolite	7.9	24.6	37.4	***	0.978C - 391	500	400 - 950	Ads	B	***	D	Exp Data
Vissershok Saprolite	7.9	24.6	37.4	***	0C	0	0 - 400	Y	B	***	D	Exp Data

3.5 Conclusions

- ➔ Batch studies were found to be the most suitable method for determining attenuation standards for heavy metals and soluble organics.
- ➔ Establishing a method for the organic compounds was more complex than for the heavy metals. A new method was developed based on steam distillation, but there was insufficient time to conduct exhaustive validation of the method.
- ➔ Comparison of the attenuation characteristics of heavy metals showed that attenuation of the negatively charged anion, Cr, was negligible while that of the positively charged cations, Pb and Cd was quite significant.
- ➔ The calcic Soil 3 (with its high pH) and the smectitic Soil 5 (with its high cation exchange capacity) attenuate the two cations best. The kaolinitic Soil 4 attenuates Cr more strongly than the other soils, probably as a result of the sesquioxides present.
- ➔ Phenol is slightly water soluble, and allows for investigation with batch studies. Phenol attenuation seems to be linked to organic matter content in the soil.
- ➔ The information contained in the compiled matrix tables indicates that linear adsorption describes the sorption of the studied heavy metals Pb and Cd most accurate. Furthermore, the adsorption isotherms obtained during this study compares favourably with a number of isotherms observed in literature. However, differences exists that are attributed to the physical derivation of these isotherms using either batch or column methods.

3.6 Recommendations

Investigation of the selected contaminants uncovered a number of obstacles to research of this nature, both scientific and logistic. In the light of new perspectives gained, it is evident that this is a research area requiring urgent attention.

Contaminant attenuation capacities should be determined for specific soil materials, and then for profile combinations. The shake up test is a fast, economical indication of attenuation potential, but should be confirmed using field experiments.

The column studies used are a simple, inexpensive way of assessing attenuation potential in a specific soil environment. A useful control for these column studies would be to pond uncontaminated soil columns with distilled water. These results could then be used as a benchmark for migration times. The steam distillation extraction method developed for organic compounds has a lot of potential. This method needs to be validated for different soil:contaminant combinations.

Further investigation is required to narrow the gap between understanding of contaminant attenuation and the extent of its impact on the South African environment. In the meantime, the results of this study should at least alert decision-makers as to the potential contamination hazard of the chemicals investigated.

CHAPTER 4

FIELD SCALE INVESTIGATION

BY O T N SILILO

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4. FIELD SCALE INVESTIGATION OF THE CONTAMINANT ATTENUATION CHARACTERISTICS OF THE SOIL/AQUIFER SYSTEM

4.1 Introduction

Field studies were conducted to examine whether or not contaminant attenuation processes, as indicated by literature could be confirmed at the field scale. The approach adopted was to assess contaminant concentration changes along the main flow path. The basis of this approach is that if natural attenuation is occurring, the contaminant concentration will decrease with distance from the source.

Two types of studies were conducted: field infiltration experiments and sampling at sites where waste disposal activities have occurred over several years.

4.2 Field infiltration experiments

4.2.1 *Objectives of field infiltration experiments*

The main objective of the field study was to obtain data on the migration and attenuation of contaminants from the surface, through the unsaturated zone to the water table.

4.2.2 *Study area*

The study site is located on the Cape Flats aquifer, which consists of Quaternary-age deposits, mainly silica sand underlain by impervious pre-Cambrian Malmesbury Shales or Cape Granite. Sedimentation initially occurred in a shallow marine environment, subsequently progressing to intermediate beach and wind blown deposits, and finally aeolian and marsh (peat) conditions. A characteristic feature of the sediments is the presence of shelly material over most of the area. The sand body is generally stratified horizontally. Portions of the area are covered by calcareous sands and surface limestone deposits, while silcrete, marine clays and bottom sediments of small inland water bodies occur sporadically. At the study site, the sands consist mainly of moderately sorted medium grained quartzitic sands with subordinate shelly and biogenic fragments. A number of calcretised horizons are present within the sand units. The measured fraction of organic carbon (f_{oc}) of the sands varies between 0.0029 and 0.0042. In situ permeability tests in the area yielded saturated hydraulic conductivity values ranging between 20 m and 40 m/d. The water table is about 8 m deep.

The climate is typically Mediterranean with the winter rainy season from May to August. The average rainfall recorded at various stations in the Cape Flats ranges from 500-700 mm/annum.

The study plot, 3 m x 1.5 m, is located approximately 30 m away from a domestic waste site. Adjacent to the waste site is a pond (Figure 4.1) in which unauthorised dumping of various types of waste has occurred over the years. During the rainy season, the pond fills up with water.

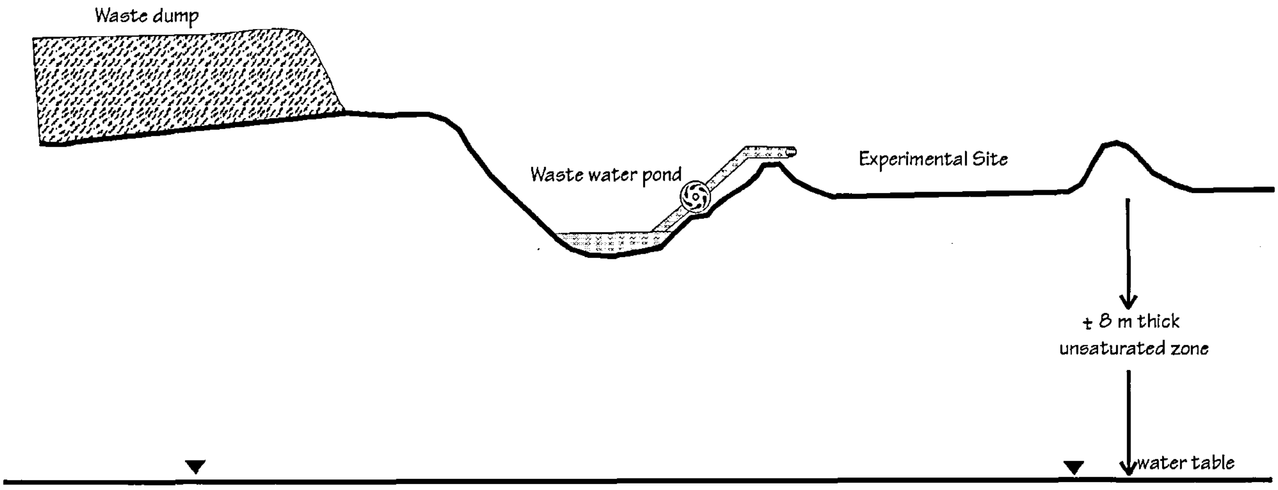


Figure 4.1 : Cross section through the study site (not to scale)

4.2.3 *Method of study*

A groundwater observation well installed at the site was used to obtain samples from the saturated zone while suction lysimeters were used in the unsaturated zone. A neutron probe access hole was also installed to help monitor the migration of the wetting front during experimentation.

Lysimeters

Lysimeters (porous suction samplers) are the most frequently used type of in situ pore liquid samplers. A review of lysimeters has been given by Liator (1988), Everett and McMillion (1985) and Wilson *et al.* (1995). The principles of their operation are as follows: when placed in the unsaturated zone, the pores in the porous sampler of a lysimeter will form a continuum with pores in the surrounding medium. When a vacuum greater than soil water suction is applied within the sampler, a hydraulic gradient is created toward the sampler. If menisci of the liquid in the soil or porous cup are unable to withstand the applied suction, liquid water will be drawn across the porous wall into the cup. The ability of the menisci to withstand applied suction decreases with increasing pore radii of the porous segment. If the maximum pore radii are too large, the menisci are not able to withstand the applied suction and as a result, they break down and air enters the sampler. Once water has collected in the sampler, it can be drawn to the surface by applying pressure to the pressure-vacuum line.

The design of the lysimeters used in this study is shown in Figure 4.2. The lysimeters were assembled by heat shrinking a 5 cm ceramic porous cup on to the bottom end of a 60 cm long and 5 cm diameter PVC cylindrical tube. The upper end was fitted with an airtight 5 cm PVC cap. The latter was then fitted with two 6 mm plastic tubing. One of the tubes, the sampling line, was fitted such that it extended from the bottom of the porous cup while the other tube, the pressure vacuum line, terminated just below the end cap. The pressure line was fitted with a 0.25 kPa non-return valve to maintain a vacuum within the lysimeter. After construction all lysimeters were checked to ensure that they were free of any leaks.

In order to install lysimeters on the site, a number of boreholes were drilled by rotary percussion, without adding any water. The general procedure of installation was as follows: silica powder was poured into the hole to cover the base. The lysimeter assembly was then lowered down until the porous cup rested on the silica powder. Additional silica was then added until the porous cup was completely covered by silica. The hole was then backfilled with native sand material, tamping thoroughly in the process. A total of 6 lysimeters were installed at the following depths from the surface: 1, 2, 3, 4, 5 and 6 m.

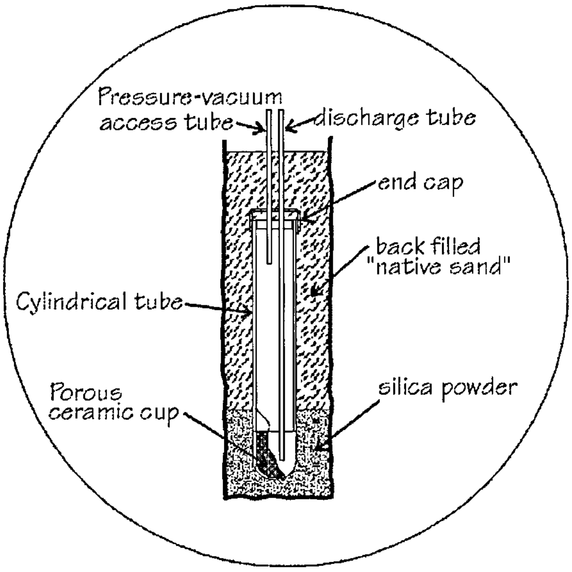


Figure 4.2 : Lysimeter design and installation

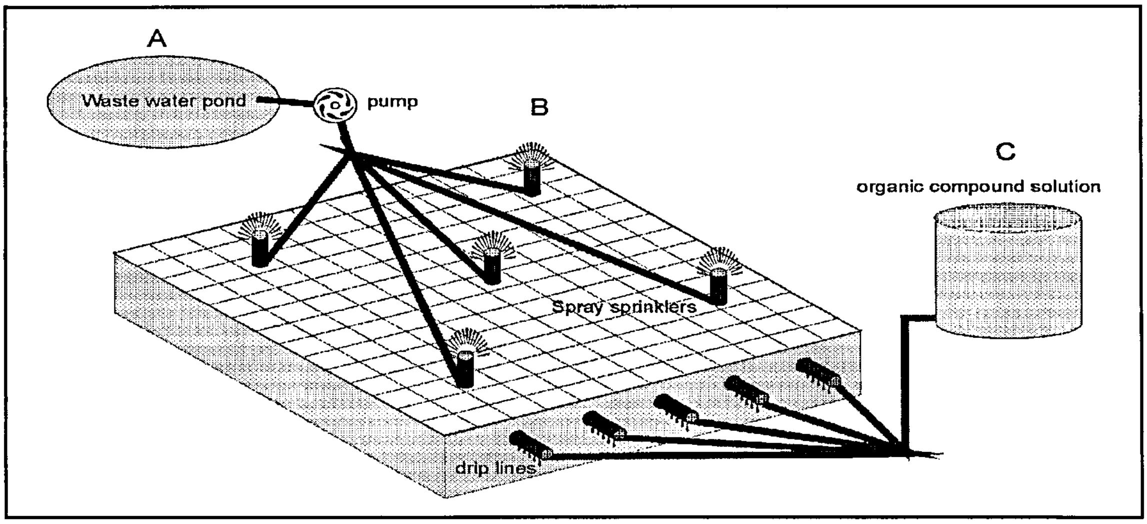


Figure 4.3 : Field experimental setup showing sprinkler system

Sprinkler system

The site was instrumented with two types of sprinkler system. The first type consisted of four spray sprinklers which were placed on the surface while the second type consisted of five drip lines, which were buried about 5 cm below the soil surface (Figure 4.3).

Infiltration experiments

The leachate/runoff mixture from pond A (Figure 4.3) was used to drive the infiltration process. During the course of the experiment, four organic compounds: toluene, butyric acid, phenol and aniline were introduced artificially. The organic compound solutions were prepared by mixing 16 g of a given compound with 400 litres of water giving 40 mg/L solutions. The general characteristics of selected organic compounds used in the study are shown in Table 4.1.

Table 4.1 : General characteristics of selected organic compounds used in the study

Parameter	Toluene[a]	Aniline[b]	Phenol[a]
Formula weight	92.14	93.13	94.11
Log octanol : water partition coefficient (Log K_{ow})	2.73	0.90	1.48
Log K_{oc}	2.06	1.41	1.43
Solubility in water (mg/L)	515	34 000	82 000
Henrys constant atm.m^3/mol	0.007	0.136	2.7×10^7

Butyric acid is highly soluble in water

[a] Montgomery and Welkom (1991)
[b] Montgomery (1991)

Just before infiltration experiments were initiated, soil moisture samples were collected from all the lysimeters and the observation borehole. The sampling procedure for the lysimeters involved applying a vacuum to the vacuum line using a vacuum pump while the sampling line remained shut. After 1 hour, the sampling (or discharge) line was opened and pressure applied to the pressure line. This caused the sample to move up to the surface through the discharge line. The samples were then collected in sample bottles and immediately stored in cooler bags. The samples were then transported to the laboratory where they were refrigerated at 4° C until they were analysed. Lysimeters at 3 m and 6 m did not yield any samples.

Neutron probe readings were also taken to get an indication of initial moisture conditions.

The infiltration experiments were conducted in four phases, with each phase involving introduction of a different organic compound. During each phase, irrigation was initiated by pumping wastewater from pond A on to the field plot B at a rate of 1.0 l/s. A total of 7 m^3 of wastewater was irrigated during the experiment. Twenty minutes after the onset of each irrigation cycle, 400 litres of the organic compound solution from tank B was introduced via the buried drip lines at a rate of 0.9 l/s.

At the end of each irrigation cycle, neutron probe measurements were taken. The objective of the latter was to observe progressive moisture changes during the experiment.

Two days after the experiment, sampling of the borehole and lysimeters commenced. The sampling procedure followed is as described above. Again, lysimeters at 3 m and 6 m did not yield any samples.

Method of analysis

For organic analysis, the EPA method 3500 was used as a basis for the extraction of the water samples. The water samples were extracted three times with 10 ml methylene chloride. All extraction glassware had been heated to 400° C and pre-rinsed with methylene chloride. The use of a wrist-action shaker for 10 minutes was utilised. The extracts were combined and dried with anhydrous sodium sulphate, prior to injection.

The combined extracts were injected into a Varian Saturn 2000 Gas Chromatograph-Mass Spectrometer. EPA method 8260 was used as a basis for the GC-MS analysis. A 30 m DB-5 column was used. The GC was temperature programmed from 30° C (6 min hold) to 70° C at 7° C/min and then to 280° C at 10° C/min. The mass spectrometer was set to scan from 40 to 450 mass units, at 0.810 s/scan. The injection port temperature was set at 260°C and the transfer line between GC and MS at 280° C. The ion trap of the MS was set at 120° C and the trap manifold was set at 45° C.

Peak identities were determined by comparison of mass spectra obtained for the extracts against mass spectra of external standards. Compound concentrations were determined by constructing calibration curves of external standards, using the peak areas under each reconstructed ion peak for the specific standard, as designated by EPA 8260.

Recovery efficiencies were calculated by spiking de-ionised water samples with known amounts of standards. These results were used to calculate the final compound concentrations.

4.2.4 *Results*

Figure 4.4 shows the interpreted neutron probe readings, giving the change in moisture content with depth. It is evident from the graph that the wetting front had migrated beyond 3 m in under 4 h.

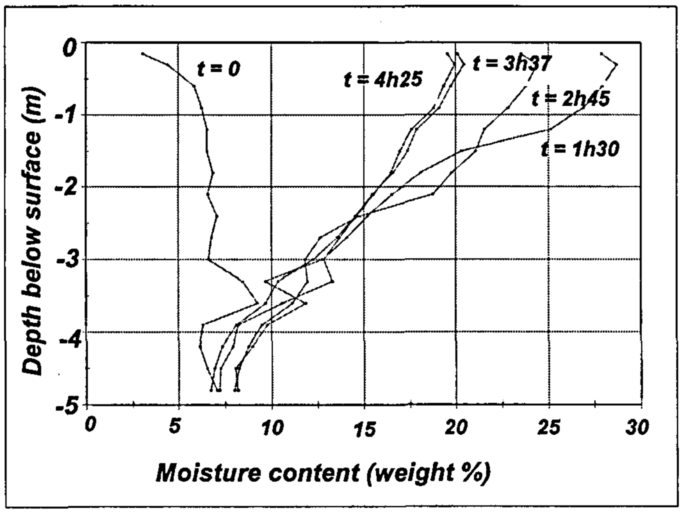


Figure 4.4 : Neutron probe moisture content vs. depth. t = time after infiltration started

Table 4.2 shows the aliphatic hydrocarbons that were identified in the wastewater from pond A. It is noted that concentration of various organic compounds in the pond are likely to vary. As this variation in concentration was not determined, the data in Table 4.2 should be viewed as semi-quantitative.

Table 4.2 : Organic contaminants (mg/l) in wastewater

Decane	1.06
Tridecane	1.42
Tetradecane	0.95
Pentadecane	0.36

The organic compounds shown in Table 4.2 were not detected in the soil water and groundwater samples which were collected before the infiltration experiments were initiated. They were, however, detected in all the soil water samples and the groundwater samples which were collected after the infiltration experiment. Shorter-chain alkanes (decane and undecane) were detected at 1 m and 4 m (Table 4.3).

Table 4.3 : Aliphatic hydrocarbons (mg/l) detected in soil water and groundwater samples

	Depth from the surface				
	1m	2m	4m	5m	Ground-water (~8m)
Decane	0.18	ND	0.16	ND	ND
Undecane	0.22	ND	0.25	ND	ND
Dodecane	0.41	1.36	1.08	1.41	0.63
Tridecane	0.49	1.70	1.73	1.68	0.83
Tetradecane	0.29	1.17	0.91	1.01	0.48
Pentadecane	0.14	0.44	0.38	0.35	0.16

ND = not detected
Detection limit = 0.005 mg/L.

Of the organic compounds added at the surface, aniline and butyric acid were not detected in the water samples. Phenol was only detected at 1 m (0.2 mg/l). Toluene was detected at 4 m and its derivatives at 1 m (Table 4.4).

Table 4.4 : Toluene and its derivatives (mg/l)

	Depth from the surface (m)	
	1 m	4 m
Toluene	ND	0.01
Benzoic acid	0.01	ND
Benzyl alcohol	0.77	ND

4.2.5 *Discussion*

The infiltration experiments were conducted to examine the vertical movement of organic compounds at this site. The main interest here was to examine whether the concentration of these compounds would decrease with depth during infiltration, and especially whether these compounds would penetrate through the 8 m thick unsaturated zone to reach the water table. The aliphatic hydrocarbons, although not the main focus of this study, have provided evidence that some organic contaminants will migrate rapidly through the unsaturated zone in this area. These compounds were detected in the groundwater two days after the infiltration experiment. This finding implies that groundwater pollution may be occurring in this area as a result of water seepage from the wastewater pond.

Results of the organic contaminants added during the experiment indicate possible attenuation. Butyric acid and aniline were not detected in any of the water samples. Phenol was only detected at 1 m and was not detected at depth.

It is interesting to note that toluene had penetrated up to a depth of 4 m. The organic compounds benzoic acid and benzyl alcohol identified at 1 m are known to be biodegradation products of toluene (Montgomery and Welkom, 1991). As noted by Muszkat (1993), although known to be biodegradable, toluene was added to the list of pollutants of major concern due to their persistence and transportability.The fraction of organic carbon (f_{oc}) of the sands (0.3 - 0.4 %) is relatively low, as such sorption is not likely to be high.

A number of assumptions were made in assessing these results. Firstly, it was assumed that the flow was strictly vertical and lateral movement of water was minimal. Results of the neutron probe measurements provide a basis to justify this assumption because a rapid vertical movement of the wetting front was observed. It was also assumed that sorption of organic compounds on the silica powder and the porous cups was minimal and that the volatilization of the organic compounds during sampling was insignificant.

4.3 Migration and attenuation of contaminants at waste disposal facilities

4.3.1 *Objectives of sampling at waste disposal facilities*

Sampling of soil and/or water was conducted at sites where waste disposal activities have occurred over several years to examine whether or not a reduction in contaminant concentration, and hence natural attenuation, could be discerned. Sampling was conducted at

- ☐ industrial liquid waste evaporation pans
- ☐ industrial liquid waste - flood spreading site
- ☐ industrial liquid waste- leaking point source
- ☐ domestic solid waste disposal site.

The site descriptions and sampling results are discussed below.

4.3.2 *Industrial liquid waste evaporation pans*

Sampling was conducted at the Vissershok waste disposal site, a Class 1 site situated approximately 20 km north of Cape Town. It was commissioned in 1974 to service the Cape Town area. The site has a number of liquid waste evaporation pans, which were used in the past for the disposal of a range of heavy metals from aluminium, scrap, electroplating, fencing and tanning industries. Data on the composition and properties of the waste which was disposed in these pans is not available.

Augered soil samples, up to a depth of 1.6 m, were collected from two pans for chemical analysis. Typical chemical profiles are shown in Figures 4.5 and 4.6. It is evident from the figures that metals have migrated more than 1.6 m below the ponds.

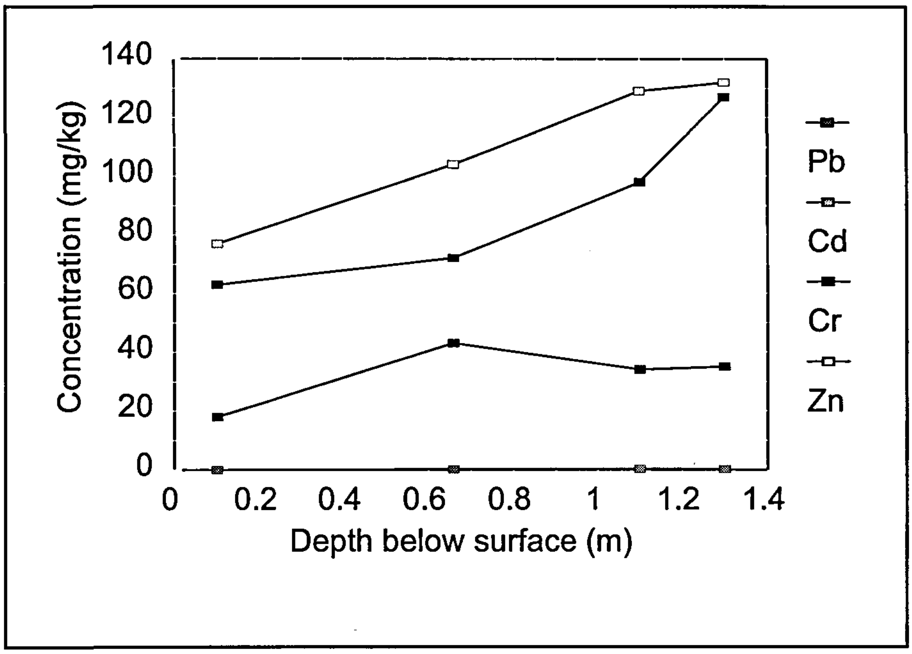


Figure 4.5 : Plot of metal concentrations vs depth

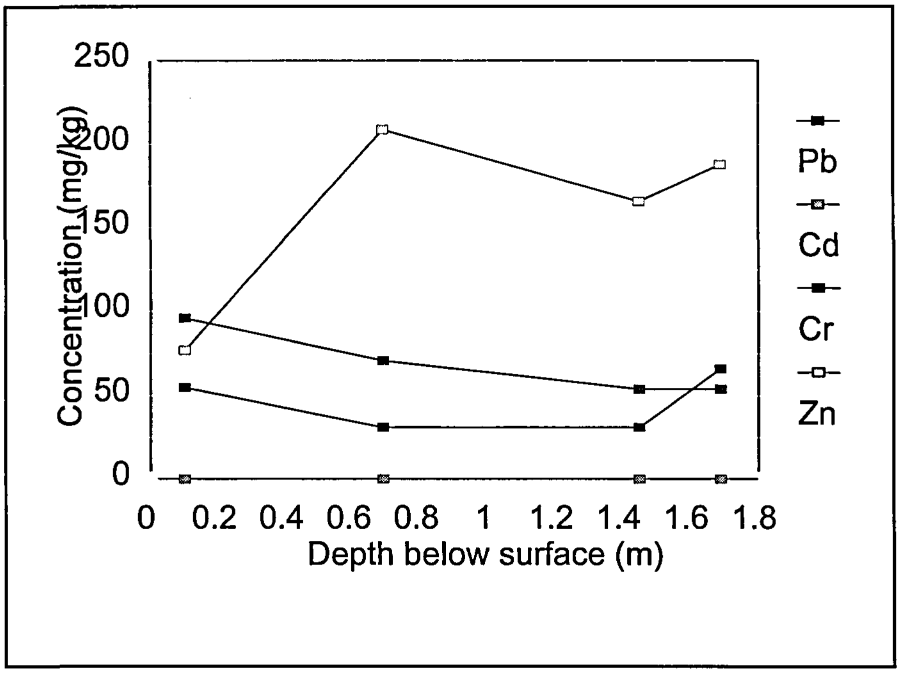


Figure 4.6 : Plot of metal concentrations vs depth

The loading history is not known. This makes it difficult to speculate as to what the dominant factors were in the migration and attenuation of the metals below the pans. It is important, however, to note that by definition, a Class 1 site should be able to contain both the waste and leachate in the site or in the immediate surroundings thereof. The fact that metals have been detected at significant concentrations 1.6 m below the pans, indicates that the attenuation potential of the clay is not as high as might have been assumed.

4.3.3 *Industrial liquid waste - flood spreading (Site X)*

Site X, situated on the Cape Flats, has a metal plating plant. Effluent from the latter is treated by precipitating most of the dissolved metal content by coagulation with a flocculant. The flocculant is filtered out, pressed and disposed of in a Class 1 disposal site. The remaining filtered effluent contains varying amounts of dissolved copper, zinc, chromium, nickel and cadmium. This effluent is disposed of by flood spreading in the permeable Cape Flats sands. Typical effluent concentrations are shown in Table 4.5. Periodically, the effluent disposal area is left to dry and the surface crust scrapped off and disposed in a Class 1 site.

Table 4.5 : Average effluent concentrations (Site X)

pH	EC (mS/m)	Cd (mg/l)	Cu (mg/l)	Cr (mg/l)	Ni (mg/l)	Zn (mg/l)
5.6	286	0.2	4.2	16.2	0.1	1.8

Soil samples were collected in the unsaturated zone to examine the changes in metal concentration with depth. Table 4.6 shows typical results. Most of the metals precipitate at the surface. The metal concentrations in the unsaturated zone are relatively low.

Table 4.6 : Metal concentrations in the unsaturated zone

Depth (m)	Cd (mg/kg)	Cu (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Zn (mg/kg)
Surface	4	39	21	16	12
0.2	3	4	5	7	6
0.4	2	3	3	6	8
0.6	2	4	6	4	5
0.7	2	3	6	5	5

Groundwater samples were collected in augered holes (Table 4.7). The concentrations are relatively low indicating low mobility in the area.

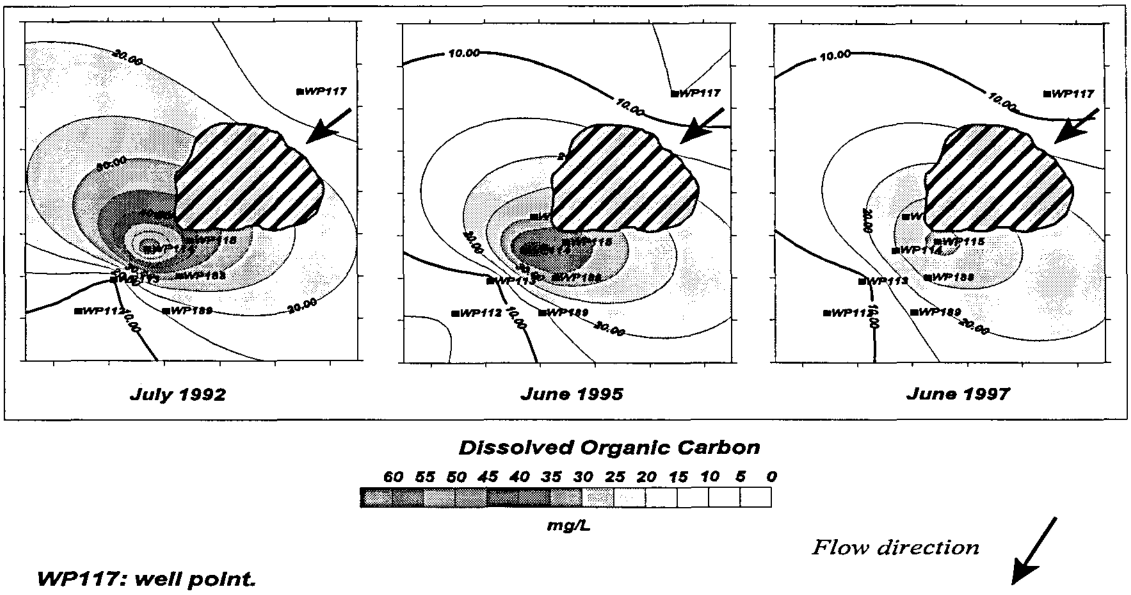
Table 4.7 : Metal concentrations in water samples from augered holes (July 1996)

Sampling point	Cd (mg/l)	Cu (mg/l)	Cr (mg/l)	Ni (mg/l)	Zn (mg/l)
1	<0.01	0.19	0.08	0.05	<0.05
2	<0.01	1.06	0.08	0.06	<0.05
3	0.130	0.61	0.05	0.04	<0.05

The results here show the role of pH buffering. Although the effluent may be acidic, the high buffering capacity of the sands means pH of the sand will not change substantially. Since high pH favours metal precipitation and sorption, migration of this class of contaminants is likely to be low in this area.

4.3.4 *Domestic solid waste disposal site - Site Y*

The waste disposal site (Site Y) was brought into operation in 1975. The site was used for the disposal of domestic refuse, building rubble and non toxic industrial wastes such as textiles, paper and cardboard. The site was officially closed in 1988 and in the following year a groundwater monitoring programme was initiated. A set of 8 well points were installed around the waste site (seven down-gradient and one up-gradient). Figure 4.7 shows DOC contour diagrams from 1992 to 1997. It is evident that a decline in concentration has occurred over the period, suggesting that contaminant attenuation is occurring.



July 1992 *June 1995* *June 1997*

WP117: well point.

Flow direction

CHECK PROPORTIONS

Figure 4.7 : Changes in DOC distribution with time

4.3.5 *Industrial liquid waste - Site Z*

The main industrial activities at Site Z include metal plating and dyeing activities. The effluent from the metal plating process is treated on site in settling tanks. Solutes leaking from one of the tanks caused groundwater contamination in the area. The site is located above a shallow unconfined sandy aquifer.

Plots of EC, heavy metals Ni, Zn and DOC are shown in Figures 4.8 - 4.11. It is evident that salinity as shown by electrical conductivity has caused the most significant contamination at the site. The heavy metal pollution is highly localized. The pollution shows a marked decline a few metres from the source, indicating that metals are not very mobile in this area. The organic compounds show similar behaviour (Figure 4.11). In Figure 4.12 two chromatograms are presented to further illustrate the attenuation of organic compounds in the aquifer. WP1, near the source, shows contamination with a number of aromatic hydrocarbons while WP2, 60 m down-gradient is uncontaminated.

