MODELING LANDFILL CAP INFLUENCE ON NATURAL ATTENUATION

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SUMMARY: Placement of low-permeability caps over old landfills will not only prolong the contaminating lifespan of these landfills indefinitely, but may also have an adverse influence on the natural attenuation of leachate plumes in groundwater. A groundwater redox model (BIOREDOX3D) is used to show that the placement of low-permeability caps at some unlined landfills may have a detrimental impact on groundwater quality, providing evidence that the implications of this remedy warrant serious consideration for the future.

1.0 INTRODUCTION

A principal concern associated with landfill leachate is the deterioration of groundwater quality below landfills (Christensen et al., 1994). Field studies have shown that landfill leachate may contain significant concentrations of chlorinated ethenes (e.g. Christensen et al., 1994). Studies have also shown that at old landfill sites, where organic contaminants have leached to underlying aquifers, natural attenuation (particularly biodegradation) has, in some cases, effectively neutralized the downgradient migration of organic contaminants (e.g. Lyngkilde and Christensen, 1992b; Carey et al., 1996).

A common perception is that placement of a low-permeability cap over these unlined landfills is necessary in order to reduce the flux of leachate to underlying aquifers. However, a reduction in leachate flux will significantly decrease the availability of landfill-derived microbial substrates in groundwater below the landfill, and therefore, may reduce the biodegradability of chlorinated ethenes already present in the underlying aquifer. As will be shown in this study, it is conceivable that the reduction in biodegradability, caused by the placement of a low-permeability cap, may result in even greater migration of existing contaminant plumes downgradient from the landfill.

Bishop (1996) identified aerobic, permeable soil covers as an alternative to the conventional low-permeability caps. At present, however, regulations require that expensive, low-permeability caps be constructed over new and existing landfills, even when natural attenuation has been documented to be effectively buffering the leachate impact to underlying aquifers. The future construction of low-permeability caps at existing landfill sites may represent hundreds of millions of dollars in expenditures to be committed over the coming decades. Given that these landfill caps may provide little benefit at some sites (with respect to aquifer restoration), it is imperative that the effects of these low-permeability caps be studied further.

Assessment of the complex processes that control the effects of low-permeability caps on waste stabilization and groundwater attenuation requires a comprehensive, multidisciplinary study. This paper presents a preliminary assessment of the influence that low-permeability caps may have on the

attenuation of leachate plumes in groundwater. The purpose of this initial assessment is to identify the need for further studies relating to low-permeability cap implications.

This study is based on a simple model scenario of a hypothetical landfill, with an emphasis on the redox-dependent migration of chlorinated ethenes typically detected in old sanitary landfills, including perchloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (DCE), and vinyl chloride. The biodegradability of these chlorinated ethenes is discussed, the landfill scenario is developed, a numerical model is utilized to compare the impact on groundwater quality for high- and low-permeability cap configurations, and further areas for study are identified.

2. BIOGEOCHEMISTRY OF LEACHATE PLUMES

2.1 Coupling Between Biodegradation and Redox Potential

The oxidation of a primary substrate results in an electron transfer from the substrate (also referred to as the electron donor) to available electron acceptors. This electron transfer results in the release of energy which is utilized for microbial metabolism. Typical electron acceptors available in groundwater, in the order of those that release the greatest energy to those that release the least energy, are as follows: dissolved oxygen, nitrate, manganese (IV) oxide and iron (III) hydroxide coatings on soil sediments, dissolved sulfate, and carbon dioxide (Baedecker and Back, 1979; Lyngkilde and Christensen, 1992a). Long-term oxidation of the primary substrate depletes the supply of available electron acceptors in a step-wise, or sequential manner, such that the redox potential in groundwater becomes more reducing during biodegradation processes.

The biogeochemistry of leachate plumes has been extensively documented by Baedecker and Back (1979), Lyngkilde and Christensen (1992a), and Christensen et al. (1994). Landfill-derived organic carbon (TOC) is thought to be the primary substrate for microbial degradation in leachate plumes, although the organic matter leaching from older landfills is only slowly biodegradable because of the absence of volatile organic acids which become depleted in the early stages of landfill stabilization (Christensen et al., 1994).

