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ATTENUATION OF LANDFILL LEACHATE BY A NATURAL MARSHLAND SYSTEM

by

François La Forge

A thesis
submitted under the supervision of

Dr. Leta Fernandes

in partial fulfilment of the
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UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

À la mémoire de mon père
Roland La Forge
(1941-1973)

et à ma mère
Louise Bélanger La Forge

ATTENUATION OF LANDFILL LEACHATE BY A NATURAL MARSHLAND SYSTEM

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ABSTRACT

Since the early 1980's, leachate originating from the Alice and Fraser municipal landfill has been discharging in a natural marshland system located some 300 meters downgradient from the waste disposal site. However, monitoring of the water quality within the marshland indicates that the contaminant level has not yet surpassed background concentration downstream from the main impact area. A mathematical model was developed in an attempt to predict the mobility of several contaminant species within the marshland environment. Parameters needed for the predictive model were gathered based on the physical configuration of the landfill and marshland associated with laboratory derived data on the attenuation capacity of the marshland soil matrix.

The behaviour, transport and ultimate fate of contaminants in organic soil is greatly affected by their participation in sorption reactions. The adsorption potential of lead, zinc, calcium, sodium and pentachlorophenol (PCP) by marshland soil was evaluated in laboratory through both, batch and column experiments. Most contaminants were found to fit either the Freundlich or Langmuir isotherm model. High retardation factors, exceeding 2000 for lead and approaching 100 for both zinc and PCP were measured. However, desorption experiments indicate that the adsorption process for certain compounds, such as PCP, can be partly reversible.

A multidimensional finite-difference model based on the Advection-Dispersion Equation was used to predict the migration of the above mentioned contaminants. The model is adapted to the hydrologic characteristics of the marshland, emphasizing subsurface flow, dilution as well as the adsorption capacity of the organic soil. Initial modeling results indicate that marshland soil has the capacity to substantially retard the migration of several contaminant species typically found in landfill leachate. The predictive capacity of the model will eventually be evaluated based on the contaminant migration plume observed at the actual marshland site. Calibration of the model is necessary to better reflect the complex reactions associated with marshland system.

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NOTATIONS

A: Water addition rate (m/day)

C: Solute concentration (g/m^3)

C': Concentration of solute sorbed on the porous medium (g/cm^3)

C_e: Concentration of material being adsorbed remaining in solution at equilibrium (kg/m^3)

C_i: Background concentration (g/m^3)

C_o: Input concentration (g/m^3)

D_L: Longitudinal dispersion coefficient (m^2/s)

D_T: Transverse dispersion coefficient (m^2/s)

D_V: Vertical dispersion coefficient (m^2/s)

d: Surface water depth (m)

E: Evapotranspiration rate (m/day)

$erfc(x)$: Complementary error function

f_{oc}: Weight fraction of organic carbon in the soil

f_{om}: Percent organic matter content

G: Represent the sink term

I: Infiltration rate (m/day)

K: Hydraulic conductivity (m/s)

K_d: Linear distribution coefficient for the solute with the soil (m^3/kg)

K_F : Freundlich adsorption coefficient (m^3/kg)

K_h: Horizontal hydraulic conductivity (m/s)

K_L: Isotherm coefficient corresponding to the enthalpy of adsorption (m^3/kg)

K_{oc}: Partition coefficient of a compound between organic compound and water (g solute sorbed/g soil organic carbon)/g solute/m^3 solution)

K_v: Vertical hydraulic conductivity (m/s)

M: Mass of solid on which adsorption is taking place (g)

n_f: Freundlich isotherm exponent (unitless)

P: Precipitation rate (m/day)

Q: Surface water flow rate (m/day)

Q^o: Isotherm coefficient corresponding to the mass of sorbate per unit mass of sorbent at mono-layer coverage (m^3/kg)

R_F: Retardation factor (unitless)

S : Mass of solute sorbed per bulk unit dry mass of soil (mg/kg)

t: Time (s)
V: Superficial velocity of surface water (m/day)
V_c: Velocity of the solute front where the solute concentration is one-half of the original value (C/Co = 0.5) (m/s)
V_{gw}: Average velocity of the ground water (m/s)
V_h: Average velocity of the ground water in the horizontal direction (m/s)
V_x: Average groundwater velocity in the x direction (m/s)
w: Wetland width (m)
X: Mass of material absorbed on solid phase (mg)

α: Hydraulic friction law coefficient ($m \cdot d^{-1} \cdot m^{\beta}$)
β: Hydraulic friction law exponent (unitless)
θ: Soil porosity (unitless)
θ_e: Effective porosity (unitless)
ρ_b: Dry bulk mass density of the soil (kg/m^3)
$\left(\frac{\partial h}{\partial z}\right)$: Hydraulic gradient (m/m)

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Water is indispensable for life on this planet and the history of mankind is directly linked to the availability of this precious resource. In the beginning, the main parameter of concern of this resource was quantity and where it was abundant civilisation flourished. But soon another parameter of water became of prime concern; it's quality. As well as being the essence of life, water can be the bearer of disease and death. Contaminants of all sorts have been dumped, spilled, sprayed or misplaced in our environment, thus greatly affecting the quality of surface and groundwater. A better control of man made waste is crucial in order to protect the integrity of our environment.

Managing the more than one million kilograms of solid waste being generated daily in North America is a doubting task. If not properly controlled, serious environmental degradation of lands and waters is inevitable. Since the beginning of the 20th century, the favoured mean of waste management in the industrial world has been to concentrate the refuse in specially designed landfill site or open pits. The logic was, and still is, that by concentrating the waste in one area, a better control of the contaminants could be achieved. Properly designed and constructed landfill incorporate proven technology to guard against the release of contaminants into the air, surface and groundwater. Although engineers have control on the design and materials used in constructing landfills, they have to contend with the geology and meteorological characteristics of the site, which greatly influences the migration potential of contaminants.

As water from precipitation infiltrates the buried waste, there is some dissolution of the refuse resulting in the formation of a strongly polluted solution known as leachate. If the landfill is not lined with impermeable soil or membrane, or if there is no collection system in place, the leachate will migrate through the waste and underlying soil eventually reaching the groundwater system. Transported by the bulk flow of the groundwater, the leachate will form a plume of contamination that can reach several kilometres.

In many instances, contamination of water resources is not detected until years after land disposal of the solid waste has begun, owing primarily to the slow movement of the contaminants in the conveying groundwater. Nonetheless, the literature is saturated with case studies where migrating leachate has caused serious groundwater degradation, severely impacting important aquifers and even in some case causing serious health threat to man, as was the case at the infamous Love Canal Site (Russel et al., 1987).

As a pollutant is transported in groundwater it can be removed or altered by several chemical, physical and biochemical reactions. Certain contaminants tend to be rather non reactive while other might be strongly attracted to the solid phase of the aquifer or again they might easily biodegrade to non toxic compounds or less harmful substances. The fate and mobility of contaminants in groundwater is of primordial concern, and proper knowledge of these mechanisms is essential to accurately evaluate the potential hazard of each contaminant and to initiate remedial processes if warranted.

1.2 USE OF NATURAL WETLANDS FOR THE TREATMENT OF POLLUTED WATER

It has been reported that the unique combination of physical and chemical properties that wetland soils possess enable them to significantly adsorb contaminant that might be present in the water. In the past few decades, planned use of natural wetlands for treatment of secondary effluent has been studied and implemented in several countries (Hammer, 1989; Brodrick et al., 1988; and Coupal and Lalancette, 1976). More recently, some researcher (McLelland and Rock, 1988; Cameron, 1978; and Lidkea, 1974) have investigated the capacity of wetland soil to attenuate landfill leachate with varying degrees of success.

As surface water in streams originating from many landfill sites percolates through wetland systems, the vegetation cover in the wetland provides an obstruction to the flow, thereby allowing greater infiltration of contaminants through the unsaturated upper soil zone down to the groundwater table. The long-range spreading of contaminants takes place mostly in the saturated zone where dissolved contaminants are carried along by the prevailing flow, mainly in the horizontal direction i.e. the surface water flow direction. The distance that can be covered by a contaminant in a certain time period depends on the velocity of flow and the reactive nature of the contaminants. A coupling of a surface hydrology water balance model with a groundwater flow model is required to simulate the overall behaviour of the landfill/wetland system.

Modelling the behaviour of pollutants during the flow of water through wetlands is essential for predicting the fate of and designing restoration strategies for existing contaminants, and for designing and locating future waste disposal sites. The complex interactions between biota, soil and water are driven first and foremost by the hydrology of the wetland. Hence, development of hydrological models which are tractable and can adequately predict the contaminants flow rates is essential to the understanding of wetland ecosystem affected by attenuation capability. The two-dimensional groundwater flow equation for a solute undergoing convection, dispersion and sorption can be used to approximate the attenuation of contaminants in surface and subsurface waters (Domenico and Schwartz, 1990; Freeze and Cherry, 1979). However, its application to peat-covered systems is lacking. Hence, the corresponding range of parameter values required to facilitate the simulation of contaminant plumes for various time periods in order to predict the long-term attenuation capacity of peatland systems is still unknown.

1.3 RESEARCH OBJECTIVES

The main research objective of this study is to investigate the long-term attenuation capacity of natural wetlands. While it has been reported that the unique combination of physical and chemical properties that wetland soils possess enables them to significantly adsorb contaminant that might be present in the water, the long-term efficiency of such system has seldom been researched.

By investigating the pollution migration through a natural wetland located downgradient from the Alice and Fraser landfill site (Pembrooke, Ontario), it is foreseen that a predictive mathematical model will be developed to simulate the long-term attenuation capacity of the wetland. The mathematical model will be adjusted based on data collected through laboratory experiments on the adsorption capacity of the marshland soil associated with field data on the water chemistry of the marshland, which was continuously monitored for the past decade.

Such mathematical models could eventually be used to simulate the short and long-term attenuation of various landfill contaminants during their migration through a landfill/wetland system. These models are required to better evaluate the environmental viability of implementing landfills, or other waste producing operations, in the vicinity of marshlands.

1.4 PRACTICAL SIGNIFICANCE

This research will be innovative by implementing a quantitative modelling approach for the simulation of contaminant transport through organic soil-covered wetland/landfill systems. The advantages and or disadvantages of locating landfill sites in vicinity of wetlands shall be better understood and suggestions regarding the future locations of waste disposal sites shall be provided.

1.5 RESEARCH METHODOLOGY

A mass balance analysis involving measurements of meteorological and hydrological variables, and contaminant concentrations shall be carried out for the unsaturated upper soil layer in order to determine the rate of landfill leachate migration to the water table in a wetland area. This leakage rate shall then provide the source term for the two-dimensional groundwater flow equation for a solute undergoing convection, dispersion and sorption. Calibration of the model parameters shall be achieved through field measurements of contaminant concentrations at different locations within the wetland system, and a companion laboratory column study designed to simulate the natural process. The numerical solution of the transport equation shall employ the finite-difference technique. The expected contaminant plumes extent for various future time periods shall then be simulated.

The above analyses shall first be applied to a selected landfill/wetland system situated in Ontario (Alice and Fraser landfill site, Pembrooke, Ontario) for model calibration and validation. A schematic representation of the present study is shown on Figure 1.1.

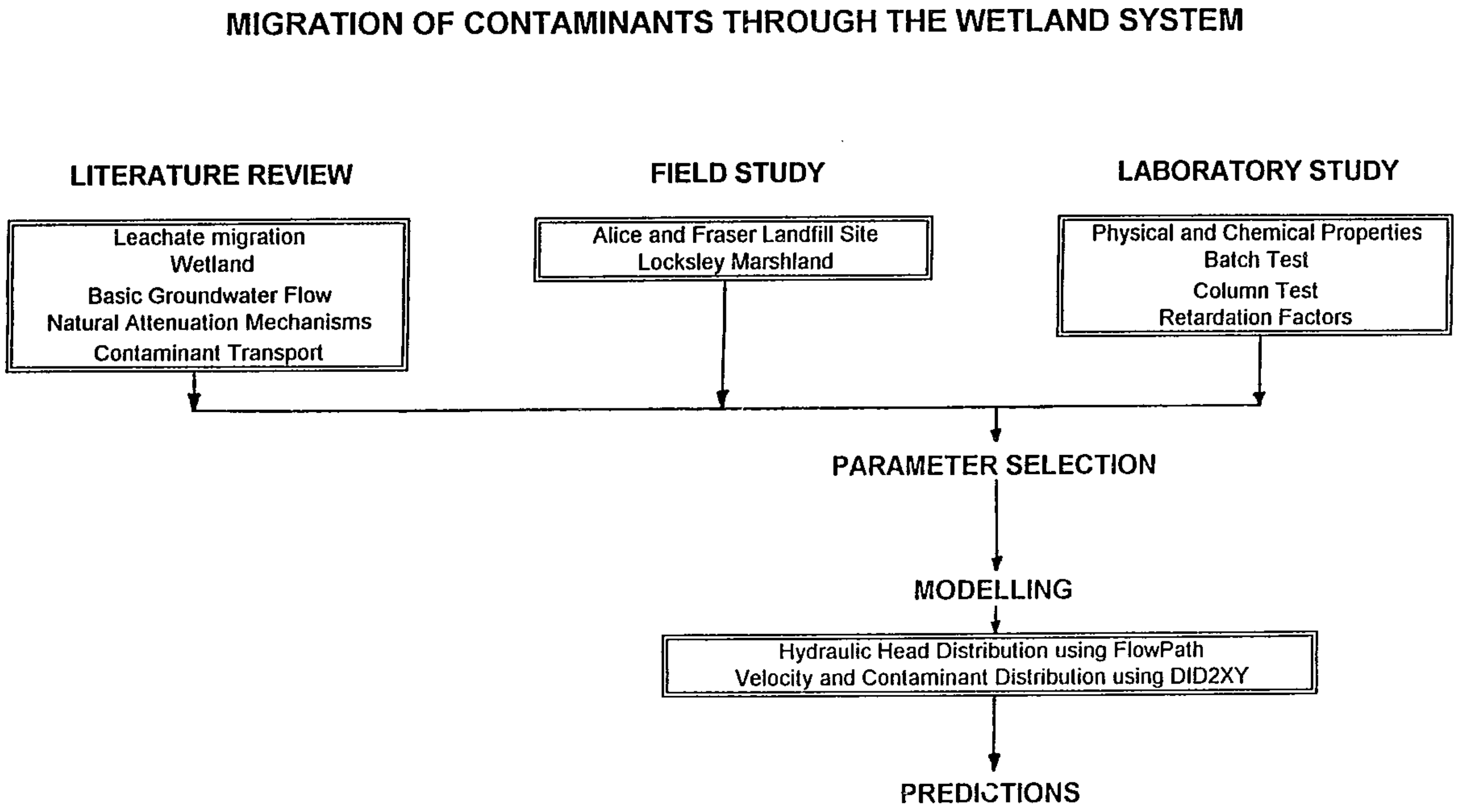

Figure 1.1. Schematic Representation of the Present Study

CHAPTER 2

LITERATURE REVIEW

2.1 LEACHATE MIGRATION: GENERAL CONCEPTS

2.1.1 Solid waste generation history.

Since the dawn of civilisation, man has used the resources of the earth to support life with minimal consideration to the environment. In the beginning, the disposal of human and other waste did not pose a significant problem, since the population was small and the amount of land available for the assimilation of wastes was large. But as the population increased, and the phenomenon of urbanisation regrouped a larger concentration of people in towns and cities, the production of wastes soon overshadowed the assimilative capacity of the surrounding land. Man was left to live among it's own waste, in putrid condition where rats and flies were rampant. The lack of any plan for the management of the waste led to large scale epidemics, such as the Black Death, that killed half of the Europeans in the fourteenth century (Tchobanoglous et al., 1993).

The relationship between improper waste disposal and the spread of disease eventually became evident in the nineteenth century, at which point public officials started to implement public health control measures. High in their list of priorities were the collection, transportation and eventually the disposal of waste in such a way as to minimize it's impact.

In the early 1900's several disposal techniques were implemented. Among those there was dumping on land, dumping in water, plowing into the soil and even feeding to hogs (Tchobanoglous et al., 1993). But as the environmental and ethical implication of those managing technique surfaced, several of them were discarded, so that nowadays the majority of the solid waste generated is being disposed on land in what is commonly called a sanitary landfill.

2.1.2 Solid waste generation rate and disposal technique

It is estimated that on average 2 to 4 kilograms of waste per person per day is being generated in North America (Tchobanoglous et al., 1993; Rathje, 1989). Katie Kelly, in her book Garbage (1973), asserted that the amount of municipal solid waste (MSW) produced in the United States annually would fill five million trucks; these placed end to end would stretch around the world twice. To process such an enormous volume of waste, a whole industry of waste management was developed.

The general operating procedure is to dispose of the waste on land in a matter that minimizes environmental hazards. This is achieved by concentrating the waste in one area by compaction in a series of cells that are covered daily with a layer of soil. Several layers of these cells are generally superimposed until the disposal site reaches its ultimate capacity. At the end of the operative life of the landfill, a final soil cover is applied to limit the infiltration of precipitation and to stabilize the structure.

2.1.3 Production of leachates.

One of the greatest potential environmental impact of a landfill is the pollution of the underlying groundwater by the movement of contaminant originating from the waste. Precipitation that infiltrates the waste can release contaminants from the refuse by physical, chemical and microbial processes, producing leachate, which is a concentrated solution of organic and inorganic substances. The composition of the leachate will be controlled by the type of waste deposited in the landfill. A typical leachate composition from a municipal landfill is presented in Table 2.1 (Tchobanoglous et al., 1993)

TABLE 2.1
Typical Composition of Municipal Landfill Leachate

Constituent	Concentration (mg/L)	
	Range	Typical
BOD_5	2,000 - 30,000	10,000
TOC	1,500 - 20,000	6,000
COD	3,000 - 45,000	18,000
Total Suspended Solid	200 - 1,000	500
Organic Nitrogen	10 - 600	200
Ammonia Nitrogen	10 - 800	200
Nitrate	5 - 40	25
Total Phosphorus	1 - 70	30
Ortho Phosphorus	1 - 50	20
Alkalinity as $CaCO_3$	1,000 - 10,000	3,000
pH	5.3 - 8.5	6
Total Hardness as $CaCO_3$	300 - 10,000	3,500
Calcium	200 - 3,000	1,000
Magnesium	50 - 1,500	250
Potassium	200 - 2,000	30
Sodium	200 - 2,000	500
Chloride	1,000 - 3,000	500
Sulphate	100 - 1,500	300
Total Iron	50 - 600	60

If allowed to migrate freely from the landfill, leachate may pose a severe pollution threat to groundwater. A multitude of case studies related to groundwater contamination from improperly designed waste disposal sites abound in the literature. Incidents like the Love Canal disaster, which forced the evacuation of over 200 families (Princeton University, 1984) or the contamination of the Gloucester landfill site (Devlin and Gorman, 1987) emphasize the environmental hazard of leachate migration.

2.1.4 Leachate collection and treatment schemes

In an attempt to limit the migration of leachate out of the landfill boundaries, all of the recently designed waste storage facilities rely on synthetic or natural liners to prevent any leakage at the base of the landfill. The collected leachate is then treated by on-site processes or shipped for off-site treatment. But in older landfill sites such collection system are generally not in place, and the leachate being produced is free to migrate out of the landfill boundaries, eventually contaminating the underlying aquifer.

Remedial technologies for the treatment of contaminated groundwater abound in the literature (Domenico and Schwartz, 1990; Mackay and Cherry, 1989) and generally require either the containment of the pollutants, the total removal of the contaminants or in-situ treatment of the polluted water. These treatment processes can be effective in some situations but are often quite expensive and require a high degree of expertise and can also be time consuming.

Constructed and natural wetlands are emerging as a possible inexpensive alternative to conventional wastewater treatment processes. Used since the early 1950's to treat municipal wastewaters, wetlands have shown that they can be used to retard the migration potential of several contaminants, with minimal manipulation by man. In the past decade, the use of wetlands for the treatment of landfill leachate has been gaining popularity.

2.2 WETLANDS: FORMATION, PROPERTIES AND CONTAMINANT INTERACTION

2.2.1 General

Public demands for more stringent wastewater effluent standards, including removal of nutrients as well as organic and suspended solids, have forced governments and scientists to develop alternative and innovative wastewater treatment technologies more adapted to smaller communities. One such alternative is the planned use of wetlands for tertiary water treatment. This natural treatment system has been studied and implemented in several countries for the treatment of municipal wastewater with generally favourable results. Wetlands appear to perform all of the biochemical, physical and chemical transformations of wastewater that usually take place in conventional wastewater treatment plants, but at a fraction of the cost. Nonetheless, the use of natural wetlands for treatment of high strength waste, has been questioned by some ecologists and environmentalists, who see in this practice possible detrimental effects to the fauna and flora of that sensitive ecosystem.

Wetland based treatment system is still in it's infancy and more research is required to better understand the complex hydrology and numerous exchange reactions that are endemic to such environments.

2.2.2 Wetland Definition

There are several definitions for wetlands in the literature, most revolving on the degree of "wetness", the soil composition or the dominant endemic plant species. The Ontario Ministry of Natural Resources (MNR) has defined wetlands as "lands that are seasonally or permanently covered by shallow water as well as lands where the water table is close or at the surface, in either case the presence of abundant water has caused the formation of hydric soils and has favoured the dominance of either hydrophilic or water tolerant plants" (MNR, 1984). The four botanical types of wetlands recognised are swamps (wooded), bogs (mossy peat), fens (sedges) and marshes (emergent, floating and submerged plants). One wetland may contain all four types.

The substratum of wetlands usually consists of a mixture of partly decomposing plant matter associated with varying concentrations of sand, silt and clays. Based on the organic fraction of the soil, the substratum can be defined as peat (over 80% organic material) or as organic soil (organic concentration between 5 and 80%) (Landva et al., 1983).

Due to the shortage of oxygen generally encountered in this water-logged environment, the rate of decomposition of the plant matter can be less than the rate of accumulation, thus resulting in a build up of partly decomposed plant material (Hamblin, 1985). Depending on the geological life of the wetland, the organic deposit can vary from a few centimetres to tens of meters. The structure of the organic fraction can range from a fibrous type, characterized by recognizable plant remains, to a woody structure, and finally to an amorphous structure based on the parent plant matter and age of deposition. In general, as the degree of decomposition increases, the organic material becomes less and less fibrous, until it gets transformed into an amorphous mushy substance without any discernible structure (Landva et al., 1983).

2.2.3 Wetland Distribution in Canada

There are over 111 millions hectares of wetlands in Canada, representing approximately 12% of the total land area of the country (Tarnocai, 1985). Wetlands are found in almost all geographic regions, although they are less common in the high Arctic. The geographical dispersion of wetlands in Canada, as described by Tarnocai (1985), is presented in Table 2.2.

TABLE 2.2
Peatlands Distribution in Canada

Province and Territories	Peatland area		
	ha x 10^3	% of land area within designated areas	% of total Canadian Peatlands
Alberta	12,673	20	11
British Columbia	1,289	1	1
Manitoba	20,664	38	19
New Brunswick	120	2	<1
Newfoundland	6,429	17	6
Northwest Territories	25,111	8	23
Nova Scotia	158	3	<1
Ontario	22,555	25	20
Prince Edward Isl.	8	1	<1
Quebec	11,713	9	11
Saskatchewan	9,309	16	8
Yukon Territory	1,298	3	1
Canada	**111,328**	**12**	

2.2.4 Attenuation Capacity of Wetlands

2.2.4.1 General

Wetland soil is a rather complex material containing a mixture of organic and inorganic constituents which has been exploited by man for years, first as a fuel source and more recently as a waste water treatment process. In the past 25 years, considerable attention has been focused on the potential of peat and other organic soils in environmental pollution control. The particular combination of physical and chemical properties of organic soils associated to it's abundance and relative low cost make it an attractive medium for pollution treatment.

Tchobanoglous and Shroeder (1987) and Rogers et al. (1985) concluded that removal of several contaminants including biochemical oxygen demand (BOD), suspended solids (SS), nitrogen, phosphorus, trace metals and pathogens is possible in a well managed wetland treatment system. This reduction of pollutants is accomplished by diverse treatment mechanisms that are inherent to wetland environment. The unique structure or organic soil, consisting of a mixture of sediments, plants and micro-organisms enables wetland to treat the contaminants by sedimentation, filtration, chemical precipitation, adsorption, as well as microbial degradation and uptake by vegetation.

The planned use of natural wetland treatment of secondary effluent has been studied and implemented in several parts of the world. Just in the United States over 400 wetland treatment systems exist in the Southeast and another 100 occur in the Great Lakes states (Bastian et al., 1989). In Canada several dozen of such treatment systems have been implemented from Cootes Paradise, Ontario to Hay River, Northwest Territories (Hautzsche, 1985).

Following the success obtained in wastewater treatment using natural wetlands, several researchers started to investigate the potential use of such system for treatment of municipal landfill leachate (McLelland and Rock, 1988; Cameron, 1978; and Lidkea, 1974). The findings of these studies indicate that considerable attenuation of major pollutants is attainable.

2.2.4.2 Attenuation of Metal

The concentration of heavy metals (lead, zinc, cadmium, nickel, copper and chromium) vary in landfill leachate and are of great concern since these elements may be highly toxic to plants, animal and man. Therefore it is essential that they be removed from leachate before it is released into receiving water bodies. Studies have shown that wastewater passing through a wetland will remove up to 90 % of the heavy metals (Rogers et al., 1985, Dissanayake and Weerasooriya, 1981).

According to McLellan and Rock (1988), peat has a large specific surface area (>200 m^2/g) and is highly porous (90-95%), properties that are analogous to activated carbon. In addition, peat is also reported to have excellent ion exchange properties, being similar to natural zeolites. The key to peat's high ion exchange capacity lies in it's organic composition. Schnitzer and Khan (1978) reported that although the organic matter usually comprises less than 5% of the soil, it usually accounts for 30 to 65% of the cation exchange capacity (CEC) of mineral soils and more than 50% in organic soils. Also, the organic material found in wetlands contains lignin and cellulose as major constituent (Viraraghavan and Ayyaswami, 1989). These components bear polar functional groups such as aldehydes, alcohols, ketones, and phenolic hydroxides that can be involved in chemical bonding reactions.

A study by Cameron (1978) and Lidkea (1974) indicated that the peat's removal capacity for any given metal depends on the chemical characteristics of the leachate and the presence of natural contaminants in the peat. Testing at very high hydraulic loading value, they found that 700 kg of peat would be required to remove 90% of the tested metal ions from 3785 litres of high strength leachate. Lidkea (1974) found that lowering the hydraulic loading from 21 to 7.57 m/d improved the peat's adsorption capacity by only 8.6%. However Lidkea (1974), did not investigate very low hydraulic loading, although in an earlier review of peat's ability to treat polluted water, Ruel et al., (1973) concluded that it can compete with other adsorbents provided that low flow rate are maintained and the quantity of wastewater to be treated is small.

McLellan and Rock (1988) investigated the effectiveness of peat to treat two different leachates, one from a municipal refuse fill and the other one from a fill which receives mainly oil and fly ash, at low hydraulic loading (41 mm/d) and a hydraulic retention time of approximately 7 days. The effects of contact time and initial metal concentration were determined by performing isotherm tests after 1 and 24 hours. The results from the 24 hours isotherms indicated that the increased contact time resulted in adsorption increase ranging from 5% for Pb, up to 142% for Cr, at initial concentrations of 500 mg/l. For initial concentrations of 50 mg/l, the increases in adsorption with time ranged from 7.5% for Cu, up to 370% for Cr. It was also observed that the total adsorption of metals by peat increased with increasing concentrations and longer contact times. For leachate, it was observed that the total adsorption of metals increased with time, however for some individual species adsorption was reduced due to metal interaction and competition for adsorption sites.

Several other factors affecting the adsorption potential of wetland soil, such as temperature, pH and additives, have been investigated using batch adsorption and column experiments, and are further detailed in the following references (Dumontet et al., 1990; Cameron, 1978; and Bunzel et al., 1976).

2.2.4.3 Attenuation of Organic Compounds

Leachate solution generated from the dissolution of the buried solid waste at sanitary landfills, is usually characterized by the presence of high concentration of organic compounds. The organic content in most cases accounts for about 40 to 60% of the total constituent. These organic compounds usually consist of the remains of biologically produced compounds in addition to a variety of synthetic organic mixtures. Organic contaminants are of great concern since they have been found to be health risk, even at low concentration.

Peat has proved to be an effective filtering medium of organic constituents in landfill leachate. Significant reductions in BOD greater than 85% and coliform bacteria reductions of 99% were reported (Surakka and Kamppi, 1971). Phenol can also be effectively adsorbed by peat; in one experiment the phenol content in a wastewater was reduced from 40 to 5 mg/l and in another from 0.22 to 0.14 mg/l (Mueller, 1972). Its effectiveness in reducing BOD was proven further by experiments conducted on slaughter-house and dairy wastewaters. A 150 mm layer of peat removed up to 90% of organic matter of slaughter-house wastewater (Silva, 1972). By utilizing a series of filter systems containing layers of peat (300 mm), sand (300 mm) and gravel (300 mm) a reduction of 40 % in BOD was obtained from dairy wastes.

The high attenuation of organic compounds by organic soil can be attributed mainly to hydrophobic sorption. Organic present in trace quantities in groundwater are mostly sorbed on existing solid organic compounds present in the porous medium (de Marsily, 1986). Biological degradation has also been linked to the attenuation of several organic compounds.

Several researchers have investigated the fate and mobility of pentachlorophenol (PCP) in groundwater. Banerji et al., (1986) studied the adsorption of pentachlorophenol on Missouri soil to determine its potential for migration into groundwater. Through batch adsorption experiments using low concentration PCP (0.1 to 10 mg/l) they were able to confirm that PCP was easily adsorbed and that the adsorption fitted the Freundlich isotherm form. In the same experiment Banerji et al., showed that PCP is highly susceptible to pH and organic content of the soil. PCP, a weak organic acid was found to adsorb more as pH decreased and as the organic content increased. Hamaker and Thompson (1972) concluded that weak acids, such as PCP, are much more highly adsorbed when in the free acid form as compared to the anion. As pH decreases, increased adsorption of PCP by organic matter could be attributed to the hydrogen bonding of molecular PCP with the COOH, carbonyl (C=O), and amide (NH_2) groups of organic matter. Hydrophobic bonding could further promote PCP adsorption onto organic matter as pH decreases since both PCP and organic colloids become less polar. Based on adsorption coefficients obtained in the batch adsorption experiment, Barnerji et al., (1986) concluded that significant retardation of a PCP contamination plume would occur during groundwater flow through the soil tested.

Similar results were obtained by Parker and Jenkins (1986), when they studied the removal of trace level organic by slow rate land treatment. In their experiment a total of 16 organic substances including PCP were treated by a slow-rate land treatment system operating in a cold temperate zone. The removal efficiency of the system for PCP exceeded 99 % with most of the contaminant being limited to the top 15 cm of the infiltration soil.

Following the accidental spill of 18,000 litres of chlorophenol/phenate solution at a sawmill in the Okanagan river district, a series of field studies were undertaken to properly defined the migration process of the contaminant in the underlying aquifer. Patterson and Liebscher (1987) simulated the spill in the laboratory using column test in an effort to reproduce the migration data obtained by the field measurement. The column experiment succeeded relatively well in simulating the retardation of PCP in the shallow aquifer. Retardation factors determined in the laboratory were in the same range as the ones determined from fields investigation. The success of the experiment permits to conclude that laboratory experiment can be a useful and valid technique for simulating the processes of contaminant migration in the subsurface.

2.3 BASIC GROUDWATER FLOW EQUATIONS AND PRINCIPLES

2.3.1 Background

In order to properly evaluate the migration potential of contaminants at a particular site, it is essential to properly understand the relationships that exist between the soil, water and contaminants phases. Details of basic groundwater flow equations and principles are presented in Appendix "A".

Mathematical modelling of contaminant transport generally requires an adaptation of the Advection-Dispersion Equation (ADE). For a one dimensional groundwater flow and solute transport in a homogeneous isotropic medium, the ADE states:

$$\frac{\delta C}{\delta t} = D_L \frac{\delta^2 C}{\delta x^2} - V_x \frac{\delta C}{\delta x} \qquad (2.1)$$

where: C: is the solute concentration (g/m^3)

D_L: is the longitudinal dispersion coefficient (m^2/s)

V_x: is the average groundwater velocity in the x direction (m/s)

t : is the time since start of solute invasion (s)

The ADE has been used to predict the breakthrough of contaminants in a multitude of laboratory and field experiments. The experimental results and predictions of the model were generally in good agreement where the targeted contaminant was conservative (Domenico and Schwartz, 1990).

Contaminants can be considered in two broad classes; conservative and reactive. Solutes that do not react with the soil and/or native groundwater are categorized as being conservative. On the other hand, reactive substances can undergo chemical, physical, biological or radioactive changes that will tend to reduce the overall concentration of the solute.

The ADE model as described in Equation (2.1) does not account for the retardation potential of reactive substances. To better reflect the particular transformation occurring during the transport process a sink term was introduced in the ADE:

$$\frac{\delta C}{\delta t} = \frac{\delta}{\delta x}\left\{ D_L \frac{\delta C}{\delta x} \right\} - V_x \frac{\delta C}{\delta x} - G \qquad (2.2)$$

where : G: represent the sink term (g/m^3/s)

As can be seen from the above development, the overall consequence of the sink term is to account for the removal of the solute from the solution phase, which for some contaminants results in retardation of the contaminant compared to the groundwater flow. This retardation phenomenon will be described in greater details in the following discussion.

2.3.2 Natural attenuation mechanisms in groundwater

As contaminated water passes through an aquifer, several reactions can occur between the solid and liquid phases of the environment, resulting in a retardation of the contaminant front compared to the groundwater velocity. This natural attenuation can be explained by several physical, chemical and biological processes of which adsorption, biodegradation, cation and anion exchange, filtration and precipitation are the most common.

Adsorption is probably the major factor controlling the movement of many hazardous substances through subsurface systems and into groundwater aquifers (Princeton University, 1984). Adsorption is defined as the process of adhesion by molecules onto the surface of individual soil particles. According to Tchobanoglous and Schroeder (1987), important factors that affect the adsorption process are the properties of the soil (chemical characteristics, organic fraction, porosity, temperature and pH) and the pollutant (negative log of equilibrium coefficient (pK), solubility and the distribution coefficient (K_d)). The adsorption process is limited by the surface capacity of the soil. When the soil surface reaches its adsorption capacity, no more contaminants can be adsorbed and, in some cases, constituents that are already adsorbed on the soil can be desorbed and re-enter the groundwater (Bagchi, 1987). The system strives toward attaining an equilibrium between adsorbed and desorbed phases based on the relative amounts of the pollutant in each of the solid and liquid phases. The partition coefficient (K_p) was used to define the equilibrium point between the two phases (Banerji et al., 1986; Princeton University, 1984; Hamaker and Thompson, 1972).

Biological uptake is a mechanism by which micro-organisms adsorb and breakdown or retain contaminant and can thereby attenuate the pollution level of groundwater. Microbial growth in soil was shown to have tremendous impact on contaminant attenuation in a particular environment. Processes performed or mediated by soil micro-organisms are numerous and documented in several papers (Larsson and Lemkemeier, 1989; Bagchi, 1987; Smith and Novack, 1987).

The exchange reactions (cation and anion) can be defined as the exchange of ions of one type by ions of another type without disturbing the mineral structure of the soil (Bagchi, 1987). Experimentally it is difficult to distinguish the exchange type reaction from the adsorption mechanism, so that the term adsorption-exchange reactions is often used. There is, however, a basic difference between the two processes. Adsorption will lower the total dissolved solids (TDS) of the groundwater, whereas exchange reaction will simply change the type of ions present in solution without lowering the TDS concentration; the ionic strength of the solution may change however.