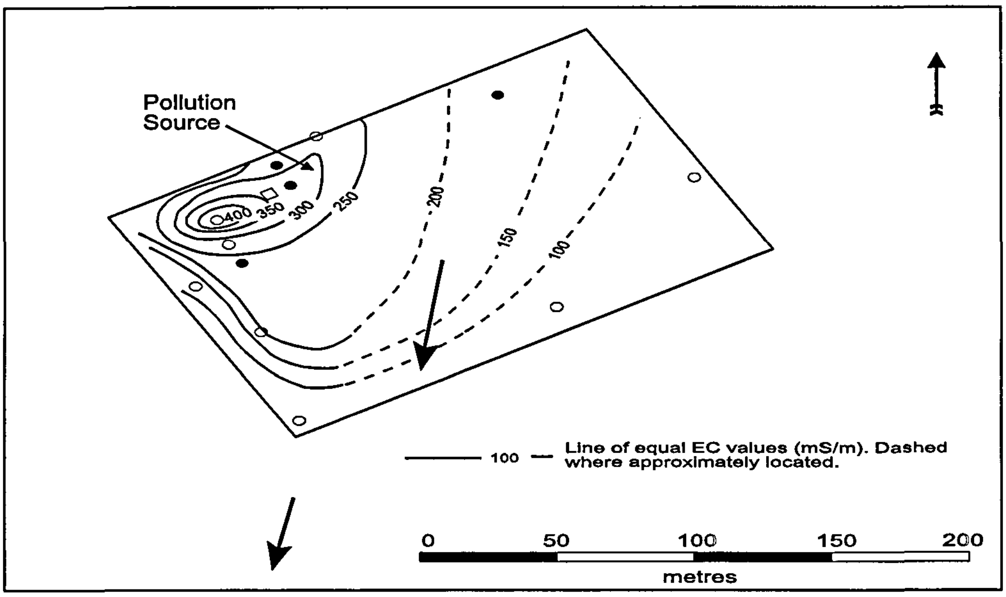


Figure 4.8 : Map showing electrical conductivity values, July 1996

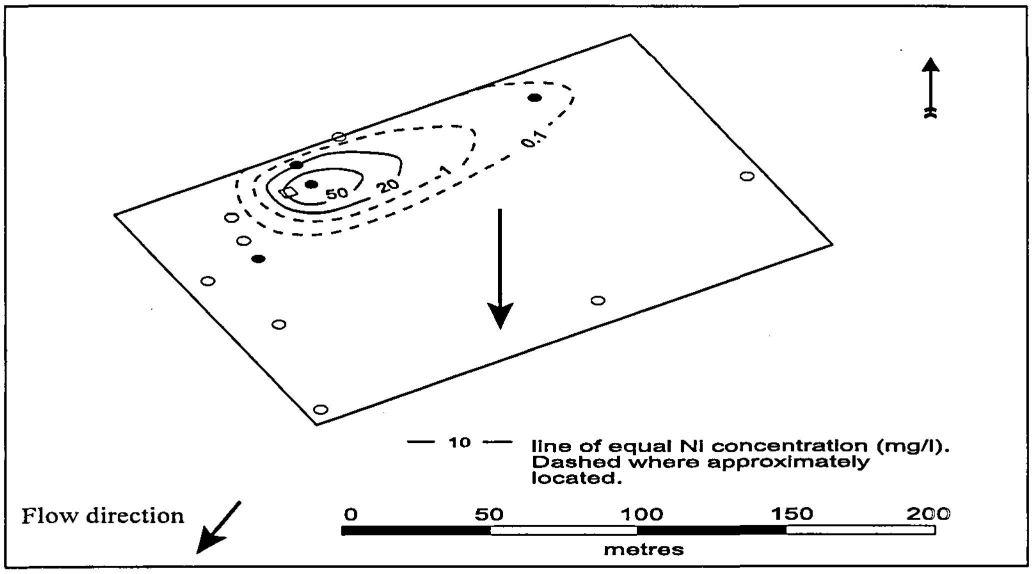


Figure 4.9 : Map showing nickel concentrations, July 1996

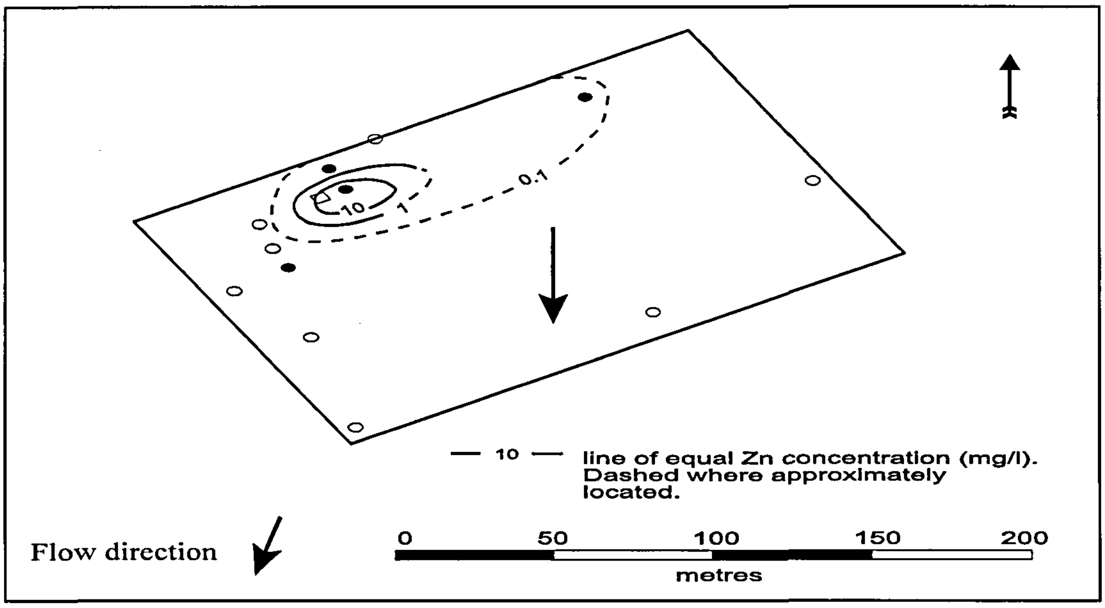


Figure 4.10 : Map showing zinc concentrations, July 1996

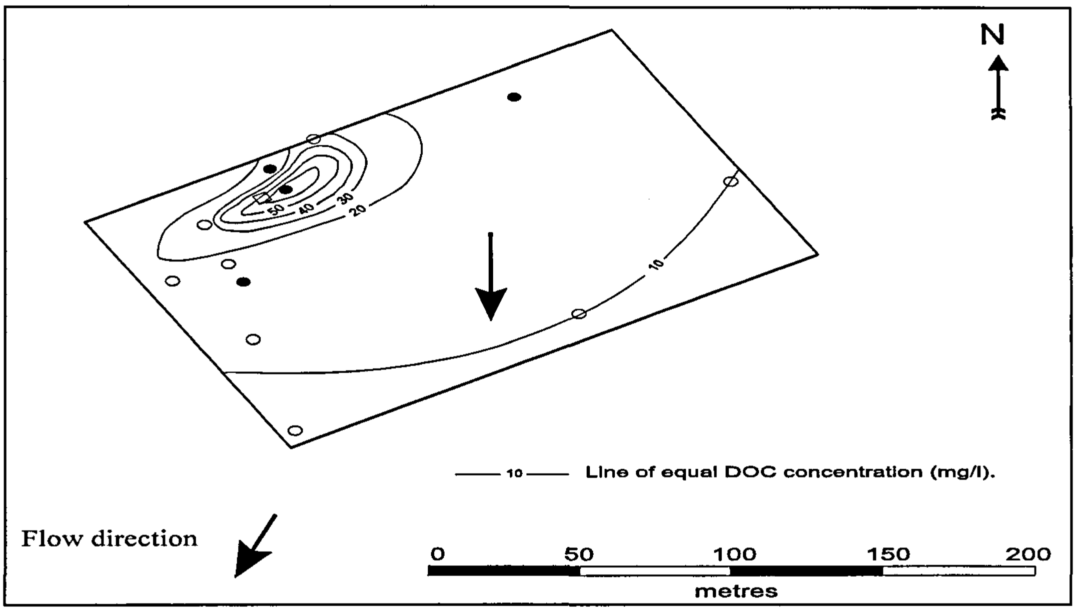


Figure 4.11 : Map showing dissolved organic concentrations, July 1996

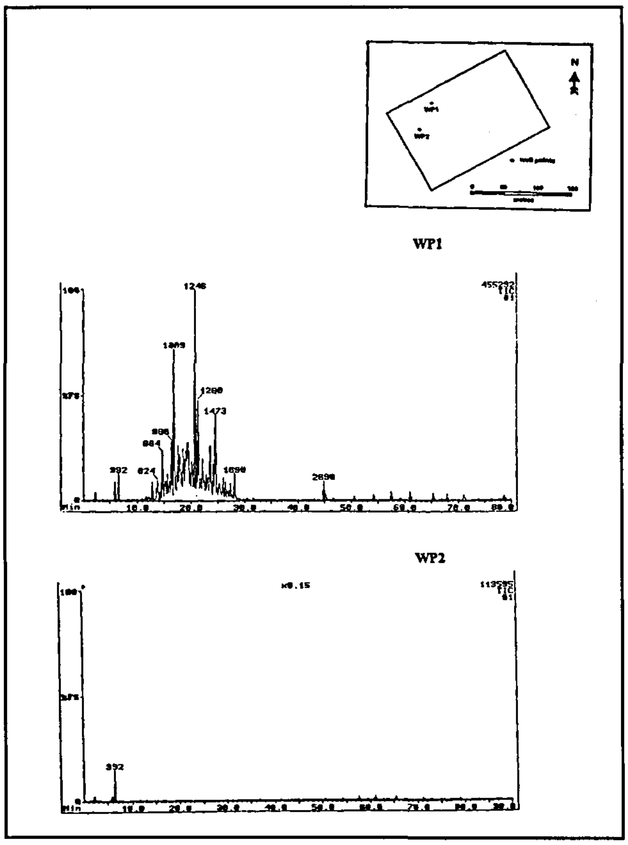


Figure 4.12 : Chromatograms of two water samples from WP1, near the source and WP2, 60 m away

CHAPTER 5

SOLUTE TRANSPORT MODELLING

BY B EIGENHUIS

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A	$[L^2]$	Cross-sectional area (Equation 2.25)
b1	$[Wm^{-1}K^{-1}]$	Empirical thermal conductivity parameter
b2	$[Wm^{-1}K^{-1}]$	Empirical thermal conductivity parameter
b3	$[Wm^{-1}K^{-1}]$	Empirical thermal conductivity parameter
Cn	$[Jm^{-3}K^{-1}]$	Volumetric heat capacity of solid phase
Co	$[Jm^{-3}K^{-1}]$	Volumetric heat capacity of organic matter
Cw	$[Jm^{-3}K^{-1}]$	Volumetric heat capacity of liquid
C_0	$[M/L^3]$	Concentration (Equation 2.36, 2.42 - 2.44)
d	[-]	Wilmot's coefficient of agreement
D	$[L^2/T]$	Diffusion-dispersion coefficient (Equation 2.28)
Dg	$[L^2/T]$	Diffusion coefficient of gas phase
D_L	[L]	Longitudinal dispersivity
D_T	[L]	Transverse dispersivity
Dw	$[L^2/T]$	Diffusion coefficient in free water
kg,1	[-]	Constant relating solution and gas concentration
kg,2	[-]	Constant relating solution and gas concentration
kg,3	[-]	Constant relating solution and gas concentration
k_s	[L/T]	Saturated hydraulic conductivity
ks,1	$[L^3/M]$	Constant relating solution and adsorbed concentration
Ks	[L/T]	Saturated hydraulic conductivity
L	[L]	Column length (Equation 7.1)
n	[-]	Soil water retention function exponent (Equations 2.9, 2.12)
P	[kPa]	Atmospheric pressure
q	$[L^3/T]$	Flowrate through laboratory column (Equation 7.1)
Rc	[-]	Retention capacity of NAPL in dry soil
Ti	[°C]	Initial temperature
tp	[s]	Pulse time
v	[L/T]	Velocity of solute through soil
α	[-]	Empirical constant (values of 1.35 to 1.4 in equation 2.2)
β_k	[-]	Adsorption isotherm constant
η_k	[-]	Empirical constant in adsorption isotherm
λL	[L]	Longitudinal thermal dispersivity
λT	[L]	Transvers thermal dispersivity
$\mu w,1$	[1/T]	First order rate constant for solute 1 in the liquid phase
$\mu' w,1$	[1/T]	First order rate constant for chain solute 1
ρ	$[M/L^3]$	Bulk density
Θn	[-]	Volumetric solid phase fraction
Θo	[-]	Volumetric organic matter fraction

5. SOLUTE TRANSPORT MODELLING

5.1 Introduction

The increasing severity and complexity of subsurface contamination problems has resulted in growing demands for predictive transport models through both the unsaturated and saturated zones. Computer modelling offers an economic and effective way of making generalised predictions of contaminant fate and in addition, offers an opportunity to investigate the likely variability in behaviour in a much wider range of conditions than is possible experimentally.

A typical management procedure is to solve (remediate) an environmental problem would be to observe the characteristics of the problem and to derive and evaluate different solutions. The role of modelling in such a scenario would be to predict the results of these solutions, thereby allowing the selection of the best solution by comparing different simulation results. Numerical models can also be used to assess the contaminant attenuation capacity of a specific unsaturated soil above the water table. These attenuation capacity estimates can be used in groundwater vulnerability mapping. Models can also be used to calculate the time lag for a contaminant to reach the water table.

The main aim of the modelling aspect of this project was to develop procedural guidelines for modelling soil pollutant transport in the unsaturated zone. Specific aims were:

☐ to identify factors and processes that will influence attenuation capacity

☐ to select a suitable numerical model that addresses contaminant attenuation in the subsurface

☐ to perform a sensitivity analysis on the selected model

☐ to validate the model on a laboratory and a field scale

☐ to use the model to predict the movement of contaminants leaching through soil at a field site

☐ to develop software to aid in the modelling process

☐ to calculate the attenuation capacity of soil from modelling results

5.2 Methods and results

5.2.1 *Modelling contaminant attenuation*

From the literature survey, it was concluded that the attenuation influencing parameters or factors that need to be addressed by a holistic modelling effort, or at least be described when not considered in modelling, can be listed as follows :

A Physical parameters and factors :

- ➔ The number of different soil textures
- ➔ Fluid retention as a function of the percentage sand, silt and clay
- ➔ Bulk density and the percentage organic carbon
- ➔ Permeability
- ➔ Convection
- ➔ Longitudinal and transversal dispersivity
- ➔ Diffusion
- ➔ Fluid density and viscosity
- ➔ Preferential flow as expressed by the fluid retention function.

B Chemical parameters and factors :

- ➔ pH
- ➔ Sorption (Described by a retardation factor or linear, Langmuir or Freundlich isotherms, including different mechanisms such as CEC, adsorption, organic complexation, co-precipitation and competitive adsorption)
- ➔ Multiple cation exchange reactions
- ➔ Solute concentration in the soil prior to further solute addition

C Biological parameters and factors :

- ➔ Transpiration (calculated by considering both meteorological conditions and crop properties)
- ➔ Type of vegetation
- ➔ The characteristics of the root zone

D Climatic parameters and factors :

- ➔ Temperature
- ➔ Precipitation
- ➔ Evaporation
- ➔ Solute concentration of the precipitation

E Other parameters and factors :

- ➔ Time

- ➔ Zero, first and second order reaction kinetics describing transformation processes such as: (a) volatilization, (b) dissolution, (c) precipitation, (d) adsorption, (e) desorption, (f) mobilization, (g) immobilization and (h) degradation

5.2.2 *A comparison of numerical simulation models*

In order to find a suitable computer code, a range of available models were examined in terms of their capabilities. The guidelines for the screening of solute transport models were based on recommendations by Moolman (1993). The criteria included the following : (a) the model must be able to describe the movement of water and solutes in soil in *two or three dimensions*, (b) the model type must be *mechanistic or functional*, (c) *climatic parameters* must be considered, (d) the model must be able to mathematically describe (e) *multiple* (f) *inorganic* and/or (g) *organic* solute movement on a *(h) field scale*, allowing for (I) *transient* conditions.

In addition to the above criteria, information from Wagenet and Rao (1990) was used to evaluate eleven selected models in terms of their characterizing parameters. The models compared were: VS2D (Lappala *et al.*, 1987), SWMS_2D (Simunek *et al.*, 1994), 3DADE (Leij and Bradford, 1994), SWASAL (Kabalt and Bolt, 1989), GEOCHEM (Sposito and Mattigod, 1979), MINTEQ (Westall *et al.*, 1976; Allison *et al.*, 1991), RIOCATS (Poulsen and Moldrup, 1994), SWARTRE (Wesseling *et al.*, 1989), CHAIN_2D (Simunek and van Genuchten, 1994), SWMS_3D (Simunek *et al.*, 1995) and CHAIN_3D. All the models investigated in this study were summarized similarly as shown in Table 5.1 for CHAIN_2D and two similar models.

Table 5.1a : Major selection criteria and characterizing parameters required by three simulation models

Type of Model	(Res.)	(Res.)	(Res.)
PARAMETER	CHAIN_2D	SWMS_3D	CHAIN_3D
Model Characteristics			
1, 2 or 3 Dimension Model	2D	3D	3D
Model Class (Laboratory / Field / Both)	B	B	B
Transient or Equilibrium State	T	T	T
Multiple or Singular Solute	M	S	M
Inorganic or Organic or Both	B	B	B
Physical Parameters			
Multiple soil layers	Y	Y	Y
Diffusion coefficient	Y	Y	Y
Saturated water content (θ_s)	Y	Y	Y
Field capacity water content (θ_{fc})	N	N	N
Hydraulic properties (K-ψ-θ)	Y	Y	Y
Boundary flexibility	Y	Y	Y
Bulk density	Y	Y	Y
Organic carbon content	Y	Y	Y
Heat flow parameters	Y	N	Y
Fluid density	N	N	N
Fluid viscosity	N	N	N
Longitudinal dispersivity	Y	Y	Y
Transversal dispersivity	Y	Y	Y
Preferential flow	N	N	N
Drains	Y	Y	Y
SCS curve number	N	N	N

Table 5.1b : Major selection criteria and characterizing parameters required by three simulation models

Type of Model PARAMETER	(Res.) CHAIN_2D	(Res.) SWMS_3D	(Res.) CHAIN_3D
Chemical Parameters			
pH	N	N	N
Cation exchange capacity (CEC)	N	N	N
Sorption (Linear, Freundlich, Langmuir)	Y	Y	Y
Competitive adsorption	Y	N	Y
Multiple cation exchange	Y	N	Y
Initial soil solution solute concentration	Y	Y	Y
Biological Parameters			
Wilting point water content (θ_{wp})	Y	Y	Y
Root density distribution	N	N	N
Maximum root depth	Y	Y	Y
Solute uptake relationships	Y	Y	Y
Biological degradation rate	Y	Y	Y
Climatic Parameters			
Daily precipitation or irrigation amounts	Y	Y	Y
Precipitation or irrigation rates	Y	Y	Y
Daily pan evaporation	Y	Y	Y
Daily maximum temperature	N	N	N
Daily minimum temperature	N	N	N
Snowmelt	N	N	N
Precipitation solute concentration	Y	Y	Y
Soil temperature	Y	N	Y
Hours of sunlight	N	N	N

Table 5.1c. Major selection criteria and characterizing parameters required by three simulation models

Type of Model PARAMETER	(Res.) CHAIN_2D	(Res.) SWMS_3D	(Res.) CHAIN_3D
Kinetic Rate Parameters			
Zero, first or second order reaction	Y	Y	Y
Sorption	Y	Y	Y
Normalized sorption coefficient (K_{oc})	Y	Y	Y
Distribution coefficient (K_d)	Y	N	Y
Volatilization	Y	Y	Y
Henry's constant (K_H)	Y	N	Y
Saturated vapour density	N	N	N
Aqueous solubility	N	N	N
Gas phase diffusion coefficient	Y	N	Y
Degradation	Y	N	Y
Temperature dependant	Y	N	Y
Mobilization / Immobilization	Y	Y	Y
Dissolution / Precipitation	Y	Y	Y
Management Parameters			
Solute	Y	Y	Y
Application date	Y	Y	Y
Application rate	Y	Y	Y
Depth of incorporation	Y	Y	Y
Multiple applications	Y	Y	Y
Crop (production systems)	N	N	N
Soil tillage effects	N	N	N
Time management	Y	Y	Y

As a result of this comparison, the CHAIN_2D model was selected since the computer code met all the expectations as described by the compiled selection criteria.

5.2.3 CHAIN_2D *sensitivity analysis*

The CHAIN_2D computer code (Simunek *et al.*, 1994) is a mechanistic model that can be used to simulate water and solute movement in a three-dimensional variably saturated soil, exhibiting radial symmetry about the vertical axis. The ANSI standard FORTRAN 77 program numerically solves the Richard's equation for saturated-unsaturated flow, while the convection-dispersion equation is incorporated in the model to account for solute and heat transport. CHAIN_2D accounts for variably saturated water flow, heat transport and the movement of *multiple* (maximum 6) solutes involved in sequential first-order decay reactions. The flow equation incorporates a sink term to account for water uptake by plants. The water flow part of the model can deal with prescribed head, gradient, and flux boundaries, as well as boundaries controlled by climatic conditions. Free drainage boundary conditions and a simplified representation of nodal drains using results of electric analog experiments are also included. The heat transport equation considers transport due to conduction and convection with flowing water. The solute transport equations consider convective-dispersive transport in the liquid phase, as well as diffusion in the gaseous phase. The transport equations also include provisions for nonlinear non-equilibrium reactions between the soil and the liquid phases, linear equilibrium reactions between the liquid and gaseous phases, zero-order production, and two first-order degradation reactions : one which is independent of other solutes, or one which provides the coupling between solutes involved in the sequential first-order decay reactions (Simunek *et al.*, 1994).

The governing flow and transport equations are solved numerically using Galerkin-type linear finite-element schemes. Depending on the size of the problem, the matrix equations resulting from discretization of the governing equations are solved using either Gaussian elimination for banded matrices or the conjugate gradient method for symmetric matrices, or the ORTHOMIN method for asymmetric matrices. Computer memory requirements are a function of problem definition.

The sensitivity of CHAIN_2D model simulation output to changes in input parameter values, was investigated by using the program to numerically simulate the movement of water and a dissolved solute over a five day period in the upper part of a nonuniform soil profile for a single-ring infiltration experiment. The soil profile consisted of a 40 cm thick A-horizon, and a B/C-horizon which extended to a depth of 300 cm. The hydraulic parameters of the two soil layers in the Hupselse Beek area in the Netherlands (Hopmans *et al.*, 1989), are given in Table 5.2. The values of the parameters shown in Table 5.2, were calculated using a closed-form equation (Van Genuchten, 1980).

In the sensitivity study, the soil profile had an initial temperature of 20°C, whereas the infiltrated water had a temperature of 30°C and contained an organic (parent) compound (the pesticide aldicarb (solute 1)) which is known to degrade by oxidation into two sequential daughter products (sulphone (solute 2) and sulfoxide (solute 3)). Each of the three solutes also undergoes hydrolytical first-order decay that leads to products which were not simulated or monitored during their subsequent transport (i.e., oximone, sulphone oximone and sulfoxide oximone). All solutes adsorb onto the solid phase, while volatilization also takes place for aldicarb and sulfoxide. The sensitivity analysis evaluates effects of changes in the values of the input parameters on the model output for variably-saturated water flow, heat movement, and solute transport in a layered and radially symmetric dimensional soil profile for the parent solute only.

The differential rates of movement of solutes through soils results in areas of different concentrations of the solute in the soil. In Figure 5.1, areas of the same concentration are represented by concentration profiles in a two-dimensional area consisting of soil width as the x-axis and soil depth as the y-axis. The surface area under such a concentration profile was calculated using the SURFER software package. This surface area represents half of the total area in which solute is present in the case where two-dimensional transport is considered. If three-dimensional solute transport is considered, the calculated area is directly proportional to the volume of soil in which a solute is present. Changes in surface area were used to evaluate the effects of different input parameter values on the heat and solute movement. The parameters which were investigated are summarized in Tables 5.3 and 5.4. For each sensitivity run, the values in these tables were used as the *central input value* which were sequentially increased and decreased by five 10% steps, while keeping all other values constant.

Results of the sensitivity analyses were presented using a graphical representation known as the "spider diagram" (Figure 5.2) (Addiscott, 1993) in which the "legs" of the spider show the extent and direction of the effects of changes in input parameters from a *central value* for each parameter. SURFER was used to calculate the surface area bounded by the profile with an arbitrary concentration of 0.05 cm^3/cm^3. In order to generate data for the spider diagram, the surface areas obtained from the non-central input values were expressed as percentages of the surface area obtained for the central input parameter for each day of the five day period. This percentage calculation procedure was repeated for all of the increased or decreased input values for the specific input parameter and the spider diagram data (sensitivity percentages) were calculated by subtracting 100% from each of the calculated percentages (non-central areas as a percentage of central areas).

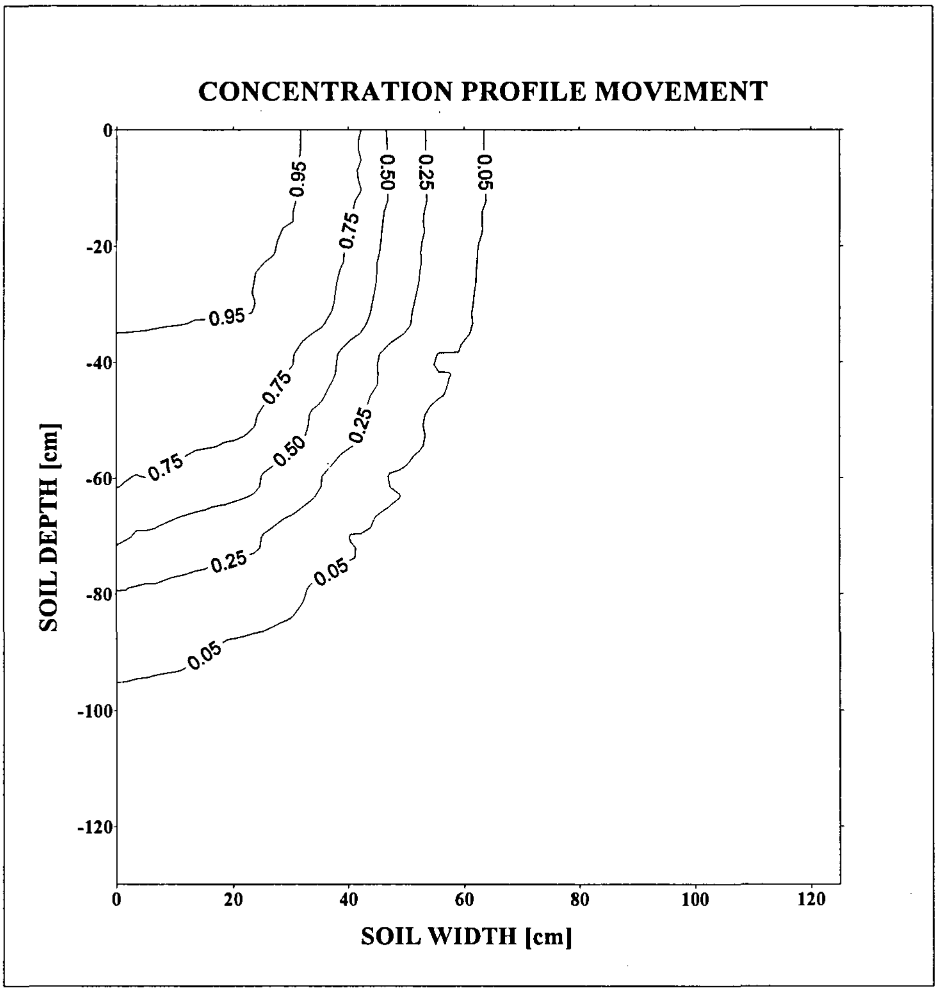

Figure 5.1 : Concentration contours in cm^3/cm^3 showing the area bounded by the 0.05 cm^3/cm^3 concentration profile five days after the start of the infiltration experiment.

Table 5.2 : Hydraulic parameters for two soil layers (Hopmans *et al.*, 1989).

Hydraulic Parameter	A Horizon	B/C Horizon
Residual water content; $\theta_r = \theta_a$[-]	0.0001	0.0001
Maximum water content; $\theta_s = \theta_m = \theta_k$[-]	0.399	0.339
Coefficient of soil water retention function; α [1/cm]	0.0174	0.0139
Exponent in the soil water retention function; n [-]	1.3757	1.6024
Hydraulic conductivity; $K_s = K_k$ [cm/min]	0.0207	0.0315

Table 5.3 : Heat transport input parameters and associated central values for two soils evaluated in the sensitivity analysis of CHAIN_2D.

Parameter / Variable Name	Code or symbol	Value for A Horizon	Value for B/C Horizon
Volumetric solid phase fraction	Θ_n [-]	0.600	0.660
Volumetric organic matter fraction	Θ_o [-]	0.001	0.001
Longitudinal thermal dispersivity	λ_L [m]	0.005	0.005
Transverse thermal dispersivity	λ_T [m]	0.001	0.001
Thermal conductivity empirical parameter	b1 [$Wm^{-1}K^{-1}$]	0.243	0.243
Thermal conductivity empirical parameter	b2 [$Wm^{-1}K^{-1}$]	0.393	0.393
Thermal conductivity empirical parameter	b3 [$Wm^{-1}K^{-1}$]	1.534	1.534
Volumetric heat capacity of solid phase	Cn [$Jm^{-3}K^{-1}$]	1.92×10^6	$1.92 * 10^6$
Volumetric heat capacity of organic matter	Co [$Jm^{-3}K^{-1}$]	2.51×10^6	$2.51 * 10^6$
Volumetric heat capacity of liquid	Cw [$Jm^{-3}K^{-1}$]	4.18×10^6	$4.18 * 10^6$
Initial temperature	Ti [°C]	20	20
Prescribed temperature boundary condition	To [°C]	30	30

Table 5.4 : Input parameters and associated central values evaluated in the sensitivity analysis of CHAIN_2D.

Parameter Name	Code or symbol	Value
Bulk density	ρ [kg/m^3]	1300
Diffusion coefficient in free water	D_w [m^2/day]	0.00374
Diffusion coefficient in the gas phase	D_g [m^2/day]	0.432
Longitudinal dispersivity	D_L [m]	0.005
Transverse dispersivity	D_T [m]	0.001
Constant relating solution and adsorbed concentration for solute 1.	$k_{s,1}$ [m^3/kg]	0.0001
Constant relating solution and adsorbed concentration for solute 2.	$k_{s,2}$ [m^3/kg]	0.00005
Constant relating solution and adsorbed concentration for solute 3.	$k_{s,3}$ [m^3/kg]	0.0002
Constant relating solution and gas concentration for solute 1.	$k_{g,1}$ [-]	$1.33*10^{-7}$
Constant relating solution and gas concentration for solute 2.	$k_{g,2}$ [-]	0.0
Constant relating solution and gas concentration for solute 3.	$k_{g,3}$ [-]	$1.33*10^{-3}$
First order rate constant for solute 1 in the liquid phase	$\mu_{w,1}$ [1/day]	0.2
First order rate constant for solute 2 in the liquid phase	$\mu_{w,2}$ [1/day]	0.01
First order rate constant for solute 3 in the liquid phase	$\mu_{w,3}$ [1/day]	0.005
First order rate constant for chain solute 1	$\mu'_{w,1}$ [1/day]	0.36
First order rate constant for chain solute 2	$\mu'_{w,2}$ [1/day]	0.024
First order rate constant for chain solute 3	$\mu'_{w,3}$ [1/day]	0.0024
Thickness of stagnant boundary layer	d [m]	0.005

The sensitivity analysis results for bulk density, saturated hydraulic conductivity and the exponent of the soil water retention (SWR) function are shown in Figures 5.2 to 5.4 while the results for the remaining parameters are presented in Table 5.5. In Figures 5.2 to 5.4, the x-axis represents the percentage change in input parameter from the central value to values less and/or greater than that of the central value. The y-axis represents the percentage change in the total area under the concentration profile in relation to the surface area calculated from results obtained using a central input parameter value. The results in Table 5.5 are the mean values of percentage change in soil profile area over the five day period for a 20% increase in input parameter value.

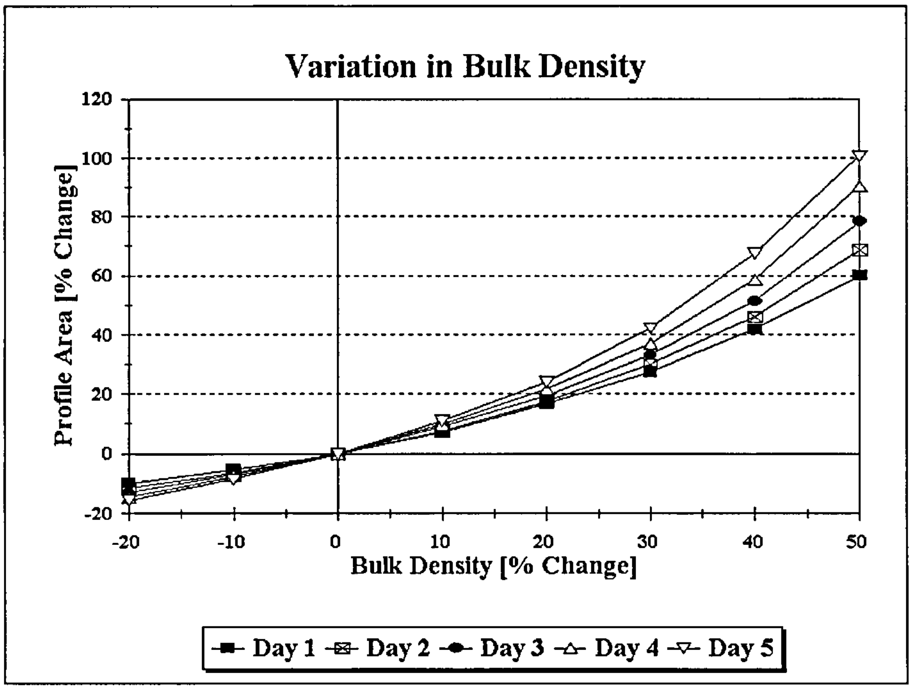

Figure 5.2 : Relationships between changes in bulk density and the percentage change in soil profile area over a five day period.

