ASSESSMENT OF THE POTENTIAL FOR THE BACTERIAL DEGRADATION OF TETRACHLOROETHENE AND TRICHLOROETHENE IN THE VADOSE ZONE OF TWO VEGETATED SLIMES DAMS

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ABSTRACT

The aim of this project is to assess the potential for the bacterial degradation of tetrachloroethene (PCE) and trichloroethene (TCE) in the vadose zone of two vegetated slimes dams, Dam 2 and Dam 3/4. The focus is on the reductive dechlorination of PCE and TCE; however, the degradation of dichloroethene (DCE) and vinyl chloride (VC), which are the carcinogenic daughter products of reductive dechlorination, via oxidation, is also investigated. The spatial and temporal variability of the reductive dechlorination and oxidation potentials within the dams are measured, and the influence of the vegetation on this degradation is determined.

The spatial variation in the reductive dechlorination potential in the vadose zone is ascertained by modifying a points system originally devised for the groundwater. The resultant points system includes the water content, redox potential, pH, temperature, the carbon source (including the measurement of soil organic matter and BTEX compounds) and the pollutants and daughter products, all of which are measured at various sites and depths on each dam. The spatial variation in the potential for oxidation in the vadose zone is determined based on the redox potential measurements. To establish the change in the potential for reductive dechlorination and oxidation between seasons, temporal measurements of redox potential are made using permanently installed redox electrodes. Since the dams have differing vegetation maturities, the effect of vegetation on the potential for bacterial degradation is ascertained by comparing the potentials for reductive dechlorination and oxidation between each dam.

The most important parameters in determining the potential for reductive dechlorination and oxidation in the vadose zone at the dams are the redox potential and the quantity of BTEX compounds. Reductive dechlorination is dominant within the measurement profile at Dam 3/4 due to a higher distribution of BTEX compounds and a lower redox potential, while at Dam 2 oxidation is dominant due to a lower distribution of BTEX compounds and a higher redox potential within the measurement profile. This is attributed to a higher vegetation maturity on Dam 2 compared to Dam 3/4. The temporal measurements of redox potential indicate that the seasonal fluctuation in degradation mechanisms is unlikely, except at isolated depths near the base of the measurement profile at Dam 2. Due to the role of vegetation in promoting

oxidation, in the past the conditions in Dam 2 would likely have resembled those currently at Dam 3/4, and Dam 2 is an indication of what Dam 3/4 is likely to be like in the future. Consequently, in the future Dam 3/4 is likely to promote oxidation over more of the profile which will lead to the degradation of DCE and VC. However, before oxidation commences, reductive dechlorination should be promoted at both dams until the PCE and TCE is degraded to acceptable limits, to prevent their continued presence.

PREFACE

The research described in this dissertation was carried out in the School of Bioresources Engineering and Environmental Hydrology, University of KwaZulu-Natal, Pietermaritzburg, under the supervision of Professor Simon Lorentz.

I hereby certify that the research reported in this dissertation represents original work by the author and has not otherwise been submitted in any form for any degree or diploma to any University. Where use has been made of the work of others it is duly acknowledged in the text.

Signed _____
Andrew Robert Gemmell

Date _____

Signed _____
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Date _____

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LIST OF ACRONYMS AND ABBREVIATIONS

µg/kg	Micrograms per kilogram
BEEH	Bioresources Engineering and Environmental Hydrology
BTEX	Benzene, Toluene, Ethylbenzene and Xylene isomers (o-Xylene, m-Xylene and p-Xylene)
DCE	Dichloroethene, which has three isomers: 1,1-Dichloroethene, cis-1,2-Dichloroethene and trans-1,2-Dichloroethene
DNAPL	Dense Non-Aqueous Phase Liquid
Eh	Redox potential relative to the standard hydrogen reference electrode
g/cm^3	Gram per cubic centimetre
g/g	Gram per gram
GC-MS	Gas Chromatography-Mass Spectrometry
KCl	Potassium Chloride
LNAPL	Light Non-Aqueous Phase Liquid
mg/l	Milligram per litre
mV	Millivolt
NAPL	Non-Aqueous Phase Liquid (includes LNAPLS and DNAPLS)
nM	Nanomolar
PCE	Tetrachloroethene (previously called perchloroethylene)
ppm	Parts per million
Redox	Reduction/oxidation
SOM	Soil Organic Matter
TCE	Trichloroethene
TOC	Total Organic Carbon
VC	Vinyl Chloride
VOC	Volatile Organic Compound (including PCE, TCE, DCE, VC and BTEX compounds)
VWC	Volumetric Water Content

GLOSSARY OF TERMS

Anthropogenic	Man-made
Carcinogenic	A chemical or substance that produces or incites cancer
Chlorinated ethene	Includes PCE, TCE, DCE and VC
Chlorinated solvent	Any liquid organic compound that contains chlorine atoms. Includes PCE, TCE, DCE, trichloroethane and chlorobenzenes
Daughter product	A compound that results directly from the biodegradation of another
Diffusion	The process whereby molecules move from a region of higher concentration to a region of lower concentration as a result of Brownian motion
Dissolved-phase	NAPL that has dissolved
Electron Acceptor	A compound capable of accepting electrons during redox reactions. Includes oxygen, nitrate, iron (III), manganese (IV), sulphate, carbon dioxide, or in some cases the chlorinated ethenes. Microorganisms obtain energy by transferring electrons from electron donors to an electron acceptor
Electron Donor	A compound capable of supplying electrons during redox reactions. Includes fuel hydrocarbons (e.g. BTEX compounds) and native organic carbon. Microorganisms obtain energy by transferring electrons from electron donors to an electron acceptor
Free-phase	NAPL which is sufficiently saturated to flow as a body in the subsurface
Mineralization	The breakdown of organic compounds into inorganic materials (such as carbon dioxide, water and chloride)
Parent Compound	Compound undergoing biodegradation
Vadose Zone	The geologic media between land surface and the regional water table

1. INTRODUCTION

The study area is a waste disposal site situated at the Umbogintwini Industrial Complex near Durban, South Africa. The waste site includes five interconnected effluent precipitation and settling dams which cover an area of 20 hectares and contain more than one million tons of waste material (Duthe, 2004), and is currently being remediated, using an evapotranspiration cover and hydraulic control, to limit contaminant movement out of the dams and to limit contaminated groundwater migration (Duthe, 2004). The focus of the project is on two of these dams, Dam 2 and Dam 3/4. The primary contaminants of concern within these dams are tetrachloroethene (which was previously called perchloroethylene, and thus has the acronym PCE) and trichloroethene (TCE) and their degradation daughter products, dichloroethene (DCE) and vinyl chloride (VC) (Duthe, 2004). These compounds, particularly VC, can cause liver damage and cancer and as a result pose an environmental threat. Sites contaminated with PCE and TCE are difficult to remediate using traditional methods due to the physico-chemical properties of the compounds and as a result research into innovative methods to treat sites contaminated with these types of compounds has become a priority in the remediation field (Chappell, 1997). One of these methods is the use of natural attenuation. Although natural attenuation is not included as an element within the current remediation strategy at the site, it is regarded as a potential mitigatory measure effective in source reduction at the site (Duthe, 2004). Bacterial degradation plays an important role in natural attenuation (WSRC, 2004), and as a result bacterial degradation is the focus of this project.

The aim of this project is to assess the potential for the bacterial degradation of PCE and TCE in the contaminated vadose zone of the two vegetated slimes dams. The vadose zone is the focus of this project since this area is the source of the majority of the contamination (Duthe, 2004). The most efficient bacterial degradation of PCE and TCE occurs when the reductive dechlorination of PCE and TCE is followed by the oxidation of the resultant daughter products (DCE and VC), since this results in the complete degradation of PCE and TCE to harmless by-products (Wiedemeier *et al.*, 1998). Since the initial step in this process is reductive dechlorination and this mechanism requires very specific conditions to occur, the focus of the project will be to assess the potential for the reductive dechlorination of PCE and TCE. However, the potential for the oxidation within the dams will also be assessed since this mechanism degrades DCE and VC, and is particularly important since this mechanism

degrades VC which is more carcinogenic than PCE, TCE and DCE (USEPA, 2004a; USEPA, 2006a; USEPA, 2006b). Both dams are vegetated so as to act as evapotranspiration covers (Duthe, 2004), and because the potential for degradation via reductive dechlorination and oxidation can be affected by vegetation (Collins *et al.*, 2002; Nengovhela *et al.*, 2006), and each of the dams are vegetated at different densities (Lubke, 2006; Oliver, 2006), the affect that vegetation has on the potential for reductive dechlorination and oxidation at each dam will be assessed by comparing the potential for degradation at each dam.

The potential for reductive dechlorination will be determined by modifying a points system which was initially created by Wiedemeier, *et al.* (1998) to assess the potential for the reductive dechlorination of chlorinated solvents in groundwater. The method relies on the fact that reductive dechlorination causes predictable changes in groundwater chemistry, and points are allocated depending on the values of each parameter that affects the potential for reductive dechlorination; the higher the points total, the better the chances for the reductive dechlorination. Since the points system was developed for chlorinated-solvent contaminated groundwater, and the focus of this project is on the vadose zone, the points system will be modified for use in the vadose zone. In addition, the points system will be modified to focus more specifically on PCE and TCE contamination. The trend of each parameter included in the vadose zone points system will be measured and described down the profile at various sites on Dam 2 and Dam 3/4 to establish the spatial variability of the reductive dechlorination potential. Since the vadose zone points system includes the measurement of redox potential, which can be used to determine the potential for the oxidation of DCE and VC (Patrick *et al.*, 1996; AFCEE, 2004; WSRC, 2004; Pierzynski *et al.*, 2005), the spatial variation of the oxidation potential will also be ascertained. In addition to measuring the parameters that spatially affect reductive dechlorination and oxidation, temporal measurements of redox potential will be made which can be used to establish the seasonal variation in the redox potential which plays an important role in determining the potential for reductive dechlorination and oxidation throughout the year. Since the dams have differing vegetation densities, the spatial and temporal variation measurements will then be used to compare the potential for reductive dechlorination and oxidation between Dam 2 and Dam 3/4, which will give an indication of the effect that vegetation has on the potential for bacterial degradation.

In Chapter 2 the site will be described in more detail, including a description of the contaminants in, and the vegetation on, Dam 2 and Dam 3/4. In addition, the remediation

strategy currently being used at the site will be described. PCE and TCE will then be described in Chapter 3; including how these contaminants and their daughter products can be removed from the site through the mechanisms of reductive dechlorination and oxidation, under the influence of vegetation. The method of modifying the points system devised by Wiedemeier *et al.* (1998) to determine the potential for the reductive dechlorination of PCE and TCE in the vadose zone at the site will then be described in Chapter 4, including a description of each of the parameters used in the vadose zone points system. The use of the redox potential, which is included in the vadose zone points system, to assess the potential for the oxidation of DCE and VC will also be described. In addition, a description of the temporal measurement of redox potential, and its use in determining the seasonal variation in the reductive dechlorination and oxidation potentials, will be described. The results of the spatial and temporal measurements of each of the parameters used to determine the potential for reductive dechlorination and oxidation within Dam 2 and Dam 3/4 will then be summarised and described in Chapter 5. In Chapter 6 the potential for reductive dechlorination in each of the dams will be established using the vadose zone points system which assimilates the spatial measurements of each of the parameters, and the potential for oxidation in each of the dams will be established based in on the spatial measurements of the redox potential. In addition, the seasonal variability of the reductive dechlorination and oxidation potentials, based on the temporal measurements of redox potential, will be described. The results will then be discussed, including a comparison of the dams to establish the effect that vegetation has on the potential for reductive dechlorination and oxidation. Thereafter, general conclusions and recommendations will be described in Chapter 7 and Chapter 8.

2. DESCRIPTION OF STUDY SITE

The waste site is situated at the Umbogintwini Industrial Complex approximately 4.5 km south-west of Durban International Airport (Lorentz, 2001). It is a chemical disposal site that comprises a drum disposal area and a slimes dam area. The slimes dams were in operation from the late 1950s and were decommissioned between 1994 and 1998 (Duthe, 2004). The slimes dam area is made up of a five interconnected effluent precipitation and settling dams, which cover 20 hectares and contain more than one million tons of waste material (Duthe, 2004). The dams were filled with lime slurry containing dissolved calcium chloride and saturated with dissolved and free phase organic reactants (Duthe, 2004), and now consist of up to 20 m of waste. The main chemicals of concern in the dams are PCE, TCE, DCE and VC, and the main inorganic chemicals of concern are mercury and arsenic (Duthe, 2004). Dam 1 was closed in July 1998 and Dam 2 was closed in 1994. Dam 3/4 is made up of two dams, both of which were closed at the end of 1998, but are now considered as a single dam. Dam 6 was also closed in 1998 (Duthe, 2004; Lubke, 2006). Since closing, the dams have dried, both naturally and through engineered actions, to a point which has allowed the growth of vegetation. Plants have been introduced through natural colonisation and through the planting of indigenous vegetation. Any alien vegetation is actively removed from the dams (Oliver, 2006). The focus for this project was on Dam 2 and Dam 3/4. Dam 2 was investigated in more detail since this dam has the highest density of vegetation, which affects the potential for bacterial degradation (Schnoor, 1997; USEPA, 2000; ITRC, 2001; McCutcheon and Schnoor, 2003; USEPA, 2003; Nengovhela *et al.*, 2006), and as a result had five measurement sites. In addition, Dam 3/4 was sampled at two sites. Dam 3/4 was included since this dam has been more recently vegetated than Dam 2 and hence has a lower density of vegetation, and as a result the effects of vegetation on the potential for bacterial degradation can be determined by comparing the results measured at Dam 2 to those measured at Dam 3/4.

Dam 2 includes co-disposed chlorinated hydrocarbons, heavy metals and phosphates. The dam was closed in 1994, and was quickly colonised with a mixture of indigenous and alien invasive vegetation, most likely as a result of the high levels of phosphates in the dam (Oliver, 2006), and now has a dense cover of trees, and a lower density of shrubs, herbaceous plants and grasses (Lubke, 2006). The vegetation can be separated into a *Cynodon nlemfuensis*

(African Stargrass) grass community, trees scattered in regular pattern with largely *Cynodon nlemfuensis* under-storey, and high density forest trees with herbaceous under-storey. Trees range from 2 m to 16 m in height with the dominant tree species being *Tremma orientalis* (Pigeon Wood), *Milletia grandis* (Ironwood), *Ficus thonningi* (Common Wild Fig) *and Calodendrum capense* (Cape Chestnut). A few tree species reach heights of 25 m, such as *Ficus thonningii* (Lubke, 2006). A vegetation map of Dam 2, including the five measurement sites (Sites 21, 22, 23, 24 and 25) used in this study, is shown in Figure 2.1, and a photograph of the dam is included in Figure 2.2.

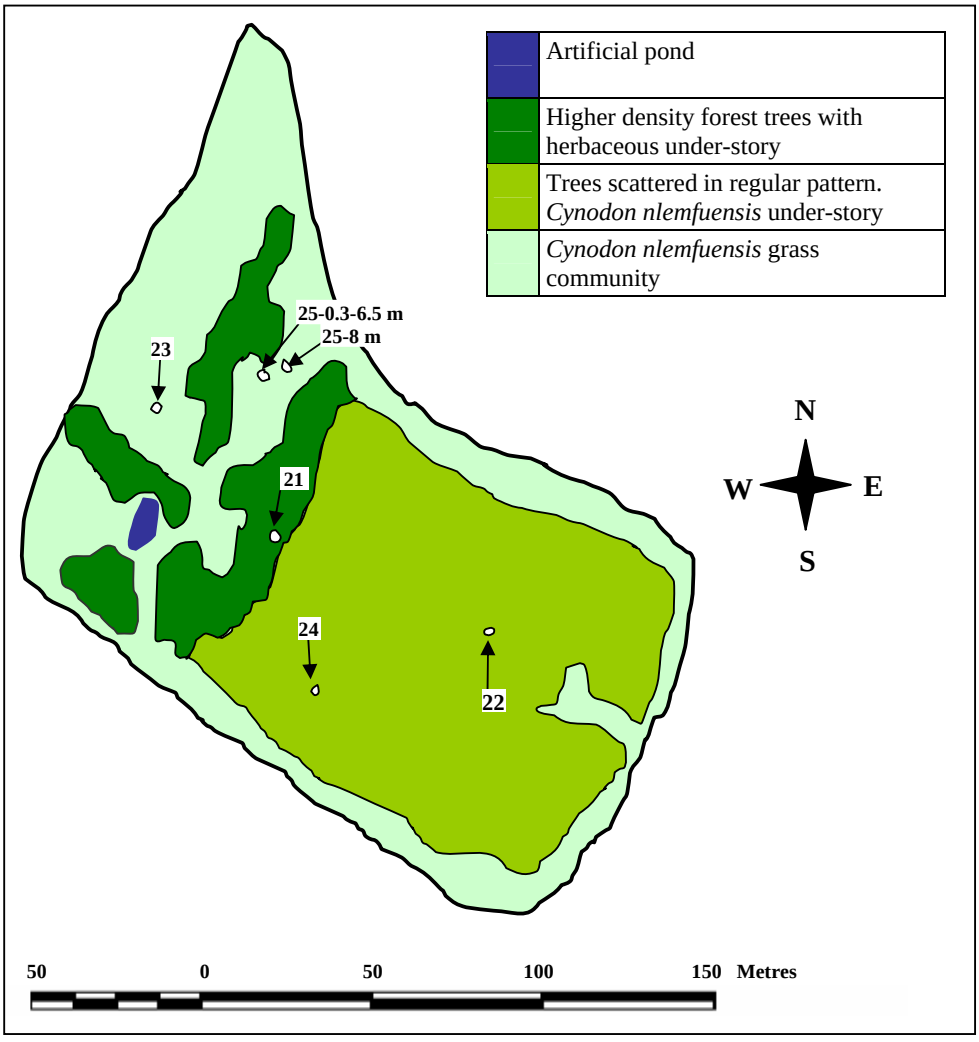

Figure 2.1 Vegetation map of Dam 2, including the five measurement sites (after Lubke, 2006).

Figure 2.2 Photograph of Dam 2 taken near Site 25 in 2006.

Dam 3/4 is a combination of two dams, Dam 3 (the eastern portion) and Dam 4 (the western portion), which are separated by a low berm dissecting the total dam area (Lubke, 2006). Since Dam 3/4 was initially divided, each dam received slightly different waste applications (Oliver, 2006); however, both contain primarily co-disposed industrial chemical waste and chlorinated hydrocarbons (Oliver, 2006). Dam 3/4 was closed in December 1998 and was actively vegetated, starting in late 2000, using indigenous vegetation species that had naturally colonised Dam 2 (Oliver, 2006). The dam is dominated by grassland interspersed with woody tree species and herbaceous plants (Lubke, 2006). The vegetation on Dam 3/4 can be separated into a *Cynodon nlemfuensis* (African Stargrass) dominated grassland community, a higher density of trees with either *Cynodon nlemfuensis* or *Imperata cylindrica* (Cogon Grass) dominated under-storey, an *Imperata cylindrica* dominated grassland community with some areas having a higher density of *Bidens pilosa* (Cobblers Peg), trees scattered in a regular pattern with largely *Imperata cylindrica* dominated grass community, and a small *Phragmites australis* (Common Reed) patch. Dominant tree species include *Ficus thoningii* (Common Wild Fig), *Tremma orientalis* (Pigeon Wood) and *Ficus sur* (Cape Fig). A number of alien woody species are scattered along the western boundary, namely gum trees *(Eucalyptus grandis sp)* and *Cassuarina equisetifolia* (Horsetail Tree). The trees are largely about 3 m in height, but some gum trees reach up to 15 m (Lubke, 2006). A vegetation map of Dam 3/4 is shown in Figure 2.3, and includes the two measurement sites (Site 341 and 342) used in this study. These study sites represent each of the dams that now make up Dam 3/4;

Site 341 represents Dam 3 and Site 342 represents Dam 4. A photograph taken near each of the measurement sites is included in Figures 2.4 and 2.5.

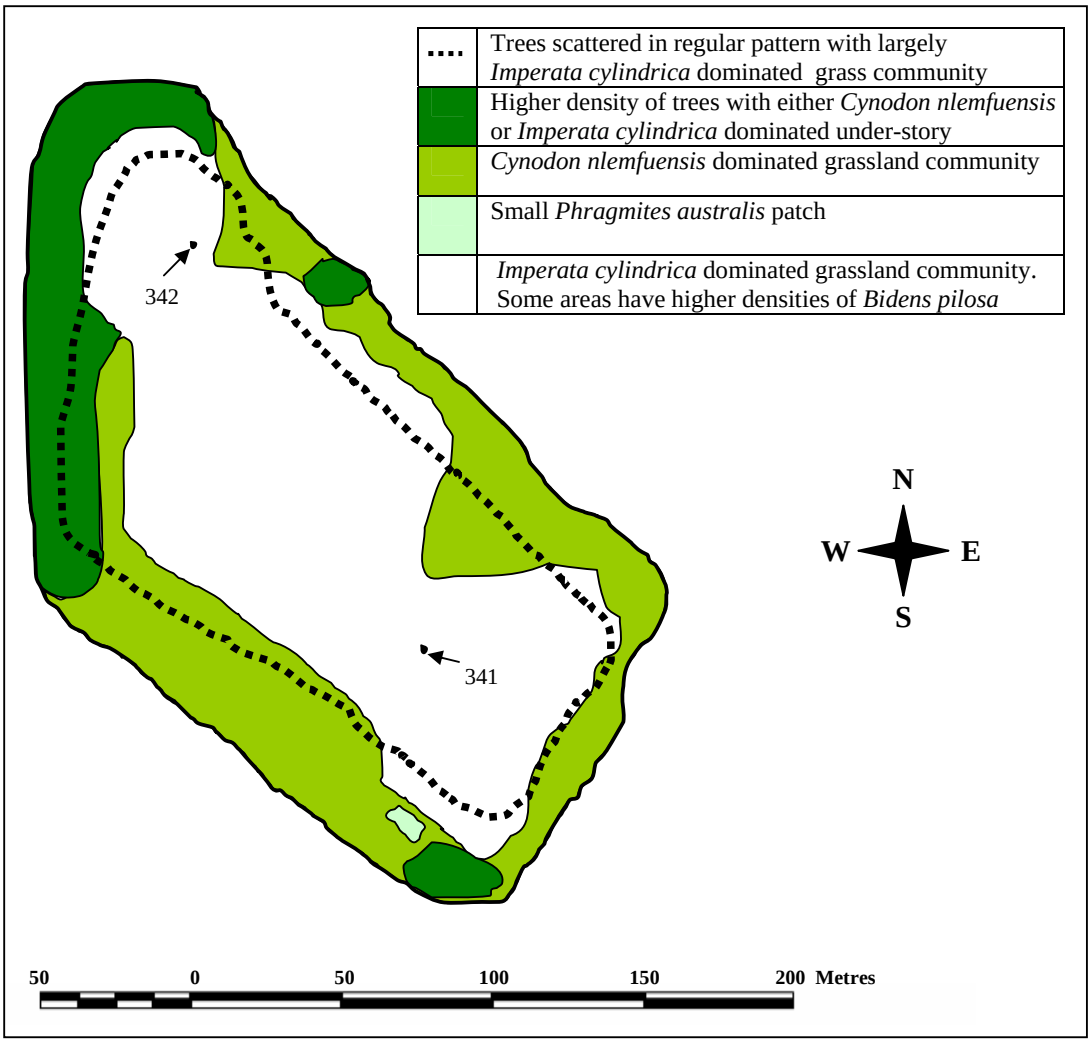

Figure 2.3 Vegetation map of Dam 3/4, including the two measurement sites (after Lubke, 2006).

Figure 2.4 Photograph of Dam 3/4 taken near Site 341 in 2006.

Figure 2.5 Photograph of Dam 3/4 taken near Site 342 in 2006.

The construction of the dams, although acceptable at the time, is not acceptable according to current Department of Water Affairs and Forestry (DWAF) requirements for the disposal of hazardous waste. As a result, the site is classified as a hazardous waste site (H:H), and needs to be closed. The DWAF standard for closure of H:H areas requires capping with an impervious plastic sheet; however, the option of using an evapotranspiration cap to control surface water percolation at the slimes dam area is considered a sustainable and viable option, and DWAF agreed to consider this alternative provided that it can be demonstrated that the vegetation will sufficiently reduce the leaching of harmful chemicals (Lorentz, 2003). For the evapotranspiration cap at the slimes dams to be considered a viable option, the evapotranspiration from the vegetation must limit deep percolation to within the limits required of a physical cap as stipulated by the Resource Conservation and Recovery Act (RCRA) in the United States of America (Pivetz, 2001). To determine the ability of the site to function within this limit, the seepage fluxes were simulated at 8 m for a period of over three years at Dam 2 and Dam 3/4 by Lorentz *et al.* (2006). The study concluded that the evapotranspiration cover was capable of reversing hydraulic gradients within the profile and transpiring water from below the root zone. At Dam 2 this led to an accumulated seepage of 12 mm between February 2002 and December 2005 (approximately 3 mm/year) which is comparable to the minimum requirement seepage rates for RCRA engineered covers. At Dam 3/4 the accumulated seepage was 80 mm between August 2002 and December 2005 (approximately 23 mm/year), which exceeds the RCRA requirement for engineered covers. The seepage rate is higher at Dam 3/4 compared to Dam 2 since there is currently less vegetation on this dam to intercept and transpire water; however, the seepage rate is expected to decrease as the vegetation matures on this dam. Due to the favourable performance of the evapotranspiration covers, their use at the site is being pursued at the site. Apart from the evapotranspiration cover, other remedial actions have been in progress. Abstraction wells were installed to contain the migration of contaminated groundwater, dewatering boreholes on or adjacent to the dams were installed to reduce the hydraulic head in the dams to reduce contaminant movement out of the dams, and stormwater control was improved to divert clean stormwater away from the dams (Duthe, 2004). In addition, natural attenuation has been shown to be occurring at the site and, although natural attenuation was not included as an element within the remediation strategy, it is regarded as a potential mitigatory measure effective in source reduction (Duthe, 2004). Natural attenuation includes dispersion, advection, degradation, sorption, volatilisation and plant uptake (WSRC, 2004). The

biological processes resulting in the reduction in contaminant concentrations are plant uptake (and subsequent degradation and volatilisation) and degradation through bacterial activity. The focus of this project is on the utilisation of bacterial degradation to reduce the contaminant concentrations at the site. Due to the difficulty in measuring plant uptake, and the subsequent plant degradation and volatilisation, these processes are not quantified in this investigation; however, these processes will be referred to as possible reasons for contaminant removal.

The vadose zone is defined as "the geologic media between land surface and the regional water table" (Stephens, 1996). Hence, the vadose zone consists of the subsurface region above the water table, including the capillary fringe (Looney and Falta, 2000). Using the rest water level measured in each of the two piezometers placed in the slimes material on each of Dam 2 and Dam 3/4, the depth of the vadose zone was calculated as being between 17.25 m and 8.59 m below ground level in Dam 2, and between 10.39 m and 14.8 m below ground level in Dam 3/4 (Duthe, 2004). Since Dam 2 and Dam 3/4 are both approximately 18 m to 18.5 m deep (Duthe, 2004), the majority of the slimes dams can be classified as the vadose zone. In addition, considering the measurements taken in 2003 by Duthe (2004) at Dam 2 and Dam 3/4 (listed and graphically represented in Appendix C), which included measurement depths throughout the slimes dams, it is evident that the PCE and TCE concentrations at Dam 2 peak between 13 m and 15.2 m, while at Dam 3/4 they peak between 2 m and 8.5 m; the DCE and VC concentrations peak between 6 m and 13.5 m at Dam 2 and between 2 m and 6.5 m at Dam 3/4. Since these depths lie in the vadose zone, this zone is the source of the highest concentrations of the primary contaminants of concern within the slimes dams. It is for these reasons that degradation in the vadose zone of the slimes dams is the focus of this project.

In the following chapter, after describing PCE and TCE and their behaviour which leads to difficulty in remediating sites contaminated by these compounds using traditional methods, the bacterial degradation of PCE and TCE, and their daughter products (DCE and VC), in the vadose zone will be described. Because the dams are vegetated, which affects the potential for bacterial degradation, the affect of vegetation will also be described.

3. BACTERIAL DEGRADATION OF PCE AND TCE IN THE VADOSE ZONE

The complete bacterial degradation of PCE and TCE and their daughter products occurs through three different mechanisms: reductive dechlorination, oxidation, and cometabolism (Wiedemeier *et al.*, 1998). At a given site one or all of these mechanisms may be operating (AFCEE, 2002). These mechanisms are aided in various ways in the vadose zone through the actions of plants and their roots systems (Schnoor, 1997; USEPA, 2000; ITRC, 2001; McCutcheon and Schnoor, 2003; USEPA, 2003; Nengovhela *et al.*, 2006). These methods can also be aided by the use of engineered actions, such as additions to the subsurface to create zones for enhanced degradation. However, since these engineered actions are not currently being pursued at the study site, these will not be described in any detail in this chapter; nevertheless, some of these will be described in the recommendations outlined in Chapter 8.

A description of PCE and TCE, including a description of their behaviour that leads to difficulty in remediating sites contaminated by these compounds using traditional methods, will be included in the following sections. In addition, the bacterial degradation mechanisms required for the complete degradation of PCE and TCE to harmless by-products, under the assistance of plants, will be described.

3.1 Description of PCE and TCE

In the industrialised nations, PCE and TCE are the most frequently found chlorinated contaminants in groundwater (Kastner, 1991). PCE is a colourless organic liquid with a mild, chloroform-like odour. Major releases of PCE are from the dry cleaning industry where PCE is used in dry-cleaning products, and from industrial metal cleaning or finishing where PCE is used as a solvent (USEPA, 2004a). TCE is a colourless or blue liquid and, like PCE, has a chloroform-like odour. The greatest use of TCE is to remove grease from fabricated metal parts and some textiles (USEPA, 2004b). The most important danger of PCE and TCE as environmental contaminants is that both pose a potential threat to humans, and drinking contaminated water in excess of the maximum concentration level (set at five parts per billion) over a lifetime can cause liver problems (USEPA, 2004a) and can increase the risk of cancer (Chappell, 1997; ATSDR, 2003).

An examination of the physico-chemical properties of PCE and TCE reveals the behaviour of these chemicals. These properties are summarized in Table 3.1.

Table 3.1 Physico-chemical properties of PCE and TCE (after USACE, 2002)

Physico-chemical Property	**PCE**	**TCE**
Liquid density (g/cm^3)	1.625	1.46
Water solubility (mg/l)	150	1100
Henry's Law constant ($atm\text{-}m^3/mol$)	0.023	0.0103
Log octanol-water coefficient (Kow)	3.14	2.42

Referring to Table 3.1, the densities of PCE and TCE are greater than water, and hence a release of these contaminants will move downward through the subsurface until a low permeability feature impedes its progress, which results in the formation of a pool of dense non-aqueous phase liquid (DNAPL) together with a trail of contamination within the downward path (Russell *et al.*, 1992). Because the Log octanol-water partition coefficient (defined as the amount of sorption possible on a unit carbon basis) is relatively low for PCE and TCE, little retardation by soil or aquifer organic materials occurs (Russell *et al.*, 1992); thus, once dissolved, PCE and TCE are easily transported through the subsurface. In addition, because PCE and TCE are relatively insoluble in water, both act as a persistent source of contamination that can take many years and large amounts of money and energy to treat using traditional remedial methods (Chappell, 1997). The Henry's Law constant, which describes the relative tendency of a compound to volatilise from liquid to air, for PCE and TCE is high enough to allow for efficient volatilisation of these compounds into the atmosphere (Russell *et al.*, 1992). Lastly, most DNAPLs (including PCE and TCE) are non-wetting fluids with respect to soils or geologic material (Lorentz, 2004) and, as a result, PCE and TCE in the subsurface are often present as non-wetting globules which are unresponsive to the driving forces of water flow (Lorentz, 2004).

Due to the behaviour of PCE and TCE, these two chemicals are particularly difficult to treat using traditional remediation methods such as "pump and treat". Consequently, research into innovative methods to treat sites contaminated with these types of compounds has become a priority in the remediation field (Chappell, 1997). Included in these innovative methods is the use of natural attenuation, during which bacterial degradation plays an important role (WSRC, 2004). Since PCE and TCE are so similar, both in chemical structure (USEPA, 1998) and in

chemical behaviour (Russell *et al.*, 1992), the mechanisms of bacterial degradation are the same for PCE and TCE. Bacterial degradation overcomes the limitations of traditional remediation methods by being relatively low cost (USEPA, 1995; Wiedemeier *et al.*, 1996); *in situ* (ESTCP, 2002b); low impact (USEPA, 1995; Wiedemeier *et al*., 1996; ESTCP, 2002b); and because degradation lowers the concentration in the dissolved phase, the concentration gradient between the non-aqueous phase and dissolved phase is increased, thereby promoting increased dissolution and hence increased degradation of the DNAPL contamination (ESTCP, 2002b). The benefits of bacterial degradation during the remediation of sites contaminated with PCE and TCE is the reason why bacterial degradation was focused on in this project. However, a concern during the bacterial degradation of PCE and TCE is that DCE and VC often accumulate as daughter products of this degradation (ESTCP, 2002b), and these compounds, like PCE and TCE, are carcinogenic and can cause liver damage. Most importantly, VC is regarded as being a more potent human carcinogen than PCE, TCE and DCE (USEPA, 2004a; USEPA, 2006a; USEPA, 2006b), with the United States Environmental Protection Agency (USEPA) setting the maximum concentration level at 2 parts per billion and estimating that drinking 1 ppm of vinyl chloride over a lifetime will cause 9 570 cases of cancer in a population of 100 000 people (Chappell, 1997). It is for this reason that when a site contaminated with PCE or TCE is remediated, it must be ensured that degradation does not cease at DCE and VC, but continues to a point where only harmless by-products of degradation remain. The mechanisms of PCE and TCE microbial degradation will be described in the following section, including the degradation DCE and VC, which ensures the complete mineralization of PCE and TCE.

3.2 Mechanisms Involved in the Bacterial Degradation of PCE and TCE and their Daughter Products

Microorganisms obtain energy by transferring electrons from an electron donor to an electron acceptor. Chlorinated ethenes (which include PCE, TCE, DCE and VC) can be degraded during these processes; during the mechanism of microbial reductive dechlorination they are used as electron acceptors, and during the mechanism of microbial oxidation they are used as electron donors. In addition, chlorinated ethenes can be degraded via cometabolism. Cometabolism differs from the reductive dechlorination and oxidation since during this mechanism the degradation is catalysed by an enzyme or cofactor produced during the microbial metabolism of another compound (Wiedemeier *et al.*, 1998), and hence the

degradation is fortuitous and there is no benefit to the microorganism. Cometabolism is not considered to be a significant mechanism for the bacterial degradation of chlorinated ethenes because it is slow (Gossett and Zinder, 1996; cited in Wiedemeier *et al.*, 1998), and the conditions suitable for cometabolism are rarely observed in non-engineered circumstances, (WSRC, 2004) such as the study site; consequently, only reductive dechlorination and oxidation will be described as options for the bacterial degradation of PCE and TCE and their daughter products at the site.

3.2.1 Reductive dechlorination

During reductive dechlorination highly chlorinated ethenes, such as PCE and TCE, are degraded through their use as electron acceptors (Wiedemeier *et al*., 1996). The chlorinated ethenes are utilised by the bacteria much in the same way as oxygen is used in aerobic respiration. During this mechanism, as represented in Figure 3.1, a chlorine atom is removed from the chlorinated ethene and is replaced with a hydrogen atom. As a result hydrogen is oxidised, and the chlorinated ethene is reduced (ESTCP, 2002b). During this mechanism, PCE can be reduced to TCE, TCE to DCE (which has three isomers, 1,1-DCE, cis-1,2-DCE and trans-1,2-DCE), DCE to VC, and VC to ethene (Kastner, 1991; USEPA, 1998; Sorenson *et al.*, 1999; Godsey *et al.*, 2003). However, because there is a decreasing reductive potential with decreasing number of chlorine substituents (Vogel *et al*. 1987; cited in WSRC, 2004; Bouwer 1994; McCarty and Semprini 1994; Vogel 1994), the rate of reductive dechlorination decreases as the degree of chlorination decreases, and as a result PCE is the most susceptible to reductive dechlorination while VC is least susceptible (Vogel and McCarty, 1985). Hence, the dechlorination of PCE and TCE to DCE can occur under mildly reducing conditions, while the transformation of DCE to VC, or the transformation from VC to ethene requires more strongly reducing conditions (Vogel *et al*., 1987; cited in WSRC, 2004). It is for this reason that DCE and VC are often not degraded and accumulate in the contaminated zone (WSRC, 2004). The specific redox conditions required for the reductive dechlorination of PCE and TCE will be described in more detail in Chapter 4.

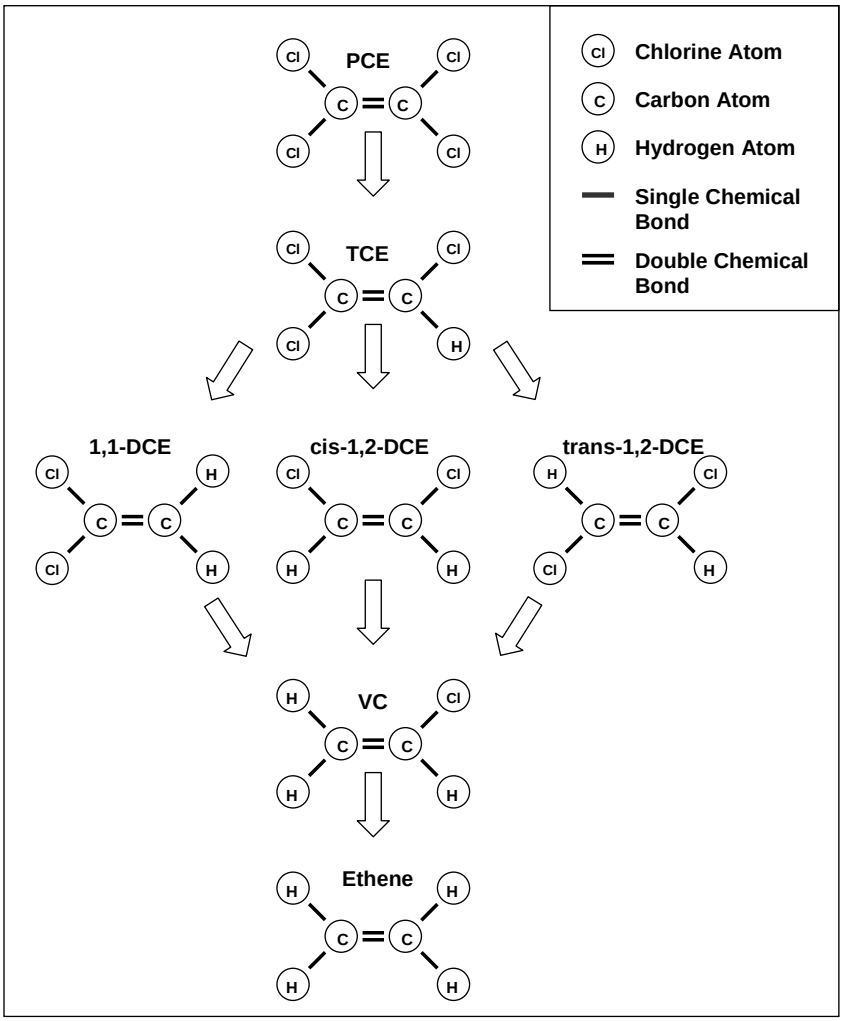

Figure 3.1 The reductive dechlorination process (after Wiedemeier, 1998).