Filtration is a mechanism by which the groundwater constituent are physically trapped in the pore structure of the soil. The filtration potential will essentially depend on the pore size and hydraulic gradient of the water. This mechanism will only be operative whenever chemical precipitation, biological growth and other processes produce undissolved solid particles (Bagchi, 1987).

Chemical precipitation involves a phase change in which dissolved chemical species are crystallized and deposited from solution because their total concentration exceeds their solubility limit. Several factors will determine the solubility limit of a contaminant, including temperature, ionic species and their concentration, redox potential and pH. It is important to note that adsorption will normally be the dominant mechanism at micro concentration while precipitation will be dominant at macro concentration.

All of the above mentioned mechanisms will influence the mobility of pollutants in groundwater. Defining the relevance and extent of each process is essential in properly defining the migration potential of a contaminant.

2.3.3 Mathematical modelling of the attenuation

2.3.3.1 Fundamental principles

The problem of predicting contaminant migration of reactive substances is compounded by the combined interaction of several processes (adsorption, biodegradation, exchange reaction , and others...). In models that include the effects of advection, dispersion and reactions, the reaction term rarely describes more than the effects of adsorption (Gilham and Cherry, 1982).

To adequately evaluate the effect of the adsorption process on the mobility of pollutants in groundwater, a contaminant transport model has to be developed. Most authors (Domenico and Schartz, 1990; Fetter, 1988; Banerji et al., 1986) treat adsorption as a linear function to simplify the governing groundwater transport equation, and attribute a respective retardation factor for a given contaminant. The retardation factor is given by the following equation (Freeze and Cherry, 1979):

$$R_F = \frac{V_{gw}}{V_c} = 1 + \frac{\rho_b}{\theta} K_d \tag{2.3}$$

where: R_F = Retardation factor (unitless)
V_{gw} = Average velocity of the ground water (m/s)
V_c = Velocity of the solute front where the solute concentration is one-half of the input concentration (C/Co = 0.5) (m/s)
θ = Soil porosity (unitless)
ρ_b = Dry bulk mass density of the soil (kg/m^3)
K_d = Linear distribution coefficient for the solute with the soil (m^3/kg)

This model will predict how many times slower the contaminant will be moving compared to the groundwater.

In order to properly evaluate the retardation factor, it is first necessary to establish the linear distribution coefficient (K_d) of the system. Numerous researchers have studied the distribution coefficient K_d (Domenico and Schwartz, 1990; Fetter, 1988; Grove and Stollenwerk, 1987). Most adsorption model are based on an equilibrium controlled chemical reaction. The most common type of equilibrium controlled solute transport model is the type described by a linear sorption isotherm.

Most mathematical expression describing the adsorption process attempt to relate this phenomena to various other parameters involved in the process. The most common forms of equilibrium adsorption equation are the Freundlich and the Langmuir models, while for organic compounds the octanol-water partitioning coefficient is often used.

2.3.3.2 Freundlich adsorption model

The most commonly encountered model used to describe the adsorption of a solute from solution was proposed by Freundlich in the 1920's. The Freundlich adsorption isotherm is an empirical expression that has been proven useful under widely varying conditions (Tchobanoglous and Schroeder, 1987). The mathematical expression is:

$$S = \frac{X}{M} = K_F C_e^{n_f} \tag{2.4}$$

Where : S = Mass of solute sorbed per bulk unit dry mass of soil (mg/g)
X = Mass of material absorbed on solid phase (mg)
M = Mass of solid on which adsorption is taking place (g)
K_F = Freundlich adsorption coefficient (m^3/kg)
C_e = Concentration of material being adsorbed remaining in solution at equilibrium (kg/m^3)
n_f = Freundlich isotherm exponent (unitless)

The empirical coefficients in the Freundlich Equation (2.4) are obtained by plotting (X/M) versus (C_e) on log-log paper.

If the slope of the log-log Freundlich isotherm is found to be equal to one, then $n_f=1$ and the isotherm is said to be linear. The Freundlich coefficient K_F is identical to the soil distribution coefficient K_d (Equation 2.3). The retardation factor is then given by:

$$R_F = 1 + \frac{\rho_b}{\theta} K_F \qquad \text{(when } n_f=1\text{)} \qquad (2.5)$$

If the slope of the log-log Freundlich isotherm is not linear ($n_f \neq 1$) then the retardation factor R_F will be a function of the solute concentration in the solution phase.

$$R_F = 1 + \left\{ \frac{\rho_b K_F C_e^{n_f - 1}}{\theta} \right\} \qquad (2.6)$$

2.3.3.3 Langmuir adsorption model

Another common sorption equilibrium relation is given by the Langmuir Equation which is based on the assumption the adsorbent surface is saturated when a monolayer has been adsorbed. The Langmuir adsorption isotherm is given by the following expression (Walter et al., 1991 and Grove and Stollenwerk, 1987):

$$S = \frac{X}{M} = \frac{K_L Q^o C_e}{1 + K_L C_e} \qquad (2.7)$$

where : K_L = Isotherm coefficient corresponding to the enthalpy of adsorption (m^3/kg)

Q^o = Isotherm coefficient corresponding to the mass of sorbate per unit mass of sorbent at mono-layer coverage (m^3/kg)

The slope of this isotherm is given by:

$$\frac{\partial S}{\partial C_e} = slope = \frac{K_L Q^o C_e}{(1 + K_L C_e)^2} \tag{2.8}$$

At low concentration the slope approaches $K_L Q^o$, which is a constant. At high concentration the slope approaches zero as the medium will not sorb additional solute. The corresponding retardation factor is:

$$R_F = 1 + \frac{\rho_b}{\theta}\left\{\frac{K_L Q C_e}{(1 + K_L C_e)^2}\right\} \tag{2.9}$$

2.3.3.4 Hydrophobic sorption

The adsorption models previously described were initially developed to illustrate the behaviour of ions in water. Although these models have been used to describe the adsorption potential of organic compounds (Banerji et al., 1986; Uchrin and Katz, 1986), other models based on the hydrophobic character of non-polar organic molecules have been employed to describe the sorption process of organic compounds. Organics present in trace quantities in groundwater are mostly sorbed on existing solid organic compounds present in the porous medium (de Marsily, 1986).

This sorption process often can be modelled with a linear isotherm based on the organic fraction of the soil. Just as for ions, an equilibrium partition coefficient (K_p) equivalent to the distribution coefficient (K_d) can be evaluated. The dimensionless K_p coefficient is defined as follow:

$$K_p = K_{oc} f_{oc} \tag{2.10}$$

where: K_{oc}= Partition coefficient of a compound between organic compound and water (g solute sorbed/g soil organic carbon)/g solute/m^3 solution)

f_{oc}= Weight fraction of organic carbon in the soil

The K_{oc} coefficient is directly related to the octanol/water partition coefficient (K_{ow}) which have been reported for several contaminants (Jafvert et al., 1990; Lyman et al., 1982).

Knowing the organic carbon fraction of the soil the equilibrium partition coefficient (K_p) can be calculated. Once the partition coefficient is evaluated, the retardation factor R_F can be estimated using Equation (2.3). This particular method is often used to gather rapid information of the adsorption potential of a soil-contaminant system when experimental results are lacking.

2.3.3.5 Adsorption evaluation based on column study

Although batch laboratory studies provide useful information on the adsorption potential of contaminants, continuous flow column experiments provide an alternate method of simulating the natural environment (Eckenfelder, 1989). Column type continuous flow operations try to simulate as closely as possible the natural conditions (Domenico and Schwartz, 1990; Weber, 1972). In addition, moving pore fluids in the column actively redistribute the products of reaction unlike batch experiments.

As long as experimental artefacts are eliminated or minimized and appropriate mathematical models are used to analyze the data, batch and column procedures should yield comparable K_d values. If this was the case, then column tests are to be favoured, especially because they permit an assessment of non-equilibrium sorption during flow.

2.3.4 Advection-Dispersion Equation with Sorption

The migration of reactive contaminants in groundwater has been modified by incorporating the retardation term represented in Equations (2.3, 2.5, 2.6 and 2.9) into the previously defined Advection Dispersion Equation.

$$\frac{\delta C}{\delta t} = \frac{1}{R_F}\frac{\delta}{\delta x}\left\{D_L \frac{\delta C}{\delta x}\right\} - \frac{V_x}{R_F}\frac{\delta C}{\delta x} \qquad (2.11)$$

Writing the above equation explicitly for a two-dimensional solute transport gives:

$$\frac{\delta C}{\delta t}=\frac{1}{R_F}\frac{\delta}{\delta x}\left\{D_{Lx}\frac{\delta C}{\delta x}\right\}+\frac{1}{R_F}\frac{\delta}{\delta y}\left\{D_{Ly}\frac{\delta C}{\delta y}\right\}-\frac{V_x}{R_F}\frac{\delta C}{\delta x}-\frac{V_y}{R_F}\frac{\delta C}{\delta y} \tag{2.12}$$

provided that the dispersion tensor $[D_{Lx}]$ is aligned with the coordinates, in which case $[D_L]=\begin{bmatrix} D_{Lx} & 0 \\ 0 & D_{Ly} \end{bmatrix}$. If $[D_{Lx}]$ is homogeneous, then:

$$\frac{\delta C}{\delta t}=\frac{D_{Lx}}{R_F}\frac{\delta^2 C}{\delta x^2}+\frac{D_{Ly}}{R_F}\frac{\delta^2 C}{\delta y^2}-\frac{V_x}{R_F}\frac{\delta C}{\delta x}-\frac{V_y}{R_F}\frac{\delta C}{\delta y} \tag{2.13}$$

The overall effect of the sorption process is to reduce the rate of contaminant flux by decreasing the value of the transport parameters D_L and V in the ADE. It should be emphasized that the main appeal of Equations (2.11), (2.12) and (2.13) are it's mathematical convenience and the fact that simple laboratory test can be used to obtain the retardation factor. The ADE constitutes the mathematical foundation of the contaminant transport model. Now the methodology available to solve this equation can be considered.

2.4 CONTAMINANT TRANSPORT MODELLING IN WETLANDS

2.4.1 General

As the use of natural wetlands for wastewater treatment of remote centres becomes more common, an emphasis on predictive modelling, as part of a preliminary environmental impact study is becoming more prevalent. Predictive models on the potential contaminant migration within wetlands are still in their infancy, and the few models that are available are generally site specific. The complexity of modelling contaminant transports in wetlands is directly related to the complexity of the hydrology of such systems.

The complex interactions between biota, soils and water are governed first and foremost by the hydrology of the wetland (Kadlec and Hammer, 1981). In order to further understand the attenuation capacity of wetland system, it is essential to properly characterize the hydrologic cycle of this environment. Water flow through a wetland system is controlled by the slope, water depth, types of vegetation, and by the degree and type of channelization (Kadlec and Hammer, 1982).

Three main flow paths are possible within wetland; groundwater, overland and channel flow. Each flow pathways is characterised by a distinct chemical, physical and biological environment and a characteristic contact time between the water and the soil matrix. These different environments play a very important role in the problem of ecosystem dynamics of wetland systems.

2.4.2 General Structure of a Wetland Model

The complexity of the hydrology of wetlands makes it necessary to consider phenomena of a rather different nature simultaneously. Mathematical models which describe separate processes of water transport by channel flow, overland flow and groundwater flow as well as variation of water quality parameters, have to be combined in one system, since all these processes are related (Minsk et al., 1982). The complexity of simultaneously modelling different flow paths is not only related to the physical, chemical and biological particularities of each environment, but also by the modelling structure which controls the number of space variables, considered time intervals and other features.

2.4.3 Existing Wetland Models

Wetland models were developed rather late compared to river, lake or even groundwater models, mainly because of the complexity of these ecosystems. Initial wetland modelling started in the mid 1970's (Mitsch, 1983; Mitsch et al., 1982), when sufficient data on the functioning of wetland environment became available. Since then, the number of wetland models published has steadily increased, mainly due to increasing interest for the natural environment.

The diversity of wetlands types is matched by a wide diversity of models used to describe and simulate these ecosystems. Particularly, this has resulted in models being limited to specific regions or types of wetland.

The dynamic of surface water flow in wetlands has been studied intensively by Hammer and Kadlec (1986) and Kadlec et al. (1981). They developed a mathematical model for overland flow through vegetated area. In their model, water is assumed to move as a thin sheet across the vegetative mat that forms the wetland and that the rate of flow is controlled by the ground slope, water depths, type of vegetation and by the degree and type of channelization. A friction law model was used with consistent accuracy at their test site, where:

$$V = \alpha d^{\beta}\left(\frac{\partial h}{\partial z}\right) \tag{2.14}$$

where:
V = Superficial velocity of surface water (m/day)
α = Hydraulic friction law coefficient ($\mathrm{m \cdot d^{-1} \cdot m^{\beta}}$)
d = Surface water depth (m)
β = Hydraulic friction law exponent (unitless)
$\left(\frac{\partial h}{\partial z}\right)$ = Hydraulic gradient (m/m)

When this rate equation is used in conjunction with the mass balance for wetland, the following equations results:

$$w\phi_s\left(\frac{\partial h}{\partial t}\right) = \frac{\delta}{\delta z}\left(\alpha d^{\beta+1} w \frac{\partial h}{\partial z}\right) + w(P - E + A - I) \tag{2.15}$$

$$Q = -\frac{\delta}{\delta z}\left(\alpha d^{\beta+1} w \frac{\partial h}{\partial z}\right) \tag{2.16}$$

where:
Q = Surface water flow rate (m/day)
w = Wetland width (m)
ϕ_s = Effective porosity (unitless)
P = Precipitation rate (m/day)
E = Evapotranspiration rate (m/day)
A = Water addition rate (m/day)
I = Infiltration rate (m/day)

These partial differential equations were solved with a Crank-Nicolson finite difference approximation technique. Although the model was capable of adequately predicting the water depth, pool size and the movement of surface waters, several important flow paths such as channel flow and groundwater flow were not being modelled.

Water movement through wetland soil has been modelled by several researchers (Hemod and Nuttle, 1990; Siegel and Glaser, 1987) using Darcy's Law, where:

$$V = \frac{K}{\theta_e}\left(\frac{\partial h}{\partial z}\right) \tag{2.17}$$

where: θ_e = Effective porosity (unitless)

While contaminant transport in groundwater is simulated using the Advection-Dispersion Equation where:

$$\frac{\delta C}{\delta t} = D\frac{\delta^2 C_i}{R_F \delta x^2} - \frac{\delta C_i}{R_F \delta x} \tag{2.18}$$

Generally, the main problem associated with modelling of groundwater transport is related to the difficulty in adequately measuring the above mentioned parameter which tend to vary substantially from wetland to wetland, and even as a function of depth within a distinct wetland. Up to now, very little modelling efforts have been made to simultaneously model the different flow paths encountered within one wetland.

2.5 SUMMARY

The use of natural marshland for treatment of secondary effluent, and more recently high strength waste, has been gaining popularity over the past quarter century. It has been amply documented that the particular properties of the marshland soil associated with the generally high retention time of the water phase, permit a high attenuation potential for several contaminants.

The hydrology of wetlands is a complex process which is rarely quantified because of the multiple flow paths involved and the unsteady nature of the system. In addition, the chemical and biological characteristics of wetlands are closely tied to the hydrologic conditions, such as retention time, the water depth and the seasonal patterns of flooding. Contaminant migration studies in such a system is still in it's infancy and is directly related to the complex hydrology of the wetlands.

For the purpose of this study, emphasis was placed on the migration potential of contaminants within the saturated portion of the marshland soil, since most of the attenuation potential occurs within this environment. Once proper understanding of this flow path is achieved, incorporation of the overland and channel flow processes could be undertaken to complement our model.

CHAPTER 3

MATERIALS AND METHODS

3.1 GENERAL

The main objective of this study is to investigate the attenuation capacity of the Locksley Marshland system, which is presently receiving leachate originating from the Alice and Fraser Landfill site. However, this attenuation potential is often site dependant, and laboratory analysis is frequently required to evaluate the treatment capability of a particular marshland.

In order to adequately characterize the attenuation potential of the Locksley Marshland system, it is essential to first establish the physical, geological and hydrogeological setting of the Alice and Fraser landfill site. A proper understanding of the field characteristics is essential to characterize and eventually model the migration potential of contaminants associated with a landfill. The physical and chemical properties of the native marshland soil are, on the other hand, best defined by laboratory experiments.

This chapter is subdivided in two major sections, presenting the work conducted on both the field and laboratory scale. Section 3.2 briefly presents the physical setting of the Alice and Fraser landfill site as well as the contaminant plume migration history. The laboratory program set-up to investigate the physico-chemical properties of the Locksley Marshland is presented in section 3.3.

3.2 THE ALICE AND FRASER LANDFILL SITE

3.2.1 Site Setting

The Township of Alice and Fraser landfill site is located some 12 km south-west of the city of Pembroke, in the province of Ontario, Canada (Figure 3.1). The landfill site covers an area of 1.25 km^2 within which are located 3 waste containment sites (industrial, dry and municipal waste), as well as a buffer zone. The lands surrounding the landfill site are sparsely populated, and are composed of wooded areas with occasional farm lands.

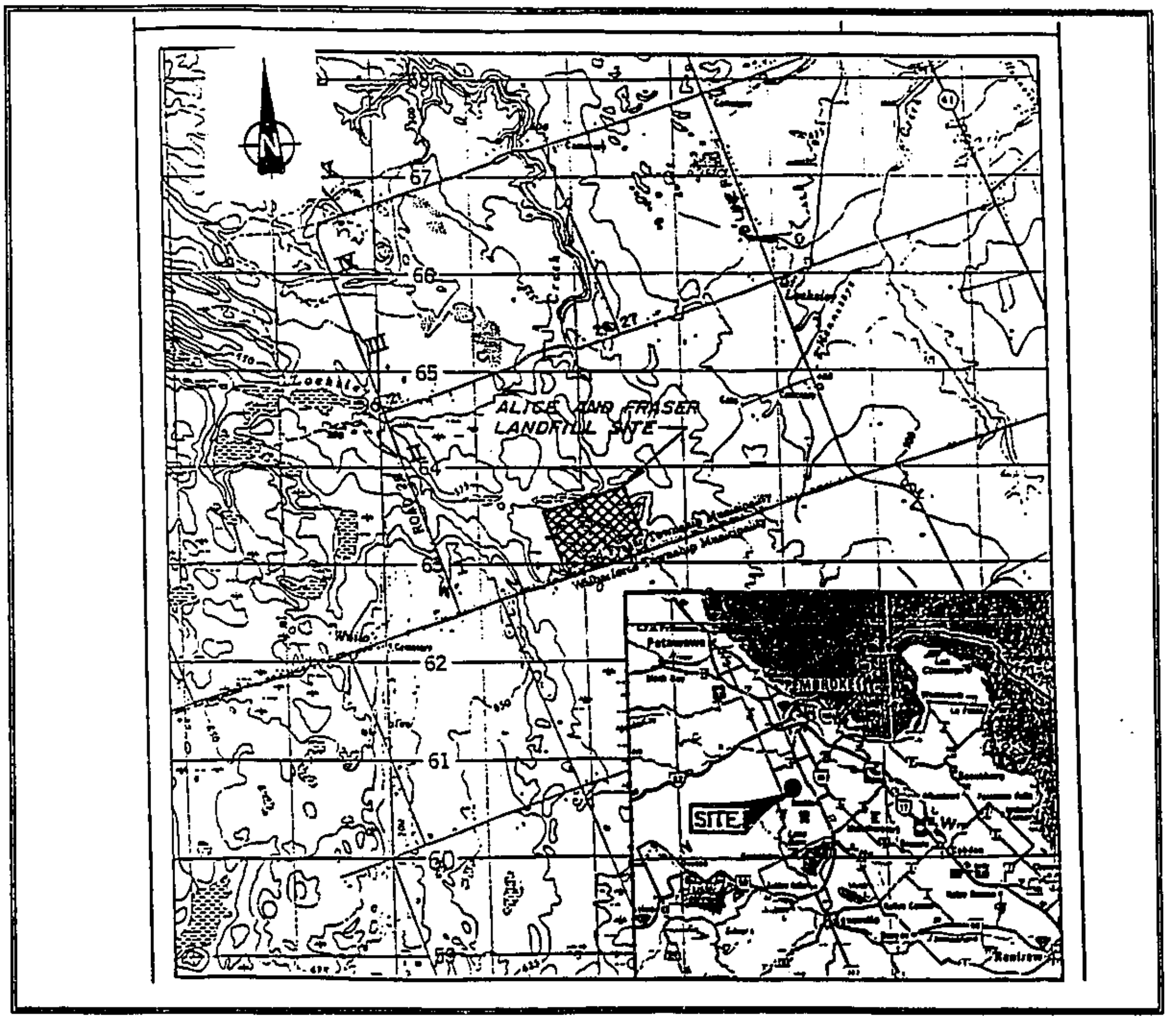

Figure 3.1: Alice and Fraser Landfill Site Setting

3.2.2 Physiography and geology

The Alice and Fraser landfill site is located in the physiographic region known as the Algonquin Highlands (Chapman and Putnam, 1973), which is characterized by rough, rounded knobs and ridges of Precambrian bedrock overlain by variable thicknesses of overburden materials. The landfill site is underlain by extensive sandy granular overburden deposits, the thickness of which is governed by variable ground surface topography and irregular bedrock surface.

The soil on site consists primarily of fine to medium sands, sand and gravel, and silty sands. These soils are believed to have been deposited under glacio-fluvial conditions during the last ice age. These glacio-fluvial sediments directly overlay the granite gneiss bedrock at this site, with very little or no glacial till encountered above the bedrock surface. The bedrock underlying the site consists of fine to coarse grained granite-gneiss (Golder Associate Ltd., 1992).

The thickness of the sandy granular overburden varies from approximately 6 m along the south boundary of the landfill site and decrease from 3 to 1.5 m between the landfill and the Locksley Marshland located to the north. Due to the irregular nature of the underlying bedrock, the overburden can reach over 10 meters thickness due to bedrock depression in some areas.

The topography and drainage in the area of the landfill is dominated by a high till ridge to the west of the landfill which rises to about elevation 123 m; by the easterly and then northerly flowing marshland tributary headwaters to the Locksley Creek system at a general elevation of about 86 m; and by lower lying land below elevation 80 m to the east and north-east of the site. The operating landfill area naturally stood at about elevation 95 m along Alice Concession I road, sloping gradually northward to the marshland. North of the marshland and west of Locksley Creek a topographical high area rises to about elevation 96 m.

Surface water flows onto the landfill site from south of Concession I road in a stream course along the west boundary of the site and, together with contributing flows from other poorly drained sub-watersheds, enters the on site Beaver Meadow marshland. Two stream courses also lead from the operating area of the landfill to the marshland; the east most stream course is intermittent and flows only during wet periods of the year. The marshland discharges from its eastern end, and flows northward as Locksley Creek for some 1.2 km where it passes beneath Concession II road. Surface water from a second marshland system enters Locksley Creek just south of Concession II road. Locksley Creek eventually discharges to the Indian River some 4.5 km further downstream.

3.2.3 Beaver Meadow Marshland

The on-site marshland is some 1.3 km in length from its west end to where it leaves the landfill site property to the north-east. The ground surface elevation in the topographic depression in which the marshland is located is at about elevation 85 m. The width of the marshland is about 15 to 20 m at its western end and typically about 60 to 70 m over the remainder, then it widens into a broad expanse at its eastern end where the flow system turns northward.

Except in areas of continuously ponded water, the marshland is covered with a thick growth of marsh grass and cattails as well as infrequent thickets of old trees. Hand auger investigations indicate that the marshland is underlain by a variable thickness of organic soils which ranged from 0.5 to 1.2 m with thickest layers observed in the central portion and decreasing toward the fringes. Sandy soils were encountered below the organic soil.

3.2.4 History of Landfilling

Landfilling operations at the Alice and Fraser site started in 1977. Prior to this date, the site was used for extraction of granular borrow materials in pits which reportedly extended to depths ranging form 4 to 8 m below ground surface.

The Alice and Fraser site contains 3 distinct waste disposal areas; the dry waste area, the solid industrial waste area and the municipal landfill area.

The dry waste area which was historically used for construction and demolition waste, brush, wood and asphalt, covers an area of some 100 by 100 m. This disposal area reached a thickness of 3.5 m before being permanently closed with a geomembrane hydraulic barrier in 1990.

The solid industrial waste area covering an area of about 90 m^2 is located just west of the landfill site office. The waste disposed in this area consisted predominantly of paper, wax, sulphur compounds as well as steel drums (some empty and others containing paint sludges) originating from the local match industries. The solid industrial waste area was permanently closed in 1990, at which time the thickness of refuse reached 5 m. The surface of the industrial waste area was then graded to promote runoff.

Of the three waste disposal areas the municipal landfill is by far the largest, the footprint of which occupies an area of some 350 by 250 m. The refuse deposited in the municipal landfill is composed essentially of both residential and commercial solid waste, of which paper, food waste, ashes, and food packaging is dominant. The thickness of the municipal landfill reached 10 m in 1991, and is still being operated as of 1994.

3.2.5 Previous Site Studies

Hydrogeological studies at the Alice and Fraser landfill site began in 1975 when Greer Galloway Ltd. initiated a preliminary subsurface investigation involving a grid pattern of auger holes and a limited number of piezometer installation. Since that time several organisation including the Ontario Ministry of the Energy and the Environment (MOEE), Water and Earth Sciences Ltd., as well as Golder Associates Ltd. have installed a monitoring network that consisted of over 50 boreholes with piezometers, dispersed across the site. In addition to these monitoring wells, all domestic wells located within several kilometres of the landfill site have been regularly monitored since 1976.

Eleven surface water sampling stations were implemented across the entire landfill site, with 3 additional sampling stations located north of the landfill site along the Locksley Creek system. This ground and surface water monitoring network has been used over the fifteen year operation of the Alice and Fraser landfill site to monitor the migration of the leachate plume.

3.2.6 Leachate Chemistry and Extend of Plume Migration

Leachate is being generated at the Alice and Fraser landfill site primarily by infiltration of precipitation (rainfall and snowmelt) through the waste. The leachate is then drawn downward due to the forces of gravitation, until it reaches the groundwater table and enters the groundwater flow system and migrate under the horizontal and vertical hydraulic gradient.

The leachate plume was found to follow the local groundwater flow which travels in a north-east direction in both the overburden and bedrock. An average groundwater velocity of about 30 to 40 m per year was measured in the overburden material while a velocity of 10 to 20 m per year was estimated in the bedrock formation (Golder Associate Ltd., 1992).

The approximate limits of impacted overburden groundwater based on 1991-92 chemical data is shown in Figure 3.2. The limits of the impacted area were defined using the conservative parameter chloride which is highly mobile at a similar velocity to that of groundwater flow; boron and barium were also used where required to differentiate between groundwater impact associated with the landfill waste disposal areas and that associated with other potential sources such as road deicing.

The overburden impact area is assumed to include all of the groundwater beneath the three landfilled areas on the site, and extends beyond these areas in the direction of groundwater flow. The most heavily impacted portion of groundwater beyond the waste disposal area is indicated to be about a 100 m wide band centred around the main leachate impacted surface water stream, which leads from the municipal waste area to the marshland, and very minor impact further to the east. This portion of the overburden plume has reached the on-site marshland where it discharges into the surface water system.

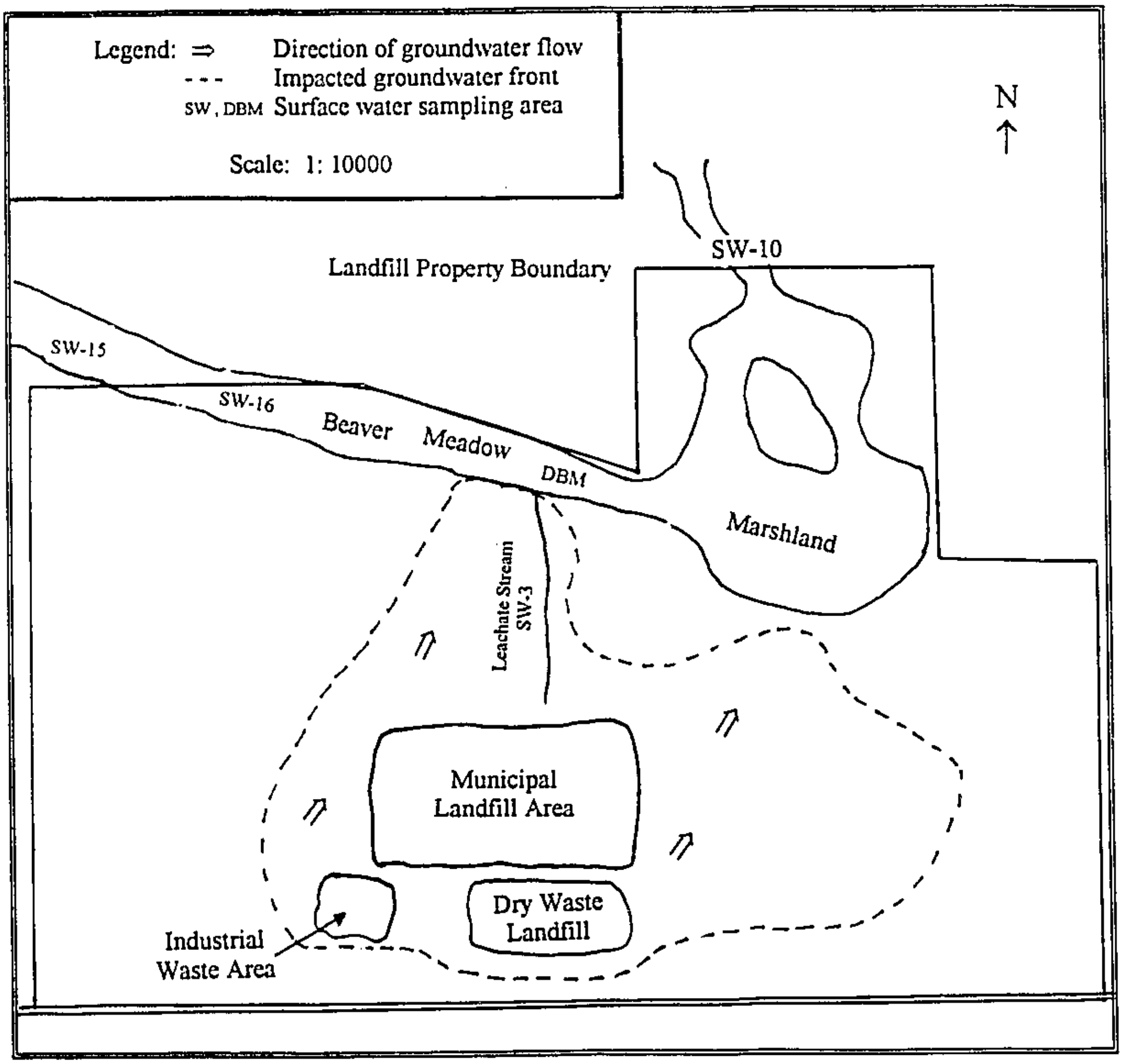

Figure 3.2: Leachate Plume Migration

The area of impacted overburden groundwater associated with the landfill waste disposal is currently contained within the landfill site boundaries and will expand further onto the property towards the north/north-east until it eventually reaches the on-site marshland groundwater discharge area where it enters the surface water system.

The large on-site marshland receives leachate impacted waters, mainly as surface water via the main leachate impacted stream course which originates at the base of the landfill. Impacted groundwater which follows the alignment of the stream course has also been discharging, albeit to a lesser degree, into the marshland since 1988.

The concentration versus time data for the main leachate impacted surface water stream indicate that concentrations for various parameters were at a maximum in the early to mid 1980's, and have either decreased, or varied over a relatively narrow range since that time. In the on-site marshland, downgradient from where landfill leachate impacted waters enter, the water quality has been consistent over time and within the range of parameter concentration contained in the Provincial Water Quality Objectives (PWQO) in natural background waters in the vicinity of the site. There is no indication of decline between 1977 and 1993 in the performance of the on-site natural marshland system to attenuate landfill leachate constituents with respect to PWQO objectives. This confirms that the on-site marshland north of the landfilled areas has, so far, been capable of attenuating the leachate generated by the landfill.

3.3 LABORATORY SET-UP

3.3.1 General

As previously stated, the assimilation potential of soil is often site dependant, and laboratory analysis are generally required to evaluate the attenuation capability of a particular marshland soil. In order to adequately characterize the attenuation potential of the Locksley Marshland it is essential to evaluate the physico-chemical properties of the native soil. A comprehensive laboratory program was set-up to investigate these properties. This program includes the following analyses:

1) The evaluation of the basic characteristics of the Locksley Marshland soil using standard laboratory analysis procedures.

2) Batch adsorption isotherm studies were undertaken using the marshland soil and several contaminant solutions. This investigation was carried out to quantify the adsorption potential of the marshland soil when in contact with various contaminants typically present in landfill leachate. The distribution coefficient of lead, zinc, calcium, sodium, chloride and pentachlorophenol (PCP) were determined.

3) Soil column experiments were undertaken to establish the breakthrough characteristics and the retardation factors of the above mentioned contaminants as they were leached through cells containing marshland soil. Furthermore, the migration profiles of the contaminant species were determined by analysing the pore water and the soil matrix within the columns.

The ultimate goal of the laboratory analysis is to estimate the primary parameters needed to implement the contaminant migration model.

3.3.2 Soil Collection

The soil used in the laboratory experiments was collected from a section of the Locksley Marshland located 700 m upstream from the main leachate stream . The soil sample location was chosen based on its accessibility and the natural state of the soil, unaffected by the landfill leachate.

The sampled soil was submerged by 0.1 to 0.15 m of water, had a dark colour, spongy texture and a distinctive organic odour. Once brought to the surface the organic soil was manually sorted to remove any large pieces of wood, gravel or other non representative materials. The soil was then placed in a 22 litres plastic pale and closed with an air tight lid. The collected soil was then transported to the University of Ottawa, where the soil was stored in a refrigerated room at a temperature of 4°C prior to laboratory analysis.

3.3.3 Soil Characteristics

The soil collected from the Locksley Marshland was characterised for moisture content, dry bulk density, organic content, total porosity, inorganic fraction and grain size distribution. All analyses were performed at the University of Ottawa following standard testing procedures as described in Table 3.1.

Due to the compressible and highly saturated nature of the marshland soil, undisturbed samples could not be gathered. Therefore great care had to be taken in measuring moisture content, bulk density and porosity, which would normally require undisturbed samples.

Prior to analysis, the soil was initially screened through a sieve with a 10 mm opening to remove any large pieces of rock or wood that might have skewed some of the laboratory results.

TABLE 3.1
Soil Characteristics: Method of Analysis

Soil Characteristics	Method of Analysis
Moisture content	ASTM D2974-87
Dry bulk density	Riley (1989)*
Organic content	ASTM D2974-87
Porosity	Riley (1989)*
Inorganic fraction	ASTM D421
Grain size analysis	ASTM D422

* Riley (1989), Laboratory Methods for Testing Peat.

3.3.4 Batch Adsorption Experiment

3.3.4.1 General

Batch adsorption experiments were used in determining the adsorption kinetics, adsorption isotherms and adsorption reversibility of several contaminant mixtures in contact with the organic soil present in the Locksley Marshland. These studies were conducted at room temperature (21°± 0.5°C) in the Environmental Pollution Laboratory at the University of Ottawa.

3.3.4.2 Soil Preparation

The marshland soil was dried at 90°C for over 48 hours using a Fischer Isotemp gravity-convection wall oven (model 110). The temperature was not raised above 90°C to prevent any loss of volatile organic matter. The dried soil was then lightly crushed using a 0.6 m long piece of PVC tubing (0.1 m diameter). The dried and crushed soil was then stored in an air tight container awaiting the adsorption experiments.