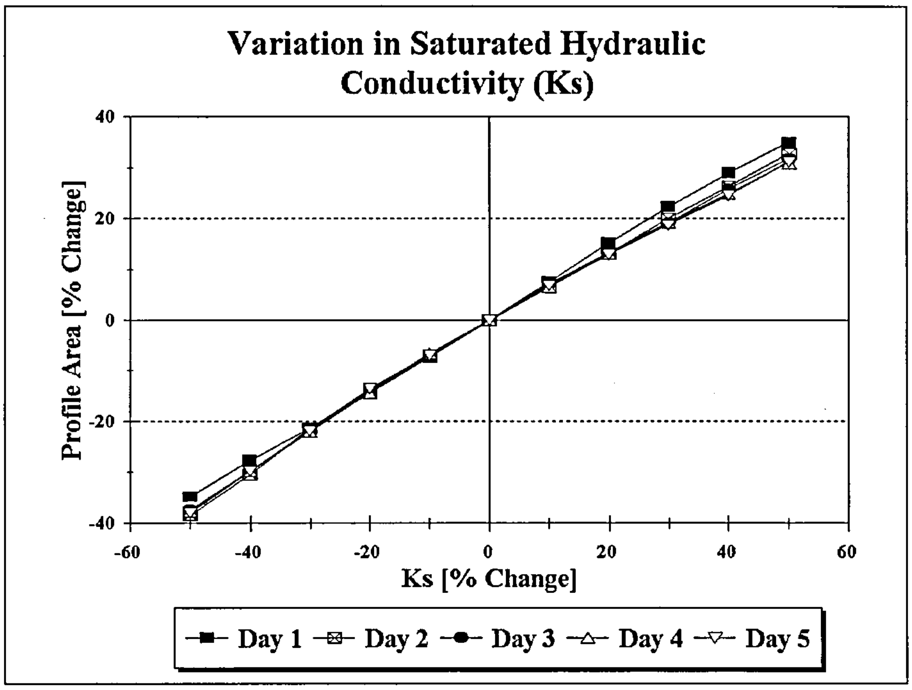

Figure 5.3 : Relationships between changes in saturated hydraulic conductivity (Ks) and the percentage change in soil profile area over a five day period.

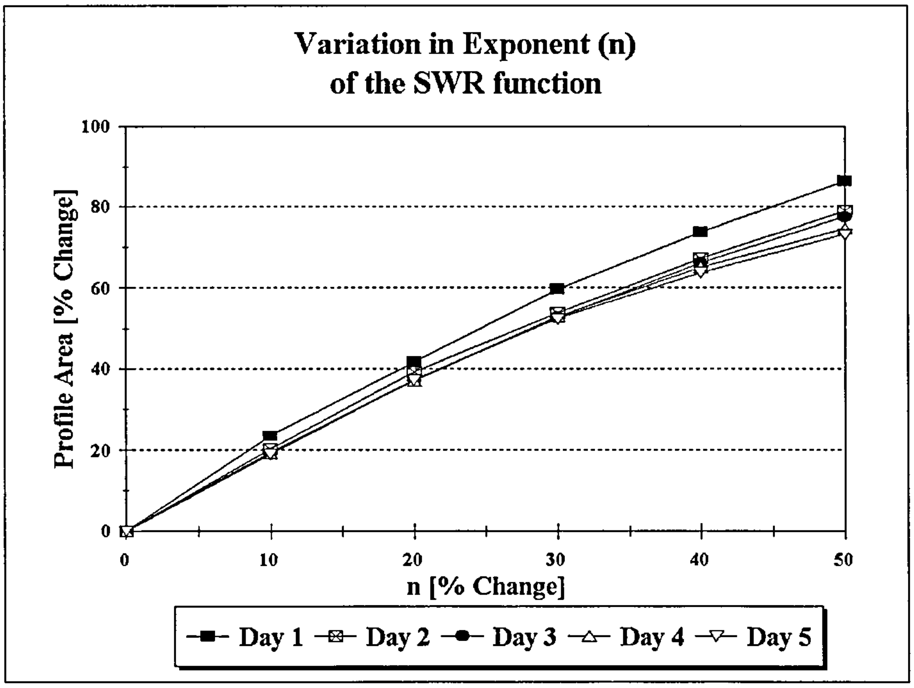

Figure 5.4 : Relationships between changes in the SWR function's exponent (n) and the percentage change in soil profile area over a five day period.

Table 5.5 : CHAIN_2D sensitivity analysis results in absolute mean values for the percentage change in soil profile area in relation to a 20% increase in the central input parameter value.

Parameter	% Change	Parameter	% Change
α [-]	1.0	D_T [m]	0.01
b1 [$Wm^{-1}K^{-1}$]	0.1	Henry k_{g1} [-]	0.0
b2 [$Wm^{-1}K^{-1}$]	0.05	Ks [m/day]	18.0
b3 [$Wm^{-1}K^{-1}$]	0.5	λ_L [m]	0.0
ρ [kg/m^3]	20.0	λ_T [m]	0.0
β_k [-]	3.0	$\mu'_{w,1}$ [1/day]	5.0
Cn [$Jm^{-3}K^{-1}$]	0.3	$\mu_{w,1}$ [1/day]	2.0
Co [$Jm^{-3}K^{-1}$]	0.0	n [-]	40.0
Cw [$Jm^{-3}K^{-1}$]	1.0	Θ_n [-]	0.25
D_g [m^2/day]	0.0	Θ_o [-]	0.0
D_w [m^2/day]	1.5	$k_{s,1}$[m^3/kg]	5.0
D_L [m]	0.5		

In terms of the magnitude of the effect of the parameters examined on parent solute movement, the sensitivity analysis indicate that the parameters can be arranged in the following sequence: $(n,\alpha) >$ Ks $\approx$ Bulk Density > Climate >> Adsorption Isotherm > First Order Kinetics > Diffusion Coefficient in Water > Volumetric Heat Capacity of Liquid > Longitudinal Dispersivity $\approx$ B3 (Coefficient of Thermal Conductivity Function) > Volumetric Heat Capacity of the Solid Phase > Volumetric Solid Phase Fraction > B1 $\approx$ B2 $\approx$ Beta (Adsorption Isotherm Constant) $\approx$ Transversal Dispersivity > Volumetric Organic Matter Fraction $\approx$ Transversal Thermal Dispersivity of Material $\approx$ Longitudinal Thermal Dispersivity of Material $\approx$ Henry's Coefficient $\approx$ Dg = 0.

This sequence stresses the importance of the hydraulic properties of the soil, climate and bulk density factors in the movement of contaminants in soil. When considering the chemical parameters, the change in input parameter value for the adsorption isotherm has shown a more pronounced sensitivity than that of the first order kinetic parameter. The significance of changes in temperature related parameters are less important than parameters already mentioned in this paragraph. The above parameter sequence allows a modeller to decide on the most significant parameters that should be included in a modelling effort, eliminating parameters that would result in high observation costs and contribute relatively little to the accuracy of the modelling result.

5.2.4 *Laboratory scale model validation*

In order to model the attenuation of solutes in the field experiment as accurately as possible, it was important to determine the solute adsorption kinetics from column *breakthrough studies.* The results of the sensitivity analysis of CHAIN_2D provided guidelines for the selection of the important parameters and factors to be measured in the column experiment. These parameters chosen were: Ks (saturated hydraulic conductivity), n (exponent of the soil water retention (SWR) function), α (coefficient of the SWR function), ρ (soil bulk density), D (diffusion coefficient) and k_s (adsorption isotherm coefficient).

The equipment used in this study are shown in Figure 5.5. The two solution tanks have a volume of 30 litres each. Tank A was used to make up the feedstock solution by dissolving a salt of a given heavy metal in water, or the leachate of interest. This resulted in a solution with a known concentration. Solution tank B was filled with clean distilled water or Coastal Park leachate containing no heavy metals. The laboratory column was packed to a known density with a soil obtained from the Swartklip waste disposal site. The quantity of soil was weighed and the volume of the column was calculated. Since the adsorption kinetic parameters are determined from miscible displacement studies, the soil in the column was saturated with the liquid of interest. This was effected by switching on the liquid circulation pump and filling the header tank with the liquid from tank B. The valve from the header tank was then opened and the liquid flowed in at the bottom and moved upwards until the column was saturated. The liquid from the column then flowed through the EC probe and into the leachate tank.

To enable introduction of a pulse of solute (adsorption section), the valve at the bottom of the column was closed to keep the column saturated. The pump was switched off and the header tank was drained into the leachate tank. The header tank overflow pipe was fitted to tank A and the header tank was filled with the solution from tank A. The air in the feedpipe to the column was removed by allowing the solution in the header tank to flow to the leachate tank. The valve to the leachate tank was closed and the valve to the column opened. The solution from tank A then flowed through the column.

The flow rate through the column was monitored by observing the solution level in the tank at chosen time intervals. Leachate samples were taken at specific time intervals and the EC of the leachate logged. In cases where there was more than one solute present in the solution, *the observed EC value provided an indication as to when the maximum* of the solute breakthrough curve was reached. After this maximum had been reached, the pump was switched off and the header tank drained into the leachate tank after the valve to the column had been closed. The first two centimetres of the top section of the soil in the column was drained of liquid by opening the valve to the leachate tank and closing it again. A small soil sample (*intermediate sample*) was taken at the top of the column, in order to determine the total adsorbed metals for this intermediate soil sample.

In order to start the *desorption* section of this procedure, the header tank was flushed with distilled water and the overflow changed to tank B again. The pump was started and the valves changed to allow the liquid to flow through the column. The liquid level in tank B and the EC at the column outlet were observed at chosen time intervals and samples were taken to determine the concentration of the heavy metal or metals with AAS. After the EC meter indicated that all the solute had been washed out of the pores of the soil region, the experiment was stopped and soil samples (*final samples*) were taken in the column for analysis of the total adsorbed metals (EPA method, Risser and Baker (1990)). In cases where the leachate samples could not be analysed immediately, the leachate was acidified by adding three drops of HNO_3 to prevent the solute from precipitating in the sample bottle.

The intermediate adsorbed solute concentration was used to validate the model as well as the column output concentration values determined from samples taken during the breakthrough experiment. The mobility of the heavy metals in the soil was studied for (1) distilled water containing heavy metals and (2) a *leachate*, obtained from the *Coastal Park waste site* (in the vicinity of the Swartklip site).

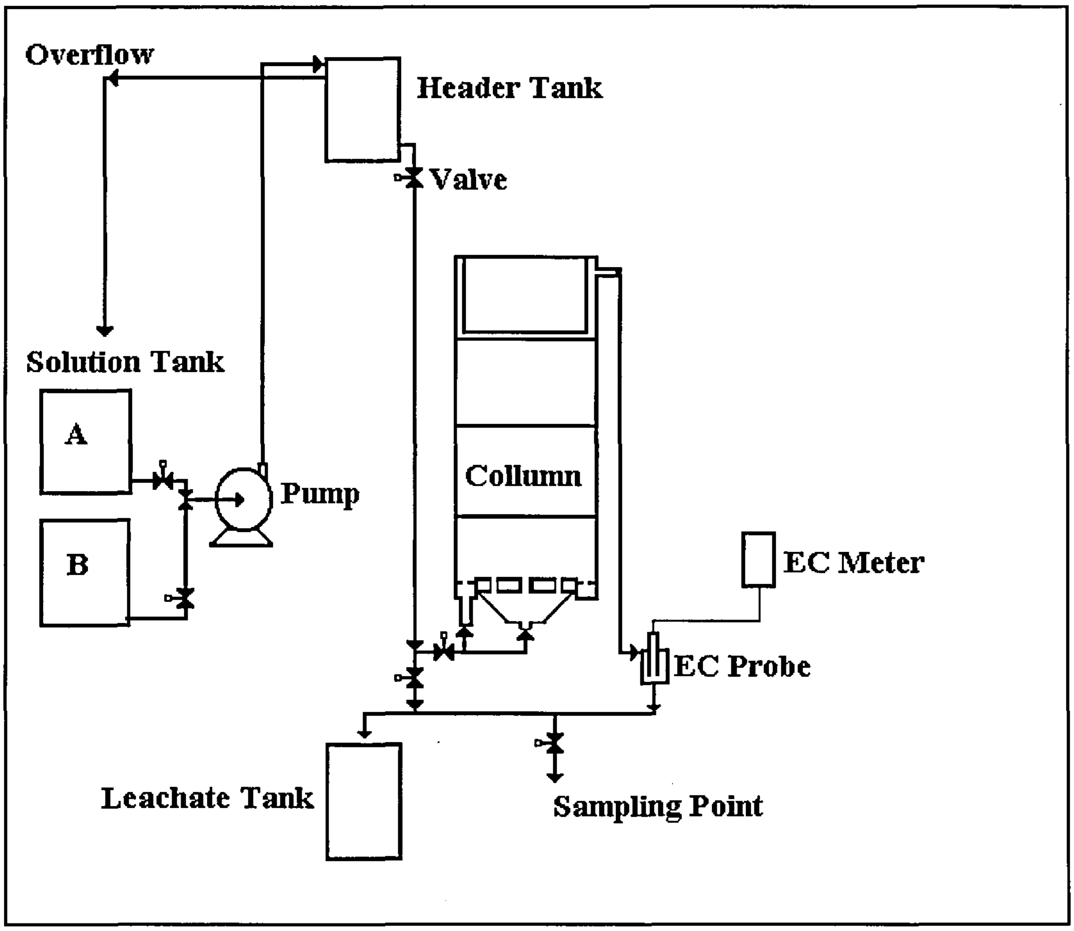

Figure 5.5 : Laboratory column setup.

The results of laboratory column breakthrough studies were obtained for Pb [$Pb(NO_3)_2$], Cd [$Cd(NO_3)_2$] and Cr [$K_2Cr_2O_7$] in distilled water.

CFITIM (Van Genuchten, 1981) was used to calculate all the necessary data from the experimental breakthrough curves. The observed and CFITIM fitted data for Pb are shown in Figure 5.6. The results, obtained from the CFITIM parameter estimation exercises are shown in Table 5.6 (k_s for Exp 13 (Pb), Exp 12 (Cd) and Exp 6 (Cr)).

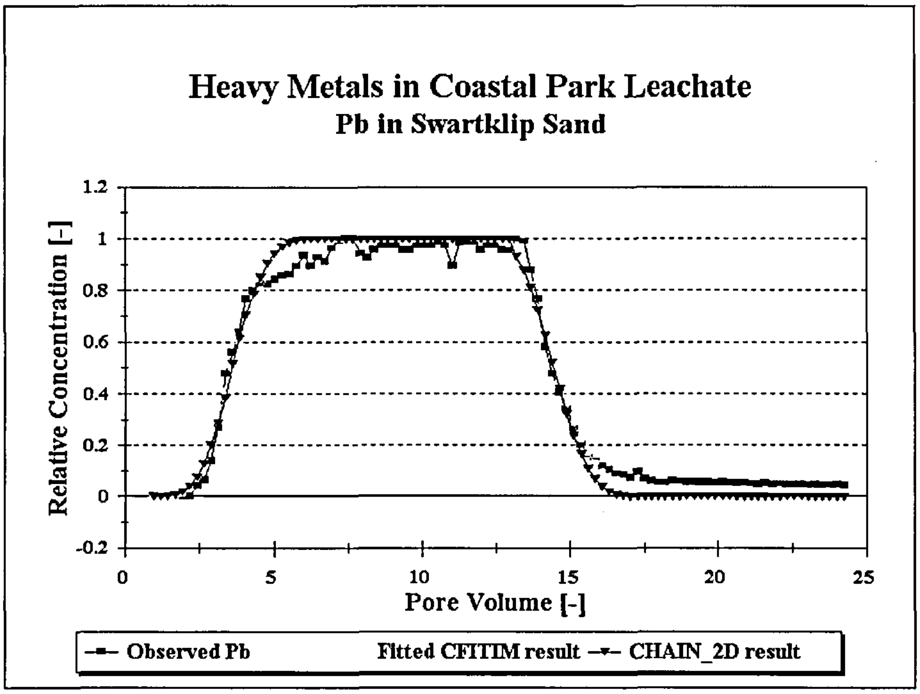

Figure 5.6 : Observed and CFITIM fitted data for Pb in distilled water.

The results of laboratory column breakthrough studies for heavy metals in Coastal Park leachate are presented in Table 5.7 for Pb [$Pb(NO_3)_2$], Cd [$Cd(NO_3)_2$] and Cr [$K_2Cr_2O_7$] in Coastal Park leachate (analysis of leachate shown in Table 5.9). The adsorption isotherm coefficient results, obtained from the CFITIM parameter estimation exercises (Table 5.7, k_s for Exp 14 (Pb), Exp 15 (Cd) and Exp 11 (Cr)) show smaller values of k_s in Coastal Park leachate than in distilled water (Table 5.6). It is possible that some of the constituents of the leachate prohibit the adsorption of heavy metal cations on the sand surface to a certain extent.

The EPA (Risser and Baker, 1990) method was used to analyse the initial, intermediate and final soil adsorbed concentrations of the soil used in the column studies. For distilled water, the Pb attenuation capacity of the Swartklip sand solid phase (Table 5.8) was determined as 7.2E-3 gram Pb per gram Swartklip sand, using the intermediate samples. Attenuation capacity values for Cd and Cr in the solid sand phase are also listed in Table 5.8, showing a relatively small value for Cr. For the Coastal Park leachate, the Pb attenuation capacity of the Swartklip sand solid phase (Table 5.8) was determined as 5.5E-4 gram Pb per gram Swartklip sand, which is significantly smaller than for the same experiment in distilled water.

Attenuation capacity values for Cd and Cr in the solid sand phase are also listed in Table 5.8, showing a relatively small value for Cr.

Other important results obtained for the purpose of validating the model are the soil moisture retention curve shown in Figure 5.7, while the Coastal Park leachate analysis is shown in Table 5.9. The RETC parameter estimation results are shown in Table 5.10. The CHAIN_2D model was validated using the data presented in Figure 5.6 and the Wilmot (1981) coefficient of agreement. This coefficient of agreement was found to be equal to 0.9959 showing a good agreement between the observed and predicted data, thereby validating the CHAIN_2D model on a laboratory scale.

The results obtained from the laboratory column experiments for Coastal Park leachate were not used for validation purposes.

Table 5.6 : Calculated and observed data obtained from the laboratory column study for distilled water and Swartklip sand (Experiments 13, 12 and 6).

Parameter code	Exp 13 Pb	Exp 12 Cd	Exp 6 Cr	Equation
A [cm^2]	12.946	12.946	153.938	πr^2
q [cm/min]	1.0	1.0	0.433	*
n [-]	2.537	2.537	2.537	*
α [-]	0.0574	0.0574	0.0574	*
P [-]	739.92	230.045	64.758	$P = vL/D$
D [cm^2/min]	0.0525	0.1689	0.4238	$D = vL/P$
L [cm]	18.0	18.0	30.0	*
v [cm/min]	2.159	2.159	0.915	$v = q/\theta$
R_c [-]	10.873	32.82	0.943	$R=1+\rho k/\theta$
$k_s = k_d$ [cm^3/g]	3.24	10.442	≈ 0	$k=\theta(R-1)/\rho$
β_k [-]	1.0	1.0	1.0	*
η_k [-]	0.0	0.0	0.0	*
θ [cm^3/cm^3]	0.465	0.465	0.473	*
ρ [g/cm^3]	1.417	1.417	1.396	*
T_1 [cm^3]	12.47	45.37	1.97	*
tp [min]	103.96	378.25	64.59	T_1L/v
Pb c_0 [g/l]	2.4	0.0	0.0	*
Cd c_0 [g/l]	0.0	0.25	0.0	*
Cr c_0 [g/l]	0.0	0.0	0.1506	*

Table 5.7 : Calculated and observed data obtained from the laboratory column study for Coastal Park leachate and Swartklip sand (Experiments 14, 15 and 11).

Parameter code	Exp 14	Exp 15	Exp 11	Equation
	Pb	Cd	Cr	
A [cm^2]	12.946	12.946	153.938	πr^2
q [cm/min]	1.0	1.0	0.325	*
n [-]	2.537	2.537	2.537	*
α [-]	0.0574	0.0574	0.0574	*
P [-]	23.859	155.437	41.094	$P = vL/D$
D [cm^2/min]	1.6288	0.25	0.5022	$D = vL/P$
L [cm]	18.0	18.0	30.0	*
v [cm/min]	2.159	2.159	0.688	$v = q/\theta$
R_c [-]	3.577	7.823	0.722	$R=1+\rho k/\theta$
$k_s = k_d$ [cm^3/g]	0.846	2.24	≈ 0	$k=\theta(R-1)/\rho$
β_k [-]	1.0	1.0	1.0	*
η_k [-]	0.0	0.0	0.0	*
θ [cm^3/cm^3]	0.465	0.465	0.472	*
ρ [g/cm^3]	1.417	1.417	1.398	*
T_1 [cm^3]	12.47	12.47	1.37	*
tp [min]	103.965	103.965	59.738	T_1L/v
Pb c_0 [g/l]	0.672	0.0	0.208	*
Cd c_0 [g/l]	0.0	0.18	0.158	*
Cr c_0 [g/l]	0.0	0.0	0.117	*

Table 5.8 : Adsorbed metals in Swartklip Sand at three different stages of the laboratory column studies.

Experimental adsorbed concentration	Adsorbed Metal Concentration (EPA Method) [g/g AC]					
	Distilled Water			Coastal Park Leachate		
	Pb	Cd	Cr	Pb	Cd	Cr
	Exp 13	Exp 12	Exp 6	Exp 14	Exp 15	Exp 11
Initial	4E-6	1E-5	4E-6	4E-6	1E-5	4E-6
Intermediate	7.2E-3	2.5E-3	1.1E-6	5.5E-4	4E-4	4E-7
Final	5.6E-3	9.5E-4	1E-6	3.6E-4	1.2E-4	4E-7

Table 5.9 : Coastal Park leachate analysis, as obtained from the Scientific Services Branch of the City Engineer's Department.

Coastal Park Leachate Analysis (1996-04-09) City of Capetown, Scientific Services Branch.		
Constituent (Cell nr 2)	Unit	Value
Chloride	Cl [mg/l]	2700
Alkalinity	CaCO3 [mg/l]	6750
Sodium	Na [mg/l]	1150
Potassium	K [mg/l]	1658
Calcium	Ca [mg/l]	76
Magnesium	Mg [mg/l]	128
Copper	Cu [μg/l]	< 25
Chromium	Cr [μg/l]	133
Lead	Pb [μg/l]	0
Cadmium	Cd [μg/l]	7
pH	[-]	8.0
Conductivity	[mS/m]	1259
Phenols	[mg/l]	< 0.1

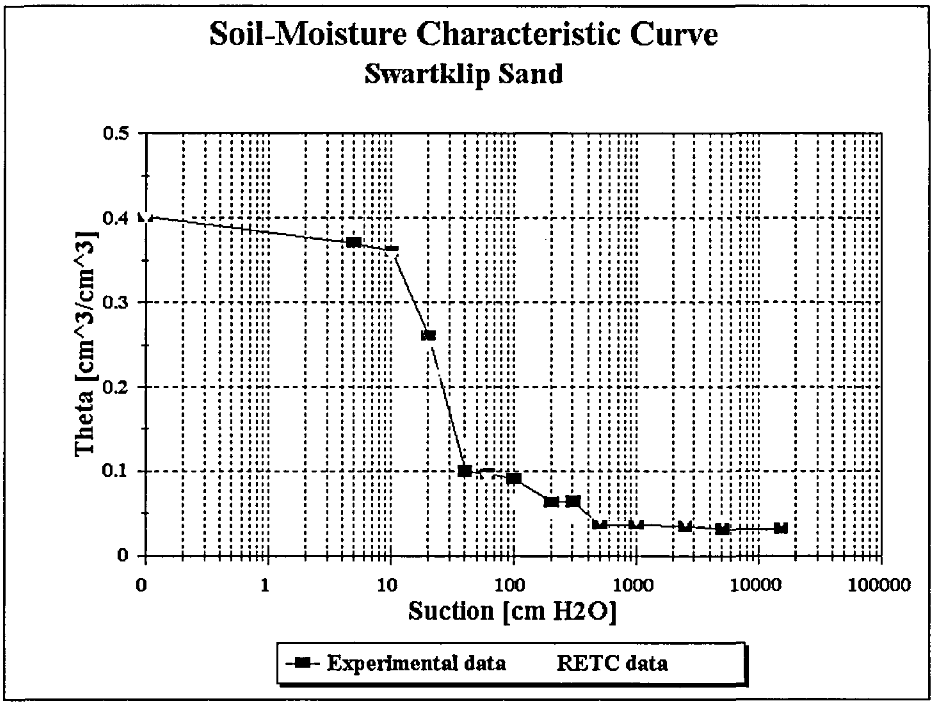

Figure 5.7 : Laboratory soil column characteristic soil moisture curve.

Table 5.10 : Model Validation Parameters.

Parameter	Value
θs	0.4 [-]
α	0.0574 [-]
n	2.537 [-]
Ks	0.0493 [cm/s]
ρ	1.5 [g/cm^3]

5.2.5 *Field scale model validation*

In order to use the CHAIN_2D model to make predictions at the field scale, it was important to validate the model on a field scale. In this case, soil moisture content data obtained during the field infiltration experiment. The positional information of the installed lysimeters is provided in Table 5.11. A detailed site description is given in Section 4.2.

The Swartklip experimental site was modelled as a one dimensional soil area with an atmospheric upper boundary and a constant level water table as a lower boundary. On site rainfall data was obtained by using an MCS Data logger and a tipping bucket rain gauge. The Cape Town International Airport (11 km away) has a fully operational weather station and the data obtained for this station were requested from the South African Weather Bureau. Physical soil data were measured both on site and in the laboratory. These data, together with laboratory results and the information acquired from the infiltration experiment was transformed into a single file for CHAIN_2D.

The validation was performed by running the CHAIN_2D model, using an annotated GRID.IN input file and comparing only the model soil moisture results with the Troxler neutron probe measurements. During the simulation it was assumed that evaporation took place at a rate of 3 mm per day and that the depth to the water table staid constant. The infiltration rate (Prec) was set to 1.08E-1 [cm/min] representing the 7 m^3 of leachate irrigated on the soil surface area of approximately 36 m^2 in the 180 min period. The final atmospheric record was prescribed at 380 minutes, representing the time at which the simulation ended. During this final period, no infiltration took place and the evaporation rate was constant as mentioned above.

Table 5.11 : Swartklip experimental site description

Borehole	Coordinate (X) [m]	Coordinate (Y) [m]	Sample Depth [m]	Porous Cup Depth [m]
SW2	3.9	1.5	-------	--------
PC1	0.8	0	1	1.1
PC2	2.18	0	2	1.77
PC3A	2.95	-0.2	3	2.77
PC3B	5.1	0.45	3	2.97
PC3C	7.7	0	3	2.97
PC4	3.8	0.2	4	3.87
PC5	6.8	0.68	5	4.87
PC6	6.9	-0.2	5	5.47
PC7	6.1	-0.6	8	7.17

The CHAIN_2D soil moisture validation curve are shown in Figure 5.8. The soil water content at depths between 60 cm to 120 cm shows comparable values for both the Troxler readings and the model simulation results.

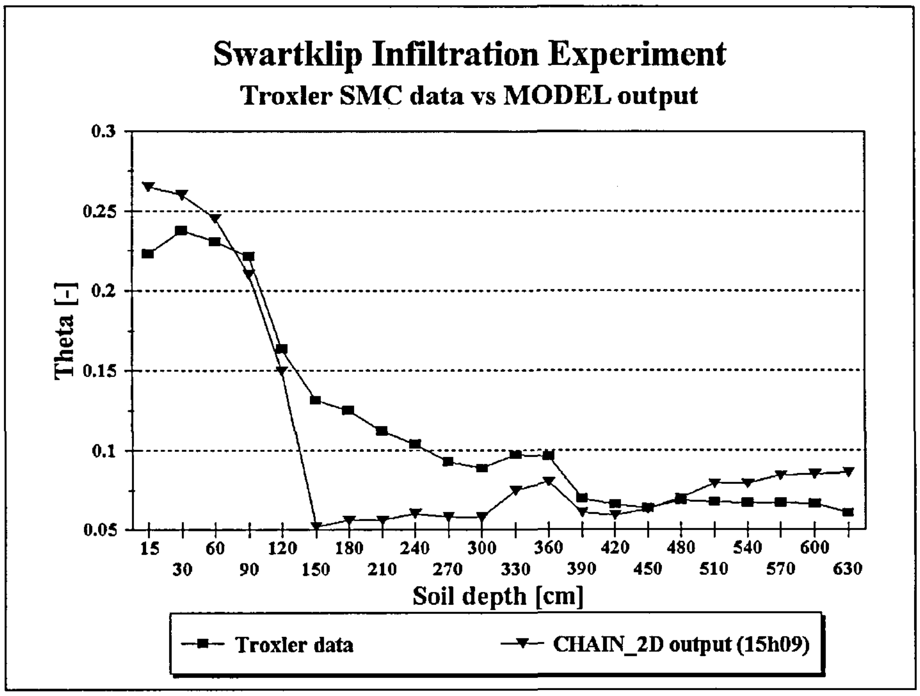

Figure 5.8 : CHAIN_2D validation soil moisture content curves for the printing time of 273 minutes (Wilmot's d = 0.934).

Since soil properties of the sand differed with depth, it was decided to use *five* different soil layers in the simulation. These soil types were demarcated by specific soil lines at specific depths.

In Figure 5.9 it can be seen that there are *five* different depth sections where the saturated hydraulic conductivity (SHC) is relatively constant. The saturated hydraulic conductivity of the soil below the surface was approximated by changing the average hydraulic conductivity (obtained from the Darcian experiments on the non disturbed samples (Table 5.12)) in relation to the change in bulk density.

Other soil moisture content influencing parameters are n and α. The product of these parameters showed the same type of curve (see Figure 5.10) when average values for use in the CHAIN_2D simulation were calculated for the five soil regions. MODEL2D calculated the initial matric suction values (hInit [cm]) after the initial soil moisture content profile data was provided as input.

Table 5.12 : Non disturbed saturated hydraulic conductivity.

Non Disturbed SHC [cm/s]	
PC1	0.0309
PC2	0.0264
PC3A	0.0262
PC3B	0.0181
PC3C	0.0205
PC4	0.0168
PC5	0.0193
PC6	0.0192
PC7	0.0192

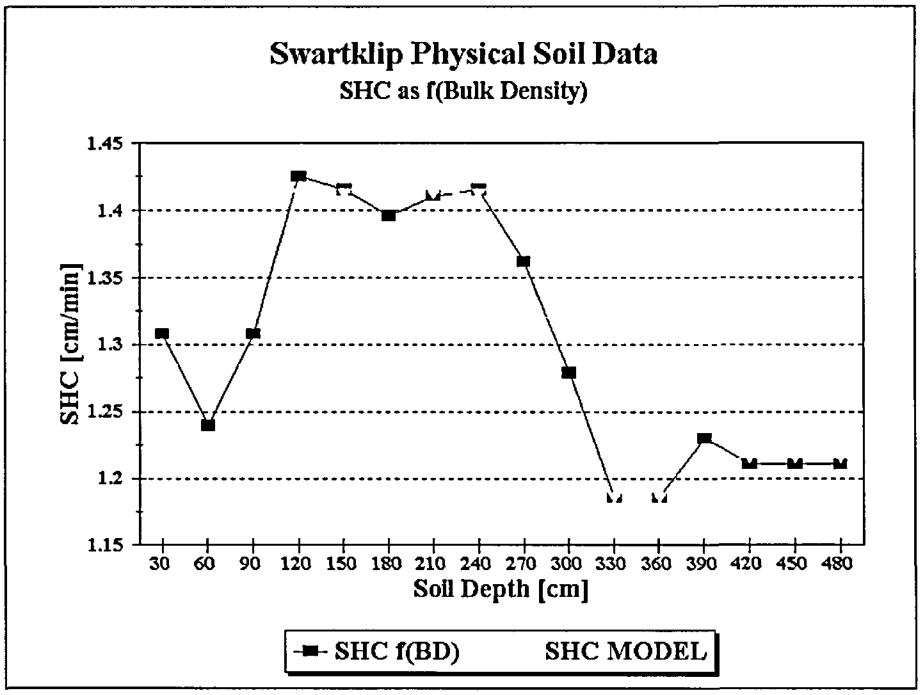

Figure 5.9 : Experimental site saturated soil hydraulic conductivity depth distribution.

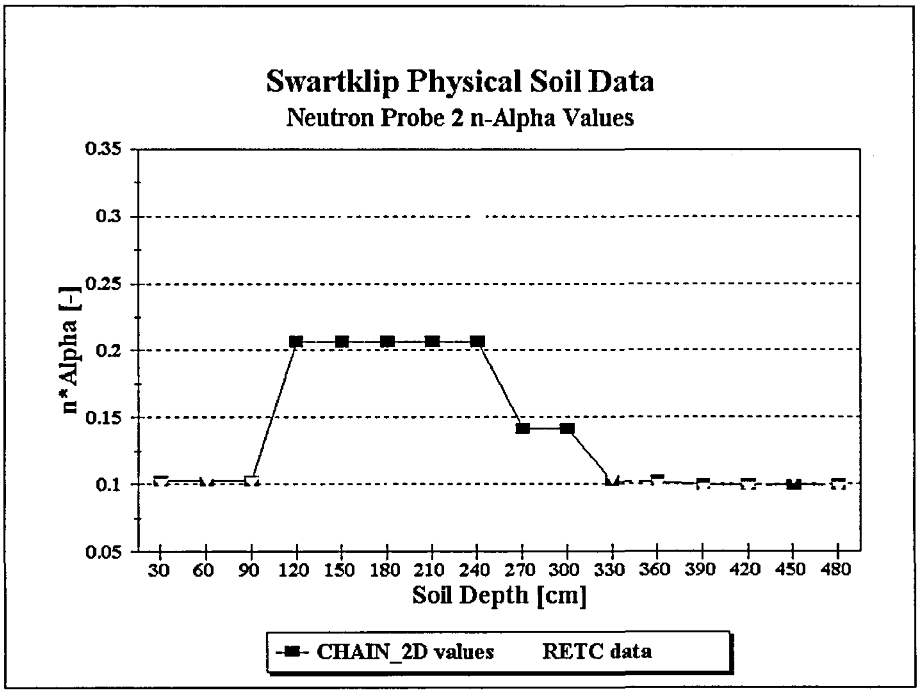

Figure 5.10 : Depth distribution of n x α values for the second neutron probe access tube.