3.2.2 Oxidation

The decreasing potential for reductive dechlorination with decreasing number of chlorine substituents, as discussed in the previous section, often results in the accumulation of DCE or VC (ESTCP, 2002b). However, DCE and VC can be degraded if the mechanism of oxidation follows reductive dechlorination. This is because, converse to reductive dechlorination, the tendency of chlorinated ethenes to undergo oxidation increases with a decreasing number of chlorine substituents (Vogel *et al.*, 1987; cited in WSRC, 2004). As a result, under aerobic and moderately anaerobic conditions, DCE and VC can be oxidised into harmless by-products (Wiedemeier *et al.*, 1998; WSRC, 2004) such as carbon dioxide, water and chloride (Dinicola *et al.*, 2002). The redox conditions required for the oxidation of DCE and VC will be described in more detail in Chapter 4.

3.3 Affect of Vegetation on Bacterial Degradation

In the vadose zone, plants play a unique role in bacterial degradation by enhancing the subsurface environment by providing nutrients and exudates to the bacteria, and by creating an ecology in soils that is suitable for degradation. These will be described in the following paragraphs. These alternations of the soil environment by plants aids in the degradation of contamination in and around the root zone. This degradation, aided by plant roots, is called rhizodegradation.

Plants may release exudates, such as proteins and enzymes, to the soil environment that increases rates of bacterial degradation. They can be produced and exuded by plants, or by soil organisms associated with the plant roots such as bacteria, yeast, and fungi. Organic contaminants, including chlorinated ethenes, can be directly metabolized by these proteins and enzymes. This metabolism may then result in the production of compounds that act as a source of energy for the plants and soil organisms (Donnelly and Fletcher, 1994; cited in ITRC, 2001). Apart from proteins and enzymes, plants can also add organic carbon to the soil through the decay of plant biomass. The organic carbon provides energy for the soil organisms thereby enhancing their activities (ITRC, 2001), and helps to retard organic chemical transport (Schnoor, 1997). In the vadose zone the organic carbon is often expressed as soil organic matter (SOM) (Plank, 2001).

The plants also create an ecology in soils that is suitable for bacterial degradation. This can be achieved through various means. One of these is the moderation of soil moisture. In sites that are waterlogged, such as the study site, the plants can act to dry out the profile through water uptake during evapotranspiration (USEPA, 2000). The plants also affect the redox potential. This can occur through the release of oxygen from root cells (Vorenhout *et al.*, 2004) and due to the formation of preferential pathways for water and gasses (Pivetz, 2001), which increases aeration (Nengovhela *et al.*, 2006). However, plants may also produce anaerobic conditions just below the root zone, since the vegetation can introduce relatively high concentrations of organic carbon, which serves as the primary substrate for microorganism growth, and the increased microbial activity can result in the depletion of dissolved oxygen, and the creation of anaerobic conditions (USEPA, 2003). The plants also affect the ecology by increasing the surface area where active microbial degradation can be stimulated (USEPA, 2000), buffering

the pH, biosorbing or chelating metals, and by ensuring that enzymes remain protected inside the plant or sorbed to plant surfaces (Schnoor, 1997).

Apart from the plants aiding the bacteria in degradation during rhizodegradation by providing exudates and nutrients to the bacteria and by creating an ecology in soils that is suitable for bacterial degradation, the plants can also be directly involved in the removal of the contaminants. Plants achieve this through the removal of contamination during plant uptake and subsequent volatilisation via phytovolatilisation, or degradation via phytodegradation (USEPA, 2000). Phytovolatilisation involves the uptake of a dissolved contaminant from the soil environment, and its translocation into the leaves where it is released to the atmosphere through the process of transpiration (ITRC, 2001). Once volatilized, many organic chemicals are then rapidly degraded in the atmosphere during photodegradation (ITRC, 1999). Phytovolatilisation can apply to most organic compounds, such as PCE and TCE and their daughter products (Chappell, 1998; McCutcheon and Schnoor, 2003). In phytodegradation the compound is taken up by the plant roots and transported to the aboveground biomass, where it is used by the plant in various metabolic processes that help to catalyze degradation. The breakdown products are subsequently stored in the plant. Most BTEX compounds and chlorinated ethenes (such as PCE, TCE, DCE and VC) are susceptible to phytodegradation (ITRC, 2001; McCutcheon and Schnoor, 2003; USEPA, 2005a).

Since the processes of rhizodegradation, phytovolatilisation and phytodegradation require the activities of plant roots, these processes are limited to the area affected by the root zone. At the site the maximum mean rooting depths for each vegetation type at the site were determined by Lubke (2006), and from this the zone of influence of the roots can be estimated. The root systems of grasses, which dominate on Dam 3/4, were found by Lubke (2006) to extend to a maximum mean depth of 637 mm, and hence the zone of influence of the roots will be limited to approximately the upper 1 m of the profile at Dam 3/4. At Dam 2, the influence of the roots will most likely be concentrated in the upper 2 m of the profile since trees dominate on this dam, and their roots were found to extend to a maximum mean depth of 1340 mm (Lubke, 2006). In addition, the study by Lubke (2006) established that Dam 2 has the highest root mass, namely 26.24 grams per litre. The deeper root systems and higher root mass present at Dam 2 is due to the fact it has been vegetated longer than Dam 3/4, which has allowed for the development of a more mature vegetation population.

As was described, in the bacterial degradation of PCE and TCE, complete mineralization of these contaminants occurs when reductive dechlorination is followed by the oxidation of the resultant daughter products. The methods used to determine the potential for the reductive dechlorination of PCE and TCE, and the oxidation of DCE and VC, in the vadose zone of Dam 2 and Dam 3/4 will be described in the following chapter.

4. METHODOLOGY

Since PCE and TCE are initially degraded in the environment via reductive dechlorination, and this process requires some very specific environmental conditions to occur (Wiedemeier *et al.*, 1998), the focus of this project was to determine the potential for the reductive dechlorination of PCE and TCE. The focus was also on the vadose zone since this zone is the source of the majority of these contaminants at the site (Duthe, 2004). To assess the potential for reductive dechlorination in the vadose zone within Dam 2 and Dam 3/4 at the site, a points system devised by Wiedemeier *et al.* (1998) to determine the potential for the reductive dechlorination of chlorinated solvents (including PCE and TCE) in groundwater was modified for use in the vadose zone. Since the points system includes the measurement of redox potential, which can be used to estimate if a soil promotes oxidation (Patrick *et al.*, 1996), the determination of the potential for the oxidation of DCE and VC within the vadose zone was also included. In the following sections the original points system will be described, as will the modification of the points system to allow it to be used in the vadose zone to assess the potential for the reductive dechlorination of PCE and TCE. In addition, the method of sampling and analysis of each of the parameters used in the vadose zone points system will be summarised, including the use of redox potential in determining the potential for oxidation.

4.1 Adaption of the Points System for Use in the Vadose Zone

The original points system devised by Wiedemeier *et al.* (1998) allows the investigator to establish if the reductive dechlorination of chlorinated solvents such as PCE, TCE, DCE, trichloroethane and chlorobenzenes is likely to be a viable remedial option in groundwater. The points system is designed to recognize the geochemical environments where reductive dechlorination is possible. Points are awarded for each parameter measured, depending on certain limits. The points are then totalled, and if the total is above certain thresholds the evidence proving the occurrence of reductive dechlorination is either inadequate, limited, adequate or strong. The points system is summarised in Table 4.1. It outlines each of the parameters that affect the potential for reductive dechlorination, giving a brief description of its importance, its concentration threshold measured in the most contaminated zone, and the point value (which gives an indication of the relative importance).

Table 4.1 Analytical parameters and weighting for anaerobic bacterial degradation processes (after Wiedemeier *et al.*, 1998)

Analysis	Concentration in Most Contaminated Zone	Interpretation	Value
Oxygen*	<0.5 mg/l	Tolerated, suppresses reductive pathway at higher concentrations	3
Oxygen*	>5 mg/l	Not tolerated; however, VC may be oxidized aerobically	-3
Nitrate*	<1 mg/l	At higher concentrations may compete with reductive pathway	2
Iron II*	>1 mg/l	Reductive pathway possible; VC may be oxidized under Fe(III)-reducing conditions	3
Sulphate*	<20 mg/l	At higher concentrations may compete with reductive pathway	2
Sulphide*	>1 mg/l	Reductive pathway possible	3
Methane*	<0.5 mg/l	VC oxidizes	0
	>0.5 mg/l	Ultimate reductive daughter product, VC Accumulates	3
Redox Potential* against Ag/AgCl electrode	<50 mV	Reductive pathway possible	1
	<-100 mV	Reductive pathway likely	2
pH*	5<pH< 9	Optimal range for reductive pathway	0
	5>pH>9	Outside optimal range for reductive pathway	-2
TOC	>20 mg/l	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
Temperature*	>20 ^{o}C	At T >20 ^{o}C biochemical process is accelerated	1
Carbon Dioxide	>2x background	Ultimate oxidative daughter product	1
Alkalinity	>2x background	Results from interaction between CO_2 and aquifer minerals	1
Chloride*	>2x background	Daughter product of organic chlorine	2
Hydrogen	>1 nM	Reductive pathway possible, VC may accumulate	3
Hydrogen	<1 nM	VC oxidized	0
Volatile Fatty Acids	>0.1 mg/l	Intermediates resulting from bacterial degradation of more complex compounds; carbon and energy source	2
BTEX*	>0.1 mg/l	Carbon and energy source; drives dechlorination	2
Tetrachloroethene		Material released	0
Trichloroethene*		Material released	0
		Daughter product of PCE	2$^{\#}$
DCE*		Material released	0
		Daughter product of TCE If cis is > 80% of total DCE it is likely a daughter product 1,1-DCE can be chemical reaction product of trichloroethane	2$^{\#}$
VC*		Material released	0
		Daughter product of DCE	2$^{\#}$
1,1,1-Trichloroethane*		Material released	0
Dichloroethane		Daughter product of trichloroethane under reducing conditions	2
Carbon Tetrachloride		Material released	0
Chloroethane*		Daughter product of dichloroethane or VC under reducing conditions	2
Ethene/Ethane	>0.01 mg/l	Daughter product of VC/ethene	2
	>0.1 mg/l		3
Chloroform		Material released	0
		Daughter product of Carbon Tetrachloride	2
Dichloromethane		Material released	0
		Daughter product of Chloroform	2

* Required Analysis

$^{\#}$ Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL)

The points system has very important benefits in determining the potential for reductive dechlorination:

- This system summarises all the parameters affecting reductive dechlorination (Wiedemeier *et al.*, 1998)
- The thresholds are indicative of the geochemical conditions affecting microbial activity
- The points give an indication of the relative importance of each of the parameters.

The parameters can be grouped into three broad divisions: Environmental conditions, a carbon source, and the contaminants and daughter products. The environmental conditions are the conditions required by the microbes to degrade the contaminants via reductive dechlorination. They are:

- Redox conditions, involving the measurement of the terminal electron acceptors (oxygen, nitrate, iron II, sulphate, sulphide and methane), hydrogen and the redox potential
- pH
- Temperature.

The carbon source is the source of energy for the microbes involved in the degradation of chlorinated solvents. There are three potential carbon sources in the reductive dechlorination of chlorinated solvents:

- Total organic carbon (TOC)
- BTEX compounds
- Volatile fatty acids.

The chlorinated solvents and their daughter products are as follows:

- Tetrachloroethene, trichloroethene, DCE, VC, ethene, chloride and carbon dioxide
- 1,1,1- Trichloroethane, dichloroethane and chloroethane
- Carbon Tetrachloride, chloroform and dichloromethane
- Alkalinity, which is an indication of zones of daughter product production in groundwater, because reductive dechlorination results in CO_2 production, which drives the dissolution of rock, which increases alkalinity.

This points system was used by SRK (2000) to determine the potential for reductive dechlorination in the saturated portion of the dams and in the groundwater below them. The saturated zone begins between 17.25 m and 8.59 m below ground level in Dam 2, and between 10.39 m and 14.8 m below ground level in Dam 3/4 (Chapter 2). The study indicated that the complete reductive dechlorination of PCE and TCE to ethene was occurring, primarily due to the reducing conditions (absence of competing electron acceptors) and an adequate supply of electron donors (BTEX compounds being the primary substrate). However, external to the slimes dams, the groundwater had a lower concentration of BTEX compounds, leading to a reduced potential for reductive dechlorination

Although the points system was applied to the dams in 2000, this only included the saturated zone and did not include the vadose zone. To determine the potential for the reductive dechlorination of PCE and TCE in the vadose zone at the site, this points system was again used, with some modification, even though it was not initially devised for the vadose zone. This was done because the initial investigations for this project indicated that no other quantitative methods, based on the measurement of geochemical parameters, were available to assess the potential for reductive dechlorination in the vadose zone. However, this points system is very useful for use in the vadose zone. The original points system uses the measurement of the environmental conditions, the carbon source, as well as the degree of degradation of the contaminants of concern, to establish the potential for reductive dechlorination of chlorinated solvents. Since the environmental conditions and carbon source for the bacteria, as well as the contaminant degradation mechanisms for chlorinated ethenes, are essentially the same within the groundwater and the vadose zone, the points system only needs to be slightly modified for use in the vadose zone, as described later in this section.

Since 8.25 m was the maximum depth able to be practically reached using a standard portable soil auger using extensions, the focus of this project was the profile from the surface to the 8.25 m depth. Because the depth of the vadose zone is between 17.25 m and 8.59 m below ground level in Dam 2, and between 10.39 m and 14.8 m below ground level in Dam 3/4 (Chapter 2) the 8.25 m sample profile does not include the entire vadose zone. However, considering the measurements taken in 2003 by Duthe (2004) at Dam 2 and Dam 3/4 at various depths throughout the slimes dams (listed in Appendix C), it is evident that the PCE and TCE concentrations in the upper 8.25 m are a good representative of the distribution deeper in the profile. At Dam 3/4 the concentrations of PCE and TCE peaked between 2 m

and 8.5 m, and at Dam 2, although the PCE and TCE concentrations peak between 13 m and 15.2 m, the upper 8.25 m contains the second highest concentrations. The concentrations of the daughter products (DCE and VC) followed a similar trend within the dams. It is for this reason that the upper 8.25 m of Dam 2 and Dam 3/4 is a good representative of the concentrations of PCE and TCE, and their daughter products, in the vadose zone of the dams. In addition, since the measurements for the points system should be made in the most contaminated zone (Wiedemeier *et al.*, 1998), the upper 8.25 m of both dams is suitable.

The behaviour of PCE and TCE in the vadose zone differs from the behaviour of these compounds in the groundwater due to the unsaturated nature of this zone. Knowledge of the movement of these parent compounds in the vadose zone is important since their distribution affects the distribution of the daughter products, which are used in the points system to determine the potential for bacterial degradation. The movement of PCE and TCE in the vadose zone at the study site needs to be low since in the use of the points system it is assumed that the down-profile movement of PCE and TCE in the vadose zone is limited, and that the concentrations of the these compounds and their daughter products at each depth is representative of that depth, and have not originated in significant quantities from other depths. The movement of the contaminants in the vadose zone occurs via three primary mechanisms (USEPA, 2006c): 1) The percolation of water containing dissolved contaminants through the unsaturated zone, 2) the migration of vapour-phase contaminant through the unsaturated zone, and 3) the free-phase DNAPL migration through the unsaturated or saturated zone. Based on these three mechanisms, the movement of PCE and TCE is likely to be limited within Dam 2 and Dam 3/4 due to the following reasons:

1. Movement due to percolation, especially in the lower profile in each dam, is likely to be minimal due to the low water fluxes estimated (Chapter 2). The seepage fluxes, simulated at 8 m for a period of over three years by Lorentz *et al*. (2006), were approximately 3 mm/year at Dam 2 and 23 mm/year at Dam 3/4. The low seepage rate is an indication that down-profile movement of dissolved contaminants due to water percolation is likely to be minimal.
2. Due to the fine nature of the material and high water holding capacity measured at the site (Lorentz *et al.*, 2006), the vapour phase migration is likely to be slow, and is only likely to be significant in the upper portions of the profile where the porosity is high and the water content is low. These characteristics will be described in more detail in Chapter 5.

3. Although free-phase DNAPL PCE and TCE could be present at both dams, their movement down-profile due to their dense nature is likely to be limited. Since the dams were closed, the profile has dried (Duthe, 2004) and any mobile DNAPL is likely to have already migrated down-profile. Any remaining DNAPL is likely to be less mobile and trapped in the pore spaces as residual phase product (USEPA, 2006c) since the material at the site is fine (Lorentz *et al.*, 2006), and the opportunity for DNAPL entrapment is high. As a result any free-phase DNAPL movement is likely to be minimal.

Since the original points system was devised to be applied to chlorinated solvents in groundwater and this project is focussed on PCE and TCE degradation in the vadose zone, the points system needed to be altered. This is because not all parameters measured in the groundwater can be measured in soil samples taken from the vadose zone, some parameters are irrelevant at the site, parameters measured in groundwater samples are often in different units from those measured in soil samples, and bacteria in the vadose zone are affected by different conditions. In the alteration of the original points system for use on PCE and TCE degradation in the vadose zone, parameters were excluded, added or modified, and these changes are described in the following paragraphs.

The parameters that were excluded include the terminal electron acceptors, hydrogen, volatile fatty acids, and some of the chlorinated solvents and their daughter products. The terminal electron acceptors (oxygen, nitrate, iron II, sulphate, sulphide and methane) and hydrogen, which give an indication of whether the reductive pathway is possible, were not measured because no laboratories were available to measure these parameters in soil samples. However, this is unlikely to be critical because the redox potential was measured which also gives an indication of whether the reductive pathway is possible (Wiedemeier *et al.*, 1998), and the redox potential can be used as an estimate of the terminal electron acceptor processes that are dominant (Pierzynski *et al.*, 2005). In addition, the redox potential has an advantage over the use of the terminal electron acceptors in that it can indicate the intensity of reduction (Patrick *et al.*, 1996). With regard to the carbon source, the volatile fatty acids were not measured. This is because BTEX compounds, not volatile fatty acids, are seen to be the dominant anthropogenic carbon source at the site (Duthe, 2004). As a result the dominant sources of carbon for bacteria at the site are organic carbon and BTEX compounds. In terms of the chlorinated solvents and their daughter products, 1,1,1- trichloroethane, dichloroethane, chloroethane, carbon tetrachloride, chloroform and dichloromethane could all be excluded

since they are not daughter products of PCE and TCE degradation, and are not involved in the degradation of PCE, TCE, or their daughter products. Because DCE and VC, which are daughter products created during the reductive dechlorination of PCE and TCE, cannot be present at the site as a result of material released since DCE was never dumped at the site and VC is so volatile that if it had been dumped onto the dams it would have volatilized immediately (Duthe, 2006), the option of having DCE and VC as a material released was removed from the points system. Hence, any DCE and VC measured in the dams occur as a result of the reductive dechlorination of PCE and TCE. Unlike DCE and VC, TCE is present at the site as a waste material, and as a result it cannot be shown that TCE is a daughter product of the reductive dechlorination of PCE, and thus no points are awarded to this parameter. Carbon dioxide and alkalinity, both of which provide evidence of oxidation, were not measured due to a lack of background conditions to compare against. However, carbon dioxide and alkalinity are not listed as a "required analysis" by the points system, and as a result their exclusion is not critical. In addition, ethene and chlorine were not measured. Both of these daughter products indicate that reductive dechlorination is occurring. Ethene could not be measured since this parameter needs to be measured in water samples, and no suitable boreholes and piezometers were available on the dams in 2006. Chloride could not be measured on site because there are no background conditions within the slimes dams to compare against. However, since the measurement of ethene is not listed as a "required analysis" by the points system, and since the other daughter products of PCE and TCE degradation are being measured, the omission of ethene and chloride is not critical.

Apart from excluding parameters, one parameter was added to the points system. This was the water content, which was measured as a percent saturation. This parameter was not included in the original Wiedemeier *et al.* (1998) points system since this system was created for use in groundwater. However, in the vadose zone, where the material is not saturated, the water content is important since it affects the redox potential at a high percent saturation, and affects microbial activity at a low percent saturation. As water content increases, the redox potential will decrease (Nengovhela *et al.*, 2006) and according to Maier (2000), at a water content higher than 81% saturation the slow rate of oxygen diffusion through water limits oxygen replenishment, thereby promoting anaerobic conditions (Richard, 2005). Since reductive dechlorination is an anaerobic process (Wiedemeier *et al.*, 1998), environments having a water content above 81% saturation thus have the potential to promote reductive dechlorination and since this threshold is a conservative value, as will be described in

Section 4.2.1, reductive dechlorination is expected to be highly likely. At water contents below 38% saturation water availability to the bacteria becomes limiting, thereby reducing their activity (Maier, 2000). This will result in lowered rates of reductive dechlorination. To include the effect of water content on reductive dechlorination required the creation of thresholds and points for this parameter. Since the potential for reductive dechlorination is reduced at water contents below 38% saturation, a negative point was allocated to values below this threshold. At water contents above 81% saturation, the potential for reductive dechlorination is more likely, thus one point was allocated to water contents above this threshold. The water content will be described in more detail in Section 4.2.1.

In addition to excluding and adding parameters, some were modified. These included the modification of the thresholds used for total organic carbon (TOC), BTEX compounds, and the redox potential; and the modification of the points awarded to the redox potential to take into account the exclusion of the terminal electron acceptors. The measurements of TOC were made in the vadose zone, and hence are measured as a percent (measured as milligrams of total organic carbon per milligrams of air-dried soil); however, in the original points system the measurements are in milligrams of total organic carbon per litre of water (mg/l). In addition, TOC was converted to a soil organic matter (SOM) value by multiplying by 1.724, the van Bemmelen conversion factor (Nelson and Sommers, 1996), since SOM is the primary natural source of carbon to bacteria in soils during reductive dechlorination (Rosenbrock *et al.*, 1997; Wiedemeier *et al.*, 1998; Ma *et al.*, 2003). As a result new thresholds need to be devised to account for these changes made to the total organic carbon measurements. According to Laing (2006), soil microbes require at least 2.5% TOC for increased growth. Using the van Bemmelen conversion factor, this equates to 4.31% SOM. Since in the Wiedemeier *et al.* (1998) points table two points were given to TOC concentrations above 20 mg/l, which enhances reductive dechlorination, the same points will be given to any SOM measurements above 4.31%, as this will also enhance reductive dechlorination. The BTEX compounds parameter was modified so as to allow the threshold, used in water samples, to be used in the measurements made in the waste material samples. To do this the units were converted to a single unit - parts per million (ppm) - and the measurements were converted to a concentration in the interstitial water, which is available to the bacteria. Since the BTEX compounds threshold, measured as milligrams per litre (mg/l) is equivalent to ppm if one ignores the small density differences between pure water and the majority of environmental water samples (USEPA, 2006d), no conversion of the threshold was required. To determine

the concentration of the BTEX compounds in the interstitial water, the concentration (measured as micrograms per kilogram (µg/kg) using headspace GC-MS, and described in Section 4.2.5) was divided by the water content (measured as gram per gram (g/g) on a dry-weight basis). The interstitial water BTEX compounds concentration was then converted from µg/kg to ppm by dividing by 1000. This calculation is shown in Appendix C. With regard to the redox potential, the thresholds were modified since the original points system measures the redox potential against an Ag/AgCl electrode; however, the standard is to measure the redox potential against a standard hydrogen electrode. As a result, the thresholds in the points system were modified by adding +199 mV to the thresholds so as to represent the standard hydrogen electrode (Patrick *et al.*, 1996). Thus the thresholds of +50 mV and -100 mV became +249 mV and +99 mV respectively. This conversion will be described in more detail in Section 4.2.2. In the alteration of the original points system for use in the vadose zone, by either excluding, adding or modifying parameters, the major change is the removal of each of the terminal electron acceptors (oxygen, nitrate, iron II, sulphate, sulphide and methane), which acted as an indication of the redox conditions within the dams. In the original points system, if it is assumed that the primary pollutants are PCE and TCE, the points allocated to the environmental factors affecting reductive dechlorination are approximately double that of the chlorinated ethenes and their daughter-product concentrations, and the points allocated to the chlorinated ethenes and their daughter products are, in turn, double that of the carbon source available to the microbes. Since between two and three points are allocated to each of the terminal electron acceptors, their removal from the points system takes the focus off the redox conditions in the environmental factors, thereby significantly reducing the importance of the environmental factors in determining the potential for reductive dechlorination of PCE and TCE. To rectify this, in the vadose zone points system instead of the redox potential of less than +50 mV having one point allocated and a redox potential below -100 mV having two points allocated, as was the case in the original points system (Wiedemeier *et al*, 1998), a redox potential below +249 mV (which in the vadose zone points system replaces +50 mV) is allocated four points and eight points is allocated to a redox potential below +99 mV (which replaces -100 mV in the vadose zone points system). This returns the dominance of the redox potential in the environmental factors affecting reductive dechlorination, and maintains the ratio between the environmental conditions, carbon source and PCE, TCE and their daughter products. The resultant vadose zone points system, after excluding, adding and modifying parameters, is summarised in Table 4.2.

Table 4.2 Modified analytical parameters and weighting for anaerobic bacterial degradation processes

Parameter	Analysis	Concentration in Most Contaminated Zone	Interpretation	Points
Redox Potential	Eh	< 249 mV	Reductive pathway possible	4
		< 99 mV	Reductive pathway likely	8
Carbon Source	SOM	> 4.31%	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
	BTEX	> 0.1 ppm	Carbon and energy source; drives dechlorination	2
pH	pH	5 < pH < 9	Optimal range for reductive pathway	0
		5 > pH > 9	Outside optimal range for reductive pathway	-2
Temperature	Temperature	> 20 ^{o}C	Above 20 ^{o}C biochemical processes accelerated	1
Pollutants and Daughter Products	PCE		Material released	0
	TCE		Material released	0
	DCE		Daughter of TCE	2$^{\#}$
	VC		Daughter of DCE	2$^{\#}$
Water Content	Percent Saturation	> 81%	Promotes anaerobic conditions	1
		< 38%	Reduces microbial activity	-1

$^{\#}$ Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL)

Since the original points system was altered, the original use of the points system; where the points allocated were totalled and the totals were compared to thresholds which described the evidence for reductive dechlorination as either inadequate, limited, adequate or strong (Wiedemeier *et al.*, 1998); cannot be used. This is because parameters have been excluded, added and modified to the original points system and, as a result, the thresholds described by Wiedemeier *et al.* (1998) to describe the evidence for reductive dechlorination are no longer applicable. However, the vadose zone points system is still very useful since the points system allocates points for all of the important parameters that promote reductive dechlorination, thereby indicating which of the parameters promote and prohibit reductive dechlorination throughout the study site. In addition, points allocated to all of the parameters at a measurement location can be totalled as an indication of the relative potential for reductive dechlorination. Each of these parameters and their measurement will be described in Section 4.2.

Apart from the parameters used in the vadose zone points system being useful in determining the potential for reductive dechlorination of PCE and TCE, the measurement of the redox potential is also useful in determining the potential for oxidation at the site (Vepraskas and Faulkner, 2001). The mechanism of oxidation is important at the site since the mechanism of reductive dechlorination often results in the accumulation of DCE and VC (WSRC, 2004),

which can be problematic due to the highly carcinogenic nature of VC (Chappell, 1997; ATSDR, 2003). As a result, the use of redox potential in determining the potential for oxidation will also be described in the following section.

4.2 Description of Parameter Measurements

As described, to establish the potential for reductive dechlorination in the vadose zone at Dam 2 and Dam 3/4, the following parameters were measured: Water content, redox potential, pH, temperature, carbon source (including the measurement of soil organic matter and BTEX compounds) and the pollutants and daughter products (PCE, TCE, DCE and VC). In addition, the redox potential measurements were used to assess the potential for oxidation in the vadose zone of each of the dams. The measurement of these parameters was divided into two scales: Temporal measurements and spatial measurements.

Temporal measurements were undertaken for the redox potential. The temporal measurement of redox potential is important since this is the most dominant parameter in determining the potential for reductive dechlorination, as indicated by Table 4.2, and is the only parameter used to determine the potential for oxidation. Since the redox potential is affected by the water content (Maier, 2000; Nengovhela *et al.*, 2006) which is affected by seasons, the temporal measurements of the redox potential is an important indicator of the seasonal change in the potential for reductive dechlorination and oxidation. To monitor the redox potential temporally, redox electrodes were manufactured and installed at Dam 2, as is described in Appendix A. The site chosen was near Site 21, shown in Figure 4.1, which lies near a stand of fig trees and grassland and is representative of the general vegetation population and conditions present on the dam. The electrodes were installed at various depths (0.3 m, 0.5 m, 1 m, 2 m, 4 m, 6.5 m and 8.25 m) so as to establish the trend down the profile. Measurements were taken on a fortnightly to monthly basis between September 2005 and August 2006. The temporal measurement of redox potential will be described in more detail in Section 4.2.2.

Spatial measurements were done to assess the horizontal and vertical variability of all the parameters that affect the reductive dechlorination potential. This involved the measurement of gravimetric water content and bulk density (used to determine the porosity and VWC, which are used to calculate the water content measured as percent saturation), redox potential, temperature, pH, the carbon source (including the measurement of soil organic matter and

BTEX compounds) and the contaminants and daughter products (PCE, TCE, DCE and VC). In addition, the redox potential measurements were used to assess the spatial variation in the oxidation potential. All of these measurements were done on a once off basis between late May and early June 2006 at various locations on each dam, and over a profile depth of 8.25 m. As was described in Chapter 2, the focus of the project was to determine the potential for bacterial degradation within Dam 2, and Dam 3/4 was included since it has a lower density of vegetation, which allowed for a determination of the effects of vegetation and the associated root zone microbial populations on the degradation potential based on a comparison of the measurements made at each dam. Since Dam 2 was the focus it had five measurement sites, while Dam 3/4 had only two. In general the dams have a similar waste composition since they were interconnected and had similar waste applications (Chapter 2); however, since Dam 3/4 was initially divided into two separate dams, which had slightly different treatments (Oliver, 2006), the two sample sites at Dam 3/4 include each of the old dams to include any possible variation. The measurement site locations, sample dates and depths on each dam are listed in Table 4.3 and are shown in Figure 4.1. Since the waste applied to each dam was initially in a liquid form (Duthe, 2004), the intermittent addition of waste is likely to have lead to stratification. In addition, the vegetation growth has been generally uniform across each dam, leading to an expected uniform degree of natural attenuation across each dam. As a result the levels of each of the parameters measured are not expected to change significantly horizontally within Dam 2 and within each of the dams that now make up Dam 3/4. To obtain samples from the sites an auger head with a “bucket” of 100 mm outside diameter, attached to extensions reaching a maximum of 8.25 m, was used to reach a depth just short of the desired sampling depth. The auger bucket was modified by technicians in the School of Bioresources Engineering and Environmental Hydrology (BEEH) at the University of KwaZulu-Natal to have openings cut into the sides to allow for easier removal of the clay-like material. A corer head attached to similar extensions was then used to take a core sample, which was brought to the surface. The corer head, specifically constructed by technicians in the School of BEEH at the University of KwaZulu-Natal, had an opening in the side so as to allow for the extraction of an undisturbed sample. The auger and corer heads are shown in Figures A-4 to A-6 in Appendix A. Measurements for temperature and redox potential were made using a hand-held meter directly from the core sample, and as soon after sampling as possible to limit any atmospheric affects on redox potential or temperature. Samples from the core were then placed in relevant storage containers, kept cool if necessary, and sent to laboratories for analysis of pH, soil organic matter, gravimetric water content,

bulk density, and volatile organic compounds (VOCs). The sampling and analysis of each of these processes will be described in more detail in Sections 4.2.1 to 4.2.6.

Since Dam 2 and Dam 3/4 have differing vegetation densities, and plants affect the water content, redox potential, pH and organic matter content, and affect the concentrations of PCE, TCE, DCE, VC and BTEX compounds in the vadose zone (Chapter 3), and these parameters were measured at both dams both temporally and spatially, the influence that vegetation has on the degradation potential within the vadose zone of Dam 2 and Dam 3/4 can be determined by comparing the measurements of these parameters at each dam, as will be described in Chapter 6. The influence of vegetation on these parameters will be described in Chapter 5.

The method of measurement and analysis of the various parameters to establish temporal and spatial variability of the parameters affecting the potential for reductive dechlorination and oxidation in the vadose zone at Dam 2 and Dam 3/4 are summarised in the following sections.

Table 4.3 Site locations, sample dates and sample depths

Dam	**Site**	**Latitude (Degrees South)**	**Longitude (Degrees East)**	**Sampling Date**	**Depths (m)**
Dam 2	21	30.89684293	-30.01857015	25-26 May 2006	0.3, 0.5, 1, 2, 4, 6.5, 8.25
	22	30.89751246	-30.01876085	01-02 June 2006	0.3, 0.5, 1, 2, 4, 6.5, 8.25
	23	30.89645673	-30.01830423	06 June 2006	0.3, 0.5, 1, 2
	24	30.89698681	-30.01891093	07 June 2006	0.3, 0.5, 1, 2, 4, 6.5, 8.25
	25 (1 m-6.5 m)	30.89679156	-30.01821163	09 June 2006	0.3, 0.5, 1, 2, 4, 6.5
	25 (8 m)	30.89684826	-30.01818862	28 June 2006	8
Dam 3/4	341	30.89579485	-30.01761247	23-26 June 2006	0.3, 0.5, 1, 2, 4, 6.5, 8
	342	30.89495515	-30.01618318	30 June 2006	0.3, 0.5, 1, 2, 4, 6.5, 8.25

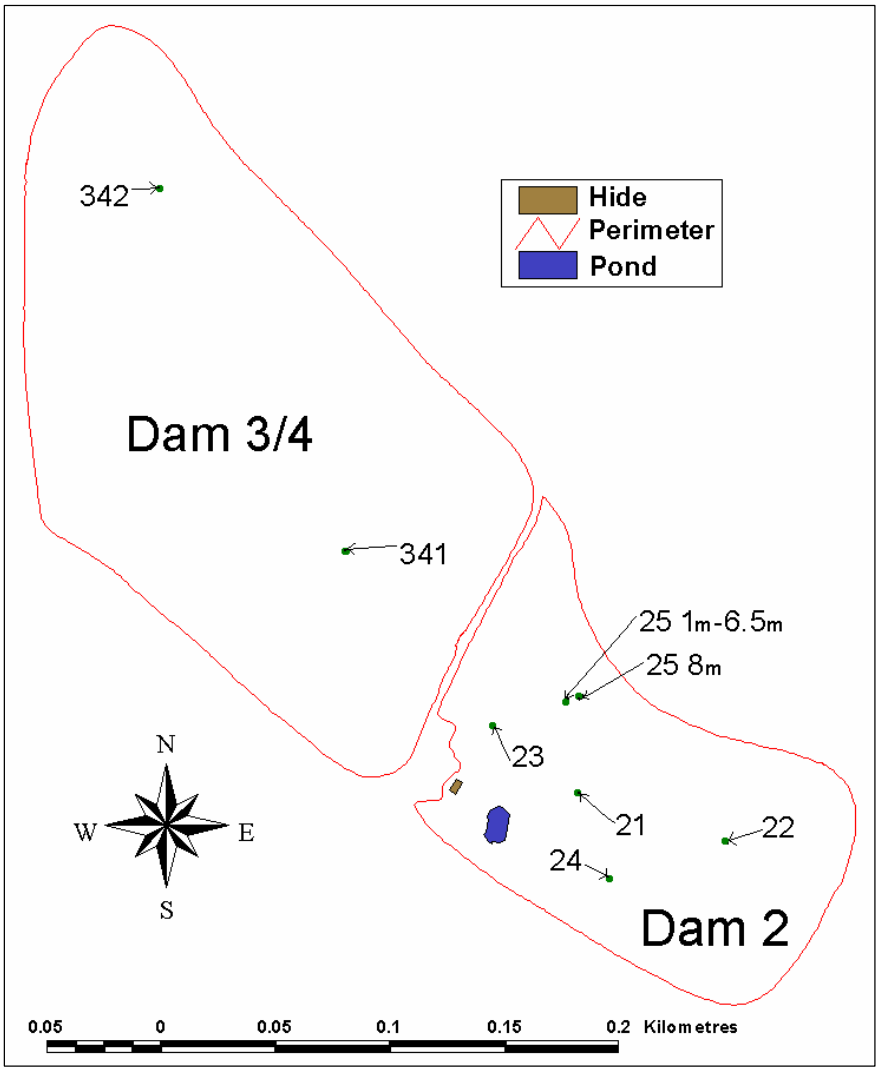

Figure 4.1 Location of measurement sites on Dam 2 and Dam 3/4.

4.2.1 Water content

In this project, the water content was measured as a percent saturation, which is the volume of pore spaces filled with water (Maier, 2000). In the vadose zone, where the material is not saturated, the water content is important since it affects the redox potential at a high percent saturation, which promotes anaerobic conditions and reductive dechlorination; while at a low percent saturation microbial activity is reduced, thereby lowering the rate of reductive dechlorination (Maier, 2000).

Since water content is inversely proportional to oxygen concentration (Nengovhela *et al.*, 2006), as the water content increases the redox potential decreases. According to Maier

(2000), at a water content higher then 81% saturation the slow rate of oxygen diffusion through water limits soil aeration, thereby promoting anaerobic conditions (Richard, 2005), and consequently has the potential to promote reductive dechlorination. However, this is a conservative value. This is because at a low bulk density there is more water in the soil at a set water saturation than in a soil with a high bulk density (Maier, 2000) and thus in materials with a low bulk density (such as the site, where the bulk density ranges from 0.22-0.56 g/cm^3 as indicated by Tables B-2 to B-8 in Appendix B) the oxygen diffusion constraints become important at a lower water saturation than for a material with a higher bulk density (Maier, 2000). Because of the effect of bulk density, the percent saturation above which aeration becomes limiting to microbial respiration can range from 60% saturation to 97% saturation (Gupta and Larson, 1982; Hillel, 1982; Linn and Doran, 1984; Neilson and Pepper, 1990). Due to the low bulk density of the material at the site, the threshold of 81% represents a very high amount of water in the material at the site, and the diffusion of oxygen will be highly limited. Hence, at the 81% saturation threshold anaerobic conditions are highly likely, resulting in a high potential for reductive dechlorination. Apart from the effects of a high water content on reductive dechlorination, a low water content also affects the potential for reductive dechlorination. At a water content below 38% saturation, water availability to the bacteria becomes limiting, thereby reducing their activity (Maier (2000), potentially resulting in a lowered reductive dechlorination rate. Percent saturation (%) is calculated using the volumetric water content (%) and porosity according to the following equation (Barton and Schipper, 2001):

$$\text{Percent saturation} = \text{Volumetric water content} / \text{porosity} \qquad (4.1)$$

The volumetric water content (VWC) is calculated by multiplying the gravimetric water content by the bulk density of the material (Barton and Schipper, 2001). Samples for gravimetric water content determination were obtained from cored soil samples taken from the relevant depth, and were stored in air-tight plastic bags to prevent evaporative losses, and were sent to the School of BEEH at the University of KwaZulu-Natal for analysis by the author. In this method a wet sample is weighed then dried (at 105 ^{o}C for 48 hours), and reweighed to determine the amount of water removed. Gravimetric water content (%) is then obtained using the following equation (Jury and Horton, 2004):

$$\text{Gravimetric water content} = \frac{\text{wet soil weight} - \text{dry soil weight}}{\text{dry soil weight}} \times 100 \qquad (4.2)$$

The samples for bulk density determination were obtained at each depth using the corer, and it was ensured that the sample core was handled and stored so as to maintain the structure, which is required when determining the sample volume. The cores then had the dry bulk mass and the volume determined by the technician in the School of BEEH at the University of KwaZulu-Natal, and the bulk density (g/cm^3) was calculated by dividing the weight by the sample volume. The porosity was calculated by using the following equation (Barton and Schipper, 2001):

$$\text{Porosity} = 1 - (\text{bulk density} / \text{particle density}) \qquad (4.3)$$

The bulk density used was that measured for the VWC determination. The particle density was assumed to be 2.65, the value for silica, which was verified by measurement to be a good representative of the density of the material at the site (Lorentz, 2006).