3.3.4.3 Reagent

In view of the strong variability of the leachate concentration observed at the Alice and Fraser Landfill site, it was decided that synthetic stock solutions would be prepared for both the batch adsorption and the column experiments. By employing a laboratory controlled spiked solution the concentration level could be precisely adjusted and enough solution could be produced.

Three stock solutions were formulated in order to investigate the chemical properties of three types of contaminants: heavy metals, cations and anions and organic compounds.

The heavy metal solution was prepared with laboratory grade lead nitrate ($Pb(NO_3)_2$) and zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$). Both compounds were dissolved in distilled water to produce an approximate concentration of 100 mg/l of lead and zinc.

The cations solution consisted of a mixture of laboratory grade calcium chloride ($CaCl_2$) and sodium chloride (NaCl) dissolved in distilled water. A resulting concentration of approximately 100 mg/l of calcium and sodium was obtained. The cations stock solution also contained a concentration of chloride approaching 250 mg/l.

The organic spiked solution was produced using purified grade (99+0.5%) pentachlorophenol (C_6HCl_5O). The PCP was dissolved in 0.1N NaOH and diluted to a concentration of approximately 8 mg/l following a procedure developed by the National Research Council of Canada (Lu, 1992). The pH of the solution was adjusted to 7 with dilute sulphuric acid.

All stock solutions were prepared to produce between 10 and 20 litres of synthetic wastewater. Additional stock solutions were prepared in the same fashion when needed during the course of the experimental phase. The use of distilled water instead of natural groundwater for the liquid phase is judged to be a conservative approach. The chemical composition of the synthetic stock solutions is presented in Table 3.2

TABLE 3.2
Synthetic Solution Constituent

Synthetic Stock Solution	Compound Used	Chemical Composition	Mass Required (mg/L)	Targeted Contaminant	Approximate Concentration (mg/L)
Heavy Metal Solution	Lead nitrate Zinc nitrate	$Pb(NO_3)_2$ $Zn(NO_3)_2$ $6H_2O$	159.85 454.96	Pb Zn	100 100
Cations and Anions Solution	Calcium chloride Sodium chloride	$CaCl_2$ NaCL	276.93 254.45	Ca Na Cl	100 100 250
PCP Solution	Pentachlorophenol	C_6HCl_5O	8	PCP	8

3.3.4.4 Batch Experimental Set-Up

Batch kinetic and adsorption studies were all carried out in 125 ml Erlenmeyer flasks to which was added a determined mass of dried soil and 100 ml of either the heavy metal, cations or the PCP spiked solutions. The contact between the soil and the stock solution was obtained by gentle agitation with a rotary shaker adjusted to 200 rpm. The experimental set-up is presented in Figure 3.3.

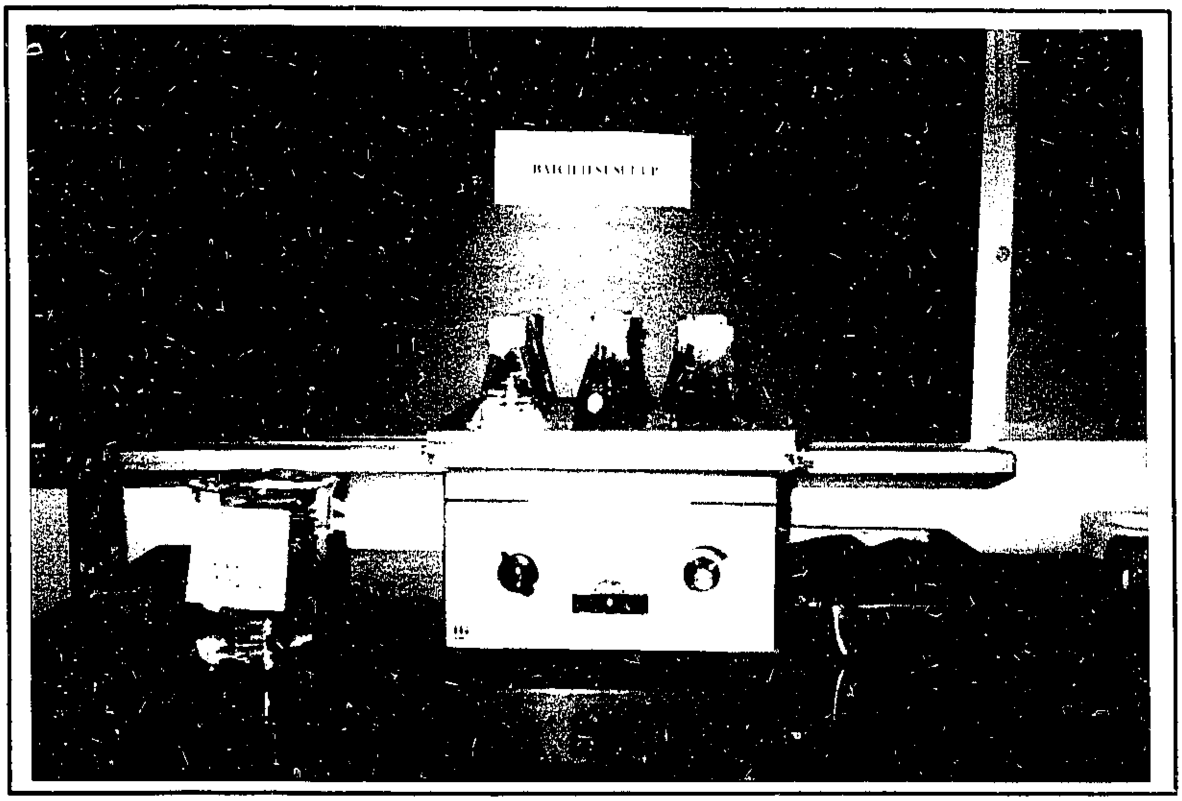

Figure 3.3: **Batch Test Apparatus (Photo)**

After a pre-determined time period, the settled slurry was transferred from the Erlenmeyer flask to a centrifuge tube and accelerated to 5000 rpm (3000 G) for a period of 10 minutes in a refrigerated centrifuge in order to separate the solid from the liquid phase. An aliquot of 20 ml of the supernatant was then collected and stored in glass scintillation vials for determination of contaminant concentration. The heavy metal, cation and anion solutions were analysed using an Inductively Coupled Argon Plasma Spectrograph (ICP), Model 975, at the University of Ottawa, while the PCP analysis was performed at the National Research Centre using a High Performance Liquid Chromatography (HPLC) as described by Lu (1992).

3.3.4.5 Kinetics of Contaminant Adsorption Analysis

In order to establish the time required for the adsorption reaction to reach equilibrium between the solid and liquid phases, a kinetic plot of time versus contaminant concentration remaining in solution was examined. The kinetic analysis was achieved using 1 g of dried soil mixed with 100 ml of each of the three spiked solutions. The mixture was then agitated as described in section 3.3.4.4. The contact time between the soil and the spiked solution was fixed at 1, 6, 12, 24, 36 and 48 hours after which the contaminant concentration remaining in solution was evaluated. A plot of concentration versus time was then drawn to establish the time required to reach equilibrium for each contaminant species (lead, zinc, calcium, sodium and PCP).

3.3.4.6 Adsorption Isotherm

To develop the adsorption isotherms, duplicates of varying mass of dried soil (0.25, 0.5, 1, 2 and 4 g) were added to 125 ml Erlenmeyer flasks containing 100 ml of the stock solution. After gentle agitation for the desired contact time as established by the kinetic plot, an aliquot of the supernatant was sampled and analyzed using the procedure described in section 3.3.4.4. The result of the adsorption isotherm was then used to develop the Freundlich and Langmuir isotherms for each contaminant-soil mixture.

3.3.4.7 Desorption Analysis

In order to investigate the reversibility of contaminant adsorption by the surface soil, a series of desorption experiments were conducted on the same samples previously used for the adsorption isotherm determination. The desorption of contaminants was achieved by centrifuging the entire sample used in the adsorption test to remove a majority of the supernatant, and then replacing it with 100 ml of distilled water. This sample was then slowly mixed for a period of 24 hours before being re-sampled and analyzed. The above mentioned procedure was repeated a second time with distilled water and a contact time of about 20 hours. The contaminant fraction migrating from the soil to the liquid phase could then be evaluated, indicating the potential reversibility of the adsorption phenomenon.

The desorption analysis was limited to pentachlorophenol, since ample studies have been reported on the desorption potential of heavy metals, and the low adsorption rate observed for calcium and sodium (Mclelland and Rock, 1988; Cameron, 1978).

3.3.5 Column study

3.3.5.1 General

Although batch laboratory studies provided useful information on the adsorption potential of contaminants by the collected soil, continuous flow column experiment provides a more reliable method of simulating the natural environment (Eckenfelder, 1989;Warith, 1987). Column type continuous flow operations try to recreate as close as possible the soil/water ratio encountered in nature (Domenico and Schwartz, 1990; Weber, 1972). In addition, moving pore fluids in the column actively redistribute the products of reaction unlike batch experiment.

In this investigation, laboratory leaching cells were designed to simulate saturated flow of leachate through the Locksley marshland soil. A total of 10 cells were constructed at the University of Ottawa. Each cell consisted of a hollow Plexiglas cylinder 3 mm thick, with an inside diameter of 100 mm and a total length of approximately 100 mm. A Plexiglas top cap and bottom plate were screwed to the top and bottom of each cylinder and fitted with rubber O-rings to prevent water leakage. The stock solution was stored in a 0.235 litres constant head reservoir located at the top of the cell, while the effluent was drained from the bottom at atmospheric pressure. A schematic representation of a laboratory leaching cell is presented in Figure 3.4.

A specially designed holding rack was constructed to permit five cells to be operated simultaneously as shown on Figure 3.5. This experimental set-up enabled simultaneous monitoring of all five cells.

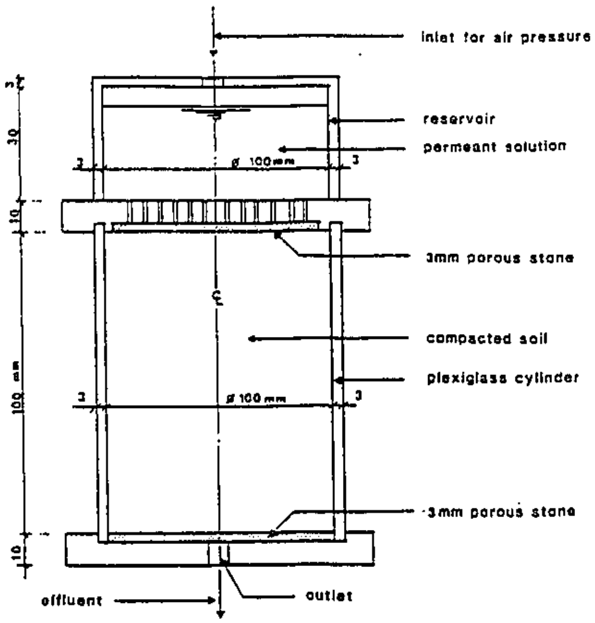

Figure 3.4: Schematic Representation of the Laboratory Column Apparatus

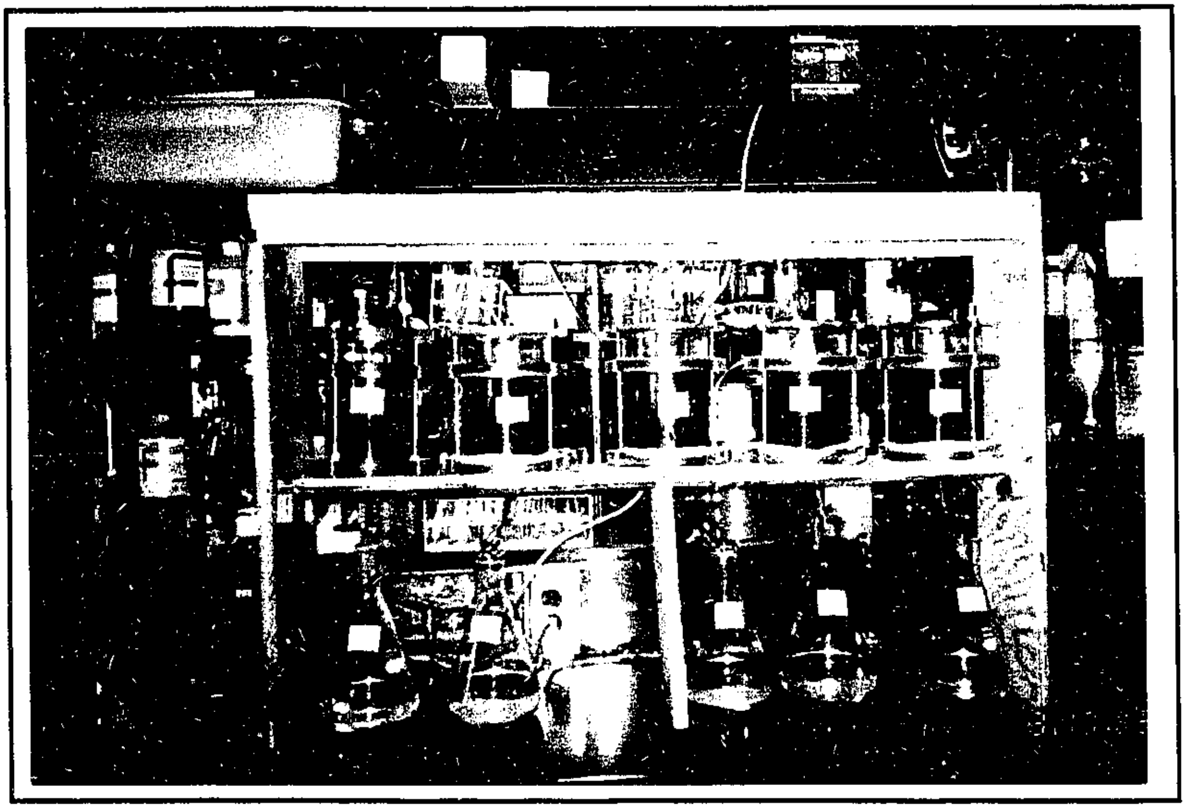

Figure 3.5: Column Study Experimental Set-Up (photo)

3.3.5.2 Soil Preparation

Theoretically, a column experiment should contain soil that is in the same physical state as is observed in field conditions. However, due to the un-cohesive nature and high water content of the Locksley Marshland soil, it was not feasible to collect undisturbed soil for insertion in the soil column. A technique to adequately place the remoulded soil in the column had to be developed. Two main conditions had to be met for the soil preparation procedure to be judged acceptable:

1) The hydraulic conductivity of the soil should be in the range characteristic of marshland soil.

2) There should not be a variation in hydraulic conductivity greater than one order of magnitude between the different cells being constructed. This is necessary if correlation are to be made between cells.

Initial trials were attempted using the disturbed soil as collected. The organic soil was placed in the column in 20 mm lifts and compacted by hand until the entire cell was filled. A permeable geotextile membrane was placed at the bottom and top portion of the cell to ensure uniform distribution of the permeant solution on the soil surface and to prevent the migration of soil particles out of the system during the leaching phase. Distilled water was then allowed to permeate through the cell, and percolation rates were monitored for several days. This technique produced highly variable hydraulic conductivities, spanning 5 orders of magnitude between cells (1×10^{-5} to 1×10^{-10} m/s).

The problem of reproducing cells having similar hydraulic conductivities is mainly due to the highly compressible nature of the organic soil. When intense compaction was applied to the soil layers, the material compressed, rendering the soil practically impermeable. When light compaction was applied to the soil layers, a large percentage of voids were left intact, promoting preferential drainage within the column. After experimenting with different compaction techniques, it was decided to somehow try to homogenise the soil sample prior to inserting it in the column. Several researchers (McLellan and Rock, 1988; Poots et al., 1976) were confronted with the same problem and circumvented it by initially homogenising the soil by first drying the material and then reducing it to a fine powder. This particular soil preparation technique was attempted.

The Locksley Marshland soil was dried at 90°C for 48 hours as described in section 3.3.4.2. The cells were then filled with the crushed soil without any compaction. An average mass of 400 g of dried soil was needed to fill the cell. Afterward a constant water head was applied to the cell, until complete saturation was achieved, at which point the bottom opening of the cell was opened, permitting the percolation process to begin.

It was observed that a hydraulic conductivity in the range of 9×10^{-7} to 9×10^{-8} m/s was generated using the dried soil technique. It was further noticed that this method was easy to implement and the results were fairly consistent. This cell filling procedure was adopted for all of the column leaching experiments that followed.

It is however important to note that entrapped air might have been present within the soil columns using this technique. This situation may have caused some oxidation and would lower the porosity of the soil matrix, thus increasing the velocity of the migrating water phase. For further studies it is highly recommended that cell be previously flushed with CO_2 to achieve true saturation prior to any leaching experiment.

3.3.5.3 Testing Procedure

A series of five cells were prepared as described in section 3.3.5.2 in order to analyse the leaching effect for each of the three stock solutions. Four of the cells were used to pass the stock solution, while the fifth cell was used as a control, passing only distilled water. Cell identification and corresponding source solution are presented in Table 3.3.

TABLE 3.3
Column Study
Cell Identification Table

Cell Identification Number	**Stock Solution Used as Influent**
1 to 4	Heavy Metal Solution
5	Distilled Water
6 to 9	Cation Solution
10	Distilled Water
11 to 14	PCP Solution
15	Distilled Water

Before allowing the stock solution into the cells, the cells were initially saturated with distilled water and the hydraulic conductivity of each cell was monitored for a period of several days until the flow rate was stabilised. Once all cells were saturated and possessed similar hydraulic conductivities, the column leaching experiment were commenced by switching the column input from distilled water to the spiked solution in four of the five leaching cells. The spiked solution was continuously pumped into the column with a Dekastaltic pump which was adjusted on a daily basis to maintain a constant head of solution in the cell reservoir. A schematic representation of the column experiment configuration is presented in Figure 3.6.

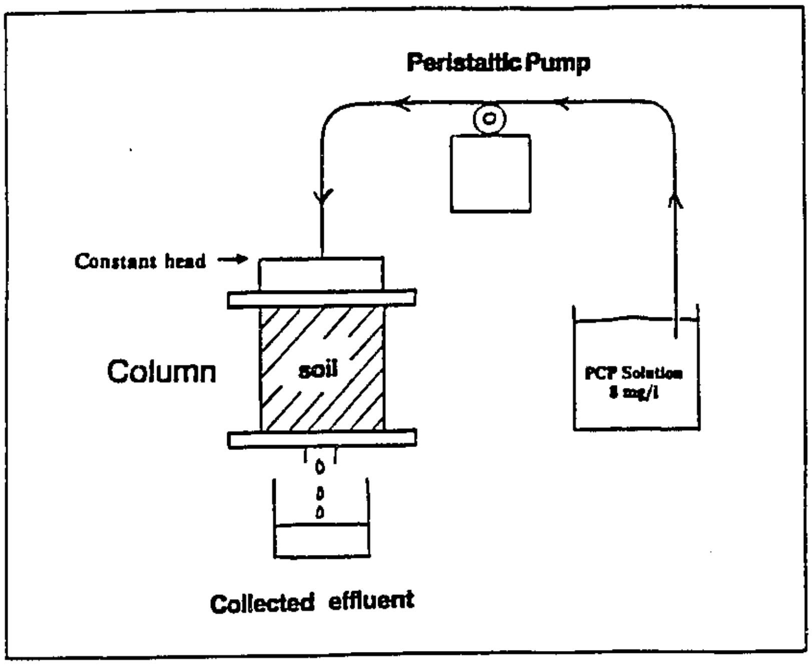

Figure 3.6: **Schematic Representation of the Leaching Column Experiment Configuration**

Monitoring of the column effluent was achieved using a five step approach:

a) Effluent measurement: The total volume of percolated solution collected was measured and tabulated on a daily basis. If the percolation rate decreased during the course of the test, the effluent measurement was taken at a larger time interval.

b) Effluent sampling: A sub-sample of approximately 50 to 70 ml of column effluent was collected using a pipette after effluent measurement.

c) Filtration: It was necessary to filtrate the effluent solution to remove any small particles of soil that might have migrated out of the cell. To achieve this, the collected effluent was then transferred to a centrifuge tube and accelerated at 3000 G (5000 rpm) for a period of 10 minutes, in order to separate the solid from the liquid phase. An aliquot of the supernatant was then collected and stored in glass scintillation vials for contaminant concentration analysis.

d) Acidification: Effluent samples originating from the heavy metal impacted cells were acidified using nitric acid to decrease the pH level below 2. The pH of the solution was measured using a Fisher Accumet pH meter (Model 210). This procedure was followed in order to avoid any precipitation of the heavy metals present in the solution. No additional treatment was required for the cations and PCP impacted effluent.

e) Storage: The treated effluent samples were then stored in glass vials and refrigerated at 4°C, until chemical analysis could be performed.

The column effluent generated from the heavy metal and cation stock solutions were analyzed for a matrix of 9 metal ions including lead, zinc, calcium and sodium using an Inductively Coupled Argon Plasma Spectrograph (ICP), Model 975. The effluent generated from the PCP stock solution was analysed with a High Performance Liquid Chromatography (HPLC). Breakthrough curves were constructed based on the results of these analysis.

3.3.5.4 Cell Termination

One of the objectives of the column study was to observe the migration of the targeted contaminant from the top portion of the cell down to the collected effluent. It was therefore decided to continue the leaching process until the targeted contaminants could be detected in the effluent. For the cations solution, calcium and sodium were observed in the effluent within 2 days, while for the PCP and heavy metal solution, none of these targeted contaminants were observed in the effluent after a respective leaching time of 76 and 120 days .

Once disconnected the packed soil was removed from the columns and cut into 5 equal layers (from top to bottom). Each layer of soil was then placed in ziplock bags and frozen until analysis for the pore water and soil matrix could be undertaken.

3.3.5.5 Pore Water Analysis

In order to establish the distribution of contaminants with depth in the water phase of the cell column, soil samples originating from the different soil layers were mechanically compressed in order to extrude the pore water. The collected water sample were then filtered and treated following the procedure described in section 3.3.5.3. The pore water was then analyzed for the targeted contaminants.

3.3.5.6 Soil Digestion

The distribution of contaminants adsorbed by the soil matrix was determined by digesting soil sample taken from the layered soil column. The digestion analysis was conducted on soil samples previously drained of their pore water as described in section 3.3.5.5. The soil samples were then dried at a temperature of 90°C for a period of 24 hours in a Fischer Isotemp oven. The samples were crushed using a mortar and pestle to a size small enough to pass a 160 micrometer sieve. A 5 g sample of each layer was weighed to the nearest 0.01 g and then placed into nalgene beakers. A total of 2 ml of distilled water and 5 ml of nitric acid were added to each of these samples. The nalgene beakers were then placed on a hot plate at a setting of 200°C and left overnight in order to allow the reaction between the nitric acid and the organic matter to ensue.

The next step involved the addition of 3 ml of perchloric acid (HClO4) and 10 ml of hydrofluoric acid (HF) to these sample which were again left for 2 days on a hot plate at a temperature setting of 150°C. Finally the resulting digested matter remaining in the beakers was mixed with 2 ml of concentrated HCl and distilled water to a total of 25 ml. The resulting solution was analysed for metals using the ICP technique.

The soil digestion analysis permitted us to quantify the adsorption capacity of the Locksley Marshland soil and its distribution profile through the cell.

CHAPTER 4

EXPERIMENTAL RESULTS AND DISCUSSION

4.1 GENERAL

In this chapter the results obtained from the laboratory analysis described in Chapter 3 are presented and discussed. Emphasis will be placed on establishing the relative importance of the adsorption process on the mobility of several contaminant species known to be present in landfill leachate. The results and analyses are presented in four sections. The first three sections (4.2, 4.3 and 4.4) describe the laboratory results, while the fourth section (4.5) provides analysis and discussion on the various attenuation mechanisms affecting the targeted contaminant species.

In the first three sections, the experimental results shall include the following:

(1) The basic physical and chemical properties of the natural Locksley Marshland soil and the characteristics of the stock solutions.

(2) Results of batch adsorption experiments which define the attenuation capacity of the marshland soil associated with different contaminants (heavy metals, majors cations and anions as well as organic compounds).

(3) Results of leaching column studies with characteristic breakthrough curves, which define the saturation capacity of the marshland soil with respect to the various contaminant species.

4.2 BASIC PHYSICAL AND CHEMICAL PROPERTIES

4.2.1 Basic Soil Characteristics of the Locksley Marshland

The soil sampled from the Locksley Marshland was investigated in the laboratory to establish its primary properties. Visually the soil had a distinctive dark brown colour, a spongy texture and an organic odour was also detected. When squeezed by hand, about 70% of the material escaped between the fingers, leaving plant residues such as roots and fibres within the palm of the hand. This initial visual inspection permitted to establish that the collected soil had a notable organic fraction, typical characteristic of marshland environments. The basic properties of the Locksley Marshland soil, as measured using standard testing procedures described in section 3.3.3, are presented in Table 4.1.

TABLE 4.1

BASIC PROPERTIES OF THE LOCKSLEY MARSHLAND SOIL

Organic matter content (%)	**20 - 30 %**
Moisture content	**75 - 80 %**
Organic carbon content (%)	**14-17%**
Porosity (%)	**75 - 85 %**
Dry bulk density	**450 kg/m3**

Grain size analysis of the inorganic fraction

Grain size (µm)		% passing
2000		100
600		97
300		82
75		54
50		45
5		20
1		6

The results of this preliminary laboratory investigation lead to the conclusion that the material sampled from the Locksley Marshland was in fact an organic soil, having an organic fraction varying from 20 to 30%. Landva et al. (1983) defined a soil with an organic fraction varying from 5 to 80% as being an organic soil while peat is defined as having an organic fraction greater than 80%.

The inorganic fraction of the collected soil consists of a fine sand and silt matrix, while the organic portion is made up of partly decomposed plant matter that originates from the wooden area that borders the Locksley Marshland.

The concentration of heavy metals and other alkali earth metals naturally adsorbed within the marshland soil matrix was determined by digesting a 5 g sample using the procedure described in section 3.3.5.6. The resulting chemical concentration of these metals, as determined by an Inductively Coupled Argon Plasma Spectrograph, is presented in Table 4.2.

TABLE 4.2
Chemical Composition of Natural Locksley Marshland Soil

Parameter	Concentration Range (mg/L)
Pb	9 - 11
Zn	45 - 46
Ca	12,000
Na	12,400 - 13,500
Ba	41 - 51
Cu	20 - 22
Mg	2,400 - 2,600
Mn	268 - 278
Sr	168 - 178

The chemical composition of the Locksley Marshland soil is similar in constitution to other marshland soils as described by Rana and Viraraghavan (1987) and Cameron (1978). High concentration of calcium, sodium and magnesium are noted while heavy metals levels are generally quite low.

4.2.2 Characteristics of the Stock Solutions

Due to the complex nature and the various chemical species which are generated from municipal landfills, it is neither facile nor feasible to detail all compositional features of such leachates. In this study, the various contaminant species were divided into three main categories: (1) Heavy Metals, (2) Major Cations and Anions, and (3) Organic Compounds. But only some individual contaminants, representative of each of the above mentioned categories were chosen for the batch adsorption and column studies. The selection of these contaminants was based on two main fundamental criteria:

(1) Occurrence of these contaminants in the leachate solution generated at the landfill site.

(2) Potential hazardous effect expected in the case of contaminant breakthrough to the environment.

The elements analyzed in this study were the following:

Heavy Metals:	Lead (Pb) and Zinc (Zn)
Major Cations and Anions:	Sodium (Na), Calcium (Ca) and Chloride (Cl)
Organic Compound:	Pentachlorophenol (PCP)

The chemical composition of the synthetic stock solution of heavy metals, cations and PCP were determined on various occasions during the batch and column study experiments to ensure their chemical integrity. The results of the chemical analysis presented in Table 4.3, indicate that the prepared solutions were relatively stable, varying marginally during the course of the experiments.

TABLE 4.3
Stock Solutions
Chemical Characteristics

Stock Solution	Parameter	Concentration Range (mg/L)	Mean Concentration (mg/L)	Standard Deviation (mg/L)	Number of Observation
Heavy Metals	Pb	105 - 120	110.2	6.9	5
	Zn	91 - 114	98.8	10.6	5
Major Cations and Anions	Na	113 - 114	113.5	0.7	2
	Ca	110 - 113	111.5	2.1	2
	Cl	249 - 250	249.5	0.7	2
Organic	PCP	6.2 - 8.7	8	0.8	8

The pH of the stock solutions were evaluated on a regular basis, as well as the pH for both the batch adsorption and soil column experiments. Although the pH was continually monitored throughout this project, it was not considered as a variable for this study. Variation in pH were naturally obtained by interaction between the stock solutions and the marshland soil, no attempts were made at externally modifying the pH. The results of the pH analyses are presented in Table 4.4.

TABLE 4.4
pH Analyses

	Stock Solution		Batch Adsorption		Column Study	
Stock Solution	Average pH	Standard Deviation	Average pH	Standard Deviation	Average pH	Standard Deviation
Heavy Metals	5.1	0.1	5.6	0.2	7.3	0.4
Major Cations and Anions	5.9	0.1	5.7	0.2	5.6	0.3
Organic	7.5	0.1	6.6	0.1	5.8	0.2

4.3 RESULTS FROM THE BATCH ADSORPTION EXPERIMENTS

4.3.1 Adsorption Kinetic Studies

Kinetic studies were undertaken to establish the time required for the adsorption process to reach equilibrium between the solid and liquid phases. In theory, the rate of transfer of contaminants from a solution to the soil matrix is related to the surface tension of the soil and the diffusion properties of the targeted contaminants, as well as the temperature, pH and ionic strength of the solution. Thus the time required to reach equilibrium will vary depending on the nature of the soil and the chemical being monitored. Following the procedure described in section 3.3.4.5, the kinetic plots of lead, zinc, calcium, sodium and pentachlorophenol were developed and are presented in Figures 4.1 (a, b and c).

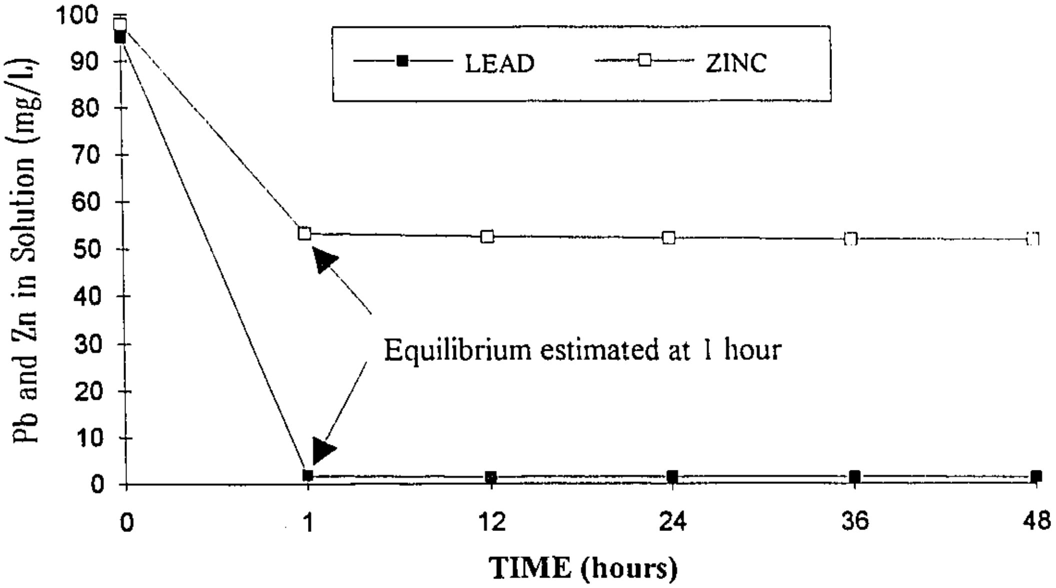

Figure 4.1a: Kinetic Plot of Time Versus Heavy Metal Concentrations Remaining in Solution

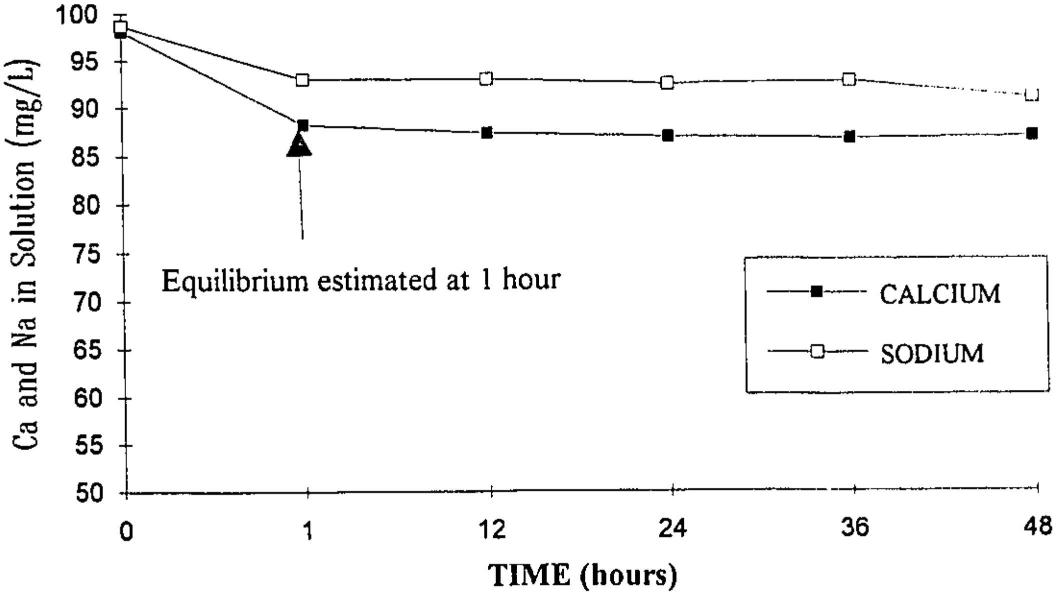

Figure 4.1b: Kinetic Plot of Time Versus Cations Concentrations Remaining in Solution

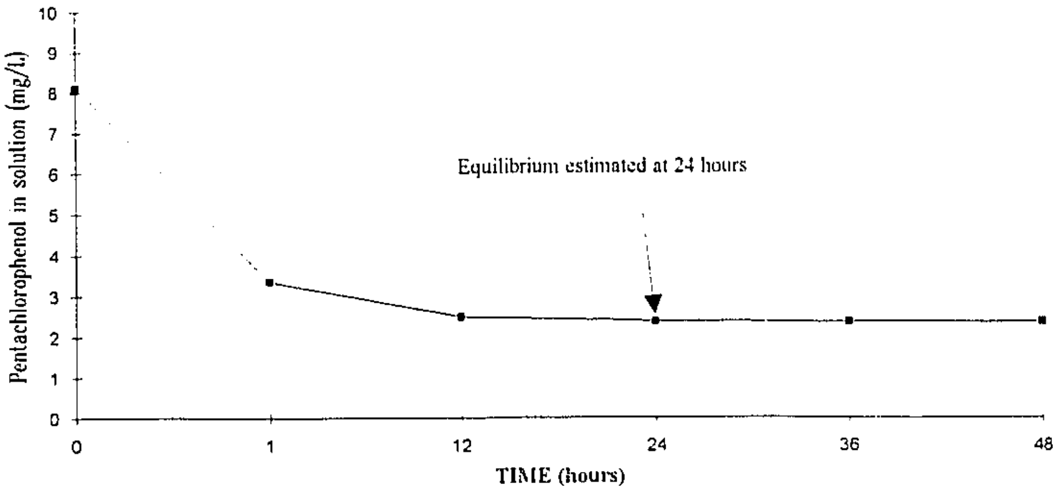

Figure 4.1c: Kinetic Plot of Time Versus PCP Concentrations Remaining in Solution

The results obtained from the adsorption kinetic studies indicate that the contaminant adsorption generally reaches equilibrium within 24 hours, with up to 98% of the adsorption process completed within 1 hour of contact time for lead, zinc, sodium and calcium. These results are in accordance with the findings of several researchers (Viraraghavan and Mathavan, 1990; McLellan and Rock, 1988; and Viraraghavan and Ayyaswami, 1988), who observed that the adsorption phenomenon in organic soil is generally completed within a few hours of contact time.