5.2.6 *Model Predictions*

Model predictions for the Swartklip Waste Site were performed using adsorption kinetic data from the laboratory, the physical data obtained at the site and data from the field experiments. The heavy metal behaviour characteristics observed for the spiked Coastal Park leachate in laboratory soil columns were used in the simulations. The actual time required for the solutes to reach the allowable maximum concentration (according to the World Health Organization, WHO (Appelo and Postma, 1993)) at the water table was obtained by performing simulation runs with the above mentioned data. The point at which the concentration reaches the maximum allowable WHO value was used to estimate the solute residence time.

The CHAIN_2D model simulated the movement of heavy metals in the leachate through the Swartklip soil. It took 6452 (4.5 days), 5242 (3.65 days) and 2342 (1.63 days) minutes for Pb, Cd and Cr respectively to reach the maximum allowable WHO concentration at the ground water table. The corresponding volumes of leachate that infiltrated through the atmospheric boundary were calculated as 174.2 m^3 (696 cm), 141.5 m^3 (566 cm) and 63.2 m^3 (252 cm) for Pb, Cd and Cr respectively. These results confirm the attenuation capacity values observed during the laboratory experiments in that, if a soil attenuates more of a certain solute, it will take more time to reach the bottom of the soil profile or water table, than a solute that is less, or not at all attenuated.

5.2.7 *Development of MODEL2D*

MODEL2D was developed to reduce the time spent on arranging and preparing input and output data from CHAIN_2D. The result of the sensitivity analysis was used to provide guidelines for selecting the most significant input parameters for use in MODEL2D. MODEL2D was also developed to assist the user in generating the input files for CHAIN_2D. The less significant input parameters were assigned values of zero in the input files. One example is provided to illustrate the use of MODEL2D (See Appendix 3).

During the development of MODEL2D, it was found that the output data of three other computer models was needed to prepare input data for CHAIN_2D. The programs RETC and CFITIM were developed by van Genuchten (1981). RETC is used to calculate n and α values, or hydraulic parameters values, while CFITIM is used to calculate adsorption kinetic parameter values. The program ETO was developed during this project to calculate time series values for evaporation, using meteorological data. The interaction between the models and programs is illustrated in Figure 5.11.

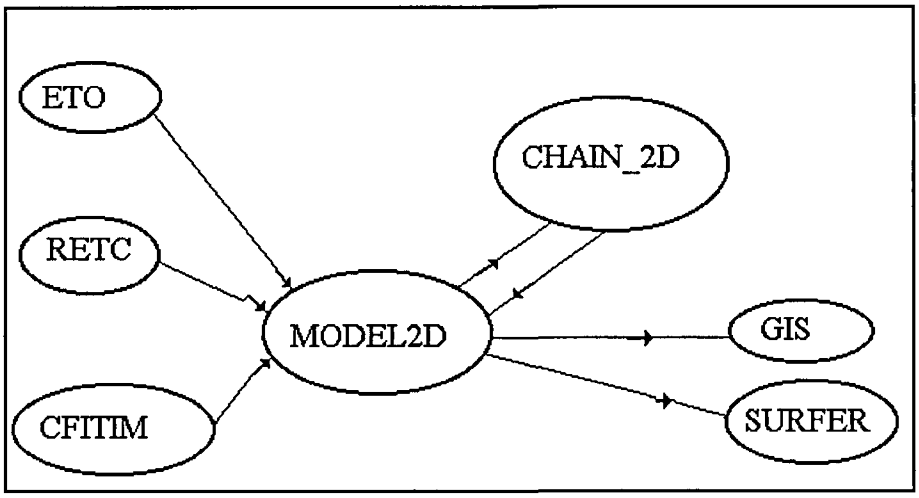

Figure 5.11 : A diagram to illustrate the interaction between the models and programs.

MODEL2D can accommodate five different model setups with specific relevant boundary conditions applying to the specific model. The five model setups are as follows:

☐ MODEL1 simulates a laboratory soil column experiment with water and solute movement. Multiple solutes (max 3) can be considered in the saturated/unsaturated environment. This model may be used to validate model output by comparing actual experimental results to model output data.

☐ MODEL2 simulates the movement of solutes and water through soil or soils with an atmospheric boundary and a water table. Atmospheric and watertable depth data must be provided, as well as initial soil water content, solute concentration and adsorbed solute concentration in the case of the two-site non-equilibrium adsorption model.

- ☐ MODEL3 simulates the movement of solutes and water through soil or soils with an atmospheric boundary and a drain. Information is required regarding the physical dimensions of the drain. Soil between the impermeable and atmospheric boundaries is considered. Initial soil water content and solute concentration must be provided.
- ☐ MODEL4 simulates the movement of solutes and water through soil with an atmospheric boundary and a seepage face bottom boundary. The movement of water is controlled by the physical properties of the soil materials in the soil region. A water table can thus develop, resulting in positive pressure head values in the soil beneath the water table.
- ☐ MODEL5 simulates the movement of solutes and water through soil with an atmospheric boundary and an impermeable bottom boundary. A water table may form if the difference between precipitation and evaporation is positive for a specific time period. Water flow with or without solutes is possible.

5.2.8 *Calculation of the attenuation capacity*

The attenuation capacity of a soil is defined as the maximum amount of solute that can be adsorbed by the soil. This capacity is expressed in units mass solute per mass soil (g/g). Throughout this study, values for solute attenuation (less than maximum, as well as the maximum value) were calculated by multiplying the solute concentration in space and time by the adsorption isotherm coefficient k_s. CHAIN_2D does not calculate the attenuation capacity or solute attenuation values automatically and the user of such a model must perform this task. If a large amount of data points are considered, this task is time consuming and tiresome. CHAIN_2D provides a mass balance from which the total amount of solute present in a specific area or volume of soil can be obtained.

Values for the *attenuation capacity* (Intermediate : Table 5.8) of the Swartklip sand for Pb, Cd and Cr in distilled water and Coastal Park leachate, were obtained from the laboratory experiments. The attenuation capacity (EPA results) for Pb in Coastal Park leachate was found to be 5.5E-4 [g/g]. This value is 96.75% of the value obtained by multiplying the distribution coefficient k_s with the column inlet concentration c_0 for this specific experiment. This implies that the total error in the CFITIM results, laboratory observations and AAS analytical results was smaller than 3.5%, suggesting that the experiments were accurately performed.

5.2.9 *Procedural guidelines for modelling solute transport*

The procedure that should be followed when modelling solute transport is as follows:

- ☐ Collect soil samples at selected positions and depths for particle size analysis and chemical analysis (EPA method).
- ☐ Obtain saturated hydraulic conductivity at different positions at the soil surface by performing a Darcian type experiment on undisturbed samples obtained from the field site.
- ☐ Install access tubes for the neutron moisture probe. These access tubes are to be used to measure both the soil moisture content and the bulk density using the gamma-ray probe.

- ☐ Calculate the soil moisture retention characteristics using the RETC (Van Genuchten, 1980) program with the data for RETC calculated using equations published by Rawls and Brakensiek (1991). These results are then used as input for the CHAIN_2D model.

- ☐ Data on the movement of chemicals at the field site must be collected by sampling soil moisture.

- ☐ The reaction kinetic data for the pollutant of interest must be investigated and determined using data obtained from a laboratory column experiments. The CFITIM (Van Genuchten, 1981) program should then be used to estimate parameter values for the reaction kinetics.

- ☐ The saturated hydraulic conductivity at positions below the soil surface can be approximated by expressing the saturated hydraulic conductivity as a function of the bulk density.

- ☐ use a fine nodal incrementation of the soil depth at the contact level of two different soil layers (*if the distance between two vertical nodes is too large and these nodes are in soil layers of different characteristics, the simulation model converged very slowly to a solution*).

- ☐ The MODEL2D program can be used to prepare the input files needed for a CHAIN_2D simulation run and the simulation started from within MODEL2D. The SURFER package can then be used to present the simulation results graphically.

5.3 Summary

- ☐ The CHAIN_2D model was selected as a suitable code for simulating the movement of water and solutes in the vadose zone. The model was used in this study without any modifications.

- ☐ The sensitivity analysis of CHAIN_2D model to changes in input parameters showed that the most important parameters influencing the attenuation of heavy metals in soils were soil moisture retention, saturated hydraulic conductivity, climate, soil bulk density and the adsorption isotherm coefficient.

- ☐ The CHAIN_2D model was successfully validated on a laboratory scale using data from soil column breakthrough curves. The order of adsorption of the heavy metals considered was as follows : Pb > Cd > Cr. This sequence was found to be valid for both distilled water solutions and the Coastal Park leachate. The Wilmot coefficient of agreement used in the laboratory validation of the model was calculated as $d = 0.9959$ showing a good agreement between the laboratory data and the CHAIN_2D predictions.

- ☐ The CHAIN_2D model was also validated on a field using soil moisture content data. The validation was not as successful as the laboratory scale validation.

- ☐ Using the CHAIN_2D model, the attenuation capacity of the Swartklip sands for Pb and Cd were predicted to be 0.295 and 0.813 (g/kg) respectively.

CHAPTER 6

A METHODOLOGY OF USING GIS FOR SOIL/VADOSE-ZONE ATTENUATION STUDIES

BY J CONRAD

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6. A METHODOLOGY OF USING GIS FOR SOIL/VADOSE-ZONE ATTENUATION STUDIES

6.1 Introduction

The vulnerability of an aquifer to pollution is related to the hydraulic accessibility of the saturated zone and the ability of the porous media to attenuate a given contaminant. The porous media properties that are important in contaminant attenuation were summarized in Chapter 2 and these include surface area, particle size, structure, mineralogy, organic and mineral coatings. Depending on the properties, a given soil will have an attenuation capacity for a given contaminant. Therefore, if one knew the geographical distribution of soils, a rapid assessment can be made of areas with high or low attenuation potential. The tools of choice in this regard are computerised Geographical Information Systems (GIS). A GIS can be described as a system of hardware, software, and procedures designed to support the capture, management, manipulation, analysis, modelling and display of spatially referenced data for solving planning and management problems of varying degrees of complexity. The advantages of a GIS are that both the spatial distribution of features and associated attribute data for those spatial features are linked and stored. This enables the analysis and modelling of spatially distributed data bases. For this project a GIS is then well suited for displaying and deriving the distribution of qualitative soil properties that impact on soil attenuation capacity, as digital Land Type information is available on a regional and national scale. In addition, as GIS's are computer based, a rapid inspection of results obtained from modelling different soil property combinations is possible.

6.1.1 *Aims of present study*

The main aim of the GIS component of this study was to develop a methodology for generating regional scale maps of vadose zone attenuation characteristics for use by planners. The original proposal included the following GIS specific objectives:

- ➔ use available data sets to produce soils characteristic maps
- ➔ produce qualitative attenuation maps for a given group of contaminants.

6.2 Approach

6.2.1 Soils Characteristic Maps

6.2.1.1 Introduction

In the original proposal, the proposed GIS approach was to be based on "national soil data bases". However, no soil maps exist at a scale larger than 1 : 2 500 000 for South Africa. It was thus decided that Land Type information would be used as this was the next best option. The Land Types for the entire country have been mapped at a scale of 1 : 250 000 and captured in digital format.

The Western Cape was chosen as the study area for the GIS component of this project, as field sampling and laboratory analysis was carried out from areas within the Western Cape. Thus the GIS derived results could be verified with this field and laboratory work. The actual limits of the study area were defined by the extent of the 1 : 250 000 Cape Town map sheet (3318). This area is between latitudes 33° 00' S and 34° 30' S and longitudes 17° 45' E and 19° 00' E.

6.2.1.2 Land Type maps

A Land Type denotes an area that can be shown at a 1 : 250 000 scale which displays a marked degree of uniformity with respect to terrain form, soil pattern and climate. One Land Type differs from another in terms of either terrain form, soil pattern or climate. Different occurrences of the same Land Type may be separated from one another by other Land Types. The Land Type map was compiled by superimposing the climate map on the pedosystem map (Land Type Survey Staff, 1987). Due to the fact that soil properties have high spatial variability, modal profiles were not used in this project. A full description of how the Land Type concept originated and how they are derived is included in Appendix 4.

The advantages of using Land Type data for mapping soil attenuation capacity include the following:

✔ the Land Types have been mapped for the whole country, thus any methodology developed for the Western Cape map sheet can possibly be extrapolated nationally;
✔ the Land Types have been mapped at a scale of 1 : 250 000, which is usable for regional planning purposes;
✔ the spatial and attribute data is accurately captured and well maintained, by the Institute of Soil, Climate and Water (ISCW) of the Agricultural Research Council;
✔ the data is in Arc/Info format, thus easily transferable and usable by the researchers who are also Arc/Info users;
✔ the Land Type data base is very well administered and requests for Land Type data are processed and delivered quickly.

The main disadvantage of using Land Type data is that the *soil type* distribution within each Land Type is not actually mapped and thus the position of each unique soil type is not known. However, the percentage of land covered by each soil type is known. Due to financial constraints, there are no immediate plans by the ISCW to map the soil type boundaries for South Africa.

The information that is available per soil type within each Land Type includes the following:

➔ CEC - Cation Exchange Capacity;
➔ OM - Organic Matter;
➔ FE - sesquioxides;
➔ clay percentage;
➔ presence of lime, and
➔ duplex character.

For each of the above soil characteristics, the values were grouped into classes by the ISCW (Table 6.1):

Additional data per Land Type that is available from the ISCW includes:

- ➔ soil category;
- ➔ soil depth (mm), and
- ➔ SCS (run-off potential).

The soil categories for the Western Cape map sheet are included in Appendix 5.

Table 6.1 : The class subdivisions of each Land Type parameter

CEC		**OM**		**Fe**		**Clay**		**CO3**		**Duplex**	
Class	cmol (+)/kg	Class	%C	Class	%	Class	%	Class	Lime	Class	
1	0 - 2	1	0 - 2	1	0.0 - 0.5	1	0 - 6	Y	present	1	weak
2	2 - 4	2	2 - 10	2	0.5 - 2.5	2	6 - 15	N	not present	2	moderate
3	4 - 8	3	> 10	3	> 2.5	3	15 - 35			3	strong
4	> 8					4	35 - 55				
						5	> 55				

A list was made of all the soils that occur within the 3318 Cape Town 1:250 000 Land Type map. By evaluating the inherent properties of the different soil series, and by evaluating all the analytical information available on this map, a table was drawn up by the ISCW where the required attributes were assigned to each soil. The fields in this table are: SOILSERIE, CEC, OM FE, CLAY, CO3 and DUPLEX and have been classed according to Table 6.1. A subset of this Table is included below (Table 6.2):

Table 6.2 : The classification of soil properties according to soil type

SOILSERIE	CEC	OM	FE	CLAY	CO3	DUPLEX
Av21	3	1	2	1	N	-
Av22	3	1	2	1	N	-
Av23	3	1	2	2	N	-
Av24	3	1	2	2	N	-
Av25	3	1	2	2	N	-
Av26	3	1	3	3	N	-
Bv26	3	1	3	3	N	-
Bv36	3	1	3	3	N	-
Cf10	1	1	1	1	N	-
Cf11	2	1	1	2	N	-
Du10	3	1	2	3	Y	-
Es15	2	1	1	2	N	3

etc.

However, this table cannot be used as the spatial distribution of the soil series is not known and therefore a Land Type based approach has to be used. The soil series attributes were assigned to each soil within the Land Types. The percentages of soils with similar attributes were added. The fields used in this file are LANDTYPE (key field which links to the spatial data), CEC, OM, FE, CLAY, CO3 and DUPLEX as defined in Table 1, as well as PERCENT (the percentage occurrence of the specific combination of attributes and LANDCLASS, where R stands for rock and A stands for all other non-soil land classes (pans, streambeds, coarse deposits etc.). An example of the data base structure is given in Table 6.3 below:

Table 6.3 : An example of the attribute data base for the Land Type spatial data

LANDTYPE	CEC	OM	FE	CLAY	CO3	DUPLEX	PERCENT	LANDCLASS
Ab16	1	1	2	1	N	-	19.30	
Ab16	2	1	1	1	N	-	4.35	
Ab16	2	1	1	2	N	-	8.51	
Ab16	2	1	1	2	Y	-	1.00	
Ab16	2	1	2	2	N	-	2.35	
Ab16	3	1	1	3	N	-	4.35	
Ab16	3	1	2	3	Y	-	3.95	
Ab16	3	1	3	3	N	-	41.60	
Ab16							5.15	A
Ab16							9.44	R
Ab18	1	1	1	1	N	2	7.40	
Ab18	2	1	1	2	N	-	8.22	
Ab18	2	1	2	2	N	-	10.00	
Ab18	3	1	2	2	N	-	27.48	
Ab18	3	1	2	3	N	-	2.80	
Ab18	3	1	2	3	N	3	1.05	
Ab18	3	1	3	3	N	-	27.00	
Ab18	4	1	2	4	N	-	11.75	
Ab18							0.70	A
Ab18							3.60	R
		etc.						

From Table 6.3 it can be seen that, for example, Land Type Ab16 contains 10 different soil types and the areal percentages of these soil types per Land Type are also listed. However, the geographic position of the soil types within the Land Type entity is not known. To represent the soil characteristics spatially, area weighted averages and ranges were calculated for each of these characteristics per Land Type. Using Land Type Ab16 and the data in Table 6.3, the area weighted average is calculated using the following equation:

(1) $AWA = \sum(SP * P) / \sum P$

where: AWA = Area Weighted Average
SP = Soil Property Class
P = Soil Property Percent
(excluding A and R classifications).

The range per Land Type is calculated from the following equation:

(2) $R = SP_{(max)} - SP_{(min)}$ R = Range.

An example of the data base file created for Clay content per Land Type is given below in Table 6.4:

Table 6.4 : Area weighted averages and ranges per Land Type

landtype	area wghtd ave	clay-range
Ab16	2.31	2
Ab18	2.49	3
Ab21	2.89	2
Ab22	2.51	3
Ab23	2.90	2
Ab24	2.90	2
Ab26	2.91	2
Ac15	2.60	1
Ac17	2.72	2
Ac18	2.90	2
Ac19	2.96	2

etc.

Such a data base file and map coverage was generated for:

- → clay content per Land Type;
- → average Organic Matter per Land Type (most soils within the Western Cape are Class 1, i.e. 0 - 2 % C);
- → average CEC per Land Type;
- → iron content per Land Type.

Four maps were generated from the above data bases, including a map showing areas where the presence of lime has been recorded. Figure 6.1 is a map of the Land Types occurring within the Cape Town 1 : 250 000 map sheet, Figure 6.2 shows the areas where lime is present, Figure 6.3 shows the Clay content per Land Type, Figure 6.4 shows average Organic Matter content per Land Type, Figure 6.5 shows the average Cation Exchange Capacity per Land Type and Figure 6.6 shows the iron oxide concentrations per Land Type. For Figure 6.3 to Figure 6.6 the area weighted average values are mapped according to the classes as given by the ISCW. Included on these maps is a hatching indicating the range. The higher the range the higher the spread of values from which the average was derived. Appendix 6 contains a listing of the code used for calculating area weighted averages and ranges per land type.

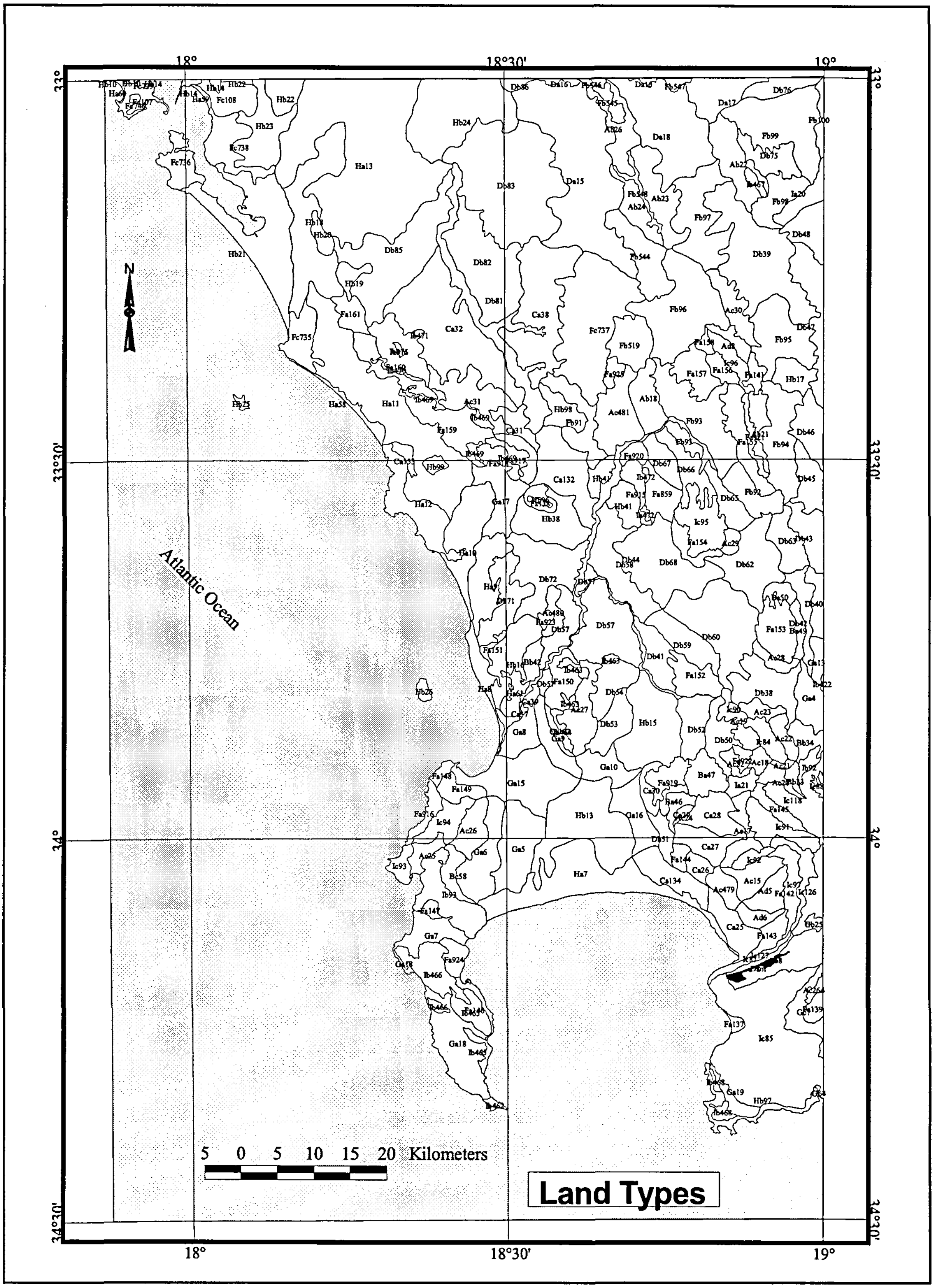

Figure 6.1 : Land Type map for the 1 : 250 000 Cape Town map sheet (3318)