With the biodegradation of organic-rich leachate in groundwater below landfills, a sequence of redox zones of increasing redox potential may develop downgradient from the source area as follows:

1. methanogenic zone (methane produced from the reduction of carbon dioxide);
2. sulfidogenic zone (sulfate-reducing);
3. ferrogenic zone (Fe(III)-reducing);
4. manganogenic zone (Mn(IV)-reducing);
5. nitrate-reducing zone; and
6. aerobic zone.

The occurrence and extent of each individual redox zone is site-specific, and will depend on substrate migration pathways, kinetics of the redox processes, hydraulic retention times, and the availability of various electron acceptors in groundwater. Local geochemical processes, including mineral dissolution/precipitation and aqueous complexation, may influence the bioavailability of electron acceptors, particularly sulfate. Ultimately, the site-specific distribution of redox zones downgradient from the source area will control the degree of natural attenuation of organic contaminants in

groundwater (Lyngkilde and Christensen, 1992b). This demonstrates the two-way coupling between the biodegradation of organic compounds and redox conditions in groundwater.

2.2 Biodegradability of Chlorinated ethenes

2.2.1 Biodegradation Mechanisms

Reductive dechlorination is one of the principal mechanisms involved in the biodegradation of chlorinated ethenes under anaerobic conditions, and thus is expected to be important for the attenuation of chlorinated ethenes in leachate plumes. Reductive dechlorination is defined as the transfer of electrons from the electron donor to the chlorinated ethene compound, which acts as a secondary electron acceptor. Common electron donors that facilitate reductive dechlorination include dissolved organic carbon (either native to the soil, or derived from anthropogenic sources such as landfill leachate) and petroleum hydrocarbons.

The anaerobic reduction of PCE and TCE to ethene (through sequential intermediate products of DCE and vinyl chloride) has been observed at many sites (Ellis, 1996), although the transformations may be incomplete; the processes responsible for dechlorination past DCE are not yet well understood (Gossett and Zinder, 1996). McCarty (1996) provides a general review of the redox-dependent biodegradability of chlorinated ethenes. In summary, the complete transformation from PCE and TCE to ethene will occur only under methanogenic conditions. Under less reducing conditions, such as in the ferrogenic or sulfate-reducing zones, PCE and TCE may be transformed to DCE, but will not be transformed further to vinyl chloride or ethene. Reductive dechlorination of these chlorinated ethenes will not occur in the nitrate-reducing zone.

The aerobic co-metabolism of chlorinated ethenes is generally of little significance unless a suitable electron donor (e.g. methane, ammonia, or phenol) is present (McCarty, 1996). Thus it is important to consider that, in the absence of a suitable electron donor, PCE, TCE, and DCE appear to be essentially non-degradable if they reach the nitrate-reducing or aerobic zones. However, it is possible for vinyl chloride to be oxidized under aerobic conditions, or under anaerobic conditions where iron (III) is the electron acceptor (Bradley and Chapelle, 1996). Vinyl chloride is also readily and very efficiently co-metabolized aerobically by methane, phenol, or toluene oxidizers (McCarty, 1996).

2.2.2 Relative Rates of Biodegradation

Given that the secondary process of reductive dechlorination occurs simultaneously with the primary transfer of electrons from available donors to inorganic electron acceptors, the rate of reductive dechlorination is dependent on the concentrations of the primary substrates and inorganic electron acceptors because these species control the intracellular availability of electrons (Wrenn and Rittmann, 1995). Based on a kinetic model proposed by Wrenn and Rittmann (1995), the rates of reductive dechlorination are directly proportional to the concentrations of primary substrates, and are indirectly proportional to the concentrations of available electron acceptors because of competitive inhibition. Therefore, a significant decline in the concentration of TOC in a leachate plume, as would occur when a low-permeability cap is placed over a landfill, is expected to result in a significant reduction in the anaerobic biodegradation rates of chlorinated ethenes already present in the aquifer. The implications of this reduction in biodegradability are shown later in this paper.

In general, the rates of reductive dechlorination are most rapid under methanogenic conditions, and become slower with increasing redox potential (Semprini et al., 1995). Also, a higher degree of chlorination generally results in a faster rate of reductive dechlorination (Vogel et al., 1987). Thus the reduction of PCE and TCE occurs at faster rates than the reduction of vinyl chloride. Based on a survey of many sites where the reductive dechlorination of chlorinated ethenes had been identified, Ellis (1996) determined the average half-lives for PCE, TCE, DCE, and vinyl chloride to range from 1.0 to 1.3 years. Based on a similar survey, Wilson et al. (1996) identified the upper range for "reasonable" rates of attenuation of chlorinated ethenes to be 7.3 y^{-1} (equivalent to a half-life of approximately 1 month).