4.3.2 Adsorption Isotherm Data Analysis

4.3.2.1 General

Sorption processes involve an array of phenomena which can alter the distribution of contaminants within the different phases of a system. The interchange of mass associated with such processes impact the fate and transport of many inorganic and organic substances (Weber, et al., 1991). Each combination of contaminant, sorbing phase and set of local conditions will yield a unique mass distribution.

Several mathematical relationships have been developed to describe the distribution of solute between liquid and solid phases. The most common form of adsorption equations are the Freundlich and Langmuir models which were described in section 2.3.3. The main advantage of these adsorption models is that they provide a rapid and relatively accurate mean to assess the initial potential of a soil to remove a particular contaminant from solution.

A series of adsorption isotherms were examined to evaluate the adsorptive capacity of the marshland soil when in contact with several contaminants. The laboratory procedure for the batch adsorption studies are presented in section 3.3.4.6. The contact time between the soil and the stock solution was of 1 hour for the heavy metal, the cation and anion solutions, while a contact time of 24 hours was maintained for the PCP solution, as determined by the kinetic plots shown on Figures 4.1 (a, b and c). The results of the adsorption isotherm will be presented in the following subsections based on the contaminant species investigated.

4.3.2.2 Adsorption of Heavy Metals

The raw data collected from batch adsorption experiments employing the heavy metals are presented in Appendix B.

The high attenuation capacity of the marshland soil towards heavy metals, as observed during the batch adsorption experiments, is emphasized in Figure 4.2. A mere 1 g of the marshland soil reduced the overall concentration of lead in solution by more than 98%, from an initial level of 95 to 1.8 mg/L within one hour of contact time. Zinc ions were also heavily attenuated with increasing soil mass, but not as effectively as lead. A 4 g mass of the marshland soil reduced the overall concentration of zinc by 88% within one hour of contact time.

The resulting adsorption isotherm for lead is presented in Figure 4.3. The minimum detection limit on S is also shown on the graph (detailed calculations are presented in Appendix C). As shown on the graph, the low detection limit indicate that all the measured points are considered to be significant. The minimum detection limit was measured for all of the isotherm performed and are discussed in detail in Appendix C.

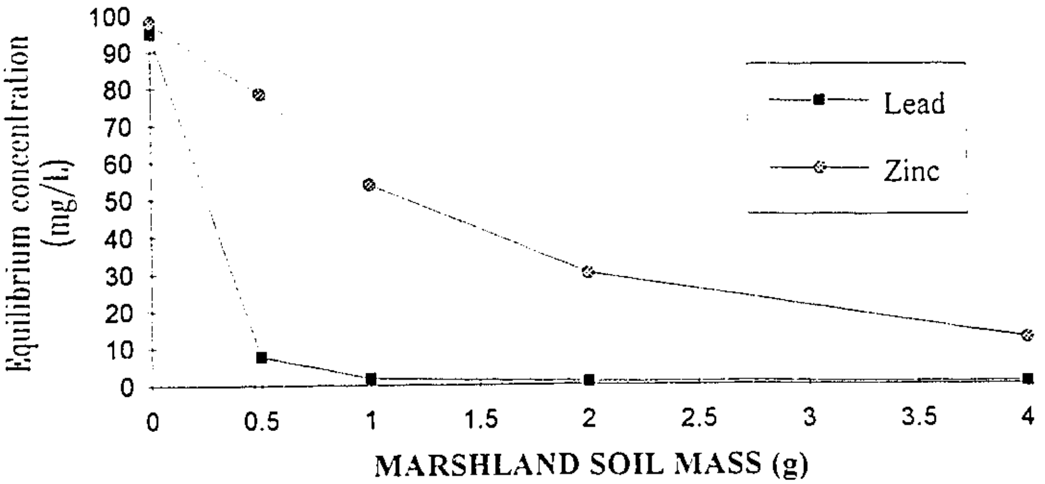

Figure 4.2: Heavy Metals Attenuation by Marshland Soil -- Batch Adsorption Study

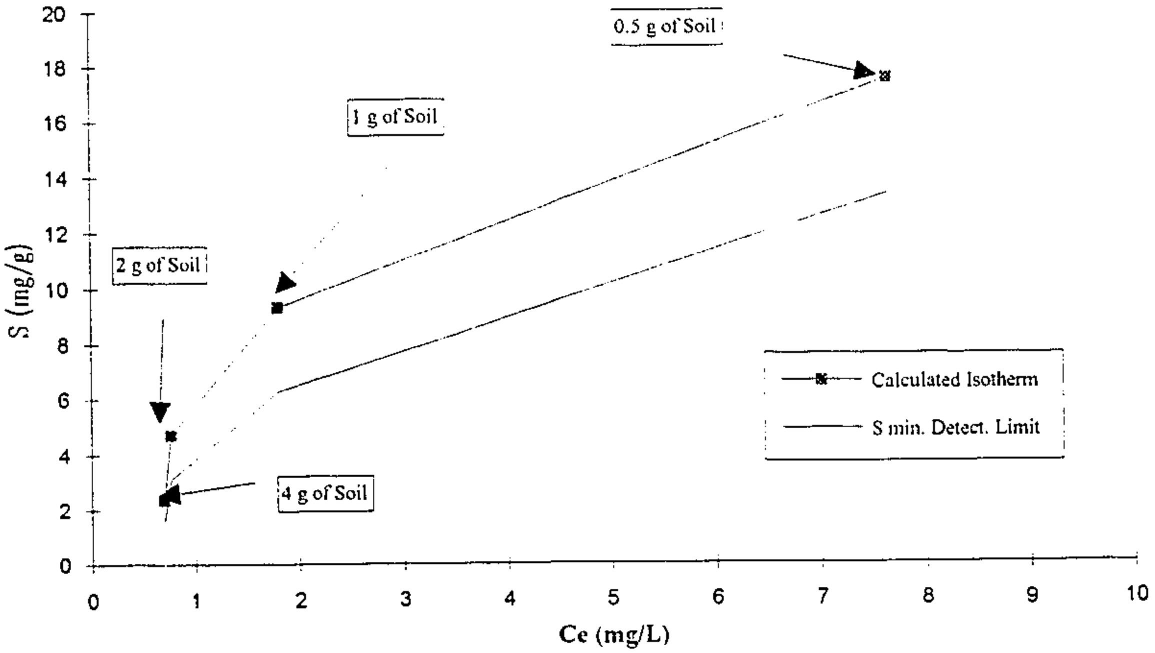

Figure 4.3: Lead Isotherm with Minimum Detection Limit

Based on the data collected an analysis for the adsorption potential of both lead and zinc using the Freundlich and Langmuir models was undertaken. Plots of these isotherms are shown in Figures 4.4 (a and b) and 4.5 (a and b).

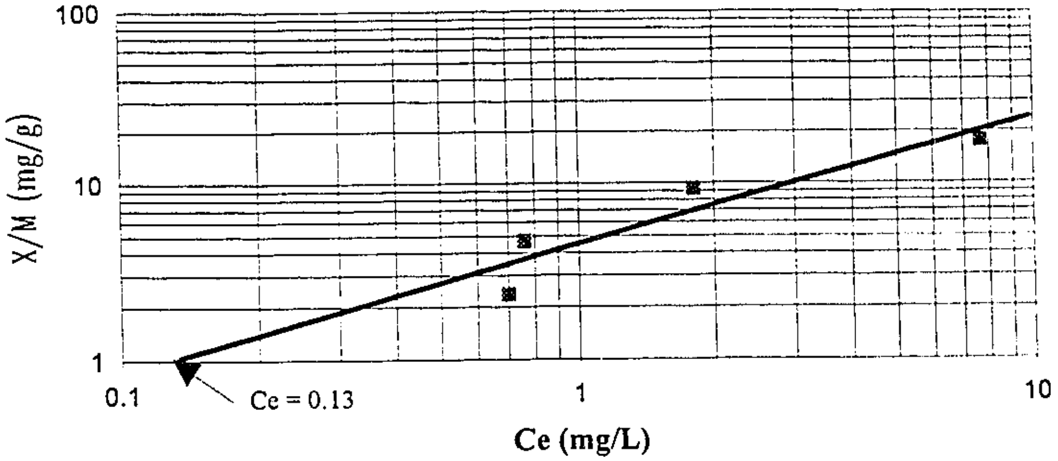

Figure 4.4a: Freundlich Isotherm for Lead

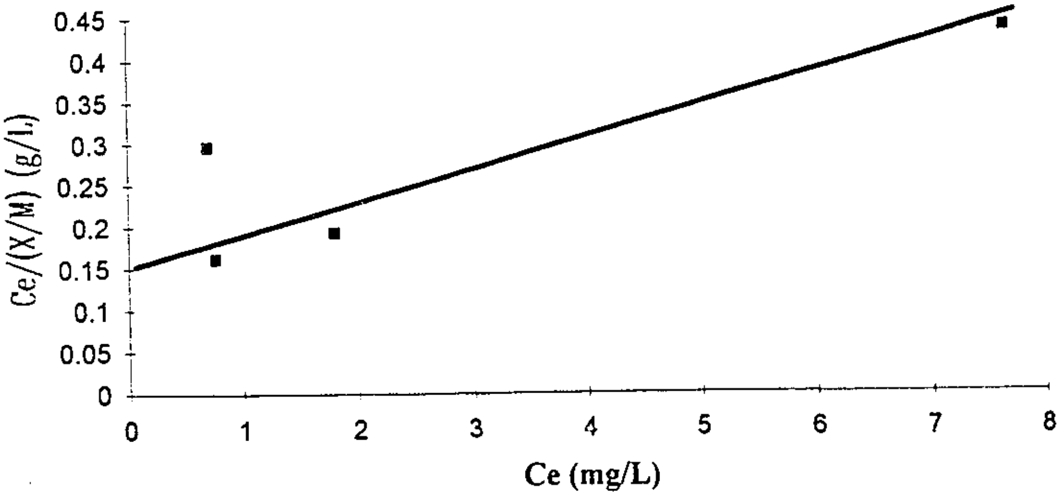

Figure 4.4b: Langmuir Isotherm for Lead

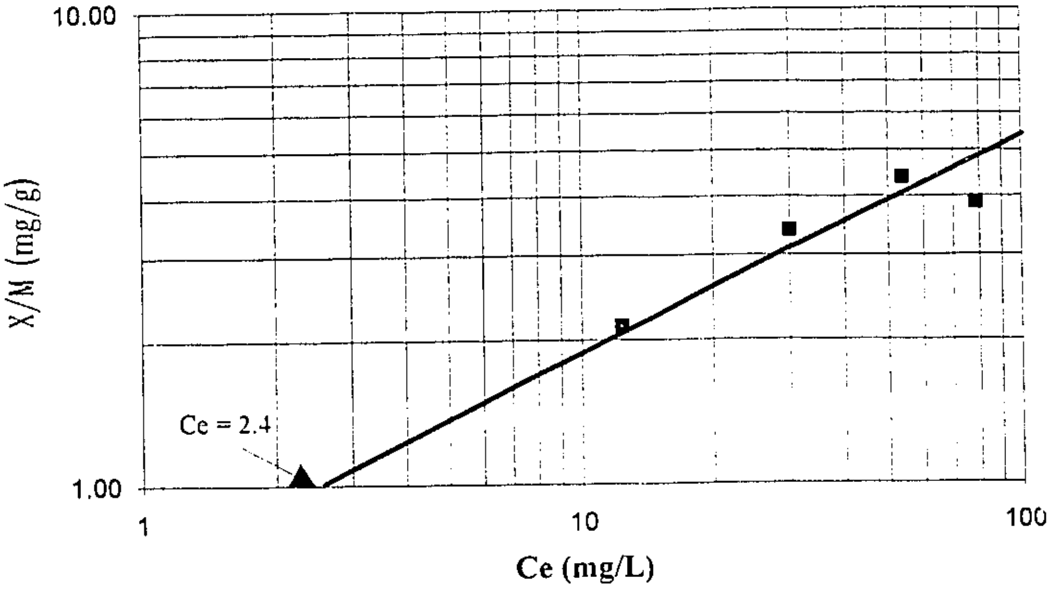

Figure 4.5a: Freundlich Isotherm for Zinc

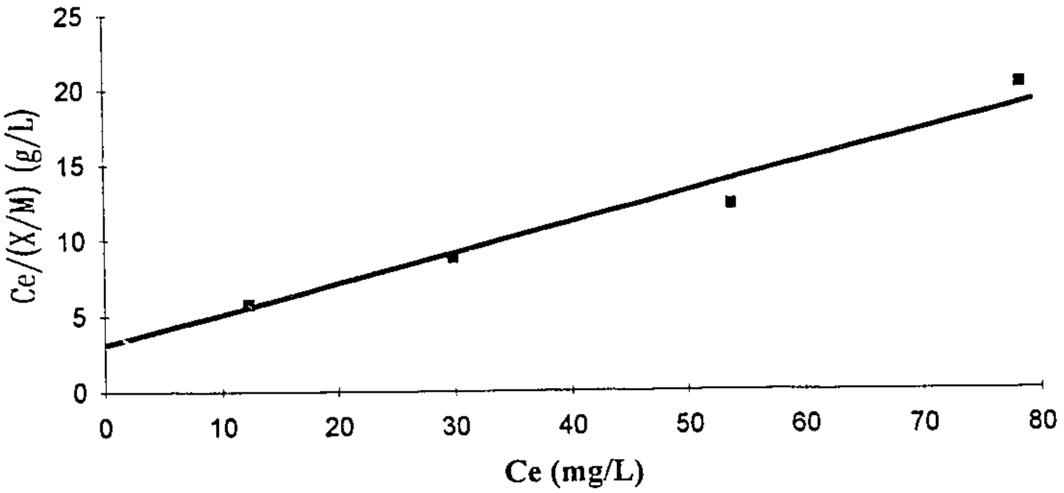

Figure 4.5b: Langmuir Isotherm for Zinc

The analysis of the data showed that the adsorption of both lead and zinc followed the Freundlich and Langmuir isotherms. This indicates that the adsorption process is of a simple, monolayer type characteristics of chemisorption (Viraraghavan and Mathavan, 1989). The Freundlich and Langmuir equations derived through the batch adsorption analysis of heavy metals are presented in Table 4.5, with associated regression equations.

TABLE 4.5

Freundlich and Langmuir
Model Parameters for Heavy Metals

Parameter	Isotherm	Isotherm Equation	Regression Equation	Correlation Factor
LEAD	Freundlich	(x/m) = 4.65CeY(0.706)	Log (x/m) = 0.649 + 0.722 log Ce	0.9
	Langmuir	(x/m) = 8.068Ce/(1+0.332Ce)	Ce/(x/m) = 0.185 + 0.0312 Ce	0.85
ZINC	Freundlich	(x/m) = 0.75CeY(0.437)	Log (x/m) = -0.0327 + 0.3594 log Ce	0.92
	Langmuir	(x/m) = 0.0277Ce/(1+0.0052Ce)	Ce/(x/m) = 2.490 + 0.2123 Ce	0.98

Both adsorption isotherms indicate that the Locksley Marshland soil has a high affinity to adsorb heavy metals. The higher the K_F (Freundlich Adsorption Coefficient) value is, the higher the adsorptive capacity. Based on these results, it can be concluded that both lead and zinc will be substantially retained on the organic soil matrix.

4.3.2.3 Adsorption of Major Cations and Anions

A batch adsorption investigation was also realised using a stock solution containing an initial concentration of 100 mg/L of calcium as well as sodium ions and 250 mg/L of chloride. Data collected from this batch study is presented in Appendix B.

Sodium and calcium ions were not adsorbed as efficiently as were the heavy metals. Figure 4.6 illustrates the attenuation potential of both cations as measured during the batch adsorption experiments. As a result of one hour of contact with 4 g of the marshland organic soil the calcium and sodium concentrations of the stock solution decreased by 13 and 5% respectively .

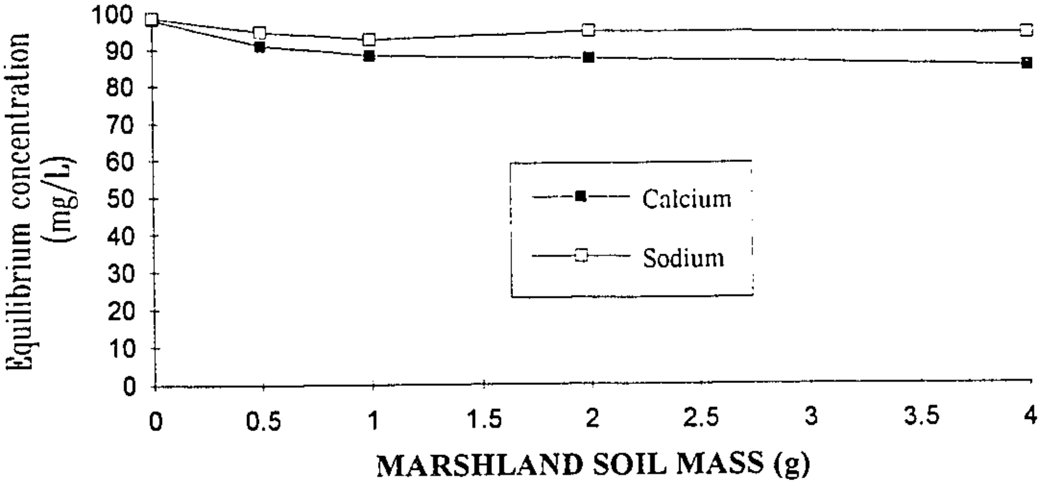

Figure 4.6: Major Cations Attenuation by Marshland soil -- Batch Adsorption Study

Plots of the Freundlich and Langmuir models derived from the laboratory data are shown in Figures 4.7 (a and b) and 4.8 (a and b).

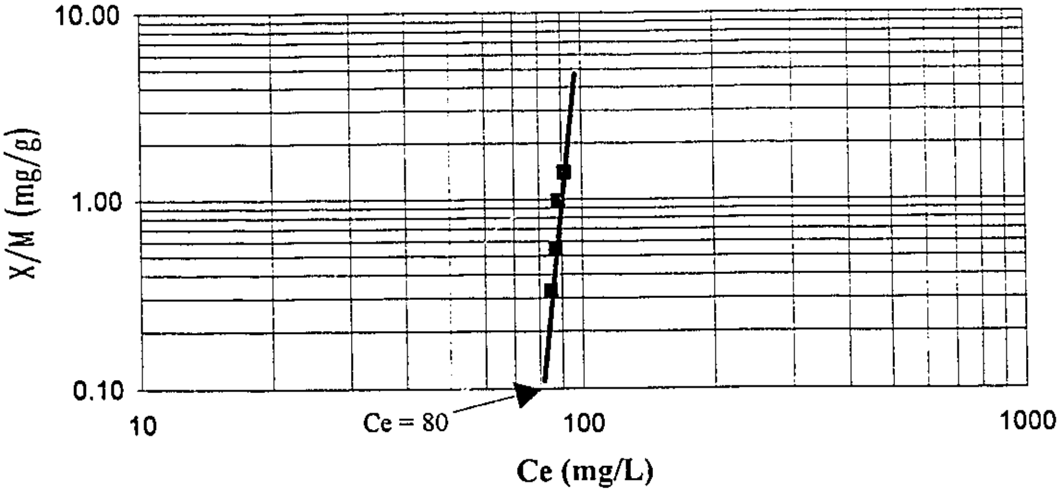

Figure 4.7a: Freundlich Isotherm for Calcium

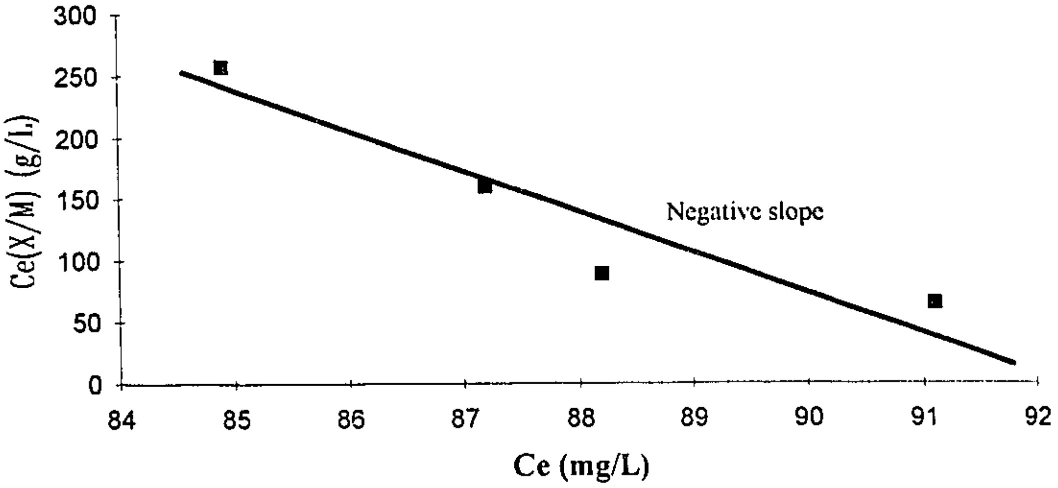

Figure 4.7b: Langmuir Isotherm for Calcium

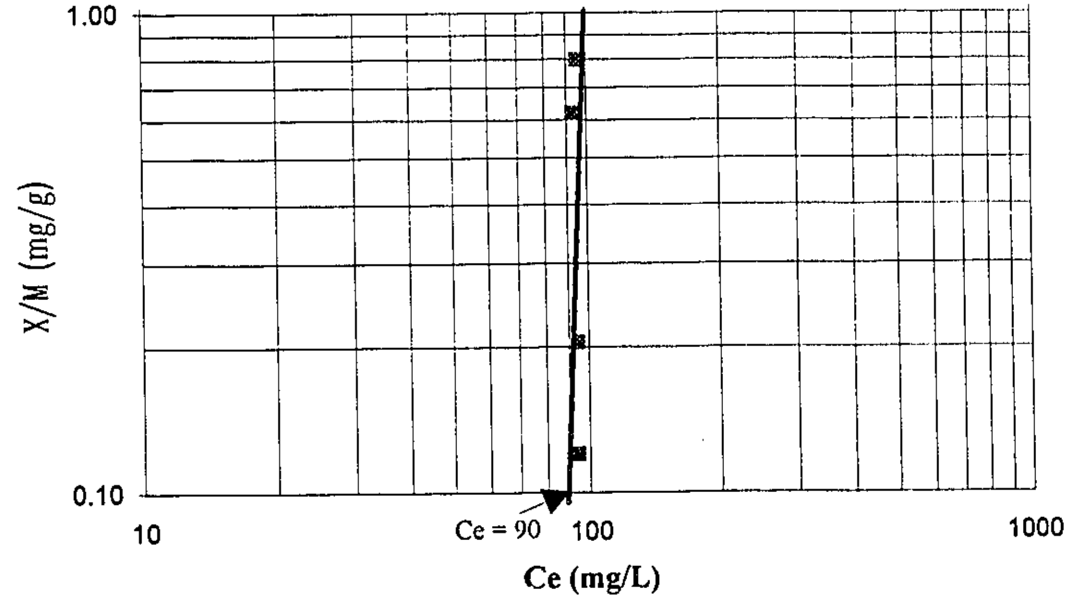

Figure 4.8a: Freundlich Isotherm for Sodium

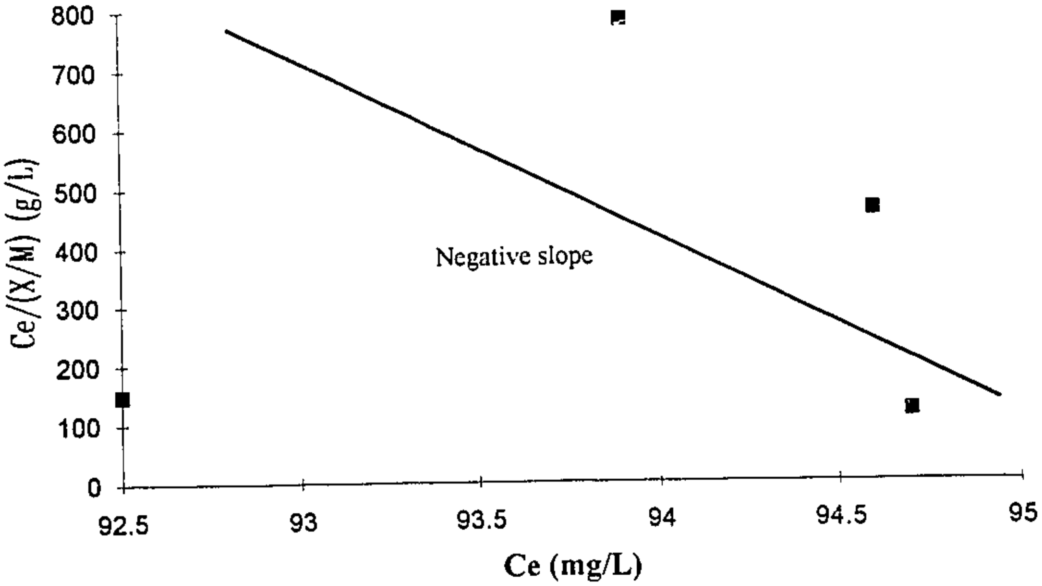

Figure 4.8b: Langmuir Isotherm for Sodium

The analysis of the previous adsorption isotherms indicate that the marshland soil has very little affinity to adsorb calcium or sodium. The slopes of the Freundlich isotherms are nearly vertical, conferring extremely low K_F values, while the Langmuir isotherms are inappropriate based on the negative coefficients of the slopes. The Freundlich equations derived from the batch adsorption analysis of calcium and sodium are presented in Table 4.6, with the associated regression equations.

TABLE 4.6
Freundlich and Langmuir Model Parameters for Cations Solution

Parameter	Isotherm	Isotherm Equation	Regression Equation	Correlation Factor
Calcium	Freundlich	(x/m) = 9.5E-41 CeY(20.5)	Log (x/m) = 41.2 + 21.1 Log Ce	0.96
Sodium	Freundlich	Kf tends toward 0	Log (x/m) = 29.3 - 15.1 Log Ce	-0.18

The exceeding low values of the Freundlich coefficients emphasize the weak adsorption potential of these ions to the soil matrix of the Locksley Marshland.

4.3.2.4 Adsorption of Pentachlorophenol

The data collected during the batch adsorption analysis of PCP are presented in Appendix B.

Based on the batch adsorption experiments, it seems that the marshland soil is well suited for the attenuation of PCP. As shown on Figure 4.9, the concentration of PCP decreases swiftly as a function of the mass of organic soil present in solution. A reduction of over 95% in PCP level was achieved with 4 g of marshland soil within 24 hours of contact.

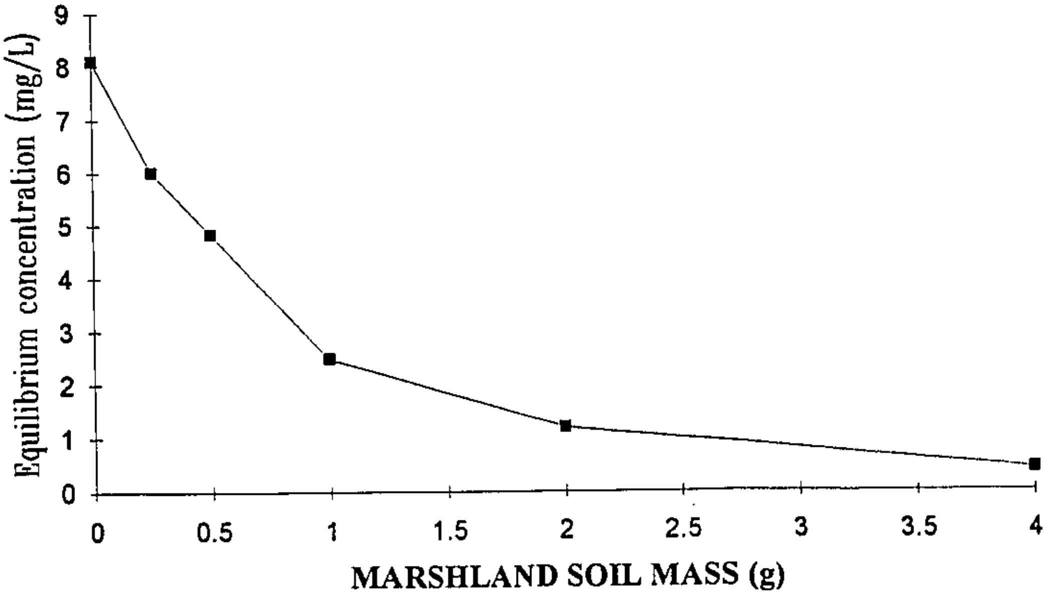

Figure 4.9: Pentachlorophenol Attenuation by Marshland soil – Batch Adsorption Study

The collected data was analyzed for the Freundlich and Langmuir models. The plots of these isotherm models are shown in Figures 4.10 and 4.11.

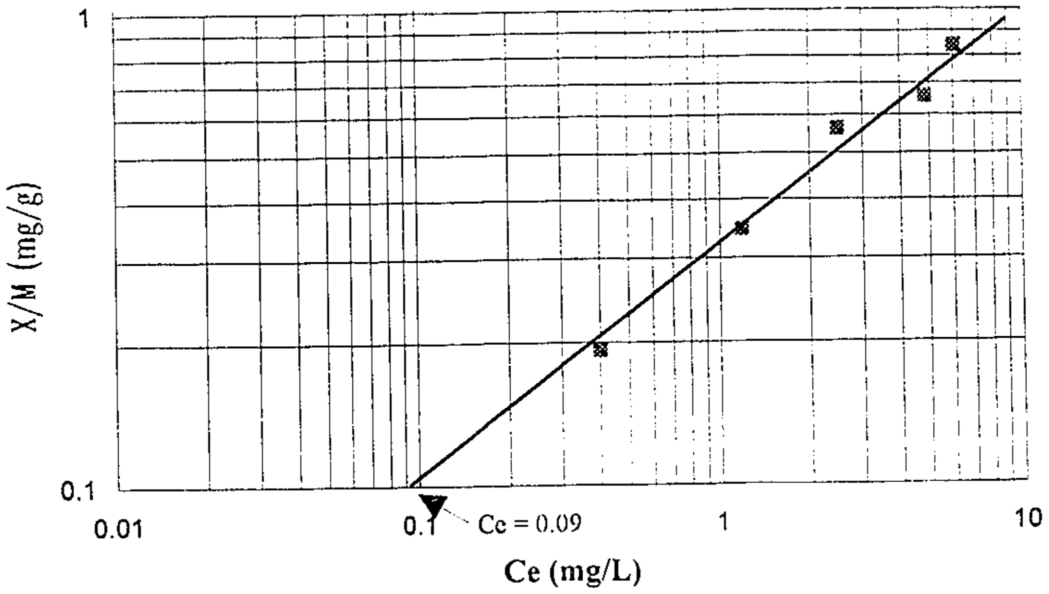

Figure 4.10: Freundlich Isotherm for Pentachlorophenol

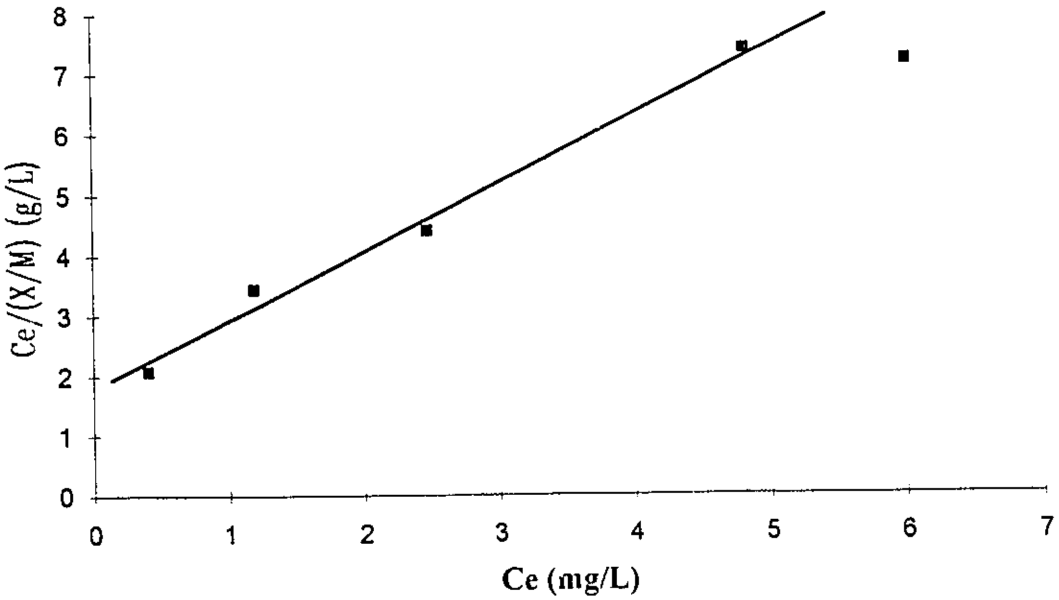

Figure 4.11: Langmuir Isotherm for Pentachlorophenol

Based on the previous graphs it can be seen that both models can be used to describe the adsorption process of PCP. The adsorption isotherm equations derived from the above plots are presented in Table 4.7.

TABLE 4.7
Freundlich and Langmuir Model Parameters for Pentachlorophenol Solution

Parameter	Isotherm	Isotherm Equation	Regression Equation	Correlation Factor
PCP	Freundlich	$(x/m) = 0.333CeY(0.5)$	$Log (x/m) = -0.498 + 0.523 Log Ce$	0.99
	Langmuir	$(x/m) = 0.555Ce/(1+0.626Ce)$	$Ce/(x/m) = 2.056 + 0.9506 Ce$	0.975

Although the marshland soil investigated had a high adsorption capacity towards PCP, the process was observed to be partially reversible. Based on the data obtained by the desorption test, as detailed in section 3.3.4.7, between 20 and 90% of the PCP initially adsorbed by the marshland soil was eventually desorbed after a short contact time with distilled water. The results of the desorption analysis for PCP are presented in Figure 4.12.

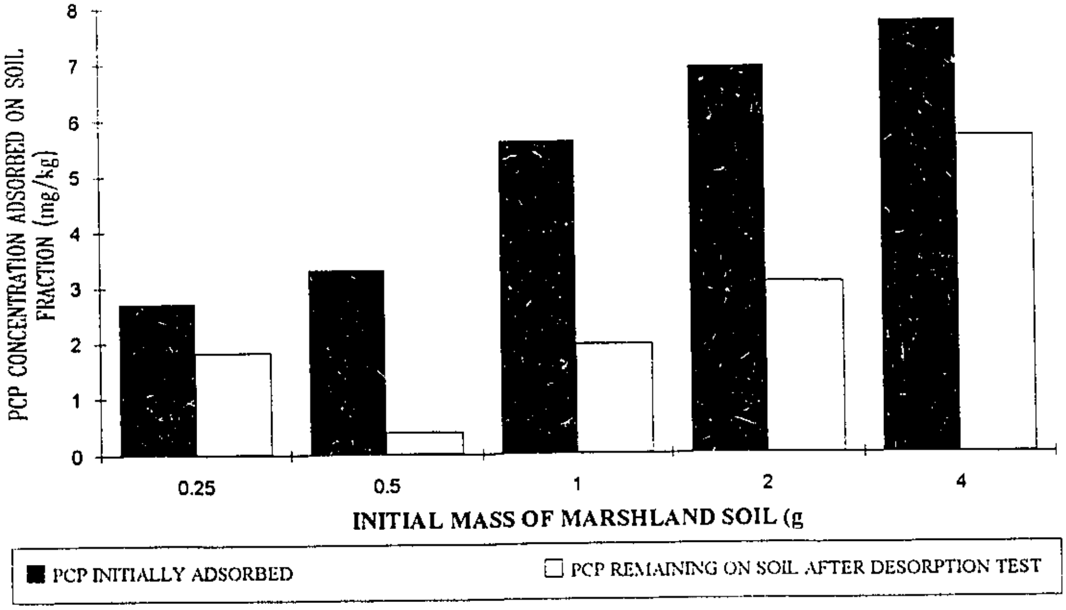

Figure 4.12: **PCP Concentration Adsorbed on the Soil Before and After the Desorption TEST**

4.4 COLUMN STUDY RESULTS

As described in section 3.3.5, a total of fifteen cells were constructed to monitor the migration potential of several contaminants through the Locksley Marshland soil. The results of these column studies are presented in the following subsections.