4.2.2 Redox potential

The redox potential plays an important role in the degradation of PCE and TCE since the complete degradation of these compounds to harmless by-products requires the occurrence of reductive dechlorination and oxidation, both of which require very specific redox conditions to occur (Chapter 3). In addition, the redox potential is affected by the water content (Maier, 2000; Nengovhela *et al.*, 2006) which is affected by seasons. As a result, both the spatial variability and the temporal variability of this parameter were investigated. Since the conditions required to promote reductive dechlorination are more difficult to achieve in the vadose zone than oxidation, the focus is on determining the potential for reductive dechlorination at the site. However, due to the importance of oxidation in preventing the accumulation of the carcinogenic daughter products during the reductive dechlorination of PCE and TCE, the potential for oxidation at the site will also be described.

Since the terminal electron acceptors (oxygen, nitrate, iron II, sulphate, sulphide and methane) could not be measured, the measurement of redox potential was used as an indication of which degradation pathway is possible (Section 4.1). The redox potentials at which common

reduction half reactions for native terminal electron acceptors occur are summarised in Table 4.4. After the depletion of dissolved oxygen, anaerobic microbes will use nitrate as a terminal electron acceptor, followed by manganese (IV), iron (III), sulphate, and finally carbon dioxide (methanogenesis) (AFCEE, 2004). As each subsequent electron acceptor is utilized the ground water becomes more reducing and the redox potential decreases (Wiedemeier *et al.*, 1998). However, it should be noted that the redox potential at which each reaction occurs differs depending on the author (Mitsch and Gosselink, 1993; cited in Vorenhout *et al.*, 2004; Wiedemeier *et al.*, 1998; AFCEE, 2004; Pierzynski *et al.*, 2005); hence, the values serve only as an approximation. It should also be noted that the trends in redox potential vary with soil pH and temperature, as noted in Table 4.4. The variation in redox potential with pH usually necessitates the use of an Eh-pH diagram (Garrels and Christ, 1965), however this variation was taken into account since the redox potentials listed in Table 4.4 assume a pH of 7 (Pierzynski *et al.*, 2005), and all measurements of redox potential made in this study (both temporal and spatial) were converted to a value equivalent of pH 7, thus this variation can be ignored. In addition, the variation with temperature is relatively minor (Patrick *et al.*, 1996) and can be ignored. The importance of pH and temperature in altering the redox potential will be described in more detail later in this section, as will the correction of the redox potential for the effects of pH.

Table 4.4 Redox reactions of primary importance in waterlogged soils (after Pierzynski *et al.*, 2005)

Element	**Oxidised species**	**Reduced species**	**Redox Potential (Eh) for Reaction (mV)***
O	O_2 [$½O_2 + 2e^- + 2H^+ \leftrightarrows H_2O$]	H_2O	+700 to +400
N	NO_3^- [$NO_3^- + 2e^- + 2H^+ \leftrightarrows NO_2^- + H_2O$]	NH_4^+, N_2O, N_2	+220
Mn	Mn^{4+} (manganic: MnO_2) [$MnO_2 + 2e^- + 4H^+ \leftrightarrows Mn^{2+} + 2H_2O$]	Mn^{2+} (manganous: MnS)	+200
Fe	Fe^{3+} (ferric: $Fe(OH)_3$) [$FeOOH + e^- + 3H^+ \leftrightarrows Fe^{2+} + 2H_2O$]	Fe^{2+} (ferrous: FeS, $Fe(OH)_2$)	+120
S	SO_4^{2-} (sulphate) [$SO_4^{2-} + 8H^+ 7e^- \leftrightarrows ½S_2^{2-} + 4H_2O$]	S^{2-} (sulphide: H_2S, FeS)	-75 to -150
C	CO_2 (carbon dioxide) [$CO_2 + 8e^- + 8H^+ \leftrightarrows CH_4 + 2H_2O$]	CH_4 (methane)	-250 to -350

* Redox potentials are approximate values and will vary with soil pH and temperature.

- Measuring redox potentials in the field

The standard method of measuring redox potentials in soils is through the use of a platinum electrode, a reference electrode, and a meter to indicate the voltage (Patrick *et al.*, 1996). When the platinum electrode is coupled with a half cell of known potential (the reference electrode), reducing systems tend to transfer electrons to the electrode while oxidising systems tend to take electrons from the electrode. When measuring the redox potential this flow of electrons is prevented, and the resultant potential between the platinum electrode and the reference electrode is measured with a meter that responds to electromotive force or potential (Patrick *et al.*, 1996). Using these components, the redox potential was measured using two different methods: The use of a portable hand-held redox meter to get once off measurements of redox potential in augured samples taken from various depths and sites to indicate the spatial variability, and the use of permanently installed redox electrodes placed at various depths at a single site to continuously measure the redox potential to determine the temporal variability.

In the spatial measurement of redox potential a portable meter was used by the author. The use of a portable meter for the measurement of redox potential was described by Olness *et al.* (1989; cited in van Bochove *et al.*, 2002). The portable meter used in this project was a microcomputer pH meter (HI8424 microcomputer pH meter by HANNA instruments), which had a platinum redox electrode (HI3230 redox electrode by HANNA instruments) attached. The reference electrode is built into the electrode. The meter measures the redox potential to an accuracy of ±0.2 mV at 20°C (Hanna Instruments, 2005). Since the meter was calibrated at the factory (Hanna Instruments, 2005), calibration of the microcomputer was not required. Prior to the measurements the platinum tip of the electrode was inspected for damage, and any coatings were removed by lightly abrading the tip with a very fine sandpaper (1200 grit). To obtain a redox reading using the hand-held meter, the platinum electrode was pushed directly into a newly obtained sample core, and once the reading had stabilised (typically taking a few minutes), the reading was noted. Although the material was dry in the upper 0.5 m, which typically necessitates the addition of distilled water, or the use of a dilute salt solution - as described by Patrick *et al.* (1996) - to prevent a junction potential from being established, these measures were not used in the spatial measurements of redox potential since this was deemed unnecessary based on the temporal measurements of redox potential (as indicated in Table B-1 in Appendix B) which will be described in the next paragraph. This indicates that the material was moist enough in the drier upper profile not to form a junction potential. The

measurement of redox potential was then converted to an Eh value, and corrected for the effects of pH, which will be described later in this section.

The use of the permanently installed electrodes to establish the temporal variability of the redox potential required the use of a platinum electrode, a reference electrode (REF321 Reference Electrode made by Radiometer Analytical), and a voltmeter able to measure in the millivolt range (in this project a hand-held voltmeter made by Fragram® was used). Since redox electrodes of the type required for this project are not commercially available, they were constructed by the author using a method modified from Vepraskas and Cox (2002). In this method a length of platinum wire is inserted into a brass brazing rod that is attached to a length of copper wire. This step was done with the help of a technician from the School of BEEH at the University of KwaZulu-Natal. A specifically made PVC tip and PVC conduit tubing was then added to protect each electrode from damage. The electrodes were then tested for accuracy using a standard redox potential solution, where it was ensured that the readings were within 47 mV of the reference value at 28 ^{o}C (Austin and Huddleston, 1999). To install the electrodes at the site, a hole of identical diameter to the redox electrode was augured and the electrode was pushed down the hole into the undisturbed material. This was done by the author with the help from a field technician from the School of BEEH at the University of KwaZulu-Natal. The electrodes were installed at 0.3 m, 0.5 m, 1 m, 2 m, 4 m, 6.5 m and 8.25 m (Section 4.2). Due to the prohibitively high expense of the electrodes, the temporal variation in redox potential was only measured at one site at Dam 2, and not at Dam 3/4; however, as will be explained in Chapter 5, the site at Dam 2 was a suitable representation of the conditions at the dam, and the trends measured could be extrapolated to Dam 3/4. The site chosen at Dam 2 to install the electrodes was situated very close to Site 21, which lies between a fig tree stand and a grassland section. This site was chosen since it is situated in an area representative of the general vegetation present on Dam 2, and as a result any affects of vegetation on the redox potential at this dam will be taken into account. A photograph of the redox electrodes installed at Site 21 is shown in Figure A-3 in Appendix A. To measure the redox potential using these permanently installed electrodes, a method described by Patrick *et al.* (1996) was used. The reference electrode was pushed a short distance into the waste material at the surface, within 2 m of the surface position of the electrodes. If the waste material was moderately dry (not moist or wet), a small volume of material was broken up and distilled water added to form a paste, into which the reference electrode was pushed. If the waste material was dry or highly weathered (which was often the case with the surface

layers at Dam 2), a salt solution (5 g potassium chloride in 100 ml distilled water) was used to moisten the hole to prevent a junction potential from being established. To obtain a reading using the redox electrodes, the voltage between the reference electrode and the electrode was measured using the voltmeter. Once the millivolt reading stabilised to a slow rate of drift (slower than about 6 mV per minute, which typically took less than five minutes to occur), the measurement was noted. At a later stage each reading was converted into an Eh value, and corrected for the effects of pH. This will be described later in this section. A more detailed description of the construction, protection, testing and installation of these electrodes is described in Appendix A. To rule out any potential errors that could occur during the measurement of the redox potential using the described method, the effect of various factors on the measurements were tested, as was noted in Table B-1 in Appendix B. The distance between the reference electrode and the redox electrode was altered from within 0.1 m to within 2 m of the surface position of each without any significant change (less than 10 mV) to the redox potential reading. In addition, the hole into which the reference electrode was inserted had different additions to moisten the hole (no additions, distilled water, and a dilute KCl salt solution), all of which did not alter the redox potential reading, indicating that the material was moist enough in the drier upper profile not to form a junction potential.

- Conversion and correction of redox potential measurements

In this study the redox potential measurements were converted to measurements that would have been obtained had a standard hydrogen electrode been used, and they were corrected for the effects of pH.

The standard hydrogen electrode is considered as the standard reference electrode; however, it is not a convenient electrode for field or routine laboratory work As a result, Ag/AgCl or calomel reference electrodes are used for field work, and the measurements are converted to a measurement that would have been obtained if a standard hydrogen electrode had been used, called Eh (Vepraskas and Cox, 2002). Since an Ag/AgCl reference electrode was used in this study, +199 mV was added to all readings to convert the measurement to an Eh (Patrick *et al.*, 1996). In addition, since the points system devised by Wiedemeier *et al.* (1998) uses thresholds based on measurements made using an Ag/AgCl reference, to standardise these thresholds for use in the vadose zone points system they were also converted to an Eh. Hence, the thresholds of +50 mV and -100 mV become +249 mV and +99 mV respectively (Section 4.1).

The redox potential is affected by the pH of the environment, with the predicted change in Eh being 59 mV per pH unit. As a result, this value can be used to adjust measured redox potentials for comparison at a given pH, so as to standardise the measurements (Patrick *et al*., 1996). This was done for all measured redox potentials, with all the Eh measurements converted to a value equivalent to pH 7. The adjustment of Eh (mV) was achieved using the following equation:

$$\text{Eh at pH 7} = \text{Eh} + ((\text{pH} - 7) \times 59) \qquad (4.4)$$

For the spatial variation measurements, the Eh measured at each depth was converted using the pH measured at the equivalent depth. In the case of the temporal variation measurements, in which the redox potential was continually monitored, the pH could not be continuously measured due to the prohibitive depths of redox electrode installation and the need to maintain an undisturbed environment around the electrodes. As a result, to correct the temporal measurements of Eh, the pH values obtained at the equivalent depths during the sampling for the spatial variation measurements, done on 25 May 2006, at Site 21 (approximately 2 m from the electrodes) were used, under the assumption that the pH did not vary significantly during the time period that the temporal measurements of redox potential were made. The pH measurements will be described in Section 4.2.3.

The redox potential is also affected by temperature; however, the redox potential is not usually corrected for this affect since the error involved from this source is relatively small compared to other inherent errors in the system (Patrick *et al*., 1996), and as a result the correction for temperature was not made in this study.

- Determination of the potential for reductive dechlorination and oxidation using redox potential measurements

As described, the complete mineralization of PCE and TCE is most efficient when the reductive dechlorination of PCE and TCE is followed by the oxidation of the daughter products (DCE and VC). The oxidation can be either aerobic or anaerobic (Wiedemeier *et al*., 1998; WSRC, 2004). The conditions required for reductive dechlorination and oxidation to occur require very specific redox conditions.

According to Bouwer (1994; cited in AFCEE, 2004) reductive dechlorination may occur in the range of nitrate reduction to iron reduction (which according to Table 4.4 occurs from +220 mV to +120 mV), and is most rapid and complete under the highly reducing conditions of sulphate reduction to methanogenesis (occurring below -75 mV according to Table 4.4). However, in the points system devised by Wiedemeier *et al.* (1998), these thresholds are different. The points system states that reductive dechlorination is possible below a redox potential of +249 mV, and is considered more likely below a redox potential of +99 mV. Since it was noted that the redox potential at which each terminal electron acceptor reaction occurs differs depending on the author (Mitsch and Gosselink, 1993; cited in Vorenhout *et al.*, 2004; Wiedemeier *et al.*, 1998; AFCEE, 2004; Pierzynski *et al.*, 2005), the constraints used described by Wiedemeier *et al.* (1998) were used since these are used in the original points system.

With regard to oxidation, according to Table 4.4 aerobic oxidation will occur above +400 mV, where oxygen is present as an oxidised species. In terms of anaerobic oxidation, WSRC (2004) states that the potential for the oxidation of highly reduced contaminants is greatest under aerobic conditions and least under methanogenic conditions. Because DCE and VC are relatively reduced compounds, a similar pattern of decreasing oxidation potential under increasingly anaerobic conditions is expected. In addition, since DCE and VC have differing chlorine numbers, anaerobic oxidation of VC will be more likely than anaerobic oxidation of DCE for each electron-accepting condition (WSRC, 2004). Hence, the anaerobic oxidation of VC occurs under mildly reducing conditions such as iron- and manganese-reduction (between +400 mV and +120 mV according to Table 4.4) (AFCEE, 2004); and DCE is anaerobically oxidised under manganese-reducing conditions (between +400 mV and +200 mV according to Table 4.4), which occurs without an initial reduction to VC (WSRC, 2004).

These thresholds for reductive dechlorination, aerobic oxidation and anaerobic oxidation are summarised in Figure 4.2. Since there is an overlap in the redox potential thresholds determining the occurrence of the reductive dechlorination of PCE and TCE, and the anaerobic oxidation of DCE and VC, as indicated by Figure 4.2, there is the possibility for conditions to exist to promote mixed microbial populations, in which some utilise reductive dechlorination and others utilise anaerobic oxidation. This would allow for the co-occurrence of reductive dechlorination and anaerobic oxidation where the degradation of PCE and TCE

occurs at the same time as the daughter products, reducing the accumulation of the daughter products. This co-occurrence of degradation occurs between +249 mV and +200 mV for PCE, TCE, DCE and VC, and from +200 mV and +120 mV for PCE, TCE and VC.

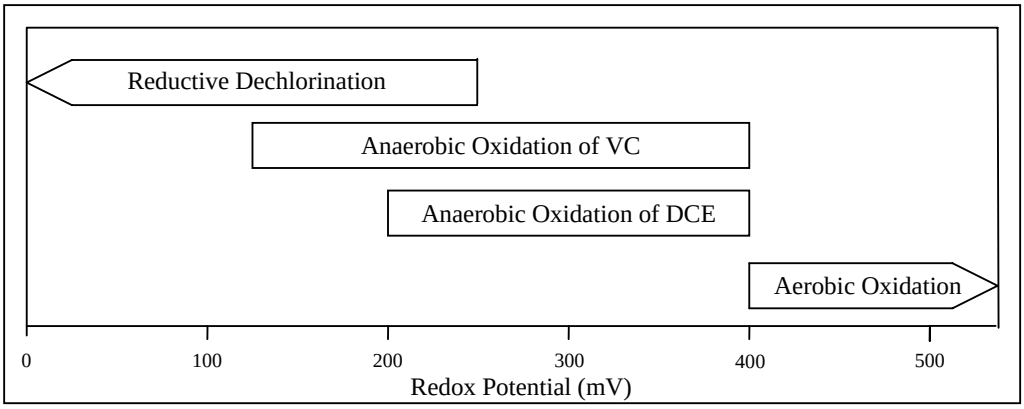

Figure 4.2 Occurrence of degradation mechanisms at different redox potentials.

4.2.3 pH

The pH has an effect on the presence and activity of microbial populations. Microbes capable of degrading chlorinated ethenes (including PCE and TCE) generally prefer a pH ranging from 6 to 9 standard units (Wiedemeier *et al.*, 1998). To determine the pH at the site, samples were obtained from the cored samples taken from the relevant depths, and were stored in airtight bottles and sent to the School of BEEH at the University of KwaZulu-Natal for analysis of pH by the author. All the pH measurements were made using a method described by YSI international (YSI, 2001), which measures the pH of a 1:1 soil suspension in the presence of a 0.01 molar concentration $CaCl_2$ salt solution. The pH was measured in the presence of a $CaCl_2$ salt due to the following benefits:

- The pH of the sample is independent of dilution over a wide range of sample to solution ranges (Peech, 1965)
- The pH is almost independent of the soluble salt concentration for nonsaline samples (Hendershot *et al.*, 1993) and thus truly reflects the degree of base saturation or the lime status of the sample regardless of the time of year that the sample was taken (Peech, 1965)
- Since the 0.01 molar concentration $CaCl_2$ solution is approximately equivalent to the total electrolyte concentration of the soil solution of a non-saline soil at optimum field water content, the pH measured represents more closely the pH of the sample solution under actual field conditions (Peech, 1965)

- Because the suspension remains flocculated, errors due to the liquid junction potential are minimised (Peech, 1965)
- No significant differences in sample pH determination are observed for moist or air-dried samples (Hendershot *et al.*, 1993).

It should be noted however; that the pH measured in a solution with a 0.01 molar concentration $CaCl_2$ salt added is about 0.5 pH units lower than that measured using only distilled water (Peech, 1965).

Prior to measuring the pH, the pH electrode was calibrated using pH 7 and pH 10 standard solutions to ensure accuracy. To measure the pH, using the method described by YSI (2001), 5 g of soil and 5 ml of distilled water were added to a 50 ml beaker and mixed thoroughly. After letting stand for ten minutes, a drop of $CaCl_2$ solution (made up to one molar concentration, to take into account the dilution effect) was added to the soil solution and stirred intermittently for 30 minutes. The pH was then measured using a portable meter (HI8424 microcomputer pH meter by HANNA instruments) and a pH electrode (HI1230B by HANNA Instruments). A temperature probe (HANNA instruments) was inserted into the sample when measuring the pH to take into account the affects of temperature on pH (Peech, 1965). The meter measures the pH to an accuracy of ±0.01 pH at 20°C (Hanna Instruments, 2005).

4.2.4 Temperature

Temperature affects the metabolic activity of bacteria. At temperatures greater than 20 ^{o}C biochemical processes are accelerated, resulting in faster rates of reductive dechlorination (Wiedemeier *et al.*, 1998). The temperature was measured by the author immediately after the material was sampled, by using a portable meter (HI8424 microcomputer pH meter by HANNA instruments) and a temperature probe (by HANNA instruments), which was pushed directly into the sample core to obtain a reading. Since the meter was calibrated at the factory (Hanna Instruments, 2005), the calibration of the temperature electrode was not required. The meter measures the temperature to an accuracy of ±0.4°C at 20°C (Hanna Instruments, 2005).

4.2.5 Carbon source

During the reductive dechlorination of chlorinated ethenes, a major requirement is the presence of a carbon source to the bacteria. This carbon can be from natural sources, or from anthropogenic sources (Wiedemeier *et al.*, 1998). The natural carbon source was measured as soil organic matter (SOM). With regard to the anthropogenic sources of carbon, BTEX compounds are likely to be the most important at the site (Duthe, 2004), and so only these were measured. The measurement of SOM and BTEX compounds will be described in the following sections.

4.2.5.1 Soil organic matter

The measurement units for TOC differ between the original points system (where the carbon sources was quantified in groundwater) (Wiedemeier *et al.*, 1998) and the measurements made in the vadose zone (where the carbon source is quantified in solid samples); consequently, new thresholds were devised (Section 4.1). In addition, the TOC was converted to a soil organic matter (SOM) value by multiplying by 1.724, which is called the van Bemmelen conversion factor (Nelson and Sommers, 1996). SOM was used since it is the primary natural source of carbon to bacteria in soils (Rosenbrock *et al.*, 1997; Wiedemeier *et al.*, 1998; Ma *et al.*, 2003). The term SOM encompasses all of the organic components of natural soil, such as intact plant and animal tissues and microorganisms, dead roots and other recognizable plant residues, and organic substances no longer identifiable as plant tissues (Plank, 2001). The amount of SOM in the surface layer of mineral soils can vary from less than 1% in coarse-textured sandy soils to more than 5% in fertile grasslands. Warm, humid climates, as found at the site, are conducive to microbial activity throughout most of the year and, as a result, SOM does not accumulate extensively. Hence, the organic matter content is typically less than 3% in these areas (Plank, 2001). According to Laing (2006), soil microbes require at least 2.5% TOC for increased growth. Using the van Bemmelen conversion factor, this equates to 4.31% SOM.

The samples for SOM analysis were obtained from the cored samples, taken from the relevant depths, and stored in airtight plastic bottles, and kept cool to minimise microbial activity which would otherwise use up the organic carbon store. The TOC content was determined by a technician in the Department of Soil Science at the University of KwaZulu-Natal using the

Walkley-Black oxidation procedure which measures the TOC as a percent (measured as milligrams of total organic carbon per milligrams of air-dried soil). This procedure measures the active or decomposable organic carbon in the soil because plant residues and humus are oxidised, while carbon present as graphite and charcoal is not. Because the correction factor used in the Walkley-Black procedure (1.33 in this case, used to take into account the incomplete oxidation of organic carbon during this procedure) is variable depending on the soil used, the procedure should be considered to give an approximate or semi-quantitative estimate of organic carbon in soil (Nelson and Sommers, 1982). The TOC was then converted to an SOM content using the van Bemmelen factor (Nelson and Sommers, 1996).

4.2.5.2 BTEX compounds

Anthropogenic sources of carbon are important in reductive dechlorination since they result in rapid and extensive degradation of PCE, TCE and DCE (Wiedemeier *et al.*, 1998). The BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) are likely to be the primary source of anthropogenic carbon at the site (Section 4.1). According to Wiedemeier *et al*. (1998), a concentration of BTEX compounds above 0.1 mg/l (which can be taken as being equivalent to 0.1 ppm, as described in Section 4.1) results in an enhanced potential for reductive dechlorination.

The samples for BTEX compound analysis were obtained from the core samples, which were obtained from the relevant depths, and placed into glass vials, with airtight lids with rubber septa. They were kept cool to prevent volatilisation of the compounds, and were analysed for benzene, toluene, ethylbenzene, and xylenes by the Centre for Specialised Environmental Analysis at the CSIR in Modderfontein, South Africa, using headspace Gas Chromatography-Mass Spectrometry (GC-MS) based on the United States Environmental Protection Agency (US EPA) methods 5021 and 8260 for volatile organic compounds. The concentrations of benzene, toluene, ethylbenzene, and xylenes were then summed to ascertain the total concentration of BTEX compounds in the material. The concentration of the BTEX compounds in the interstitial water of the material (which is available to the bacteria) was then calculated by dividing the total concentration of BTEX compounds (measured as µg/kg) by the water content (measured as g/g on a dry-weight basis), and converted to ppm. This calculation is described in Appendix C.

4.2.6 Pollutants and daughter products

The measurement of the pollutants and daughter products was used to establish their type, concentration, and distribution at the site (Wiedemeier *et al.*, 1998). If TCE, DCE and VC are present at any concentration, and can be shown to be the daughter products of PCE, TCE and DCE respectively (as opposed to originating in the waste material released into the site), there is a strong indication of reductive dechlorination occurring.

As with the BTEX compounds, the samples for the analysis of the pollutants and daughter products were obtained from the cored samples, which were taken from the relevant depths, and were placed into glass vials, with airtight lids with rubber septa, and kept cool to prevent volatilisation. They were analysed for PCE, TCE, DCE and VC by the Centre for Specialised Environmental Analysis at the CSIR in Modderfontein, South Africa, using the same methods as were described for the BTEX compounds.

Using the methods described in this chapter, the spatial variability of all the parameters that determine the potential for reductive dechlorination at Dam 2 and Dam 3/4 were measured. The measurement of redox potential was also used to establish the spatial variability of the oxidation potential. In addition to the spatial measurements, the temporal variation in the redox potential was used to ascertain the seasonal variation in the potential for reductive dechlorination and oxidation. These results will be summarised and described in the following chapter. Since vegetation affects some of the parameters, this influence will also be described in the following chapter.

5. RESULTS

Spatial measurements were made at various sites and depths at Dam 2 and Dam 3/4 to determine the spatial variability of all the parameters that affect the reductive dechlorination of PCE and TCE and the oxidation of DCE and VC. The parameters measured to establish the potential for reductive dechlorination were water content, redox potential, pH, temperature, the carbon source (including the measurement of soil organic matter and BTEX compounds) and the pollutants and daughter products; and the measurement of redox potential was used to assess the potential for oxidation. These spatial measurements will be described in the following sections. Where depths or sites differ significantly from elsewhere in each dam, they are discussed in more detail. This is especially applicable to the sample sites at Dam 3/4 which include each of the two dams that originally made up the present dam, and as a result are not as homogenous as the measurement sites at Dam 2; hence, where necessary, Sites 341 and 342 are described separately. In addition to the spatial measurements, the temporal variation in reductive dechlorination and oxidation was measured using the continuous measurement of redox potential since the redox potential is useful as an indicator of the seasonal change in the potential for reductive dechlorination and oxidation (Section 4.2 in Chapter 4). The temporal measurement results will also be described in the following sections. Since plants can affect the water content, redox potential, pH and the organic matter content, and affect the concentrations of PCE, TCE, DCE, VC and BTEX compounds through phytoremediation mechanisms (Section 3.3 in Chapter 3), and these parameters are used in the determination of the potential for reductive dechlorination and oxidation, the influence that vegetation has on each of these parameters will be included in this chapter.

5.1 Water Content

Since the soil water content was not described in the original points system by Wiedemeier *et al.* (1998) because the points system was devised for groundwater and not the vadose zone, thresholds were devised to quantify the affect of water content on reductive dechlorination in the vadose zone (Section 4.1 in Chapter 4). At water contents higher then 81% saturation reductive dechlorination is expected to be promoted, and one point was allocated to this threshold; while at water contents below 38% saturation, the potential for reductive

dechlorination is expected to be reduced, and one negative point was allocated to this threshold.

At Dam 2, the water content was only calculated at Site 22 due to the difficulty in obtaining samples for the analysis of the materials physical properties. However, this is unlikely to be problematic due to the stratification of wastes and the uniform degree of natural attenuation expected over each dam (Section 4.2), which is expected to lead to the parameters, including water content, not changing significantly horizontally within each dam. The only possible exception is the 8 m depth at Site 25, which was noted as being unusually dense compared to the other depths at 8.25 m (as noted in Table B-6 in Appendix B), which would typically lead to a higher percent saturation. However, the measured gravimetric water content measured at 8 m at Site 25 was noted as being lower then the rest of the profile, as shown in the results summarised in Table B-6 in Appendix B, which will result in a percent saturation that is not likely to be significantly different from the same depth at other sites at Dam 2. Due to the expected similarity in the water contents at each corresponding depth down the profile between the sites at Dam 2, all the sites were assumed to have the same water content as Site 22 at each respective depth, so as to allow for a comparison using the points system, which will be described in Chapter 6. At Dam 3/4 both sites were sampled to determine the water content down the profile because Dam 3/4 was initially divided into two dams, which had slightly different waste applications and thus water contents, and the sample sites lie on each of the old dams. The water content measurements for each dam are summarised and described in the following sections. The data are shown in Appendix B.

- **Dam 2**

At Site 22 the water content could not be established for the 0.3 m depth as it was too dry and the sample crumbled. Since the vadose zone points system requires a full set of results down the profile, the value needs to be estimated. It can be assumed that the 0.3 m depth had a lower water content then the 0.5 m depth (which had a value of 38.8% saturation) due to the dry nature of the sample, and thus a water content below 38% saturation was assumed.

Looking at the trend in water content in Figure 5.1, it generally increases with depth at Site 22. Since the porosity does not change significantly down-profile (as shown in Table B-3 in Appendix B), the change in water content down the profile is more likely because evaporation and root water uptake occurs from the upper profile, while deeper in the profile

the material acts as a water store. The water content is below 38% saturation in the upper 0.3 m which will lead to a lowered reductive dechlorination potential at this depth. In addition, since the 0.5 m and 1 m depth are close to the 38% saturation threshold, low rates of reductive dechlorination could occur at these depths in the future if the profile dries further. At 6.5 m and 8.25 m the percent saturation was higher than 81% saturation, which will promote anaerobic conditions and a higher potential for reductive dechlorination. However, a high water content does not always lead to conditions that promote reductive dechlorination, as will be described in Section 5.2.

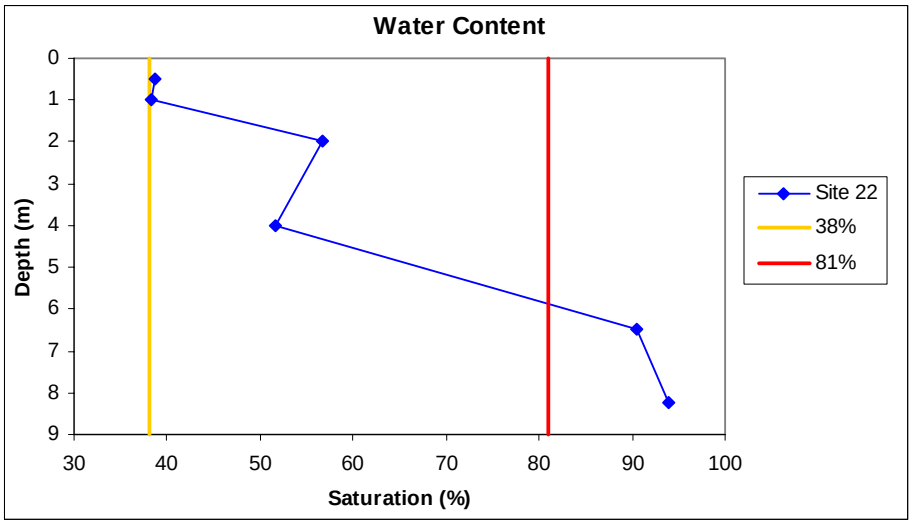

Figure 5.1 Percent saturation results for Site 22 at Dam 2, including thresholds, to determine spatial variability.

- **Dam 3/4**

At Dam 3/4 the samples at 2 m at Site 341 and 1 m at Site 342 needed to be discarded because the bulk density values were erroneous, likely due to slightly disturbed samples which necessitated the estimation of the sample volume, which lead to errors. In addition, some values (8.25 m at Site 341 and 4 m and 6.5 m at Site 342) could not be measured because the material was either too soft or too coarse to get an adequate core sample to test the physical properties of the samples. Hence, the values at these depths need to be estimated, since the vadose zone points system requires a full set of results down the profile. Because the 2 m depth at Site 341 is unlikely to be similar to the 4 m depth due to the coarse layer being present at 4 m (as noted in Table B-7 in Appendix B), the missing value at 2 m is most likely to be similar to the 1 m depth. At 8 m at Site 341 the material was too coarse to obtain a sample (also noted in Table B-7 in Appendix B), and since this coarse layer holds less water (as will be described in the following paragraph), the missing value at 8 m was assumed to

have a similar water content as 6.5 m, which is close to this depth and was also noted as being coarse in Table B-7 in Appendix B. At Site 342 the erroneous value at 1 m can be assumed to be similar to the values measured at the 0.5 m depth since in the field notes (Table B-8 in Appendix B) this depth was noted as not being significantly different from the 0.3 m and 0.5 m depths. At 4 m the material was noted in the field notes (in Table B-8 in Appendix B) as having a softer texture than the 6.5 m sample. It is likely that the soft nature of the material at this depth is due to the same reasons as the 2 m depth, which was also soft, and hence the 4 m depth was given a value equal to the 2 m depth. At 6.5 m and 8.25 m the material became slightly more dense, as noted in the field notes (Table B-8 in Appendix B), thus the missing 6.5 m depth was assumed equal to the 8.25 m depth.

Referring to Figure 5.2, at Site 341 the profile was wetter near the surface (the water content peaked at 0.5 m) and became dryer down the profile, which is unlike the trend at Dam 2. The high water content in the upper 0.5 m may be due to the lower porosity and high volumetric water content (VWC) at these depths, as indicated in Table B-7 in Appendix B. The lower porosity results in the pore spaces quickly being filled by water after even a small precipitation event. In addition, since Dam 3/4 is dominated by grasses (Lubke, 2006), there is less water uptake in the upper profile compared to Dam 2 which is dominated by trees (Lubke, 2006). The cause of the deeper profile being dry may be due to the coarse layer noted at 4 m to 8 m. This may be a tar residue layer, as will be described in Section 5.5.2, which was disposed of at the site (Duthe, 2004), and which accounts for the black nature of the material at these depths (noted in Table B-7 in Appendix B). This layer was noted as being made up of coarse particles in a softer matrix which had a low water holding capacity (as indicated by the lower VWC results for the 4 m and 6.5 m depths as summarised in Table B-7 in Appendix B) which leads to a low percent saturation. The water content is below the 38% saturation threshold at the depths of 4 m, 6.5 m and 8 m (since the missing 8 m depth was assumed equal to the 6.5 m depth), and as a result, the potential for reductive dechlorination will be limited at these depths. The water content is above the 81% saturation threshold in the upper 0.5 m; hence, anaerobic conditions are likely, which will lead to an increased potential for reductive dechlorination. However, as will be described in Section 5.2, a high water content does not always lead to conditions that promote reductive dechlorination.

The water content results in Figure 5.2 indicate that unlike Site 341, Site 342 has a drier upper profile, where the water content is low in the upper 1 m. This is likely to be due to the lower

VWC and higher porosity at these depths (which are summarised in Table B-8 in Appendix B). At 2 m and 4 m the water content was high, caused by a high VWC which is close to porosity. This lead to a waterlogged material with a soft texture (as noted in Table B-8 in Appendix B) due to the fine textured, highly porous material at the site (Lorentz *et al.*, 2006). At 6.5 m and 8.25 m the material became drier than the 2 m and 4 m depths due to a high porosity which leads to a lower water saturation. The water contents are all above the 38% saturation threshold, thus the water content will not be limiting to the bacteria at this site. The water content is above 81% saturation at 2 m and 4 m (since the missing 4 m value was assumed equal to the 2 m depth), and as a result the potential for reductive dechlorination is increased. However, this does not always lead to conditions that promote reductive dechlorination, as will be described in Section 5.2.

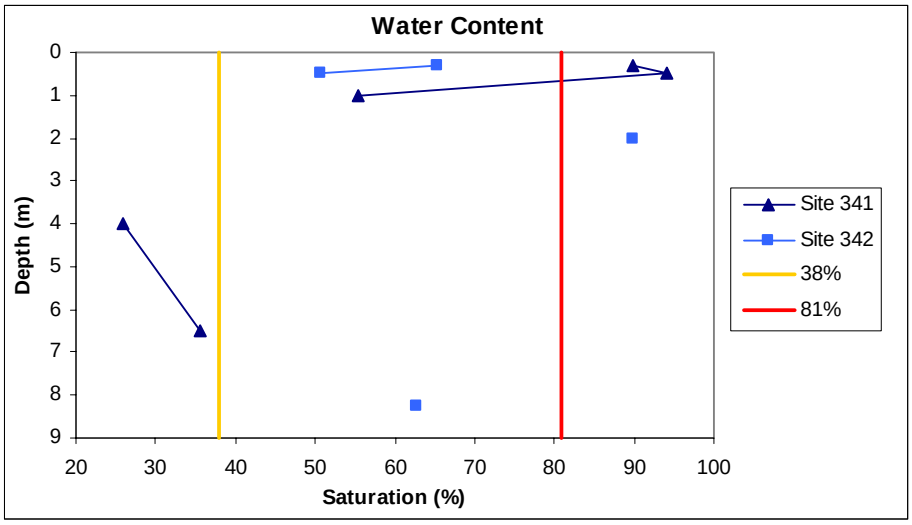

Figure 5.2 Percent saturation results at Dam 3/4, including thresholds, to determine spatial variability.

Since the measurements were made in the dry winter season, the water content on both dams is likely to increase once summer commences. This is more likely in the upper profile where the water content is more easily affected after precipitation events. The effect of water content on the redox potential, both spatially and temporally, will be described in the following section.

5.2 Redox Potential

Due to the importance of redox potential in determining the potential for reductive dechlorination and oxidation, and because the redox potential is affected by seasons

(Section 4.2.2 in Chapter 4), the redox potential was investigated both spatially and temporally at the dams. According to Wiedemeier *et al.* (1998), reductive dechlorination is possible below a redox potential (measured as Eh) of +249 mV, but is considered more likely below a redox potential of +99 mV. Aerobic oxidation occurs above +400 mV; and the anaerobic oxidation of DCE and VC occurs from +400 mV to +200 mV and from +200 mV to +120 mV for VC (AFCEE, 2004; WSRC, 2004; Pierzynski *et al.*, 2005). Since the thresholds for reductive dechlorination and anaerobic oxidation overlap, there is the possibility for conditions to exist to promote mixed microbial populations, in which some utilise reductive dechlorination and others utilise anaerobic oxidation which would allow for the co-occurrence of reductive dechlorination and anaerobic oxidation (Section 4.2.2 in Chapter 4). The results of the spatial and temporal redox potential measurements will be described in the following sections.

5.2.1 Spatial variation measurements

The spatial measurements of redox potential were made using a hand-held meter with a redox electrode attached (Chapter 4). The results for each dam are summarised and described in the following sections, and the redox potential data are shown in Appendix B.