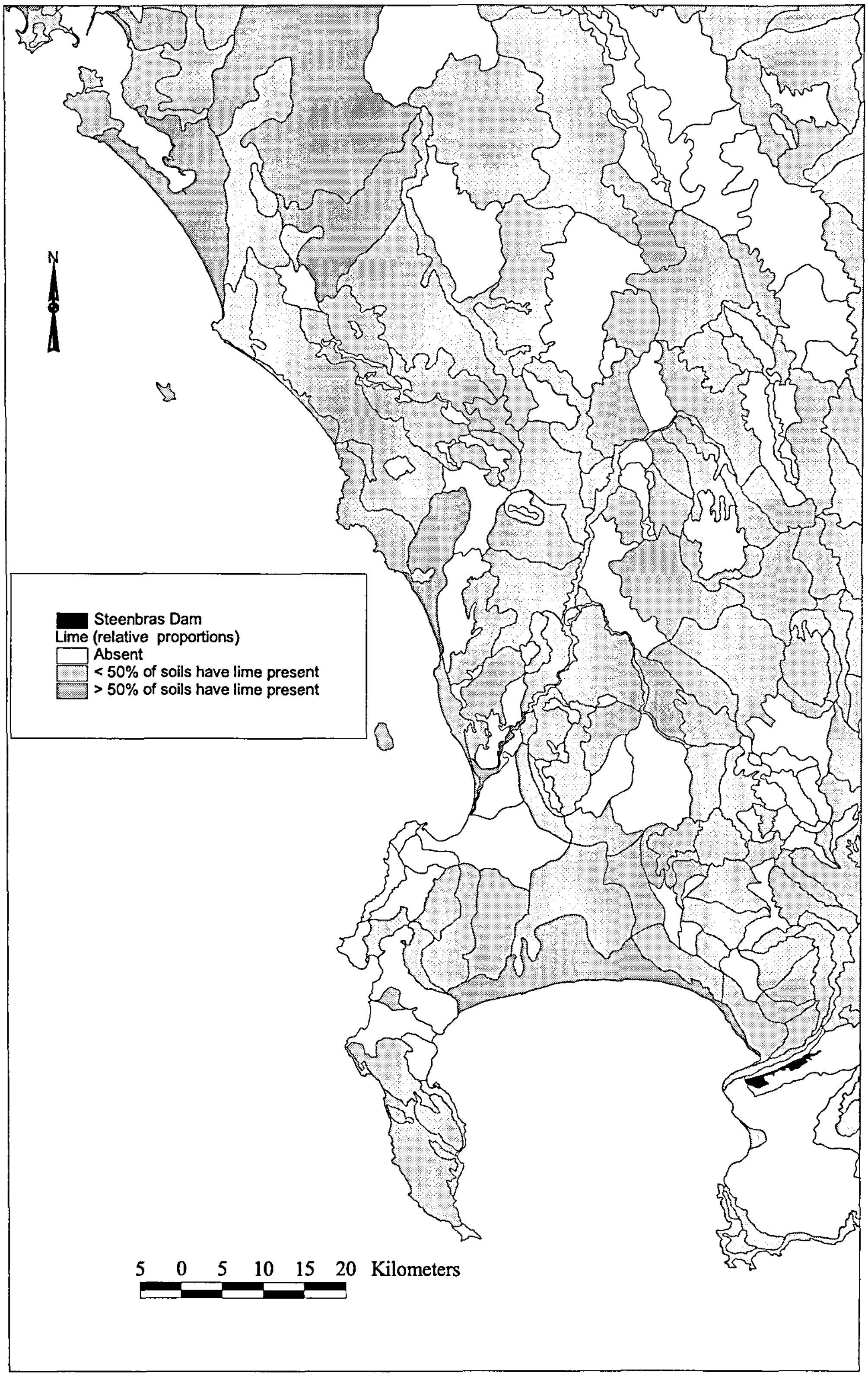

Figure 6.2 : The presence of lime within the Cape Town map sheet

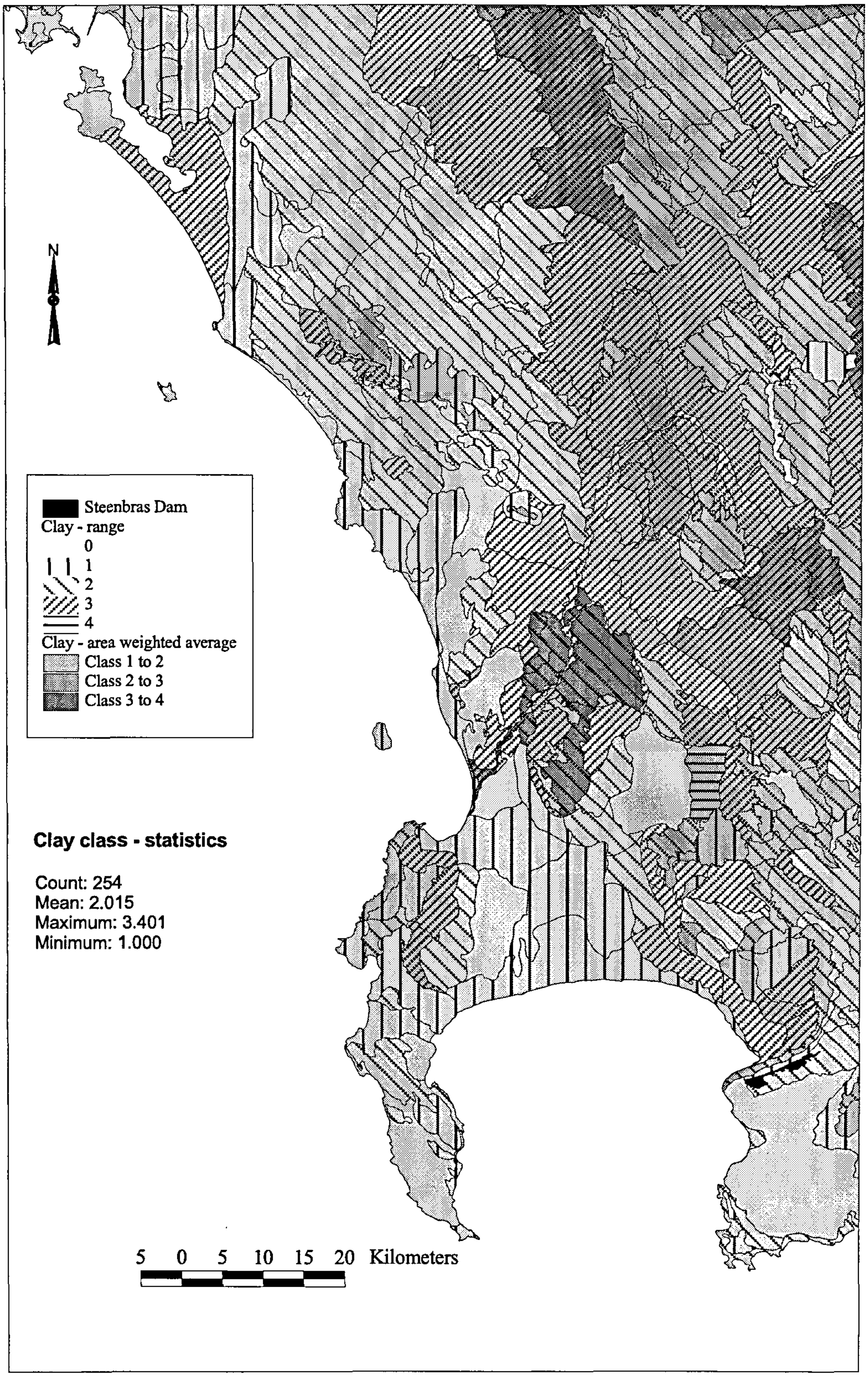

Figure 6.3 : Clay content per Land Type

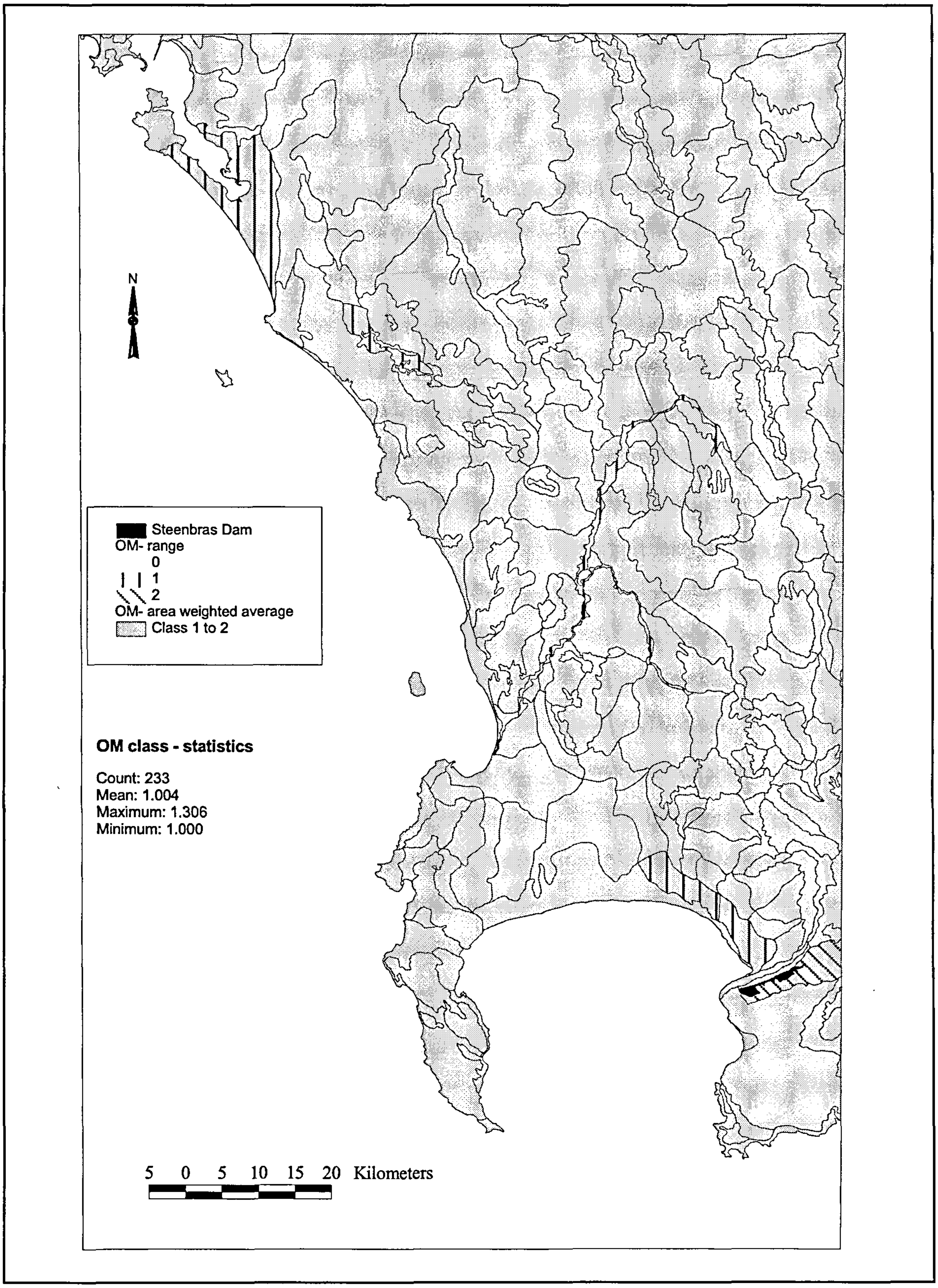

Figure 6.4 : Average organic matter content per Land Type

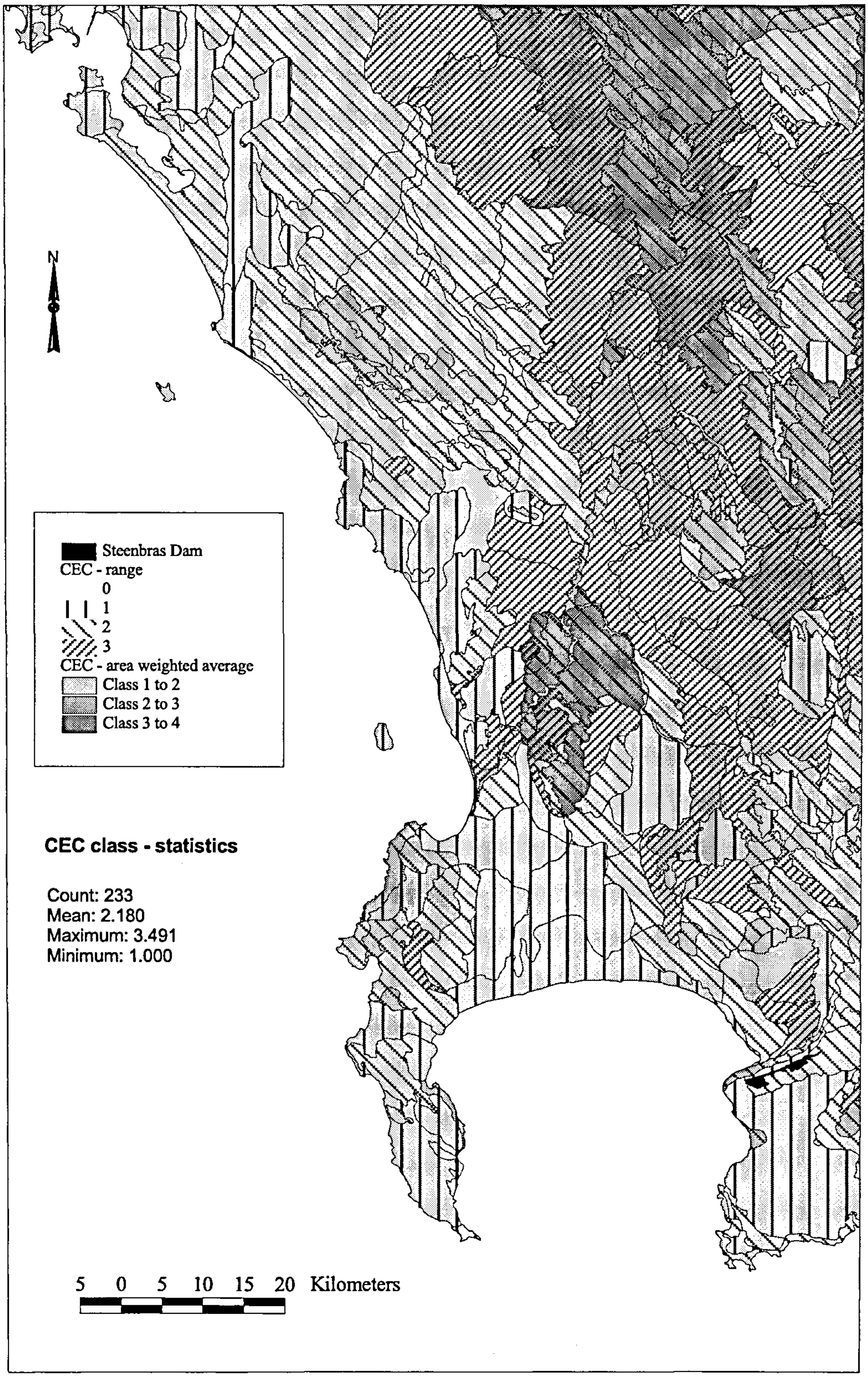

Figure 6.5 : Average Cation Exchange Capacity per Land Type

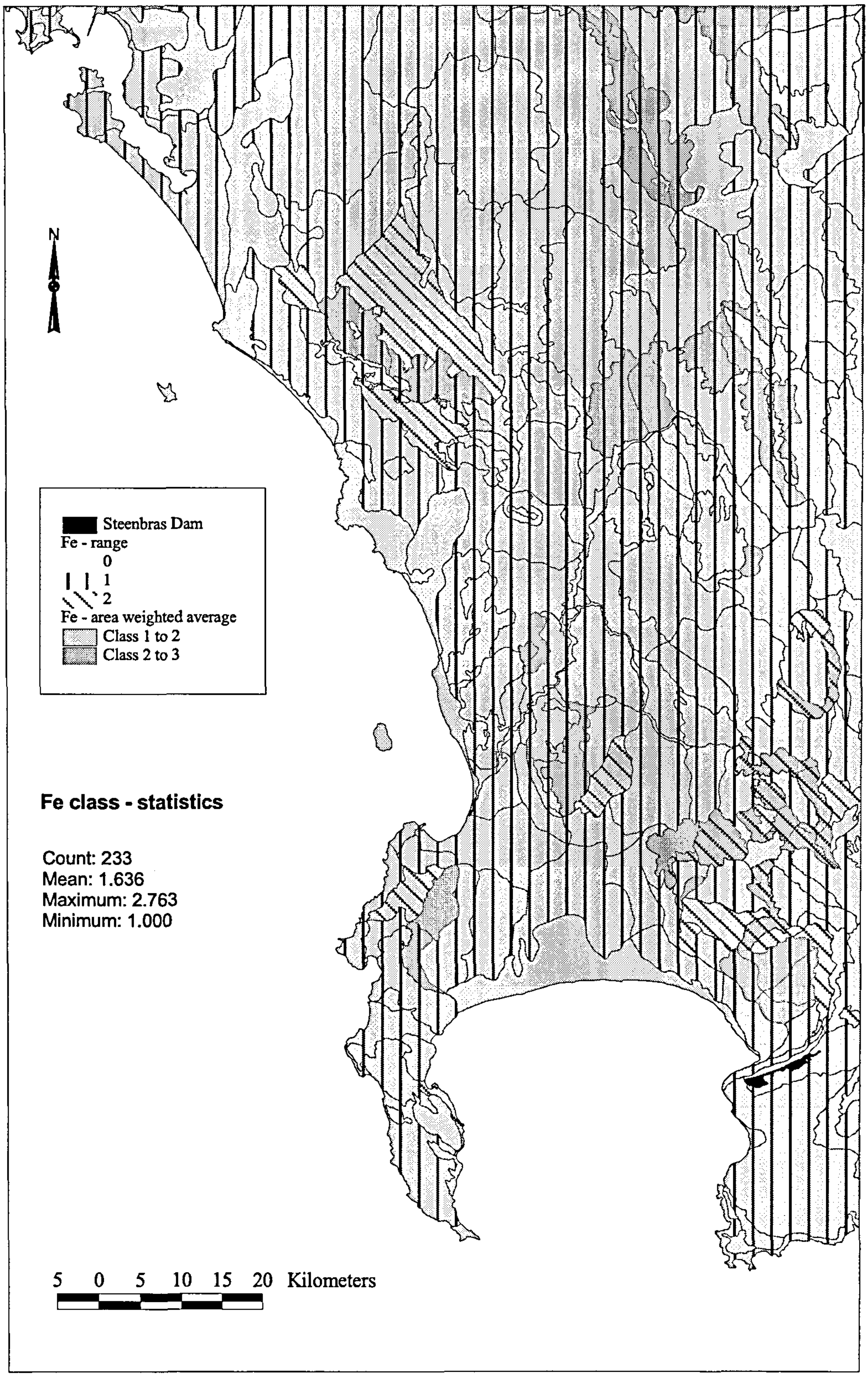

Figure 6.6 : Iron oxide concentrations per Land Type

6.2.2 *Qualitative Contaminant Attenuation Maps*

The soils information maps generated above were used to obtain a qualitative indication of the attenuation potential of cation and anion forming elements. The sections below describe how this was carried out.

6.2.2.1 Cation forming elements

For cation forming elements clay content plays a primary role. Fuller (1978) found that clay rich soils were very effective in attenuating these elements, while sandy soils were ineffective. Thus clay content can be used to obtain a qualitative indication of attenuation potential of cation forming elements. The higher the clay content, the higher the attenuation potential.

The qualitative attenuation potential of cation forming elements was calculated according to the clay content classes per Land Type as shown in the Table 6.5:

Table 6.5 : Attenuation Potential assigned according to clay content

Clay class per LT	Attenuation Potential
1 - 2	(low)
2 - 3	(medium)
3 - 4	(high)

Figure 6.7 is a map showing the attenuation potential for cation forming elements based on the classification given in Table 6.5.

6.2.2.2 Anion forming elements

For anion forming elements soil hydroxide (Fe) content plays a primary role (Fuller, 1978). In general the higher the soil hydroxide content, the higher the attenuation of anion forming anion forming elements. Soil pH is more important for attenuation of anion forming elements than it is for cation forming elements. Unfortunately data is not available for soil or Land Type pH values, however the presence of lime can be taken as an indicator of soil pH.

Iron oxide content was used to determine the qualitative attenuation potential of anion forming elements as shown in Table 6.6.

Table 6.6 : Attenuation Potential assigned according to iron oxide content

Fe oxide class per LT	Attenuation Potential
1 - 1.5	(low)
1.5 - 2.5	(medium)
2.5 - 3	(high)

Figure 6.8 shows the attenuation potential for anion forming elements, based on iron oxide content (Table 6.6) and a hatching indicates the presence of lime.

6.2.2.3 Polar, cationic and anionic organic molecules

The generalized behaviour of the various classes of organic compounds in soil is summarized in Table 2.4. For non-ionic, non-polar organic compounds, the sorption potential is related to the amount of organic matter present in a given soil. Unfortunately, only one class for average organic matter per Land Type was provided by the ISCW for the Western Cape soils. As such these data cannot be used to derive qualitative attenuation potential for the various Land Types.

For cationic and anionic organic molecules, cation exchange plays a major role in the sorption process. The derived CEC per Land Type can therefore be used as a basis of estimating the attenuation potential of this class of compounds (see table 6.7 and Figure 6.9).

Table 6.7: Attenuation Potential assigned according to Cation Exchange Capacity

CEC class per LT	Attenuation Potential
1 - 2	(low)
2 - 3	(medium)
3 - 4	(high)

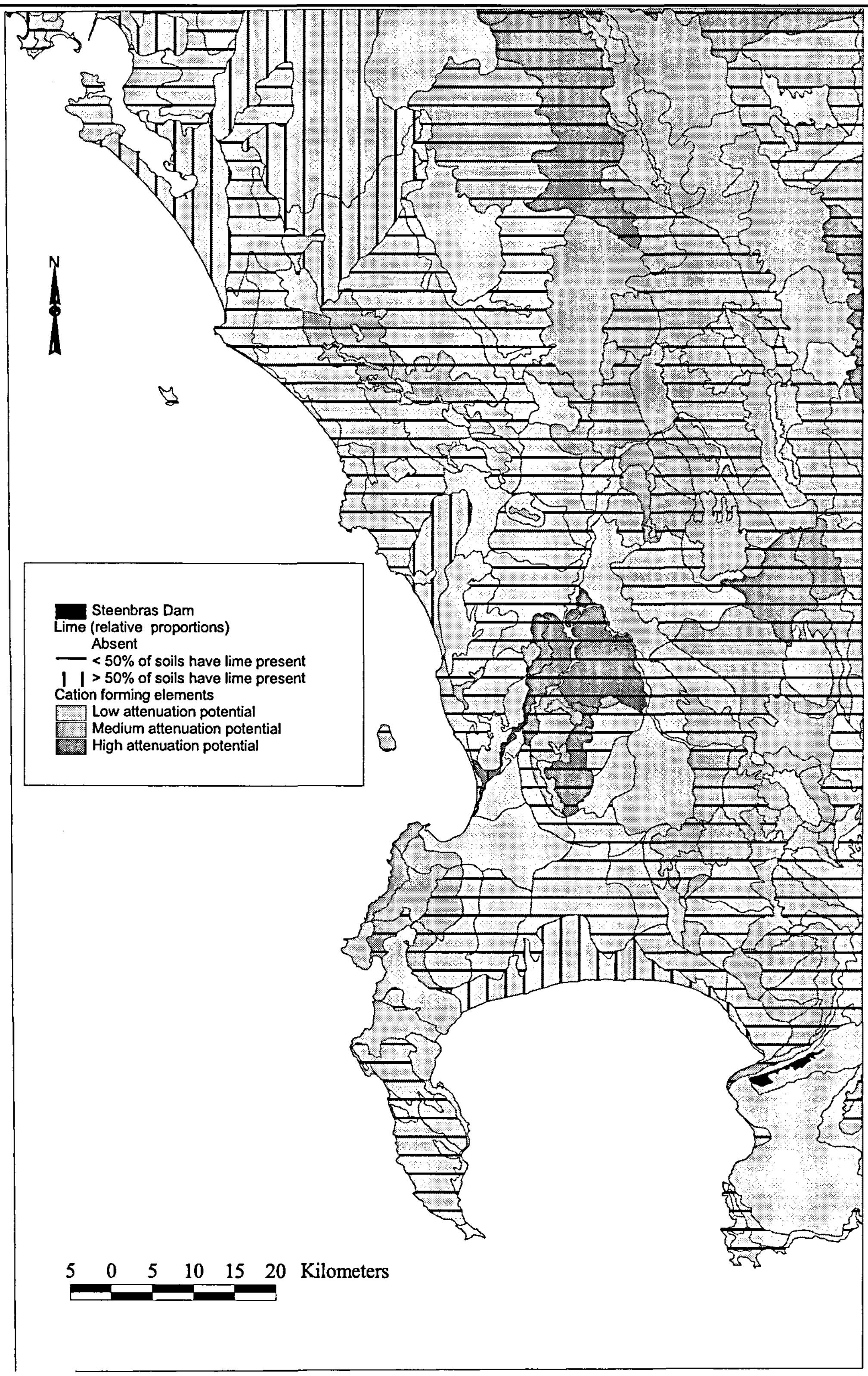

Figure 6.7 : Attenuation potential of cation forming elements

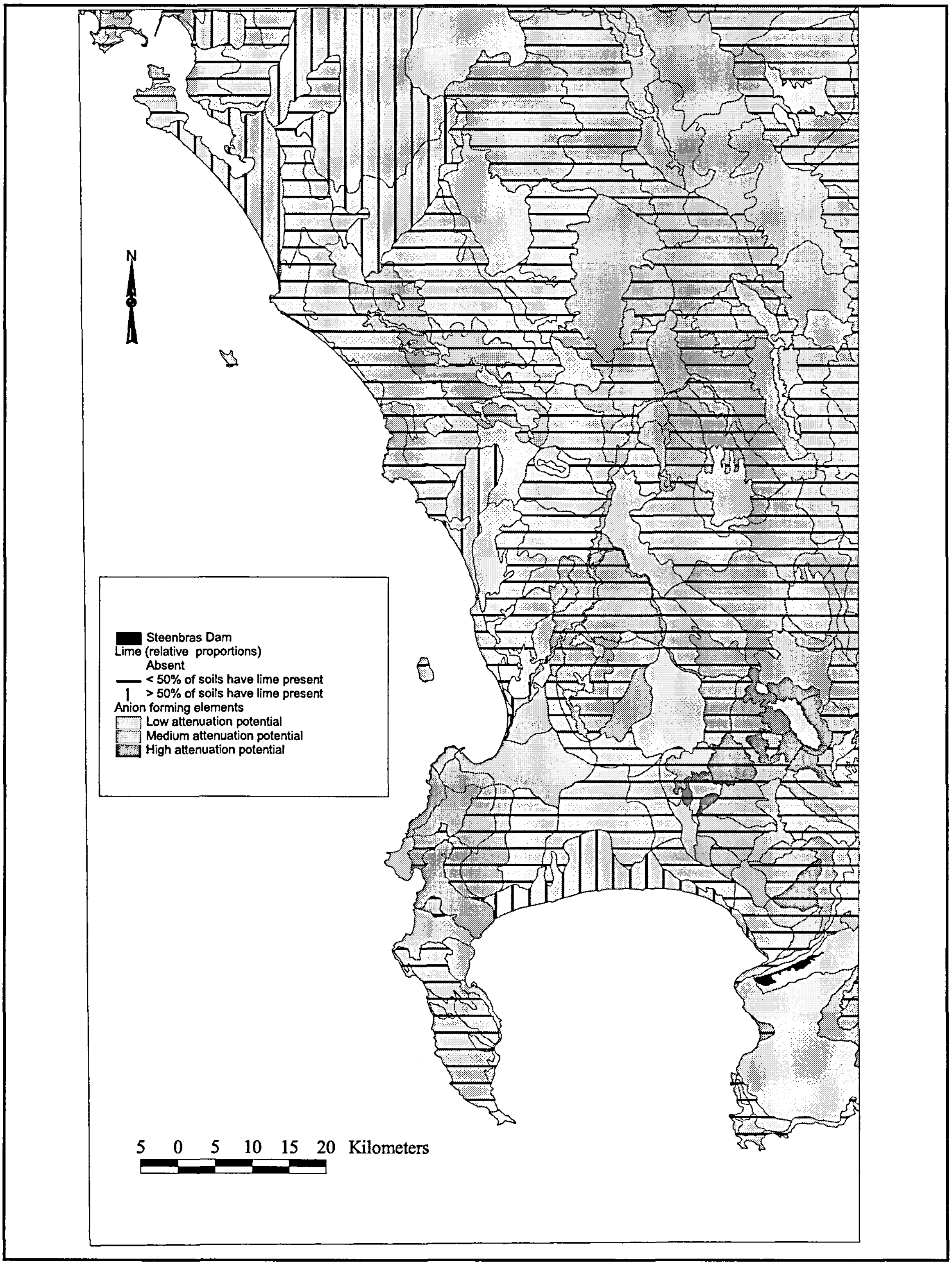

Figure 6.8 : Attenuation Potential of anion forming elements

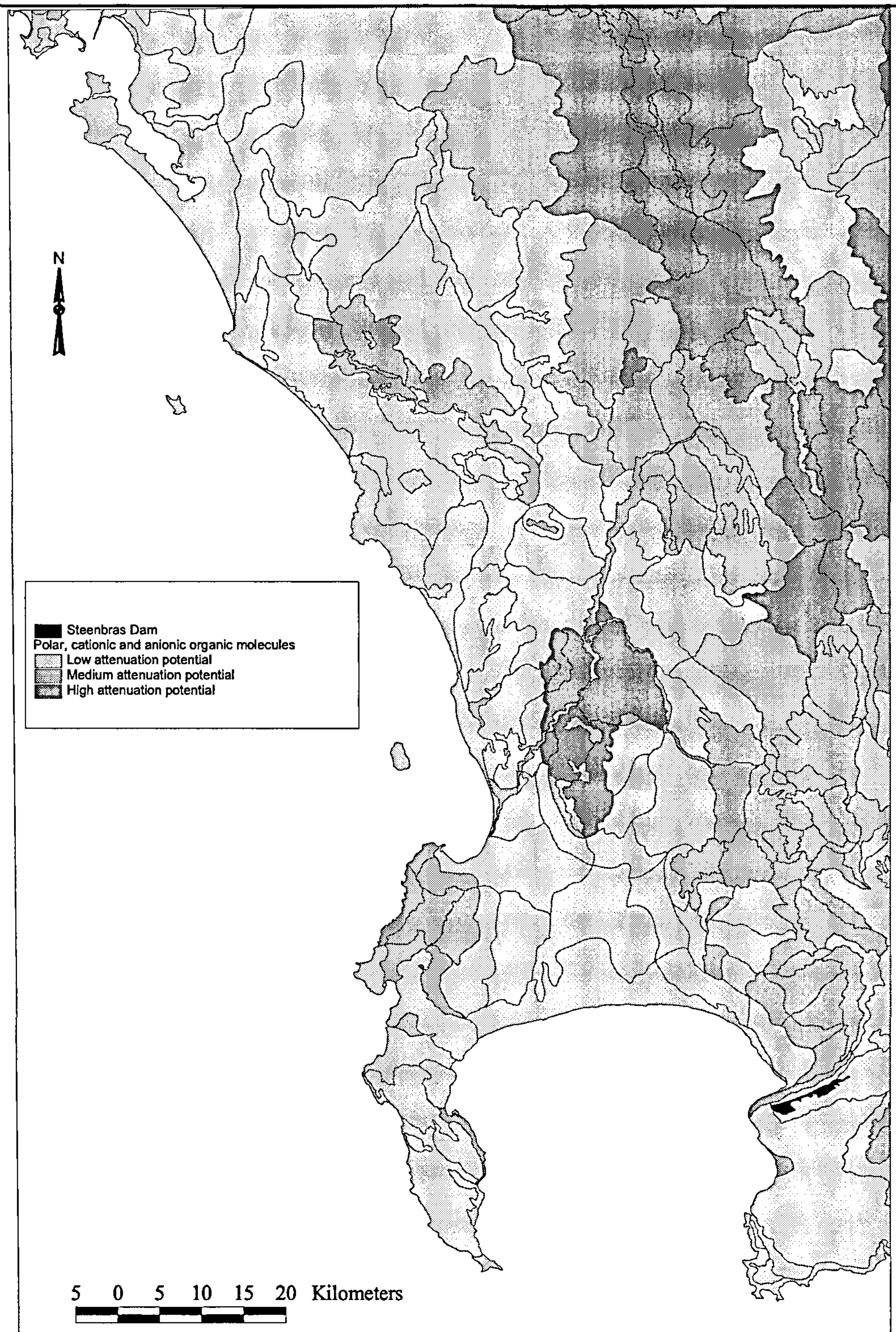

Figure 6.9 : Attenuation Potential of polar, cationic and anionic organic molecules

6.3 Discussion

6.3.1 *The merits of using GIS in the attenuation studies*

Mapping of the attenuation potential of the vadose zone will have significant benefits for regional planning purposes. It can give a broad overview of where certain types of activities can be placed. The land type coverages used here can be used to indicate potentially suitable areas for further more detailed investigations. It is noted that ISCW has now embarked on a 1:50 000 scale mapping of soil types in the peri urban areas.

In addition, with the analytical capabilities of a GIS the existing data that has been derived can be looked at in combination with geological and/or hydrogeological maps to map aquifer vulnerability to pollution. In other words the results from the vadose zone attenuation potential study could provide input into the DRASTIC methodology as the "I" layer or "Impact of Vadose Zone" layer, thereby enhancing the quality of aquifer vulnerability determinations.

6.3.2 *The limitations of using GIS in the attenuation studies*

The likelihood of a soils map being produced for the entire country at a reasonably large scale is very small. The Land Type data set is the best at the moment and will be for many years. The limitations of these data must be appreciated when making interpretations. In other words since the spatial distribution of the soil types is not known within the Land Types, a more qualitative and stochastic approach has to be used to derive the attenuation potential. The results based on this approach cannot be used on a site specific basis. For site specific work, soil analyses and interpretation of the results would be best accomplished using an Expert System model. An Expert System has been developed as one of the products of this research project.

6.3.3 *Procedure summary*

- → The data used for calculating soil attenuation capacity potential was based on the Land Type data from the ISCW;
- → For each Land Type, the soil type characteristics are provided in classes, with a percentage areal distribution of each soil type for the Land Type;
- → The area weighted average and range, was calculated for Cation Exchange Capacity, Organic Matter, Fe Content and Clay Content per Land Type. Appendix 6 contains the Arc Macro Language code for carrying out these calculations;
- → For the cation forming elements the combination of clay percentage was used;
- → For the anion forming elements hydroxides (Fe) and the occurrence of carbonate were used.

6.4 Conclusions

The definition of using a GIS procedure has been made challenging, with the lack of a soils data set at a resolution of greater than 1 : 2 500 000. It has also been difficult for the researchers to determine which soil characteristics influence attenuation capacity and to quantify these influences. In addition, spatial variability of soil characteristics is very high and in regional mapping this important aspect is essentially ignored. The only way of addressing this issue has been to indicate standard deviations on the maps of soil characteristics. The results produced can be used on a regional basis, and not for site specific purposes. The results obtained in qualitatively assessing soil attenuation capacity can be used in conjunction with other relevant data sets for determining aquifer vulnerability to pollution and aquifer risk management.

6.5 Recommendations

The results that have been generated are valuable as regional information for planners and decision makers, however they need to be verified with the field results obtained. In addition, the results obtained from the laboratory study need to be incorporated, in some way, into the GIS methodology. The possibility of using the modal profile results from the ISCW should also be investigated further. The current work that has been applied to the Western Cape map sheet, can be extrapolated to national coverage, as the Land Type data set is available for the whole country at a scale of 1 : 2 500 000.

CHAPTER 7

A PROTOTYPE SOIL/VADOSE-ZONE ATTENUATION DECISION-SUPPORT SYSTEM

BY K O' H MURPHY

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7. A PROTOTYPE SOIL/VADOSE-zONE ATTENUATION DECISION-SUPPORT SYSTEM

7.1 Introduction

7.1.1 *Preamble*

The precise evaluation of the attenuation potential of soil at a site in terms of a specific contaminant is likely to be a time-consuming and expensive task. At times, an approximate indication of attenuation potential is all that is needed, such as in feasibility-stage and candidate-site-identification investigations. Information derived from maps, reports and a site visit may be sufficient to derive approximate or site-relative attenuation-potential evaluations. If needed, this information could be further supported by simple soil tests.

Relevant expert knowledge is needed for interpretation of this information, but is not normally readily available. Expert systems may be used to trap this expertise and make it readily available in a form that can be utilised for specific types of tasks.

This chapter reports on a study that was conducted to determine the feasibility of developing a prototype, expert-systems based, decision support software for use when assessing the contaminant attenuation potential of soils.

7.1.2 *Aims and Objective*

The specific aims were to determine the feasibility of developing:

(a) a prototype expert system designed to provide simple decision support for the preliminary identification of sites or areas which are likely to have soils with certain chemical characteristics important for contaminant-attenuation assessment purposes (this assumes no soils analysis is as yet available);

(b) a prototype expert system which performs as a relative contaminant-attenuation assessor.

7.2 Method

7.2.1 *Knowledge representation and system design*

Prior to building expert-systems based software, it was necessary to

(1) identify suitable "problem-domains". This entailed establishing what type of information was available, and if such information was sufficient to develop a working expert-system.

(2) identify the key issues and goals, and establishing logical links between them

Tasks which were conducted during expert-system development included:

- ☐ determining whether any conflicting information exists;
- ☐ establishing whether there was sufficient information to derive a satisfactory answer;
- ☐ identifying what further information was required to improve an outcome;
- ☐ making a choice between relevant algorithms, equations, tabulated information or "rules of thumb" to derive required results;
- ☐ selecting the best way to present results, such as: simple numbers together with qualifying text, textual information as comments, tabulated data, mathematical graphs, bar charts, or weighted lists.

7.2.2 *Prototype expert-systems development*

An "object-oriented" expert-system development tool, Leonardo, was used to establish a decision "tree" consisting of logical links between major issues and goals, then at the branch "nodes", components were built with specific tasks to accomplish, dependent on values assigned to other nodes and to specific parameters defined within the system. Components usually consisted of "chunks-of-logic", procedures, algorithms, data classes and information processing functions.

Components' major functions were to assign values to parameters, to obtain required data, to display results, to manipulate the available information in order to obtain the results required where this was possible, and where not, to assign a value to the node to show this. Components often needed to be modified or re-positioned within the system to give the required performance.

Individual components were then tested, at first individually, then within the portion of the network where their functionality was critical. When the whole system was functional, the components were "fine tuned" and the network itself changed around so as to make the system run in a logical manner. Finally, the display was changed so as to be as "user-friendly" as possible. To this end, a bar-chart display was added.

7.3 Results and Discussion

In the prototype expert systems developed here, 'sorption potential' is defined as the relative capability of a specific soil to take up a contaminant from a solution while 'leaching potential' is defined as a relative potential of a contaminant to move downwards in percolating soil water.

Two prototype expert systems have been developed. These are described below.

(a) Expert system that presents comments on climate, vegetation, topography and soil texture/colour.

Task: Determine how climatic, topographical, vegetation, and soil-texture and soil-colour data can be used within an expert system to deduce the presence of important soil characteristics for contaminant-attenuation purposes.

Possible uses of this expert system could be:

(i) to give preliminary indications of soil characteristics based on colour and texture of soil layers exposed in an excavated hole;

(ii) to give a preliminary indication of areas where investigation for suitable areas for waste disposal could be carried out, based on soil colour and on expected chemical soil characteristics.

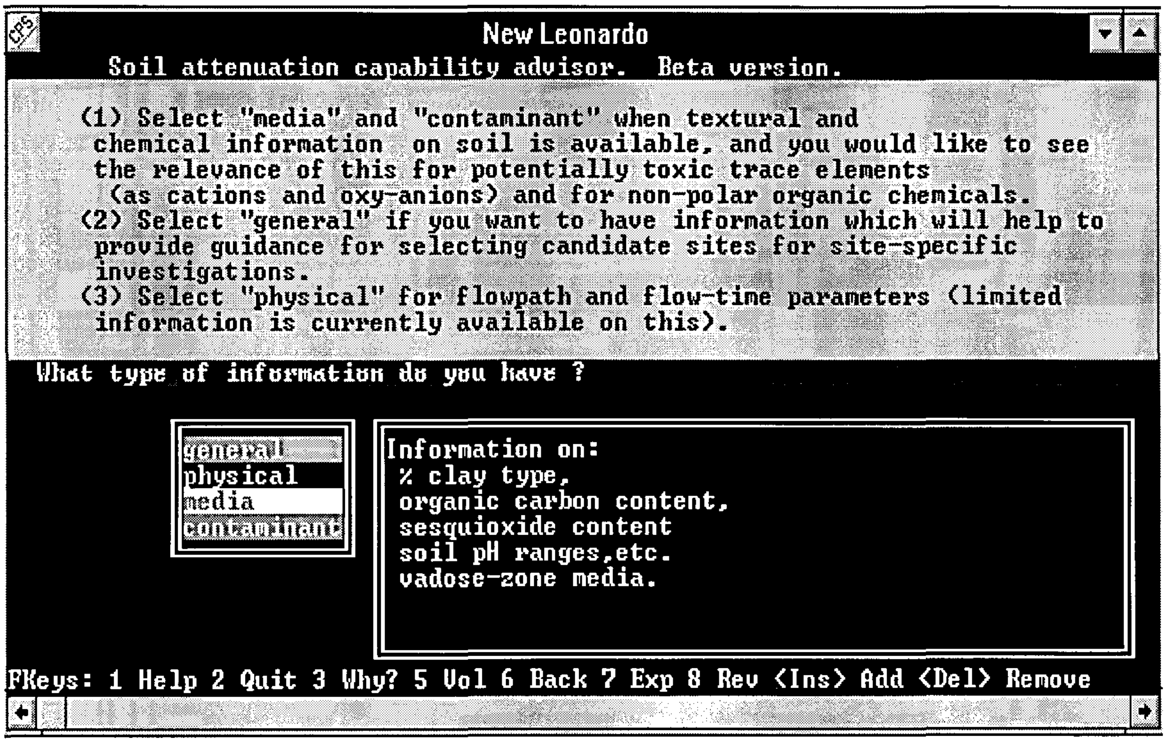
Given simple information on topography, climate, vegetation cover, soil texture and soil colour, the prototype expert system presents comments on likely pH values, soil-solution buffering, organic carbon content, presence of sesquioxides, clays, carbonates, etc. (See **Table 7.1**). An example of a question screen which enables a user to select categories for which there is information available is shown in **Figure 7.1** and **Figure 7.2**[1]. In the latter figure a highlighted item, topography, has been selected. Questions relating to the selected items will then be asked in order to present comments which help determine parameters influencing the likely suitability of soils for attenuating contaminants and/or comments which help to identify suitable places to take soil samples. **Figure 7.3** shows comments which are applicable to an arid climate, sparse vegetation, a site at the base of a steep slope, and the presence of shrinking, aggregated clays. This expert system consists mostly of simple interpretive logic to link each answer to a specific set of comments.