4.4.1 Heavy Metals

The migration patterns of lead and zinc were analyzed through a series of leaching tests conducted between June and September 1991. Cells No. 1 to 4 were used to permeate the heavy metals stock solution while Cell No 5. was used as a control, permeating only distilled water. Basic data on the sampling and chemical characteristics of the influent and effluent solution are presented in Appendix D.

Results from the leaching tests confirmed that the heavy metals are strongly retained by the soil matrix. Throughout the course of the leaching experiment, which lasted approximately 3 months, no lead or zinc were detected in the columns effluent. All of the heavy metals permeated through the cell were retained by the soil matrix. It is however interesting to observe that the concentration of calcium and magnesium tend to increase with time even though no such compounds were present in the influent solution, as further detailed in section 4.5.3.2. A detail graphical illustration of the breakthrough curves related to Pb and Zn leaching experiments is provided in Appendix C. A typical breakthrough curve registered for Cell No. 4 is presented in Figure 4.13.

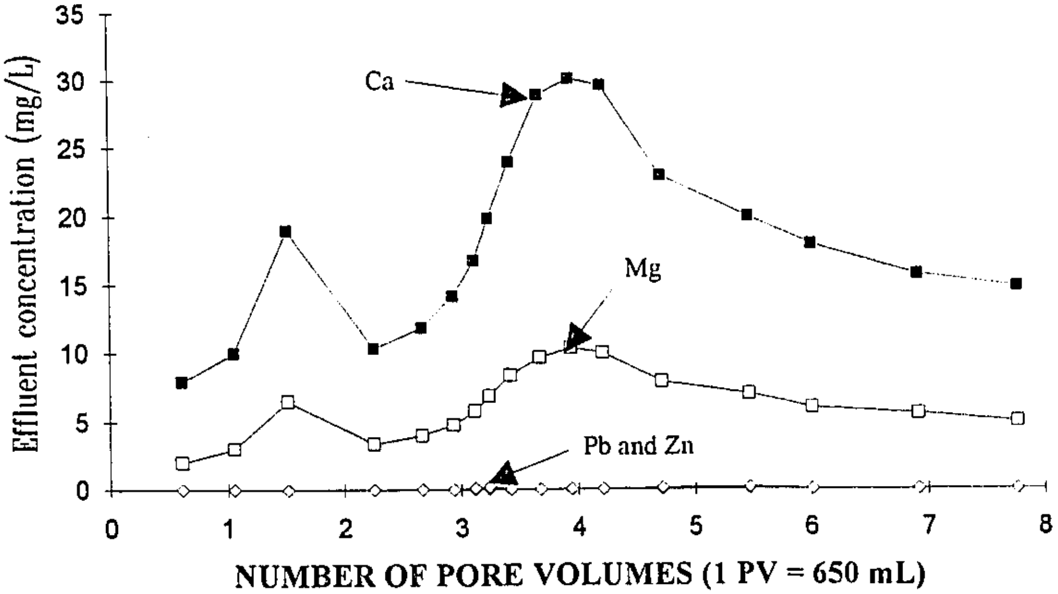

Figure 4.13: **Breakthrough Curves Associated with Cell No 4**

Following the procedure described in section 3.3.5.5 the pore fluid of Cell No. 2 and 4 were extracted in order to evaluate the concentration variation of lead and zinc with depth within the soil column. Results obtained from the chemical analysis of the extracted pore fluid are presented in Figures 4.14 and 4.15.

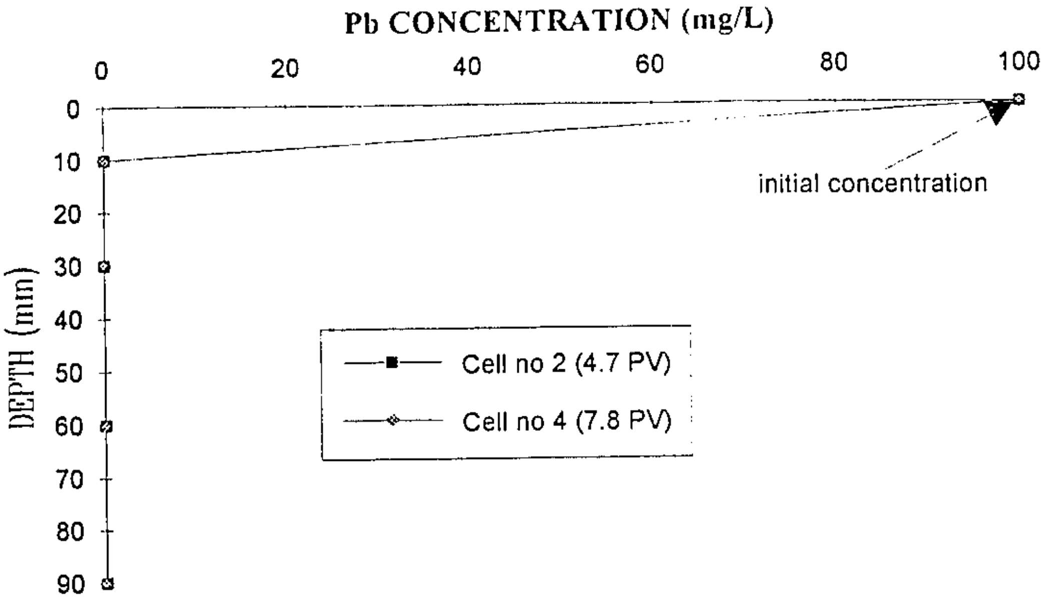

Figure 4.14: Lead Migration Profiles Within The Pore Fluid

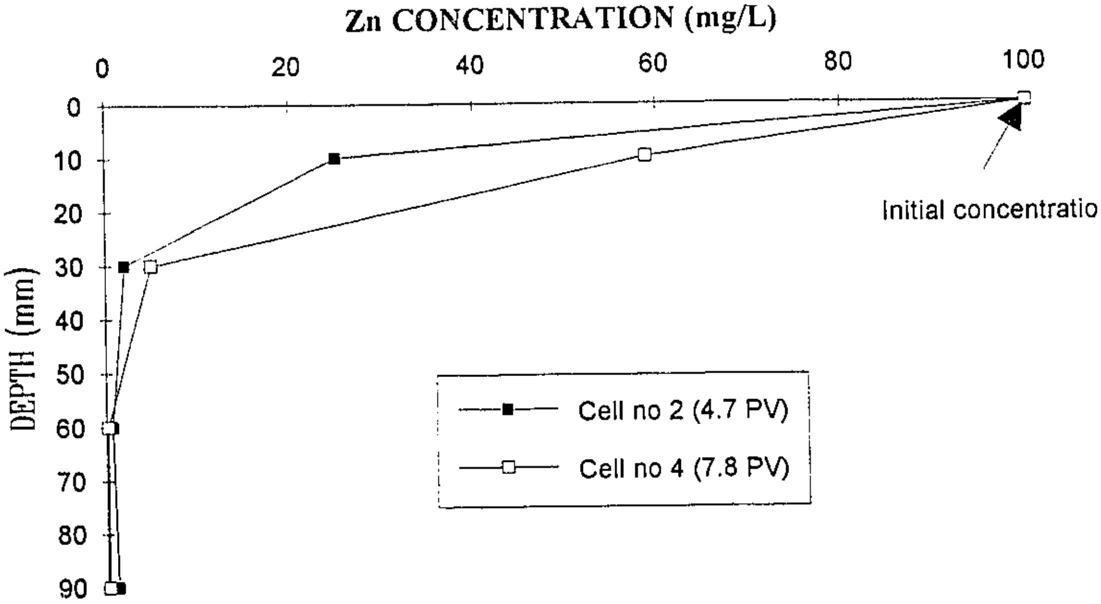

Figure 4.15: Zinc Migration Profiles Within The Pore Fluid

The results showed that significant amounts of the heavy metals were retained in the top portions of the soil columns. The lead ions are effectively retained on the marshland soil, since only trace amounts (<0.1 mg/L) are detected in the pore fluid. However, zinc seems to be somewhat more mobile since low concentration of the ion was detected down to a depth of 30 mm in the top layers of the soil columns.

In order to establish the fate of the heavy metals within the leaching cell, a digestion analysis of the soil matrix, as described in section 3.3.5.6, was undertaken. It is expected that the analysis will demonstrate a high concentration of lead and zinc in the upper layer of the soil matrix. This is anticipated based on the low concentration of heavy metals detected in the column effluent and the pore fluid. The results obtained from the digestion analysis of Cell No. 2 and 4 are presented in Figures 4.16 and 4.17, respectively.

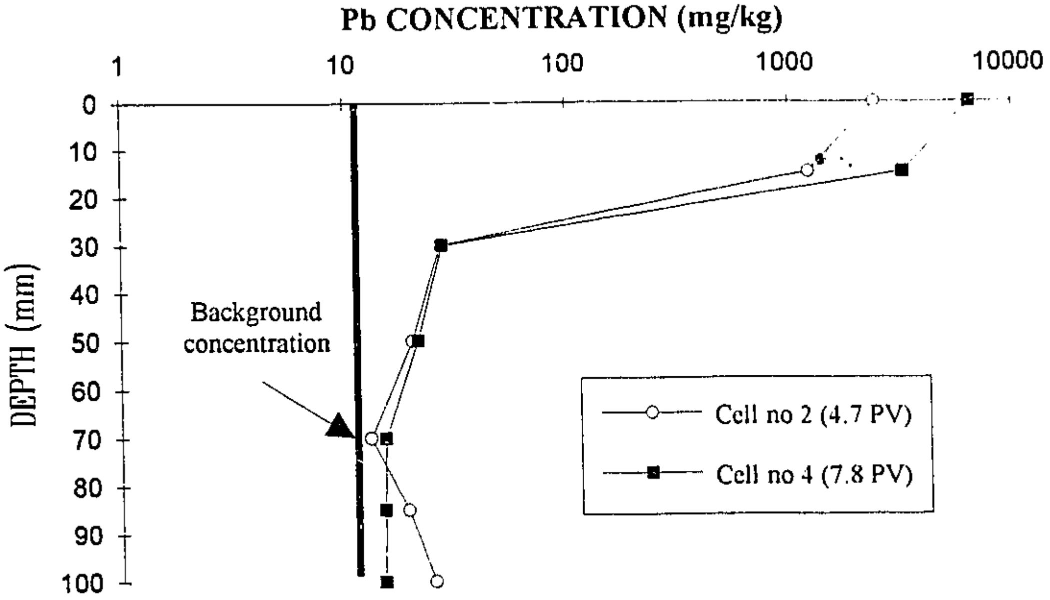

Figure 4.16: Lead Migration Profiles Within The Soil Matrix

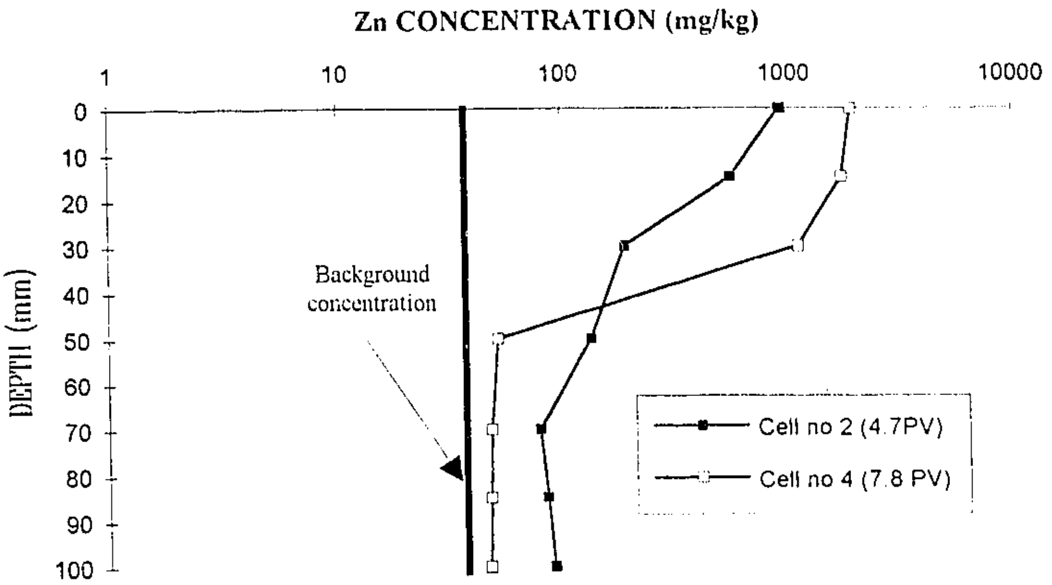

Figure 4.17: Zinc Migration Profiles Within The Soil Matrix

The data obtained from the digestion analysis confirmed that both lead and zinc are being preferentially adsorbed by the top layer of the soil column. Exceedingly high concentration of lead and zinc reaching 6560 and 1960 mg/kg respectively were detected in the top 20 mm of Cell No. 4. The concentration decreased to background level at a depth of 50 mm for lead and at a depth of 70 mm for zinc.

Mass balance analyses were carried out to establish the validity of the methodology used. By comparing the total influx of contaminant entering the cells with the mass of contaminants detected in the effluent, pore fluids and soil matrix it was possible to estimate the total recovery for each compound. A total recovery of 75% and 95% was achieved for lead in Cell no 2 and 4 respectively, while a total recovery of 45% and 53% was achieved for zinc for these same cells. Mass balance analyses calculations are presented in Appendix E.

4.4.2 Major Cations and Anions

The mobility of some major cations and anions was investigated through a series of leaching test. A synthetic solution of calcium, sodium and chloride was leached through Cell No. 6 to 9 to establish the migration profile of these elements in marshland soil. Cell No. 10 was used as a control, passing only distilled water. The raw data collected from the leaching test are presented in Appendix D.

Results from the leaching test indicate that the calcium and sodium cations as well as the chloride anion required little time to migrate through the cells. Figure 4.18 shows a plot of the breakthrough curve obtained for Cell No. 6. This plot is typical of the migration profiles observed during the cations and anion leaching program. Illustration of the breakthrough curves of the other cells are presented in Appendix D.

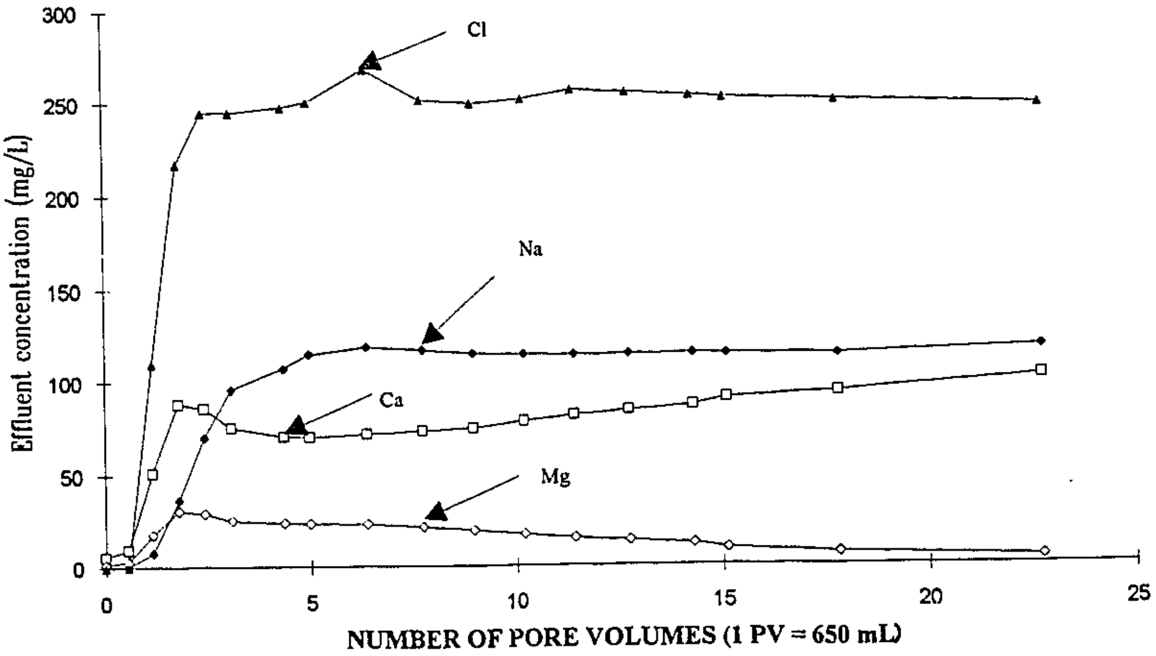

Figure 4.18: Breakthrough Curves Associated with Cell No 6

As expected, the breakthrough of chloride is observed after approximately 1 pore volume, indicating that the attenuation of the chloride ions was negligible across the length of the soil column. This low attenuation was expected because Cl is considered to be a mobile and non-interacting anion, i.e. a conservative contaminant. Therefore, the main purpose of investigating the behaviour of the chloride ions in this study was to evaluate the effect of dispersivity operating in the soil column. As detailed in section 2.3.1, dispersivity can influence the migration velocity of a contaminant front through porous media. The dispersivity associated with the migration of the chloride ion is investigated in detail in section 4.5.3.3.

As for the cations studied, both calcium and sodium appeared in the effluent rather rapidly. The breakthrough of calcium was observed at approximately 1.4 pore volumes, while for sodium the breakthrough appeared at approximately 2.4 pore volumes.

Upon examination of Figure 4.18 it is interesting to note that the concentration of Na in the effluent is slightly above the stock solution concentration. Since the relative concentration ($C_{effluent}/C_{influent}$) is greater than 1.0, one has to conclude that some sodium must have been eluted from the soil matrix. The most plausible explanation of these results rests with the cation exchange process(es), i.e. the replacement of the sodium ions in the exchangeable sites by preferential cations such as calcium.

The pore fluid extracted from the different soil layers of each columns indicate that the concentration of calcium and sodium are relatively constant throughout the soil column, varying within a 20% range. Plots of the cations concentration as a function of cell depth are presented in Figures 4.19 and 4.20.

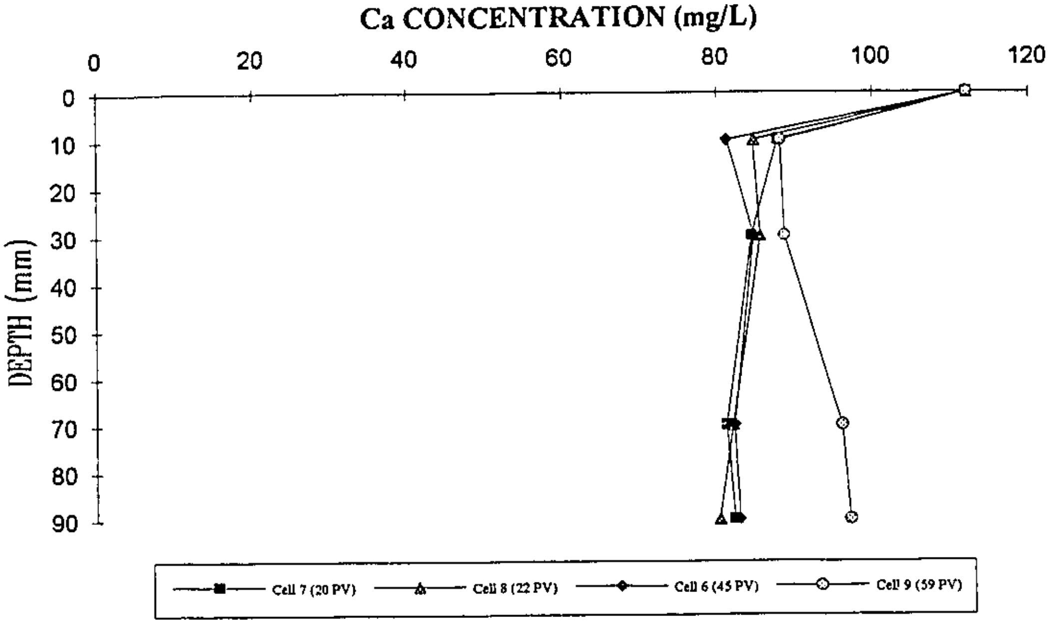

Figure 4.19: Calcium Migration Profiles Within The Pore Fluid

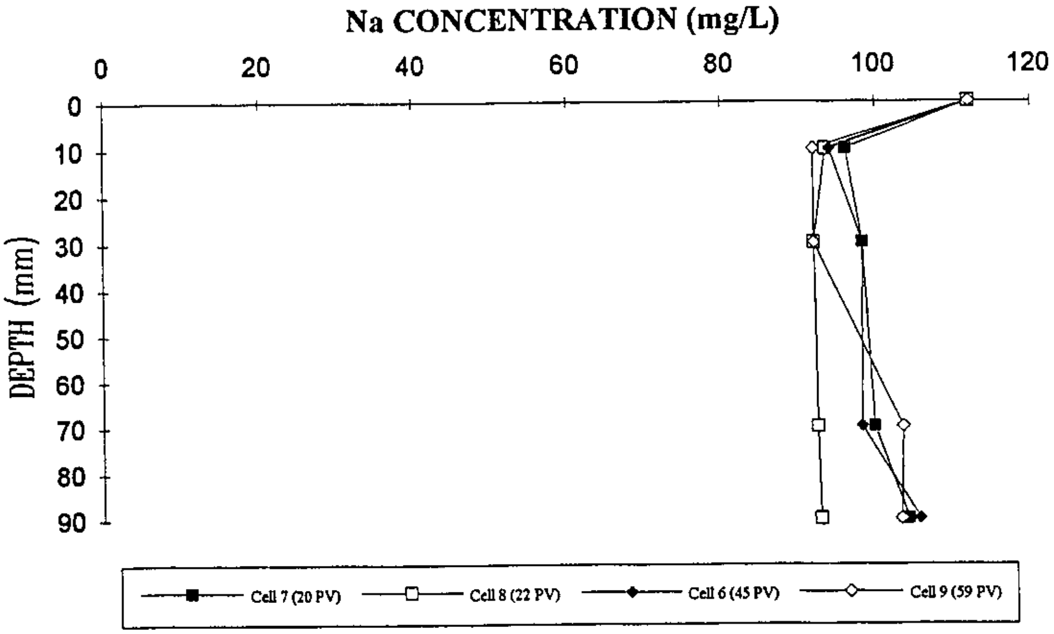

Figure 4.20: Sodium Migration Profiles Within The Pore Fluid

The same cations concentration distribution observed from pore fluid analysis was also observed from soil digestion analysis. An uniform distribution of both calcium and sodium are observed along the cell depth as shown on Figures 4.21 and 4.22.

Interestingly when comparing the digestion results of the cations impacted soil to natural soil, one can see that the calcium level of the impacted cells increased by approximately 10%, while the concentration of sodium decreased by almost 20%. The decrease in sodium levels within the soil matrix indicate once again that some desorption of sodium occurs during the leaching process.

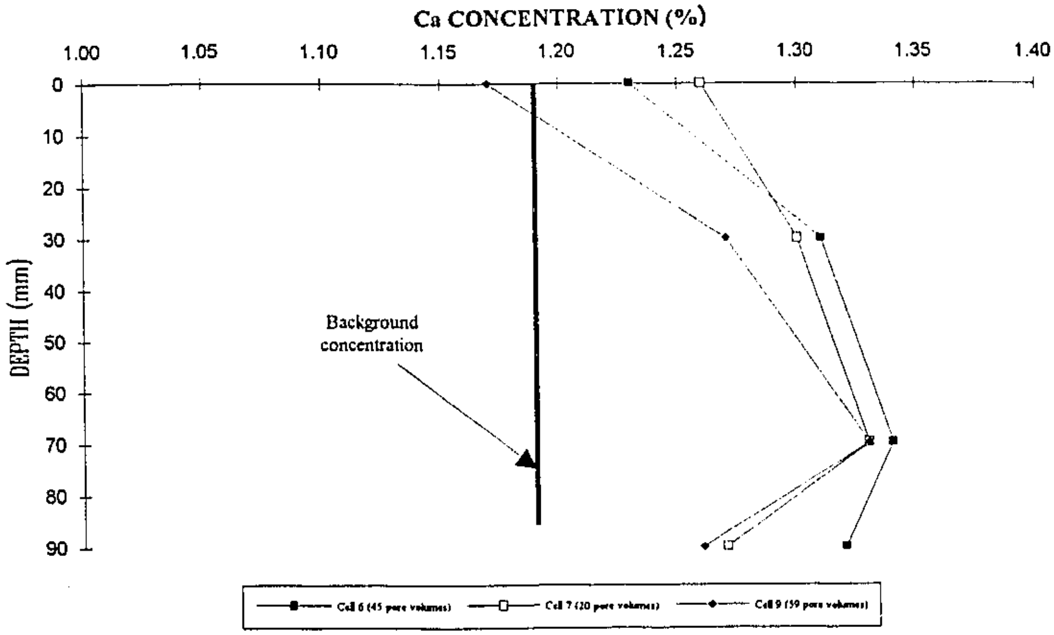

Figure 4.21: Calcium Migration Profiles Within The Soil Matrix

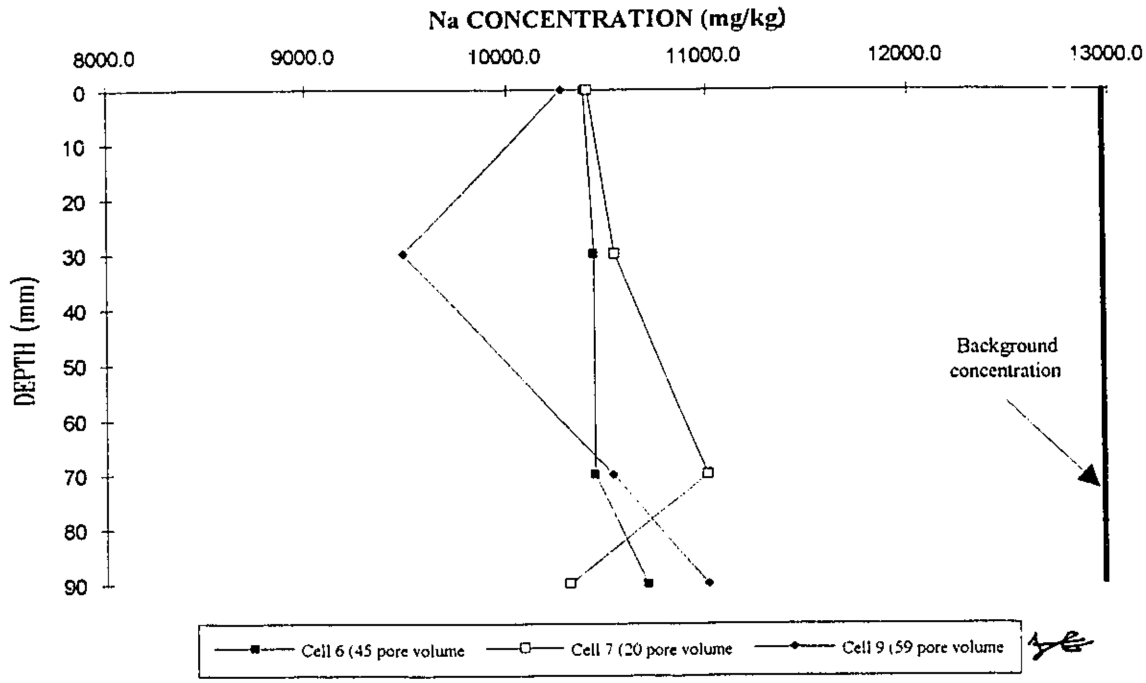

Figure 4.22: Sodium Migration Profiles Within The Soil Matrix

4.4.3 Pentachlorophenol

Leachate solution generated from the dissolution of the buried solid waste at municipal landfills is usually characterized by the presence of a high concentration of organic compounds. In order to investigate the migration potential of an organic compound through marshland soil, a series of leaching tests were conducted using a synthetic organic solution containing pentachlorophenol (PCP).

Following the column leaching procedure developed in section 3.5, a series of 5 cells were prepared. Cell No. 11 to 14 monitored the PCP migration while Cell No. 15 was used as a control. The raw data gathered during the 4 months period of the leaching experiments are presented in Appendix D.

Results from the leaching tests indicate that the PCP solution is being strongly adsorbed by the soil matrix. No detectable levels of PCP were measured in the column effluent, even in Cell No. 11 which leached over 24 litres of the PCP stock solution over a period of 4 months. All of the PCP initially present in solution was adsorbed by the marshland soil. The extreme reactivity of PCP is highlighted in Figure 4.23, where the PCP breakthrough curve of Cell No. 11 is plotted against a non reactive contaminant (chloride) which was previously analyzed. The breakthrough curves of the remaining cells are presented in Appendix D.

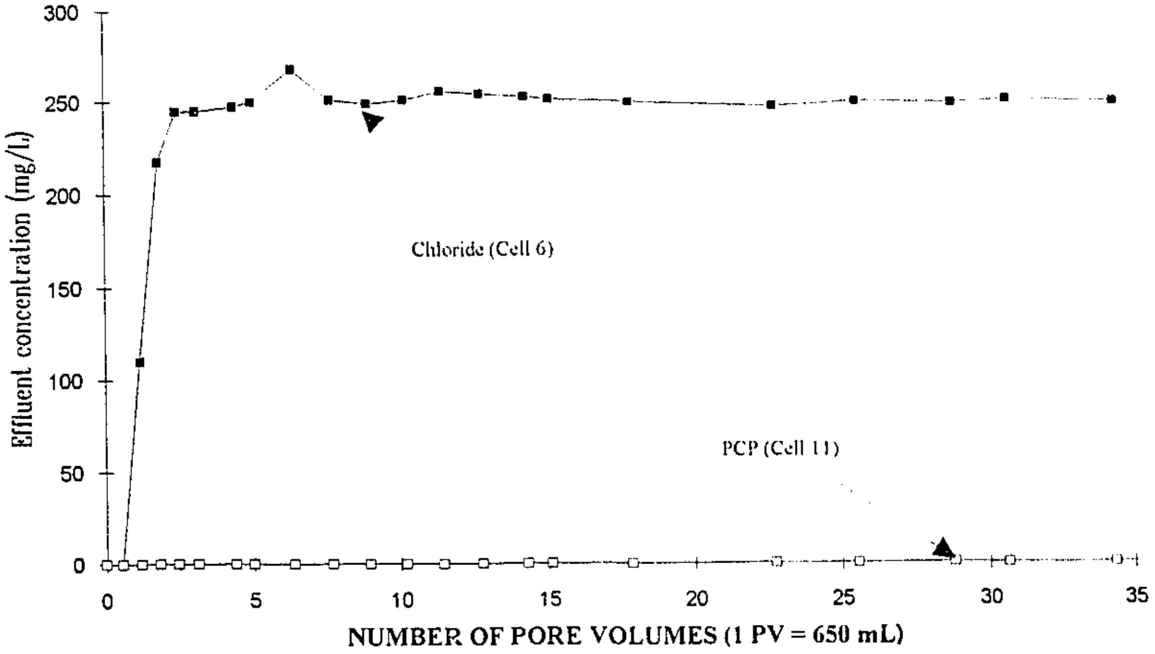

Figure 4.23: Breakthrough Curves Associated with Cell No 11

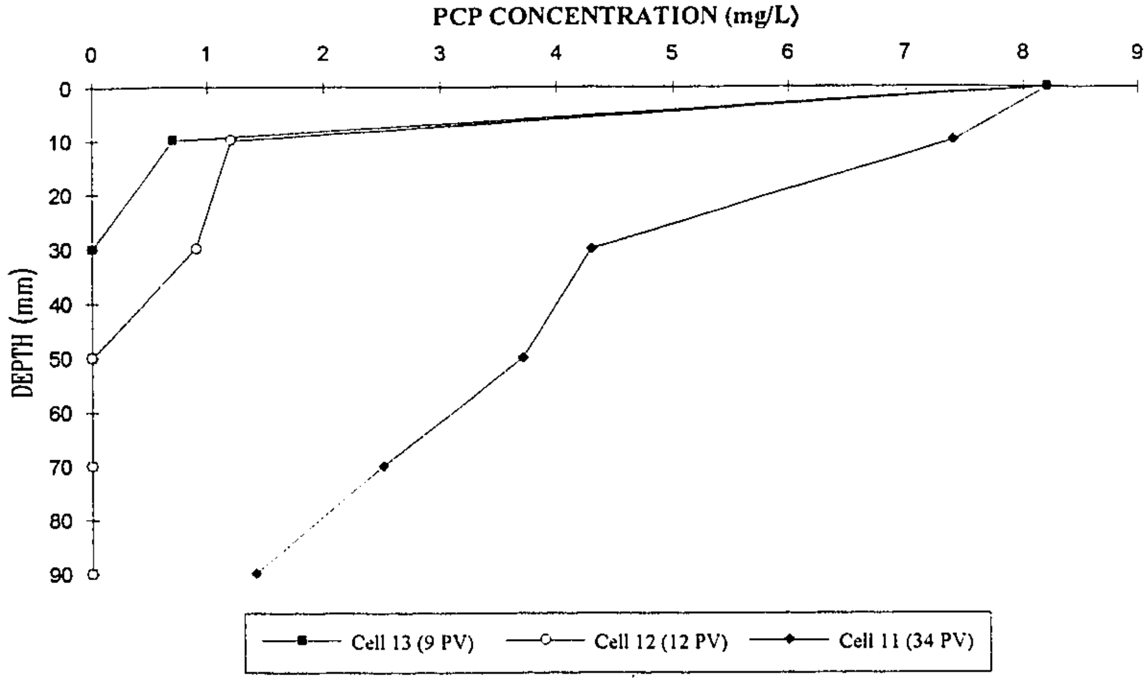

Figure 4.24: **Pentachlorophenol Migration Profiles Within The Pore Fluid**

The pore fluids of Cell No. 11 to 13 were then extracted and analyzed for PCP concentration. A plot of the pore fluid concentration as a function of cell depth is presented in Figure 4.24.

The results of the pore fluid analysis indicate that the PCP is retained in the top portion of the organic soil column. Only when available adsorption sites are saturated, the PCP front can migrate downward. In Cell No. 11, which was operated for 4 months, the distribution of PCP follows an exponential function. Based on the distribution of the PCP within Cell No.11, one can conclude that the PCP front had almost reached the effluent level when the leaching test was terminated.

The data obtained from the digestion of Cell no 11, presented in Figure 4.25, confirmed that PCP is being preferentially adsorbed by the top layers of the soil column. A mass balance analysis carried out on Cell no 11 indicate a recovery of about 35% for PCP. This low recovery could be attributable to other processes such as biodegradation, or again due to sorption on the walls of the column itself which was made out of Plexiglas.