- **Dam 2**

Considering the spatial trends of the redox potential at Dam 2, summarised in Figure 5.3, it can be seen that in general the redox potential decreases with depth. This is most likely due to the presence of roots in the upper profile and the high water content in the lower profile (Section 5.1). The roots in the upper profile promote a high redox potential by adding oxygen (Vorenhout *et al.*, 2004) and create preferential pathways which increases aeration (Pivetz, 2001; Nengovhela *et al.*, 2006). The proximity to the atmosphere further increases aeration. Unexpectedly, at the 0.3 m depth the redox potential is often lower than slightly deeper in the profile, despite being closer to the atmosphere. The reason for this may be that the roots slightly deeper in the profile add oxygen to the profile, which allows for a higher redox potential (Vorenhout *et al.*, 2004), while at 0.3 m the dry nature of the material leads to a lower root activity. The high water content in the lower profile leads to a reduced redox potential, since Nengovhela *et al.* (2006) indicated that the oxygen concentration is inversely proportional to the water content. However, the effect of water content is not as much as expected. At Site 22 (which was assumed to represent the water content at all sites at Dam 2),

the water content was above 81% at 6.5 m and 8.25 (Section 5.1). According to Maier (2000), this should lead to anaerobic conditions, which has the potential to promote reductive dechlorination at these depths; however, the redox potential is only low enough to promote reductive dechlorination at 8 m at Site 25. The reason for the higher than expected redox potentials at 6.5 m and 8.25 m may be due to oxygen replenishment from the upper layers which have a high redox potential. This is an indication that a high water content does not necessarily lead to conditions that promote reductive dechlorination. This will be described in more detail in Chapter 6. The reason for the lower redox potential at the isolated depth of 8 m at Site 25 cannot be conclusively given, but may be due to this depth being noted in the field notes in Table B-6 in Appendix B as being particularly dense, which would limit oxygen transport, leading to a lower redox potential. Unfortunately no bulk density measurements were able to be made at this depth to support this assumption. Referring to the redox potential thresholds, aerobic oxidation will occur in the upper 4 m to 6.5 m of Dam 2, and anaerobic oxidation will occur below 4 m to 6.5 m. At 8 m at Site 25, the redox potential is low enough for the possible reductive dechlorination of PCE and TCE, and to allow for the anaerobic oxidation of VC. The reductive dechlorination of PCE and TCE and the oxidation of DCE and VC will be described in more detail in Chapter 6.

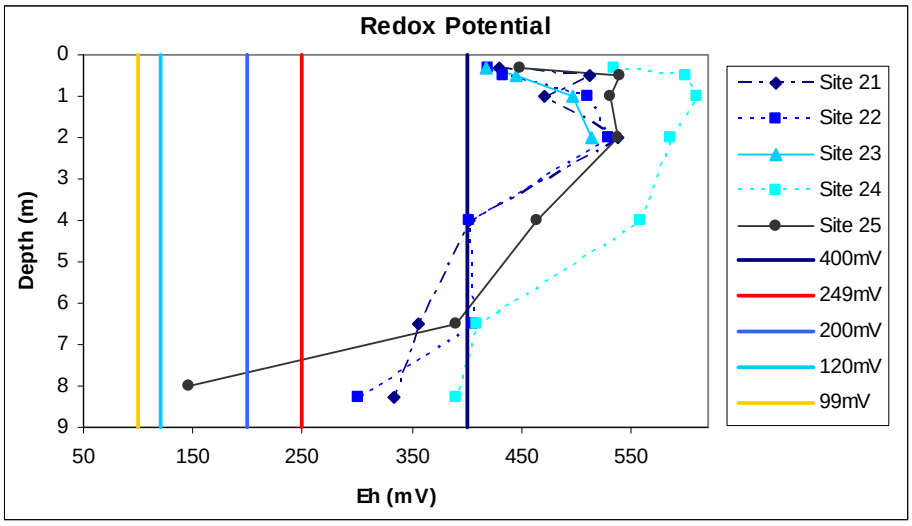

Figure 5.3 Redox potential results at Dam 2, including thresholds, to determine spatial variability.

- **Dam 3/4**

At Dam 3/4, as with Dam 2, there is a general decrease in the redox potential with depth, as is evident in Figure 5.4. In the upper profile the high redox potential is due to the actions of roots which add oxygen to the profile, and due to the proximity to the atmosphere. As with

Dam 2, the redox potential at 0.3 m is lower then the 0.5 m depth, possibly due to less root activity in this shallow depth due to the dry nature of this depth. However, unlike Dam 2, in the lower profile the low redox potential is due to the presence of a black layer, most likely to be a tar residue layer, rather than the high water content. Tar residue was disposed of at the site (Duthe, 2004), and provides a source of BTEX compounds at and below 2 m, which act as an enhanced carbon and energy source to bacteria (Wiedemeier *et al.*, 1998), thereby promoting enhanced microbial activity which leads to a reduction in oxygen levels and the decrease in redox potential (Eberts *et al.*, 2003). The distribution of the BTEX compounds will be described in more detail in Section 5.5.2. Unexpectedly, at 4 m at Site 341 and 6.5 m at Site 342, the redox potential increases before continuing the expected trend of a decrease in redox potential with depth. The reason for this has not been conclusively determined, however, it may be due to a unique chemistry at this depth. As with Dam 2, the effect of a high water content in promoting anaerobic conditions and reductive dechlorination in this dam is not as much as expected. At Site 341 the water content is above the 81% saturation threshold in the upper 0.5 m, and at Site 342 the water content is above 81% saturation at 2 m and 4 m (Section 5.1). As a result it would be expected that anaerobic conditions and possibly reductive dechlorination would be promoted at these depths. This is the case at 2 m and 4 m at Site 342; however, as shown by the redox potential results, the redox potential is higher than expected in the upper 0.5 m of Site 341. The higher redox potential in the upper 0.5 m, despite the high water content, is likely due to oxygen addition from the atmosphere and the shallow plant roots on this dam. This is an indication that a high water content does not necessarily lead to conditions that promote reductive dechlorination. This will be described in more detail in Chapter 6. Referring to the redox potential thresholds, the tar residue layer results in redox potentials at Dam 3/4 that are typically lower than Dam 2, with all the measurements taken at and below 2 m being below +249 mV and hence in the range for possible reductive dechlorination, and four measurements being within the range for likely reductive dechlorination (2 m and 8 m at Site 341, and 2 m and 4 m on Site 342). Aerobic oxidation will occur in the upper 1 m of Site 341, and anaerobic oxidation of VC will occur at 4 m at Site 341; however, the redox potential is too low to allow the oxidation of DCE at this depth. At Site 342 aerobic oxidation occurs in the upper 1 m, and at 6.5 m the anaerobic oxidation of DCE and VC occurs. At 8.25 m at Site 342, the redox potential allows for the anaerobic oxidation of VC, but not DCE. Since anaerobic oxidation and reductive dechlorination can co-occur at some depths at this dam (4 m at 341, and 6.5 m and 8.25 m at Site 342) this promotes the degradation of PCE and TCE without the accumulation of the daughter

products. The reductive dechlorination of PCE and TCE and the oxidation of DCE and VC will be described in more detail in Chapter 6.

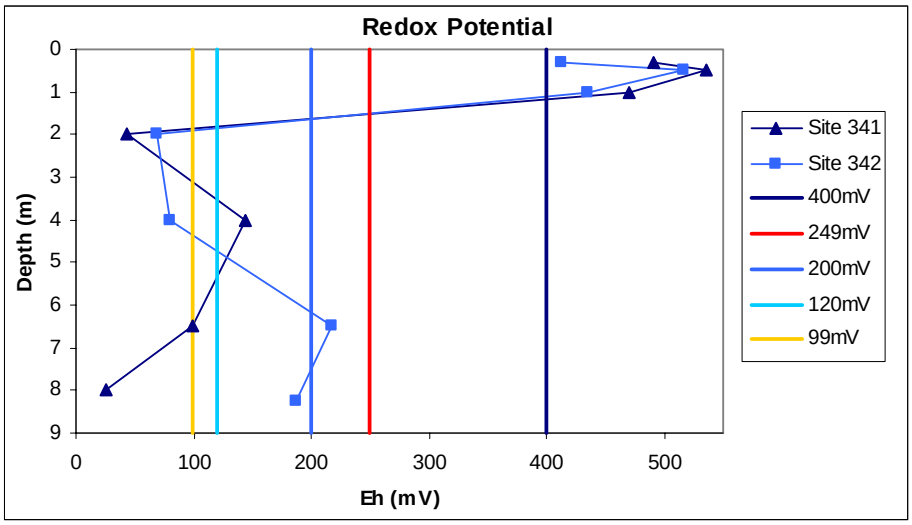

Figure 5.4 Redox potential results at Dam 3/4, including thresholds, to determine spatial variability.

Since the redox potential measurements were taken in winter, the redox potential within the profile of both dams is likely to change in summer as the water content increases, leading to a decrease in redox potential (Maier, 2000; Nengovhela *et al.*, 2006). However, as will be explained in the following section, this is unlikely to make a significant difference to the potential for reductive dechlorination or oxidation within the dams.

5.2.2 Temporal variation measurements

The temporal variability in redox potential was measured using redox electrodes permanently installed at various depths near Site 21 at Dam 2 (Chapter 4). Since problems with the electrodes may develop during installation and during the course of the measurements, a reading obtained using these electrodes (on the 16 May 2006) was compared to those made during the spatial measurements using the more dependable hand-held meter on the 25th and 26th May 2006, so as to establish possible errors with the redox electrodes. Possible problems include the electrode not being water tight, the platinum not having a good connection to the brass rod, and the copper wire not being soldered on correctly (Vepraskas and Cox, 2002). The summary of the comparison results are given in Table 5.1. The comparison indicates that the readings made by the electrodes and portable meter are similar (ranging between 6 mV and 86 mV difference), except for the readings at 1 m, the reading made with the new

electrode at 2 m, and the reading at 8.25 m; where there is a difference of 246 mV, 106 mV and 92 mV respectively. The new 2 m electrode was installed after the other electrodes, as a comparison to the original 2 m probe. The difference in readings with the 1 m and new 2 m depth electrodes is most likely due to an error, and as a result these measurements were ignored. With the 8.25 m electrode, referring to Table B-1 in Appendix B, it is evident that the first two electrode measurements at 8.25 m were unexpectedly low, and increased significantly by the next readings. The reason for this cannot be determined, and as a result this electrode was also ignored due to possible errors. The results, excluding the erroneous values and adjusted for the effects of pH, are summarised in Figure 5.5.

Table 5.1 Comparison of measurements taken with portable meter and permanently installed electrodes

Depth (m)	Eh (mV) measured with portable meter	Eh (mV) measured with electrodes	Difference (mV)
0.3	429	515	-86
0.5	513	519	-6
1	471	225	246
2	537	468	69
New 2 m	537	431	106
4	402	450	-48
6.5	355	398	-43
8.25	334	426	-92

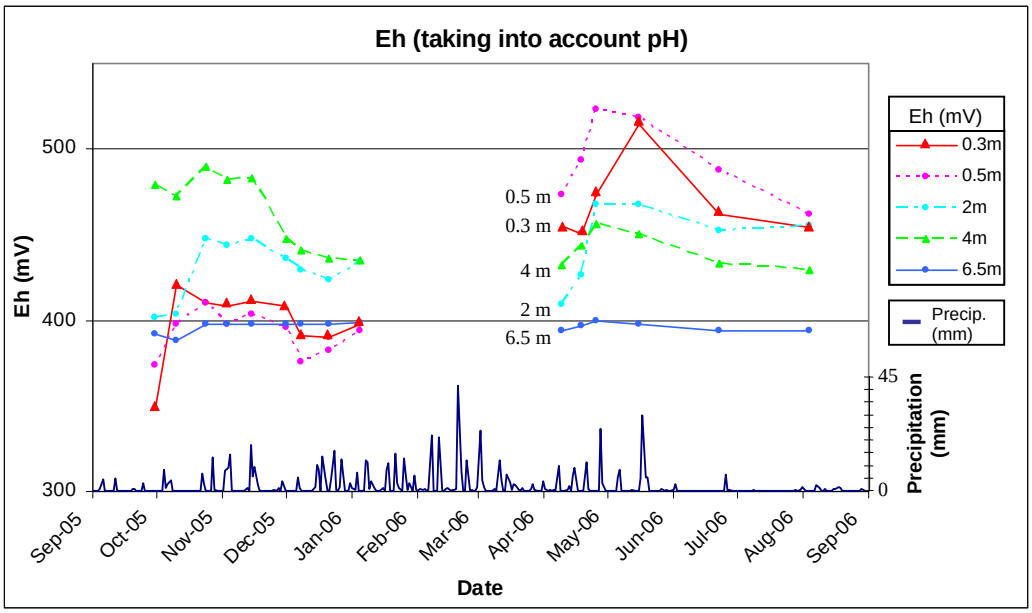

Figure 5.5 Redox potential results from various depths at Site 21 at Dam 2, including precipitation measurements, to determine temporal variability.

As was described in Section 5.1, the water content affects the redox potential; as a result, Figure 5.5 includes the redox potential results (excluding the erroneous electrodes) and the precipitation that occurred during this time to serve as an indicator of the effect of seasons on the redox potential. The precipitation values are summarised in Table B-9 in Appendix B. Referring to Figure 5.5 it is evident that there in general redox potential decreases with depth. As was described in the spatial results of redox potential in the previous section, this is as a result of increasing water content and decreasing root density with depth at Dam 2, where the electrodes were installed. The temporal trend in redox potential in Figure 5.5 indicates that from October 2005 to January 2006 the redox potential gradually decreased as the wet summer season began, since the increased precipitation increased the profile water content which reduced oxygen diffusion. From January 2006 to April 2006, although the measurements are missing since no field work was permitted during this period, the high precipitation during this period may have initially increased the redox potential, particularly in the surface soils, due to oxygen dissolved in the precipitation (Nengovhela *et al.*, 2006), and then slowly the redox potential may have decreased as the oxygen was used by bacteria and the wetter profile reduced oxygen diffusion. This may also explain the peak in the redox potential in late April and May 2006 where there is another peak in the precipitation, and the subsequent decrease in the redox potential towards September 2006. The effect of precipitation is more evident in the upper profile, as is evident in Figure 5.5 where the redox potential in the upper 0.5 m varies more between winter and summer then does the lower depths. According to Table B-1 in Appendix B, the redox potential decreased from winter (where the measurements taken on 23 June 2006 were used) to summer (where the measurements taken on 05 January 2006 were used) by 64 mV, 94 mV and 18 mV at 0.3 m, 0.5 m and 2 m respectively; while at 4 m and 6.5 m the readings increased by only 2 mV and 5 mV respectively. This is possibly because the upper profile is more easily affected by smaller precipitation events; while the deeper layers act as a water store, which receive less water than the surface soils, and are only affected after extreme precipitation events. Using the redox potential thresholds described in the previous section, the fluctuations within the profile between seasons does not bring the redox potential to within levels to promote reductive dechlorination; hence these results indicate that the possibility of seasonal redox potential fluctuations from those that promote reductive dechlorination to those that promote oxidation is unlikely. However, since the spatial measurements using the portable redox electrode (summarised in Figure 5.3) indicate that the co-occurrence of reductive dechlorination and the anaerobic oxidation of VC is possible at 8 m at Site 25, the degradation

of PCE and TCE without the accumulation of VC is a possibility in isolated zones in the lower profile within Dam 2.

Since the redox electrodes were only installed at Dam 2, the measurements need to be extrapolated to Dam 3/4 to determine the potential change in redox potential at this dam between seasons. However, the affect of seasons on the redox potential is expected to be less significant on this dam. This is due to the dominance of oxidation in the upper 1 m, and the influence of the tar residue layer at and below 2 m at this dam, which will result in a low degree of fluctuation of the redox potential. In the upper 1 m the activities of plant roots and the proximity of these depths to the atmosphere leads to an increased redox potential (Section 5.2.1). Consequently, although the redox potential will possibly decrease, it is unlikely to decrease by the amount required to bring the redox potential to levels that would promote reductive dechlorination (which requires a decrease of at least 164 mV, according to Table B-1 in Appendix B), and hence only oxidation is likely in the upper 1 m during the year. The tar residue layer present at various depths at and below 2 m acts as a source of BTEX compounds, which, as will be described in Section 5.5.2, leads to enhanced bacterial activity and the development of anaerobic conditions at and below 2 m, as was evident in Figure 5.4. Since the low redox potential at and below 2 m is likely to be determined primarily by the high levels of bacterial activity and not a high water content, the change in seasons is expected to have an insignificant affect on the redox potential. As a result, the redox potential at and below 2 m will remain within the range of promoting reductive dechlorination, and the anaerobic oxidation of VC will continue to be promoted at 4 m at Site 341 and at 8.25 m at Site 342, and the anaerobic oxidation of DCE and VC will be also continue to be promoted at 6.5 m at Site 342, as was described in the previous section. This will allow for the co-occurrence of reductive dechlorination and anaerobic oxidation at 4 m at 341, and at 6.5 m and 8.25 m at Site 342, which will lead to the degradation of PCE and TCE without the accumulation of VC.

5.3 pH

The pH is important in reductive dechlorination since it has an effect on the presence and activity of microbial populations. Reductive dechlorination of PCE and TCE is enhanced at pH values ranging from 5 to 9 standard units (Wiedemeier *et al*., 1998). The pH results for

each dam are summarised and described in the following sections. The pH data are shown in Appendix B.

- **Dam 2**

In general, the pH increases down the profile at Dam 2, as is evident in Figure 5.6. In the upper 2 m, the pH remains within the range to promote increased degradation, and does not vary significantly between the sites and depths, possibly due to the buffering effect that vegetation has on pH (Schnoor, 1997). The pH was out of range at 4 m to 8.25 m at Sites 21, 22 and 24, and at 6.5 m and 8 m at Site 25, where the pH was above pH 9, and thus enhanced reductive dechlorination will not be promoted at these depths.

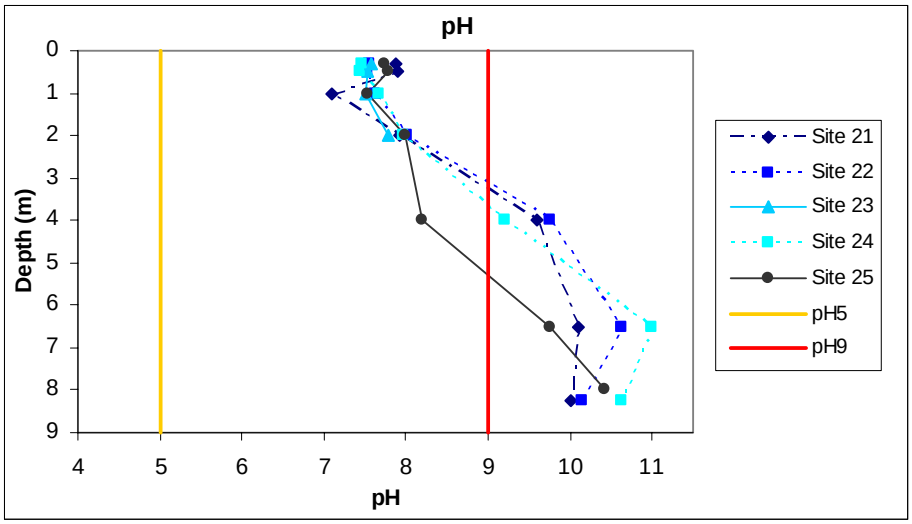

Figure 5.6 pH results at Dam 2, including thresholds, to determine spatial variability.

- **Dam 3/4**

At Dam 3/4, as with Dam 2, the general trend in pH shows an increase with depth, as is evident in Figure 5.7. Site 341 had all the pH measurements within the range for enhanced reductive dechlorination, while Site 342 had measurements above pH 9 at 6.5 m and 8.25 m, and hence these deeper depths do not promote enhanced reductive dechlorination. Unlike Dam 2, the pH in the upper 2 m of Dam 3/4 varies more between depths and sites, ranging from pH 6 to pH 8. This is possibly due to the recent vegetation of this dam (Lubke, 2006), which may not have had enough time to buffer the pH (Schnoor, 1997), and due to the slightly different wastes applied at each of the dams that now make up Dam 3/4, into which each of the measurement sites are placed. Site 341 differs from Site 342 and all the sites at Dam 2 in that although at mid-profile the pH values are similar to Site 342 and the sites at

Dam 2, at 0.3 m, 6.5 m and 8 m the pH is significantly lower than the other sites. The reason for this is unknown, but may be as a result of a different chemistry at these depths at Site 341.

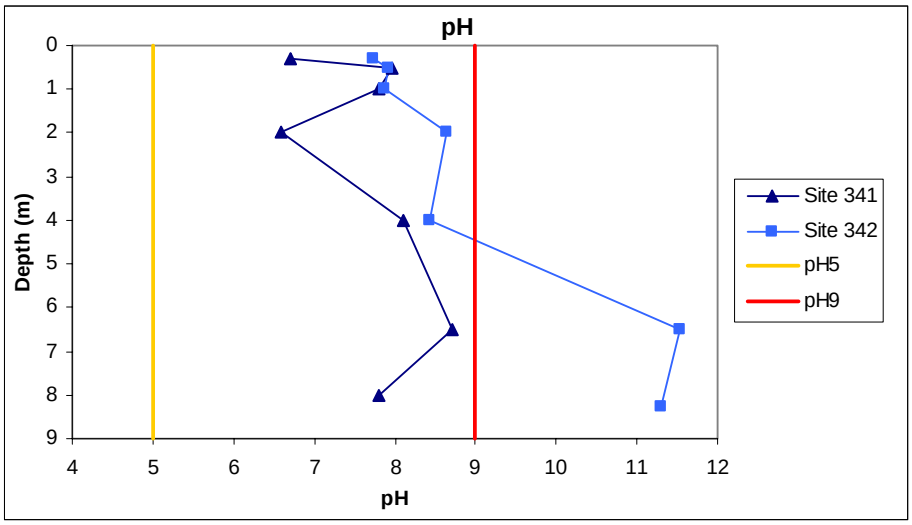

Figure 5.7 pH results at Dam 3/4, including thresholds, to determine spatial variability.

5.4 Temperature

The temperature affects reductive dechlorination by enhancing the metabolic rate of bacteria, since biochemical processes are accelerated at temperatures above 20 ^{o}C (Wiedemeier *et al*., 1998). The temperature measurements for each dam are summarised and described in the following sections. The data are shown in Appendix B.

- **Dam 2**

Referring to Figure 5.8, the trend in temperature at Dam 2 shows a general increase with depth. This may be due to a combination of effects including higher levels of microbial activity in the deeper profile which would lead to an increase in temperature (Laing, 2007), heating of the profile by the suns radiation, and a loss of heat from the surface. The only depths not above the 20 ^{o}C threshold, and which will not have an increased rate of reductive dechlorination, is 0.3 m at Sites 22 and 25. However the temperature is between 20 ^{o}C and 21 ^{o}C at 0.3 m at Sites 21, and at 0.5 m at Site 24, and hence these shallow depths could possibly fall below 20 ^{o}C, especially at night, due to radiation losses from the surface. Since these measurements were made in winter, this is not likely to be a problem in summer, when the general temperature of the profile should increase.

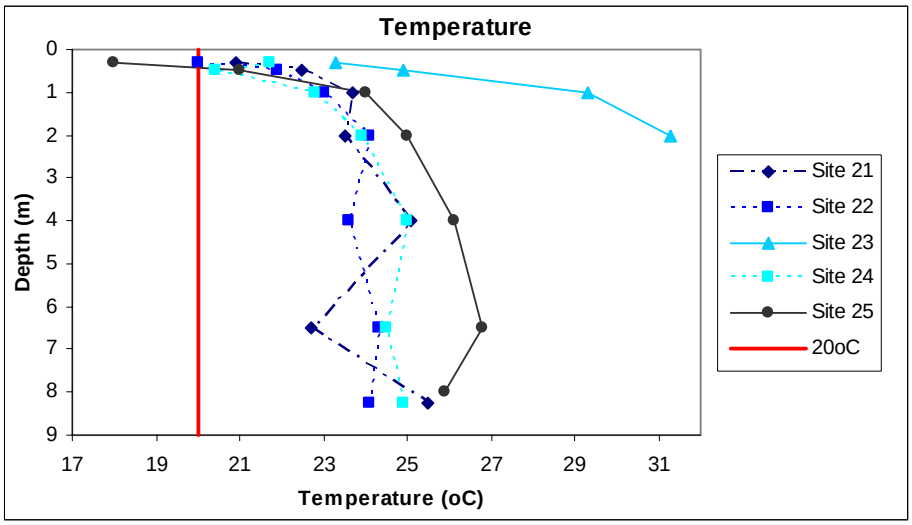

Figure 5.8 Temperature results at Dam 2, including threshold, to determine spatial variability.

- **Dam 3/4**

The trend in temperature at Dam 3/4, shown in Figure 5.9, indicates an increase with depth down to 4 m, where there is then a subsequent decrease in temperature below 4 m. The increase in temperatures in the upper 4 m may be due to similar reasons as at Dam 2 where there is heating of the profile by the suns radiation, and a loss of heat from the surface, and due to higher levels of microbial activity near 4 m which leads to an increase in temperature (Laing, 2007). The reasons for the subsequent decrease in temperature below 4 m are not certain. The temperature is only below the 20 ^{o}C threshold at 0.3 m and 8 m at Site 341 and 0.3 m at Site 342, and hence only these depths will not have an increased rate of reductive dechlorination. The temperature is between 20 ^{o}C and 21 ^{o}C at 0.5 m at Site 342, and thus could possibly fall to below 20 ^{o}C at night, especially near the surface, due to radiation losses. This is not likely to be a problem in summer, when the general temperature of the profile should increase.

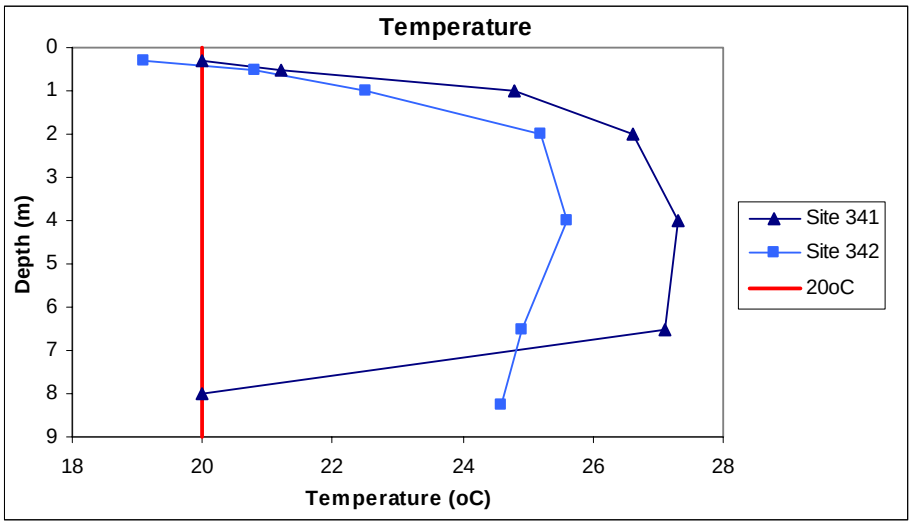

Figure 5.9 Temperature results at Dam 3/4, including threshold, to determine spatial variability.

5.5 Carbon Source

A carbon source acts as a source of energy to microbes and drives reductive dechlorination. This carbon source can be natural (organic matter) or anthropogenic (i.e.: BTEX compounds) (Wiedemeier *et al.*, 1998).

5.5.1 Soil organic matter

The thresholds for total organic carbon were altered to allow for use in the vadose zone, and were converted to represent soil organic matter (SOM) (Section 4.1 in Chapter 4). Consequently, at values of SOM above 4.31% the microbial activity is expected to be enhanced, resulting in higher rates of reductive dechlorination. The SOM measurements for each dam are summarised and described in the following sections. The data are shown in Appendix B.

- **Dam 2**

Referring to Figure 5.10, in general the SOM is highest between 0.3 m and 0.5 m at Dam 2, (except at Site 25, where the peak is at 1 m). This is likely to be as a result of the higher root activity in the upper layers, which adds SOM through the presence of root material, as well as root decay which adds humus. The SOM in some cases peaks again deeper in the profile (8.25 m at Site 22, and 4 m and 6.5 m at Site 25) which is possibly as a result of an increased

source of organic carbon at these depths, such as root material or a waste material high in organic carbon. As described by Plank (2001), in warm, humid climates (as found at the site), microbial activity is high and present throughout the year and, as a result, the SOM does not accumulate extensively. The SOM content will typically be less than 3% in these areas (Plank, 2001), which is the case throughout the profile. In addition, the SOM content is significantly less then the 4.31% threshold required for enhanced microbial growth; thus, the SOM content is insufficient to promote increased rates of reductive dechlorination. The likely reason for the low SOM content is, in addition to the effects of the warm and humid climate, because vegetation, which is the primary source of SOM, was only introduced to this dam in late December 1994 (Oliver, 2006); hence, the SOM has had little time to accumulate sufficiently.

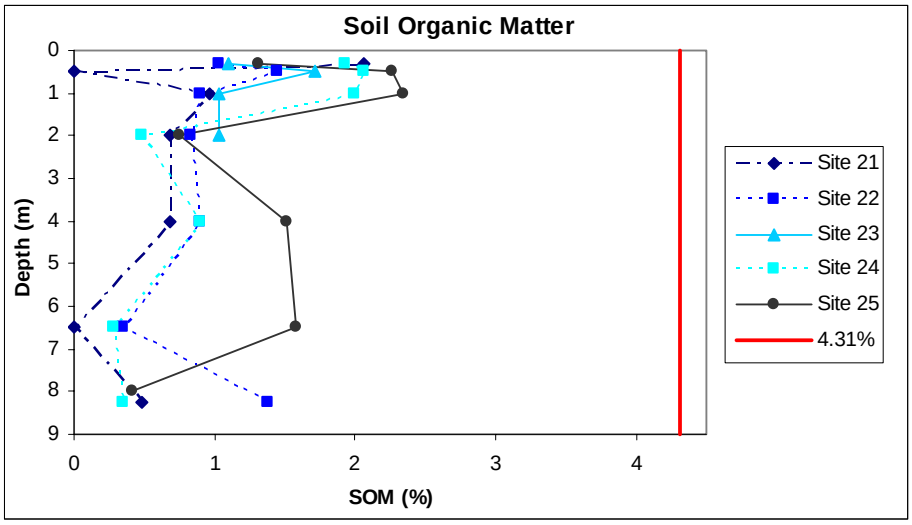

Figure 5.10 SOM results at Dam 2, including threshold, to determine spatial variability.

- **Dam 3/4**

Due to the slight differences in waste applications between each dam that now makes up Dam 3/4, at Site 341 and 342, which lie in each of these dams, the trends in SOM differ, as is evident in Figure 5.11. At Site 341 the SOM follows a general increase down the profile, peaking at 2 m and 6.5 m while at Site 342 the trend is the opposite, being higher in the upper profile. The reason for this trend may be the black layer noted at various depths in the field notes (listed in Appendix B). These depths were 2 m, 4 m and 6.5 m at Site 341, and 2 m and 4 m at Site 342. At the corresponding depths, the SOM content is higher than the rest of the profile. Hence, the black layers are most likely an organic carbon rich contaminant that was dumped into Dam 3/4, such as tar still residue that was dumped in the dams (Duthe, 2004).

Tar is high in organic carbon (Torbeyns, 2005), and as a result the tar residue will increase the SOM content. At Site 341 the SOM content is relatively high throughout the profile: SOM from plant roots maintains a high SOM content in the upper, root-rich, 1 m of profile (Lubke, 2006), while from 2 m to 8 m the tar residue layer maintains the high SOM content. At Site 342, the upper 1 m of the profile also has SOM supplied from the root zone, while at 2 m and 4 m the SOM is elevated by the presence of the tar residue layer. Beyond 4 m, where the tar residue layer ceases at Site 342, the SOM content drops significantly. This indicates the importance of the tar residue layer in the adding SOM to the deeper profile at this dam. As described previously, in warm, humid climates (as found at the site) microbial activity is high throughout most of the year, and hence the SOM does not accumulate extensively (Plank, 2001). As a result, the SOM content will typically be less than 3% in these areas (Plank, 2001), which is the case in this dam. The SOM content is also significantly lower then the 4.31% required for enhanced microbial growth (Laing, 2006) which will lead to a reduced potential for reductive dechlorination. The low SOM content is likely due, in addition to the effects of the warm and humid climate, to the recent vegetation of the dam, which began in late 1998 (Oliver, 2006), which has not allowed sufficient time for significant SOM accumulation, and due to the tar residue layer not supplying a sufficient amount of organic matter. However, despite the low amount of organic matter supplied by the tar residue layer, it is a source of BTEX compounds, which, as will be described in the following section, plays a more important role in enhancing reductive dechlorination.

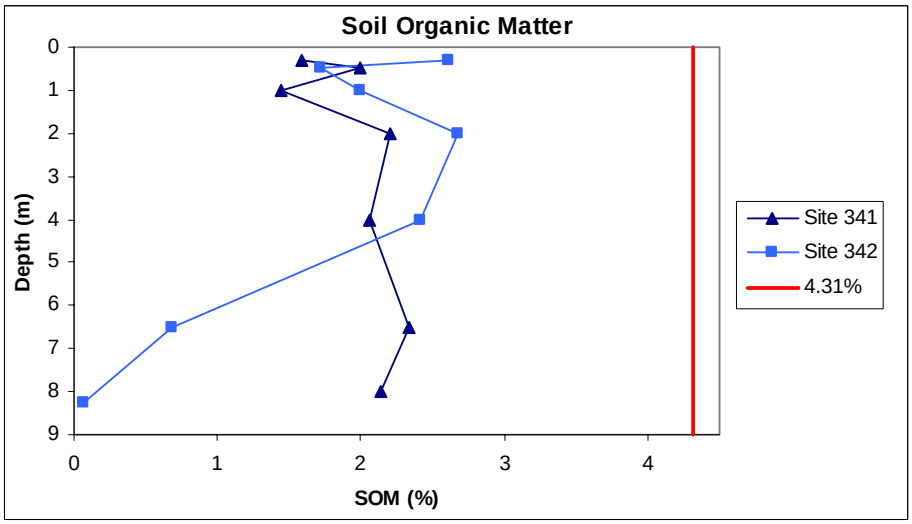

Figure 5.11 SOM results at Dam 3/4, including threshold, to determine spatial variability.

5.5.2 BTEX compounds

According to Wiedemeier *et al.* (1998), a concentration of BTEX compounds above 0.1 mg/l (which can be assumed equivalent to 0.1 ppm, as described in Section 4.1 in Chapter 4) acts as an enhanced carbon and energy source, which enhances reductive dechlorination. Due to the relatively low concentration required to enhance reductive dechlorination, BTEX compounds, when present, are an important carbon source during reductive dechlorination. The concentrations of BTEX compounds (measured in the interstitial water of the material so as to indicate the concentration available to the bacteria, as described in Section 4.1 of Chapter 4) for each dam are summarised and described in the following sections. The concentration is plotted on a logarithmic scale for ease of interpretation. Depths that were not above the detection limit were not plotted. The data are shown in Appendix C.

- **Dam 2**

Of the BTEX compounds, toluene, ethylbenzene and the xylene isomers were present at Dam 2, but benzene was not detected. In addition, the ethylbenzene and the xylene isomers are more prevalent (being found at Sites 21, 22, 24 and 25), while toluene is only detected at isolated depths at Sites 22, 23 and 25, as shown in Appendix C. The source of the BTEX compounds on this dam is undefined. There is a general increase in the concentrations of these BTEX compounds with depth, as is evident in Figure 5.12. This trend may be because free-phase BTEX compounds are classed as Light Non-Aqueous Phase Liquids (LNAPLs) (Kampbell *et al.*, 2001), which are less dense then water (Wiedemeier *et al.*, 1998) and hence will float above the saturated zone. As a result a down-profile movement of these compounds in the free-phase, through the vadose zone, may have occurred in the past. In addition, any dissolved-phase BTEX compounds may have migrated down-profile with percolating water before the vegetation was established enough to limit percolation. The low concentration of these compounds in the surface soils may also be due to the degradation and removal of BTEX compounds during phytoremediation (Collins *et al.*, 2002) during the processes of phytovolatilisation, phytodegradation and rhizodegradation (Chapter 3). The degradation and removal is predominantly from the upper 2 m of the profile due to the shallow rooting depth of the trees dominant at the site (Chapter 3). The isolated presence of toluene at 0.3 m cannot be conclusively ascertained, but may be due to the dense layer at 3.25 m (as noted in Table B-4 in Appendix B), which may have prevented any LNAPL BTEX compounds moving down-profile, thereby providing a persistent source of dissolved-phase BTEX compounds in the

upper profile, which may have been brought to the surface by root water uptake. Since then the BTEX compounds have been used up by the bacteria and through phytoremediation processes, leading to the low concentrations measured in the upper profile of Site 23. At Site 25 there is a peak in toluene, ethylbenzene and xylene isomers at 6.5 m which may be due to a superior source of BTEX compounds present in this part of the dam. Volatilisation will also lead to a reduction in concentrations in the upper profile; however, direct volatilisation from the material is not likely to play a major role, as shown by the presence of toluene in the upper 0.3 m at Site 23. Since the concentrations of BTEX compounds are above 0.1 ppm at 8.25 m at Sites 22 and 24 and 4 m to 8 m at Site 25, reductive dechlorination will be promoted at these depths (Wiedemeier *et al.*, 1998).

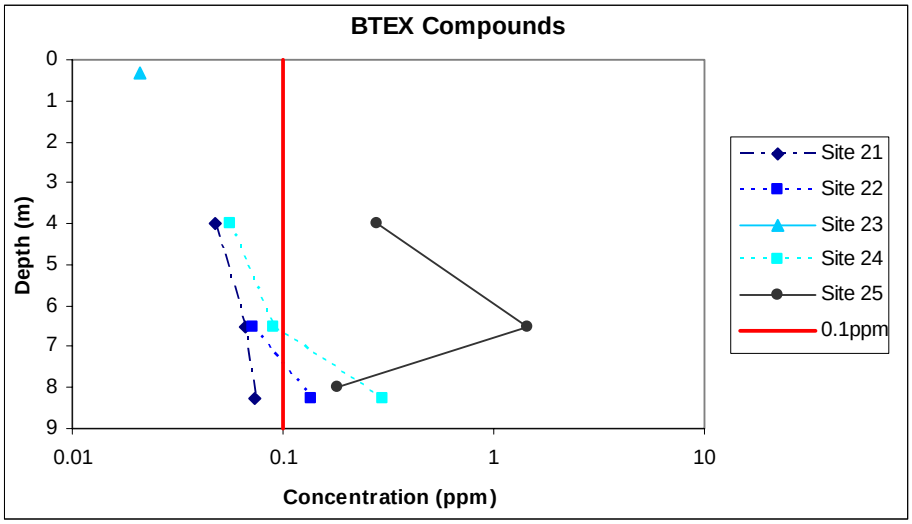

Figure 5.12 BTEX compounds results at Dam 2, including threshold, to determine spatial variability.

- **Dam 3/4**

As with Dam 2, at Dam 3/4 toluene, ethylbenzene and the xylene isomers were present, but benzene was not detected, as is evident in Appendix C. In general, there is an increase in the concentrations of these BTEX compounds with depth, as is evident in Figure 5.13. The low concentrations in the upper profile may be due to the same reasons as Dam 2, where there was a down-profile movement of the LNAPL BTEX compounds and dissolved-phase BTEX compounds in the past when there was less vegetation, and due to phytoremediation processes occurring in the root zone. Since the effect of the roots is limited to the upper 1 m of Dam 3/4 due to the predominance of grasses at this dam (Chapter 3), this explains the low concentrations of BTEX compounds in the upper 1 m. At both sites the concentrations of toluene, ethylbenzene and the xylene isomers peak at the depths corresponding to the depths

noted as having the tar residue layer present at this dam, as was described in the previous section. These depths are 2 m to 6.5 m at Site 341, and 2 m and 4 m at Site 342. This is because tar acts as a source of BTEX compounds (USEPA, 2005b), and below the tar residue layer the toluene, ethylbenzene and xylene compounds remain high (i.e. at 8 m at Site 341 and at 6.5 m and 8.25 m at Site 342), likely due to the movement of these compounds down the profile through the movement of LNAPL BTEX compounds, and through the movement of dissolved-phase BTEX compounds with percolating water. The BTEX concentrations are above 0.1 ppm at 2 m, 6.5 m and 8 m at Site 341 and from 2 m to 8.25 m at Site 342, and as a result reductive dechlorination will be promoted at these depths (Wiedemeier *et al.*, 1998).