---

[1] Information sources:

➔ Lecture notes: Prof. W. Flügel, University of Jenna, Germany (1996)

➔ Thompson, J.G., 1985: *Guidelines for the disposal of Effluent on Land in South Africa,* Informaiton Bulletin series: Soil, SIRI: Dept. of Agriculture, Pretoria



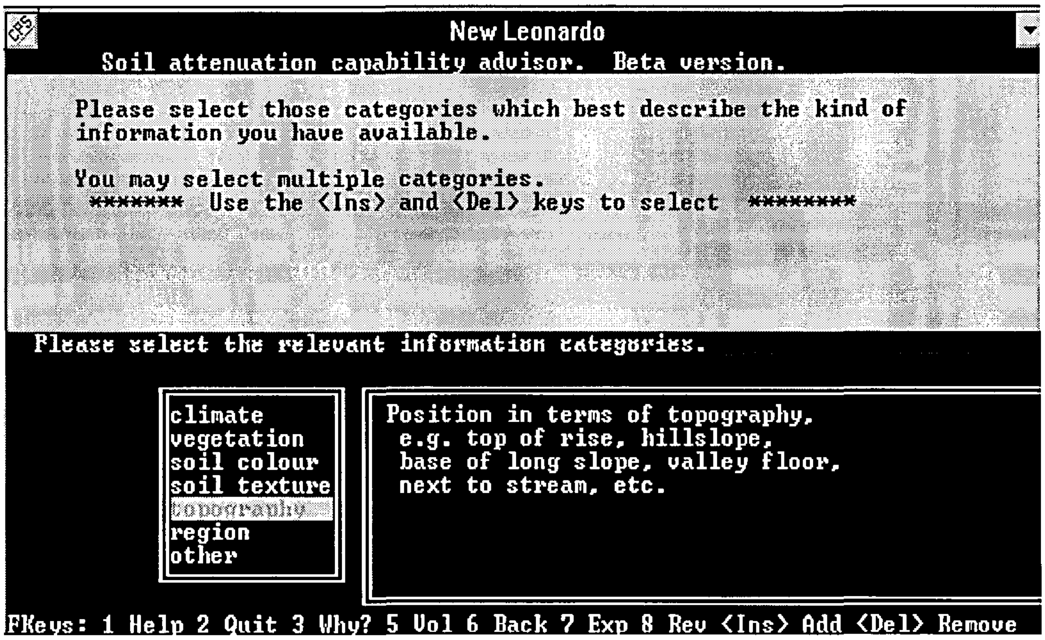
Soil attenuation capability advisor. Beta version.

(1) Select "media" and "contaminant" when textural and chemical information on soil is available, and you would like to see the relevance of this for potentially toxic trace elements (as cations and oxy-anions) and for non-polar organic chemicals.
(2) Select "general" if you want to have information which will help to provide guidance for selecting candidate sites for site-specific investigations.
(3) Select "physical" for flowpath and flow-time parameters (limited information is currently available on this).

What type of information do you have ?

Information on:
% clay type,
organic carbon content,
sesquioxide content
soil pH ranges,etc.
vadose-zone media.

Figure 7.1 : The selected items (general, media, contaminant) will cause expert systems which deal with general information, soil media and contaminant characteristics, to be run.



Soil attenuation capability advisor. Beta version.

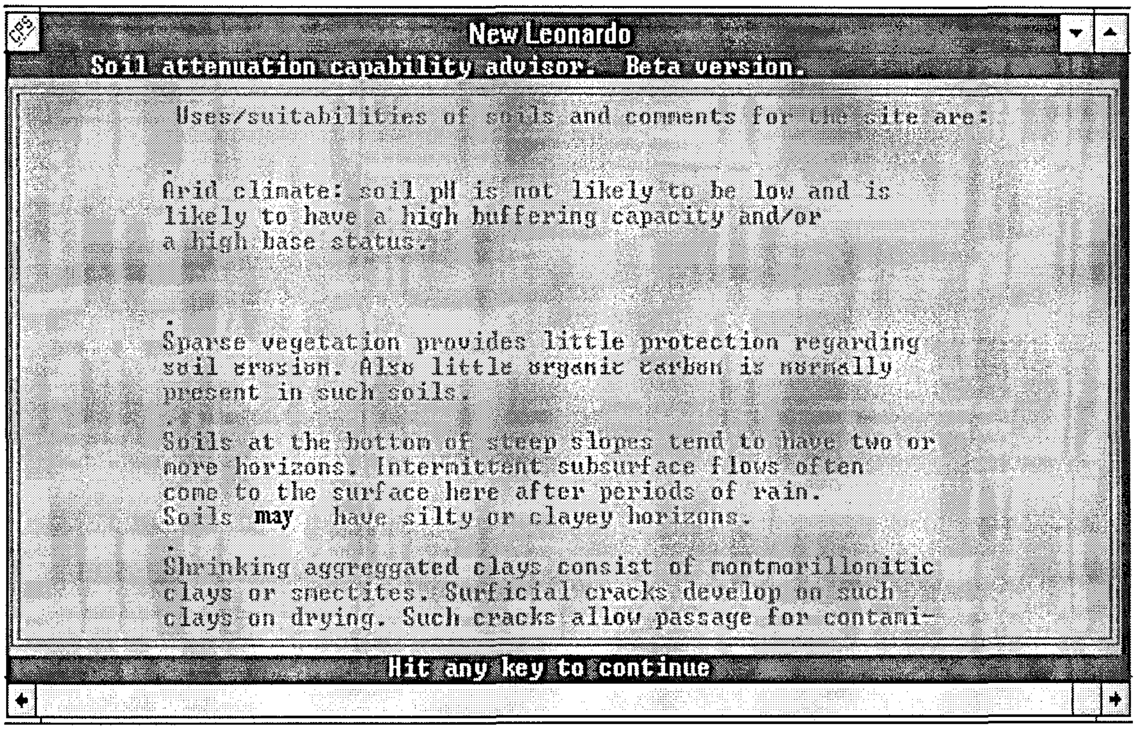
Please select those categories which best describe the kind of information you have available.

You may select multiple categories.
******* Use the <Ins> and <Del> keys to select ********

Please select the relevant information categories.

Position in terms of topography,
e.g. top of rise, hillslope,
base of long slope, valley floor,
next to stream, etc.

Figure 7.2 : A request for identification of categories of available information.One item, topography, is currently selected.



```
Soil attenuation capability advisor.  Beta version.

 Uses/suitabilities of soils and comments for the site are:

.
Arid climate: soil pH is not likely to be low and is
likely to have a high buffering capacity and/or
a high base status.


.
Sparse vegetation provides little protection regarding
soil erosion. Also little organic carbon is normally
present in such soils.
.
Soils at the bottom of steep slopes tend to have two or
more horizons. Intermittent subsurface flows often
come to the surface here after periods of rain.
Soils  may   have silty or clayey horizons.
.
Shrinking aggreggated clays consist of montmorillonitic
clays or smectites. Surficial cracks develop on such
clays on drying. Such cracks allow passage for contami-

Hit any key to continue
```

Figure 7.3 : Comments presented as result of selecting an arid climate, sparse vegetation, site at the bottom of a steep slope, and presence of shrinking, aggregated clays.

"Production rules" are generally used to code logic. An example of a readable version of such a rule follows:

```
IF
        the soil to be sampled is located at the top of a significant rise
THEN
        it is likely to be more leached than other soils in the area
AND
        it is likely to be more acidic than other soils in the area
AND
        it is generally of relatively shallow depth.
AND
        it generally has a lower clay content than other soils in the area.
```

If the precondition to the rule is true (the IF part), the statements in the THEN part of the rule are added as text to files for display and reporting purposes.

This expert system is limited to simplified textual information relating to the categories: topography, climate, vegetation cover, soil texture and soil colour, **and its current use is solely for demonstration purposes.**

It is believed that there is significant potential for further expansion, especially in a "Windows" environment, relating to information in the form of text, diagrams and pictures, and to database information.

(b) Expert system designed to estimate CEC values, sorption potential indeces and leaching potential indeces in terms of specific contaminants.

Task: Use information from a soil-sample analysis to help assess:

(i) the relative sorption potential of various inorganic cationic and anionic trace elements in soil;

(ii) the relative sorption potential and leaching potential of specific organic chemicals in soil.

Given soil-analysis data on: soil pH, organic carbon content, content of Al/Fe/Mn oxides/hydroxy-oxides/hydroxides, carbonate content, soil texture, % clay-type content, saturated vertical hydraulic conductivity, climate, etc., the prototype expert system is designed to assess the relative potential that a soil has to adsorb specific contaminants within the following contaminant groups: priority heavy metals, priority anionic inorganic species and non-volatile, non-polar synthetic organic chemicals (See **Table 7.2** and **Figures 7.4**, **7.5**, **7.6a, 7.6b** and **7.7**).

More specifically, this expert system does the following:

☐ It presents a very approximate CEC value for use when analytical results are not available. **Figure 7.8** shows a screen which presents a CEC estimate which has been derived from the organic carbon percentage-content as well as the clay type and percentage-content and which gives an opportunity for the user to enter an accurate CEC value from a soils analysis, if one is available.

☐ It uses media-attenuation characteristics and related data to assess coefficients/ parameters associated with sorption (Kd/ cec), chemical precipitation, biological degradation and vertical moisture flux, for each contaminant grouping.

It derives an approximate Kd value for the contaminant/media in question and provides a qualitative evaluation of CEC and Kd. **Figure 7.10** shows a screen display of estimated sorption potential indices for some priority inorganic ions.

☐ It estimates sorption and leaching potential indeces for organic chemicals. **Figure 7.11** shows a request for a numeric value for the Log K_{ow} of a specific organic chemical. Displayed in the top half of the screen (**Figure 7.11**) are Log K_{ow} values of some organic chemicals.

☐ It presents information on relevant attenuating mechanisms (esp. sorption/ precipitation/ degradation), in numeric, textual and graphical format. **Figure 7.12** shows comments relating to sorption properties of media types present in a specific soil sample. The graphical form presents sorption potential indeces as a multi-coloured bar chart.

- ☐ Weighting-and-rating algorithms together with sets of rules are used for relative sorption assessment purposes. As a temporary measure, numerical importance weights were estimated from multi-media soil correlation coefficients (mainly Fuller et al, 1978). Numerical ratings were approximated from contaminant sorption potential rankings in the literature.

Potential uses of this expert system are believed to be:

(i) to give a relative indication of site-suitability of specific sites for disposal of wastes containing specific contaminants, based on soil-sorption potential only;

(ii) to give preliminary indications of those contaminants that are likely to be problematic for land-users, soils, agriculture or groundwater, based on contaminant toxicity type, soil type, and the resource at risk.

Due to the extensive information in literature on CEC, this expert system addresses CEC estimation in some detail. For organic non-polar chemicals, K_d and the leaching potential index (LPI) are calculated using formulae obtained from literature. Very little information is available in the literature on estimating K^d for inorganic trace elements. In place of Kd and for relative evaluation purposes, a sorption potential index (SPI) is calculated from weighting-and-rating formulae. Parameters in these formulae have as yet to be properly evaluated, so the results need validation.

It is believed that there is significant need for further work to be done on this expert system, in order to derive validated results.

The assumptions taken in the development of the expert systems

The following assumptions have been taken in developing the logical modelling process prior to encoding the expert systems:

(1) The soil media is homogenous
(2) Soil refers to porous, unsaturated media in the vadose zone
(3) No preferential flow pathways exist within the media
(4) Sorption of contaminants is unaffected by the presence of other species in solution
(5) Sorption of contaminants is unaffected by the presence of species already sorbed onto the soil media
(6) Water is the transporting medium for contaminants

Given more information on the effect of other contaminants in the solution on sorption of particular contaminants, it is possible that item 4) above, would fall away to some extent.

The suitability of expert systems for supplying decision-support in the field of soil-contaminant attenuation are considered to be dependent on, inter alia:

☐ The availability of sufficient numeric and qualitative data, preferably tabulated, relating to the quantity of specific contaminants adsorbed/retained by soil media in terms of :

(i) the quantity of contaminant remaining in solution,

(ii) the quantity of specific sorptive material in the soil which is responsible for the sorption and

(iii) other properties of the solution and soil which affect sorption, such as pH, redox status, salinity, media-porosity/particulate-surface-area, etc.

From an expert-systems development perspective, point (ii) is very important and is often overlooked as most soil-attenuation projects have been concerned with sorption of specific contaminants on mixed-media soils, and have not been concerned with the quantification of the sorption parameters in terms of individual soil-media characteristics (clay content and type being the exception). This is especially true for soil containing carbonates and oxides/oxy-hydroxides of iron, manganese and aluminium.

☐ The availability of measurable media/environmental parameters which are either mutually independent of one another, or else if not mutually independent, the dependency relationships being clearly specified.

☐ A significant overlap existing between the needs of potential end-users of the software and the information able to be sourced from literature and available experts, and also the ability to derive required logical decision-making processes and algorithms from available information/ expertise.

7.4 Conclusions

Two prototype expert systems have been developed to address the feasibility of using expert systems as decision-support tools for vadose-zone contaminant attenuation assessment purposes. These are:

☐ A prototype expert system which uses climatic, topographical, vegetation, and soil-texture and soil-colour data in an attempt to deduce the presence of important soil characteristics for contaminant-attenuation purposes, for feasibility-level or preliminary site-screening investigations.

☐ A prototype expert system which is designed to perform as a relative contaminant-attenuation assessment aid for specific contaminants within three contaminant categories, namely: organic non-polar contaminants, heavy metals and anionic inorganic trace contaminants.

Table 7.1 : Tabulated description of the expert system that presents comments on climate, vegetation, topography and soil texture/ colour

	CLIMATE	**VEGETATION**				**TOPOGRAPHY**				**SOIL TEXTURE**	**SOIL COLOUR CHARACTERISTICS**		
Questions asked	Arid; Semi-arid; Sub- humid; Humid	Trees/bush	Grass	Sparse	Crops	Top of rise	On steep slope	Base of long slope	Bottom of valley	Percentage clay. Clay type	Red	Orange-yellow	Mottled
Comments	Comments presented on: soil pH, soil salinity, percolation rate constraints, etc.	In general: Low soil pH. Medium-high organic C. Percolation rate limits.	In general: High organic C. High base status. High Ca/Mg content.	In general: Little organic C. Potential erosion probs.	Often have a high NO3 leaching effect.	Usually get permeable, leached, shallow soils, with low pH and low clay content.	In general: Prevalence of duplex soils. Long subsoil flow path for percolating water.	Prevalence of clayey soils. Often get seasonally emerging percolating water.	Prevalence of clayey soils. Usually a relatively high base status.	Vertical hydraulic conductivity ranges.	Usually indicates a high iron-oxide content. (Sesqui-oxide soils)	Usually has high aluminium and manganese oxide content	Indicates a seasonally high water table or presence of interflow conditions

Information sources:

- Lecture notes: Prof. W. Flügel, University of Jenna, Germany (1996)
- Thompson, J.G., 1985: *Guidelines for the disposal of Effluent on Land in South Africa*, Information Bulletin series: Soil, SIRI: Dept. Of Agriculture, Pretoria.

Table 7.2 : Tabulated description of the expert system designed to estimate CECvalues, sorption potential indeces, leaching potential indeces and to qualitatively assess these values in relative terms

MEDIA CONTENT CHARACTERIS-TICS	CARBONATE CONTENT	CLAY CONTENT		ORGANIC CARBON CONTENT	SESQUIOXIDE CONTENT	SOIL PH	CEC MEASUREMENT
SPECIFIC TYPE DETAILS		Kaolinite	Montmorillonite, smectite, illite, chlorite & vermiculite				
FIRST STEP: CATION EXCHANGE CAPACITY (CEC) ESTIMATION	No estimation.	Estimate CEC at neutral pH (i).	Estimate CEC at neutral pH. (ii)	Estimate CEC at neutral pH. (iii)	Estimate CEC at neutral pH. (iv)		Sum the CEC estimates from (i) to (iv) and present the result. This result may be over -written by the user (e.g. by a CEC value from a soils analysis.)
SECOND STEP: WEIGHT CATIONS AND ANIONS. MULTIPLY WEIGHTS WITH RESPECTIVE PROPORTIONAL MEDIA CONTENTS	Weight priority cations in the order of their CO3-solubilities. Multiply weights by proportional CO3 -content of soil.	Weight priority cations and anions according to published rankings, dependent on two broad pH ranges. Multiply weights by proportional clay-content of soil.	Weight priority cations according to published sorption-potential rankings for non-kaolinite clays. Multiply weights by proportional clay-content of soil.	Weight priority cations (and some anions) according to published information regarding sorption-potential. Multiply weights by proportional organic-carbon content of soil.	Weight priority cations and anions according to published rankings, dependent on two broad pH ranges. Multiply weights by proportional sesqui-oxide content of soil.	Estimate anionic and cationic pH-correction factors for kaolinite clays, sesquioxide soils and for CEC (cations only).	Evaluate CEC qualitatively.
CALCULATION DETAILS AND DISPLAY OF RESULTS	**CATIONS:** Given comparative-importance ratings (for cations) between clays + organic carbon content (as CEC), % CO3 content and % sesquioxide content: multiply together (a) weightings for each cation applicable for each media/sorption-characteristic type, (b) the media importance-rating and (c) the % media content/100. Apply the relevant pH correction factors. Display the results as comparative sorption potential indeces on a bar graph. **ANIONS:** Given comparative-importance ratings (for anions) between kaolin clay content, sesquioxide content and organic carbon content: multiply together (a) weightings for each anion applicable for each media type (or sorption characteristic type) (b) the media rating and (c) the % media content/100. Apply the relevant pH correction factors. Display the results as comparative sorption potential indeces on a bar graph. **ORGANIC CHEMICALS:** Given log K_{ow} for an organic chemical, estimate K_d as a function of log Kow and organic carbon content. Evaluate K_d qualitatively. Given the degradation half-life for the organic chemical, estimate a Leaching Potential Index (LPI).						

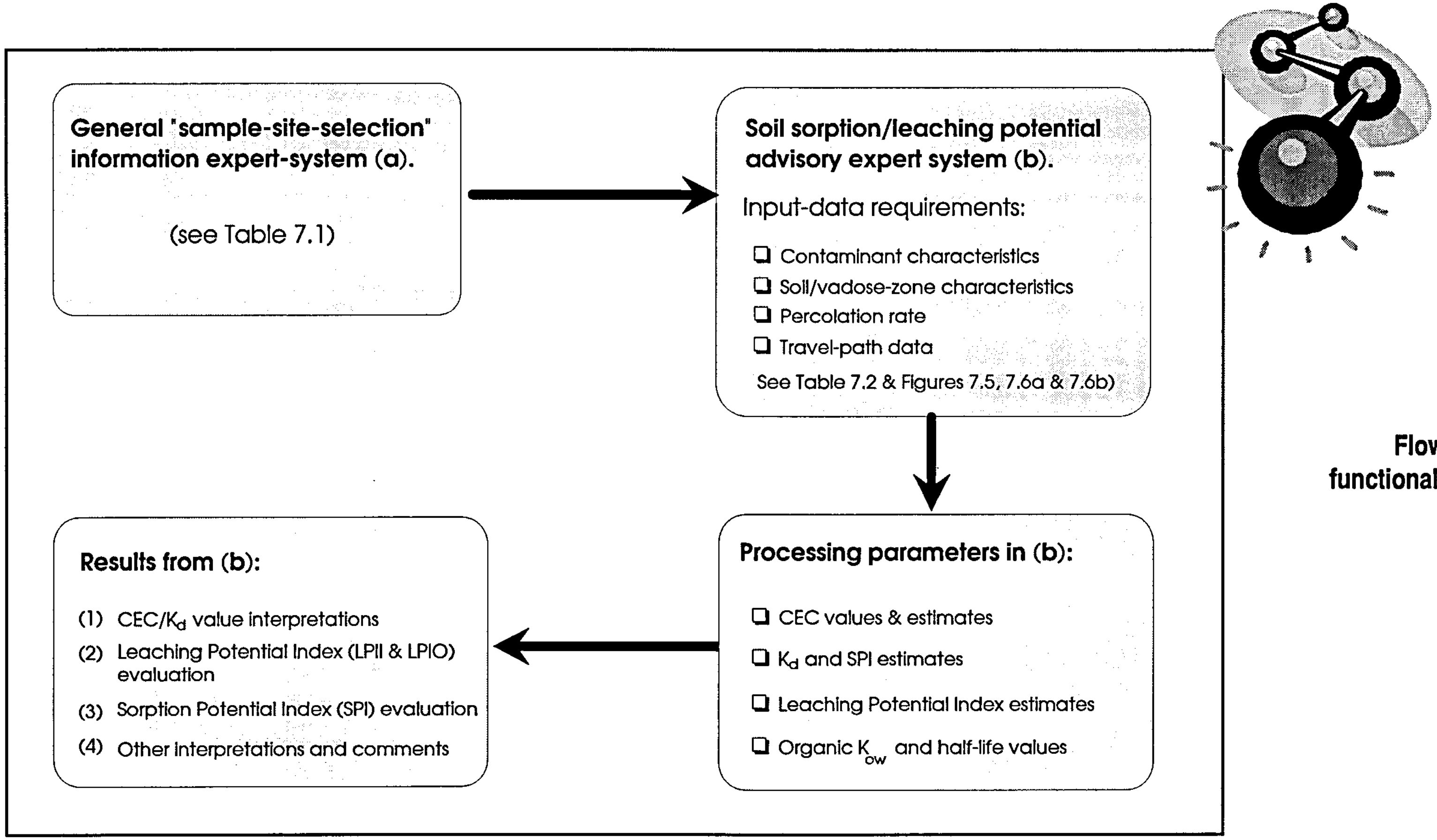
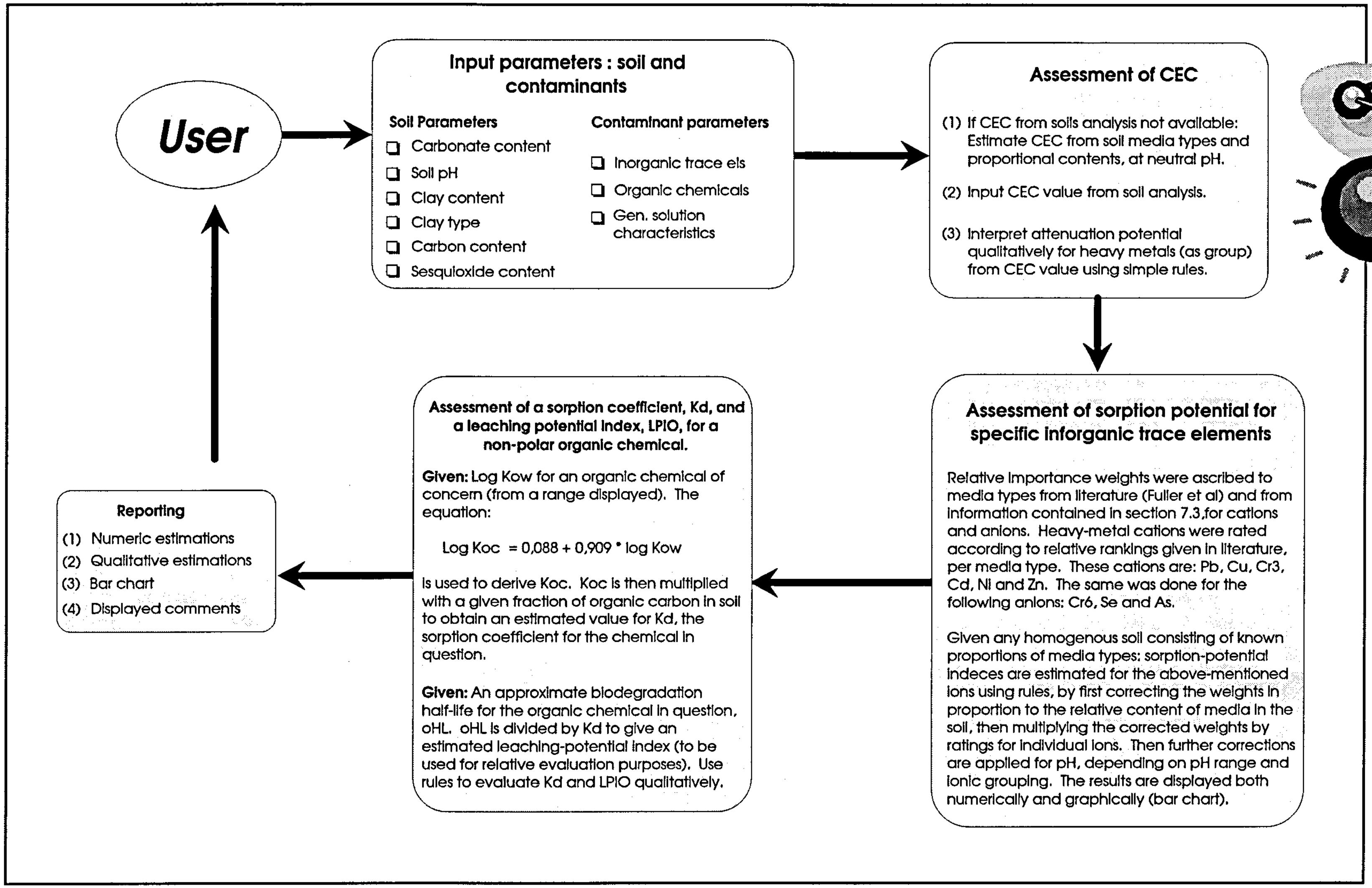


Figure 7.4 :

Flow-chart to describe the overall functionality of the two expert systems.



Input parameters : soil and contaminants

Soil Parameters

☐ Carbonate content
☐ Soil pH
☐ Clay content
☐ Clay type
☐ Carbon content
☐ Sesquioxide content

Contaminant parameters

☐ Inorganic trace els
☐ Organic chemicals
☐ Gen. solution characteristics

Assessment of CEC

(1) If CEC from soils analysis not available: Estimate CEC from soil media types and proportional contents, at neutral pH.

(2) Input CEC value from soil analysis.

(3) Interpret attenuation potential qualitatively for heavy metals (as group) from CEC value using simple rules.

Assessment of sorption potential for specific inorganic trace elements

Relative importance weights were ascribed to media types from literature (Fuller et al) and from information contained in section 7.3,for cations and anions. Heavy-metal cations were rated according to relative rankings given in literature, per media type. These cations are: Pb, Cu, Cr3, Cd, Ni and Zn. The same was done for the following anions: Cr6, Se and As.

Given any homogenous soil consisting of known proportions of media types: sorption-potential indeces are estimated for the above-mentioned ions using rules, by first correcting the weights in proportion to the relative content of media in the soil, then multiplying the corrected weights by ratings for individual ions. Then further corrections are applied for pH, depending on pH range and ionic grouping. The results are displayed both numerically and graphically (bar chart).

Assessment of a sorption coefficient, Kd, and a leaching potential index, LPIO, for a non-polar organic chemical.

Given: Log Kow for an organic chemical of concern (from a range displayed). The equation:

Log Koc = 0,088 + 0,909 * log Kow

is used to derive Koc. Koc is then multiplied with a given fraction of organic carbon in soil to obtain an estimated value for Kd, the sorption coefficient for the chemical in question.

Given: An approximate biodegradation half-life for the organic chemical in question, oHL. oHL is divided by Kd to give an estimated leaching-potential index (to be used for relative evaluation purposes). Use rules to evaluate Kd and LPIO qualitatively.

Reporting

(1) Numeric estimations
(2) Qualitative estimations
(3) Bar chart
(4) Displayed comments

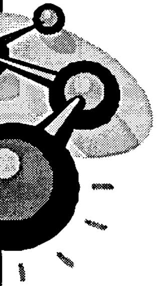


Figure 7.5 : Chart showing the functional detail of the expert system (b) the sorption/ leaching-potential advisory expert system.

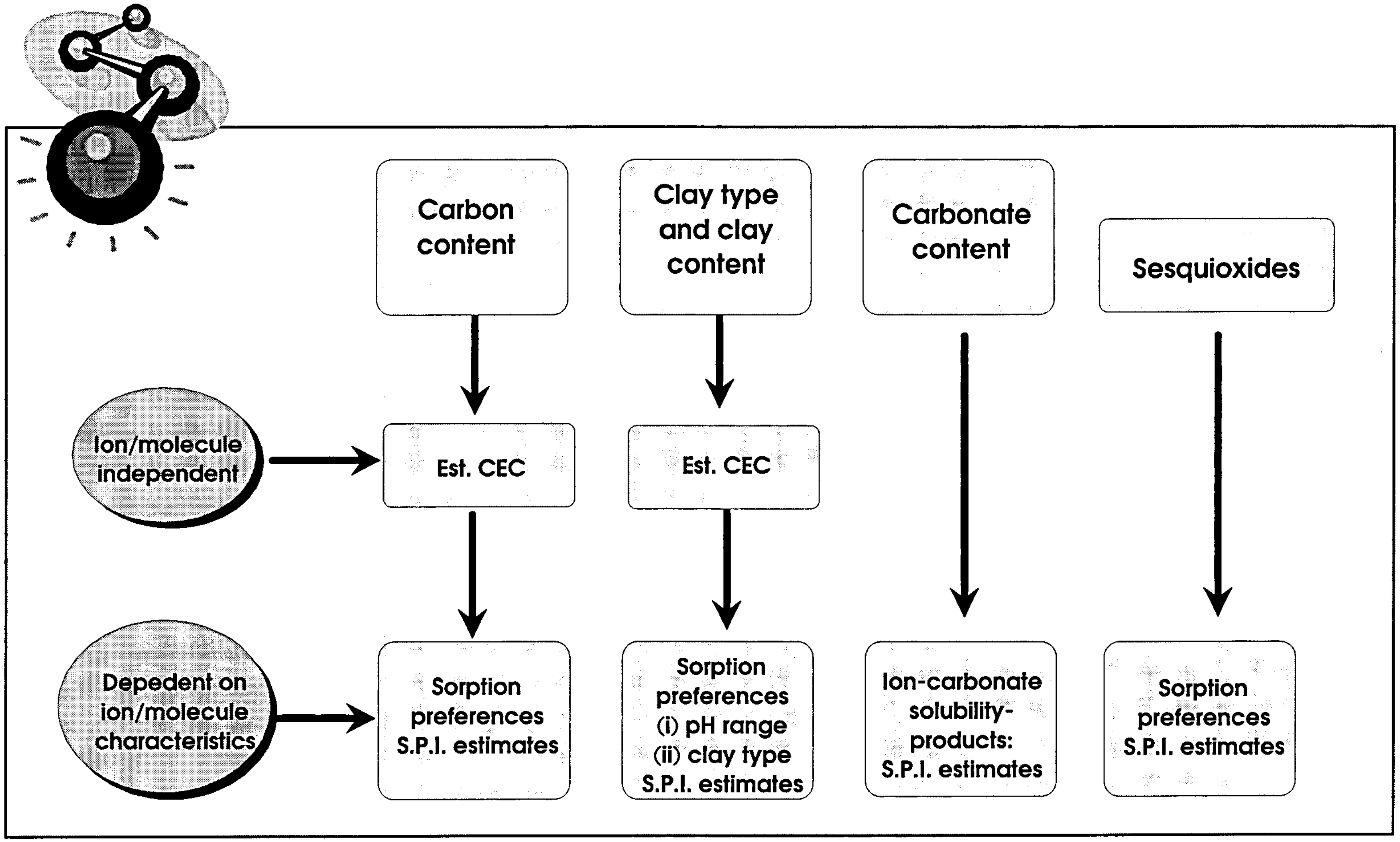


Figure 7.6a : Diagram to elucidate the functionality of that part of expert system (b), designed to estimate CEC and sorption potential indeces.