3. IMPLICATIONS OF LANDFILL CAP PERMEABILITY

3.1 BIOREDOX3D Model Development

Redox mapping is an essential task when evaluating the biodegradability of chlorinated ethenes in groundwater, particularly for landfill leachate plumes. A three-dimensional, multicomponent transport model (BIOREDOX3D) is used to provide representation of the coupling between the biodegradation of organic contaminants, and the associated redox reactions between available electron donors and acceptors. BIOREDOX3D simulates microbial redox reactions by coupling the first-order oxidation of electron donors (such as landfill-derived TOC) and the sequential reduction of available electron acceptors, including oxygen, nitrate, mineral-phase manganese oxide and ferric hydroxide coatings, sulfate, and carbon dioxide. BIOREDOX3D is also capable of representing redox- and substrate-dependent biodegradation rates for organic contaminants, and can represent the straight-chain sequential transformations commonly observed during the first-order reductive dechlorination of chlorinated ethenes such as PCE, TCE, DCE, and vinyl chloride. A detailed description of the BIOREDOX3D model is beyond the scope of this paper. Carey et al. (1997a) present a thorough review of the development, verification, and validation of BIOREDOX3D.

3.2 Model Scenario

A hypothetical landfill scenario was developed so that some of the principal processes controlling the influence of landfill cap permeability on groundwater quality could be modeled. The landfill scenario is based on an old, unlined landfill overlying a shallow, unconfined aquifer. For the purpose of this initial study, the model scenario was based on the assumption that native organic matter in the soil was insufficient to support the natural attenuation of contaminants in the leachate plume. That is, contaminants in the leachate plume would only be attenuated effectively in the presence of landfill-derived organic matter. Future studies will address the sensitivity of low-permeability cap implications for other landfill settings.

Contaminants were assumed to have leached from the uncovered landfill to the shallow aquifer over an initial 15-year period following the commencement of leachate production, at which time the landfill was assumed to be capped. The rate of leachate generation was assumed to be 0.30 metres per year (m/y) prior to the placement of the cap. BIOREDOX3D was used to predict the redox zone distribution and the extent of the chlorinated ethene plumes in the aquifer prior to the placement of the cap.

Two alternative landfill cap scenarios were modeled. The first scenario assumed the landfill was covered with a permeable cap which allowed water to continue to infiltrate into the landfill at the same rate of 0.30 m/y, to allow for enhanced stabilization of the waste. The second scenario assumed that a low-permeability cap was placed over the landfill, restricting leachate production from the landfill to the underlying aquifer to a rate of only 0.025 m/y. Both scenarios were modeled for an additional 15 years after placement of the respective caps.

To ensure a realistic assessment, the conditions assumed for this scenario were derived based on similar conditions reported for the Vejen Landfill Site in Vejen, Denmark (Lyngkilde and Christensen, 1992a; Heron et al., 1995). PCE, TCE, DCE, and vinyl chloride were selected as primary contaminants for this scenario because they are commonly detected in leachate at old landfills, and because the biodegradability of these compounds is strongly dependent on groundwater redox potential, which is directly influenced by landfill cap permeability.

A landfill leachate model was selected to represent the temporal changes in leachate quality. The leachate concentrations and flux terms for the two cap scenarios were used to formulate the contaminant source term for the groundwater model developed for this study. The landfill leachate model and groundwater model are discussed in the following sections.

3.2.1 Landfill Leachate Model

The rate of moisture infiltration into landfills has a strong influence on the rate of refuse stabilization, and thus has a direct impact on leachate constituent concentrations. A separate study is being conducted to determine the potential implications of landfill cap permeability on temporal variations in leachate quality, including the development of a leachate composition model for predicting the relative strength of the leachate source impacting underlying aquifers based on different landfill cap configurations (Carey et al., 1997b). For the purposes of this study, a simplified landfill model was utilized to provide a preliminary assessment of the implications for landfill cap permeability on the extent of groundwater impact.