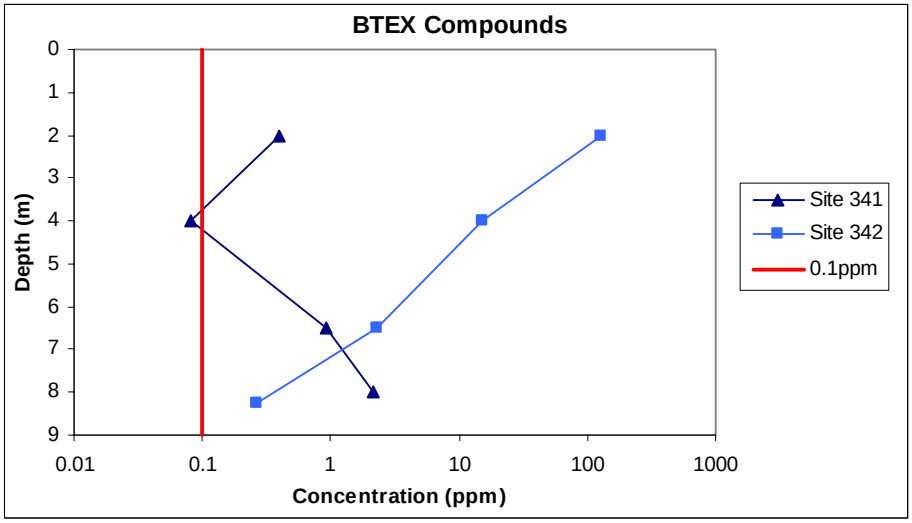

Figure 5.13 BTEX compounds results at Dam 3/4, including threshold, to determine spatial variability.

5.6 Pollutants and Daughter Products

An investigation into the concentrations of PCE and TCE and their daughter products, DCE and VC, provides an indication of the type, concentration, and distribution of the contaminants and daughter products. In addition, the presence of DCE and VC is an indication of the occurrence of the reductive dechlorination of PCE and TCE (Wiedemeier *et al.*, 1998).

The occurrence of reductive dechlorination is best ascertained by using the ratio of the parent compounds to the daughter products (Looney *et al.* 2004). To determine this ratio, the sum of the parent compound (PCE and TCE) concentrations is divided by the sum of the daughter product (DCE and VC) concentrations at each depth at each measurement site. The

calculation of this ratio is summarised in Appendix C. A ratio greater than a value of one shows that there is more parent compound then daughter product, indicating that oxidation is dominant over reductive dechlorination; while a ratio less than a value of one indicates that reductive dechlorination dominates over oxidation, which results in the accumulation of daughter products.

The results for the pollutant and daughter-product concentration measurements and the parent compound to daughter product ratio measurements done at Dam 2 and Dam 3/4 are summarised in Figures 5.14 to 5.20 and Tables 5.2 and 5.3 in the following sections. The concentrations at each site are plotted on a logarithmic scale, and bar graphs are used, for ease of interpretation. Depths that were not above the detection limit, shown in Appendix C, were not plotted.

- **Dam 2**

Referring to the parent-compound concentrations, an examination of the Figures 5.14 to 5.18 reveals that there is a general increase in the concentrations of PCE and TCE with depth. The lower concentrations of PCE and TCE in the upper profile may be due to a down-profile movement of these compounds in the dissolved-phase with percolating water in the past before the vegetation was established enough to limit percolation, and because these compounds have migrated down-profile as DNAPLs in the past due to their dense nature. The low concentrations of PCE and TCE in the upper profile may also be because these compounds were taken up by plant roots during phytoremediation mechanisms (Chapter 3). This would occur in the upper 2 m of the profile where the influence of the tree roots occurs at this dam (Chapter 3). Volatilisation directly from the surface of the dam could also lead to a reduction in the concentrations of PCE and TCE in the upper profile; however, volatilisation may not be as important as the other mechanisms since PCE and TCE are present in the upper 0.3 m of the profile. At Site 23 the concentrations of PCE and TCE are unexpectedly high. This may be because Site 23 is underlain by a dense layer at 3.25 m (as noted in Table B-4 in Appendix B), which may have trapped any DNAPL PCE and TCE in the shallow depths, thereby providing for the persistent source of dissolved-phase PCE and TCE, which could have been brought to the surface by root water uptake.

Considering the daughter products, which indicate the potential for the reductive dechlorination of PCE and TCE, generally the DCE and VC concentrations increase with

depth, as is evident in Figures 5.14 to 5.18. This is likely due to the removal of DCE and VC in the upper profile due to oxidation (indicated by the parent compound to daughter product ratio greater than a value of one) and phytoremediation mechanisms (ITRC, 2001; McCutcheon and Schnoor, 2003; USEPA, 2005a,) occurring in the upper 2 m (Chapter 3), and due to the increase in the parent compounds with depth and conditions that favoured reductive dechlorination at the lower depths of the profile (as is indicated by the parent compound to daughter product ratio that is below or close to a value of one at these depths). Volatilisation will also lead to a reduction in concentrations in the upper profile; however, direct volatilisation from the material is not likely to play a major role, as shown by the presence of DCE in the upper 0.3 m at Site 23. Since the redox potential results indicate that the oxidation of DCE and VC is likely in all the measurement depths at Dam 2, except 8 m at Site 25 where the co-occurrence of reductive dechlorination and the oxidation of VC is likely, the presence of daughter products at 6.5 m and 8.25 m at Sites 21 and 22, 4 m to 8.25 m at Site 24, 6.5 m and 8 m at Site 25, and in the upper 1 m of Site 23 indicates that reductive dechlorination occurred until the recent past which lead to the accumulation of daughter products, and only recently have conditions that promote anaerobic oxidation been promoted at these depths. Reductive dechlorination and oxidation, and the effect that these processes have on the distribution of the daughter products, will be described in Chapter 6 once the vadose zone points system has assimilated the affect of redox potential, temperature, pH, carbon sources and water content; which all influence the reductive dechlorination potential. Unexpectedly, the trend of increasing daughter-product concentrations with depth is broken at Site 23 where there is a high concentration of DCE in the upper profile despite conditions that promote oxidation, as indicated by the parent compound to daughter product ratio that is above a value of one in Table 5.2. In addition, the parent compound to daughter product ratio indicates that at Site 24 reductive dechlorination occurs at 4 m which is unlike the other sites on this dam. These differences will be explained in Chapter 6.

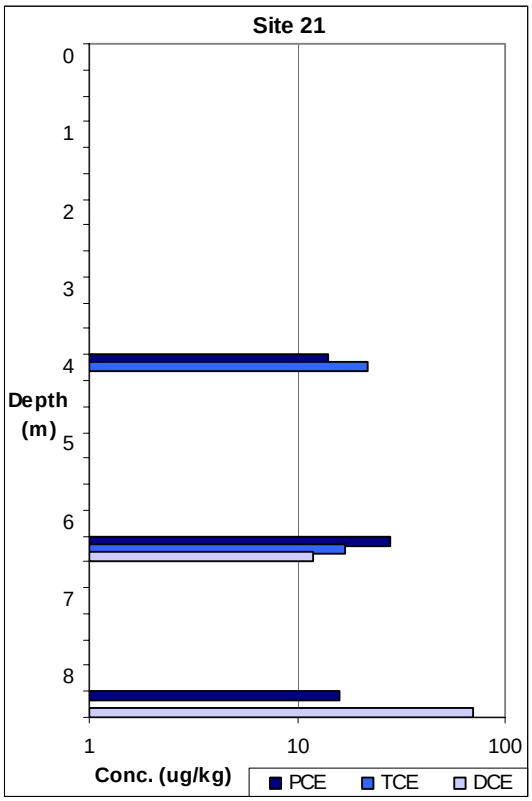

Figure 5.14 Pollutants and daughter products at Site 21.

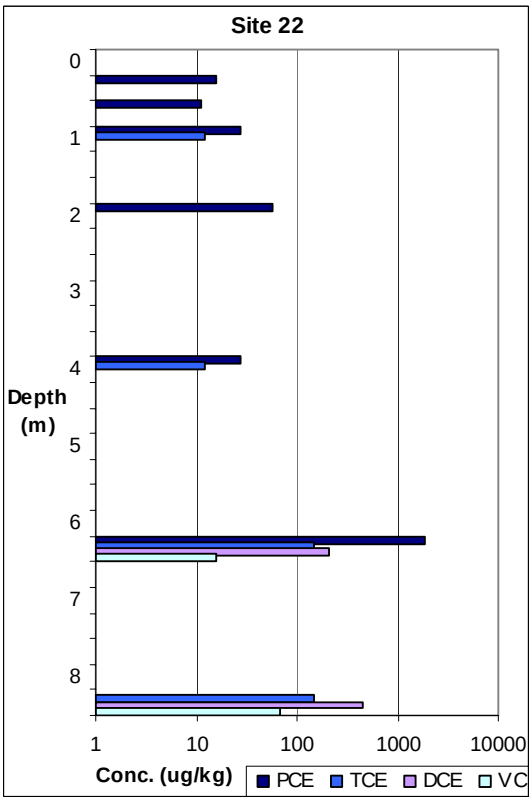

Figure 5.15 Pollutants and daughter products at Site 22.

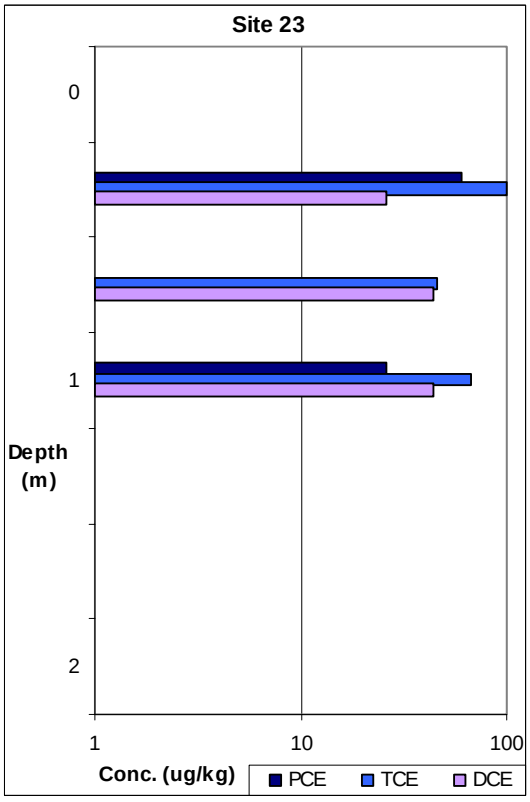

Figure 5.16 Pollutants and daughter products at Site 23.

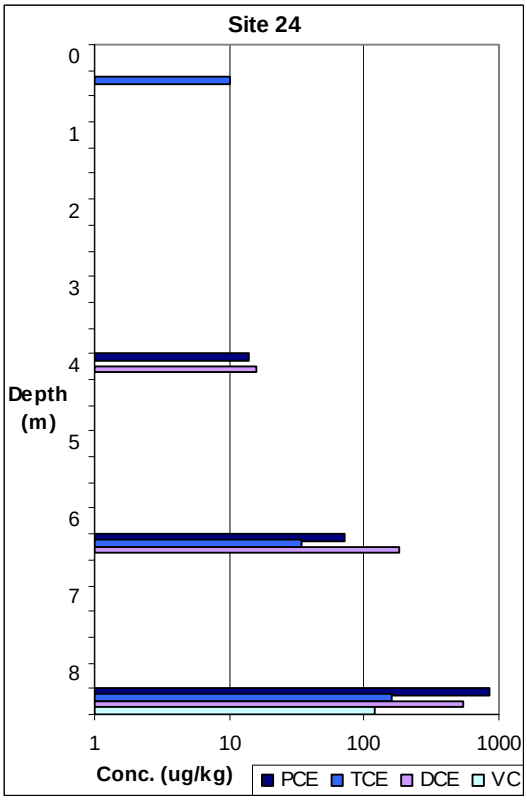

Figure 5.17 Pollutants and daughter products at Site 24.

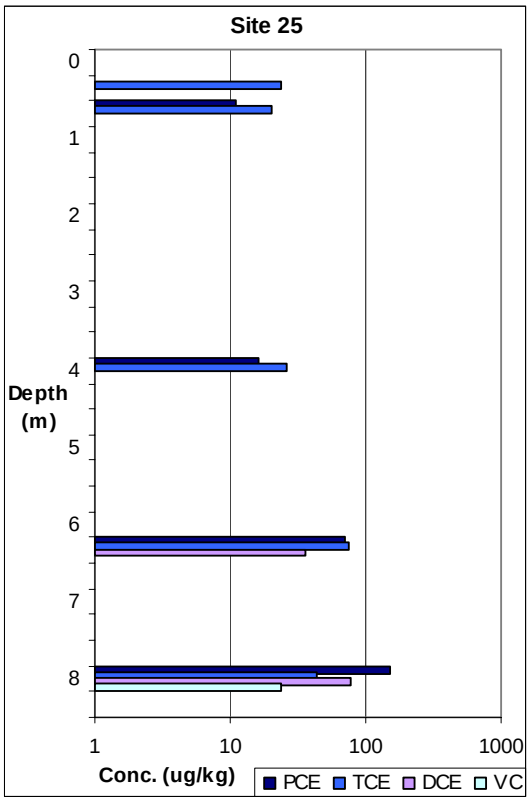

Figure 5.18 Pollutants and daughter products at Site 25.

Table 5.2 Parent compound to daughter product ratio at Dam 2 [(PCE+TCE) / (DCE+VC)]

Depth	Site 21	Site 22	Site 23	Site 24	Site 25
0.3		16	6.12	10	24
0.5		11	1.05		31
1		40	2.11		
2		57			
4	36	39	-	0.88	42
6.5	3.75	9.07	-	0.59	4.03
8	-	-	-	-	1.92
8.25	0.23	0.28	-	1.52	-

- **Dam 3/4**

As with Dam 2, at Dam 3/4 there is a general increase in the concentrations of the parent compounds with depth, which is evident in Figures 5.19 and 5.20. The lower concentrations in the upper profile are likely due to the same reasons as Dam 2, where there was a down-profile movement of these compounds in the dissolved-phase with percolating water in the past before the vegetation was established enough to limit percolation, because these compounds have migrated down-profile in the past as DNAPLs, and due to phytoremediation

mechanisms occurring in the upper profile. Phytoremediation will occur in the upper 1 m of the profile, where the influence of the grass roots at this dam occurs (Chapter 3). As described for Dam 2, although volatilisation is a possibility it is unlikely to be a significant removal mechanism, as is evident by the presence of PCE and TCE in the upper 0.5 m of the profile. Site 341 differs from Site 342 in that there are no parent compounds present in the upper 4 m of the profile, while at Site 342 they are present as shallow as 0.5 m. This is possibly due to different waste applications received at this site, with more PCE and TCE added to the upper profile of Site 342. This is possible since Site 341 and Site 342 are placed into each of the two dams that now make up Dam 3/4, both of which had slightly different waste applications. Reductive dechlorination may have removed any parent compounds in the upper profile of Site 341. Unexpectedly at 2 m at Site 342 the levels of PCE and TCE peak, despite conditions existing that should promote reductive dechlorination, as indicated by the parent compound to daughter product ratio in Table 5.3 that is close to a value of one. The reasons for this cannot be conclusively be given, but may be because the conditions have only recently promoted reductive dechlorination, and as a result there has not been sufficient time to degrade these contaminants fully.

Considering the daughter product distribution (represented in Figures 5.19 and 5.20), which indicate the potential for reductive dechlorination, there is a general increase in the DCE and VC concentrations with depth, likely due to similar reasons as Dam 2, where phytoremediation and oxidation occurred in the upper profile, and due to an increase in parent compounds with depth and conditions that favour reductive dechlorination deeper in the profile. At Site 341 reductive dechlorination is possible at 6.5 m and 8 m as is indicated by the parent compound to daughter product ratios which are close to a value of one, with the ratios also indicating that reductive dechlorination is favoured more at 6.5 m than 8 m. Since the conditions that promote reductive dechlorination involve the interaction of all the previously described parameters (redox potential, temperature, pH, the carbon sources and water content), the trends in the daughter products will be explained in Chapter 6 once the vadose zone points system has been used to assimilate the importance of all the parameters in determining the potential for reductive dechlorination. The lack of parent compounds and daughter products in the upper 4 m of Site 341 is due to reductive dechlorination and oxidation that have occurred in the past. Oxidation, as with reductive dechlorination, will be described in Chapter 6. At Site 342 the daughter products begin accumulating at and below 1 m, indicating that reductive dechlorination is promoted at and below this depth, which is

shown by the parent compound to daughter product ratio being below or close to a value of one from 1 m to 8.25 m. However, although the parent compound to daughter product ratio indicates that reductive dechlorination is occurring from 1 m to 8.25 m at Site 342, the redox potential results indicate oxidation is likely in the upper 1 m and the co-occurrence of reductive dechlorination and the anaerobic oxidation of DCE and VC occurs at 6.5 m, and at 8.25 m for VC. This indicates that reductive dechlorination occurred at these depths in the past which lead to the accumulation of daughter products, and only recently have conditions that promote oxidation been promoted. This accounts for the low concentrations of daughter products in the upper 1 m, the continued production of the daughter products at 6.5 m and 8.25 m, and the accumulation of DCE at 8.25 m at Site 342. This reductive dechlorination and oxidation will be described in Chapter 6, once the vadose zone points system has been used to assimilate the importance of all the parameters that affect the reductive dechlorination potential. There is an isolated peak in the DCE concentrations at 2 m at Site 342 which will also be explained in Chapter 6, since this is related to oxidation. In addition, the unexpected presence of VC at 4 m at Site 342 despite the absence of PCE, TCE and DCE which would act as parent compounds during reductive dechlorination will be described in Chapter 6.

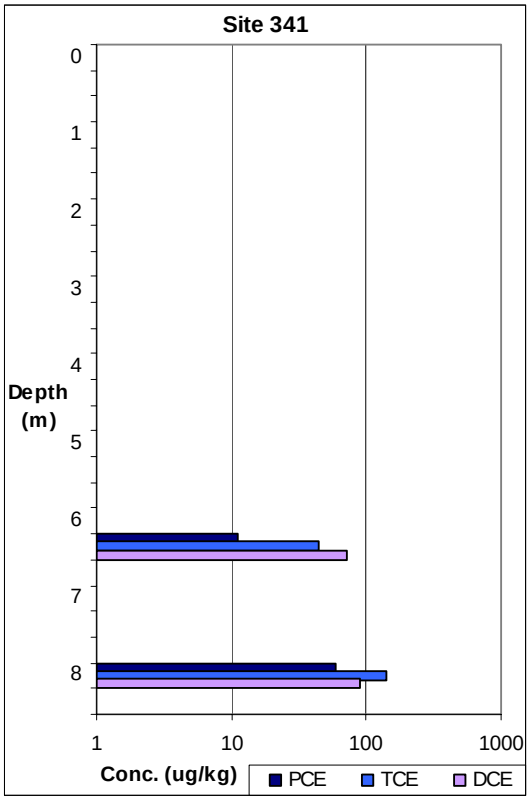

Figure 5.19 Pollutants and daughter products at Site 341.

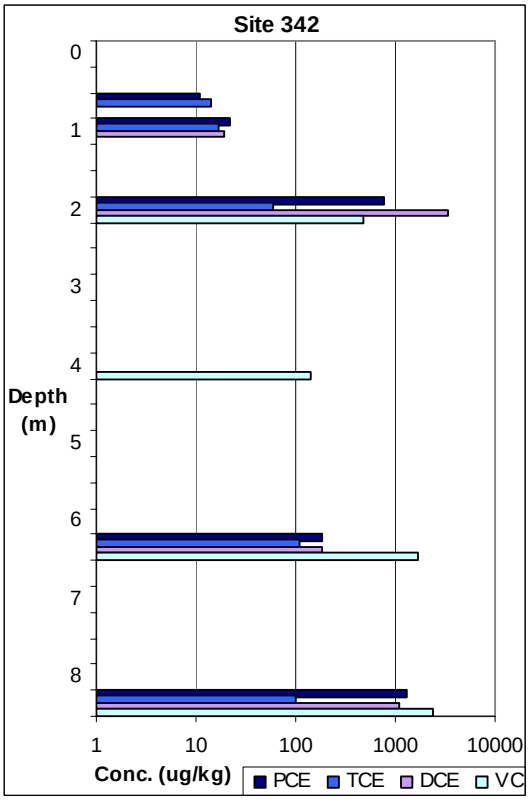

Figure 5.20 Pollutants and daughter products at Site 342.

Table 5.3 Parent compound to daughter product ratio at Dam 3/4 [(PCE+TCE) / (DCE+VC)]

Depth	Site 341	Site 342
0.3		
0.5		25
1		2.05
2		0.21
4		0.01
6.5	0.76	0.15
8	2.22	-
8.25	-	0.40

In the previous sections the spatial and temporal measurements of the parameters that affect the potential for reductive dechlorination and oxidation were outlined and discussed. In the following chapter the spatial distribution of the depths that promote reductive dechlorination and oxidation will be ascertained and described. In addition, the temporal variability of the potential for reductive dechlorination and oxidation within the dams will be described. Since vegetation affects many of the parameters that determine the potential for reductive dechlorination and oxidation, the affect of vegetation on the degradation of PCE and TCE and their daughter products will also be described in the following chapter.

6. ANALYSIS AND DISCUSSION

In this chapter the spatial distribution of depths that promote reductive dechlorination in the vadose zone at Dam 2 and Dam 3/4 will be determined by assimilating the spatial measurements of each of the parameters described in Chapter 5 using the vadose zone points system (Chapter 4). In addition to determining the potential for reductive dechlorination, the spatial distribution of the depths that promote the oxidation of DCE and VC will be ascertained based on the spatial variation measurements of the redox potential. Apart from the determination of the spatial distribution of depths that promote reductive dechlorination and oxidation, the temporal measurement of redox potential will be used to establish the seasonal fluctuation in the potential for reductive dechlorination and oxidation. The temporal measurement of redox potential is a suitable indicator of the seasonal change in the potential for reductive dechlorination and oxidation since the redox potential is affected by the water content (Maier, 2000; Nengovhela *et al.*, 2006) which is controlled by seasons, and because the redox potential is the most dominant parameter in determining the potential for reductive dechlorination as indicated by the vadose zone points table in Chapter 4, and is used to determine the potential for oxidation (AFCEE, 2004; WSRC, 2004; Pierzynski *et al.*, 2005).

Once the potential for reductive dechlorination and oxidation at Dam 2 and Dam 3/4 has been assessed, the influence of each of the parameters in determining the potential for degradation will be discussed. In addition, since the vegetation can affect some of these parameters, the influence of vegetation on the potential for degradation will be ascertained by comparing Dam 2 and Dam 3/4, and the implications for each of the dams will be discussed.

6.1 Determination of the Potential for Reductive Dechlorination

The spatial variation in the potential for reductive dechlorination was determined by using the vadose zone points system. In order to use the vadose zone points system, some of the water contents needed to be estimated due to missing water content measurements at some points on each of the dams, to ensure a fair allocation of points to each site and depth at the dams. As was described in Section 5.1 in Chapter 5, the water content was only measured at Dam 2 at Site 22, which necessitated the estimation of the water contents at the other sites at Dam 2. As was explained, the measurements are not expected to change significantly throughout Dam 2,

and as a result all the other sites at Dam 2 (Sites 21, 23, 24 and 25) were assumed to have the same water content distribution down the profile as Site 22. In addition, various depths at Dam 2 and Dam 3/4 could not be sampled, either due to the structure of the material that made it unfeasible to obtain a core sample, or due to erroneous measurements of bulk density caused by slightly disturbed samples. As a result, the missing water content values were estimated based on the values measured at other depths (Section 5.1 of Chapter 5).

Using the vadose zone points system, points were allocated using the method described in Appendix D, where the spatial results for each parameter described in Chapter 5 (summarised in Appendix B and C) were given colour coded point values based on the thresholds outlined in Table 4.2 in Chapter 4. Colour codes were used for ease of interpretation. The points were then totalled for each depth at each site; the higher the points total, the greater the potential for reductive dechlorination of PCE and TCE. The resultant point allocations, which include the estimated water content values and the point totals, are summarised in Tables 6.2 to 6.8. The tables are colour coded according to Table 6.1, which indicates the influence of the different point allocations on promoting reductive dechlorination.

Table 6.1 Key to colour coding of points result tables

Points	Influence on promoting reductive dechlorination
-2	Moderately decreased
-1	Mildly decreased
0	None
1	Mild
2	Moderate
4	High
8	Very High

Table 6.2 Points allocation to Site 21

Depth (m)	Redox Potential	Temp.	pH	Carbon Source		Water Content	Daughter Products		TOTAL
				SOM	BTEX		DCE	VC	
0.3	0	1	0	0	0	-1	0	0	**0**
0.5	0	1	0	0	0	0	0	0	**1**
1	0	1	0	0	0	0	0	0	**1**
2	0	1	0	0	0	0	0	0	**1**
4	0	1	-2	0	0	0	0	0	**-1**
6.5	0	1	-2	0	0	1	2	0	**2**
8.25	0	1	-2	0	0	1	2	0	**2**

Table 6.3 Points allocation to Site 22

Depth (m)	Redox Potential	Temp.	pH	Carbon Source		Water Content	Daughter Products		TOTAL
				SOM	BTEX		DCE	VC	
0.3	0	0	0	0	0	-1	0	0	**-1**
0.5	0	1	0	0	0	0	0	0	**1**
1	0	1	0	0	0	0	0	0	**1**
2	0	1	0	0	0	0	0	0	**1**
4	0	1	-2	0	0	0	0	0	**-1**
6.5	0	1	-2	0	0	1	2	2	**4**
8.25	0	1	-2	0	2	1	2	2	**6**

Table 6.4 Points allocation to Site 23

Depth (m)	Redox Potential	Temp.	pH	Carbon Source		Water Content	Daughter Products		TOTAL
				SOM	BTEX		DCE	VC	
0.3	0	1	0	0	0	-1	2	0	**2**
0.5	0	1	0	0	0	0	2	0	**3**
1	0	1	0	0	0	0	2	0	**3**
2	0	1	0	0	0	0	0	0	**1**

Table 6.5 Points allocation to Site 24

Depth (m)	Redox Potential	Temp.	pH	Carbon Source		Water Content	Daughter Products		TOTAL
				SOM	BTEX		DCE	VC	
0.3	0	1	0	0	0	-1	0	0	**0**
0.5	0	1	0	0	0	0	0	0	**1**
1	0	1	0	0	0	0	0	0	**1**
2	0	1	0	0	0	0	0	0	**1**
4	0	1	-2	0	0	0	2	0	**1**
6.5	0	1	-2	0	0	1	2	0	**2**
8.25	0	1	-2	0	2	1	2	2	**6**

Table 6.6 Points allocation to Site 25

Depth (m)	Redox Potential	Temp.	pH	Carbon Source		Water Content	Daughter Products		TOTAL
				SOM	BTEX		DCE	VC	
0.3	0	0	0	0	0	-1	0	0	**-1**
0.5	0	1	0	0	0	0	0	0	**1**
1	0	1	0	0	0	0	0	0	**1**
2	0	1	0	0	0	0	0	0	**1**
4	0	1	0	0	2	0	0	0	**3**
6.5	0	1	-2	0	2	1	2	0	**4**
8	4	1	-2	0	2	1	2	2	**10**

Table 6.7 Points allocation to Site 341

Depth (m)	Redox Potential	Temp.	pH	Carbon Source		Water Content	Daughter Products		TOTAL
				SOM	BTEX		DCE	VC	
0.3	0	0	0	0	0	1	0	0	**1**
0.5	0	1	0	0	0	1	0	0	**2**
1	0	1	0	0	0	0	0	0	**1**
2	8	1	0	0	2	0	0	0	**11**
4	4	1	0	0	0	-1	0	0	**4**
6.5	4	1	0	0	2	-1	2	0	**8**
8	8	0	0	0	2	-1	2	0	**11**

Table 6.8 Points allocation to Site 342

Depth (m)	Redox Potential	Temp.	pH	Carbon Source		Water Content	Daughter Products		TOTAL
				SOM	BTEX		DCE	VC	
0.3	0	0	0	0	0	0	0	0	**0**
0.5	0	1	0	0	0	0	0	0	**1**
1	0	1	0	0	0	0	2	0	**3**
2	8	1	0	0	2	1	2	2	**16**
4	8	1	0	0	2	1	0	2	**14**
6.5	4	1	-2	0	2	0	2	2	**9**
8.25	4	1	-2	0	2	0	2	2	**9**

In addition to the measurements to establish the spatial variation in the potential for reductive dechlorination, the temporal measurements of redox potential were used to determine the seasonal variation. Measurements at Dam 2 (measured near Site 21) were extrapolated to Dam 3/4 (Section 5.2.2 of Chapter 5). The potential for reductive dechlorination within Dam 2 and Dam 3/4, and its variation throughout the year will be described in the following sections.

6.1.1 Potential for reductive dechlorination at Dam 2

Referring to the point totals in Tables 6.2 to 6.6, these indicate that reductive dechlorination is possible at 8.25 m at Sites 22 and 24 and 8 m at Site 25, and that it is more likely at 8 m at Site 25. This results in the creation of daughter products at these depths. The potential for reductive dechlorination is higher at these depths due to the high concentrations of BTEX compounds which act as a carbon and energy source for bacteria which drives reductive dechlorination (Wiedemeier *et al.*, 1998), the favourable temperature which promotes microbial activity, and the high water content which should promote anaerobic conditions that promote reductive dechlorination. However, despite the water content being high enough to have the potential to promote reductive dechlorination at 6.5 m and 8.25 m at Sites 21, 22 and 24 and 6.5 m and 8 m at Site 25 (Maier, 2000), the redox potential remains too high to promote reductive dechlorination at any depths except 8 m at Site 25. This is an indication that a high water content does not necessarily promote conditions anaerobic enough to promote reductive dechlorination. Another factor that reduces the potential for reductive dechlorination in the lower profile is the high pH, which reduces microbial activity; however, the continued production of daughter products at these depths is an indication that the microbial activity is not reduced to the point that it prevents reductive dechlorination from occurring.

Since reductive dechlorination is unlikely at 6.5 m and 8.25 m at Sites 21, 22 and 24 and 6.5 m at Site 25, primarily due to the unsuitable redox potential, the presence of daughter products at these depths is thus an indication that reductive dechlorination occurred in the past, and that oxidation has recently been promoted at these depths which is still in the process of degrading the daughter products. In addition, the lower redox potential at 8 m at Site 25, which promotes reductive dechlorination and the anaerobic oxidation of VC, may be due to this depth being particularly dense (as noted in the field notes in Table B-6 in Appendix B), which would limit oxygen transport. The potential for oxidation will be described in Section 6.2. Unexpectedly, at 4 m at Site 24 DCE was measured, and since the points system does not indicate that this is likely, the reason cannot be conclusively be given, but may be because conditions were conducive to reductive dechlorination in the past but recently changed to those that favour oxidation, and the DCE has not been fully oxidised yet, as will be described in Section 6.2, when oxidation is described.

Site 23 is unlike the other sites on this dam in that DCE is present from 0.3 m to 1 m, despite the fact that the point totals in Table 6.4 indicate that reductive dechlorination is unlikely at these depths, and despite the presence of plants which can remove and degrade these daughter products through phytoremediation. The presence of these daughter products is thus an indication that reductive dechlorination occurred at these depths in the past, but recently the conditions have promoted oxidation, and hence the microbial populations are still in the process of oxidising DCE. A reason for this is that a dense layer is present at 3.25 m at Site 23 which may have trapped PCE, TCE and BTEX compounds in the upper profile in the past (Section 5.5 and 5.6 in Chapter 5). The BTEX compounds were used by the bacteria to drive the reductive dechlorination process at an enhanced rate, leading to the degradation of PCE and TCE to DCE and VC at a rate that exceeded the phytoremediation processes that removed the daughter products. Since then the BTEX compounds have been degraded and removed by the bacteria during reductive dechlorination and by plants during phytoremediation, leading to the conditions which currently promote bacterial oxidation. The potential for oxidation will be described in Section 6.2.

The temporal measurements of redox potential indicate that at Dam 2 the redox potential does not decrease between seasons to a level that will promote reductive dechlorination. However, because the spatial variation measurements indicate that at 8 m at Site 25 reductive dechlorination is possible, reductive dechlorination of PCE and TCE may be possible at isolated depths in the lower profile, especially in summer when the redox potential was shown to decrease.

6.1.2 Potential for reductive dechlorination at Dam 3/4

In the description of the spatial variation in the potential for reductive dechlorination at Dam 3/4 the measurement sites will be treated separately because each measurement site is located in each of the dams that now make up Dam 3/4, and each of these dams had slightly different waste applications. Thereafter, the temporal variation in the reductive dechlorination potential at Dam 3/4 will be described.

- **Site 341**

Referring to the point totals for Site 341 in Table 6.7, the reductive dechlorination of PCE and TCE is most likely to occur at 2 m, 6.5 m and 8 m. This is due to the favourable redox

conditions and the presence of BTEX compounds at these depths. However, the degradation at 2 m is not indicated by the production of any daughter products at this depth, and at 6.5 m and 8 m, although DCE is present, the concentrations are relatively low and no VC is produced. The lack of daughter products at 2 m may be due to the lack of parent compounds in the upper 4 m (Section 5.6 in Chapter 5), and any daughter products produced in the past may have been removed due to a down-profile movement of these compounds with percolating water before the vegetation was established enough to limit percolation. The low concentrations of DCE and lack of VC at 6.5 m and 8 m may be due to the low water content at these depths, and reduced temperature at 8 m, which has led to a lowered microbial activity and hence, lowered potential for reductive dechlorination.

In the upper 0.5 m of the profile at Site 341, although the water content was high enough to have the potential to lower the redox potential, the redox potential remained too high to promote reductive dechlorination. This is an indication, again, that a high water content does not necessarily lead to conditions that promote reductive dechlorination. The high redox potential is likely due to oxygen additions from the atmosphere and from the plant roots due to oxygen additions (Vorenhout *et al.*, 2004) and the creation of preferential pathways which allows for oxygen ingress into the soil (Pivetz, 2001; Nengovhela *et al.*, 2006). The potential for oxidation at this site will be described in more detail in Section 6.2.

- **Site 342**

The point totals in Table 6.8 indicate that at Site 342 the potential for reductive dechlorination is highest from 2 m to 8.25 m. This results in increased daughter product creation at these depths. The reductive dechlorination of PCE and TCE is promoted by the favourable redox potential and temperature, and the presence of BTEX compounds at these depths. The low redox potential from 2 m to 8.25 m is due, in part, to the high water content at 2 m and 4 m. The high water content results in a particularly low redox potential due to reduced oxygen diffusion, leading to a particularly high potential for reductive dechlorination at 2 m and 4 m compared to the other sites at Dam 2 and Dam 3/4, and also allows for a reduced redox potential at 6.5 m and 8.25 m due to limited oxygen transport from the upper layers through the 2 m and 4 m depths. This promotes reductive dechlorination at 6.5 m and 8.25 m, despite the recent promotion of oxidation at these depths (which will be described in Section 6.2), thereby allowing for the co-occurrence of reductive dechlorination and the anaerobic oxidation of DCE and VC at 6.5 m and VC at 8.25 m which accounts for the accumulation in

daughter products at these depths. Despite the pH being prohibitive at 6.5 m and 8.25 m, the presence of daughter products is an indication that the microbes are still involved in reductive dechlorination, although this may be at a reduced rate. At 4 m VC is present despite a lack of PCE, TCE and DCE which act as parent compounds. This may be because reductive dechlorination at this depth has promoted the degradation of PCE, TCE and DCE, so that they have been fully removed from this depth, but since the degradation of VC under anaerobic conditions requires conditions that are more anaerobic then required to degrade PCE, TCE or DCE (Vogel and McCarty, 1985), the redox potential may not be anaerobic enough to degrade VC, which has led to its accumulation.

Although DCE is present at 1 m at Site 342, which indicates the occurrence of reductive dechlorination, the point totals in Table 6.8 indicate that reductive dechlorination is not as likely at this depth compared to the lower depths. In addition, DCE is present at 1 m despite the potential for phytoremediation at this depth. The reason for the presence of this daughter product at 1 m may be that in the past conditions favoured enhanced reductive dechlorination that produced DCE and VC at a rate that exceeded their removal via phytoremediation, but recently conditions that promote oxidation have developed which is removing these daughter products. This enhanced degree of reductive dechlorination may have been caused by the presence of BTEX compounds at this depth, but since then the BTEX compounds have been used up by the bacteria during reductive dechlorination and plants during phytoremediation, leading to conditions that now favour oxidation. In addition, at 2 m the concentration of DCE is particularly high, which is possibly due to reductive dechlorination and only the anaerobic oxidation of VC being promoted at this depth in the past, leading to the accumulation of DCE. The development of conditions that promote oxidation at 1 m, and the co-occurrence of reductive dechlorination and anaerobic oxidation at 2 m will be described in more detail in Section 6.2, when oxidation at the site is described.

The extrapolation of the temporal variation measurements of redox potential from Dam 2 indicate that the promotion of reductive dechlorination of PCE and TCE at various depths at and below 2 m at Dam 3/4 is unlikely to fluctuate significantly between seasons due to the limited fluctuation expected in the redox potential between seasons due to the high levels of bacterial activity, promoted by the presence of BTEX compounds, which promotes a low redox potential that is not significantly affected by the changes in water content between seasons. Consequently, reductive dechlorination and the anaerobic oxidation of VC will

continue to be promoted at 4 m at Site 341 and at 8.25 m at Site 342, and reductive dechlorination and the anaerobic oxidation of DCE and VC will be also continue to be promoted at 6.5 m at Site 342. Oxidation will be described in the following section.

As is evident, the reductive dechlorination of PCE and TCE results in the accumulation of DCE and VC at both Dam 2 and Dam 3/4, which can be particularly problematic due to the highly carcinogenic effects of VC (Chappell, 1997). However, DCE and VC can be degraded through the mechanism of oxidation, which breaks down these compounds to harmless by-products (Wiedemeier *et al*., 1998; WSRC, 2004) such as carbon dioxide, water and chloride (Dinicola *et al*., 2002). The potential for oxidation throughout the Dam 2 and Dam 3/4 will be described in the following section.

6.2 Determination of the Potential for Oxidation

The presence of conditions that allow for oxidation can be determined using the redox potential measurements (Patrick *et al*., 1996). Aerobic oxidation occurs above a redox potential (measured as an Eh) of +400 mV, and the anaerobic oxidation of DCE and VC occurs from +400 mV to +200 mV and from +200 mV to +120 mV for VC (AFCEE, 2004; WSRC, 2004; Pierzynski *et al*., 2005).

The spatial distribution of depths at each dam that promote each form of oxidation were colour coded, for ease of interpretation, based on the redox potential measurements, given in Appendix B, according to steps outlined in Section D-2 of Appendix D. The key to the colour codes and the colour coded results are shown in Tables 6.9 and 6.10 respectively.

Table 6.9 Key to colour codes for oxidation potential

Degradation Mechanism	**Threshold**
Aerobic Oxidation of DCE and VC	Eh > 400 mV
Anaerobic Oxidation of DCE and VC	400 mV>Eh> 200 mV
Anaerobic Oxidation of VC	200 mV>Eh>120 mV
Oxidation Unlikely	Eh < 120 mV

Table 6.10 Summary of oxidation occurring at Dam 2 and Dam 3/4 based on redox potential measurements

Depth (m)	Dam 2					Dam 3/4	
	Site 21	Site 22	Site 23	Site 24	Site 25	Site 341	Site 342
0.3							
0.5							
1							
2							
4			-				
6.5			-				
8.25 (8 m for Site 25 and 341)			-				

In addition to the determination of the spatial variation in the potential for oxidation, the temporal variation measurements of redox potential were used to determine the seasonal variation, as was done for the determination of the potential for reductive dechlorination in Section 6.1. Since the temporal variation measurements were only made at Dam 2 (near Site 21), the measurements were extrapolated to Dam 3/4 (Section 5.2.2 in Chapter 5). The potential for oxidation within Dam 2 and Dam 3/4, and its seasonal variation will be described in the following sections.