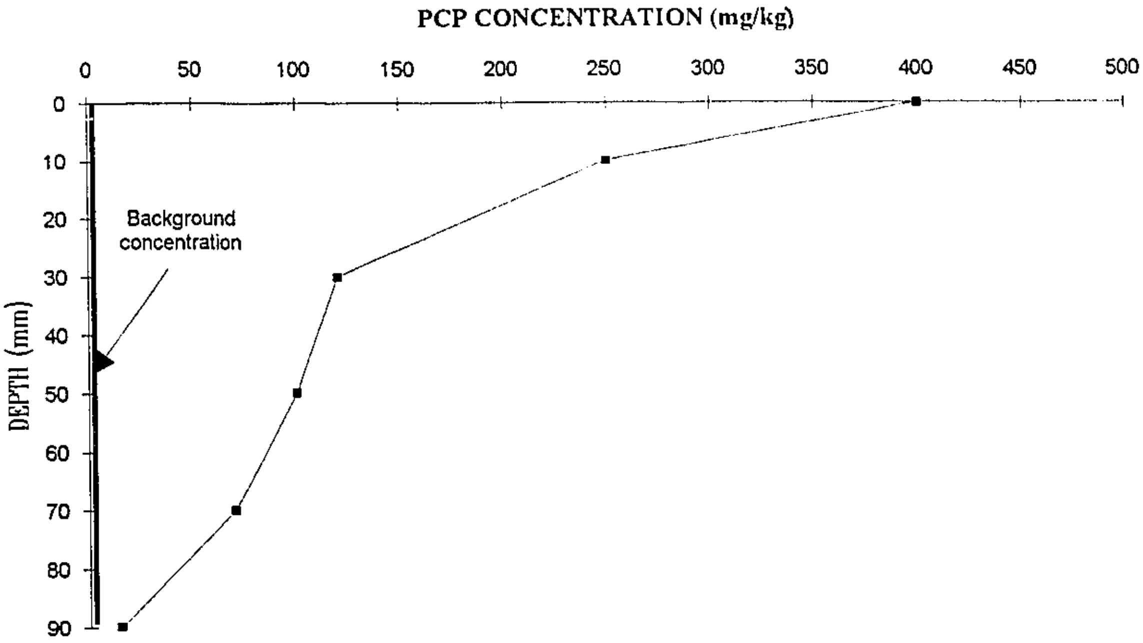

Figure 4.25: PCP Migration Profile Within The Soil Matrix (Cell no 11)

4.5 ANALYSIS AND DISCUSSION

4.5.1 General

As a pollutant is transported in groundwater it can be removed or altered by several chemical, physical and biochemical reactions. Certain organic substances tend to be rather non reactive while other might be strongly attracted to the solid phase of the aquifer or again might easily biodegrade to lesser or non toxic compounds. The fate and mobility of contaminants in groundwater is of primordial concern, and proper knowledge of these mechanisms is essential to accurately evaluate the hazard potential of each contaminant and to initiate remedial processes if need be. A detailed review of the dominant attenuation mechanisms encountered in groundwater environment is presented in Section 2.3.2.

The objective of this section is to evaluate the mobility and possible environmental impact of leachate entering the Locksley Marshland system. A discussion on the various attenuation characteristics of the marshland soil is presented based on the results obtained from the batch and column tests previously presented.

In the following sections, the behaviour of each categories of contaminant investigated (heavy metals, major cations and organic compounds) is analyzed and discussed with emphasis on the following points:

(1) The potential hazardous effect of the specific contaminant species to the environment and man.

(2) A description of the probable attenuation mechanisms controlling the contaminant migration.

(3) An evaluation of the retardation factor characteristic of the contaminants studied within the marshland system.

4.5.2 Heavy Metals

4.5.2.1 Hazard Potential

Heavy metals are often found in trace amount in groundwater and can be toxic to plants, animals and men. Even low concentration of heavy metals can be detrimental to health because of their tendency to accumulate in the tissues of both plants and animal. Since heavy metals are easily stored in the tissues of organisms, it can gradually move up in the food chain, eventually infecting humans, causing severe health effects and sometime death as was the case in the well documented heavy metals poisoning of fishermen at Minamata, Japan.

4.5.2.2 Attenuation mechanisms

The migration potential of lead and zinc through the marshland system was investigated through a series of laboratory studies. Results obtained clearly indicate that both metals are being strongly retained by the organic soil matrix. Even though there is voluminous literature on the subject of metal adsorption by organic soil, the nature of bindings of the cations to the marshland soil has been the subject of much debate. Marshland soil, such as the one sampled at the Alice and Fraser landfill site is a rich source of humic substance. This organic matter contains carboxyl, amino, quinone, hydroxyl and other groups which are involved in the chelation and formation of complexes (Dissanayake and Weerasooriya, 1981). These are the most likely and predominant reaction by which organic matter traps metal ions. Besides being excellent chelates, the humic compounds have been known to retain large quantities of metals by cation exchange and surface adsorption. The total sorption capacity of the compounds depend upon the types of metals and environmental conditions particular to a given site.

It has also been demonstrated that heavy metals can be trapped by the soil matrix due to precipitation and/or filtration mechanisms. The production of heavy metals at a landfill is generally caused by the leaching of metal ions in an acid leachate solution. As the leachate migrates out of the landfill area, mixing with groundwater and interacting with varying soil matrix, the pH of the leachate will invariably change. An increase of the leachate pH and the development of oxidizing conditions could result in the precipitation and/or complexation of the heavy metals with the soil constituent.

4.5.2.3 Potential for Heavy Metals Migration

As previously discussed, the mobility of a given contaminant through saturated soil will be determined by several processes including adsorption, biodegradation, ion exchange, filtration and precipitation. Of those processes adsorption to the soil matrix by chelation, cation exchange and precipitation, are generally the most common mechanisms of heavy metals removal in groundwater.

The data obtained on heavy metals adsorption, through batch and column experiments indicates that the adsorption capacity of lead and zinc is very high. The information gathered by the batch test studies demonstrated that the rate of adsorption generally followed the Freundlich and Langmuir isotherms form and resulted in a Freundlich adsorption coefficient (K_F) of 4.65 and 0.75 for lead and zinc, respectively.

To adequately evaluate the effect of the adsorption process on the mobility of lead and zinc in groundwater, a contaminant transport model has to be developed. As detailed in section 2.3.3, the retardation factor is then given by the following equation:

$$R_F = \frac{V_{gw}}{Vc} = 1 + \frac{\rho_b K_d}{\theta} \qquad (2.3)$$

In order to properly evaluate the retardation factor of lead and zinc through the soil investigated, it is first necessary to establish the linear distribution coefficient (K_d) of the system. But as previously stated, the adsorption process, as determined through the batch test, is better represented by a Freundlich isotherm than by a linear relation. Nonetheless, a linearization of the adsorption coefficients based on the Freundlich parameters previously determined in Table 4.4, was calculated and is presented in the following figures. This linearization was achieved by initially imputing the observed concentrations remaining in solution (Ce) in the regression equation in order to evaluate the resulting mass of solute sorbed per bulk unit dry mass of soil (X/M). Once these points have been plotted on a linear graph, the best fit line is passed. This linearization will permit an estimation of the distribution coefficient of the heavy metals in the soil for the studied range of concentration. Figures 4.26 and 4.27 shows the linearization of the Freundlich adsorption isotherms for lead and zinc respectively.

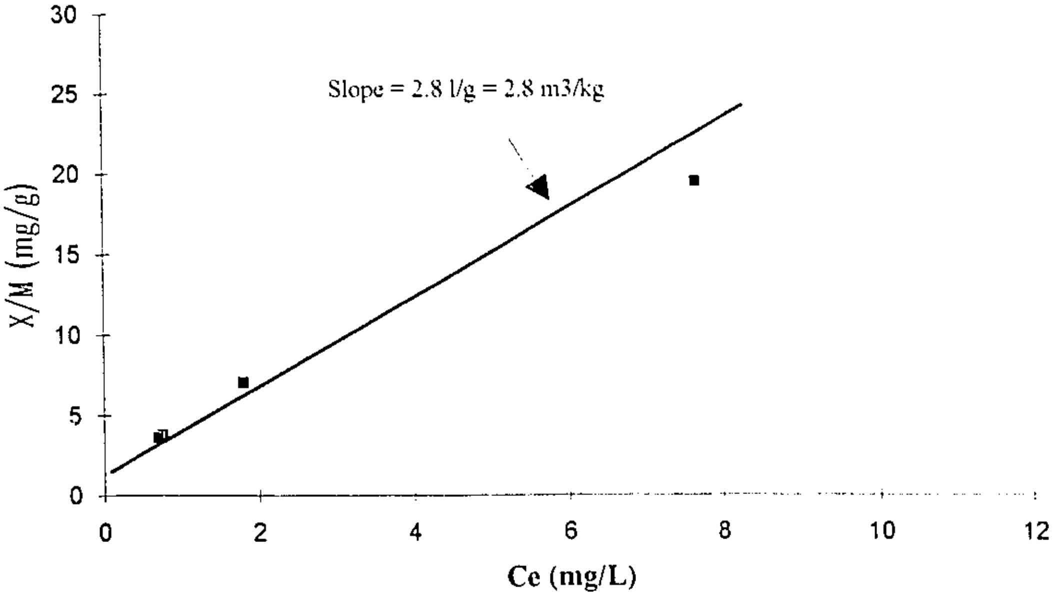

Figure 4.26: Linearization of the Adsorption Coefficient Obtained by the Freundlich Adsorption Isotherms for Lead

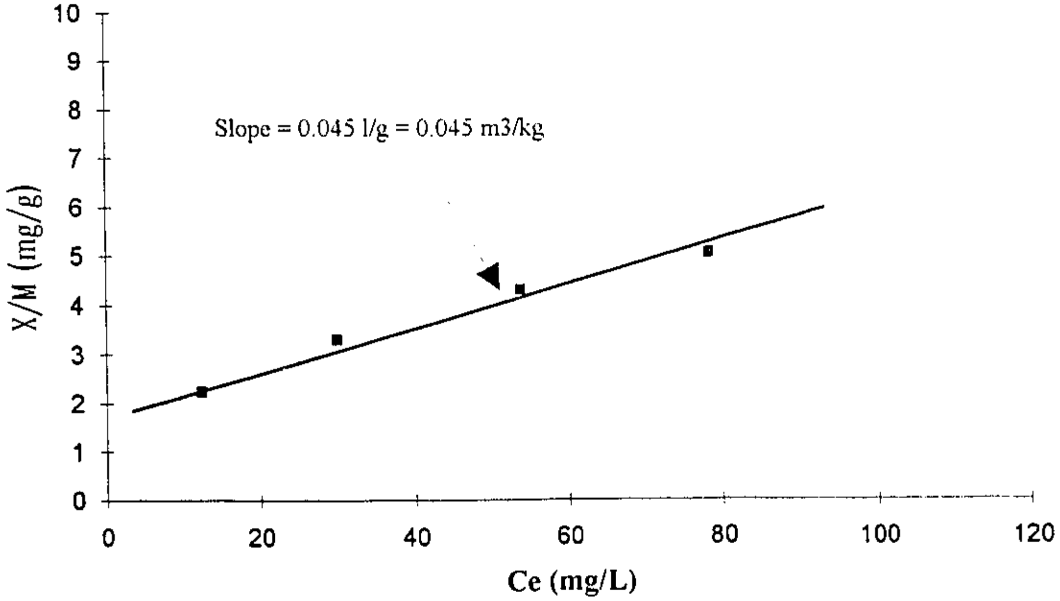

Figure 4.27: Linearization of the Adsorption Coefficient Obtained by the Freundlich Adsorption Isotherms for Zinc

Based on the previous figures, a distribution coefficient (K_d) of approximately 2.8 and 0.045 m³/kg can be anticipated for lead and zinc respectively. Knowing the porosity and the bulk density of the soil (Table 4.1) a crude estimate of the retardation factor can be calculated as follows:

Lead: $$R_F = 1 + \left(\frac{450 \text{ kg/m}^3 \times 2.8 \text{ m}^3\text{/kg}}{0.75} \right) = 1681$$

Zinc: $$R_F = 1 + \left(\frac{450 \text{ kg/m}^3 \times 0.045 \text{ m}^3\text{/kg}}{0.75} \right) = 28$$

It is therefore anticipated, based solely on the batch adsorption experiments, that a contamination plume of lead and zinc would be retarded by a respective factor of approximately 1681 and 28 compared to the average groundwater velocity. This would suggest that the contaminant plume would travel several orders of magnitude slower than the groundwater.

It is also possible to estimate the retardation factor of both lead and zinc by investigating their migration pattern during the leaching cells tests described in section 4.4. Since no heavy metals ions were detected in the column effluent, the retardation factor had to be evaluated based on the migration profiles within the pore fluids. As described in section 4.4.1, the concentration at different depth and times within each cell were tabulated. Knowing the contaminant distribution through space and time it was possible using a numerical model to back-calculate the retardation coefficients characteristics of each contaminant species. By adapting the Advection-Dispersion Equation (ADE) with sorption (referred in section 2.3.4) to a spreadsheet layout it was feasible to numerically back calculate, by trial and error, the contaminant distribution profiles obtained in the laboratory column experiments. The numerical model used for simulating the migration profiles of contaminants through the soil columns is presented in Appendix F.

The analysis of the contaminant distribution profiles enabled the evaluation of a retardation factor of approximately 2000 for lead and ranging from 83 to 105 for zinc. These results are of the same order of magnitude as the ones obtained from the batch adsorption studies.

Results from both the batch adsorption and the laboratory column analysis of the migration profile of heavy metals through the Locksley Marshland soil permitted the following estimate of the retardation factor for lead and zinc:

Lead Retardation: 1681 to 2000
Zinc Retardation: 28 to 105

The results of this investigation suggest that significant retardation of lead and zinc contamination should be foreseen, assuming a steady input of contaminated water. Desorption of heavy metals from marshland soil is however to be expected in the long-term. Research by McLelland and Rock (1988) as well as Cameron (1978) indicate that up to 50% of the heavy metals initially adsorbed by organic soil can be desorbed following contact with deionized water.

4.5.3 Major Cations and Anions

4.5.3.1 Hazard Potential

In this study, the major cations group of contaminant was represented by calcium and sodium, while chloride was chosen as a representative element of anions. These elements are generally present in relatively high concentration in groundwater and are major contributors to the overall salinity of water. The health-related problem associated with sodium and calcium are generally less serious as those caused by other contaminant group such as heavy metals (Domenico and Schwartz, 1990). However at very high concentration (>1000 mg/l) the water can become brackish and unfit for human consumption. High concentration of sodium has also been linked to cell or blood transformation with serious consequence varying from simple hypertension to heart attacks. Chloride is one of the characteristic elements found in landfill leachate. No ill effect is attributed to chloride concentration below 250 mg/l.

4.5.3.2 Attenuation mechanisms

The migration potential of calcium, sodium and chloride through marshland soil was investigated by a series of batch and column experiments. Results of these studies indicate that there is little attenuation of these elements by the Locksley Marshland soil. Attenuation of the major cations species is generally governed by the same attenuation phenomena described for the heavy metals species in the previous section. Chloride ions, on the other hand, is not affected by any adsorption processes, since it is a non-reactive contaminant.

Under certain conditions, the ions attracted to a solid surface may be exchanged for other ions in aqueous solution. The ion-exchange process can be conceptualized as the preferential adsorption of selective ions with the concomitant loss of other ions (Fetter, 1988). In marshland soil, the ion exchange sites are found primarily on the organic material. Theoretically divalent ions are more strongly bonded and tend to replace monovalent ions that might initially be attached to the soil surface. Several studies confirmed this phenomena and a general ordering of the preferential adsorption ions has been proposed (Fetter, 1988):

Pb > Zn > Ca > Mg > K > Na

The same selectivity sequence was noticed in the batch adsorption analysis of the four tested metal ions. The relative attenuation capacity of the Locksley Marshland soil with respect to lead, zinc, calcium and sodium ions is emphasized in Figure 4.28, which presents the contaminant concentration variation as a function of the mass of organic soil added to the solution.

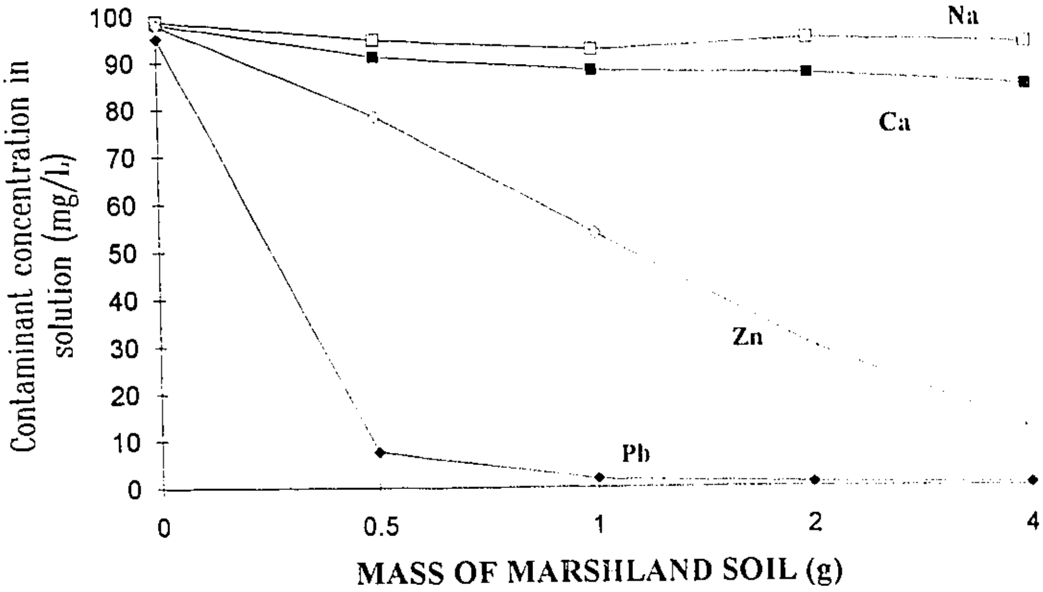

Figure 4.28: Comparison of the Attenuation of Pb, Zn, Ca and Na Based on the Batch Adsorption Analyses

Researchers such as Shotyk (1988) have noted that sodium can be leached from organic soil profiles and is probably the metallic element most rapidly removed from marshland by simple elution. It is important to note that analysis of the Locksley Marshland soil composition indicate a naturally high level of both calcium and sodium. Furthermore, during the leaching cell experiments with distilled water, both calcium and sodium were being systematically leached from the soil column. This tend to indicate that the marshland soil is essentially saturated with respect to calcium and sodium, severely limiting its capacity to accept additional cations.

4.5.3.3 Potential for Major Cations and Anions Migration

Laboratory analysis on the mobility of calcium, sodium and chloride indicate that the Locksley Marshland soil has little affinity to adsorb these elements. In fact the Freundlich and Langmuir isotherm parameters are either too low or non-representative to adequately evaluate the retardation factors of the targeted contaminants. However analysis of the leaching column data permit an approximation of the relative mobility of the targeted elements.

The breakthrough curve of chloride was observed after approximately 1 pore volume of solution displacement. This was expected, since chloride is considered to be a non-reactive contaminant, with a retardation factor of 1. Any variation of the breakthrough curve of chloride is thus attributable solely to the effects of dispersivity, as reported in section 2.3. It is possible to quantify the dispersivity coefficient of the chloride ions by numerical analysis of the Advection Dispersion Equation as mentioned in the previous section. By fixing the retardation factor to $R_F=1$ in the ADE, the dispersion coefficient D_L could thus be calculated by trial and error. When the numerically projected chloride profile matched the one obtained in the laboratory, the dispersivity coefficient was deemed to be acceptable. Following this procedure a dispersion coefficient varying from $0.7\text{x}10^{-4}$ to $1.5\text{x}10^{-4}$ m^2/day was calculated. A detailed explanation of the numerical technique is presented in Appendix F.

The retardation factor of calcium and sodium was evaluated based on the data obtained by the leaching experiments. Following the same procedure described for lead and zinc in section 4.5.2.3, the retardation factor for the major cations was estimated using the ADE formulated in a spreadsheet form. A description of the numerical scheme used to simulate the migration profiles of the cations is presented in Appendix F. The following retardation factor were thus calculated:

Calcium retardation:	1.0 to 1.25
Sodium retardation:	1.9 to 2.4
Chloride retardation:	1.0

Therefore, it is anticipated that a contamination plume of calcium and sodium would be retarded by a respective factor of approximately 1.2 and 2.2 compared to the average groundwater velocity. This would suggest that the cation contaminants plume would travel slightly slower than the groundwater, while chloride would in effect be transported at the same groundwater velocity.

4.5.4 Organic Compounds

4.5.4.1 Hazard Potential

Of the contaminants of concerns, organic compounds are near the top of the list of priority pollutants. Thousands of organic compounds have been synthesized in the past century and every year that list becomes longer. These chemicals are used in a multitude of processes including cooling agent, petroleum product, pesticides, plastics, industrial fluids, pharmaceutical processes and others. Thus it is without any surprise that some of those compounds have found their way in the groundwater, producing health hazard. Organic contamination may cause cancer in humans and animals and a host of other problems, including liver damage, impairment of cardiovascular function, depression of the nervous system, brain disorders and various kinds of lesion (Domenico and Schwartz, 1990).

In this study, pentachlorophenol was chosen as one representative of organic contamination. It is a polychlorinated aromatic compound (C_6HCl_5O) that has been used as a biocide for wood preservation since the 1930 (Jackson and Bisson, 1990). Although the use of PCP for treating consumer products was banned in 1984, the treatment of industrial products such as telephone poles and fence posts was not affected by this ban. In the past years, measurable concentrations of PCP have been reported in rainwater, river water, groundwater, air and even human urine from people not known to be associated with the production, processing or utilization of PCP (Ingram et al., 1985). Health hazards associated with contact to PCP can vary from variation in respiration, blood pressure, urinary output to motor weakness, convulsion and even death. The allowable maximum concentration for drinking water is still debatable, but the USEPA has set a value of 200 μg/l as a maximum contaminant level (Fetter, 1988) while the Canadian Council of Ministers of the Environment (CCME, 1991) have establish a maximum level criteria of 60 μg/l.

4.5.4.2 Attenuation mechanisms

The migration potential of PCP within the marshland system was investigated through a series of laboratory studies. Results obtained indicate that PCP is strongly retained by the organic soil matrix. Based on the previous literature review, it seem that the adsorption of organic compounds by organic soil is generally achieved by hydrophobic sorption and the hydrogen bonding at the molecular level with the COOH, carbonyl (C=O), and amide (NH_2) groups of organic matter. Although adsorption is the most common mechanism of PCP removal in groundwater, Smith and Novak (1987) have documented the biodegradation of phenolic compounds in the groundwater environment. However, the biodegradation process required a much longer contact time than the adsorption process.

Regardless of the attenuation mechanisms affecting PCP in marshland soil, it seems apparent that laboratory experiments can be a useful and valid technique for simulating it's migration potential in the subsurface.

4.5.4.3 Potential for Pentachlorophenol Migration

The data obtained on PCP adsorption, through batch and column experiments permit us to conclude that the adsorption capacity of PCP is very high. The information gathered by the batch test studies demonstrated that the rate of adsorption followed the Freundlich and Langmuir isotherms form and resulted in a Freudlich adsorption coefficient K_F of 0.33.

In order to properly evaluate the retardation factor of PCP through the examined soil, it is first necessary to establish the linear distribution coefficient (K_d) of the system. A linearization of the adsorption coefficients based on the Freundlich parameters previously determined was conducted and is presented in Figure 4.29. This linearization will permit a rough estimate of the distribution coefficient of the PCP within the soil for the concentration range studied.

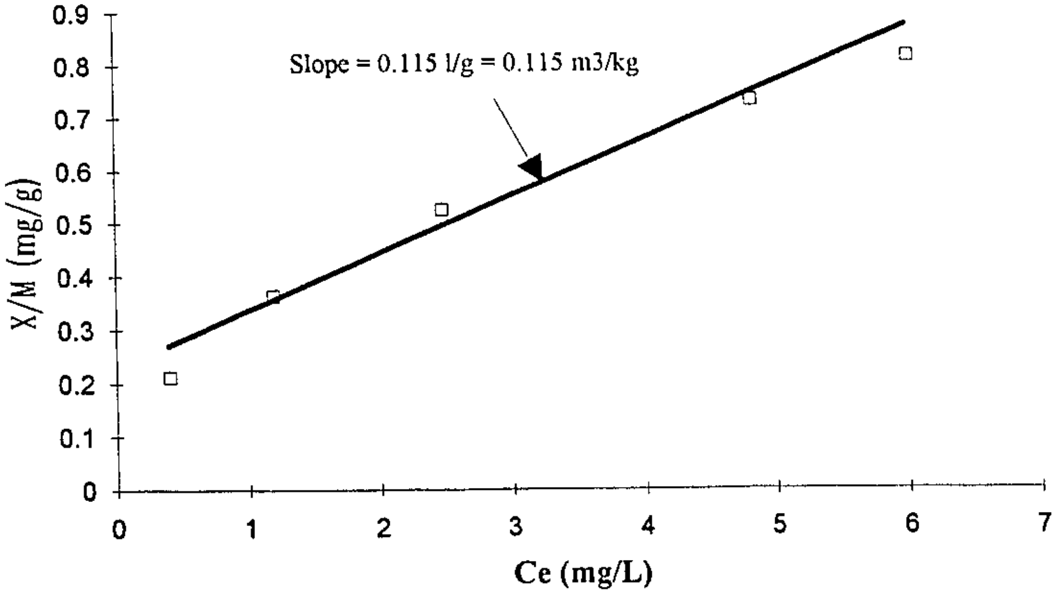

Figure 4.29: **Linearization of the Adsorption Coefficient Obtained by the Freundlich Adsorption Isotherms for PCP**

Based on the above graph, a distribution coefficient (K_d) of approximately 0.115 m^3/kg can be determined. Knowing the porosity and the bulk density of the soil (Table 4.1) an estimate of the retardation factor can be achieved as follows:

$$R_F = 1 + \left(\frac{450\ \text{kg/m}^3 \times 0.115\ \text{m}^3\text{/kg}}{0.75} \right) = 69$$

It is therefore anticipated that a contamination plume of PCP would be retarded by a factor of approximately 70 compared to the average groundwater velocity. The column experiment seems to be in accordance with this high retardation factor, since no PCP contamination was noticed in the effluent during the 4 month testing period.

By investigating the migration of PCP within the pore fluids of the leaching cells, it was possible to evaluate the retardation factor characteristic of this contaminant in the marshland soil. Following the numerical procedure discussed in section 4.5.2.3, a retardation factor varying from 93 to 150 was determined. A printout of the numerical modelling procedure is presented in Appendix F.

Based on the laboratory analysis of the migration potential of PCP through the Locksley Marshland soil the forecasted retardation factor can vary between 70 to 150.

It is however important to remember that although PCP is highly adsorbed by the organic soil it is a partly reversible process as observed in the desorption analysis. Experimental data obtained during the batch test study indicate that 20 to 90 % of the PCP initially adsorbed was desorbed once in contact with distilled water. The reversibility of the adsorption process will undoubtedly affect the long term mobility of PCP in the groundwater.

The results of this investigation suggest that significant retardation of PCP contamination should be foreseen, assuming a steady input of PCP contaminated water. It is nonetheless expected that as the contaminated water source is cut off, some of the adsorbed contaminants might return to the water phase as lower concentration water flushes through previously contaminated zones. But as explained earlier this new front of PCP tainted water reaches uncontaminated soil, the adsorption process will once again dominate the system. One can see that this repetitive cycle of sorption and desorption will significantly retard the advance of the contamination plume.

It is also expected that this prolonged period of near immobilization of pentachlorophenol in the aquifer will greatly favour the biodegradation of the chlorinated phenol. As previously noted, biodegradation of PCP has been reported as being an effective long term removal process. Thus it is therefore assumed that the combined action of the adsorption process, which is virtually instantaneous, and the slower rate of biodegradation processes should greatly reduce the migration potential of PCP.

4.6 SUMMARY

The behaviour, transport and ultimate fate of contaminants in organic soil is greatly affected by their participation in sorption reactions. The adsorption potential of lead, zinc, calcium, sodium and pentachlorophenol (PCP) by marshland soil was evaluated in laboratory through both, batch and column experiments. Most contaminants were found to fit either the Freundlich or Langmuir isotherm model. High retardation factors, exceeding 2000 for lead and approaching 100 for both zinc and PCP were measured. However, desorption experiments indicate that the adsorption process for certain compounds, such as PCP, can be partly reversible.

CHAPTER 5

IDENTIFICATION OF PARAMETERS FOR CONTAMINANT ATTENUATION AT THE ALICE AND FRASER LANDFILL SITE

5.1 GENERAL REMARKS

To predict contaminant migration in an aquifer, three main stages have to be achieved. The initial stage, which was described in Chapter 2.3, consist of the derivation of the mathematical model capable of simulating contaminant transport. The second stage is the calibration of the model for the desired problem. In this stage, characteristic parameters of the aquifer and contaminants are determined through either literature, field or laboratory investigations. The third and final stage is applying the model with the previously determined parameters for contaminant migration prediction.

In this chapter the parameter determination process for the township of Alice and Fraser Landfill site will be discussed.

The most accurate model results are obtained from simulations which are based on site specific data collection. However, in some cases it is not feasible to measure certain parameters, and satisfactory results can be obtained using laboratory derived data or again by referring to previously published data.

The township of Alice and Fraser Landfill site has been intensively monitored since 1975. Through the monitoring programs, a considerable understanding of the geology and hydrogeology of the region was acquired. An in depth description of the site is presented in Chapter 3.2.

Site specific geochemical reaction rates were also evaluated based on laboratory analysis performed on soil originating from the marshland located at the northern portion of the Alice and Fraser Landfill site. A description of the batch adsorption and column studies accomplished for this project is presented in Chapter 3 and 4.

Based on the site specific information and the laboratory results, several parameters needed for the contaminant migration model were gathered. The data was grouped into three general categories; the source specific data, the organic soil specific parameters and the initial groundwater properties. Parameters for each categories are described in the following subsections.

5.2 SOURCE SPECIFIC PARAMETERS

5.2.1 Physical Framework

The physical framework defines the geometry of the system including the thickness and areal extent of each hydrostratigraphic unit and of the contaminant source. Information on the physical framework were evaluated based on the site plan of the landfill and marshland area and the geological maps of the region. By reviewing the available data several parameters were evaluated for the landfill, the underlying sand and gravel aquifer and the marshland area. Those results are presented in Table 5.1.

TABLE 5.1
Physical Framework
Alice and Fraser Landfill Site

Physical Framework	Landfill	Sand and Gravel Aquifer	Marshland Deposit
Area	80 000 m^2	---	72 000 m^2
Depth	10 to 15 m	3 to 8 m	0.5 to 1.5 m
Length	---	---	600 m

The physical characteristics of the marshland were obtained from map analysis and field investigation of the portion of the marsh located between the main leachate stream (SW-3) and the end of the landfill property (SW-10A) as shown on Figure 3.2.

5.2.2 Leachate Production

Leachate is generated at the Alice and Fraser Landfill site primarily by the infiltration of precipitation through the waste. In order to assess the potential leachate generation from the municipal landfill area, the Hydrologic Evaluation of Landfill Performance (HELP) model was used. This model accepts climatological, soil and landfill configuration data and utilizes a solution technique that accounts for the effects of surface storage, runoff, infiltration, percolation, evapotranspiration, soil moisture storage and lateral drainage. It simulates the effects of hydrological processes on the water balance for the landfill by performing daily sequential analysis using deterministic approaches. The basic workings of the HELP model, its limitations, assumptions and sensitivity to certain parameters are discussed in detail by Gebhardt and Jankowshi (1987) and Schroeder et al. (1984). Rates of leachate generation at the Alice and Fraser Landfill site using the HELP model were provided by Golder Associates Ltd. (1992).

The HELP model established that an annual average precipitation of 60 950 m^3 per year is affecting the area of the municipal landfill under study. The amount of total evapotranspiration is indicated to represent an average of about 74 % (45 400 m^3 per year), while a leachate generation rate of 13 850 m^3 per year representing about 23% of the precipitation was evaluated for the existing conditions. Based on the open landfill configuration, the runoff is indicated to be minimal.

Table 5.2 provides a breakdown of the annual average total precipitation, evapotranspiration and leachate generation rates under the open site conditions. Also, the standard deviations are provided to illustrate the data distribution around the average values.

TABLE 5.2
Water Balance Breakdown
Alice and Fraser Landfill

	Average (m3/year)	Standard Deviation (m3/year)	Percentage
Precipitation	60950	7520	100
Runoff	0	0	0
Evapotranspiration	45410	6000	74.5
Leachate	13850	3200	22.7

Note: A small percentage of the precipitation contributes to lateral drainage and changes in water storage.

5.2.3 Hydrology of the Marshland

The estimation of the flow volume discharging from the landfill into the on-site marshland is an important parameter required to evaluate the total contaminant loading on this system. In addition, un-polluted water originating from the surrounding watershed have to be evaluated in order to properly evaluate the effects of dilution on the leachate entering the marshland. To allow a proper watershed/sub-watershed delineation, aerial photography of the landfill site and surrounding area were taken in April 1991. From this photography, topographic base plans were prepared by Golder Associates Ltd. (1992).

In order to evaluate the surface water flow throughout the marshland area, a precipitation gauging station was established at the landfill site and concrete weirs were constructed in October 1991 at two locations to allow actual flow measurements to be taken. One was located on the main leachate stream downgradient from the municipal landfill prior to its entering the Beaver Meadow, and the second was located on the Locksley Creek channel downstream of the north boundary of the landfill property i.e. off-site, but as close to the north boundary as was practically possible. Continuous flow monitoring devices were installed at each of these locations.

Calibrated surface water flow rates for different periods between 1989 and 1993 are presented in Table 5.3. These seasonal variations in the surface water flow rate must be considered for the attenuation of the contaminants by the process of dilution as further discussed in Section 5.5.

TABLE 5.3
Flows at Specific Locations
Within the Marshland

Date	Flows at Specific Locations (m3/sec)			
	SW-8	SW-3	DBM	SW-10A
August 9/89	0.007	0.002	0.016	0.02
November 17/89	0.007	0.002	0.016	0.02
April 16/90	0.007	0.003	0.045	0.051
August 4/90	0.007	0.002	0.026	0.03
Feb. 18/91	N/A	0.001	0.012	0.012
April 9/91	N/A	0.006	0.182	0.202
June 6/91	N/A	0.001	0.004	0.004
August 15/91	N/A	0.001	0.006	0.006
Oct. 21/91	N/A	0.001	0.011	0.011
Dec. 10/91	N/A	0.001	0.024	0.024
April 24/92	N/A	0.005	0.338	0.362
August 11/92	N/A	0.002	0.004	0.006
Nov. 6/92	N/A	0.001	0.007	0.007
August 28/93	N/A	0.002	0.053	0.056
Nov. 2/93	N/A	0.001	0.013	0.013

5.2.4 Initial Concentration of the Contaminants.

The concentration of contaminants at the source was evaluated based on data gathered by two monitoring wells located within the landfill area. Water sample taken from these monitoring wells were analyzed for a variety of organic and inorganic compounds over a ten year period. The leachate sample collected indicate highly variable concentration of dissolved constituents between each sampling events. Ranges in parameter concentration are presented in Table 5.4.

The main source of contaminants entering the marshland originates from a leachate impacted stream which flows from the base of the landfill to the marshland. Contaminant concentration of the stream have been monitored since 1976 at surface water sampling station SW-3. Ranges in parameter concentration for the stream based over the past five years are presented alongside the leachate values in Table 5.4. Several parameters exceed background levels, such as hardness (calcium and magnesium), alkalinity, conductivity, ammonia, TKN, phenols, chloride, barium, boron, iron, manganese, strontium, and COD.