Leachate TOC was represented as a source term for the groundwater model so that the development of redox zones downgradient from the landfill could be simulated. Based on the leachate model presented by Lu et al. (1981), the initial leachate TOC concentration was specified to be 14000 mg/L, and TOC concentrations were specified to decline exponentially with a first-order rate of 0.26 y^{-1}. The decline in concentrations was specified to occur for the first ten years of the landfill simulation. Following the initial ten year period, TOC concentrations were assumed to remain constant to reflect the additional electron donor capacity in leachate resulting from the presence of ammonium (Heron et al., 1995). The leachate concentrations for PCE, TCE, DCE, and vinyl chloride were assumed to be constant values of 250 μg/L for the entire simulation period. BIOREDOX3D also represented landfill source concentrations for oxygen, nitrate, and sulfate. The concentrations for oxygen and nitrate were assumed to be zero at all times, and the sulfate concentration was assumed to be a constant value of 400 mg/L based on an upper range reported by Christensen et al. (1994).

3.2.2 Groundwater Model

A two-dimensional cross-section of the unconfined aquifer was modeled. Groundwater flow was simulated using MODFLOW, and the leachate plume migration was simulated using BIOREDOX3D. The groundwater flow simulation is based on an average aquifer thickness of 10 metres, an average linear

groundwater velocity below the landfill ranging from 150 to 200 m/y, and uniform regional recharge to the aquifer (beyond the boundaries of the landfill) at a rate of 0.30 m/y. The rate of recharge to the shallow aquifer directly below the landfill was specified to be consistent with the landfill infiltration rates assumed for each cap configuration.

BIOREDOX3D was used to simulate the fate and transport of the leachate plume in the shallow aquifer, including a representation of the coupling between the oxidation of landfill-derived TOC and the reduction of available electron acceptors in groundwater and in the soil. TOC, PCE, TCE, DCE, and vinyl chloride are the organic leachate constituents included as solutes in the BIOREDOX3D model; inorganic electron acceptors represented as solutes in the model include dissolved oxygen, nitrate, and sulfate, as well as mineral-phase ferric hydroxide coatings on soil particles. Manganese oxides were not considered as part of this study, nor was the transport of methane downgradient from the methanogenic zone. It was assumed that carbon dioxide was non-limiting with respect to methanogenic activity.

The redox-dependent biodegradability of the chlorinated ethenes was specified in the model, using biodegradation rates consistent with the review presented in Section 2.2.2 of this paper. It was also assumed that the reductive dechlorination rates for the chlorinated ethenes decreased when the low-permeability cap was placed over the landfill, because of the corresponding decrease in TOC concentrations below the landfill. Further study is warranted to define a general relationship between reductive dechlorination rates and TOC concentrations in leachate plumes.

Figure 1 shows the dimensions and boundary conditions for the respective simulation models. Table 1a presents properties of solutes simulated for this scenario, as well as boundary and initial concentrations. Table 1b presents relevant redox half-reactions, and Table 1c presents groundwater biodegradation rates simulated for the organic leachate constituents.
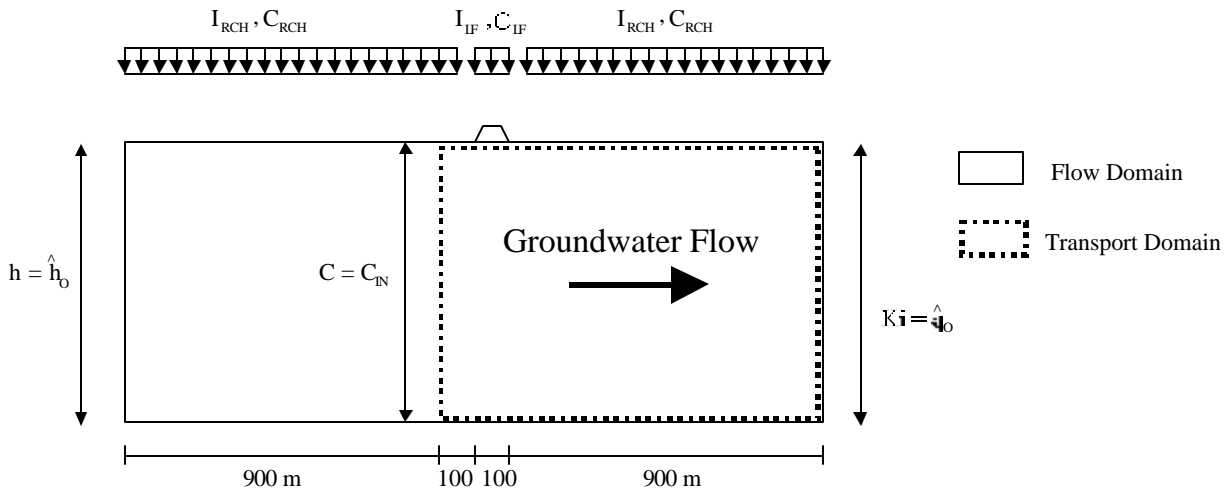