6.2.1 Potential for oxidation at Dam 2

The redox potential of the upper 8.25 m of Dam 2 allows for the oxidation of DCE and VC (be it anaerobic or aerobic), with the exception of 8 m at Site 25 which only allows for the anaerobic oxidation of VC, as indicated by Table 6.10. As a result, this dam is expected to have low concentrations of DCE and VC at all depths, except at 8 m at Site 25 where a low concentration of VC is expected. This is the case, except at 6.5 m and 8.25 m at Sites 21, 22 and 24; 6.5 m at Site 25; the upper 1 m of Site 23; and 4 m at Site 24 where the DCE and/or VC concentrations are high, and at 8 m at Site 25 where the VC concentrations are high, as is evident in the pollutant and daughter product results (Section 5.6 of Chapter 5). The unexpected accumulation of daughter products in the upper 1 m of Site 23 and various depths between 4 m and 8.25 m at the sites at Dam 2 is an indication that reductive dechlorination may have occurred at these depths without the presence of oxidation in the past, and only recently oxidation may have been promoted, which will promote the degradation of the daughter products present at these depths.

The presence of daughter products in the upper 1 m of Site 23 may be due to the dense layer at 3.25 m which may have trapped PCE, TCE and BTEX compounds in the upper profile in the past, which would have promoted reductive dechlorination at a rate that exceeded phytoremediation, leading to accumulation of daughter products, but since then the BTEX compounds have been removed by the actions of bacteria and the plants, leading to the conditions which currently promote the oxidation of these daughter products (Section 6.1.1). Between 4 m and 8.25 m at the sites, the recent promotion of oxidation at these depths may be due to oxygen replenishment from the upper layers which have a higher redox potential caused by the developing vegetation drying the profile through water uptake, increased aeration caused by the roots due to oxygen addition (Vorenhout *et al.*, 2004) and the creation of preferential pathways for oxygen transport (Pivetz, 2001; Nengovhela *et al.*, 2006), and due to the possible removal of BTEX compounds in the upper profile by phytoremediation and bacterial degradation which typically promotes the development of anaerobic conditions.

The temporal measurements of redox potential indicate that the oxidation of DCE and VC is promoted throughout the year at Dam 2, except at isolated depths near the base of the profile, as proved by the spatial variation measurements of redox potential, which indicated that at 8 m at Site 25 the redox potential decreases to a level that only promotes the anaerobic oxidation of VC. This will be more important in summer, when the redox potential was shown to decrease due to the affect of the higher water content.

6.2.2 Potential for oxidation at Dam 3/4

As was done in the determination of the spatial variation in the reductive dechlorination potential, in the description of the spatial variation in the potential for oxidation at Dam 3/4 the measurement sites will be described separately. Thereafter, the temporal variation in the oxidation potential at Dam 3/4 will be described.

- **Site 341**

At Site 341 the upper 1 m of the profile promotes the aerobic oxidation of DCE and VC, while at 4 m the co-occurrence of reductive dechlorination and the anaerobic oxidation of VC occurs, as is evident in Table 6.10. However, since the parent compounds and daughter products have already been removed from the upper 4 m (Section 5.6 in Chapter 5), oxidation is unnecessary at these depths. The lack of parents in the upper 4 m may be due to reductive

dechlorination in the past, a down-profile movement in the past, and phytoremediation occurring in the upper 1 m (Section 5.6 in Chapter 5); while the lack of daughter products may be due to the removal of any daughter products in the past due to a down-profile movement of these compounds with percolating water before the vegetation was established enough to limit percolation (Section 6.1.2), phytoremediation currently underway in the upper 1 m, and due to the oxidation that is currently promoted in the upper 1 m and at 4 m. The promotion of oxidation in the upper 1 m and at 4 m may be due to the actions of the maturing vegetation that dries the profile and adds oxygen from the developing root system, and due to the lack of BTEX compounds at these depths (which typically lead to a reduced redox potential) due to their removal through phytoremediation process in the upper 1 m and through bacterial degradation.

At 2 m at Site 341 the parents and daughters are not present, and at 6.5 m and 8 m the daughter products are present, but at a lower than expected concentration, despite only reductive dechlorination being favoured, without oxidation (Section 6.1.2).

- **Site 342**

At Site 342 the aerobic oxidation of DCE and VC occurs in the upper 1 m, the co-occurrence of reductive dechlorination and the anaerobic oxidation of DCE and VC occurs at 6.5 m, and at 8.25 m the co-occurrence of reductive dechlorination and the anaerobic oxidation of VC occurs, as is evident in Table 6.10. The co-occurrence of reductive dechlorination and anaerobic oxidation at 6.5 m and 8.25 m results in the continued production of daughter products at these depths (Section 5.6 in Chapter 5). Since the redox potential limits DCE oxidation at 8.25 m, high concentrations of this compound occur at this depth. The high concentrations of the daughter products at 6.5 m and 8.25 m may also be because oxidation has only recently been promoted at these depths, possibly due to a drying of the profile and the diffusion of oxygen down-profile from the developing vegetation root system.

Despite the fact that only oxidation is promoted in the upper 1 m of Site 342, the concentrations of the parent compounds are low and DCE is present at 1 m. The lack of the parent compounds may be due to their removal in the past due to reductive dechlorination, a down-profile movement of these compounds in the past, and phytoremediation (Section 5.6 in Chapter 5). The oxidation that now exists explains the low concentration of the daughter products. Oxidation may have been promoted in the upper 1 m due to the a reduction in

BTEX compounds which drive reductive dechlorination, possibly due to bacterial degradation and phytoremediation, and through the actions of the plants that reduce the water content and add oxygen through the actions of the roots. The isolated presence of DCE present in the upper 1 m may be because BTEX compounds present at this depth in the past promoted reductive dechlorination that produced daughter products at a rate that exceeded their removal through phytoremediation, leading to the accumulation of daughter products (Section 6.1.2); since then the BTEX compounds have been removed by the actions of bacteria and the plants, leading to the conditions which currently promote the oxidation of these daughter products, which are still in the process of being fully removed.

Reductive dechlorination, without the possibility of oxidation, occurs at 2 m and 4 m at Site 342; however, unexpectedly at 2 m the DCE concentration is high, and at 4 m VC is present in the absence of PCE, TCE and DCE (Section 5.6 in Chapter 5). The high concentration of DCE at 2 m may be because the redox in the past was higher, being between +120 mV and +200 mV which would have allowed for reductive dechlorination, and the anaerobic oxidation of VC, but not DCE. This is possible since at depths surrounding 2 m the redox is higher. The accumulation of VC at 4 m may be because reductive dechlorination occurring at this depth has led to accumulation of VC (Section 6.1.2).

Following the extrapolation of the temporal variation measurements of redox potential from Dam 2, in the upper 1 m of Dam 3/4 oxidation is likely to be possible throughout the year due to the high redox promoted due to oxygen additions from the atmosphere and the root activity, which is unlikely to decrease sufficiently in the wet summer season to prevent oxidation. In addition, the anaerobic oxidation of VC possible at 4 m at Site 341 and at 8.25 m at Site 342, and the anaerobic oxidation of DCE and VC possible at 6.5 m at Site 342 is likely to remain unchanged throughout the year due to the low fluctuation of the redox potential expected at and below 2 m at Dam 3/4 due to the high levels of bacterial activity at these depths, promoted by the presence of BTEX compounds, which promotes a low redox potential that is not significantly affected by the changes in water content between seasons at this dam.

After analysing the affect of each of the parameters on the potential for reductive dechlorination and oxidation at Dam 2 and Dam 3/4, in the following section these parameters will be discussed. Since the vegetation of each dam was initiated at different times, the vegetation is more mature on Dam 2 (Chapter 3) and, as a result, the dams will be compared

to determine the effect that vegetation, and the associated microbial populations, has on the complete degradation of PCE and TCE.

6.3 Discussion

Referring to the analysis of the spatial measurement results (Section 6.1 and 6.2), it is evident that the reductive dechlorination of PCE and TCE occurs over more of Dam 3/4 than Dam 2 and conversely the oxidation of DCE and VC occurs over more of Dam 2 than Dam 3/4. Based on the vadose zone points system, this can be attributed to differences in water content, redox potential, pH, temperature and the carbon source (SOM and BTEX compounds) between each dam. The only parameters in the vadose zone points system that do not directly affect degradation are the daughter products, since these act as an indication of reductive dechlorination and do not affect the degradation itself. However, as was established in the application of the vadose zone point system, the parameters did not all have the same influence on degradation. As was noted in the analysis of the results (Section 6.1 and 6.2), the pH, temperature, SOM and water content had a limited influence on microbial activity. Since a sensitivity analysis of the points system is outside the scope of this study, the reasons for the limited influence of these parameters will be outlined in the following section, and alterations to enhance the accuracy of the vadose zone points system will be discussed. Due to the limited influence of pH, temperature, SOM and water content, the redox potential and BTEX compounds are more dominant in determining the potential for reductive dechlorination at the dams, as will be described in Section 6.3.2. Since the redox potential and the BTEX compounds are affected by the actions of plants, this will also be described and discussed in Section 6.3.2.

6.3.1 Discussion of limiting parameters

As noted in the analysis of the results (Section 6.1), the pH, temperature, SOM and water content had a limited influence on reductive dechlorination. In the following section the reasons for the parameters having a limited influence will be reviewed and if this is due to inappropriate parameter thresholds or points, methods to rectify this will be discussed as will the possible effect of these changes on increasing the accuracy of the vadose zone points system in determining the potential for reductive dechlorination.

- **pH**

Outside the optimum pH, set between pH 5 and pH 9 (Wiedemeier *et al.,* 1998), it was expected that reductive dechlorination would be limited; however, no significant reductions were observed, as is evident in the continued degradation at 8 m at Site 25 and 6.5 m to 8 m at Site 342, as evident in the analysis of the results in Tables 6.6 and 6.8 in Section 6.1, where the pH is above pH 9. Since these thresholds are reasonable, because most natural environments have pH values between 5 and 9 standard pH units and thus most bacteria will have optima within this range (Brock and Madigan, 1991), the influence of pH is likely to be less critical in determining microbial activity at the site than initially thought. As a result, the two negative points assigned to pH values that were out of the optimal range are possibly excessive and can be reduced to one negative point, which will still reduce the reductive dechlorination potential, but to a lesser degree. This change will increase the reductive dechlorination potential at all depths that were out of range. These depths were 4 m to 8.25 m at Sites 21, 22 and 24 and at 6.5 m and 8 m at Site 25 at Dam 2 and at 6.5 m and 8.25 m at Site 342 at Dam 3/4. The effect of these changes on the reductive dechlorination potential will be described later in this section.

- **Temperature**

The 20 ^{o}C threshold used by Wiedemeier *et al.* (1998), above which the rate of the microbial processes are expected to be increased, is likely based on the temperature optima of mesophiles, which are bacteria that are typically found in soils in temperate and tropical latitudes (Brock and Madigan, 1991), and thus will be present at the study site. Since the temperature optima for mesophiles is slightly variable (Brock and Madigan, 1991), and the temperature is only lowered below 20 ^{o}C at 0.3 m at Site 25 and Site 342 (as evident in the results in Appendix B) where no reductive dechlorination was shown to be likely in the analysis of the results (Section 6.1), the role of a lower than optimum temperature in influencing the potential for reductive dechlorination is likely to be limited at the site since the temperature within the dams is not expected to decrease significantly in the future due to the warm climate at the study site. As a result, this threshold can safely be ignored, and all depths that received a point in the old points system can be removed, and the depths that did not receive a point (0.3 m at Sites 22, 25 and 342 and at 0.3 m and 8 m at Site 341) will therefore have the reductive dechlorination potential increased relative to the other depths. The effect of these changes on the reductive dechlorination potential will be described later in this section.

- **Soil organic matter**

With regard to the SOM, although the down-profile movement of organic carbon from the root zone has the potential to promote anaerobic conditions below this zone by enhancing microbial activity and hence oxygen consumption (Eberts *et al.*, 2003), which thereby increases the potential for reductive dechlorination, the SOM concentrations were consistently well below the threshold of 4.31%, with the maximum occurring at 2 m at Site 342 with a value of 2.68%. This is most likely due to the low concentrations of SOM added by the relatively immature vegetation community on Dam 2 and Dam 3/4, rather than an erroneous threshold. Consequently, the SOM is expected to increase over time and no changes are required to the thresholds or the points awarded.

- **Water Content**

At a water content below 38% saturation the microbial activity is expected to be limited due to a low water availability (Maier, 2000); however, apart from the low water content in the upper 0.3 m at Dam 2 which was expected due to evapotranspiration that has occurred at this dam, the water content is only below 38% saturation at 4 m to 8 m at Site 341 at Dam 3/4. Since the analysis of the results in Section 6.1 indicates that reductive dechlorination is still occurring at 6.5 m and 8 m at Site 341, the effect of the low water content is expected to be limited at this dam. Since no depths at Dam 2 promote reductive dechlorination at a water content below 38% saturation, the 38% threshold is less important at this dam.

In addition, although a water content above 81% saturation should limit oxygen ingress into the material leading to conditions that promote anaerobic conditions (Maier, 2000); the role of the water content in promoting reductive dechlorination is less important then initially thought, despite the 81% saturation threshold being a conservative value at the site (Section 4.2.1 in Chapter 4). This is evident at some parts of Dam 3/4 where the water content was below 81% saturation and the redox potential was anaerobic enough to promote reductive dechlorination (2 m, 6.5 m and 8 m at Site 341, and 6.5 m and 8.25 m at Site 342), and at some parts of Dam 2 where the water content was above 81% saturation and the redox was not anaerobic enough to promote reductive dechlorination (6.5 m and 8.25 m at Dam 2, with the exception of 8 m at Site 25 due to a dense layer at this depth that limits oxygen transport and thus promotes anaerobic conditions). The limited effect of the 81% water content threshold in determining the potential for reductive dechlorination can be attributed to the

high redox potential throughout the profile at Dam 2 due to the mature vegetation that promotes oxidation despite the high water content, and the dominance of BTEX compounds at Dam 3/4 that leads to a higher potential for reductive dechlorination despite the low water content. Due to the dominance of the redox potential over the BTEX compounds - as is evident in the vadose zone points system thresholds (shown in Table 4.2 in Chapter 4) where four and eight points is awarded to a favourable redox potential versus two points awarded for a favourable concentration of BTEX compounds - the high redox potential at Dam 2 limits the effect of a high water content in promoting anaerobic conditions to a greater degree than the BTEX compounds that promote anaerobic conditions at Dam 3/4, as will be described in Section 6.3.2. As a result, the influence of a high water content at Dam 2 is not as important as at Dam 3/4 since BTEX compounds dominate over a high redox potential at Dam 3/4, as will be described in the following paragraphs.

Since at Dam 2 no depths promote reductive dechlorination at water content values below 38% saturation, this threshold and the one negative point can remain unchanged at the dam, however since this threshold is site specific, in the future the threshold should be investigated to determine if the value should be decreased to be more accurate, as will be discussed in Chapter 8. In addition, as was described, due to the limited influence of a water content above 81% saturation at Dam 2 due to the high redox potential promoted by the mature vegetation, in the future this parameter can be ignored at this dam and the one point added to any water content above 81% saturation can be removed which will reduce the points awarded to depths with a water content above 81% saturation at Dam 2, which range from 6.5 m to 8.25 m. The effect of these changes on the reductive dechlorination potential will be described later in this section.

At Dam 3/4, due to the limited influence of vegetation in promoting a high redox potential, as was described, since this dam has less vegetation than Dam 2, the limited influence of water content may be because the bulk density was not included in the determination of the water content thresholds. According to Maier (2000), at a low bulk density (such as the material at the site) there is more water in a soil at a set water saturation than in a soil with a high bulk density, and as a result at the 38% and 81% saturation thresholds there is more water in the material at the site than in a material with a higher bulk density. Hence, the water content thresholds should be lowered in accordance with the bulk density. Since the bulk density is unusually low at both dams, ranging from 0.22 g/cm^3 to 0.56 g/cm^3 at Dam 3/4, while typical

values range from 1.25 g/cm^3 for clay to 1.65 g/cm^3 for sandy soils (Beasley and Huggins, 1991), the percent saturation value will be reduced to a large degree. However, since the effect of bulk density on the water content is dependant on the site specific water requirements of the bacteria populations, the precise values cannot be calculated theoretically and must be determined empirically. Consequently, to establish the effect of changing the water content thresholds, the thresholds will be lowered to a point where the anomalies at Dam 3/4 are suitably corrected, and these will be assumed to be suitable thresholds for use in this discussion. The future investigations required to ascertain a precise threshold will be discussed in Chapter 8. This process of altering the lower water content threshold (38% saturation) and the upper water content threshold (81% saturation) at Dam 3/4 will be described in the following paragraphs.

The evidence of reductive dechlorination occurring at 6.5 m and 8 m at Site 341 at Dam 3/4 despite the water content being below the lower water content threshold of 38% saturation may be because the bulk density was not taken into account when calculating the water content thresholds, and due to the depths of 4 m to 8 m at Site 341 being noted in Appendix B as being course but having a similar bulk density. As will be described later in this section, the course layer may maintain conditions that promote reductive dechlorination at 6.5 m and 8 m despite the low water content due to the course layer being less limiting in water to bacteria. If the threshold is lowered to 35% saturation the only depth that is lower than this threshold is 4 m at Site 341, which had a low potential for reductive dechlorination, and as a result this threshold is likely to be suitable. The effect of these changes on the reductive dechlorination potential will be described later in this section.

The anomaly at 2 m, 6.5 m and 8 m at Site 341 and 6.5 m and 8.25 m at Site 342 at Dam 3/4, where reductive dechlorination was promoted despite the water content not being above the upper water content threshold of 81% saturation, may also be because the bulk density was not included in the determination of the water content thresholds. In addition, the effect of a high water content on soil aeration is a dynamic process related not only to bulk density and water content, but also to biological respiration (Neilson and Pepper, 1990). Consequently, this threshold, as with the lower water content threshold, is site specific. Hence, as with the lower water content threshold, to determine the upper water content threshold it will be lowered to a point where the anomalies mentioned are suitably corrected, and this will be assumed to be a suitable threshold for use in this discussion. The value of the upper water

content threshold can be less than the literature value minimum of 60% saturation (Neilson and Pepper, 1990) since the material has an unusually low bulk density compared to typical soils, as was discussed. If the water content thresholds are lowered to 55% saturation, this rectifies the errors ascertained at Dam 3/4 except at 6.5 m to 8 m at Site 341. However, as mentioned, there is a course layer from 4 m to 8 m at Site 341 with a bulk density similar to the rest of the profile. The results summarised in Section 6.1 of Chapter 6 indicate that reductive dechlorination occurs in this course layer despite the water content being particularly low, and hence this layer may serve as a superior source of water to the bacteria. In this course layer, if the thresholds are lowered to 35% saturation then all depths will promote anaerobic conditions and reductive dechlorination, except for the 4 m depth where reductive dechlorination was shown in the analysis of the results to be unlikely; thus, this threshold is suitable in the course layer. The effect of these changes in the points and thresholds on the reductive dechlorination potential will be described in the following paragraph.

To determine the effect of changing the thresholds and the points awarded to pH, temperature and water content at Dam 2 and Dam 3/4, in Appendix E the new thresholds and points are included into the original vadose zone point results table, which was used in Section 6.1. From the tables in Appendix E, the affect of the changes to the thresholds and points on the distribution of depths that promote reductive dechlorination can be established. Comparing the totals obtained with the original and modified point systems in Tables E-2 to E-8 in Appendix E, there is no change in the distribution of depths that have a higher points total compared to other depths (i.e. depths that promote an increased potential for reductive dechlorination have a points total of eight and above using the original point system, and a total of nine and above using the modified point system), which indicates that there is no change in the distribution of depths that promote a higher degree of reductive dechlorination (i.e. 8 m at Site 25, 2 m, 6.5 m and 8 m at Site 341, and 2 m to 8.25 m at Site 342). In addition, the modified point systems point totals still indicate that at Dam 2 a high redox potential dominates and hence this dam promotes predominantly oxidation, while at Dam 3/4 the totals still indicate that the BTEX compounds play a more important role and as a result reductive dechlorination dominates. As a result, because the changes to the pH, temperature and water content points and thresholds do not change the outcome of vadose zone points system, the changes do not need to be discussed further. However, the modified point system totals indicate more clearly which depths promote reductive dechlorination. This is evident in

the points totals in Appendix E, where the depths that promoted an increased potential for reductive dechlorination in the original vadose zone points results tables had a value of eight and above, and the depths that were less likely had a maximum value of six; while in the modified vadose zone points results tables the totals that indicate an increased potential for reductive dechlorination had a value of nine and above, and the depths that were less likely had a maximum value of five. Because the changes to the vadose zone points system enhance the accuracy of the vadose zone points system, in Chapter 8 these changes will be outlined as future research needs.

6.3.2 Discussion of dominant parameters

As described in the previous section, the redox potential and BTEX compounds are dominant in determining the potential for reductive dechlorination and oxidation at the dams. Since both the redox potential and BTEX compounds are affected by the vegetation and Dam 2 was closed four years prior to Dam 3/4, thereby leading to a more mature vegetation community on Dam 2 which affects the redox potential and BTEX compounds to a greater degree than at Dam 3/4, the effect that vegetation has on the potential for reductive dechlorination and oxidation at the site can be determined by comparing the distributions of redox potential and BTEX compounds at each dam.

Referring to the analysis of the spatial measurements (Section 6.1 and 6.2), in general the redox potential is higher over more of Dam 2 than Dam 3/4 leading to a dominance of oxidation at Dam 2, while at Dam 3/4 there is a dominance of BTEX compounds which promotes a dominance of anaerobic conditions and reductive dechlorination at this dam. The BTEX compounds are present as shallow as 2 m at Dam 3/4, and as shallow as 4 m and 6.5 m at Dam 2. Since the processes of phytovolatilisation, phytodegradation and rhizodegradation can degrade BTEX compounds, the different distributions of BTEX compounds between each dam may be due, in addition to microbial degradation, to the differences in rooting depth since the roots affect the upper 1 m of Dam 3/4 and the upper 2 m of Dam 2. However, although the BTEX compounds promote reductive dechlorination at all the depths at Dam 3/4 where they are present in suitable concentrations, at Dam 2 although the BTEX compounds are present in suitable concentrations at 8.25 m at Sites 22 and 24, and 4 m to 8 m at Site 25, the potential for reductive dechlorination is only increased at 8 m at Site 25. This is possibly due to the more mature root system at Dam 2 where the roots produce preferential pathways

in the material which allows oxygen ingress and add oxygen to the upper 2 m of the profile due to root activity, and the oxygen moves down to the lower depths via diffusion leading to a higher redox potential in the lower profile which promotes oxidation. The exception at 8 m at Site 25 is likely due to this depth being noted as being more dense than elsewhere in the profile (as described in Table B-6 Appendix B) which leads to reduced oxygen transport, resulting in a lower redox potential at this isolated depth that promotes reductive dechlorination. At Dam 3/4 the shallower and less dense roots system adds less oxygen to the profile, and hence only the upper 1 m of this dam is affected by oxygen additions from the root activity and by the processes of phytoremediation. It is for this reason that Dam 3/4 has a lower redox potential and a higher distribution of BTEX compounds throughout the profile compared to Dam 2, and as a result has a higher degree of reductive dechlorination throughout the profile.

With regard to the temporal variation of the redox potential, used in the determination of the seasonal fluctuation in the potential for reductive dechlorination and oxidation (Section 6.1 and 6.2), it is evident that the variation in the redox potential between seasons is insufficient to promote the fluctuation in degradation mechanisms at Dam 2 and Dam 3/4, except at isolated depths near the base of the measurement profile at Dam 2. At Dam 2 this is due primarily to the high redox potential caused by oxygen additions from the roots due to the dominance of vegetation on this dam, which prevents a fluctuation in the redox potential to levels that promote reductive dechlorination except at isolated depths near the base of the profile; while at Dam 3/4 this is due to the low redox potential at and below 2 m due to the dominance of BTEX compounds at these depths which promotes anaerobic conditions which are unlikely to allow for the fluctuation in the redox potential to levels high enough to promote oxidation, and due to the high redox in the upper 1 m of Dam 3/4 due to oxygen additions from the atmosphere and plant roots which will not promote a fluctuation to levels that promote reductive dechlorination.

From the above discussion, it is evident that vegetation plays an important role at the site in promoting oxidation by affecting both the redox potential and the BTEX compounds through the additions of oxygen to the profile due to root activity and due to the degradation and removal of BTEX compounds through phytoremediation processes. This effect is most evident at Dam 2 where the vegetation is more mature. However, the fact that oxidation dominates at Dam 2 does not mean that Dam 2 did not support reductive dechlorination in the

past. Assuming the redox potential and BTEX compounds had a similar dominance in determining the potential for reductive dechlorination and oxidation in the past as they do currently, in the past the conditions in Dam 2 would likely have resembled those currently at Dam 3/4. Initially Dam 2 would have had a lower density of vegetation which would have lead to less oxygen added to the subsurface from the roots, and the BTEX compounds would likely have been present over more of the profile at Dam 2, as is the case at Dam 3/4, since the lack of vegetation would lead to less degradation and removal of the BTEX compounds through phytoremediation processes. The lower redox potential and higher concentrations of BTEX compounds throughout the profile would have enhanced the potential for reductive dechlorination at Dam 2. If the temporal variations in redox potential in the past were similar to what they currently are at Dam 3/4, the potential for reductive dechlorination at Dam 2 would likely not have varied enough throughout the year to promote oxidation, thereby promoting year-round reductive dechlorination in the lower profile. Since in the past Dam 2 likely resembled the conditions currently present at Dam 3/4, Dam 2 is also an indication of what Dam 3/4 is likely to be like in the future. As a result, since Dam 2 currently promotes oxidation, in the future Dam 3/4 is likely to promote oxidation over more of the profile as the vegetation matures and adds oxygen to the profile and the BTEX compounds are removed via phytoremediation and bacterial degradation. This promotion of oxidation in the future at Dam 3/4 will degrade the VC that is being accumulated, which will lead to the complete mineralization of PCE and TCE to harmless by-products. If the temporal variations of redox potential in the future at Dam 3/4 resemble those currently at Dam 2, in the future the potential for oxidation at Dam 3/4 will likely not vary enough throughout the year to promote reductive dechlorination, possibly except at isolated depths near the base of the profile, as currently occurs at Dam 2.

As discussed, oxidation is currently dominant year-round at Dam 2, and in the future oxidation is likely to be promoted year-round at both Dam 2 and Dam 3/4 due to the effects of the vegetation, which will degrade the VC that is accumulating at these dams. However, at both dams reductive dechlorination must be promoted at all depths where PCE and TCE are present until the concentrations have been reduced to acceptable levels before the conditions are allowed to promote oxidation, to prevent the continued presence of PCE and TCE at the dams. PCE and TCE are present without the mechanism of reductive dechlorination being likely, at various depths at Dam 2 ranging from 0.3 m to 8.25 m at most sites, and at 0.5 m to 1 m at Site 342 at Dam 3/4 according to the distribution of the parent compounds (Section

5.6 in Chapter 5) and the distribution of depths that promote reductive dechlorination (Section 6.1). As a result, methods to maintain the conditions that favour reductive dechlorination, as well as methods to promote the oxidation of the resultant daughter products, will be outlined as recommendations in Chapter 8. General conclusions are presented in the following chapter.

7. CONCLUSIONS

Considering the initial aim of the project, which was to assess the potential for the bacterial degradation of PCE and TCE in the contaminated vadose zone of two vegetated slimes dams at the study site, this has been achieved by determining which areas in each dam have the highest potential for the reductive dechlorination of PCE and TCE. The areas in each dam that promote the bacterial degradation of the daughter products produced during reductive dechlorination were also determined by assessing the potential for oxidation in the dams, which ensures the complete mineralization of PCE and TCE to harmless by-products. Reductive dechlorination was focussed on more than oxidation since it is the initial step in the complete degradation of PCE and TCE to harmless by-products, and this mechanism requires very specific conditions to occur. In addition to measuring the spatial variation of the potential for reductive dechlorination and oxidation, the temporal fluctuations in the potentials for reductive dechlorination and oxidation over time were assessed to establish the expected change in the potential for bacterial degradation between seasons.

To achieve the aim of measuring the spatial variation in the potential for the reductive dechlorination of PCE and TCE within the vadose zone at the site, a points system was created by modifying a points system originally devised by Wiedemeier *et al.* (1998) to ascertain the occurrence of reductive dechlorination of chlorinated solvents in groundwater. To modify this points system for use in the vadose zone, parameters were excluded, modified or added to the original points system. The resultant points system included the water content, redox potential, pH, temperature, the carbon source (including the measurement of soil organic matter and BTEX compounds) and the pollutants and daughter products, all of which were sampled at five sites at Dam 2 and two sites at Dam 3/4, at depths ranging from 0.3 m to 8.25 m. Points were allocated depending on the measured values of each parameter, based on thresholds. The higher the points total, the higher the potential for the reductive dechlorination of PCE and TCE. The spatial variation in the potential for the oxidation of the daughter products (DCE and VC) produced during reductive dechlorination was determined based on the redox potential measurements. Oxidation is particularly important since this mechanism degrades VC, which is more carcinogenic than PCE, TCE and DCE. Apart from measuring the spatial variation in the reductive dechlorination and oxidation potentials within each dam, the temporal variation in redox potential was measured as an indicator of the

seasonal change in the potential for reductive dechlorination and oxidation. The temporal variation in the redox potential was measured at one site at Dam 2 using permanently installed redox electrodes, and the measurements were assumed to represent all of Dam 2, and were extrapolated to Dam 3/4.

The analysis of the results indicated that the BTEX compounds and redox potential were the most important parameters in determining the potential for reductive dechlorination and oxidation in the dams. These parameters differed in influence at each dam, due to the effect of the vegetation, and the differences in vegetation density at each dam. Taking this into account, the affect of the parameters on the complete bacterial degradation of PCE and TCE to harmless by-products via reductive dechlorination and oxidation at each dam can be summarised as will be described in the following paragraphs. Both the spatial and temporal variation will be described.

In the upper 2 m of Dam 2 it was noted that the concentrations of the VOCs (PCE, TCE, DCE, VC and the BTEX compounds) are generally lower than elsewhere in the profile. The low concentrations of PCE, TCE and the BTEX compounds was attributed to a down-profile movement of these compounds in the past, both as free-phase NAPLs and in the dissolved-phase with percolating water. In addition, the low concentration of the VOCs was attributed to phytoremediation mechanisms, which will be discussed in more detail in Chapter 8. The vadose zone points system indicates that reductive dechlorination is possible at 8.25 m at Sites 22 and 24 and 8 m at Site 25. This is primarily due to the high concentrations of BTEX compounds, which results in the production of daughter products at these depths. However, the relatively high redox potentials at Dam 2 compared to Dam 3/4 reduced the potential for reductive dechlorination at all the sites except 8 m at Site 25. The high redox potential at all the depths except 8 m at Site 25 promotes only oxidation, despite the high water content and the presence of daughter products at various depths within Dam 2, which would otherwise promote reductive dechlorination. The daughter products of reductive dechlorination were unexpectedly present in the upper 1 m of Site 23, and at the lower depths of Sites 21, 22, 24 and 25, possibly because conditions were conducive to reductive dechlorination in the past, but recently changed to those that favour oxidation. The presence of daughter products in the upper 1 m of Site 23, despite the evidence of oxidation occurring and the actions of phytoremediation processes that can remove and degrade them, may be due to the dense layer noted at 3.25 m which may have trapped PCE, TCE and BTEX compounds in the upper

profile in the past. The BTEX compounds would have promoted the enhanced reductive dechlorination of PCE and TCE, which may have produced daughter products at a rate that exceeded their removal via phytoremediation, but since then the BTEX compounds have been removed by the actions of bacteria and plants leading to the conditions which currently promote oxidation. The reason for the presence of daughter products in the lower profile of Sites 21, 22, 24 and 25, despite oxidation occurring, may be due to the recent promotion of oxidation at these depths due to oxygen diffusion from the upper layers which have a higher redox potential caused by the maturing vegetation, and the mechanism of oxidation is still in the process of degrading these daughter products. The vegetation promotes a higher redox potential in the upper profile by drying the profile through water uptake, increasing the aeration due to oxygen additions from the roots and the creation of preferential pathways in the waste material, and due to the removal of BTEX compounds by phytoremediation and bacterial degradation which would typically promote the development of anaerobic conditions. Reductive dechlorination is only promoted at 8 m at Site 25 - where there is the co-occurrence of reductive dechlorination and the anaerobic oxidation of VC, which leads to the accumulation of DCE at this isolated depth - possibly due to this depth being noted as being particularly dense (Table B-6 in Appendix B), which would limit oxygen transport, leading to a relatively low redox potential that promotes reductive dechlorination. The temporal variation measurements of the redox potential at Dam 2 indicate that oxidation is likely throughout the measurement profile year-round, and the fluctuation in the redox potential to within levels that would promote reductive dechlorination is unlikely except at isolated depths at the base of the measurement profile (as indicated by the spatial variation measurements), where the reductive dechlorination of PCE and TCE and the anaerobic oxidation of VC may be promoted.

In the upper 1 m of Dam 3/4 it was noted that the concentrations of PCE, TCE, DCE, VC and the BTEX compounds are generally lower than elsewhere in the profile. As described, this was attributed to a down-profile movement of PCE, TCE and BTEX compounds in the past, as free-phase NAPLs and in the dissolved-phase with percolating water. In addition, the low concentrations of PCE, TCE, DCE, VC and the BTEX compounds were attributed to phytoremediation mechanisms. The phytoremediation mechanisms are active to a shallower depth compared to Dam 2 (where the removal occurred down to 2 m) due to the shallower rooting depth noted at Dam 3/4 compared to Dam 2 due to the dominance of shallow rooted grasses on Dam 3/4 and the dominance of deeper rooted trees on Dam 2. Phytoremediation

will be discussed in more detail in Chapter 8. Referring to the potential for reductive dechlorination and oxidation measured at Dam 3/4, since this dam was initially divided into two separate dams, with slightly different waste applications, the potential for reductive dechlorination and oxidation at each site (Site 341 and 342) will be described separately. At Site 341, based on the vadose zone point system results, the reductive dechlorination of PCE and TCE is most likely to occur at 2 m, 6.5 m and 8 m. This is primarily due to the favourable redox conditions caused by the high water content and presence of BTEX compounds, which results in the production of daughter products. However, the daughter products were absent in the upper 4 m. This was attributed to phytoremediation occurring in the upper 1 m, a lack of parent compounds in the upper 4 m due to reductive dechlorination and a down-profile movement of these compounds in the past, and that any daughter products were removed from the upper 4 m due to oxidation and a down-profile movement in the past. With regard to oxidation, although the aerobic oxidation of DCE and VC is promoted in the upper 1 m, and at 4 m the co-occurrence of reductive dechlorination and the anaerobic oxidation of VC is possible, since the parent compounds and daughter products have already been removed from the upper 4 m, oxidation is unnecessary. Oxidation is promoted at these depths due to the actions of the maturing vegetation in the upper 1 m that dries the profile and adds oxygen due to the developing root system, and due to the lack of BTEX compounds in the upper 1 m and at 4 m due to their removal through phytoremediation and bacterial degradation. At Site 342 the vadose zone points system indicated that the potential for reductive dechlorination of PCE and TCE exists from 2 m to 8.25 m. This is primarily due to the favourable redox potential caused by the high water content and the presence of BTEX compounds at these depths, which results in the production of daughter products. At 2 m, the high concentrations of DCE is evidence that in the past anaerobic oxidation and reductive dechlorination, instead of only reductive dechlorination, was promoted. In addition, at 4 m VC is present despite the absence of PCE, TCE and DCE which would act as parent compounds during reductive dechlorination; this was attributed to the past occurrence of reductive dechlorination at 4 m which promoted the degradation of PCE, TCE and DCE, but the redox potential may not have been low enough to degrade VC. At 6.5 m and 8.25 m the recent promotion of anaerobic oxidation due to a drying of the profile and the addition of oxygen due to the developing root system on this dam allows for the co-occurrence of reductive dechlorination and the anaerobic oxidation of DCE and VC at 6.5 m and of VC at 8.25 m, which leads to a continued production of the daughter products at these depths and the accumulation of DCE at 8.25 m. At 1 m, despite the presence of daughter products, reductive dechlorination is unlikely to be

promoted due to the high redox potential in the upper 1 m that promotes aerobic oxidation and hence is an indication that conditions have recently changed from those favouring reductive dechlorination to those favouring oxidation. The presence of daughter products at 1 m, despite the actions of phytoremediation processes that remove and degrade these daughter products, may be due to BTEX compounds present at this depth in the past which would have promoted reductive dechlorination at a rate that produced daughter products at a rate that exceeded their removal via phytoremediation but since then the BTEX compounds have been removed by the actions of bacteria and plants, leading to the conditions which currently promote oxidation. Following the extrapolation of the temporal variation measurements of redox potential from Dam 2 to Dam 3/4, the results indicate that the profile from 2 m to 8.25 m will have little change in the redox potential throughout the year, due to the high levels of bacterial activity promoted by the presence of BTEX compounds that are less affected by the seasons. As a result, the redox potential is expected to remain within a range to promote reductive dechlorination of PCE and TCE throughout the year at and below 2 m at Dam 3/4, and the potential for the anaerobic oxidation of VC at 4 m at Site 341 and 8.25 m at Site 342, and the anaerobic oxidation of DCE and VC at 6.5 m at Site 342, will continue to be promoted throughout the year. In addition, in the upper 1 m of the profile of Dam 3/4 the low influence of the water content due to the oxygen additions from the atmosphere and from plant activity will lead to a low likelihood of the redox potential decreasing significantly enough to promote reductive dechlorination, hence oxidation will be promoted year-round.

Due to the differences in the vegetation density between the dams, as well as the dominance of the BTEX compounds and the redox potential in determining the potential for reductive dechlorination and oxidation - both of which are affected by vegetation - generalisations regarding the dominance of these degradation mechanisms at each dam can be made. In general the potential for reductive dechlorination is higher at Dam 3/4 compared to Dam 2. This was attributed to a higher presence of BTEX compounds and a lower redox potential at this dam compared to Dam 2, due to the less mature vegetation community on Dam 3/4, dominated by grasses, which leads to a shallower and less dense root system. The high levels of BTEX compounds are likely due, in part, to the less mature vegetation community being less efficient at phytoremediation mechanisms, leading to the presence of BTEX compounds at and below 2 m, which promote reductive dechlorination by acting as an enhanced carbon source to the bacteria. In addition, the lower density of vegetation adds less oxygen to the profile which promotes a lower redox potential at and below 2 m. This is expected to promote

the year-round reductive dechlorination of PCE and TCE at various depths at and below 2 m at Dam 3/4. Conversely, at Dam 2, the vegetation is more mature, and is dominated by trees, which leads to a deeper and more dense rooting system. This leads to a lack of BTEX compounds in the upper 4 m to upper 6.5 m of the profile, and a redox potential that remains high enough to promote oxidation throughout the measurement profile. The low concentrations of BTEX compounds in the upper profile is likely due, in addition to microbial degradation, to the mature vegetation being more efficient at phytoremediation, and the higher redox potential throughout the measurement profile is likely due to the influence of the dense roots in the upper 2 m that add oxygen, which moves to the lower depths via diffusion. This will promote the year-round oxidation of DCE and VC throughout the measurement profile at Dam 2, except at isolated depths near the base of the measurement profile, where only the anaerobic oxidation of VC is likely in summer.