TABLE 5.4
Range in Contaminant Concentration Underlying the Landfill and in the Stream

Parameter	Units	ODWO	Measured Concentration Under the Landfill	Measured Concentration in the Leachate Stream (SW-3)
Alkalinity	mg/L	30 - 500	1600 - 7000	600 - 1700
Conductivity	uS/cm	--	4000 - 40000	2000 - 28000
Hardness	mg/L	500	1200 - 7000	1000 - 2000
pH		6.5 - 8.5	5.4 - 6.8	6 - 7.5
T°	°C	--	8 - 12	1 - 22
TKN	mg/L	--	43 - 246	2 - 42
Ammonia	mg/L	--	<0.1 - 220	1 - 22
Barium	mg/L	1	0.5	1 - 6.7
BOD	mg/L	--	--	11 - 5400
Boron	mg/L	5	0.8 - 5	0.4 - 0.8
Calcium	mg/L	--	900 - 1900	150 - 500
Chloride	mg/L	250	200 - 1400	100 - 480
COD	mg/L	--	1500 - 14000	40 - 6500
Iron	mg/L	0.3	100 - 1300	0.01 - 114
Lead	mg/L	0.05	0.05	<0.002
Magnesium	mg/L	--	100 - 600	60 - 220
Manganese	mg/L	0.05	1 - 63	<0.5 - 17
Phenols	mg/L	--	0.25 - 3.5	0.008 - 1.9
Phosphorous	mg/L	--	<0.1 - 0.3	<0.1 - 0.3
Strontium	mg/L	--	1	0.4 - 1.9
Zinc	mg/L	5	0.08 - 0.3	0.001 - 0.03

Note: ODWO stands for Ontario Drinking Water Objective (1994)

Considering the wide range of concentration usually observed in the leachate, a representative range of values will be considered in the contaminant transport model.

5.3 ORGANIC SOIL SPECIFIC PARAMETERS

5.3.1 Effective Porosity

The effective porosity (θ_e) is an important parameter, influencing the velocity and retardation of contaminant in the marshland system. The effective porosity is defined as the percentage of inter-connected pore space and is more closely related to permeability than to total porosity. The effective porosity can be evaluated through laboratory and field experiments or obtained from literature.

The effective porosity of the marshland soil is somewhat problematic to evaluate, since the organic soil contains a high percentage of pore space, of which only a small fraction is inter-connected. Organic soil samples originating from the Alice and Fraser Marshland were analyzed for total porosity as described in section 3.3.3. The total porosity of the collected soil varied between 75 and 80%.

Based on research by Loxham (1980) who studied the effective porosity of peat, approximately 30 to 40% of the total pore space is large enough and interconnected to permit groundwater flow. Loxham based his findings on photomicrograph pictures and image analysis techniques on peat samples. Other researchers (Viraraghavand and Mathavan, 1990; Shotyk, 1988) evaluated an effective porosity ranging between 33 and 45% for wetland soil.

By assuming that the pore distribution observed by Viraraghavand and Mathavan (1990), Shotyk (1988) and Loxham (1980) are representative of all peat formation, an approximation of the effective porosity of the marshland soil was calculated, resulting in an effective porosity ranging from 22 to 45%. An average effective porosity of 30% was assumed for modelling purposes.

5.3.2 Dry Bulk Density

The soil dry bulk density directly influences the retardation of solutes and is related to the soil structure. A dry bulk density of 450 kg/m^3 was measured for the organic soil originating from the marshland. The procedure used for determining the dry bulk density is presented in section 3.3.3.

Other researchers (McLellan and Rock, 1988; Chason and Siegel, 1986) obtained dry bulk density values for peat varying from 60 to 480 kg/m^3.

5.3.3 Hydraulic Conductivity

Hydraulic conductivity estimates should be based on site specific data collection, such as pumping tests. If no such results are available, which is the case for the marshland soil, typical hydraulic conductivity values can be found for similar system in the literature. David et al., (1980) established an average hydraulic conductivity, for peat soil, of 6.6 x 10^{-5} m/s while Tchobanoglous and Schroder (1987) present a range varying from 1 x 10^{-7} to 1 x 10^{-8} m/s, and Chason and Siegel (1986) put forth a range values ranging from 5.6 x 10^{-7} to 2.5 x 10^{-8} m/s.

Laboratory scale column test can also be used in estimating the hydraulic conductivity. Results obtained from numerous column test realized for this project indicates hydraulic conductivity in the range of 9 x 10^{-7} to 9 x 10^{-8} m/s. It is nonetheless important to stress that several researchers have noticed a one to two orders of magnitude difference between field and laboratory values of hydraulic conductivity (Domenico and Schwartz, 1990; Tchobanoglous and Schroder, 1987). A hydraulic conductivity of 5 x 10^{-7} m/s was assumed for modelling purposes.

5.3.4 Hydraulic Gradient

The hydraulic gradient is the change in water level elevation over a given distance. In general, it is a function of the local topography, groundwater recharge volume and location, and the volume and location of groundwater withdrawals. Further it may also be related to the porous media properties (Sharp-Hansen et al., 1990).

The hydraulic gradient was estimated from water level measurements within the marshland area. In the model development, the hydraulic gradient will be evaluated for each element of the grid, based on localized measurement of the water table. The average hydraulic gradient between the contaminants entering the marshland and the Alice and Fraser Landfill Site property limits was estimated based on site specific measurements as follows:

$$\text{Hydraulic Head} = \frac{\text{Difference in head}}{\text{Distance}} = \frac{(85.30m - 82.20m)}{600m} = 0.0052 \tag{5.1}$$

5.3.5 Groundwater Velocity

The groundwater velocity is an essential parameter to quantify transport by advection. Because groundwater velocities are difficult to measure directly, they are often approximated indirectly using measurements of heads and hydraulic conductivity with Darcy's Law. Assuming a uniform, saturated porous medium, the groundwater velocity can be expressed as:

$$V = -\frac{K}{\theta_e}\left(\frac{\partial h}{\partial z}\right) \tag{2.16}$$

The groundwater velocity will be evaluated at each finite difference grid of the system based on the discrete values of the hydraulic conductivity, effective porosity and the hydraulic gradient. The average groundwater velocity for the marshland is estimated to be 8.67 x 10^{-9} m/s (0.273 m/y).

5.3.6 Hydrodynamic Dispersion Coefficient

Hydrodynamic dispersion refers to the spreading and mixing caused by molecular diffusion and mechanical dispersion. Dispersivity, is the parameter that describes mechanical dispersion, it is a difficult parameter to determine, and several researchers have shown that values for dispersivity are scale dependant. In the absence of site specific values, as is the case for the Alice and Fraser landfill site, the dispersivity can be evaluated as a function of the distance to the downgradient receptor. By using a regression analysis based on data gathered by different researchers, the following relationship between the longitudinal dispersivity and the travel path was developed by Domenico and Schwartz (1990).

$$D_L = 0.11 \times \text{Distance travelled} \tag{5.2}$$

The longitudinal dispersivity accounts for mechanical dispersion in the predominant direction of flow. The dispersivity observed perpendicular to the main flow path are referred to as transverse (D_T) and vertical (D_V) dispersion. Sharp-Hansen et al., (1990) suggest the following ratio for D_T and D_V:

$$D_T = 3.0 D_L \tag{5.3}$$

$$D_V = 0.056 D_L \tag{5.4}$$

5.3.7 Retardation Factor

The retardation factor is used to determine the retardation due to adsorption of a contaminant relative to the bulk mass of water transporting the contaminant as previously mentioned in section 2.3.3.

Both the dry bulk density (P_b) and the soil porosity (θ) have been previously defined for the marshland soil. The contaminant distribution coefficient (K_d) will vary based on the specific contaminant monitored. Several techniques for estimating K_d have been reported in section 2.3.3. Laboratory analysis comprising of both batch and column studies were undertaken to evaluate the K_d and ultimately the retardation factor of several contaminants. Results for lead, zinc, sodium, calcium, chloride and pentachlorophenol (PCP) are presented in Table 5.5.

TABLE 5.5
Laboratory Results
Retardation Factor

Element	**Based on Batch Test Studies**		**Based on Column Study**
	K_d (m^3/kg)	**R_F**	**R_F**
Zinc	0.045	28	83 to 105
Lead	2.8	1680	2000
Sodium	--	≈1	1.9 to 2.4
Calcium	--	≈1	1.0 to 1.25
Chloride	--	≈1	1.0
PCP	0.115	69	93 to 150

5.3.8 Organic Carbon Content

It has been shown that non polar molecules tend to partition preferentially into non polar environments provided by small quantities of solid organic matter (Domenico and Schwartz, 1990). Therefore the organic carbon content of marshland soil will directly control the retardation factor of hydrophobic non polar organic contaminants as detailed in section 2.3.3.4. The fractional organic carbon content (f_{oc}) can be estimated from the percent organic matter content (f_{om}) of a given soil based on the following relationship (Lyman et al., 1982):

$$f_{oc} = \frac{f_{om}}{172.4} \tag{5.5}$$

Organic soil sampled from the marsh was analyzed for organic matter content as described in section 3.3.3. Laboratory analysis indicate an organic matter content varying from 20 to 30%. This relates to an organic carbon content varying from 0.11 to 0.17.

5.4 GROUNDWATER PROPERTIES

5.4.1 Density and Viscosity of the Fluid

For the purpose of this model, it is assumed that the density and viscosity of the fluid is the same as that of uncontaminated groundwater. This assumption is realistic since the concentration of contaminant within the groundwater is not excessive. The following values were obtained from Fetter (1988) based on a yearly average temperature of 5°C.

Density:	999.965 kg/m^3
Viscosity:	0.015188 g/(cm.sec)

5.4.2 Background Contaminant Concentration

An extensive surface and groundwater sampling program has been in place at the Alice and Fraser landfill site since 1975. In order to properly delineate the migration of leachate impacted water through the marshland, it is essential to establish the background contaminant level of the system. This is required since it is common to find elevated concentrations of some compounds originating from natural processes within the system, unrelated to the leachate migration.

The background water quality of the marshland was established based on surface water sampling at locations SW-15 and SW-16 as shown on Figure 3.2. These locations are considered to provide the best available determination of background surface water quality in the Locksley Creek system, since they are located within the marshland system and upstream of the main leachate impacted stream entry. The chemical constituents in the water at these locations are similar, and the variability in concentration over time is low.

The range of concentrations measured at SW-15 and SW-16 over the last 15 years, for selected landfill leachate indicator parameters as well as some PWQO parameters, is provided in Table 5.6.

TABLE 5.6
Background Water Quality Within the Marshland

Parameter	Units	PWQO	Measured Concentration SW15	Measured Concentration SW16	Background	Average Background
Alkalinity	mg/L		10 - 46	10 - 36	10 - 46	28
Conductivity	uS/cm		50 - 130	50 - 140	50 - 140	95
Hardness	mg/L		19 - 57	17 - 60	17 - 60	38
pH		6.5 - 8.5	6.5 - 8	6 - 8	6 - 8	7
Temperature	°C		5 - 25	0.5 - 27	0.5 - 27	14
TKN	mg/L		0.3 - 1.2	0.7 - 2.1	0.3 - 2.1	1.2
Barium	mg/L		0.01- 0.05	0.02 - 0.04	0.01- 0.05	0.03
BOD	mg/L		1 - 5	1 - 7	1 - 7	4
Boron	mg/L		<0.01	<0.01	<0.01	<0.01
Calcium	mg/L		6 - 12	5 - 14	5 - 14	10
Chloride	mg/L		3 - 20	2 - 16	2 - 20	11
COD	mg/L		40 - 85	59 - 140	40 - 140	90
Iron	mg/L	0.3	0.3 - 2.5	0.4 - 1.4	0.3 - 2.5	1.4
Lead	mg/L	0.05	<0.002	<0.002	<0.002	<0.002
Magnesium	mg/L		1 - 5	1 - 6	1 - 6	3
Manganese	mg/L		<0.01 - 0.25	<0.01 - 0.18	<0.01 - 0.25	0.13
Phenols	mg/L	0.001	<0.002 - 0.005	<0.002 - 0.004	<0.002 - 0.005	0.003
Phosphorous	mg/L	0.03	<0.1	<0.1	<0.1	<0.1
Strontium	mg/L		0.02 - 0.1	<0.01 - 0.12	<0.01 - 0.12	0.07
Zinc	mg/L	0.03	<0.01	<0.01 - 0.02	<0.01 - 0.02	0.01

Note: PWQO stands for Provincial Water Quality Objectives

From Table 5.6 it is concluded that iron and phenols may exceed PWQO in natural background waters. But nonetheless, background concentration for most compound are substantially lower than the contaminated sources concentration as presented in Table 5.4.

5.5 DILUTION PROCESS

Prior to undertaking the modelling of contaminant transport through the Locksley Marshland system, the initial contaminant attenuation due to dilution processes must be evaluated. Of all the water entering the marshland system, only a small fraction is contaminated, therefore dilution is a major attenuation mechanisms at this site. A mass balance analysis carried out on the marshland system, based on flow data gathered in Table 5.3 and the contaminant concentration within the leachate stream as well as the background concentration within the marshland as reported in Table 5.4 and 5.6, respectively, and the contaminant concentration observed at the property limit (SW-10A), enable an estimate of the attenuation related to the dilution process.

The seasonal variation in flow rates between the leachate stream (SW-3) and the marshland system (SW-10A) is illustrated in Figure 5.1, while the total attenuation ratio $\left(\frac{[SW-3]-[SW-10]}{[SW-3]-[background]}\right)$ and the attenuation due exclusively to dilution is presented in Figures 5.2 and 5.3 respectively for certain contaminants.

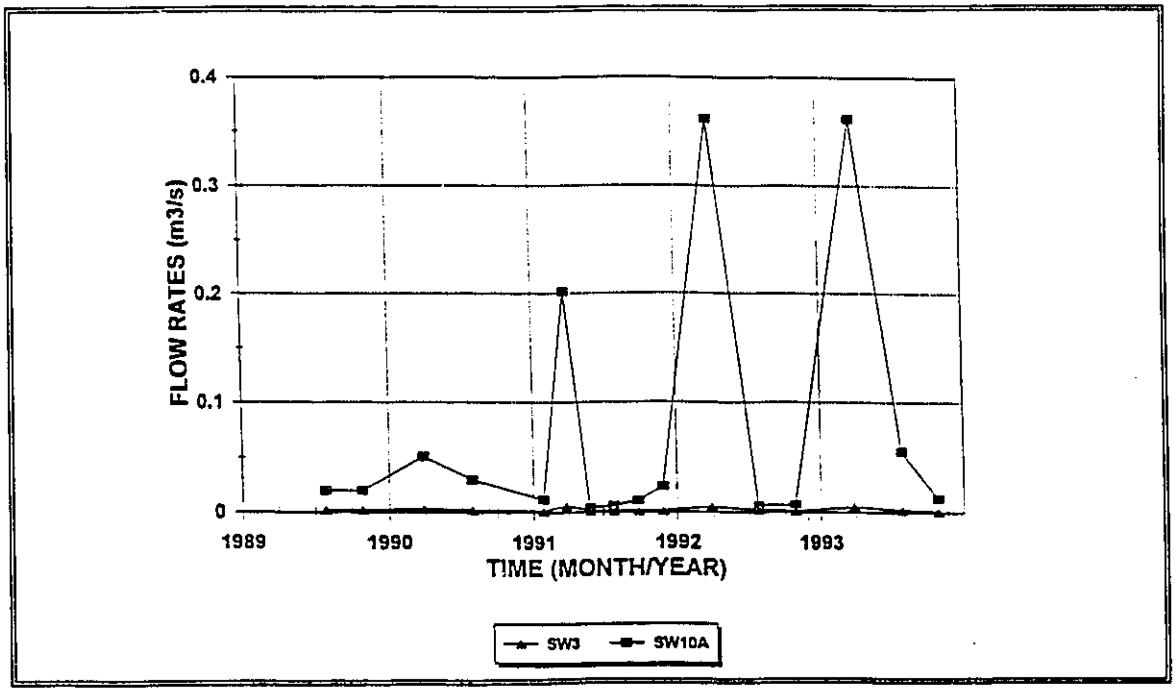

Figure 5.1: Seasonal Variation in Flow Rates

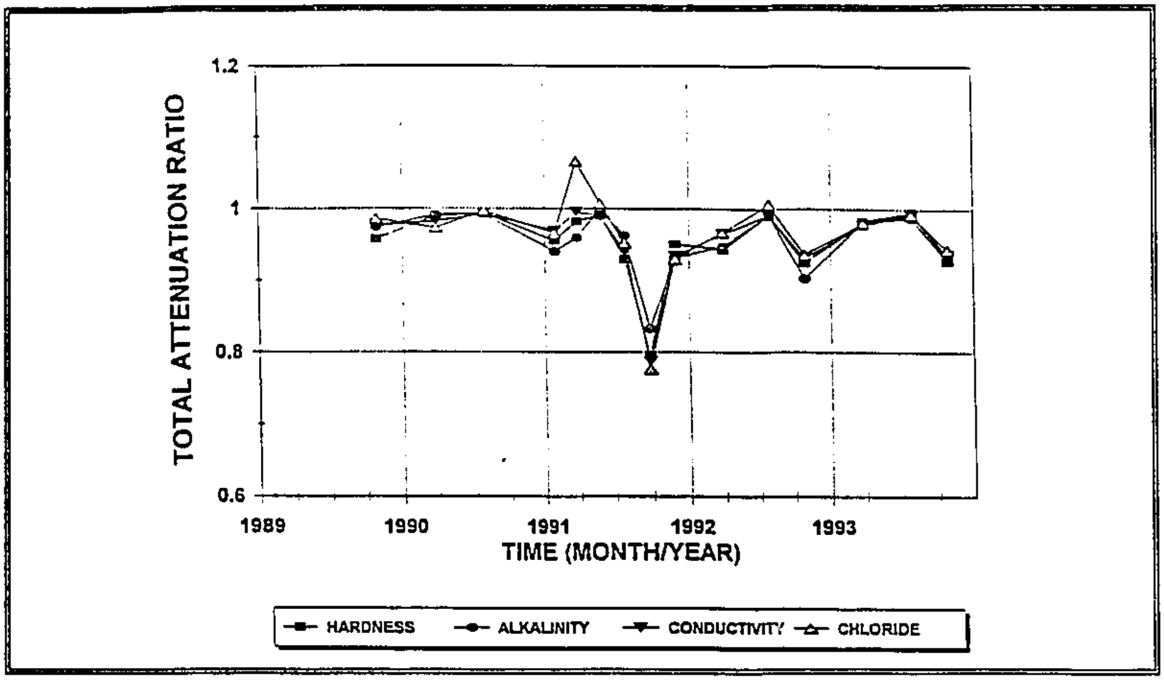

Figure 5.2: Total Attenuation Ratio

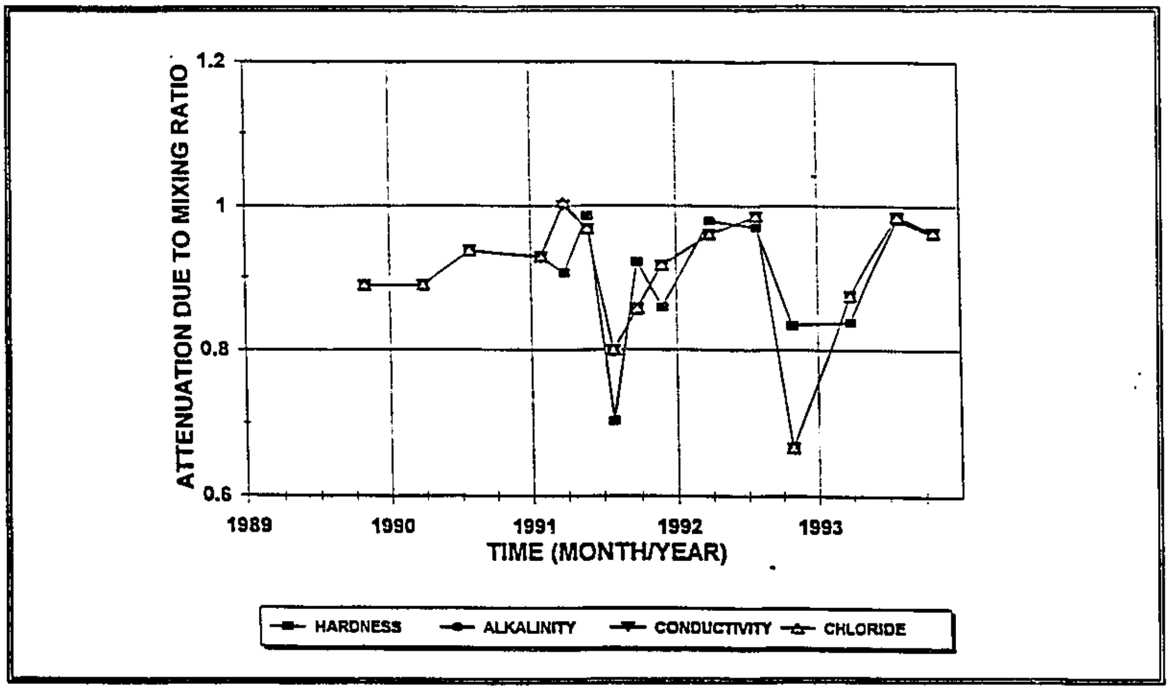

Figure 5.3: Attenuation due to Dilution

The results of this mass balance analysis indicates that the process of dilution by itself is responsible for the attenuation of between 85 to 95 percent of the contaminants monitored.

Since the dilution process is not incorporated in the computer model described in the following chapter, contaminants entering the marshland system must initially be attenuated prior to modelling. Based on the above mentioned projected dilution, the calculated contaminant concentrations at the main mixing zone, where the main leachate stream enters the marshland system, are presented in Table 5.7.

TABLE 5.7
Range in Contaminant Concentration Projected after Dilution

Parameter	Units	PWQO	Projected concentation at the mixing zone (SW-3) after dilution
Alkalinity	mg/L	30 - 500	60 - 170
Conductivity	uS/cm	--	200 - 2800
Hardness	mg/L	500	100 - 200
pH		6.5 - 8.5	6 - 7.5
Temperature	°C	--	1 - 22
TKN	mg/L	--	2 - 42
Ammonia	mg/L	--	0.1 - 2.2
Barium	mg/L	1	0.1 - 0.67
BOD	mg/L	--	1.1 - 540
Boron	mg/L	5	0.04 - 0.08
Calcium	mg/L	--	15 - 50
Chloride	mg/L	250	10 - 48
COD	mg/L	--	4 - 650
Iron	mg/L	0.3	0.001 - 11.4
Lead	mg/L	0.05	0.001
Magnesium	mg/L	--	6 - 22
Manganese	mg/L	0.05	1
Phenols	mg/L	0.002	0.2
Phosphorous	mg/L	--	0.02
Strontium	mg/L	--	0.1
Zinc	mg/L	5	0.003

Note: PWQO stands for Provincial Water Quality Objectives

5.6 SUMMARY

In this chapter identification of the parameters required for the contaminant transport model within the marshland system were developed. When possible field and/or laboratory derived data were used to characterize the physical framework of the site as well as the specific marshland soil parameters and the initial groundwater conditions. This information is essential for modelling the migration of contaminants within the Locksley marshland system. The reliability of any model will be directly affected by the reliability of the primary parameters. This is why a great deal of efforts were made to collect site specific data. However, due to several restrains, several parameters such as the effective porosity, the hydraulic conductivity and the hydrodynamic dispersion coefficient were partly derived from existing literature dealing with groundwater flow through marshland environment. Table 5.8 summarize the primary model parameters.

TABLE 5.8

CONTAMINANT TRANSPORT
PRIMARY MODEL PARAMETERS

	PARAMETER ESTIMATION PROCEDURE			
	Literature Review	Field Investigation	Laboratory Investigation	Modeler's Estimation
Initial Source Data				
Area of the landfill		80 000 m²		
Depth of the landfill		10 to 15 m		
Area of the marshland		72 000 m²		
Depth of the marshland		0.5 to 1.5 m		
Length of the marshland		600 M		
Leachate production				13 850 m3/year
Flow within the marshland		Table 5.3		
Leachate concentration		Table 5.4		
Hydraulic Properties of the Marshland				
Total Porosity (N)	70 to 90 %		75 to 80 %	
Effective Porosity (Ne)	22 to 45 %			30%
Bulk Density (Pb)	60 to 480 kg/m3		450 kg/m3	
Groundwater Velocity (V)				8.67 E-9 m/s
Hydraulic Conductivity (K)	1E-5 to 1E-8 m/s		9 E-7 to 9 E-8 m/s	5 E-7 m/s
Hydraulic Gradient (dh/dl)		0.0052		0.0052
Hydrodynamic Dispersion Coeff. (Dl)				0.11 x distance
Organic Carbon Content (foc)			11 to 17 %	
Retardation Factor (Rf)			Table 5.5	
Groundwater Properties				
Density of the Fluid	999.965 kg/m3			
Dynamic Viscosity of the Fluid	0.0152 g/(cm.sec)			
Background contaminant conc.		Table 5.6		
Projected Diluted concentration				Table 5.7

CHAPTER 6

SUBSURFACE WATER FLOW MODELLING WITHIN THE LOCKSLEY MARSHLAND

6.1 INTRODUCTION

The goal of this chapter is to present the modelling techniques utilised to simulate both the subsurfacewater flow and contaminant transport within the organic soil layer of the Locksley marshland. Contaminant transport simulation is a three-step process in which the governing equations of flow and mass transport, as described in chapter 2, are employed sequentially. First, the flow equation is solved for the head distribution. Next, the head distribution is used with the hydraulic conductivity and effective porosity for flow distributions to calculate the seepage velocity distribution using Darcy's law. Finally the contaminant transport equation is solved using the previously calculated velocity distribution.

To achieve these tasks, two distinct models were utilised. In a first step, the local flow system within the marshland was calibrated using Waterloo Hydrogeologic Software's FLOWPATH flow and pathline model. The hydraulic head distribution gathered from FLOWPATH for the marshland system was then used as input for the velocity and contaminant transport model (DID2XY). The DID2XY model was initially written by Samani (1987). This program, which resolves unsteady two dimensional solute and fluid transport in clay soil, was partly rewritten to permit a two dimensional plan analysis of the Locksley marshland.

The Locksley Marshland was modelled in an attempt to predict the long-term migration potential of the contaminants presently being leached from the Alice and Fraser Landfill site into the marshland. The predictive capacity of the model is an invaluable tool in the water resource planning for this particular marshland and could eventually be adapted to other landfill-wetland systems. The following sections describes in more detail the modelling techniques utilised to simulate the contaminant transport phenomena within the Locksley Marshland.

6.2 Models Description and Validation

6.2.1 FLOWPATH Model

FLOWPATH is a steady-state two-dimensional horizontal plane groundwater flow and pathline analysis model developed by Waterloo Hydrogeologic Software (Franz and Guiguer, 1992). FLOWPATH is based on the block-centred finite difference and the particle tracking methods. The model can simulate hydraulic head distributions, groundwater velocities as well as pathline in both confined and unconfined aquifers.

6.2.1.1 Model Assumption and Limitation.

The implementation of the two-dimensional finite difference method yields a numerical approximation of the modelled system. Upon discretization of the natural system into a large number of rectangular cells, a differential water balance is written for each cell. In the block-centred finite difference formulation, the obtained system of equations is solved for the hydraulic head at the centre of each cell. It is important to realise that all flow parameters including the calculated hydraulic head value represent an average value over the entire cell volume, neglecting any small scale variations or vertical gradient.

The two dimensional formulation does, however, lead to local inaccuracies close to surface water bodies where fully three-dimensional flow prevails. The transient behaviour of the groundwater flow system was not studied. Instead, it was attempted to provide conservative long-term estimates of the hydraulic head distribution in the Locksley marshland system.

6.2.1.2 FLOWPATH Validation

Since it's initial release in the fall of 1989, the FLOWPATH model has been updated and refined on a number of occasions transforming the model into an extremely powerful computing package that has reached a high level of recognition in the modelling community.

FLOWPATH has previously been validated against several well established computer models such as PLASM (Prickette and LonnQuist, 1971) and MODFLOW (McDonald and Harbough, 1984) for the hydraulic head distribution and with GWPATH (Shafer, 1987) for pathlines, as well as a host of analytical and semi analytical models. Results of the validation process indicates that FLOWPATH's numerical implementation solves the mathematical equations describing groundwater flow and advective particle movement correctly.

6.2.2 DID2XY Model

DID2XY is a transient two-dimensional model for the simulation of a multi-component contaminant transport in saturated soil. This model was written in FORTRAN by Samani (1987). In the model, various solute transport mechanisms such as advection, diffusion/dispersion and adsorption are considered. The migration of reactive contaminants in groundwater is modelled in DID2XY using an adaptation of the Advection Dispersion Equation. For a Two dimensional solute transport the following equations is utilized:

$$\frac{\delta C}{\delta t} = \frac{\delta}{\delta x}\left\{\frac{D_{Lx}}{R_F}\frac{\delta C}{\delta x}\right\} + \frac{\delta}{\delta y}\left\{\frac{D_{Ly}}{R_F}\frac{\delta C}{\delta y}\right\} - \left\{\frac{V_x}{R_F}\frac{\delta C}{\delta x}\right\} - \left\{\frac{V_y}{R_F}\frac{\delta C}{\delta y}\right\} \qquad (2.12)$$

To solve the non-linear partial differential equations, several finite difference methods have been used. Additional information on the DID2XY model, can be found in Samani (1987). The DID2XY model was initially designed to evaluate the contaminant migration potential in clay liners or natural clay underlying landfill sites. In order to adapt the model to the Locksley marshland ecosystem, several modifications were necessitated to transform it from a vertical profile to a horizontal plane model. A simplified flow chart describing the performance of the program is presented in Figure 6.1. A complete listing of the DID2XY computer program is presented in Appendix G.

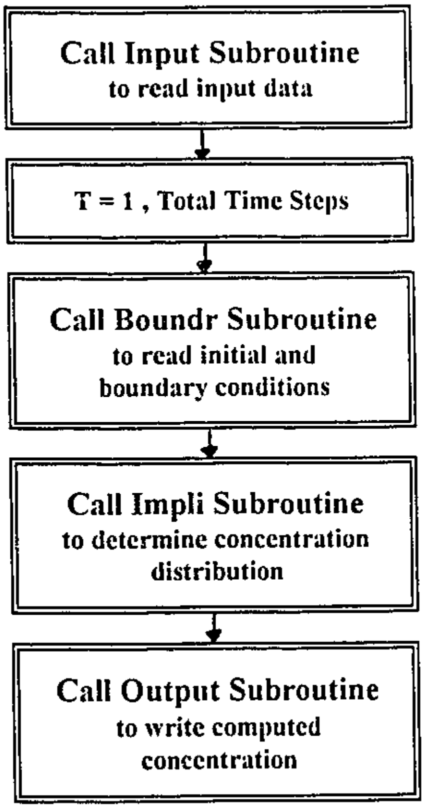

Figure 6.1: Flow Chart ot the DID2XY Numerical Model

6.2.2.1 Model Assumption

Several assumptions were made in the construction of the DID2XY transport model. They can be summarized as follows:

1- Organic soil layer is homogenous across the marshland.
2- Isothermal conditions prevails.
3- The organic soil layer is completely saturated.
4- Validity of Darcy's Law.
5- Laboratory derived data on adsorption are adequate.
6- No biological activity is affecting the contaminant migration.

Assumption 1 to 5 are judged to be acceptable for most marshland environments, and although assumption no 6 is unlikely, assuming a lack of biological activity only renders the model more conservative.

6.2.2.2 DID2XY Model Validation

The DID2XY model is not as well established as the previously described FLOWPATH model and therefore requires an in depth validation. In order to establish the accuracy of the DID2XY numerical method, the model's prediction capacity was compared with an exact analytical solution for a given situation. The validation of the DID2XY model was conducted by comparing its results with the analytical solution of the advection-dispersion equation.

The analytical solution used to check the numerical model developed in this study is the one-dimensional advection-dispersion with sorption model for the solute transport in a porous medium obtained by Ogata (1970). The relationship used by Ogata was as follows:

$$\frac{\delta C}{\delta t} = \frac{D_x \delta^2 C}{R_F \delta x^2} - \frac{V_x \delta C}{R_F \delta x} \qquad (6.1)$$

where:

$$R_F = 1 + \frac{\rho_b}{\theta} K_d \qquad (2.3)$$

With the initial and boundary conditions described below:

C(z,0) = 0
C(0,t) = Co
C(∞,t) = 0

The solution of Eq (6.1) with the above mentioned initial and boundary conditions is as follows:

$$C(x,t)=\frac{C_o}{2}\left\{erfc\left(\frac{R_F x-V_w t}{2(DR_F t)^{\frac{1}{2}}}\right)+\exp\left(\frac{V_w x}{D}\right)erfc\left(\frac{R_F x+V_w t}{2(DR_F t)^{\frac{1}{2}}}\right)\right\} \tag{6.2}$$

where $erfc(x)$is the complementary error function which is defined as:

$$erfc(x)=1-\frac{2}{\sqrt{\Pi}}\int_0^x e^{-\phi^2}d\phi \tag{6.3}$$

which can be approximated by the following equation (Kreyszig, 1988):

$$erfc(x)=1-\left\{\frac{2}{\sqrt{\Pi}}\left(x-\frac{x^3}{1!3}+\frac{x^5}{2!5}-\frac{x^7}{3!7}+-\ldots\right)\right\} \tag{6.4}$$

for x values equal to or greather than 3, the following seires is used (Peirce, 1957):

$$erfc(x)=\frac{e^{-x^2}}{x\sqrt{\Pi}}\left\{1-\frac{1}{2x^2}+\frac{1\times 3}{(2x^2)^2}-\frac{1\times 3\times 5}{(2x^2)^3}+-\ldots\right\} \tag{6.5}$$

In order to evaluate the reliability of the DID2XY model the problem described in Figure 6.2 was modelled using both the analytical and the numerical models. Concentrations at different points and time were calculated.

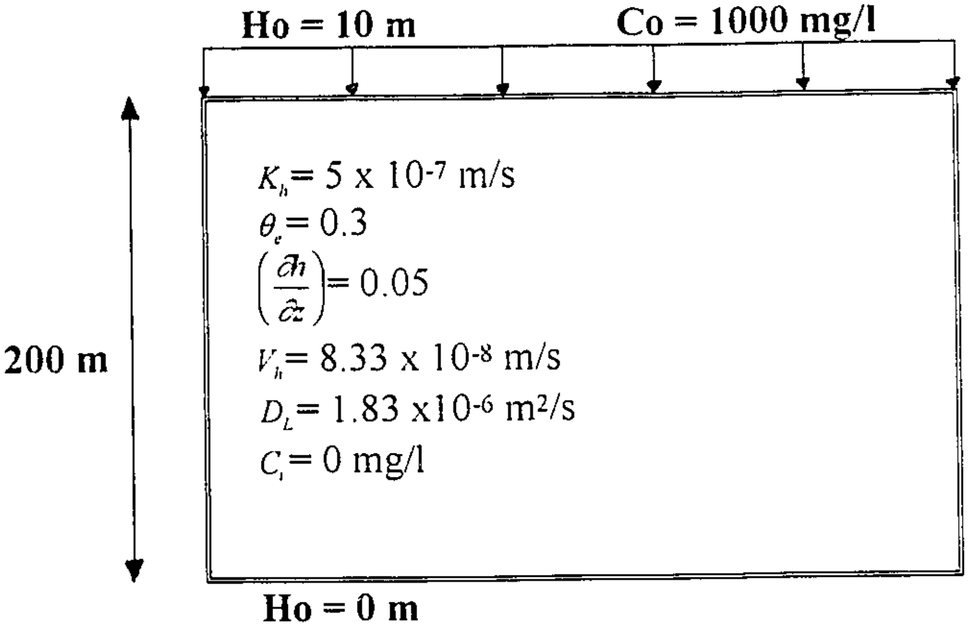

Figure 6.2: **Problem Geometry Initial and Boundary Conditions**

According to the initial and boundary conditions of the chosen problem, as shown in Figure 6.2, there are concentration and hydraulic gradients only in the vertical direction. Therefore, although the problem is presented in two dimensions, the solution is one dimensional. The soil parameters used in this example were the one obtained from the Locksley Marshland soil, as presented in Chapter 5.