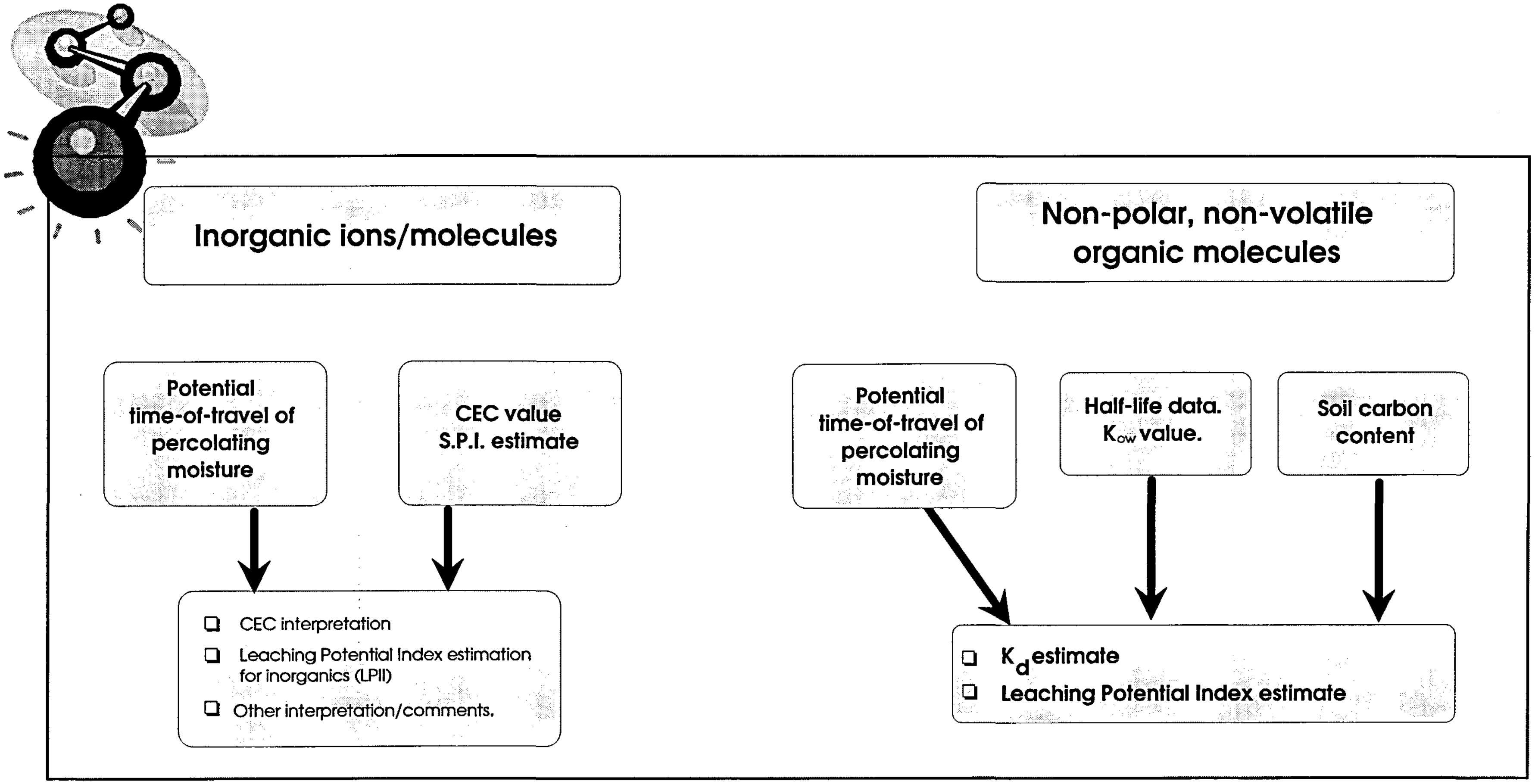
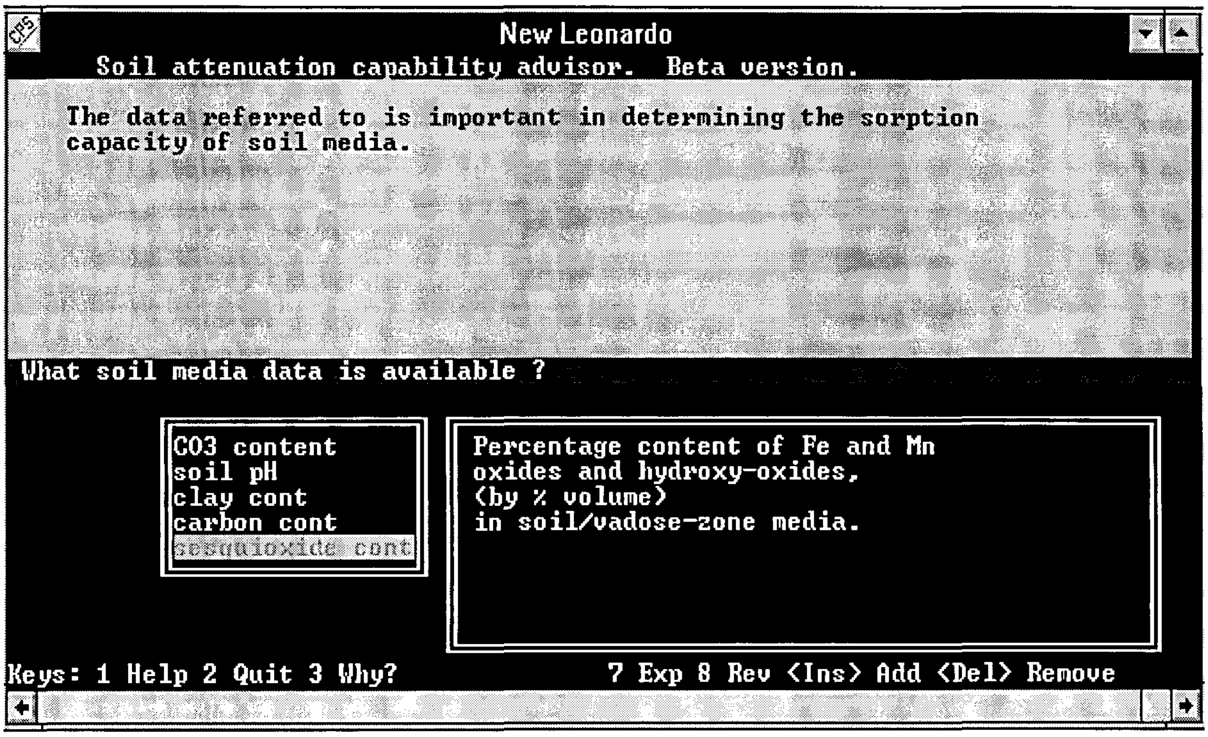
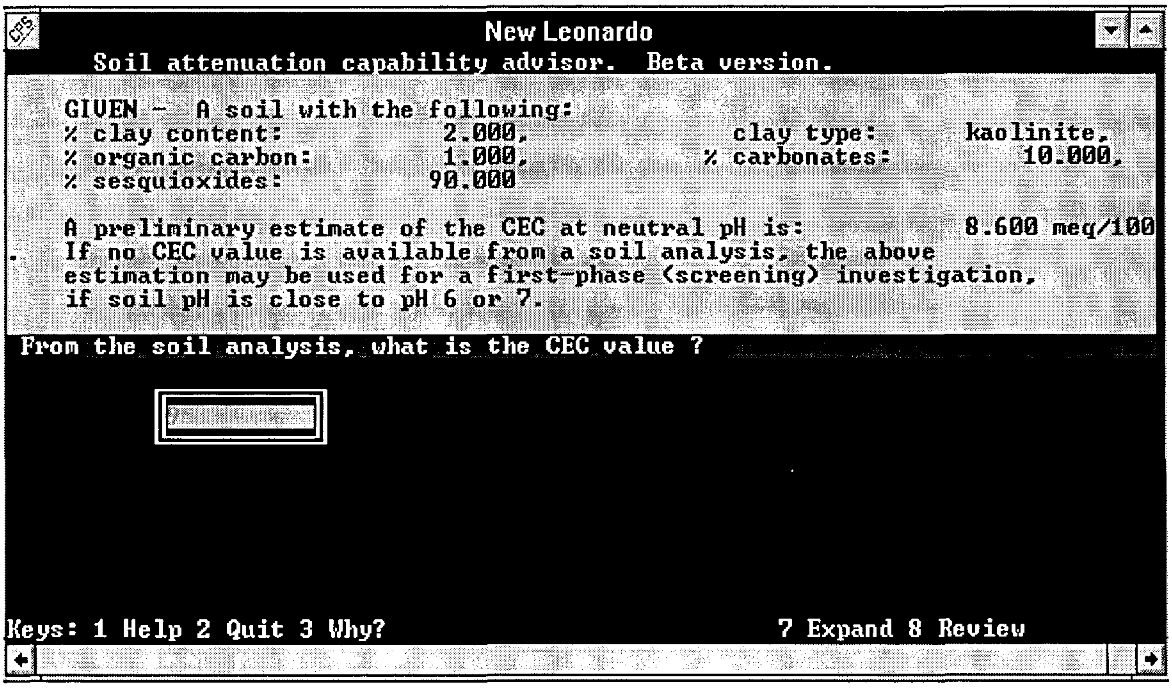


Figure 7.6b : Illustration of functionality of that part of expert system (b), designed to estimate Leaching Potential Index for inorganics and organics.



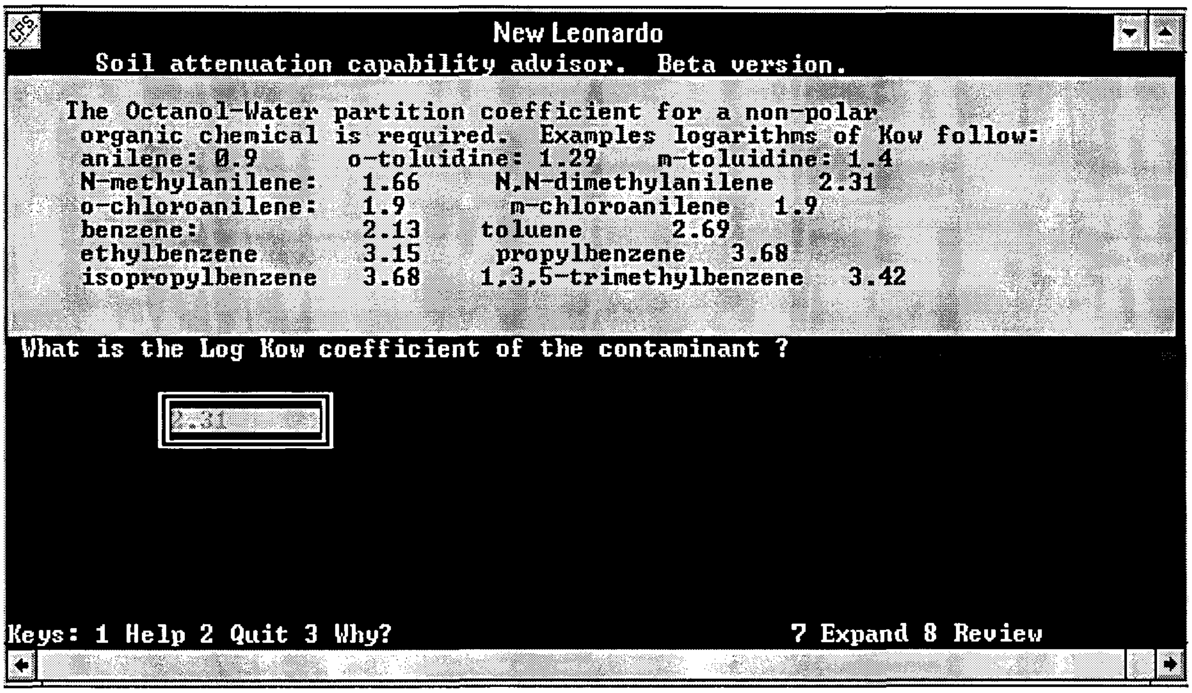
```
Soil attenuation capability advisor.  Beta version.

The data referred to is important in determining the sorption
capacity of soil media.

What soil media data is available ?

CO3 content
soil pH
clay cont
carbon cont
sesquioxide cont

Percentage content of Fe and Mn
oxides and hydroxy-oxides,
(by % volume)
in soil/vadose-zone media.
```

Figure 7.7 : Screen showing a request for selection of soil media data types.



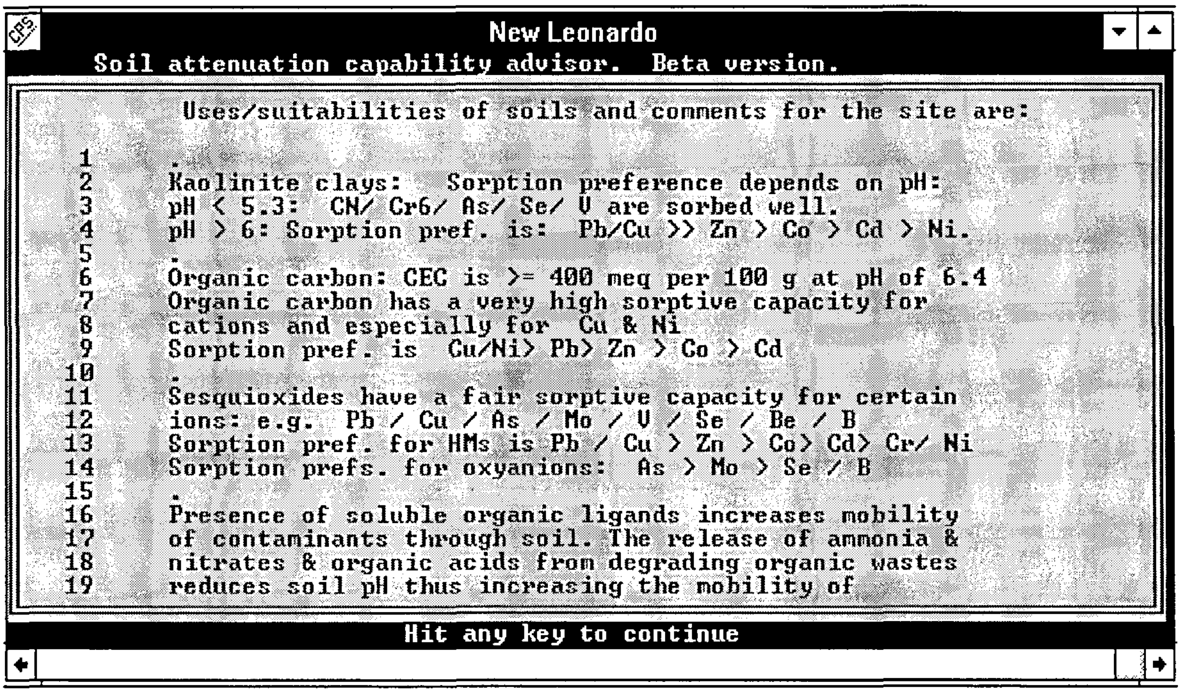
```
Soil attenuation capability advisor.  Beta version.

GIVEN -  A soil with the following:
% clay content:          2.000,          clay type:       kaolinite,
% organic carbon:        1.000,        % carbonates:        10.000,
% sesquioxides:          90.000

A preliminary estimate of the CEC at neutral pH is:        8.600 meq/100
If no CEC value is available from a soil analysis, the above
estimation may be used for a first-phase (screening) investigation,
if soil pH is close to pH 6 or 7.
From the soil analysis, what is the CEC value ?
```

Figure 7.8 : Screen showing estimated CEC value and a request for a corrected CEC value from a soils analysis, if available.



```
   Soil attenuation capability advisor.  Beta version.

    The Octanol-Water partition coefficient for a non-polar
     organic chemical is required.  Examples logarithms of Kow follow:
     anilene: 0.9       o-toluidine: 1.29    m-toluidine: 1.4
     N-methylanilene:   1.66     N,N-dimethylanilene   2.31
     o-chloroanilene:   1.9       m-chloroanilene   1.9
     benzene:           2.13    toluene        2.69
     ethylbenzene       3.15     propylbenzene   3.68
     isopropylbenzene   3.68    1,3,5-trimethylbenzene   3.42

What is the Log Kow coefficient of the contaminant ?

          2.31

Keys: 1 Help 2 Quit 3 Why?                        7 Expand 8 Review
```

Figure 7.11 : Screen showing Log K_{ow} coefficients for organic chemicals and a request for a Log K_{ow} value for the organic contaminant in question.



```
   Soil attenuation capability advisor.  Beta version.

            Uses/suitabilities of soils and comments for the site are:

  1        .
  2        Kaolinite clays:   Sorption preference depends on pH:
  3        pH < 5.3:  CN/ Cr6/ As/ Se/ U are sorbed well.
  4        pH > 6: Sorption pref. is:  Pb/Cu >> Zn > Co > Cd > Ni.
  5        .
  6        Organic carbon: CEC is >= 400 meq per 100 g at pH of 6.4
  7        Organic carbon has a very high sorptive capacity for
  8        cations and especially for  Cu & Ni
  9        Sorption pref. is  Cu/Ni> Pb> Zn > Co > Cd
 10        .
 11        Sesquioxides have a fair sorptive capacity for certain
 12        ions: e.g.  Pb / Cu / As / Mo / V / Se / Be / B
 13        Sorption pref. for HMs is Pb / Cu > Zn > Co> Cd> Cr/ Ni
 14        Sorption prefs. for oxyanions:  As > Mo > Se / B
 15        .
 16        Presence of soluble organic ligands increases mobility
 17        of contaminants through soil. The release of ammonia &
 18        nitrates & organic acids from degrading organic wastes
 19        reduces soil pH thus increasing the mobility of

                           Hit any key to continue
```

Figure 7.12 : Screen showing comments relating to sorption properties of media types present in a soil sample.

7.5 Recommendations

(i) A significant amount of information needs to be sourced regarding the quantification of sorption potential for priority anionic contaminants, especially arsenic and selenium. This information needs to relate to all soil media types, and especially for soil containing carbonates or oxides/oxy-hydroxides of iron, manganese and aluminium. This information is needed to help quantify the parameters in the SPI weighting-and-rating formulae.

(ii) In order to develop the expert systems further, more information, preferably as formulae or else able to be put in tabular form, needs to be gathered regarding the quantity of specific contaminants adsorbed in terms of :

☐ the quantity of contaminant remaining in solution;

☐ relevant quantification of specific sorptive material in the soil which is responsible for the sorption (for example, iron oxide content needs to be obtained together with soil particle surface area per unit volume: this is because sorption potential is dependent on both);

This point is believed to be very important, as most soil-attenuation projects reported on in the literature have been concerned with sorption of specific contaminants on mixed-media soils, and have not been concerned with the quantification of the sorption parameters in terms of individual soil-media characteristics (clay content and type being the exception).

☐ other properties of the contaminant-solution and of soil which affect sorption and precipitation: e.g. pH, redox status, salinity, media-porosity/particulate-surface-area, etc.

In terms of importance, all indications are that priority should be given to obtaining data on the relative effects of changes in pH on the sorption of particular contaminants on specific media (mainly on sesquioxides and kaolinite clay). Possibly second in importance: more data needs to be gathered to assess the effect of particulate surface area of soils (or maybe, soil porosity), on sorption potential. This is likely to be most relevant for sesquioxides.

CHAPTER 8

DISCUSSION AND CONCLUSIONS

CONTENTS

LIST OF FIGURES

8. DISCUSSION AND CONCLUSIONS

8.1 Introduction

To recap, the main aim of this study was to determine the contaminant attenuation capacity characteristics of various soils, aquifers and the subsurface environment as a whole for specific contaminants in order to provide a useful tool for planners, policy makers and pollution control authorities to assess groundwater pollution risks. A number of activities were conducted to achieve this aim. These included literature, laboratory, field and computer modelling studies. Information obtained from these studies was then used to address the development of GIS and expert system models.

This chapter discusses the conclusions from this study.

8.2 Literature review of contaminant attenuation in the subsurface

The literature study focussed mainly on the chemical processes that are likely to affect the fate of heavy metals and soluble organic compounds in the subsurface. For heavy metals, the main processes that are important are complexation, dissolution/precipitation, adsorption, reduction/oxidation and hydrolysis. For organic compounds, sorption and biological transformation are often the dominant reactions affecting their fate. The porous media properties that are important in attenuation include surface area, particle size, structure, mineralogy, organic and mineral coatings. The emphasis of the literature study was on chemical processes. Biological processes were only mentioned briefly. Transport processes of advection and dispersion were not considered.

The literature study showed that several factors and processes will operate in the soil/aquifer system that will affect contaminant attenuation. These processes may occur simultaneously and in certain cases will compete with each other. Thus, the fate of a given contaminant in the subsurface will be determined not only by its properties but the consequent reactivity in a variety of chemical, physical, and biologically mediated processes and the rate of its physical transport. The 'attenuation potential' of a given system is therefore, not a fixed parameter but a variable.

In order to accurately predict the attenuation and eventual location of solutes in the subsurface, a simultaneous consideration of all the important reactions and processes must be conducted. This is complex and can only be accomplished by using sophisticated computer codes, which require vast amounts of data to run. For many management problems, such data are usually not available and approximations have to be made. The latter takes advantage of the fact that if relationships between porous media properties and contaminant attenuation are known, predictions can be made with respect to the fate of a given contaminant. The relationships can be determined through laboratory experimentation, and where possible field verification. In this study laboratory studies were conducted on selected South African soils. Field verification studies were also conducted.

8.3 Laboratory studies

Laboratory studies were conducted to determine the potential for contaminant attenuation in selected soil materials. Comparison of the attenuation characteristics of heavy metals showed that attenuation of the negatively charged anion, Cr, was negligible while that of the positively charged cations, Pb and Cd was quite significant. It was also found that the calcic and smectitic soils attenuated the two cations best. For Cr, the highest attenuation occurred in the kaolinitic soil.

A matrix was compiled from literature to facilitate comparison of different physical and chemical properties of soil materials and their ability to attenuate different chemicals. Adsorption isotherms for Pb and Cd obtained from the literature compared well with isotherms obtained during this study.

More experiments are still required to identify the characteristics of porous media which can be used to predict the attenuation of selected contaminants.

8.4 Field scale studies

Field studies confirmed that attenuation of contaminants occurred at every site examined. The conclusions from the field studies are discussed below.

8.4.1 *Infiltration experiments*

The results of the organic contaminants added during the infiltration experiment showed possible attenuation. Butyric acid and aniline were not detected in any of the water samples. Phenol was only detected at 1 m and was not detected at depth. Toluene was detected at 4 m and its derivatives at 1 m. On the other hand, aliphatic hydrocarbons were detected at 8 m, two days after the infiltration experiment indicating that the subsurface environment will not be as effective in attenuating all compounds.

8.4.2 *Industrial liquid waste evaporation pans - Vissershok*

The uncertainty as to the loading history in the evaporation pans makes it difficult to speculate as to what the dominant factors were in the migration and attenuation of the metals under the pans. It is important, however, to note that metals have been detected at significant concentrations 1.6 m below the pan. The migration of contaminants to depth may be due to the fact that the attenuation capacity of the clay has been exceeded or alternatively, the attenuation potential of the clay under the pans is not as high as might have been assumed for this Class 1 site. By definition, a Class 1 site should be able to contain both the waste and leachate in the site or in the immediate surroundings thereof.

8.4.3 *Industrial liquid waste - flood spreading*

At this site, it was found that most of the metals precipitated at the surface. The metal concentrations in the unsaturated zone and groundwater were relatively low indicating low mobility in the area. The low mobility of the metals is attributed to the high buffering capacity of the sands. Since high pH favours metal precipitation and sorption, migration of metals is likely to be low in this area.

8.4.4 *Domestic solid waste disposal site*

An examination of changes in DOC both in time and in space indicates that the DOC levels are declining, suggesting that natural attenuation of organic contaminants is occurring in the aquifer.

8.4.5 *Industrial liquid waste - leaking source*

At this site, the heavy metal pollution shows a marked decline a few metres from the source, indicating that metals are not very mobile in this area. The organic compounds show similar behaviour. For the heavy metals, the low mobility is attributed to the high pH buffering capacity in the aquifer.

8.5 Solute transport modelling

Procedural guidelines for modelling solute transport in the unsaturated zone were developed from an integrated literature, laboratory and field scale studies. The CHAIN_2D computer code was selected as a suitable model and was used without any modifications. MODEL2D program was developed as a tool to assist the user in rearranging data and to act as a guide to the input data for the simulation model.

A sensitivity analysis was conducted on the selected CHAIN_2D model in order to determine the sensitivity of the model parameters to a 20% change in input parameter value. In terms of the magnitude of the effect on parent solute movement, the parameters can be arranged in the following sequence:

$(n,\alpha) > K_s \approx$ Bulk Density > Climate >> Adsorption Isotherm > First Order Kinetics > Diffusion Coefficient in Water > Volumetric Heat Capacity of Liquid > Longitudinal Dispersivity ≈ B3 (Coefficient of Thermal Conductivity Function) > Volumetric Heat Capacity of the Solid Phase > Volumetric Solid Phase Fraction > B1 ≈ B2 ≈ Beta (Adsorption Isotherm Constant) ≈ Transversal Dispersivity > Volumetric Organic Matter Fraction ≈ Transversal Thermal Dispersivity of Material ≈ Longitudinal Thermal Dispersivity of Material ≈ Henry's Coefficient ≈ $Dg = 0$.

This sequence stresses the importance of the hydraulic properties of the soil, climate and bulk density in determining the movement of contaminants in soil. When considering the chemical parameters, the change in input parameter value for the adsorption isotherm has shown a more pronounced sensitivity than that of the first order kinetic parameter. The parameter sequence above, allows the modeller to decide on the most significant parameters which should be included in a modelling effort, eliminating parameters that would result in high observation costs and contribute relatively little to the accuracy of the modelling result.

The CHAIN_2D model was validated on a laboratory scale using data from soil column breakthrough curves. These data were used with the parameter estimation program CFITIM and the results were used to calculate the adsorption isotherm coefficient (k_s [cm^3/g]) for the selected heavy metals in distilled water and Coastal Park leachate. The k_s values for Cr were smaller than zero, which indicates that the resident adsorbed Cr in the sand could be washed out of the laboratory column. No adsorption of Cr took place in the sand during the laboratory column experiments. The metals Pb and Cd were found to be *more mobile* in the sand when they were dissolved in Coastal Park leachate than in distilled water. The order of adsorption of the heavy metals was as follows : Pb > Cd > Cr. This sequence is valid for both distilled water and the Coastal Park leachate. The Wilmot coefficient of agreement used in the laboratory validation of the model was calculated as $d = 0.9959$ showing a good agreement between the observed laboratory data and the CHAIN_2D predictions.

The CHAIN_2D model was also validated on a field scale using soil moisture content data. Although the validation was less successful than the laboratory scale validation, it is noted that the infiltration experiment was less controlled than the laboratory experiments.

8.6 GIS

Using GIS, a methodology has been developed for generating regional/national scale maps of vadose zone attenuation characteristics. It has been demonstrated that land type maps, which are available at a scale of 1:250 000, can be used to derive soils information per land type. The following maps were derived:

☐ clay content per land type
☐ Fe content per land type
☐ average CEC per land type

The soils information were then used to obtain a qualitative indication of the attenuation of a given land type. This was effected by using:

☐ clay content and lime to map attenuation potential of cation forming elements
☐ hydrous oxides to map attenuation potential of anion forming elements
☐ CEC to map attenuation potential of basic organic molecules and organic cations

These maps can be used to rapidly assess/identify areas with low or high attenuation potential. When the derived soils information is combined with vulnerability maps, a means is provided for rapidly assessing groundwater pollution risks on a regional scale.

One of the major limitations of using land type maps in attenuation studies stems from the fact that the spatial distribution of the soils is not known within the land type. The results can not therefore be used for site specific work.

8.7 Prototype expert system models

Two prototype expert systems have been developed to address the feasibility of using expert systems as decision-support tools for vadose-zone contaminant attenuation assessment purposes. ***Additional work is still required on these systems. At present, their use is solely for demonstration purposes only.*** The two systems developed are:

☐ A prototype expert system which uses climatic, topographical, vegetation, and soil-texture and soil-colour data to deduce the presence of important soil characteristics for contaminant-attenuation purposes, for feasibility-level or preliminary site-screening investigations.

☐ A prototype expert system which performs as a relative contaminant-attenuation assessment aid for specific contaminants within three contaminant categories, namely: organic non-polar contaminants, heavy metals and anionic inorganic trace contaminants.

There is still need for further work on the prototype expert systems to derive validated results. More information from literature on contaminant attenuation characteristics, preferably as formulae or else in tabular form, needs to be gathered.

8.8 Final comments

The tools developed in this study can be used during investigations of aquifer pollution risks. Figure 8.1 summarizes how the tools can be used individually or in combination . The scheme shown in Figure 8.1 can be combined with information from vulnerability maps to determine groundwater pollution risks on a regional scale.

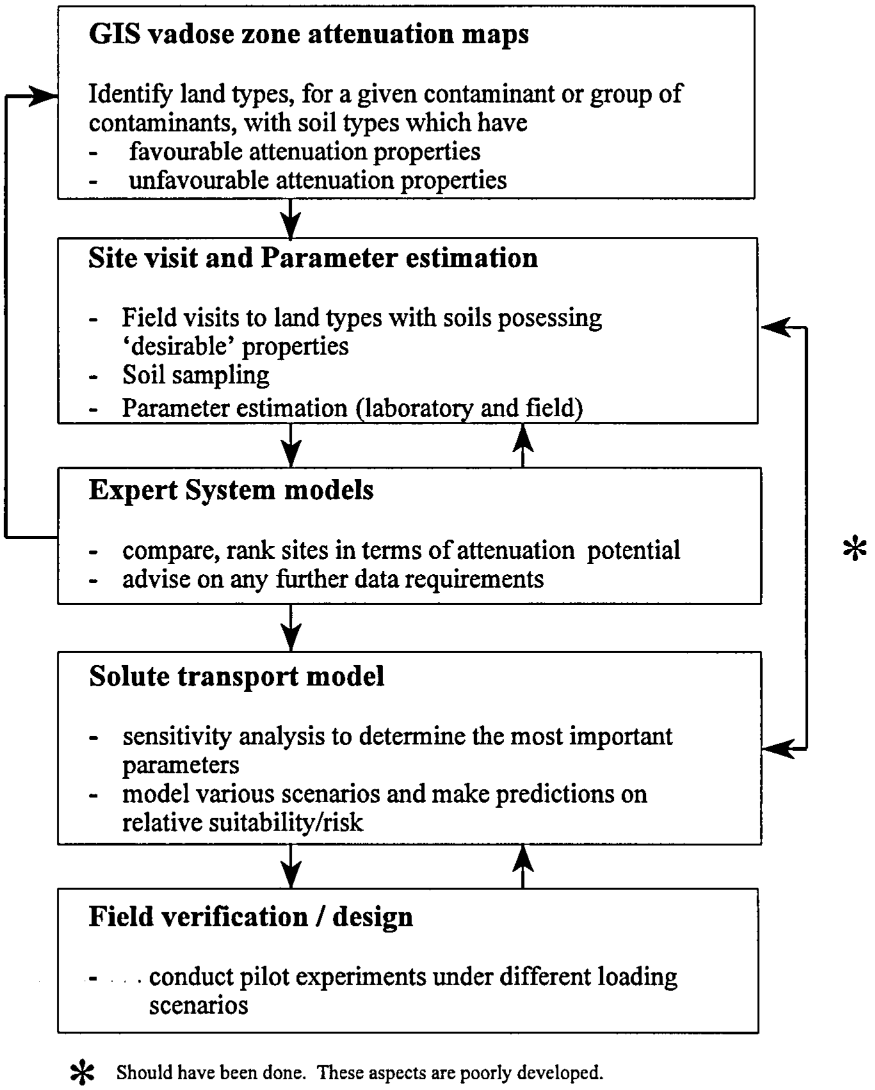


Figure 8.1: Potential application of GIS, Expert System and Solute Transport Models in attenuation studies

CHAPTER 9

RECOMMENDATIONS

CONTENTS

9. RECOMMENDATIONS

Recommendations are given in two sections: Implementation and further research.

9.1 Implementation

9.1.1 *GIS vadose zone attenuation maps*

The methodology developed in this study for generating vadose zone attenuation maps for the Western Cape should be applied to the whole country. This should be possible because land type maps which were used to generate the attenuation maps are available for the whole country at a scale of 1:250 000. In addition, the spatial and attribute data is accurately captured and well maintained by the Institute of Soil, Climate and Water (ISCW) of the Agricultural Research Council. The land type data base is very well administered by the ISCW and requests for land type data are processed and delivered quickly. The data are in Arc/Info format, thus easily transferable and usable.

The recommended approach is as follows:

☐ use available land type maps to produce soils characteristic maps.

☐ produce qualitative contaminant attenuation maps for the whole country.

The qualitative contaminant attenuation maps can be used for regional planning purposes. They can be used

☐ for land-use planning to give a broad overview of favourable or unfavourable areas for certain human activities.

☐ to indicate potentially suitable areas for further detailed investigation.

☐ in combination with geological and hydrogeological maps to assess aquifer vulnerability to pollution.

9.1.2 *Solute transport modelling*

The modelling package CHAIN_2D, which is now available at the University of Stellenbosch, can be utilized to model fate and transport of contaminants in the unsaturated zone. Specifically, the model can be used

☐ to investigate the likely variability in contaminant behaviour in a much wider range of conditions than is possible experimentally.

☐ to estimate the contaminant attenuation capacity of the unsaturated zone.

☐ to estimate the time it would take a contaminant to migrate from the surface to the water table. Using this approach, sites can be compared or ranked in terms of pollution risk.

9.2 Further research

9.2.1 *Context*

The original aim of this study was:

"to determine the contaminant *attenuation* capacity *characteristics of various soils, aquifers and the subsurface environment* as a whole for specific contaminants in order to provide *a useful tool* for planners, policy makers and pollution control authorities to assess *groundwater pollution risks.*"

This aim was quite broad and stressed attenuation characteristics. It is important to note, however, that in order to fully address groundwater pollution risks, data on aquifer sensitivity and pollution loading are also essential.

The recommendations given below are intended to serve two purposes. Firstly, to highlight areas that need immediate attention with respect to contaminant attenuation. Secondly, to highlight areas that need attention with respect to determining groundwater pollution risks.

9.2.2 *Relationships between porous media characteristics, contaminant types and contaminant attenuation*

An integrated literature, laboratory and field studies is recommended. A significant amount of literature still needs to be sourced regarding the relationships between soil characteristics, contaminant properties and contaminant attenuation. For each contaminant of interest, information on the following should be collected:

☐ mechanisms of attenuation
☐ relationships between contaminant attenuation and porous media properties
☐ relationships between contaminant attenuation and contaminant properties
☐ measured adsorption coefficients for a given contaminant and conditions under which the results are obtained, eg pH, organic carbon content, etc.

Verification of these literature based results should be conducted for South African soils at the **laboratory scale**. The laboratory tests should have an added requirement of producing results which can be used for management purposes. For this reason, it is recommended that the selection of soils should be done in close consultation with the ISCW, who are the suppliers of land type and soil maps.

The following type of experiments are recommended:

A *Experiments designed to compare and rank soils according to their attenuation potential*

☐ Batch experiments to measure the adsorptive capacity of soil materials at different pH values. If enough measurements are conducted, regression equations can be obtained which can be used for ranking.

B *Experiments designed to predict transport of contaminants in the subsurface*

☐ Batch experiments to measure the distribution coefficient (K_d) of a given contaminant

☐ column experiments designed to obtain information on transport of contaminants in porous media.

Field studies should be conducted in areas where (1) pollution incidences have been observed and (2) pollution loading is high but no groundwater pollution has occurred. The idea here is to establish the most important factors at the field scale which can be used as 'predictors' for aquifer pollution risks. It is noted that these factors may be related to *aquifer sensitivity*, contaminant attenuation characteristics or *pollution loading*.

Product

A database giving

☐ general behaviour of selected contaminants in porous media, with emphasis on South African soils/geological materials.

☐ predictors for contaminant migration in different types of soils/geological materials.

9.2.3 *Decision aids*

The data/information from above should be captured in a form that can be utilized by practitioners. GIS is best suited for this purpose.