FIGURE 1 - GROUNDWATER MODEL DOMAIN

3.3 Redox Zone Distributions

Figure 2 presents the redox zone distribution that was simulated using BIOREDOX3D, based on the initial 15 years of TOC migration from the landfill. The general sequence of redox zones simulated using

BIOREDOX3D is consistent with what was expected, and compare favorably with the redox zones observed in the shallow aquifer underlying the Vejen landfill site (Lyngkilde and Christensen, 1992a). Simulation results indicated that the redox zone distribution corresponding to a time of 15 years after the placement of the high-permeability cap (total simulation time of 30 years) was similar to Figure 2, except the methanogenic zone was longer, coincident with a decrease in the length of the ferrogenic zone, because of the gradual depletion of ferric hydroxide coatings in the aquifer. Figure 3 illustrates the simulated redox zone for the low-permeability cap scenario corresponding to a time of 15 years after placement of the cap. This figure shows how the placement of the low-permeability cap, and the corresponding decline in TOC concentrations in the aquifer, resulted in a significant shift in the redox zone distribution in the aquifer. Potential implications of this shift in redox distribution are discussed in the following section.

TABLE 1a - SOLUTE INPUT PARAMETERS

Solute	Molecular Weight (g/mol)	K_{oc} (mL/g)	Units of Concentration	Boundary and Initial Conditions			
				C_{IN}	C_{RCH}	C_{LF}	$C(x,t=0)$
TOC	12	0	mg/L	0	0	(a)	0
PCE	166	364	ug/L	0	0	250	0
TCE	131.5	126	ug/L	0	0	250	0
DCE	97	49	ug/L	0	0	250	0
Vinyl Chloride	62.5	57	ug/L	0	0	250	0
Oxygen	32	0	mg/L	7	7	0	7
Nitrate	62	0	mg/L	25	25	0	25
Ferric Hydroxide	55.85	N/A	mg/g	N/A	N/A	N/A	5
Sulfate	96.1	0	mg/L	40	40	400	40

(a) $C = 14000e^{-0.26t}$, $t \leq 10$ years; $C = 1040$ mg/L, $t > 10$ years

TABLE 1b - REDOX HALF-REACTIONS

Solute	Type	Half-Reaction
TOC	Oxidation	$CH_2O + H_2O \rightarrow CO_2 + 4H^+ + 4e^-$
Vinyl Chloride	Oxidation	$CH_2CHCl + 2H_2O \rightarrow CH_3COOH + 3H^+ + 3e^-$
Oxygen	Reduction	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Nitrate	Reduction	$NO3^- + 6H^+ + 5e^- \rightarrow 0.5N_2(g) + 3H_2O$
Ferric Hydroxide	Reduction	$Fe(OH)_3(s) + 3H^+ + e^- \rightarrow Fe^{2+} + 3H2O$
Sulfate	Reduction	$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$

TABLE 1c - BIODEGRADATION RATES

	Redox Zone Biodegradation Rate						Scenario	k_{TOC} (d^{-1})	k_{RD} (d^{-1})	k_{OXD} (d^{-1})
Organic Solute	CH_4	SO_4	Fe(III)	NO_3	O_2					