Due to the role of vegetation in promoting oxidation by maintaining a higher redox potential and in removing BTEX compounds, and since Dam 2 has been vegetated longer than Dam 3/4, before the development of the mature vegetation community at Dam 2, the conditions would likely have resembled those currently in Dam 3/4, and, more importantly, at present Dam 2 is an indication of what Dam 3/4 is likely to be like in the future once the vegetation matures. Hence, in the future Dam 3/4 is likely to promote oxidation over more of the profile, throughout the year, as Dam 2 does currently, which will lead to the degradation of the daughter products, including VC, currently accumulating in parts of Dam 3/4. However, reductive dechlorination must be promoted, on both Dam 2 and Dam 3/4, where PCE and TCE are present until the concentrations of these compounds have been reduced to acceptable levels, to prevent their continued presence. Methods to maintain the conditions that favour reductive dechlorination, as well as methods to promote the oxidation of the resultant daughter products, are outlined in the following chapter. In addition, recommendations to enhance the vadose zone points system, methods to prevent the movement of contaminated water into the groundwater, and the future research needs will be described.

8. RECOMMENDATIONS

From the analysis of the results and the discussion and conclusions obtained from these (Chapters 6 and 7), various recommendations to enhance the vadose zone points system and the bacterial degradation occurring within the vadose zone of Dam 2 and Dam 3/4 can be proposed. These recommendations are described in the following sections, and include:

- Changes to the vadose zone point systems thresholds and points
- Alterations to the subsurface to enhance reductive dechlorination
- The creation of conditions that promote the oxidation of the daughter products produced during reductive dechlorination
- The recirculation of contaminated groundwater
- The planting of indigenous vegetation to promote the hydraulic control of contaminated water.

In addition, the future research needs at the study site are presented.

8.1 Inclusion of Changes to the Vadose Zone Point System

In the discussion of the results (Chapter 6), changes to the temperature, pH and water content thresholds and points were described to improve the accuracy of the vadose zone points system in determining the potential for reductive dechlorination. The implementation and effect of these changes to the vadose zone point system are outlined in Appendix E.

In the discussion of the results (Chapter 6) it was decided that the temperature threshold of 20 ^{o}C could safely be ignored, and in the future points should no longer be given to temperatures above this threshold, because the role of a lower than optimum temperature in reducing the potential for reductive dechlorination is likely to be limited at the site since the temperature is only below this threshold at isolated depths where no reductive dechlorination was shown to be likely. Chapter 6 also indicated that the two negative points assigned to pH values that were out of the optimal range (below pH 5 and above pH 9, where microbial activity is expected to be reduced) were excessive, and should be reduced to one negative point in the future. With regard to the water content, since at Dam 2 no depths promote reductive dechlorination at values below 38% saturation, this threshold and point allocation can remain unchanged at the dam; however, it should be investigated in the future to ensure

accuracy, as will be described in Section 8.6. In addition, due to the limited influence of a water content above 81% saturation at Dam 2 in promoting reductive dechlorination, due to the high redox potential in this dam, in the future the one point added to any water content above 81% saturation could be removed at Dam 2. The influence of water content at Dam 3/4 is limited, possibly because the unusually low bulk density of the material was not included in the determination of the water content thresholds, leading to an overestimation. In addition, the limited influence of the 38% saturation threshold at Dam 3/4 may be because this occurs within a course layer that may be less limiting in water to bacteria. Consequently, the 38% saturation threshold was lowered to 35% and still received one negative point. With regard to the upper water content threshold at Dam 3/4, since the redox potential is less dominant on this dam, the water content has more influence than at Dam 2 in determining the potential for anaerobic conditions and reductive dechlorination. As a result, unlike Dam 2, points were still awarded to a high water content at Dam 3/4, however, the thresholds were lowered to take into account the unusually low bulk density of the material in the dam. Hence, the 81% saturation threshold was lowered to 55% (and 35% saturation in the course layer from 4 m to 8 m at Site 341 since it may be a superior source of water to the bacteria), and the one point awarded to this threshold remained unchanged. Since the changes to the water content thresholds are site specific, and as a result were estimated based on the results described in Chapter 6, the exact thresholds should be investigated in the future, as will be discussed in Section 8.6.

Although these changes to the temperature, pH and water content did not alter which depths had an increased potential for reductive dechlorination or which parameters are most dominant in determining the potential for reductive dechlorination, the new vadose zone point system indicated more clearly which depths promote reductive dechlorination; thus, these changes should be included in the vadose zone point system if it is used in the future.

8.2 Promotion of Conditions Required for Reductive Dechlorination

As was described in the results of the vadose zone point system (Chapter 6), the potential for reductive dechlorination is reduced at various depths at Dam 2 and Dam 3/4 due to parameters that are outside the thresholds that promote enhanced reductive dechlorination. As was indicated in the discussion of the results (Chapter 6), the most important parameters determining the potential for reductive dechlorination at the site were the redox potential and

the presence of BTEX compounds (which act as the dominant source of carbon for the bacteria), and because these parameters were outside the thresholds required for enhanced reductive dechlorination at various depths, methods will be described to enhance the redox potential and source of carbon. In addition the water content and pH were also outside the thresholds required for enhanced reductive dechlorination (Chapter 6), and as a result methods will be recommended which enhance these parameters. Although the temperature has the potential to limit reductive dechlorination, its impact is likely to be limited at the site (Chapter 6); hence, temperature alterations will not be included as an option to enhance reductive dechlorination.

8.2.1 Redox potential

At Dam 2, the redox potential is too high to promote enhanced reductive dechlorination, except for 8 m at Site 25; while at Dam 3/4 the redox potential is too high in the upper 1 m. An option to bring the redox potential to within a range to promote enhanced reductive dechlorination is to ensure that the conditions which promote microbial activity are optimised. The increased microbial activity enhances oxygen consumption, leading to anaerobic conditions (Eberts *et al.*, 2003) that may be low enough to promote reductive dechlorination. This would involve promoting conditions with the carbon sources, water content and pH within the thresholds to promote enhanced microbial activity. These alterations will be discussed in the following subsections. Due to the importance of redox potential and its temporal variability, it is recommended that this parameter be constantly monitored in the waste material.

8.2.2 Carbon source

Generally, a source of carbon is lacking in the upper 4 m at Dam 2 and upper 1 m at Dam 3/4. This is due to the low amount of SOM currently added by the vegetation; and more importantly, the lack of BTEX compounds at these depths. In addition, the concentrations of BTEX compounds are expected to decrease over time through bacterial degradation and phytoremediation mechanisms, and the SOM is not expected to increase significantly over time due to the warm, humid climate at the site which promotes microbial activity (Plank, 2001). Since these compounds act as electron donors to microorganisms, their absence in suitable concentrations reduces the potential for reductive dechlorination. As a result, organic

substrates should be added to the profile to provide a source of electron donors to promote continued reductive dechlorination. Organic substrates can take three forms: Dissolved phase substrates, slowly-soluble substrates, and solid phase substrates (ESTCP, 2002b). Dissolved phase substrates include lactate and molasses, and since they are dissolved they offer the greatest potential for uniform distribution. Slowly-soluble substrates include HRC^{TM} (a trade mark of Regenesis Bioremediation Products) and edible (vegetable) oils, and these substrates rely more on dissolution and diffusion for delivery throughout the material. In terms of the solid phase substrates, these include mulch and chitin and, being solid, these substrates are typically added in a trench or excavation (ESTCP, 2002b). Since microbial degradation depends on an adequate supply of carbon, it is recommended that this parameter be continually monitored to ensure the maximised degradation of PCE and TCE.

8.2.3 Water content

Based on the water content thresholds (described in Chapter 6 and outlined in Section 8.1) it should be ensured that the water content is maintained above 38% saturation at Dam 2 and 35% saturation at Dam 3/4 to prevent water constraints to bacteria that will limit reductive dechlorination, and at Dam 3/4 the water content should be increased to above 55% (and 35% in the course layer from 4 m to 8 m at Site 341) to ensure that anaerobic conditions that enhance reductive dechlorination are promoted. Since a high water content had a limited influence on promoting anaerobic conditions at Dam 2, the upper water content threshold can be ignored at Dam 2. These constraints should be investigated in the future, to be more accurate, as will be described in Section 8.6. The difficulty in altering the water content of the profile is that if the profile is made to be too wet there is a chance that the pollutants will leach to the groundwater. As a result, it is recommended that the water content be increased to above 38% saturation at Dam 2 and above 55% at Dam 3/4 (and 35% in the course layer from 4 m to 8 m at Site 341), to promote continued microbial activity at the dams, and anaerobic conditions at Dam 3/4, but not to a level that causes leaching. Hence, the water content of the profile and the water movement into the groundwater should be monitored to ensure leaching does not occur. Since the water content of the profile and the fluxes into the groundwater are already being investigated by Lorentz *et al.* (2006), this would entail a continuation of these measurements. To increase the water content in the dams, irrigation could be applied uniformly on the dam surface. This could be achieved using recirculated water applied through a subsurface drip irrigation system, which increases degradation and reduces the

volatilisation of the contaminants, while having the added benefit of limiting the leaching of contaminants into the groundwater, as will be described in Section 8.4.

8.2.4 pH

The pH is generally outside the thresholds for enhanced reductive dechlorination (which occurs between pH 5 and pH 9) near the base of the profile at each dam (from 4 m to 8.25 m at Dam 2, and at 6.5 m and 8.25 m at Site 342); where the pH is above pH 9, leading to reduced microbial activity. To reduce the pH at these depths to within the thresholds required for enhanced reductive dechlorination, without altering the pH in the upper profile, it is recommended that elemental sulphur or acid be injected to the relevant depths, which will lower the pH. However, during this process the groundwater should be monitored to ensure that elemental sulphur does not leach into the groundwater, and that the pH is not reduced below pH 5, which is outside the range for enhanced reductive dechlorination.

8.3 Promotion of the Oxidation of Daughter Products

If the recommendations described above are followed, the conditions will promote the reductive dechlorination of PCE and TCE. However, the most efficient method to promote the complete degradation of PCE and TCE to harmless by-products, without the accumulation of VC, is to have a mixed behaviour where reductive dechlorination is followed by oxidation downgradient (Wiedemeier *et al.*, 1998). According to Duthe (2004) external to the slimes dams the conditions in the aquifer promote oxidation, thus the groundwater will promote the degradation of VC via this mixed behaviour (Wiedemeier *et al.*, 1998). However, this is not ideal since this relies on VC addition to the groundwater, which is less controllable in terms of containment.

Another option would be to ensure that the redox potential remains within the range whereby both reductive dechlorination and anaerobic oxidation can co-exist. From +249 mV to +200 mV the reductive dechlorination of PCE and TCE and the anaerobic oxidation of DCE and VC can occur, and from +200 mV to +120 mV the reductive dechlorination of PCE and TCE and the anaerobic oxidation of VC can occur. Since VC is the most carcinogenic of these compounds, the redox potential should be maintained between +249 mV and +120 mV to ensure that this compound does not accumulate. This could be achieved by following the

methods outlined in Section 8.2. However, due to the narrow redox potential range where the co-occurrence of reductive dechlorination and anaerobic oxidation can occur, careful monitoring of the redox potential would be required which may be problematic.

Potentially the most feasible option would be through the promotion of oxidation in zones that previously promoted reductive dechlorination. If the conditions within the dams were maintained to promote the reductive dechlorination of PCE and TCE (using the methods outlined in Section 8.2) until the concentrations of PCE and TCE were low enough to be within acceptable limits, then oxidation could be promoted within the dams to degrade the resultant daughter products that accumulate during reductive dechlorination. The easiest method to promote oxidation would be through the continued presence of vegetation, ensuring the development of a mature tree population at the dams which promotes oxidation throughout the measurement profile, as is currently the case at Dam 2. The trees promote oxidation throughout the measurement profile at Dam 2 by increasing the redox potential in the root zone by adding oxygen through the actions of the roots and by removing BTEX compounds through phytoremediation processes, and this oxygen moves to the lower depths via diffusion (Chapter 6). The planting of trees at the dams will be described in more detail in Section 8.5. While reductive dechlorination and then oxidation is occurring at the dams, it must be ensured that the movement of contamination into the groundwater is limited. Since this movement is already limited due to the actions of the vegetation that acts as an evapotranspiration cover, as was demonstrated by measurements undertaken by Lorentz *et al*. (2006) and described in Chapter 2, the prevention of the contaminant movement into the groundwater would entail the continued use of the evapotranspiration cover and the monitoring of the water fluxes into the groundwater using the methods outlined in Lorentz *et al*. (2006).

8.4 Recirculation

To enhance the complete bacterial degradation of PCE and TCE through reductive dechlorination and oxidation it is recommended that recirculation of groundwater be investigated. This involves the extraction of contaminated groundwater and the reapplication onto the land surface, with or without the addition of organic substrates (which were described in Section 8.2.2). This method has the benefit of maintaining the contaminated water in the root zone where phytoremediation can occur, and helps to reduce contaminant

leaching into the groundwater (ESTCP, 2002a). Recirculation generally promotes anaerobic conditions within the subsurface which would promote the reductive dechlorination of PCE and TCE due to the organic carbon rich nature of the recirculated leachate which promotes microorganism growth, and the subsequent depletion of dissolved oxygen (Wiedemeier *et al.*, 1996); however, these systems can also be managed to promote oxidation (ESTCP, 2002a) which would lead to the degradation of DCE and VC. Once the contaminated groundwater has been extracted from the boreholes, a method of contaminated groundwater reapplication would be through the use of an irrigation system. In a study by Wilde *et al.* (2003), a drip irrigation system was successfully implemented at a site with TCE-contaminated groundwater. The drip lines could be buried below the ground surface to reduce the volatilisation of the contaminants into the atmosphere (Wilde *et al.*, 2003), which would pose a potential health risk (Chappell, 1997).

8.5 Planting

Apart from the degradation and removal of PCE, TCE, DCE, VC and BTEX compounds by plants through phytoremediation mechanisms (Chapter 3), and the effects described in Chapters 5 and 6, another role that plants play during phytoremediation is hydraulic control (USEPA, 2000). Hydraulic control involves the use of vegetation to influence the movement of groundwater and soil water through the uptake and consumption of water by the plants. Hydraulic control may influence and potentially contain the movement of a groundwater plume, reduce or prevent percolation through the vadose zone to the groundwater, and induce the upward flow of water from the water table through the vadose zone. This may limit the movement of the dissolved contamination (USEPA, 2000). To enhance the hydraulic control, planting at the site should focus on high water use trees. Most commonly poplars and cottonwoods are used since they are phreatophytic, which allows these plants to extend their roots to the water table and pump from the zone of saturation (Chappell, 1997). However, since indigenous planting is promoted at the site (Oliver, 2006), and these plants are not indigenous, it is recommended that the planting of indigenous high water use trees, especially phreatophytes, be investigated, as will be described in Section 8.6.

8.6 Future Research Needs

Since there is more water in the soil with a low bulk density than in a soil with a high bulk density at a set water saturation (Maier, 2000), and the site has a particularly low bulk density, the water content thresholds at Dam 3/4 were lowered to take this into account (Chapter 6). However, since the effect of bulk density on the water content is dependant on the site specific water requirements of the bacteria, the precise values could not be obtained and the values were estimated based on the effect of changing the water content thresholds; hence, these site specific thresholds should be investigated in the future. With regard to the lower threshold, this should be investigated to establish the water content below which water availability becomes limiting to bacteria. Although the threshold was only lowered at Dam 3/4 since there were no depths below this threshold at Dam 2 which promoted reductive dechlorination, this should be investigated for both dams to increase the accuracy of this threshold. The upper water content at which anaerobic conditions develop is dependant not only on the water content and bulk density but also on the biological respiration (Neilson and Pepper, 1990). Although water content and bulk density were measured in this project, and it was assumed that the low bulk density at the site would lower the critical water content above which anaerobic conditions will develop (Maier, 2000), these values were estimates and did not take into account the effects of the site specific water requirements of bacteria and the biological respiration. As a result, in the future, the site specific effect of the bulk density and microbial respiration on the critical water content, above which anaerobic conditions develop, should be investigated, to determine at what water content anaerobic conditions develop. Due to the limited importance of the upper water content threshold at Dam 2 due to the high redox potential that dominates the potential for reductive dechlorination, the measurement of this threshold is less critical at Dam 2.

Since the vadose zone points system considers only the reductive dechlorination of PCE and TCE, it ignores the bacterial degradation of the daughter products via oxidation. Since this project focussed more on the mechanism of reductive dechlorination, if the potential for microbial oxidation in the vadose zone is researched in more detail in the future, the parameters used to assess the potential for oxidation would need to be monitored in more detail. To do this a points system similar to the one used to determine the potential for reductive dechlorination in this project could be developed that could be used to ascertain the potential for oxidation. As was done in this project, the redox potential could be used as an

indication of where oxidation is possible. In addition, to ensure the environmental conditions are enhanced, a water content above 38% saturation at Dam 2 and 35% saturation at Dam 3/4, and a pH between 5 and 9 standard units could be stipulated, as outlined in the modified vadose zone points system (Chapter 6). The points values awarded to the redox potential, water content and pH would also need to be investigated, but are likely to be similar to the points awarded for reductive dechlorination since these parameters are likely to have a similar influence on oxidation. The environmental factors that affect bacterial activity were not included in the determination of the potential for oxidation in this project since the focus of this project was on reductive dechlorination, and the effect of these factors in determining the potential for oxidation are less significant than the redox potential (Chapter 6). However, if the potential for oxidation is investigated in more detail in the future, the lower water content thresholds and pH thresholds, and the point values, should be included to ensure accuracy.

The phytoremediation at the site not only includes rhizodegradation, phytodegradation and phytovolatilisation, but also includes hydraulic control (Section 8.5). Although the process of hydraulic control is currently being utilized through the use of the evapotranspiration cap at the site (Lorentz *et al.*, 2006), the active planting at the site does not specifically use plants that will maximize hydraulic control. As a result, in the future the planting of indigenous high water use trees at the site, especially phreatophytes, should be investigated. With regard to rhizodegradation, phytodegradation and phytovolatilisation, the low concentrations of the VOCs (PCE, TCE, DCE, VC and BTEX compounds) in the upper 2 m of Dam 2 and the upper 1 m of Dam 3/4 was attributed, in part, to these phytoremediation processes (Chapter 5). The removal of PCE and TCE is important since this occurs in the upper profile, where the potential for reductive dechlorination is low (Chapter 6). In addition, the removal of BTEX compounds via these phytoremediation processes is important since the BTEX compounds act as the dominant carbon source within the dams, and their removal lowers the potential for reductive dechlorination. However, despite the importance of these phytoremediation processes at Dam 2 and Dam 3/4, due to the difficulty in quantifying the site specific processes involved it was not included in the investigation. Hence, it is recommended that the effects of these phytoremediation processes be quantified at the study site in the future to establish the degradation and removal of PCE, TCE, DCE and VC by plants, and to assess the effect that the vegetation has on removing the BTEX compounds. This investigation should include plants currently at the site, and any plants chosen to be used to maximize the process of hydraulic control. To measure the degradation of these VOCs

through the process of rhizodegradation would involve the measurement of the concentrations of the pollutants and daughter products and the BTEX compounds in the vadose zone, using the methods outlined in Chapter 4. However, to measure the removal and degradation of the VOCs through the processes of plant uptake and subsequent phytodegradation and phytovolatilisation would require a different method. According to the USEPA (2005c) this can be done by determining the presence of the parent compound and daughter products within the plant tissues. The methods of measurement for the concentrations of the VOCs in the trunks, branches and transpiration gasses are explained in USEPA (2005c).

During this project Dam 2 was investigated in more detail than Dam 3/4 since it had the highest density of vegetation which affects the potential for bacterial degradation, with Dam 3/4 serving only as a comparison. In addition, although Dam 1 and Dam 6 at the study site are vegetated and include chlorinated ethenes (Duthe, 2004), they were not included in this project. Consequently, it is recommended that Dams 1, 3/4 and 6 be investigated in more detail in the future to better understand the potential for the complete bacterial degradation of PCE and TCE in the vadose zone, through the mechanisms of reductive dechlorination and oxidation, under the influence of vegetation.

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APPENDIX A
FIELD INSTRUMENTS

A.1 Redox Electrode Construction, Protection, Testing and Installation

- **Electrode construction**

A method described by Vepraskas and Cox (2002) was modified for this construction method. A 13 mm length of platinum wire was inserted into a drilled hole (1 mm wide and 3 mm deep) in the end of a 100 mm length of 1/8 inch diameter brass brazing rod. The platinum was soldered into the brass brazing rod using silver solder. This was done by a technician in the School of BEEH at the University of KwaZulu-Natal. Polyolefin heat-shrink tubing was then used by the author to seal the platinum and brass junction. 18 gauge insulated multi-stranded copper wire was then soldered to the exposed top of the brass brazing rod, and insulated by using another length of heat-shrink tubing.

- **Electrode protection**

To protect the electrode during insertion into the waste material, a PVC cone was constructed by a technician in the School of BEEH at the University of KwaZulu-Natal. The electrode tip was placed into the cone, and sealed into place using waterproof epoxy (Pratley® Quickset Clear). The cone and electrode was then glued into 25 mm outside diameter conduit tubing. The tubing protects the electrode from water and the waste material environment. The protective cone, electrode and protective tubing are shown in Figures A-1 and A-2. Since conduit tubing only comes in 4 m lengths (for ease of transport), when constructing electrodes to reach more than 4 m, two or more tubes needed to be joined. Instead of using conventional conduit tubing connectors which fit on the outside of the tubes, PVC internal connectors were fabricated by a technician in the School of BEEH at the University of KwaZulu-Natal. This was done to allow for a uniform outside diameter of the tubing, so a snug fit into the waste was ensured to prevent the preferential flow of water down the outside of the tubes which would affect the redox potential readings. The internal connectors were made by fabricating PVC tubes of an identical internal diameter to the PVC conduit tubes, and the conduit tubes were connected by gluing their ends onto the internal connector. The wire was then fed from the electrodes, through the conduit tube (and internal connector tubes were applicable) to the opposite end of the conduit tube. A cap at this end of the PVC conduit tubing, through which

the wire can run (made waterproof using silicone sealant) was glued in place to ensure the tubing was completely waterproof. A knot was made in the wire, immediately above and below the cap, to prevent the wire from falling into the conduit tubing and to prevent tension on the wire from pulling the platinum electrode from the PVC protective cone.

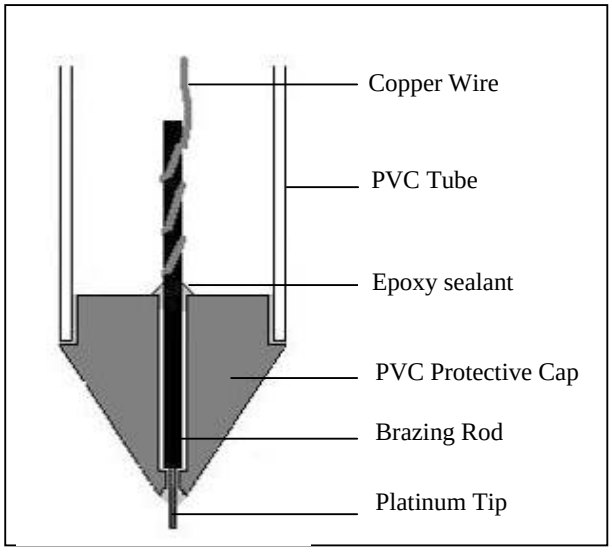

Figure A-1 Cross-section of electrode placed into protective PVC cap and PVC tubing.

Figure A-2 Photograph of PVC cap and tubing protecting the electrode.

- **Electrode testing**

Once constructed, the electrodes needed to be tested for accuracy. To do this a standard redox potential solution was used. Before testing the platinum tip was lightly abraded with a very fine sandpaper (1200 grit) to remove any coatings which may have accumulated, and which will alter the readings. The copper wire was then attached to the positive lead of a voltmeter, and the reference electrode (a Ag/Ag/Cl reference electrode in this case) to the negative lead of the voltmeter. The platinum tip and reference electrode was then placed into the standard redox potential solution (i.e. 240 mV or 470 mV solution). Properly functioning electrodes should give readings within 47 mV of the reference value at 28 ^{o}C (Austin and Huddleston, 1999). This was the case for all the electrodes.

Upon completion of the study, the electrodes should be removed and retested using the standard solution (Austin and Huddleston, 1999); however, since the probes are required for future measurements, the removal and retesting is not feasible. This is unlikely to be a problem since Austin and Huddleston (1999) proved that electrode poisoning that affects

electrode performance is not a problem for up to three to five years of permanent installation, and the electrodes have not been installed for this period of time. In addition, any poisoning or other sources of error that may have occurred during the measurement period have already been indicated by erroneous readings, and these electrodes were ignored (Section 5.2.2 in Chapter 5). As a result, this removal and retesting of electrodes is currently unnecessary.

- **Electrode Installation**

To place an electrode at each measurement depth (0.3 m, 0.5 m, 1 m, 2 m, 4 m, 6.5 m and 8.25 m) near Site 21 on Dam 2, a standard Dutch auger with a cutting head of equal diameter to the PVC tubes (25 mm outside diameter) was attached to extensions reaching a depth of up to 8.25 m. A hole was augured to a depth 50 mm short of the desired depth, and the electrode (complete with the protective conical tip and PVC conduit tubing) was pushed down the hole, 50 mm into the undisturbed waste at the bottom. This was done by the author, with help from a technician from the School of BEEH at the University of KwaZulu-Natal. A photograph of the installed electrodes is shown in Figure A-3. Only the upper 0.5 m of the conduit tubing and the insulated copper wire used to take readings are visible.

Figure A-3 Photograph of redox electrodes installed at Site 21 at Dam 2.

A.2 Auger and Corer

To obtain samples from various depths for the testing of the parameters required in this project, a specially modified auger and corer were attached to extensions to reach as deep as 8.25 m. The auger head, with a “bucket” of 100 mm outside diameter, was modified to have openings in the sides to allow for the easy removal of the clay-like waste material. This modification was done by technicians in the School of BEEH at the University of KwaZulu-Natal, and is visible in Figure A-4. The corer head, shown in Figures A-5 and A-6, was specifically constructed by technicians in the School of BEEH at the University of KwaZulu-Natal., and was made to have an opening in the side so as to allow for the extraction of an undisturbed sample, which was required for the testing of the physical properties of the waste material, required for the water content determination.

Figure A-4 Modified bucket auger, measured against a 50 cm ruler.

Figure A-5 Side view of corer, measured against a 50 cm ruler.

Figure A-6 Top view of corer, measured against a 50 cm ruler.

APPENDIX B

FIELD RESULTS

B.1 Temporal Measurements of Redox Potential

The temporal variation in redox potential was measured using redox electrodes installed near Site 21 at Dam 2, using the method described in Section 4.2.2 in Chapter 4. The results are summarised in Table B-1.

Table B-1 Temporal measurements of redox potential (against Ag/AgCl reference electrode)

Date	Eh (mV) taking into account pH								Field Notes
	0.3 m	0.5 m	1 m	2 m	New 2 m	4 m	6.5 m	8.25 m	
30-Sept-05	348	374	346	402	-	479	392	100	One day after installation. Packed holes with ash. Poor results at 0.3 m and 0.5 m could be due to dry material
10-Oct-05	421	398	318	404	-	472	388	331	Stripped wire (to show unoxidised metal), and moved reference position by 700 mm: Both alterations did not alter the readings significantly
24-Oct-05	410	411	326	448	-	489	398	357	Had just rained, and started again during measurement
03-Nov-05	408	398	313	444	-	482	398	371	Corroded and newly exposed wires gave identical readings
15-Nov-05	411	404	321	448	-	483	398	392	Grass cover around probes is more dense than previous
01-Dec-05	408	396	314	436	-	447	398	407	
08-Dec-05	391	376	312	429	-	440	398	407	Electrodes at 0.3 m and 0.5 m had a slow change of mV reading
21-Dec-05	390	383	310	424	-	436	398	409	Previous week had been wet
05-Jan-06	398	394	319	434	-	435	399	420	After rains. The wire was stripped, and at one depth used KCl, distilled water, and nothing at a dry patch on the surface. All changes made no difference to reading
06-Feb-06					439				Installed new 2 m probe today. Took a measurement 10 minutes after installing
10-Apr-06	455	474	284	409	335	432	394	410	Returned after long break
19-Apr-06	450	494	294	427	349	443	397	417	Attempted to install new 8.25 m electrode. Unsuccessful due to breakage of PVC conduit tube
26-Apr-06	473	524	296	468	367	456	400	429	Removed, tested, and reinstalled 0.3 m electrode AFTER taking measurements. Testing with 240 mV standard solution gave reading of 302 mV. Testing proved this was likely caused by a faulty reference electrode. Reference serviced by replacing filling solution and cleaning ceramic tip
16-May-06	515	519	225	468	431	450	398	426	Lysimeter installed today near measurement site
23-Jun-06	462	488	195	452	411	433	394	417	
04-Aug-06	454	462	179	455	407	429	394	418	8.25 m probe quickly reached value (1/2 a second). May be faulty

B.2 Spatial Measurements

The spatial variation measurements for Dam 2 and Dam 3/4 involved the measurement of the gravimetric water content and bulk density (used to determine the porosity and VWC, which are used to calculate the water content, measured as percent saturation), the redox potential (measured with a Ag/AgCl reference electrode and converted to an Eh, and corrected for the effects of pH), temperature, pH (measured in the presence of a $CaCl_2$ salt), and soil organic matter (which acts as a carbon source). The methods used to obtain these measurements were described in Section 4.2 in Chapter 4. The data are summarised in Tables B-2 to B-8. The spatial variation of the contaminants and daughter products (PCE, TCE, DCE and VC) and BTEX compounds (which also act as a carbon source) at Dam 2 and Dam 3/4 are described in Appendix C.

Table B-2 Spatial measurements at Site 21

Date	Depth (m)	Redox (Ag/AgCl) (mV)	Eh (mV) with pH correction	Temp. (^oC)	pH ($CaCl_2$)	SOM (%)	Gravimetric Water Content (%)	Bulk Density (g/cm^3)	VWC (%)	Porosity	Saturation (%)	Notes
25-May-06	0.3	178	428.92	20.9	7.88	2.06	69.55	-	-	-	-	
25-May-06	0.5	261	512.51	22.5	7.89	0.00	106.02	-	-	-	-	
25-May-06	1	267	471.31	23.7	7.09	0.96	116.73	-	-	-	-	
25-May-06	2	283	536.87	23.5	7.93	0.69	139.54	-	-	-	-	
25-May-06	4	50	402.40	25.1	9.60	0.69	125.64	-	-	-	-	
26-May-06	6.5	-27	354.90	22.7	10.10	0.00	186.19	-	-	-	-	
26-May-06	8.25	-43	333.59	25.5	10.01	0.48	218.43	-	-	-	-	

Table B-3 Spatial measurements at Site 22

Date	Depth (m)	Redox (Ag/AgCl) (mV)	Eh (mV) with pH correction	Temp. (^{o}C)	pH ($CaCl_2$)	SOM (%)	Gravimetric Water Content (%)	Bulk Density (g/cm^3)	VWC (%)	Porosity	Saturation (%)	Notes
01-Jun-06	0.3	187	419.04	20.0	7.56	1.03	75.69	-	-	-	-	Soil dry
01-Jun-06	0.5	202	432.86	21.9	7.54	1.44	88.90	0.3750	33.34	0.8585	38.83	Soil dry
01-Jun-06	1	274	509.58	23.0	7.62	0.89	92.54	0.3575	33.09	0.8651	38.25	Soil dry
01-Jun-06	2	271	529.59	24.1	8.01	0.83	120.62	0.3990	48.13	0.8494	56.66	
02-Jun-06	4	40	401.25	23.6	9.75	0.89	114.65	0.3844	44.07	0.8549	51.55	
02-Jun-06	6.5	-8	405.17	24.3	10.63	0.34	293.00	0.2768	81.09	0.8956	90.55	
02-Jun-06	8.25	-84	300.26	24.1	10.14	1.38	269.62	0.3082	83.09	0.8837	94.02	

Table B-4 Spatial measurements at Site 23

Date	Depth (m)	Redox (Ag/AgCl) (mV)	Eh (mV) with pH correction	Temp. (^{o}C)	pH ($CaCl_2$)	SOM (%)	Gravimetric Water Content (%)	Bulk Density (g/cm^3)	VWC (%)	Porosity	Saturation (%)	Notes
06-Jun-06	0.3	185	418.22	23.3	7.58	1.10	52.50	-	-	-	-	Soil dry
06-Jun-06	0.5	214	444.86	24.9	7.54	1.72	83.87	-	-	-	-	Soil dry
06-Jun-06	1	267	496.09	29.3	7.51	1.03	126.34	-	-	-	-	
06-Jun-06	2	268	513.61	31.3	7.79	1.03	158.81	-	-	-	-	
06-Jun-06	4	-	-	-	-	-	-	-	-	-	-	Hit a dense layer at 3.25 m. May be the dam embankment, due to sites proximity to it

Table B-5 Spatial measurements at Site 24

Date	Depth (m)	Redox (Ag/AgCl) (mV)	Eh (mV) with pH correction	Temp. (^oC)	pH ($CaCl_2$)	SOM (%)	Gravimetric Water Content (%)	Bulk Density (g/cm^3)	VWC (%)	Porosity	Saturation (%)	Notes
07-Jun-06	0.3	308	534.73	21.7	7.47	1.93	71.93	-	-	-	-	Soil dry
07-Jun-06	0.5	375	599.37	20.4	7.43	2.06	96.83	-	-	-	-	Soil dry
07-Jun-06	1	370	609.12	22.8	7.68	1.99	102.65	-	-	-	-	Soil dry
07-Jun-06	2	330	585.64	23.9	7.96	0.48	143.49	-	-	-	-	
07-Jun-06	4	230	558.80	25.0	9.20	0.89	109.74	-	-	-	-	
07-Jun-06	6.5	-25	409.41	24.5	10.99	0.28	249.36	-	-	-	-	
07-Jun-06	8.25	-23	389.58	24.9	10.62	0.34	260.62	-	-	-	-	

Table B-6 Spatial measurements at Site 25

Date	Depth (m)	Redox (Ag/AgCl) (mV)	Eh (mV) with pH correction	Temp. (^oC)	pH ($CaCl_2$)	SOM (%)	Gravimetric Water Content (%)	Bulk Density (g/cm^3)	VWC (%)	Porosity	Saturation (%)	Notes
09-Jun-06	0.3	206	448.66	18.0	7.74	1.31	54.35	-	-	-	-	
09-Jun-06	0.5	295	540.02	21.0	7.78	2.27	89.54	-	-	-	-	
09-Jun-06	1	300	530.86	24.0	7.54	2.34	99.44	-	-	-	-	
09-Jun-06	2	280	538.00	25.0	8.00	0.76	110.10	-	-	-	-	
09-Jun-06	4	195	464.21	26.1	8.19	1.51	115.28	-	-	-	-	
09-Jun-06	6.5	29	390.25	26.8	9.75	1.58	232.26	-	-	-	-	
28-Jun-06	8	-255	145.78	25.9	10.42	0.41	130.73	-	-	-	-	Auger broke before 8.25 m sampled. Re-augured close to previous site (to avoid effects of previous site which had water added to loosen stuck auger) on 28 June. Sampled at 8 m since layer was dense

Table B-7 Spatial measurements at Site 341

Date	Depth (m)	Redox (Ag/AgCl) (mV)	Eh (mV) with pH correction	Temp. (^oC)	pH ($CaCl_2$)	SOM (%)	Gravimetric Water Content (%)	Bulk Density (g/cm^3)	VWC (%)	Porosity	Saturation (%)	Notes
23-Jun-06	0.3	309	490.30	20.0	6.70	1.58	128.80	0.5518	71.07	0.7918	89.76	
23-Jun-06	0.5	280	535.64	21.2	7.96	1.99	146.00	0.5187	75.73	0.8043	94.17	
23-Jun-06	1	224	470.79	24.8	7.81	1.44	130.00	0.3674	47.76	0.8614	55.45	
23-Jun-06	2	-130.6	43.62	26.6	6.58	2.20	182.32	0.5395	98.36	0.7964	123.50	Black soil. Very anaerobic. Core sample disturbed
26-Jun-06	4	-120.3	144.19	27.3	8.11	2.06	61.46	0.3645	22.40	0.8625	25.97	Black and coarse material. Unable to get good core sample
26-Jun-06	6.5	-201	99.48	27.1	8.72	2.34	50.54	0.5556	28.08	0.7904	35.53	Black and coarse material. Unable to get good core sample
26-Jun-06	8	-220	26.20	20.0	7.80	2.13	43.75	-	-	-	-	Black and coarse material. Unable to get core sample

Table B-8 Spatial measurements at Site 342

Date	Depth (m)	Redox (Ag/AgCl) (mV)	Eh (mV) with pH correction	Temp. (^oC)	pH ($CaCl_2$)	SOM (%)	Gravimetric Water Content (%)	Bulk Density (g/cm^3)	VWC (%)	Porosity	Saturation (%)	Notes
30-Jun-06	0.3	170	412.66	19.1	7.74	2.61	119.32	0.4529	54.04	0.8291	65.17	
30-Jun-06	0.5	264	516.69	20.8	7.91	1.72	104.36	0.4097	42.75	0.8454	50.57	
30-Jun-06	1	184	434.92	22.5	7.88	1.99	155.29	0.6529	101.39	0.7536	134.53	Core sample disturbed
30-Jun-06	2	-228	68.35	25.2	8.65	2.68	143.71	0.5056	72.66	0.8092	89.78	Material very black and wet
30-Jun-06	4	-204	79.37	25.6	8.43	2.41	141.72	-	-	-	-	Material too soft for core sample
30-Jun-06	6.5	-249	217.86	24.9	11.54	0.69	242.38	-	-	-	-	Material whiter and more dense, but still too soft for core sample
30-Jun-06	8.25	-266	186.70	24.6	11.30	0.07	264.16	0.2180	57.59	0.9177	62.75	Material slightly more dense

B.3 Precipitation Measurements

The precipitation at the study site was measured by the automatic weather station on Dam 2. The total daily precipitation on each day that received precipitation from 01 September 2005 to 01 September 2006 is included in Table B-9. These dates include the months that the temporal measurements of redox potential were made at Dam 2; hence, the effects of the precipitation on the redox potential can be determined.