GIS

Using GIS, contaminant attenuation information can be combined with information on aquifer sensitivity (vulnerability) to determine aquifer pollution risks under different land-use management practises.

The GIS component should also investigate ways of incorporating solute transport modelling - through coupling with mathematical models. There are a spectrum of strategies for linking models to GIS. A continuum exists ranging from loose through tight coupling to an embedded system approach in which the GIS and the model are fully-integrated into a single software system.

In applying GIS, the significance of spatial variability must be investigated and users must be cautioned about the limitations. The spatial variability investigation should be conducted in close consultation with the ISCW.

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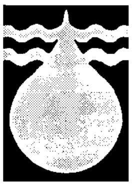


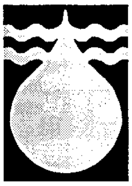
APPENDIX 1

Mobility of inorganic metals in the subsurface

Inorganic metal	Mobile	Immobile
Cadmium	**Low pH:** decreased sorption by colloids; increased solubility	**High pH:** increased sorption by colloids; decreased solubility **Reducing conditions:** precipitation of **sulphides** **Complexation:** sorption to soil organics to form organo-metallic complexes is the primary mechanism of attenuation
Chromium(VI)		**Reducing conditions:** change the oxidation state from Cr (VI) to Cr (III), which is less mobile than Cr (VI). **Oxides** and **phosphates** are insoluble
Chromium (III)	**Sulphates** and **nitrates** are soluble	Generally immobile in groundwater **Carbonates, hydroxides** and **sulphides** are insoluble
Copper	**Low pH:** decreased sorption by colloids	**High pH:** increased sorption by colloids **Sorption:** by clays, quartz, iron and manganese oxides **Complexation:** forms stable complexes with organics e.g. carbonyl and phenol groups
Lead	**Low pH:** decreased sorption by clays; increased solubility **Reducing conditions**	**High pH:** increased sorption by clays; decreased solubility **Oxidising conditions** **Complexation:** forms insoluble organic complexes **Carbonates, hydroxides** and **sulphates** are insoluble

Inorganic metal	Mobile	Immobile
Mercury	**Low pH:** decreased sorption by clays Hg has a low boiling point and may undergo volatization **Complexation:** organo-mercury compounds e.g. methyl mercury are the most common pathway for migration to humans and animals	**High pH:** increased sorption by clays; precipitation of **sulphates, hydroxides** and **nitrates** **Reducing conditions:** precipitation of sulphides **Oxidising conditions:** precipitation of chlorides **Sorption:** by clays, fine sands, iron and manganese oxides **Complexation:** rapidly and strongly complexed by covalent bonding to sulphur-containing organic compounds and inorganic soils
Manganese	**Low pH:** increased solubility of Mn (II) **Mn (II)** is soluble and mobile	**High pH:** decreased solubility of Mn (II) **Reducing conditions:** Mn (II) strongly sorbed to clays and organics **Mn (IV)** is insoluble and immobile
Silver		**Sorption:** through ion exchange by colloidal particles. **Carbonates, chlorides** and **sulphates** are insoluble
Zinc	**Sorption:** by organic colloids which are very soluble and mobile Most zinc salts are soluble	**High pH:** insoluble above pH 6.5 **Sorption:** by solid particle surfaces which are immobile **Ionic Substitution:** for Al, Fe or Mg in clay minerals **Sulphates** are insoluble
Iron	**Reducing conditions:** increased solubility See E_H/ pH field diagram for iron	**Oxidising conditions:** precipitation of hydrous oxides (These provide a major attenuation mechanism by sorption of Co, Ni, Cu, Zn, etc.) **Bacterial activity:** can cause precipitation of hydrous iron oxide

** USEPA, 1985 DRASTIC - USEPA report EPA/600/2-85/018.*



APPENDIX 2

Experimental methods for determining attenuation standards.

The initial approach chosen for determination of contaminant attenuation by the soils involved the use of packed columns. It was then suggested that 'shake-up' screening tests be used to provide an initial indication of contaminant attenuation by the soil. The advantages of the screening test are that it is fast, inexpensive, and produces reproducible results. The disadvantages are that the process has little correlation with the actual field situation, where the contaminant migrates through the soil mass. Soil column studies represent the field situation more accurately, although the soil has been disturbed and resettled in the column. The column studies would then to used to confirm the results of the screening tests under simulated field conditions.

Screening Tests

Various Quantity/Intensity (Q/I) screening tests were tested, with a view to finding a quicker, simpler and less expensive method of determining attenuation, than the column studies.

A Q/I test involves the following steps:

Make up aqueous stock solutions of the contaminants.

- ➔ Shake up mixtures of the different soil materials with the contaminant solutions.
- ➔ Centrifuge the mixture.
- ➔ Analyse the supernatant.
- ➔ Extract adsorbed contaminant from soil, and analyse.
- ➔ Calculate mass balance for each soil/contaminant combination.

Heavy Metals

This approach gave rise to two significant problems. Firstly, an aqueous stock solution of the metal, with known concentration, must be made up for contaminating the soil. However, the concentration of an unbuffered aqueous heavy metal solution will begin to drop almost immediately, as a result of precipitation in this neutral medium. The problem is normally avoided by acidifying the contaminant solution. In this case, the application of an acidified solution to the soil would alter the soil environment, and render the study meaningless or, at the very least, irreconcilable with the field situation. The alternative was to use a contaminant solution with a very high concentration, and then compare results of the supernatant analysis after centrifugation, rather than conducting a mass balance. Secondly, centrifugation of the soil suspension renders a solid, dense core of soil at the base of the tube. This makes it extremely difficult to wash the remaining contaminant solution from the sediment. This problem was overcome by simple filtration of the suspension, rather than centrifugation.

Column Studies

Design

The columns used were specially designed to measure rate of solute flow through a soil mass. Initial testing revealed, however, that the design was unsuitable for determining attenuation capacity. Various changes were made and tested, before arriving at the final design (Figure 3.1). This design not only reduced leachate loss to a minimum, but also allowed for batch sampling of the leachate.

The columns for the heavy metal studies were constructed from perspex, while those for the organic compounds were made from glass, to eliminate interaction between contaminant and column material. The soil is packed on a disc of Whatman No. 41 filter paper (Figure A2.1).

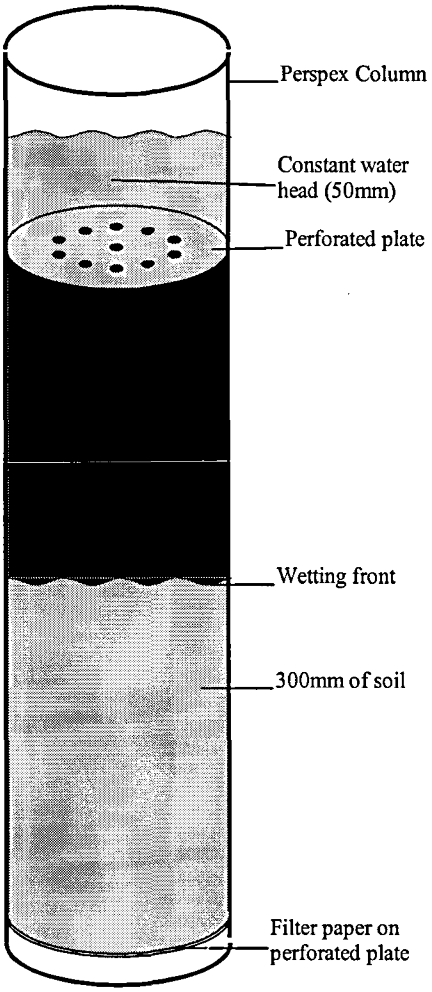
Method

The column is packed either with 30cm of sand to a bulk density of 1.5 g/cm^3, or with 30cm of clay to a bulk density of 1.3 g/cm^3 (the clay columns are shaken on a platform shaker to achieve the required bulk density), to represent the field situation. The soil is then contaminated to capacity (as determined in the screening tests), with a specific contaminant.

The columns are then ponded, simulating extreme rainfall conditions, and the recovered leachate monitored for the presence of contaminant. This ponding is repeated until no contaminant is detectable in the leachate.

On completion of the leaching studies, the soil is divided into segments, and the retained contaminant extracted for analysis. Finally, a mass balance is drawn up for each column.

Figure A2.1. Column Design



Extraction

Heavy Metals

One of the greatest obstacles of the study was finding a suitable method for extraction of the attenuated heavy metal from the soil sediment. At the Steering Committee Meeting of 14 October 1994, it was proposed that a sequential extraction method (Van der Merwe et al, 1994) be used to extract the selected heavy metals from the contaminated soil samples. A description of the method was then obtained from the Institute of Soil, Climate and Water, for testing. A revised description is presented below:

Sequential Metals Extraction (ISCW)

Procedure

Phase O: Total metals digestion

Phase I: Mobile fraction

Phase II: Slowly oxidised fraction

Phase III: Mn-oxides occluded fraction

Phase IV: Organically bound fraction

Phase V: Poorly crystallised iron-oxides occluded fraction

Phase VI: Crystallised iron-oxide occluded fraction

Phase VII: Residual fraction

Reagents

Ammonium nitrate (NH_4NO_3), 1 mol.dm^{-3}

Ammonium acetate (NH_4OAc), 1 mol.dm^{-3}

Hydroxylamine hydrochloride (NH_2OH-HCl), 0.1 mol.dm^{-3}

Ammonium EDTA [$(NH_4)_2EDTA$], 0.025 mol.dm^{-3} (pH 4.6)

Ammonium oxalate buffer [$(NH_4)_2C_2O_2.H_2O$] + Oxalic acid ($H_2C_2O_4$)],
0.2 mol.dm^{-3} (pH 3.25)

Ascorbic acid ($C_6H_8O_6$), 0.1 mol.dm^{-3}

Perchloric acid (c.$HClO_4$)

Hydrofluoric acid (c.HF)

Hydrochloric acid (c.HCl)

The method was eventually discarded in August 1995, in light of the following pitfalls and problems:

- ➔ the method is extremely time-consuming (a complete extraction takes at least seven (7) days)
- ➔ the sequential nature of the method means that any experimental error made during any stage of the method, necessitates repeating the entire procedure
- ➔ the final stage involves digestion using hydrofluoric acid (HF), an acutely corrosive chemical
- ➔ presence of HF in the final solution complicates analysis

In addition to these practical problems, comes the warning of Nirel & Morel (1990), who point out that results obtained with sequential methods, are 'operationally defined'. This means that the physicochemical conditions used during extraction procedures (strong reagents and fast kinetics) cannot be extrapolated to naturally occurring processes (weak reagents and slow kinetics). In their report, Nirel & Morel (1990) quote six publications that attempted to validate sequential techniques, using well-defined samples. In all six cases the results were negative.

The EPA Total Sorbed Metals Method (Risser & Baker, 1990) was then adopted, and is presented below:

Total Sorbed Metals Extraction (EPA)

Reagents

conc. Nitric Acid (HNO_3)
conc. Hydrochloric Acid (HCl)
30% Hydrogen peroxide (H_2O_2)
Deionised water

Method

Add 10 ml of 1:1 HNO_3 to 2 g of air-dry soil, in a 150 ml Pyrex beaker

Cover with a watch glass

Place samples on a boiling waterbath

Reflux for 15 min.

Cool the beaker

Add 5 ml of conc. HNO_3 and replace watchglass

Reflux for 30 min.

Repeat Steps 6 & 7

Evaporate solution to 5 ml (beaker partially covered)

Cool sample

Add 2 ml of deionised water, 3 ml of 30% H_2O_2

Heat gently to start peroxide reaction

If effervescence is vigorous, remove from waterbath and cool

Add 1 ml of 30% H_2O_2 and return to waterbath

Repeat Step 15 until effervescence is minimal

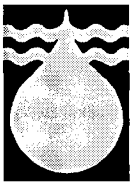
Add 5 ml conc. HCl, 10 ml deionised water

Cover with watch glass, return to waterbath

Reflux for 15 min.

Cool, filter sample through Whatman no. 41 filter paper

Dilute to 50 ml with deionised water



APPENDIX 3

Example Model 1: Laboratory Column

In this example for MODEL 1, a simulation run was performed with CHAIN_2D for a laboratory column and a non-reacting solute moving through a uniform laboratory soil column.

The user can repeat the procedure by selecting MODEL 1 from the MODEL2D menu, providing the simulation run number and by using the information presented in this example as input for the MODEL2D program. It is important that the user use the same simulation number during the simulation, since the modelling results are archived by simulation run number.

Basic simulation and soil information.

The simulation units that were chosen, were gram, centimetres and minutes. The column was 30 cm in height and 14 cm in diameter. The simulation run was performed in axis symmetrical dimensions, resulting in information for a three dimensional soil region consisting of one soil type through which one solute was moving. Depth and width increments of 1cm were chosen to generate the nodal region grid, resulting in 30 increments in the vertical (z) direction and 7 increments in the horizontal (x) direction.

Material information.

The soil hydraulic properties of sand were selected from the MODEL2D database.

Time information.

CHAIN_2D can print simulation results at user-specified times in MODEL2D to the relevant output file. The simulation run was performed for a simulation period (computer calculation time was 4 minutes) of 5 hours. Output was generated for the situation at hourly intervals after the start of the simulation. Thus five sets of output were produced.

Solute transport information.

By assuming a non-reacting solute, it does not matter (adsorption equals zero) whether the adsorption type selected is nonlinear or linear. The linear adsorption type was only selected to be able to complete the input needed by MODEL2D. The typical value for the soil bulk density of sand, selected from the menu of MODEL2D, was used. Thus, by selecting the sand as the soil matrix, the specific value is recalled from the database and no external value was necessary. The material information parameter values mentioned are dependant on the soil bulk density. If the bulk density value is changed, the simulation results might be spurious and in some cases the model will not converge. The adsorption type-1 site fraction value was set to 1.0. MODEL2D needs a value for the solute diffusion coefficient in free water, therefore a value of 0.025 was entered. Finally, the adsorption isotherm coefficient k_s [cm^3/g] value of zero was entered for no adsorption. This parameter is labelled as Ks in MODEL2D.

Initial soil conditions.

The initial column profiles consist of information on the soil solute concentration profile, the initial adsorbed solute concentration profile and the initial soil water content profile. The soil solute concentration and adsorbed solute concentrations were set to zero for all soil depths. The soil water content was manually set to the θ_r value of 0.02 (the database value) for every soil depth increment. MODEL2D calculates the pressure head values from the water content information given as input and checks that these values do not exceed 15000 centimetres head of water.

Column input flux information.

The column input flux was calculated by dividing the flowrate by the column cross sectional area. A flux value of 0.325 centimetre per minute was obtained for a 3 litre per hour flowrate. Time related records (a record contains one data point for a specific time period) for the column flux can be used as input for MODEL2D. The simulation starting time was set to time zero and the number of records were set to 2. Solute was added at the top of the column at the mentioned flux (record 1) for two hours (120 minutes). No evaporation took place (zero) and the solute concentration in the input was set to 1 gram per cubic centimetre. For the remaining time period, no solute was added (record 2) to the column and the evaporation and solute concentration values were set to zero.

Graphical presentation method and modelling results.

After the input data have been processed by MODEL2D, the necessary input files for CHAIN_2D are written by MODEL2D. CHAIN_2D then performs the simulation and the results are written to output files. The input and output files for most simulation runs are very large and some of these files (results) are discussed below.

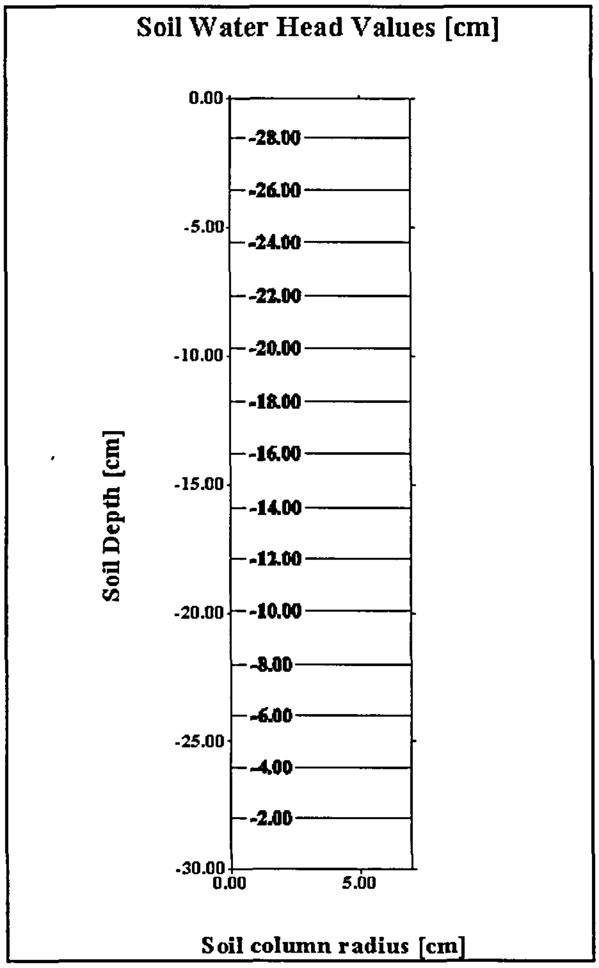


Figure A3.1 : MODEL1 result showing pressure head contours for a section of the soil in a laboratory column.

The SURFER package was used to summarise output from the MODEL2D program graphically. The soil water pressure head (H.DAT) after five hours is shown in Figure A3.1. This figure was prepared by importing the H.DAT file into the SURFER worksheet. With the exception of the output for the time interval of 300 minutes all data were deleted from the file. After saving the new file to disk, a SURFER grid file was generated and a contour plotted. The text labels were added and the resulting graphic exported as a WMF file.

The soil water content θ for the different printing times can be found in the file TH.DAT obtained from MODEL2D. The soil water solute concentration of 1 gram per cubic centimetre can be checked in the file C.OUT. In C.OUT, the soil water solute concentration is printed first, followed by the soil adsorbed solute concentration for the selected printing times. Since no solute was adsorbed, the column outlet concentration at 5 hours remained as specified at time zero. CHAIN_2D also generates a check file named CHECK.OUT. This file allows the user to ascertain if the input data was entered correctly while using MODEL2D. Data for the unsaturated hydraulic conductivity are also listed in CHECK.OUT.

In order to be able to calculate a mass balance of the water and solute, mass flow rates are required. The files A-LEVEL.OUT, BALANCE.OUT and CUM_Q.OUT provides this type of information. When maximum attenuation has been reached, the column outlet solute concentration will be the same as the inlet concentration. Further simulation results were printed in the files V_MEAN.OUT and SOLUTE1.OUT. These files are not listed, but the parameter definitions for files used in the mass balance, are listed in the CHAIN_2D manual.

Attenuation capacity.

The attenuation capacity of a soil can be calculated from a mass balance, obtained from CHAIN_2D results. Since an inert solute was used, no change from the liquid to the solid phase occurred, meaning that M_c equals zero. The value of M_{ss} can be calculated by multiplying the volume of the soil bulk region (V_s) with the bulk density. In the case of axisymmetrical flow, the AREA values obtained from the BALANCE.OUT file, are the volume of the bulk soil region. In the case of planar flow, this parameter is the area and not volume as mentioned above. Values needed to calculate AC_{ss} and AC_w for the five printing times, are presented in Table A3.1.

Table A3.1 : Attenuation capacity values at different printing times, calculated from CHAIN_2D mass balance results.

Time [min]	M_{ss} [g]	Mc_{Max} [g]	AC_{ss} [g/g]	Cw_{Max} [g/cm^3]	V_w [cm^3]	M_w [g]	AC_w [g/g]
0	6881.0	0.0	0.0	0.0	116.0	116.0	0.0
60	6881.0	0.0	0.0	1.0	2020.0	2020.0	1.0
120	6881.0	0.0	0.0	1.0	2020.0	2020.0	1.0
180	6881.0	0.0	0.0	1.0	1690.0	1690.0	1.0
240	6881.0	0.0	0.0	1.0	1670.0	1670.0	1.0
300	6881.0	0.0	0.0	1.0	1660.0	1660.0	1.0

APPENDIX 4

Land type maps

No soils map exists at a scale of larger scale than 1: 2 500 000 for South Africa as a whole. The land type maps can be used as a substitute. The land type maps have been designed to assist in assessing agricultural potential. During the years leading up to 1971 there was a growing awareness in the Dept. of Agriculture that a sound perspective of South Africa's agricultural potential was required. Essential to the attainment of this objective was a systematically compiled inventory of the natural factors that determine agricultural potential, namely; climate, terrain form and soil type. The aims of the survey became:

i) the delineation of areas, known as land types, at 1:250 000 scale such that each land type displays a marked degree of uniformity with regard to terrain form, soil pattern and climate,
ii) the definition of each land type in terms of terrain, soil and climate parameters, and
iii) an in-depth analysis of a number of soil profiles, termed modal profiles, selected to represent the range of soils encountered during the survey.

With this information it is possible to define and, with reasonable accuracy, estimate the areas of the main climate - soil - slope classes that occur in each demarcated area. Climate, terrain and soil data stored in terms of these classes, or derived from them, could be used as inputs to crop production and other models.

The land type maps were derived from inspecting existing maps and satellite imagery. The survey of the area covered by a 1:250 000 map was carried out in a stepwise fashion on each of its component 1:50 000 quarter degree sheets. With field mapping, areas called *terrain types*, each displaying a marked uniformity of terrain form, were delineated. Then the soils in each terrain type were identified and areas known as *pedosystems*, each with uniform terrain and soil pattern, were delineated. Representative or modal profiles were described and sampled for in-depth laboratory investigation. A separate map showing the *climate zones* was then drawn. This was superimposed upon the pedosystem map to arrive at a map of *land types*, each displaying marked uniformity of terrain, soil pattern and climate. On completion of these steps the land type boundaries were transferred from the 1:50 000 to the 1:250 000 maps. Finally, an inventory of each land type was compiled in terms of terrain, soil and climate parameters.

Terrain Types.

A terrain unit is any part of the land surface with homogeneous form and slope. Terrain can be thought of as being made up of all or some of the following kinds of terrain units: crest, scarp, midslope, footslope and valley bottom or flood plain. A terrain type in this context denotes an area of land over which there is a marked uniformity of surface form and which, at the same time, can be shown easily on a map at a scale of 1:250 000. Land shown on a map as belonging in a terrain type may cover only a single terrain unit (e.g. a flood plain), it may cover a single crest-valley bottom sequence (e.g. an escarpment) or it may cover a large number of crest to valley bottom sequences that repeat themselves three-dimensionally (e.g. a large area of rolling hills). Although the terrain type is not without genetic implication, morphology and not genesis is the basis for its delineation and description.

The terrain type boundaries were drawn in the office and then field-checked. The main criteria for delineation were the pattern and density of the drainage system, relief and the slope, profile and extent of each of the terrain units. The terrain inventory was made after the land type boundaries were finalised.

Pedosystems.

A pedosystem denotes land over which terrain form and soil pattern each displays a marked degree of uniformity. Soils do not occur randomly in a landscape, but follow a pattern determined by factors such as geology and topographic position, many of which in turn have either played a part in shaping the landscape or are inherent features of the landscape (e.g. a valley bottom). This inter-relationship between soils and land form is good reason for relating soils to the landscape positions in which they occur; the terrain type provides a suitable framework. In addition, terrain types are convenient compartments of land whereby the soils of a large country can be systematically surveyed, inventoried and presented. The soil composition of a terrain type was described by detailing which soil series of the Binomial System5 occur on each terrain unit (e.g. the midslope) and by giving an estimate of the area of each series on a given terrain unit.

Each terrain type was traversed systematically, normally by motor vehicle, paying attention to genetic principles such as topomorphism and the effects of geology, in an effort to identify as many as possible of the soils present. By augering, by using exposures such as road cuttings and occasional soil pits, the soils occupying the terrain units (crest to valley bottom) were identified and their positions marked on the 1:50 000 maps. Where necessary, soil samples, usually no more than one per profile, were taken for the purpose of series identification. Occasionally access to an area was impossible. In such cases an indication is given of what soils are thought likely to occur.

If the soil pattern (crest to valley bottom) was found to be roughly the same throughout, the terrain type boundary became a pedosystem boundary. Where the soil pattern changed from one part of the terrain type to another, boundaries were drawn within the terrain type to separate these different patterns (two or more) and hence pedosystems.

At this stage modal profile sites were identified, pits dug and the profiles described and sampled. Analytical facilities required that these profiles, chosen to represent the range of soils encountered during~ the survey, be limited in number.

Climate Zones.

The climate map required was one which would show the distribution of climate zones within each of which all agriculturally important climate parameters would display either a narrow range of variation or a marked regularity in pattern of variation. It soon became clear that a map of this sort at 1:250 000 scale could not be prepared within a reasonable period of time using climate measurements alone: meteorological stations are too widely scattered and in most cases record too few climate parameters.

The procedure used therefore placed great reliance on natural vegetation, soils, crop performance, altitude and topography as indicators of climate boundaries. Beginning at a point, for example in the middle of a plain, and moving in a given direction, the investigator, aided by his knowledge gained from. prior terrain form and soil surveys of the area, had to decide where to place a climate boundary. Having established a boundary, he would continue working outwards from the original starting point until he had delineated a climate zone that as far as he could determine, fulfilled the requirements set out above. Where all or several of the indicators (climate measurements, natural vegetation, altitude, topography, soils, crop performance) pointed to a climate boundary, for example along the edge of an escarpment, the task was easy and accurate, meaningful boundaries could be drawn. Over large plains where climate changes gradually, the task was more difficult and the positioning of boundaries was attended by a degree of uncertainty. In the latter instances as much reliance as possible was placed on the evidence of climate measurements, while soil and vegetation characteristics, and crop performance, helped considerably.

In placing the boundaries, the investigators were assisted to a greater or lesser extent in different parts of the country by agrometeorologists, ecologists, agricultural advisers, agronomy research scientists, pasture research scientists and foresters.

Some climate zones cover no more than a terrain unit (e.g. a plateau, a flood plain), some a single crest-valley bottom sequence, while many cover a large number of crest to valley bottom sequences that repeat themselves three-dimensionally (e.g. a large undulating plain). Certain zones, for example some plateaux, display a greater uniformity of climate than others, for example rolling hills or an escarpment. Large climate differences occur from top to bottom of an escarpment. In an area of rolling hills, climate differences occur from crest to valley bottom, N-slope to S-slope and so on. While the map does not demarcate these differences, it does provide a means of accurately referring to them and, if necessary, demarcating them on larger scale maps. For example, in a climate zone characterised by rolling hills, all the valley bottoms will have marked uniformity of climate, so also all the crests, likewise the N-slopes and so on. Points on a horizontal line along the slope of an escarpment climate zone will also display marked uniformity of climate. In this sense it is perhaps permissible to regard many of the climate zones as macro-climate zones within which meso-climate differences occur.

A number of agriculturally important climate parameters were chosen to define the climate of each zone. In a large number of zones data were not available for all the chosen parameters and in some cases no data at all were available. In the latter instance estimates of one or more components of climate are given. The chief source of data has been the data base of the Agrometeorology Subdivision of the Soil and Irrigation Research Institute (the present ISCW) which incorporates data from other organisations such as the Weather Bureau, Department of Transport, Pretoria. Improved definitions of the climate of these zones will be possible in future as the number of meteorological stations is increased. The present shortage of data does mean, however, that it is difficult to state the relationship between some zones and others in either qualitative or quantitative terms.

Land Type Map.

A land type denotes an area that can be shown at 1:250 000 scale and that displays a marked degree of uniformity with respect to terrain form, soil pattern and climate. One land type differs from another in terms of one or more of terrain form, soil pattern and climate. Different occurrences of the same land type may be separated from one another by other land types. The land type map was compiled by superimposing the climate map on the pedosystem map. The land type inventory was then compiled using data collected during the terrain, soil and climate survey phases.

A climate zone may cover a portion of a pedosystem, it may have the same boundary as a pedosystem or it may cover two or more pedosystems. In order to improve the usefulness of land type maps, solid black, broken red and solid red lines are used to show land type boundaries. Solid black indicates a pedosystem boundary; that is, the climate on either side is the same but terrain form and/or soil pattern are different on either side. Broken red indicates a climate boundary only; the pedosystem is the same on either side. Solid red is a climate and a pedosystem boundary; here the possibilities are: climate, terrain form and soil pattern are different on either side; climate and terrain form are different on either side; climate and soil pattern are different on either side. Frequently, therefore, the boundary of a single land type is shown as part solid black, part broken red and part solid red. These different lines make it possible to draw a climate zone map (by omitting solid black lines) or a pedosystem map (by omitting broken red lines) of an area.

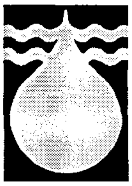
On each map a list is given of the modal profiles that are located on it- the positions of these profiles arc also shown. The co-ordinates, description and analytical data for each profile are contained in the memoir that deals with the land type inventories for the particular 1:250 000 map. On each map is a list of the numbers of the land types that occur on the map. In addition, the area (ha) of each separate occurrence of every land type is given.

Legend to the land type maps.

Broad soil patterns were chosen at the start of the survey for the purpose of constructing a common legend for the land type maps. These broad soil patterns and their associated colours have a restricted function, namely to

(i) improve the readability of the maps and
(ii) to give the reader an indication of the soils of the area.

It was also considered convenient to number the land types according to these broad soil patterns. Each land type was allocated a number by placing it in the broad soil pattern (defined in the paragraphs that follow) which accommodated it and then giving it the next available number in that soil pattern. Thus land type number Ea39 was given to the thirty ninth land type which qualified for inclusion in broad soil pattern (or map unit) Ea. Often, land belonging to the same land type occurs as islands separated by other land types. Each such separate occurrence is identified using the system Ea39a, Ea39b, etc. A single occurrence of a land type may occur on two map sheets; the same system of postscripts is used to indicate the two portions of the land type. Since these postscripts indicate different occurrences of the same land type, they are not part of the land type number. There follows a list of the soil patterns and a description of the soils to which each refers. Technical terms are explained in the book "Soil classification. A binomial system for South Africa".



Appendix 5

Soil type categories for the 3318 map sheet

#	Soil type categories
1	Soils with a humic topsoil (>2% organic carbon)
2	Freely drained structureless and red structured soils
3	Yellow-brown/red structuredless soils with a plinthic horizon
4	Imperfectly drained neocutanic soils, usually sandy
5	Shrink/swell clay soils, usually dark.
6	Dark clay soils.
7	Soils with a pedocutanic (blocky structured) horizon
8	Poorly drained soils, often shallow and often with a plinthic horizon
9	Podzols (soils with a horizon of iron/organic matter accumulation)
10	Poorly drained dark clay soils
11	Poorly drained shrink/swell clay soils, usually dark
12	Dark clay soils, often shallow, on hard/weathering rock
13	Lithosols (shallow soils on hard/weathering rock)
14	Duplex soils (soils with a sandy topsoil abruptly overlying a clayey, structured horizon), often poorly drained.
15	Wetlands soils
16	Non-soil land classes eg. rock, coarse deposits, pans, marshes and river/stream beds

APPENDIX 6

Code used for the calculated area weighted averages and ranges per land type

```
/********************************************************************************************************
/*                    W A V E . A M L
/********************************************************************************************************
/* Purpose:
/* Computes weighted averages for land types and prints them to a text file.
/********************************************************************************************************
/* Programmer: S. M. Jones
/* Date: 25 July 1997
/* Modified: 29 July 1997
/********************************************************************************************************

&args param

&severity &error &routine bailout

&s curr_work [show workspace]
&s curr_form &show &format
workspace /usr2/gis/wf00195/work

&if [exists uni_lt.txt -file] &then &s filedel [delete uni_lt.txt -file]
&if [exists %param%.txt -file] &then &s filedel [delete %param%.txt -file]

&s lt [listunique attenuation.inf -info landtype uni_lt.txt]
&s ltfile [open uni_lt.txt ltopen -read]
&s ltread [read %ltfile% ltstat]
&s %param%file [open %param%.txt %param%stat -write]
&s title 'landtype,%param% wghtd ave'
&s %param%write [write %%param%file% %title%]

/* Enter ae environment to work on atenuation.lut
display 0
arcedit
edit attenuation.inf info
&messages &on

/* Sort through records according to land type
&do &until [null %ltread%]
  &s sum = 0
  &s tot_per = 0
  sel landtype = [quote %ltread%]
  cursor open
```

```
 /* Loop through the records
 &do &while %:edit.AML$NEXT%
   &if [null %:edit.LANDCLASS%] &then &do
     &s temp_%param% = %:edit.%param%%
     &s temp_percent =  %:edit.percent%
     &s sum_temp = %temp_%param%% * %temp_percent%
     &s sum = %sum% + %sum_temp%
     &s tot_per = %temp_percent% + %tot_per%
     &end /* if landclass null
   cursor next
   &end /* do until aml$NEXT
 &format 3
 /* Calculate mean average
 &if %tot_per% ne 0 &then
   &s value [calc  %sum% / %tot_per%]
   &else &s value 0

 /* &type %value%
 /* Write to file
 &s %param%_rec [format '%1%,%2%' %ltread% %value%]
 &s %param%write [write %%param%file% %%param%_rec%]
 cursor close
 &s ltread [read %ltfile% ltstat]
 &end /* while ltstat = 0


&s fileclose [close %ltfile%]
&s fileclose [close %%param%file%]
&if [exists uni_lt.txt -file] &then &s filedel [delete uni_lt.txt -file]
save
quit /* fr%param%ae

&format 3
&messages &on

&return

/* Bailout routine
&routine bailout
&s &messages &on
&s fileclose [close -all]
```

```
quit /* frco3 ae
workspace %curr_work%
&format 3
&return; &return &error \Bailing out of AML...
```