TOC	k_{TOC}	k_{TOC}	k_{TOC}	k_{TOC}	k_{TOC}
PCE	k_{RD}	0.75 k_{RD}	0.5 k_{RD}	0	0
TCE	k_{RD}	0.75 k_{RD}	0.5 k_{RD}	0	0
DCE	k_{RD}	0	0	0	0
Vinyl Chloride	0.75 k_{RD}	0	k_{OXD}	0	k_{OXD}

no cap	7.6E-3	7.6E-3	7.6E-3
high-K cap	7.6E-3	7.6E-3	7.6E-3
low-K cap	7.6E-3	1.9E-3	7.6E-3
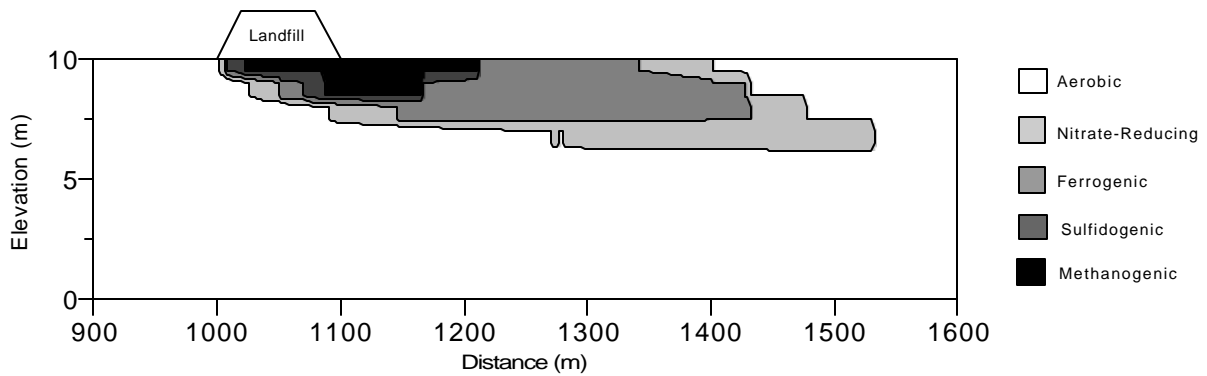
FIGURE 2 - REDOX ZONES, NO CAP (t=15 years)
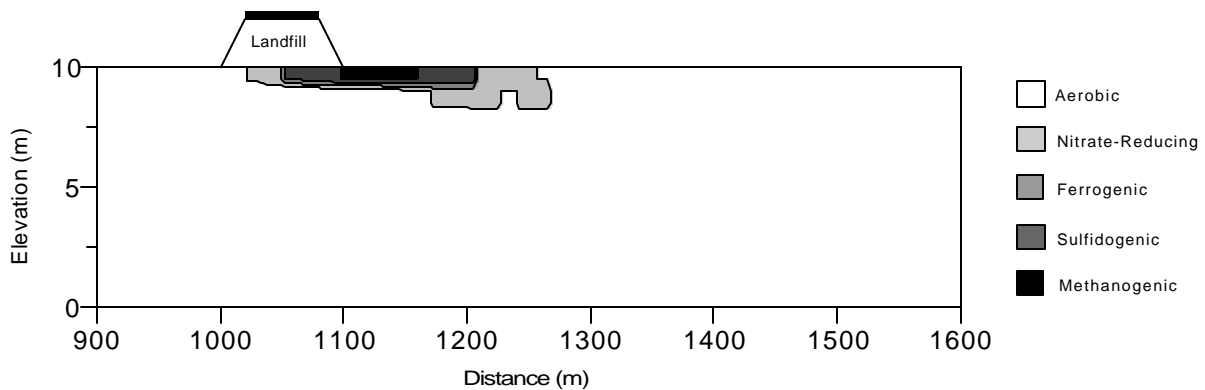
FIGURE 3 - REDOX ZONES, LOW-K CAP (t=30 years)

3.4 Effects of Landfill Cap Permeability on Ethene Plumes

For the purposes of this paper, the PCE, TCE, and vinyl chloride plumes are defined as those portions of the aquifer where concentrations of the respective compounds exceed 5 ug/L. (DCE has a higher water quality criteria than the other chlorinated ethenes, and hence will not be discussed further here). Figures 4a and 4b illustrate the extent of the PCE and TCE plumes, respectively, for the high-permeability cap scenario at a simulation time equivalent to 5 years after the placement of the permeable cap (total simulation time of 20 years). Based on the simulation results, these plumes are relatively stable in time, indicating that the natural attenuation of these contaminants is effectively limiting groundwater impact to within 300 metres from the landfill boundary. Figures 4c and 4d show the extent