Table B-9 Precipitation measurements at Dam 2

Date	Precip. (mm)	Date	Precip. (mm)	Date	Precip. (mm)	Date	Precip. (mm)
05-Sep-05	0.8	24-Dec-05	15.9	18-Feb-06	0.4	22-Apr-06	11.4
06-Sep-05	4.7	25-Dec-05	0.2	19-Feb-06	0.2	23-Apr-06	0.8
12-Sep-05	5	27-Dec-05	1.6	20-Feb-06	0.8	29-Apr-06	24.4
20-Sep-05	0.8	28-Dec-05	12.3	21-Feb-06	41.6	30-Apr-06	2.9
21-Sep-05	0.8	01-Jan-06	3.1	22-Feb-06	7.5	07-May-06	5.5
25-Sep-05	3.2	02-Jan-06	1	25-Feb-06	12.2	08-May-06	8.4
05-Oct-05	8.4	03-Jan-06	0.4	27-Feb-06	0.2	14-May-06	0.2
06-Oct-05	1.3	04-Jan-06	7.2	02-Mar-06	1.4	18-May-06	5
07-Oct-05	2.6	08-Jan-06	12	03-Mar-06	24	19-May-06	30
08-Oct-05	4.1	09-Jan-06	11.2	04-Mar-06	4.1	20-May-06	5.2
23-Oct-05	6.8	10-Jan-06	0.6	05-Mar-06	1.5	21-May-06	5.2
24-Oct-05	2.8	11-Jan-06	3.9	10-Mar-06	0.8	28-May-06	0.8
28-Oct-05	13.2	12-Jan-06	1.2	12-Mar-06	12.2	30-May-06	0.2
29-Oct-05	0.3	16-Jan-06	1	13-Mar-06	4.1	02-Jun-06	0.4
03-Nov-05	7.9	18-Jan-06	8.5	16-Mar-06	6.6	03-Jun-06	2.5
04-Nov-05	8.9	19-Jan-06	10.8	17-Mar-06	3.3	27-Jun-06	6.4
05-Nov-05	14.3	22-Jan-06	14.9	18-Mar-06	0.2	29-Jun-06	0.3
13-Nov-05	1.2	23-Jan-06	3.1	19-Mar-06	2.7	10-Jul-06	0.2
15-Nov-05	18.3	24-Jan-06	1.2	20-Mar-06	2.1	30-Jul-06	0.2
16-Nov-05	5.6	26-Jan-06	12.8	21-Mar-06	0.2	01-Aug-06	0.4
17-Nov-05	9.4	27-Jan-06	6	23-Mar-06	1	02-Aug-06	1.5
18-Nov-05	2.2	28-Jan-06	0.4	27-Mar-06	0.6	03-Aug-06	0.6
26-Nov-05	0.5	29-Jan-06	2.9	28-Mar-06	2.5	09-Aug-06	2.1
28-Nov-05	1.2	31-Jan-06	6.2	29-Mar-06	0.2	10-Aug-06	1
30-Nov-05	3.9	01-Feb-06	0.2	02-Apr-06	3.7	13-Aug-06	0.6
07-Dec-05	5.2	03-Feb-06	0.8	03-Apr-06	0.8	17-Aug-06	0.6
08-Dec-05	1.3	04-Feb-06	0.2	05-Apr-06	0.2	18-Aug-06	0.8
15-Dec-05	1.7	05-Feb-06	0.6	07-Apr-06	0.2	19-Aug-06	1.4
16-Dec-05	10.1	07-Feb-06	0.5	09-Apr-06	9.7	20-Aug-06	1
17-Dec-05	8.3	08-Feb-06	21.8	13-Apr-06	0.3	30-Aug-06	0.8
19-Dec-05	13.8	12-Feb-06	21.2	14-Apr-06	1.8	31-Aug-06	0.4
20-Dec-05	4.2	15-Feb-06	0.8	16-Apr-06	6.2		
23-Dec-05	4.6	16-Feb-06	1.2	17-Apr-06	9.1		

APPENDIX C
VOC RESULTS

C.1 2003 Results

The spatial measurements of the VOCs (including PCE, TCE, the isomers of DCE, VC, and the compounds that make up the BTEX compounds) in 2003 were made by Duthe (2004), at various depths at both Dam 2 and Dam 3/4. The samples were taken from drilled core samples and tested for VOCs by CSIR BioChemtek in Modderfontein, South Africa, using headspace GC-MS and using an in-house method based on the US EPA methods 5021 and 8260. A number of samples were analysed by purge and trap GC-MS analysis after extraction with methanol. These results are summarised in Tables C-1 to C-4. The isomers of DCE, as well as the compounds making up the BTEX compounds, were added to get a total for each. The pollutants and daughter products are graphically represented in Figures C-1 to C-4.

- **Dam 2**

Table C-1 2003 VOC results from Dam 2 near Piezometer N2

Depth range (m)	PCE (µg/kg)	TCE (µg/kg)	1,1-DCE (µg /kg)	trans-1,2 DCE (µg/kg)	cis-1,2 DCE (µg/kg)	Total DCE (µg/kg)	VC (µg/kg)	Benzene (µg/kg)	Toluene (µg/kg)	Ethylbenzene (µg/kg)	m,p-Xylene (µg/kg)	o-Xylene (µg/kg)	Total BTEX (µg/kg)
2-2.5	67	27	<25	<25	<25	<75	25	<25	<25	<25	<50	<25	<150
6-6.5	1600	970	<35	110	990	1100	1200	<35	40	400	850	560	1850
11-11.5	1300	250	<20	<20	320	320	200	<20	<20	28	53	34	115
15-15.2	2600	3200	20	140	530	690	380	<20	<20	<20	52	<20	52
19-19.5	620	43	<25	<25	<25	<75	<25	<25	<25	<25	<50	<25	<150
22	<25	<25	<25	<25	41	41	<25	<25	<25	<25	<50	<25	<150

Table C-2 2003 VOC results from Dam 2 near Piezometer N3

Depth range (m)	PCE (µg/kg)	TCE (µg/kg)	1,1-DCE (µg/kg)	trans-1,2 DCE (µg/kg)	cis-1,2 DCE (µg/kg)	Total DCE (µg/kg)	VC (µg/kg)	Benzene (µg/kg)	Toluene (µg/kg)	Ethylbenzene (µg/kg)	m,p-Xylene (µg/kg)	o-Xylene (µg/kg)	Total BTEX (µg/kg)
2-2.5	<20	<20	<20	<20	<20	<60	<20	<20	<20	<20	<40	<20	<120
8-8.5	470	82	<30	45	52	97	320	<30	<30	300	930	530	1760
13-13.5	530	750	<20	<20	210	210	59	<20	<20	<20	<40	<20	<120
18-18.5	24	<15	<15	<15	<15	<45	<15	<15	<15	<15	<30	<15	<90

- **Dam 3/4**

Table C-3 2003 VOC results from Dam 3/4 East (Near Piezometer M4)

Depth range (m)	PCE (µg/kg)	TCE (µg/kg)	1,1-DCE (µg/kg)	trans-1,2 DCE (µg/kg)	cis-1,2 DCE (µg/kg)	Total DCE (µg/kg)	VC (µg/kg)	Benzene (µg/kg)	Toluene (µg/kg)	Ethylbenzene (µg/kg)	m,p-Xylene (µg/kg)	o-Xylene (µg/kg)	Total BTEX (µg/kg)
2-2.5	700	890	59	460	78000*	78519	12000*	<25	1400	36000*	110000*	17000*	164400
4-4.5	30	27	<25	530	160	690	7700*	<25	780*	17000*	46000*	7500*	71280
8-8.5	2200	500	<25	78	630	708	2200	<25	450	2600	5600	1300	9950
13-13.5	220	<20	<20	<20	<20	<60	<20	<20	<20	<20	<40	<20	<120
15-15.2	19	83	<15	<15	130	130	97	<15	<15	36	65	18	119
18-18.5	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60

* Analysed by Purge and Trap GC-MS after Methanol extraction

Table C-4 2003 VOC results from Dam 3/4 West (Near Piezometer M5)

Depth range (m)	PCE (µg/kg)	TCE (µg/kg)	1,1-DCE (µg/kg)	trans-1,2 DCE (µg/kg)	cis-1,2 DCE (µg/kg)	Total DCE (µg/kg)	VC (µg/kg)	Benzene (µg/kg)	Toluene (µg/kg)	Ethylbenzene (µg/kg)	m,p-Xylene (µg/kg)	o-Xylene (µg/kg)	Total BTEX (µg/kg)
2-2.5	230	160	<25	<25	3200*	3200	4100*	<25	66	880*	2600*	750*	4296
6-6.5	10000*	980*	<25	93	96000*	96093	4400*	<25	15000*	280000*	930000*	130000*	1355000
10-10.5	250	160	<30	<30	470	470	960	<30	<30	140	270	80	490

* Analysed by Purge and Trap GC-MS after Methanol extraction

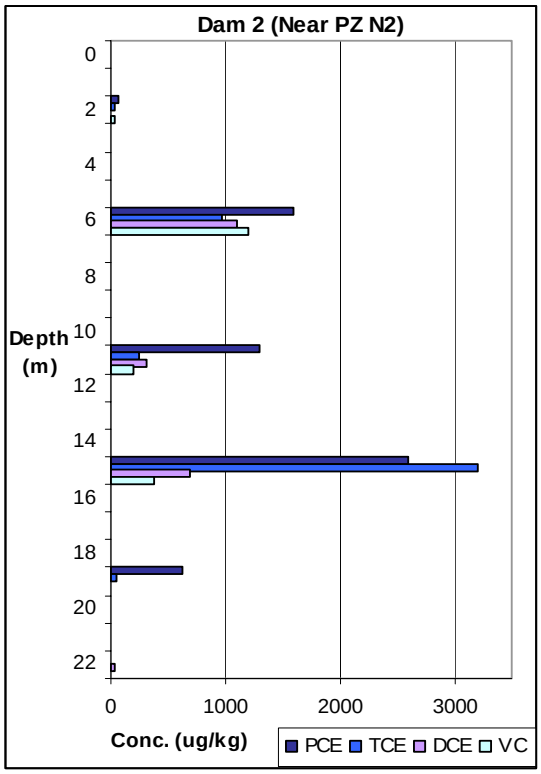

Figure C-1 Pollutants and daughter products near PZ N2 at Dam 2.

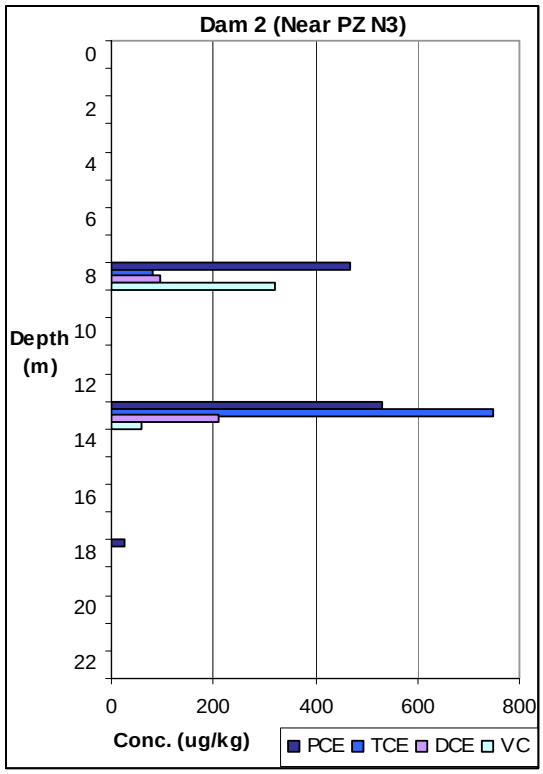

Figure C-2 Pollutants and daughter products near PZ N3 at Dam 2.

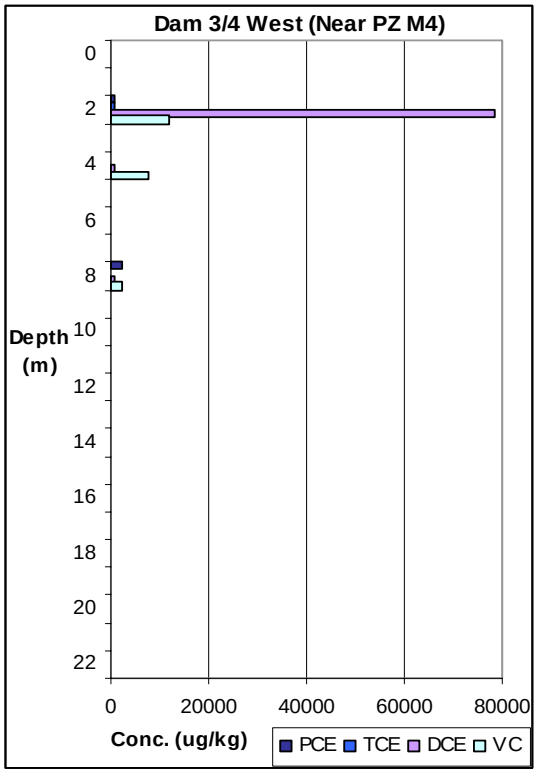

Figure C-3 Pollutants and daughter products near PZ M4 at Dam 3/4.

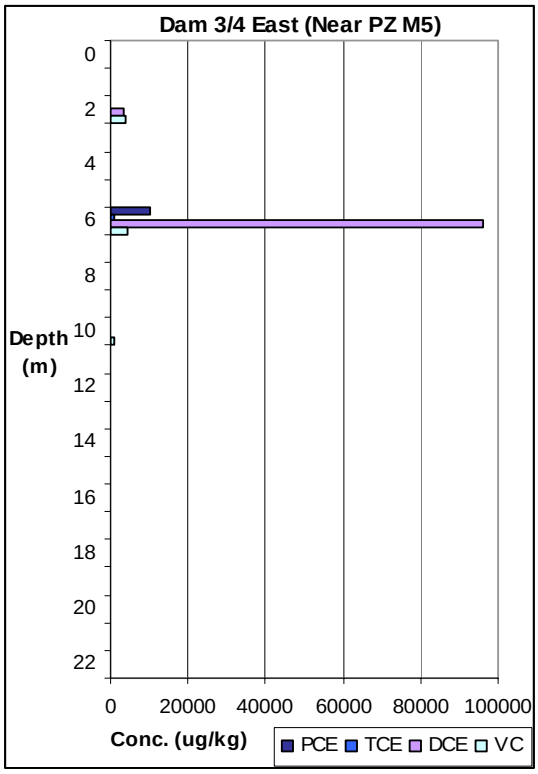

Figure C-4 Pollutants and daughter products near PZ M5 at Dam 3/4.

C.2 2006 Results

The spatial measurements of the VOCs were made in 2006 using the methods described in Sections 4.2.5 and 4.2.6 in Chapter 4, and using the same laboratory method to determine the VOC concentrations as was used in 2003. These measurements were made at each of the measurement sites at Dam 2 and Dam 3/4, and included the measurement of PCE, TCE, the DCE isomers, VC, and the compounds that make up the BTEX compounds. The results are summarised in Table C-5 and C-6. The isomers of DCE, as well as the compounds making up the BTEX compounds, were added to get a total for each.

- **Dam 2**

Table C-5 2006 VOC results from Dam 2

Site and depth (m)	PCE (µg/kg)	TCE (µg/kg)	1,1-DCE (µg/kg)	trans-1,2-DCE (µg/kg)	cis-1,2-DCE (µg/kg)	Total DCE (µg/kg)	VC (µg/kg)	Benzene (µg/kg)	Toluene (µg/kg)	Ethylbenzene (µg/kg)	m,p-Xylene (µg/kg)	o-Xylene (µg/kg)	BTEX (µg/kg)
21 - 0.3	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
21 - 0.5	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
21 - 1	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
21 - 2	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
21 - 4	14	22	<10	<10	<10	<30	<10	<10	<10	14	<20	46	60
21 - 6.5	28	17	<10	<10	12	12	<10	<10	<10	20	58	45	123
21 - 8.25	16	<10	<10	<10	70	70	<10	<10	<10	22	76	61	159
22 - 0.3	16	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
22 - 0.5	11	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
22 - 1	28	12	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
22 - 2	57	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
22 - 4	27	12	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
22 - 6.5	1900	150	<10	<10	210	210	16	<10	<10	39	99	73	211
22 - 8.25	<10	150	<10	<10	460	460	67	<10	12	65	170	120	367

Table C-5 cont. 2006 VOC results from Dam 2

Site and depth (m)	PCE (µg/kg)	TCE (µg/kg)	1,1-DCE (µg/kg)	trans-1,2-DCE (µg/kg)	cis-1,2-DCE (µg/kg)	Total DCE (µg/kg)	VC (µg/kg)	Benzene (µg/kg)	Toluene (µg/kg)	Ethylbenzene (µg/kg)	m,p-Xylene (µg/kg)	o-Xylene (µg/kg)	BTEX (µg/kg)
23 - 0.3	60	99	<10	<10	26	26	<10	<10	11	<10	<20	<10	11
23 - 0.5	<10	46	<10	<10	44	44	<10	<10	<10	<10	<20	<10	<60
23 - 1	26	67	<10	<10	44	44	<10	<10	<10	<10	<20	<10	<60
23 - 2	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
24 - 0.3	<10	10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
24 - 0.5	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
24 - 1	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
24 - 2	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
24 - 4	14	<10	<10	<10	16	16	<10	<10	<10	<10	<20	62	62
24 - 6.5	72	34	<10	<10	180	180	<10	<10	<10	42	100	84	226
24 - 8.25	860	160	<10	11	540	551	120	<10	<10	150	380	250	780
25 - 0.3	<10	24	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
25 - 0.5	11	20	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
25 - 1	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
25 - 2	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
25 - 4	16	26	<10	<10	<10	<30	<10	<10	<10	89	<20	230	319
25 - 6.5	71	74	<10	<10	36	36	<10	<10	36	560	1800	1000	3396
25 - 8	150	44	<10	<10	77	77	24	<10	<10	44	110	82	236

- **Dam 3/4**

Table C-6 2006 VOC results from Dam 3/4

Site and depth (m)	PCE (µg/kg)	TCE (µg/kg)	1,1-DCE (µg/kg)	trans-1,2-DCE (µg/kg)	cis-1,2-DCE (µg/kg)	Total DCE (µg/kg)	VC (µg/kg)	Benzene (µg/kg)	Toluene (µg/kg)	Ethylbenzene (µg/kg)	m,p-Xylene (µg/kg)	o-Xylene (µg/kg)	BTEX (µg/kg)
341 - 0.3	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
341 - 0.5	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
341 - 1	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
341 - 2	<10	<10	<10	<10	<10	<30	<10	<10	<10	190	370	160	720
341 - 4	<10	<10	<10	<10	<10	<30	<10	<10	<10	30	20	<10	50
341 - 6.5	11	44	<10	12	60	72	<10	<10	28	170	200	68	466
341 - 8	60	140	<10	<10	90	90	<10	<10	35	330	410	160	935
342 - 0.3	<10	<10	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
342 - 0.5	11	14	<10	<10	<10	<30	<10	<10	<10	<10	<20	<10	<60
342 - 1	22	17	<10	<10	19	19	<10	<10	<10	<10	<20	<10	<60
342 - 2	770	60	<10	12	3400	3412	470	<10	<10	21000	140000*	22000	183000
342 - 4	<10	<10	<10	<10	<10	<30	140	<10	180	1300	16000	4100	21580
342 - 6.5	180	110	<10	<10	180	180	1700	<10	170	770	3500	1200	5640
342 - 8.25	1300	100	<10	<10	1100	1100	2400*	<10	87	150	330	140	707

*** Above Calibration**

C.3 Calculation of BTEX Compounds Concentration in Interstitial Water

To calculate the concentration of the BTEX compounds available to the bacteria in the material, the concentration of BTEX compounds in the interstitial water of the material was calculated by dividing the total concentration of BTEX compounds (listed in Tables C-5 and C-6) by the water content (measured as g/g on a dry-weight basis, listed in Appendix B as a percent). The measurement, in micrograms per kilogram (µg/kg) was converted to parts per million (ppm) by dividing by 1000. The calculation is shown in the following tables.

Table C-7 Calculation of concentration of BTEX compounds in interstitial water at Dam 2

Site and depth (m)	BTEX conc. (µg/kg)	Water content on dry-weight basis (g/g)	BTEX conc. in interstitial water (ppm)
21-0.3	0	0.70	0
21-0.5	0	1.06	0
21-1	0	1.17	0
21-2	0	1.40	0
21-4	60	1.26	0.05
21-6.5	123	1.86	0.07
21-8.25	159	2.18	0.07
22-0.3	0	0.76	0
22-0.5	0	0.89	0
22-1	0	0.93	0
22-2	0	1.21	0
22-4	0	1.15	0
22-6.5	211	2.93	0.07
22-8.25	367	2.70	0.14
23-0.3	11	0.53	0.02
23-0.5	0	0.84	0
23-1	0	1.26	0
23-2	0	1.59	0
24-0.3	0	0.72	0
24-0.5	0	0.97	0
24-1	0	1.03	0
24-2	0	1.43	0
24-4	62	1.10	0.06
24-6.5	226	2.49	0.09
24-8.25	780	2.61	0.30
25-0.3	0	0.54	0
25-0.5	0	0.90	0
25-1	0	0.99	0
25-2	0	1.10	0
25-4	319	1.15	0.28
25-6.5	3396	2.32	1.46
25-8	236	1.31	0.18

Table C-8 Calculation of concentration of BTEX compounds in interstitial water at Dam 3/4

Site and depth (m)	BTEX conc. (μg/kg)	Water content on dry-weight basis (g/g)	BTEX conc. in interstitial water (ppm)
341-0.3	0	1.29	0
341-0.5	0	1.46	0
341-1	0	1.30	0
341-2	720	1.82	0.39
341-4	50	0.61	0.08
341-6.5	466	0.51	0.92
341-8	935	0.44	2.14
342-0.3	0	1.19	0
342-0.5	0	1.04	0
342-1	0	1.55	0
342-2	183000	1.44	127.34
342-4	21580	1.42	15.23
342-6.5	5640	2.42	2.33
342-8.25	707	2.64	0.27

C.4 Calculation of the Parent Compound to Daughter Product Ratio

To establish the parent compound to daughter product ratio the sum of the parent-compound concentrations (PCE and TCE) is divided by the sum of the daughter-product concentrations (DCE and VC), as described in Looney *et al.* (2004). This was done at each depth at each site on Dam 2 and Dam 3/4, using the 2006 results which were shown in Tables C-5 and C-6. Where no parent compounds or no daughter products were present above the detection limit the concentration was assumed negligible and a value of one was assigned to the total, so that the ratio could be calculated. Where neither parent compounds nor daughter products were above the detection limit, the ratio was not calculated. The calculation of this ratio is shown in Tables C-9 and C-10. Measurements below the detection limit are not shown, to simplify the tables.

- **Dam 2**

Table C-9 Calculation of Parent Compound to Daughter Product Ratio at Dam 2

Site and depth (m)	PCE (µg/kg)	TCE (µg/kg)	Total Parent (PCE+TCE) (µg/kg)	DCE (µg/kg)	VC (µg/kg)	Total Daughter (DCE+VC) (µg/kg)	Parent:Daughter ratio (PCE+TCE) / (DCE+VC)
21-0.3							
21-0.5							
21-1							
21-2							
21-4	14	22	36			1	36
21-6.5	28	17	45	12		12	3.75
21-8.25	16		16	70		70	0.23
22-0.3	16		16			1	16
22-0.5	11		11			1	11
22-1	28	12	40			1	40
22-2	57		57			1	57
22-4	27	12	39			1	39
22-6.5	1900	150	2050	210	16	226	9.07
22-8.25		150	150	460	67	527	0.28
23-0.3	60	99	159	26		26	6.12
23-0.5		46	46	44		44	1.05
23-1	26	67	93	44		44	2.11
23-2							
24-0.3		10	10			1	10
24-0.5							
24-1							
24-2							
24-4	14		14	16		16	0.88
24-6.5	72	34	106	180		180	0.59
24-8.25	860	160	1020	551	120	671	1.52

Table C-9 cont. Calculation of Parent Compound to Daughter Product Ratio at Dam 2

Site and depth (m)	PCE (µg/kg)	TCE (µg/kg)	Total Parent (PCE+TCE) (µg/kg)	DCE (µg/kg)	VC (µg/kg)	Total Daughter (DCE+VC) (µg/kg)	Parent:Daughter ratio (PCE+TCE) / (DCE+VC)
25-0.3		24	24			1	24
25-0.5	11	20	31			1	31
25-1							
25-2							
25-4	16	26	42			1	42
25-6.5	71	74	145	36		36	4.03
25-8	150	44	194	77	24	101	1.92

- **Dam 3/4**

Table C-10 Calculation of Parent Compound to Daughter Product Ratio at Dam 3/4

Site and depth (m)	PCE (µg/kg)	TCE (µg/kg)	Total Parent (PCE+TCE) (µg/kg)	DCE (µg/kg)	VC (µg/kg)	Total Daughter (DCE+VC) (µg/kg)	Parent:Daughter ratio (PCE+TCE) / (DCE+VC)
341-0.3							
341-0.5							
341-1							
341-2							
341-4							
341-6.5	11	44	55	72		72	0.76
341-8	60	140	200	90		90	2.22
342-0.3							
342-0.5	11	14	25	0		1	25
342-1	22	17	39	19		19	2.05
342-2	770	60	830	3412	470	3882	0.21
342-4			1	0	140	140	0.01
342-6.5	180	110	290	180	1700	1880	0.15
342-8.25	1300	100	1400	1100	2400	3500	0.40

APPENDIX D
ANALYSIS OF RESULTS

D.1 Determination of Reductive Dechlorination Potential

Based on thresholds and points given in Table 4.2 in Chapter 4, and summarised in Table D-1, the spatial results of each parameter measured (taken from Appendix B and C) were allocated a colour coded point value, using Table D-2. Colour codes are used for ease of interpretation.

In order for the point system to be used, missing water content measurements needed to be estimated at some sites and depths at each of the dams. This was done for all the depths at Sites 21, 23, 24 and 25, which were assumed equal to Site 22 since the measurements were only made at Site 22. In addition the values at 0.3 m at Site 22; 2 m and 8 m at Site 341; and 1 m, 4 m and 6.5 m at Site 342 were estimated based on the values measured at other depths in the profile (Section 5.1 in Chapter 5).

The colour coded summary of results, including the estimated water content measurements, is shown in Tables D-3 to D-9, and these were used to create the point tables in Chapter 6, which indicate the potential for reductive dechlorination within the dams.

Table D-1 Summary of thresholds and points for each parameter

	Analysis	Threshold	Points
Redox Potential	Eh	< 249 mV	4
		< 99 mV	8
Carbon Source	SOM	> 4.31%	2
	BTEX	> 0.1 ppm	2
pH	pH	5 < pH < 9	0
		5 > pH > 9	-2
Temperature	Temperature	> 20 ^{o}C	1
Daughter Products	DCE	Present	2
	VC	Present	2
Water Content	Percent Saturation	> 81%	1
		< 38%	-1

Table D-2 Colour code interpretation for point values

Points	Influence reductive dechlorination potential
-2	Moderately lowered
-1	Mildly lowered
0	None
1	Mildly promoted
2	Moderately promoted
4	Highly promoted
8	Very Highly promoted

Table D-3 Summary of results for Site 21 including colour codes

Depth (m)	Eh (mV)	Temp. (°C)	pH	Carbon Source		Saturation (%)	DCE (ppm)	VC (ppm)
				SOM (%)	BTEX (ppm)			
0.3	428.92	20.9	7.88	2.06	<0.06	-	<0.03	<0.01
0.5	512.51	22.5	7.89	0	<0.06	-	<0.03	<0.01
1	471.31	23.7	7.09	0.96	<0.06	-	<0.03	<0.01
2	536.87	23.5	7.93	0.69	<0.06	-	<0.03	<0.01
4	402.4	25.1	9.6	0.69	0.05	-	<0.03	<0.01
6.5	354.9	22.7	10.1	0	0.07	-	0.012	<0.01
8.25	333.59	25.5	10.01	0.48	0.07	-	0.07	<0.01

Table D-4 Summary of results for Site 22 including colour codes

Depth (m)	Eh (mV)	Temp. (°C)	pH	Carbon Source		Saturation (%)	DCE (ppm)	VC (ppm)
				SOM (%)	BTEX (ppm)			
0.3	419.04	20	7.56	1.03	<0.06	-	<0.03	<0.01
0.5	432.86	21.9	7.54	1.44	<0.06	38.83	<0.03	<0.01
1	509.58	23	7.62	0.89	<0.06	38.25	<0.03	<0.01
2	529.59	24.1	8.01	0.83	<0.06	56.66	<0.03	<0.01
4	401.25	23.6	9.75	0.89	<0.06	51.55	<0.03	<0.01
6.5	405.17	24.3	10.63	0.34	0.07	90.55	0.21	0.016
8.25	300.26	24.1	10.14	1.38	0.14	94.02	0.46	0.067

Table D-5 Summary of results for Site 23 including colour codes

Depth (m)	Eh (mV)	Temp. (°C)	pH	Carbon Source		Saturation (%)	DCE (ppm)	VC (ppm)
				SOM (%)	BTEX (ppm)			
0.3	418.22	23.3	7.58	1.1	0.02	-	0.026	<0.01
0.5	444.86	24.9	7.54	1.72	<0.06	-	0.044	<0.01
1	496.09	29.3	7.51	1.03	<0.06	-	0.044	<0.01
2	513.61	31.3	7.79	1.03	<0.06	-	<0.03	<0.01

Table D-6 Summary of results for Site 24 including colour codes

Depth (m)	Eh (mV)	Temp. (°C)	pH	Carbon Source		Saturation (%)	DCE (ppm)	VC (ppm)
				SOM (%)	BTEX (ppm)			
0.3	534.73	21.7	7.47	1.93	<0.06	-	<0.03	<0.01
0.5	599.37	20.4	7.43	2.06	<0.06	-	<0.03	<0.01
1	609.12	22.8	7.68	1.99	<0.06	-	<0.03	<0.01
2	585.64	23.9	7.96	0.48	<0.06	-	<0.03	<0.01
4	558.8	25	9.2	0.89	0.06	-	0.016	<0.01
6.5	409.41	24.5	10.99	0.28	0.09	-	0.18	<0.01
8.25	389.58	24.9	10.62	0.34	0.30	-	0.551	0.12

Table D-7 Summary of results for Site 25 including colour codes

Depth (m)	Eh (mV)	Temp. (°C)	pH	Carbon Source		Saturation (%)	DCE (ppm)	VC (ppm)
				SOM (%)	BTEX (ppm)			
0.3	448.66	18	7.74	1.31	<0.06	-	<0.03	<0.01
0.5	540.02	21	7.78	2.27	<0.06	-	<0.03	<0.01
1	530.86	24	7.54	2.34	<0.06	-	<0.03	<0.01
2	538	25	8	0.76	<0.06	-	<0.03	<0.01
4	464.21	26.1	8.19	1.51	0.28	-	<0.03	<0.01
6.5	390.25	26.8	9.75	1.58	1.46	-	0.036	<0.01
8	145.78	25.9	10.42	0.41	0.18	-	0.077	0.024

Table D-8 Summary of results for Site 341 including colour codes

Depth (m)	Eh (mV)	Temp. (°C)	pH	Carbon Source		Saturation (%)	DCE (ppm)	VC (ppm)
				SOM (%)	BTEX (ppm)			
0.3	490.3	20	6.7	1.58	<0.06	89.76	<0.03	<0.01
0.5	535.64	21.2	7.96	1.99	<0.06	94.17	<0.03	<0.01
1	470.79	24.8	7.81	1.44	<0.06	55.45	<0.03	<0.01
2	43.62	26.6	6.58	2.2	0.39	-	<0.03	<0.01
4	144.19	27.3	8.11	2.06	0.08	25.97	<0.03	<0.01
6.5	99.48	27.1	8.72	2.34	0.92	35.53	0.072	<0.01
8	26.2	20	7.8	2.13	2.14	-	0.09	<0.01

Table D-9 Summary of results for Site 342 including colour codes

Depth (m)	Eh (mV)	Temp. (°C)	pH	Carbon Source		Saturation (%)	DCE (ppm)	VC (ppm)
				SOM (%)	BTEX (ppm)			
0.3	412.66	19.1	7.74	2.61	<0.06	65.17	<0.03	<0.01
0.5	516.69	20.8	7.91	1.72	<0.06	50.57	<0.03	<0.01
1	434.92	22.5	7.88	1.99	<0.06	-	0.019	<0.01
2	68.35	25.2	8.65	2.68	127.34	89.78	3.412	0.47
4	79.37	25.6	8.43	2.41	15.23	-	<0.03	0.14
6.5	217.86	24.9	11.54	0.69	2.33	-	0.18	1.7
8.25	186.7	24.6	11.3	0.07	0.27	62.75	1.1	2.4

D.2 Determination of Oxidation Potential

The redox potential thresholds which determine the three forms of oxidation likely to be occurring within Dam 2 and Dam 3/4 (Section 6.2 in Chapter 6), are summarised in Table D-10. This table was used to colour code the redox potential results, measured as an Eh and corrected for pH, which are shown in Appendix B. The colour coded redox potential results are summarised in Table D-11. These colour codes, used for ease of interpretation, were used in the oxidation results table in Chapter 6 to indicate the potential for oxidation within the dams.

Table D-10 Colour codes for oxidation potential

Threshold	Degradation Mechanism
Eh > 400 mV	Aerobic oxidation of DCE and VC
400 mV>Eh> 200 mV	Anaerobic oxidation of DCE and VC
200 mV>Eh>120 mV	Anaerobic oxidation of VC
Eh < 120 mV	Oxidation unlikely

Table D-11 Summary of redox potential results for Dam 2 and Dam 3/4 including colour codes

Depth (m)	Dam 2 Eh (mV)					Dam 3/4 Eh (mV)	
	Site 21	Site 22	Site 23	Site 24	Site 25	Site 341	Site 342
0.3	428.92	419.04	418.22	534.73	448.66	490.3	412.66
0.5	512.51	432.86	444.86	599.37	540.02	535.64	516.69
1	471.31	509.58	496.09	609.12	530.86	470.79	434.92
2	536.87	529.59	513.61	585.64	538	43.62	68.35
4	402.4	401.25	-	558.8	464.21	144.19	79.37
6.5	354.9	405.17	-	409.41	390.25	99.48	217.86
8.25 (8 m for Site 25 and 341)	333.59	300.26	-	389.58	145.78	26.2	186.7

APPENDIX E

MODIFICATIONS TO VADOSE ZONE POINTS SYSTEM

Due to the limited importance of pH, temperature and water content, the points and thresholds of the vadose zone points system were modified in the discussion of the results in Chapter 6. The changes to the vadose zone points system (shown in Table 4.2 in Chapter 4) are summarised in Table E-1. The effects of these changes to the original vadose zone points system results tables (Section 6.1 in Chapter 6), are summarised in Tables E-2 to E-8, where the changes to points awarded are highlighted and the new totals are included as a comparison to the original totals.

Table E-1 Changes to the thresholds and points for pH, temperature and water content

	Thresholds		Points	
	Old	**New**	**Old**	**New**
pH	5 > pH > 9	5 > pH > 9	-2	-1
Temperature	> 20 ^{o}C	No threshold	1	0
Water Content	< 38% saturation at Dam 3/4	< 35% saturation at Dam 3/4	-1	-1
	> 81% saturation at Dam 2	No threshold at Dam 2	1	0
	> 81% saturation at Dam 3/4	> 55% saturation at Dam 3/4 (> 35% saturation in course layer at 4 m to 8 m at Site 341)	1	1

Table E-2 Changes to original vadose zone points table for Site 21

Depth (m)	**Eh**	**Temp.**	**pH**	**Carbon Source**		**Water Content**	**Daughter Products**		**NEW TOTAL**	**OLD TOTAL**
				SOM	**BTEX**		**DCE**	**VC**		
0.3	0	0	0	0	0	-1	0	0	**-1**	**0**
0.5	0	0	0	0	0	0	0	0	**0**	**1**
1	0	0	0	0	0	0	0	0	**0**	**1**
2	0	0	0	0	0	0	0	0	**0**	**1**
4	0	0	-1	0	0	0	0	0	**-1**	**-1**
6.5	0	0	-1	0	0	0	2	0	**1**	**2**
8.25	0	0	-1	0	0	0	2	0	**1**	**2**

Table E-3 Changes to original vadose zone points table for Site 22

Depth (m)	Eh	Temp.	pH	Carbon Source		Water Content	Daughter Products		NEW TOTAL	OLD TOTAL
				SOM	BTEX		DCE	VC		
0.3	0	0	0	0	0	-1	0	0	**-1**	**-1**
0.5	0	0	0	0	0	0	0	0	**0**	**1**
1	0	0	0	0	0	0	0	0	**0**	**1**
2	0	0	0	0	0	0	0	0	**0**	**1**
4	0	0	-1	0	0	0	0	0	**-1**	**-1**
6.5	0	0	-1	0	0	0	2	2	**3**	**4**
8.25	0	0	-1	0	2	0	2	2	**5**	**6**

Table E-4 Changes to original vadose zone points table for Site 23

Depth (m)	Eh	Temp.	pH	Carbon Source		Water Content	Daughter Products		NEW TOTAL	OLD TOTAL
				SOM	BTEX		DCE	VC		
0.3	0	0	0	0	0	-1	2	0	**1**	**2**
0.5	0	0	0	0	0	0	2	0	**2**	**3**
1	0	0	0	0	0	0	2	0	**2**	**3**
2	0	0	0	0	0	0	0	0	**0**	**1**

Table E-5 Changes to original vadose zone points table for Site 24

Depth (m)	Eh	Temp.	pH	Carbon Source		Water Content	Daughter Products		NEW TOTAL	OLD TOTAL
				SOM	BTEX		DCE	VC		
0.3	0	0	0	0	0	-1	0	0	**-1**	**0**
0.5	0	0	0	0	0	0	0	0	**0**	**1**
1	0	0	0	0	0	0	0	0	**0**	**1**
2	0	0	0	0	0	0	0	0	**0**	**1**
4	0	0	-1	0	0	0	2	0	**1**	**1**
6.5	0	0	-1	0	0	0	2	0	**1**	**2**
8.25	0	0	-1	0	2	0	2	2	**5**	**6**

Table E-6 Changes to original vadose zone points table for Site 25

Depth (m)	Eh	Temp.	pH	Carbon Source		Water Content	Daughter Products		NEW TOTAL	OLD TOTAL
				SOM	BTEX		DCE	VC		
0.3	0	0	0	0	0	-1	0	0	**-1**	**-1**
0.5	0	0	0	0	0	0	0	0	**0**	**1**
1	0	0	0	0	0	0	0	0	**0**	**1**
2	0	0	0	0	0	0	0	0	**0**	**1**
4	0	0	0	0	2	0	0	0	**2**	**3**
6.5	0	0	-1	0	2	0	2	0	**3**	**4**
8	4	0	-1	0	2	0	2	2	**9**	**10**

Table E-7 Changes to original vadose zone points table for Site 341

Depth (m)	Eh	Temp.	pH	Carbon Source		Water Content	Daughter Products		NEW TOTAL	OLD TOTAL
				SOM	BTEX		DCE	VC		
0.3	0	0	0	0	0	1	0	0	**1**	**1**
0.5	0	0	0	0	0	1	0	0	**1**	**2**
1	0	0	0	0	0	1	0	0	**1**	**1**
2	8	0	0	0	2	1	0	0	**11**	**11**
4	4	0	0	0	0	-1	0	0	**3**	**4**
6.5	4	0	0	0	2	1	2	0	**9**	**8**
8	8	0	0	0	2	1	2	0	**13**	**11**

Table E-8 Changes to original vadose zone points table for Site 342

Depth (m)	Eh	Temp.	pH	Carbon Source		Water Content	Daughter Products		NEW TOTAL	OLD TOTAL
				SOM	BTEX		DCE	VC		
0.3	0	0	0	0	0	1	0	0	**1**	**0**
0.5	0	0	0	0	0	0	0	0	**0**	**1**
1	0	0	0	0	0	0	2	0	**2**	**3**
2	8	0	0	0	2	1	2	2	**15**	**16**
4	8	0	0	0	2	1	0	2	**13**	**14**
6.5	4	0	-1	0	2	1	2	2	**10**	**9**
8.25	4	0	-1	0	2	1	2	2	**10**	**9**