of the PCE and TCE plumes, respectively, for the low-permeability cap scenario at the same simulation time (5 years after cap placement). These figures clearly indicate that a significant portion of the PCE and TCE plumes have migrated to a greater extent downgradient from the landfill. Analysis of the model results indicates that the re-distribution of the redox zones resulted in portions of the PCE and TCE plumes extending beyond the new boundary of the ferrogenic zone, where PCE and TCE are non-degradable. The model predicted that vinyl chloride would be attenuated more strongly than the PCE and TCE plumes because of the efficient oxidation of this compound in the ferrogenic and aerobic zones.
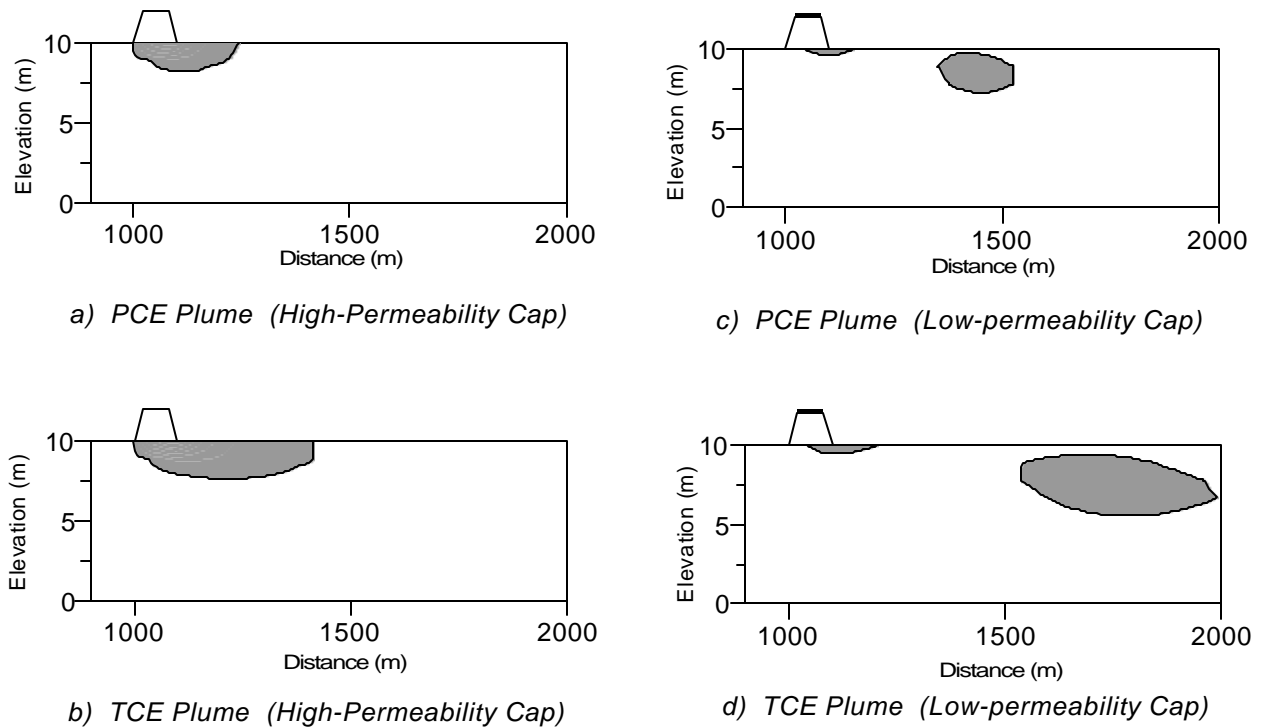

a) PCE Plume (High-Permeability Cap)

c) PCE Plume (Low-permeability Cap)

b) TCE Plume (High-Permeability Cap)

d) TCE Plume (Low-permeability Cap)

FIGURE 4 - COMPARISON BETWEEN LANDFILL CAPS (t=20 years)

4. SUMMARY

This study describes potential implications associated with low-permeability landfill caps. A numerical model was used to simulate conditions where the placement of a low-permeability cap may cause a detrimental impact to groundwater quality. Although this initial assessment is based on a specific setting, it provides important evidence that serious consideration should be focused on the risk and cost implications of low-permeability caps. Particular attenuation should be paid to alternative remedies (such as aerobic, permeable caps) that can be engineered to suit site-specific conditions and to provide more cost-effective remedial solutions.

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