The results obtained by the analytical solution and the two-dimensional numerical (DID2XY) solution related to concentration distribution after 10 years for a retardation factor (R_F) of 1 and 5 are shown in Table 6.1. A graphical comparison of the results produced by the analytical solution and the numerical model is presented in Figure 6.3.

TABLE 6.1
Analytical and Numerical Solution of Contaminant Concentration After 10 Years

Distance from the Source (m)	Retardation factor $R_F = 1$		Retardation factor $R_F = 5$	
	Analytical Sol. (mg/L)	DID2XY Sol. (mg/L)	Analytical Sol. (mg/L)	DID2XY Sol. (mg/L)
0	1000	1000	1000	1000
10	909.31	907.5	626.44	617
20	788.75	784.9	286.44	292.8
30	648.11	643.2	91.94	110
40	501.54	497.5	20.21	33.9
50	363.78	362.4	2.93	8.8
60	246.39	248.4	0.29	1.9
70	155.34	160.3	0.02	0.4
80	90.95	97.5	0	0.07
90	49.33	55.9	0	0
100	23.06	30.4	0	0
110	11.50	15.6	0	0
120	4.93	7.6	0	0
130	1.95	3.5	0	0
140	0.71	1.5	0	0
150	0.23	0.7	0	0
160	0.07	0.3	0	0
170	0.02	0.1	0	0
180	0.005	0.04	0	0
190	0	0	0	0
200	0	0	0	0

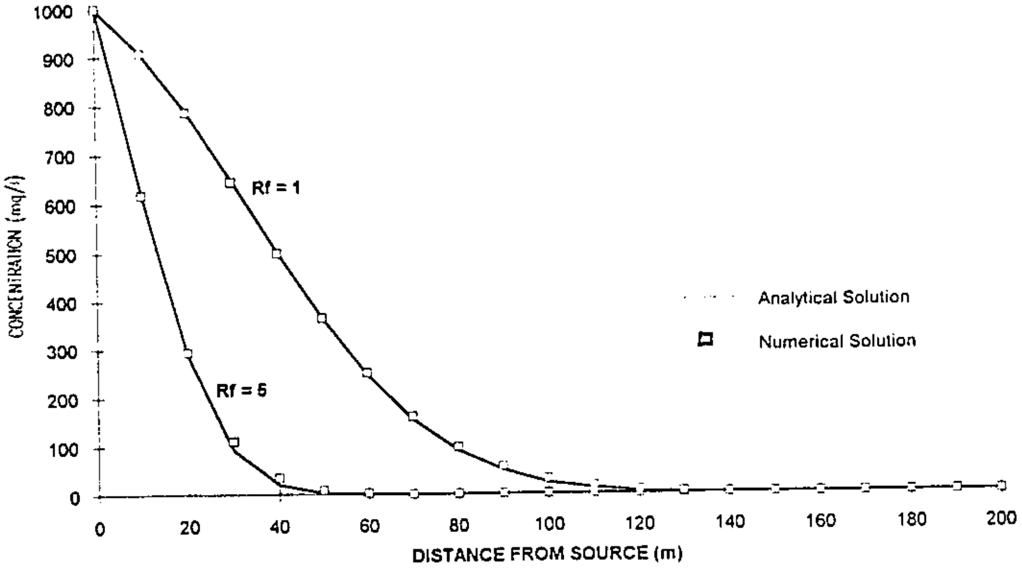

Figure 6.3: Comparison of Numerical (DID2XY) and Analytical Solutions

Comparing the analytical solution with the numerical solution obtained with DID2XY shown in Figure 6.3, it can be argued that the numerical model used can provide predictions that are reliable, at least for simple field situation as the one depicted above.

It is important to stress that the validation of the DID2XY model was achieved for a 1 dimensional situation. However, for the purpose at hand, which is the migration potential within the soil matrix of a marshland, this approach is deemed acceptable since longitudinal flow will be prevalent in such environment.

Having established the validity of both the FLOWPATH and DID2XY models through literature review and simple mathematical comparison, an attempt will now be made at modelling the Locksley Marshland. The methodology used to evaluate the migration potential of several contaminants presently being leached in the marshland are detailed in the following sections.

6.3 MODELLING OF THE LOCKSLEY MARSHLAND

6.3.1 General

Contaminant transport modelling within the Locksley Marshland was achieved using both the FLOWPATH and DID2XY models previously described. The FLOWPATH model was initially used to define the hydraulic head distribution throughout the marshland boundaries while the DID2XY model was used to calculate the velocity distribution and concentration variation as a function of both time and space.

Parameters needed for modelling were gathered when possible from both field and laboratory analysis of the Locksley marshland, or based on literature derived values as presented in Chapter 5. These parameters were used as initial input values for both the FLOWPATH and the DID2XY models. Figure 6.4 illustrates the process for a two-dimensional simulation of flow and contaminant mass transport.

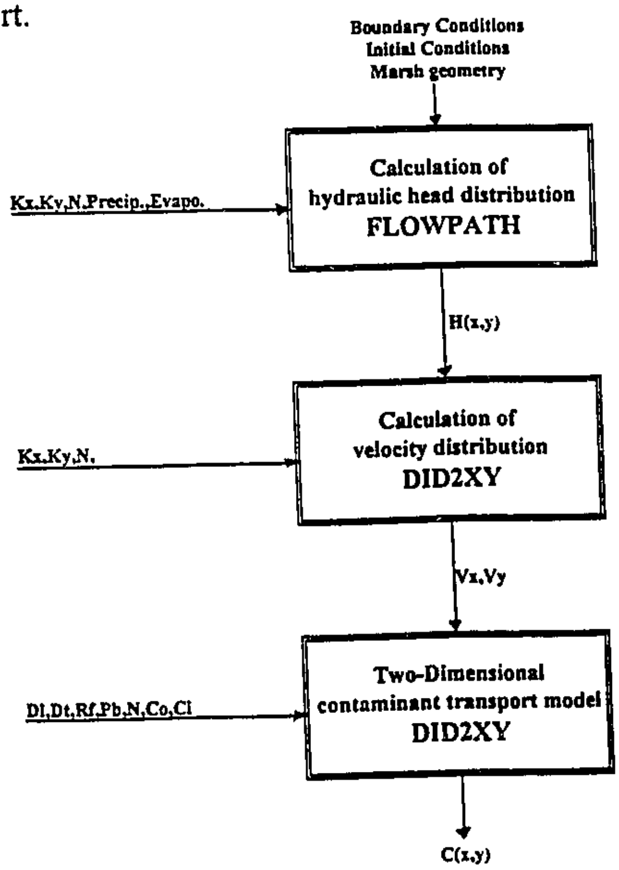

Figure 6.4: Flow Chart of theLocksley Marshland Model

6.3.2 Hydraulic Head Distribution Modelling

6.3.2.1 Grid Design and Boundary Conditions

In order to accurately simulate the subsurface water flow pattern within the Locksley marshland system, the FLOWPATH model was designed in such a way as to correctly reproduce the geometrical and boundary conditions of the system. To achieve this, the grid design was constructed to reproduce the aerial configuration of the marshland as well as the variable topographical relief. Figure 6.5 presents the section of the Locksley marshland that is under study with some surface elevation as determined by field investigations.

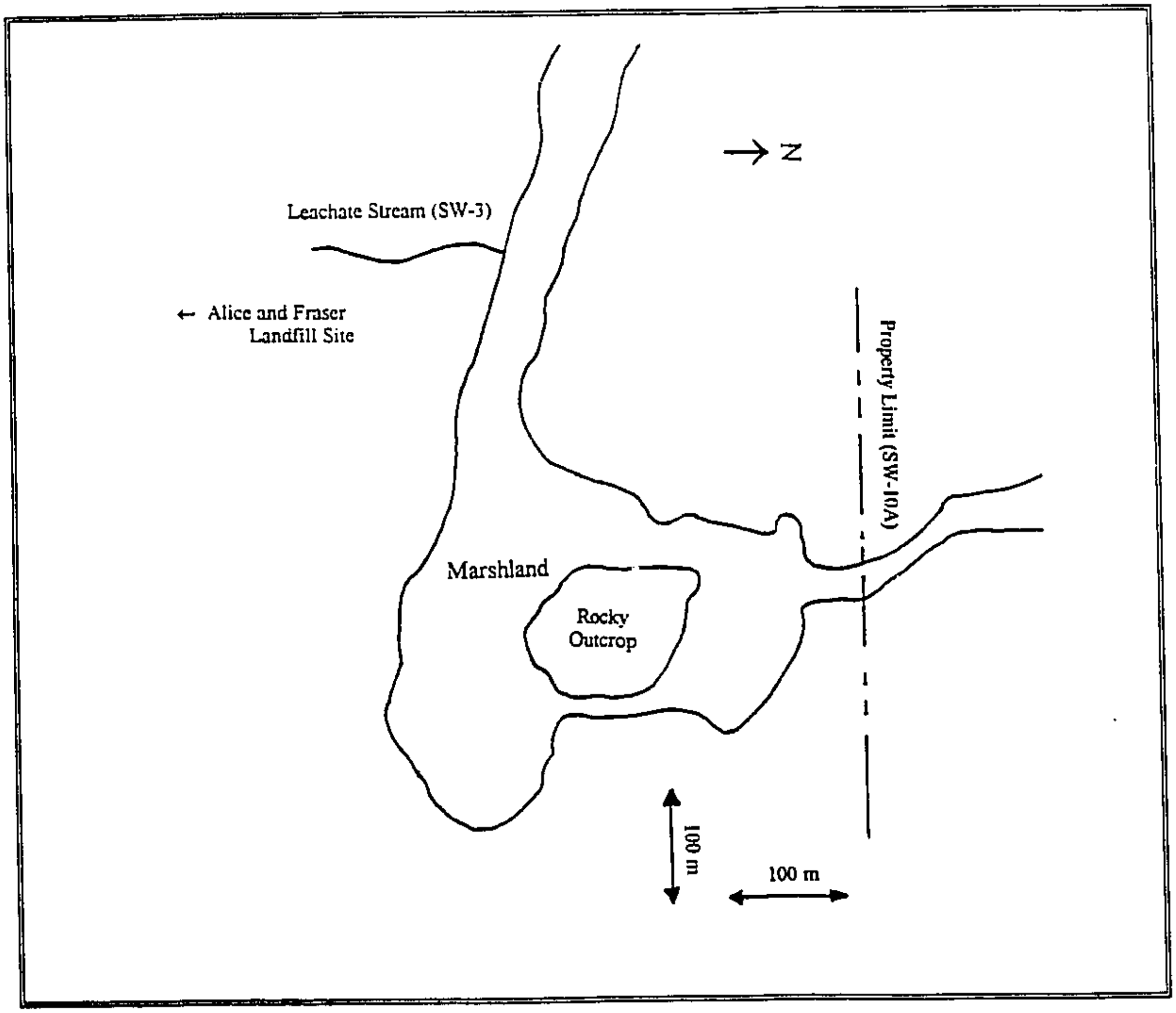

Figure 6.5 Configuration of the Locksley Marshland System

The grid network constructed to simulate the Locksley marshland presented in Figure 6.5 consisted of over 500 cells the majority of them having dimensions of 13 m x 13 m. The model covers an area of 67 700 m^2. Constant head boundaries were assumed at both the western and northern limits of the marshland, while the perimeter of the marsh was simulated by an impermeable boundary, since no groundwater flux is assumed to enter the system. This assumption is based on the very low hydraulic conductivity of the organic soil deposit covering the bottom of the marshland. For modelling purposes, it was assumed that the water table was located at the surface, which is typically the case at most wetland sites. The resulting grid network is presented in Figure 6.6.

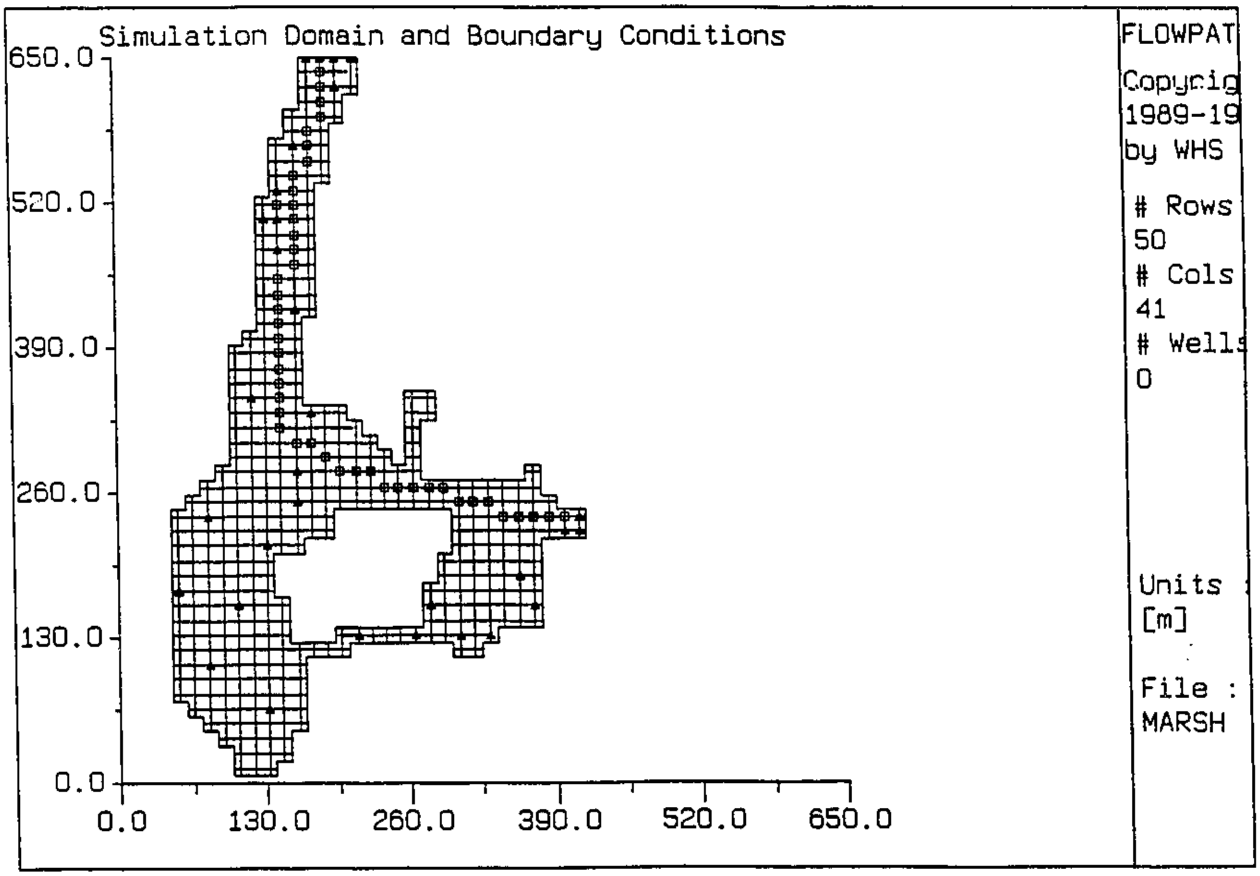

Figure 6.6: **FLOWPATH's Grid Network Representing the Locksley Marshland System**

6.3.2.2 Surface water and Groundwater Recharge

The interaction between surface water features and groundwater can be a dominant characteristic in wetland hydrology. Data on the surface water drainage pattern for the Locksley marshland was gathered through field investigation and aerial photography. Two weirs were constructed within the marshland to add additional information on the flow rate within some of the main channels of the marsh.

Analysis on the thickness and permeability of the organic soil deposit found at the Locksley marshland site, indicates that the deposit acts as a relatively impermeable layer which severely limits groundwater recharge in the marsh system. It was therefore concluded that most of the water entering the marshland originates from surface drainage of the adjoining watershed.

In the FLOWPATH simulation model, the interaction of subsurface water and surface water is modelled using the principle of a leaky aquifer. With this approach it is possible to account for the fluid flux between the marshland channel and the underlying organic soil deposit. The position of the channels in the wetland were estimated based on aerial photography, and a typical water depth of 0.3 m has been measured by probing inspection.

Monthly temperature and precipitation data spanning the last 20 years are available for the Locksley marshland site, and are presented in Table 6.2. An average annual synthetically generated precipitation of 770 mm with a standard deviation of 12% has been measured. The resulting annual groundwater recharge rate amounts to approximately 190 mm/year, which represents 25 % of the total precipitation. The remaining 75 % is accounted for in evapotranspiration (50%) and runoff (25%).

TABLE 6.2
Temperature and Precipitation Data for the Locksley Marshland Site

Month	Total Precipitation (millimetres)	Temperature (°C)
January	48.3	-11.8
February	44.7	-10.5
March	43.4	-3.6
April	57.4	5.2
May	61.8	12.3
June	80.5	17.6
July	64.8	20.2
August	77.1	19
September	87.6	14.2
October	68	7.9
November	65.9	0.8
December	70.8	-8.5
Mean Annual	**770**	**5.2**

6.3.2.3 Hydraulic Conductivity and Porosity Distribution

For modelling purpose, it was assumed that both the hydraulic conductivity and porosity of the organic deposit remained constant laterally across the marshland. While it is true that a substantial decrease in both parameters is expected to occur as a function of depth within the organic soil deposit, it was decided to model only the upper 0.3 m of the deposit, where most of the subsurface water flow occurs, and where variation of both hydraulic conductivity and porosity tend to be minimal. As discussed in section 5.3 a hydraulic conductivity of 5×10^{-7} m/s and an effective porosity of 30% were assumed for modelling purposes.

6.3.2.4 FLOWPATH Simulation

Once all the parameters were inputted in the model, FLOWPATH was activated to calculate the hydraulic head distribution across the Locksley marshland site, assuming steady state condition. The hydraulic head distribution as calculated by FLOWPATH is presented in Figure 6.7 .

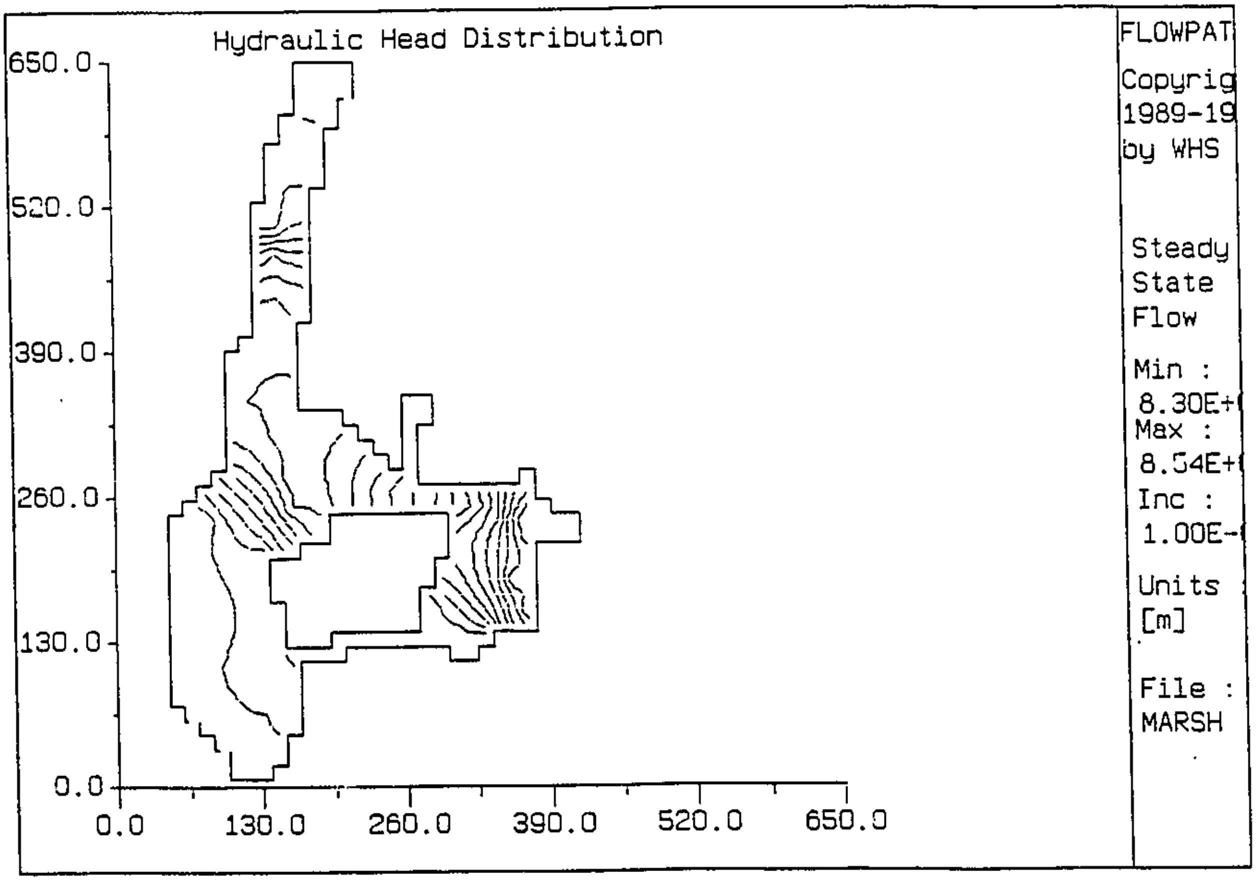

FIGURE 6.7 **Hydraulic Head Distribution Across the Locksley Marshland**

The FLOWPATH model was also used to provide a visual description of the subsurface water flow regime in the organic soil covering the marshland. In a steady-state flow field with no areally distributed recharge, pathlines coincide with streamline. In order to investigate the preferred transport pathways of contaminants in the marshland, a series of tracers were positioned along the transversal section of the marshland, corresponding at the main discharge area of the highly impacted surface stream (SW-3). The FLOWPATH model calculated the preferential transport paths of the subsurface water within the marshland system as presented in Figure 6.8.

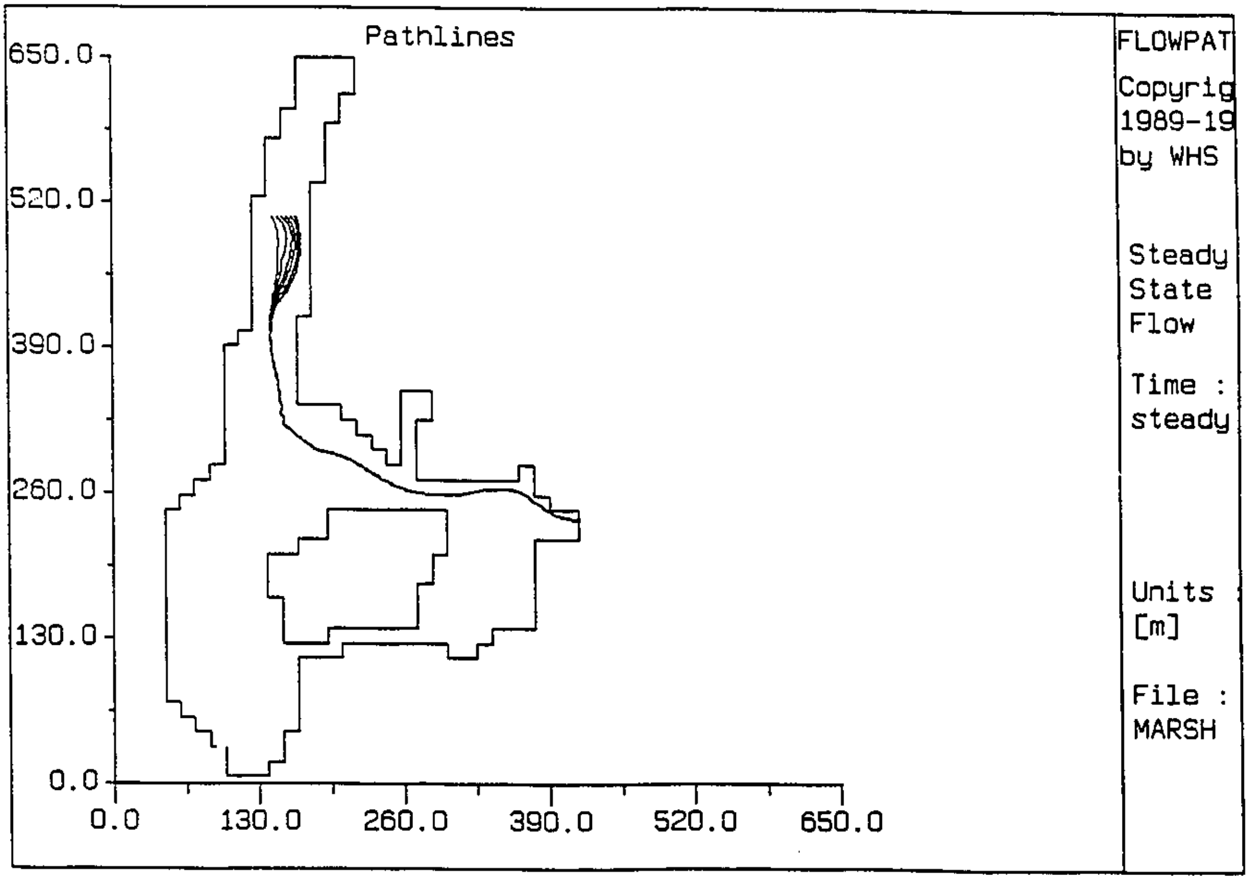

Figure 6.8: **Transportation Pathways of Contaminants Within the Locksley Marshland**

By superimposing Figures 6.7 and 6.8, the hydraulic head distribution along the main flowpath could thus be evaluated. The hydraulic head distribution between the main contaminant source and the property limits, as determined by FLOWPATH, is presented in Table 6.3.

TABLE 6.3
Hydraulic Head Distribution as a Function of the Distance from the Main Contaminant Source

Distance from Source (m)	Hydraulic Head as calculated from FLOWPATH (m)
0	85.30
30	84.95
60	84.80
90	84.68
120	84.63
150	84.60
180	84.58
210	84.55
240	84.53
270	84.50
300	84.40
330	84.30
360	84.20
390	84.05
420	83.90
450	83.70
480	83.40
510	83.10
540	82.90
570	82.70
600	82.20

FLOWPATH's output was then used as input for the DID2XY model for both the velocity and contaminant transport simulations to follow.

6.3.3 Contaminant Transport Modelling

6.3.3.1 General

Having established the hydraulic head distribution throughout the sector of the marshland under study, implementation of the DID2XY program was initiated to evaluate the migration potential of selected contaminants. The input data required by the computer program DID2XY for the prediction of solute transport are presented in Table 6.4.

TABLE 6.4
Input Data Required for
The DID2XY Numerical Model

	Input Parameter	Notation	Value
Soil and Media Characteristics	Hydraulic conductivity (m/s)	Kx, Ky	5.0 E -7
	Effective porosity	Ne	0.3
	Dry soil density (kg/m3)	Ps	450
	Hydrodynamic dispersion (m)	Dl, Dt	Sect. 5.4.6
	Distribution coefficient (ml/g)	Kp	Table 5.5
	Retardation factor	Rf	Table 5.5
Hydraulic Head Distribution	As determined from FLOWPATH (m)	H(i,j)	Table 6.2
Contaminant Concentration	Pollutant source concent. (mg/l)	Ci	Table 5.7
	Background concentration (mg/l)	Co	Table 5.6
Geometry	Source length (m)	Lenl	Table 5.1
	Marsh width (m)	Len	Table 5.1
	Marsh length (m)	Dep	Table 5.1
Matrix Dimension	X - direction (m)	Delx	Variable
	Y - direction (m)	Dely	Variable
Time Projection	Time step interval (s)	Delt	Variable
	Total time of projection (s)	Nts	Variable

6.3.3.2 Contaminant Migration Potential

The mobility of lead, zinc, calcium, sodium, chloride and pentachlorophenol was simulated with the DID2XY model. The initial and boundary conditions used in the analysis are shown in Figure 6.9.

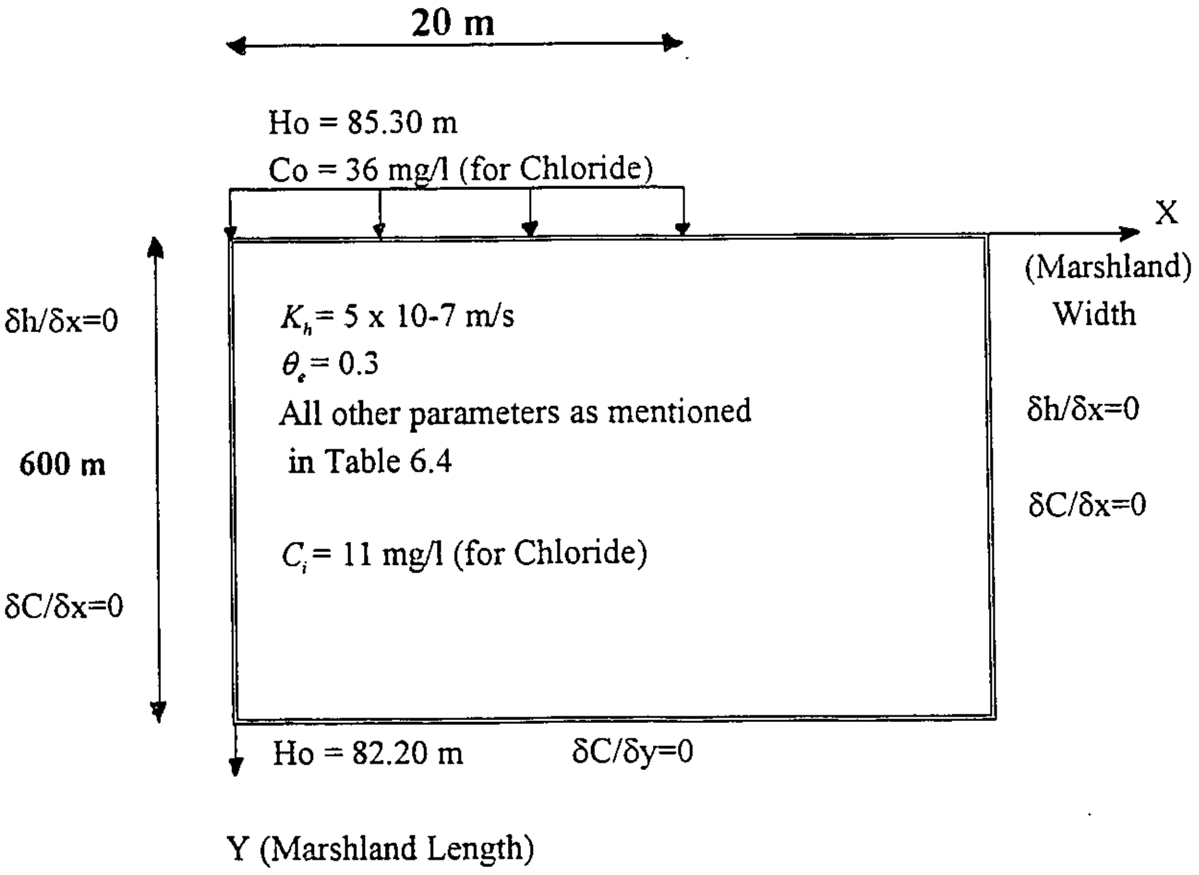

Figure 6.9: **Locksley Marshland Model Initial and Boundary Conditions**

In Figure 6.9 the Y-axis represents the length of the marshland along the main flow path as depicted in Figure 6.8, and the X-axis shows the average lateral width of the Locksley marshland. The origin has been chosen at the junction of the main surface impacted stream and the marshland. Contaminant concentration are kept constant at the upper boundary, simulating the continuous flow of the leachate stream.

6.3.3.3 Results and Discussion

The DID2XY model was used to simulate the migration potential of lead, zinc, sodium, chloride and pentachlorophenol within the subsurface water phase of the Locksley Marshland system. The analysis was performed to predict migration after 1, 10, 50 and 100 years. The DID2XY output file for chloride simulation after 1 year is shown in it's entirety in Appendix "H". The mobility of the contaminants is illustrated in the following figures, where the concentration contour lines are shown as a function of contaminant migration time.

The migration potential of chloride as a function of time (1, 50 and 100 years) is presented in Figures 6.10 to 6.12. The preceding figures illustrate the migration pattern of a non reactive contaminant. As shown of these figures, the migration potential of chloride is somewhat limited. Even after a period of 100 years, the migration front of chloride reached only a distance of approximately 260 m. This slow migration potential is directly related to the low hydraulic conductivity of the marshland soil media and the low hydraulic gradient observed within this segment of the marshland.

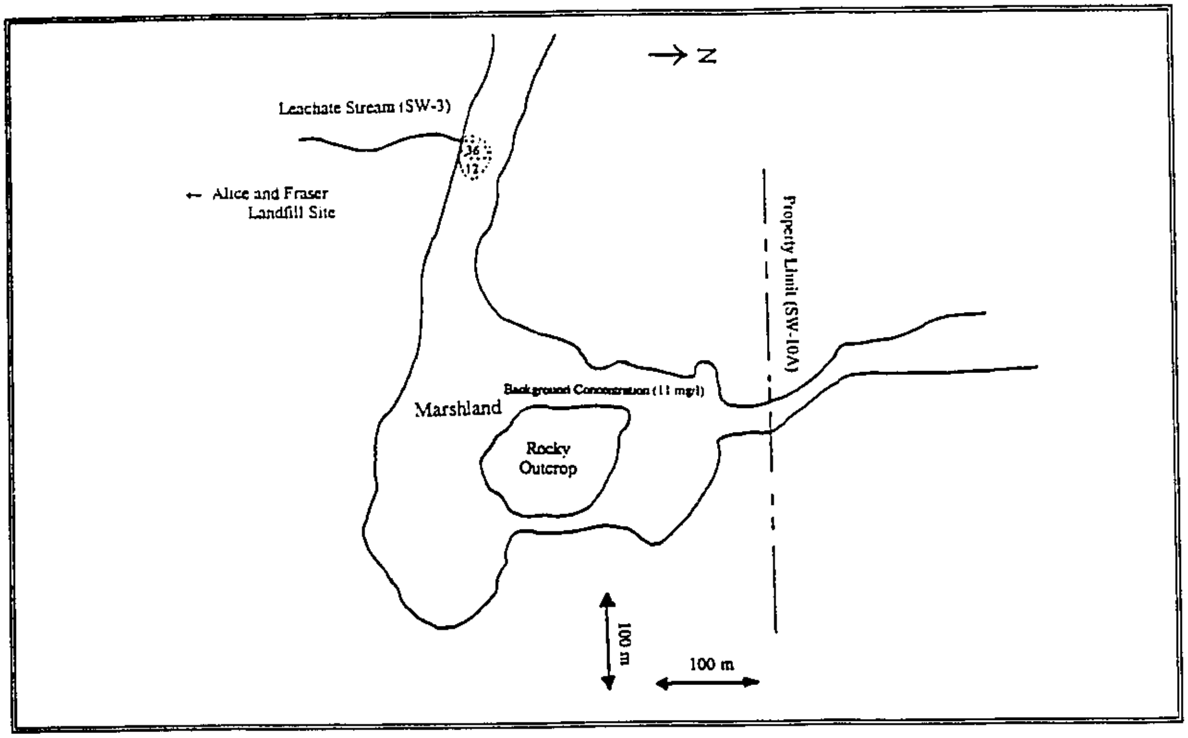

Figure 6.10: Concentration Contours (mg/l) for Chloride after 1 Year

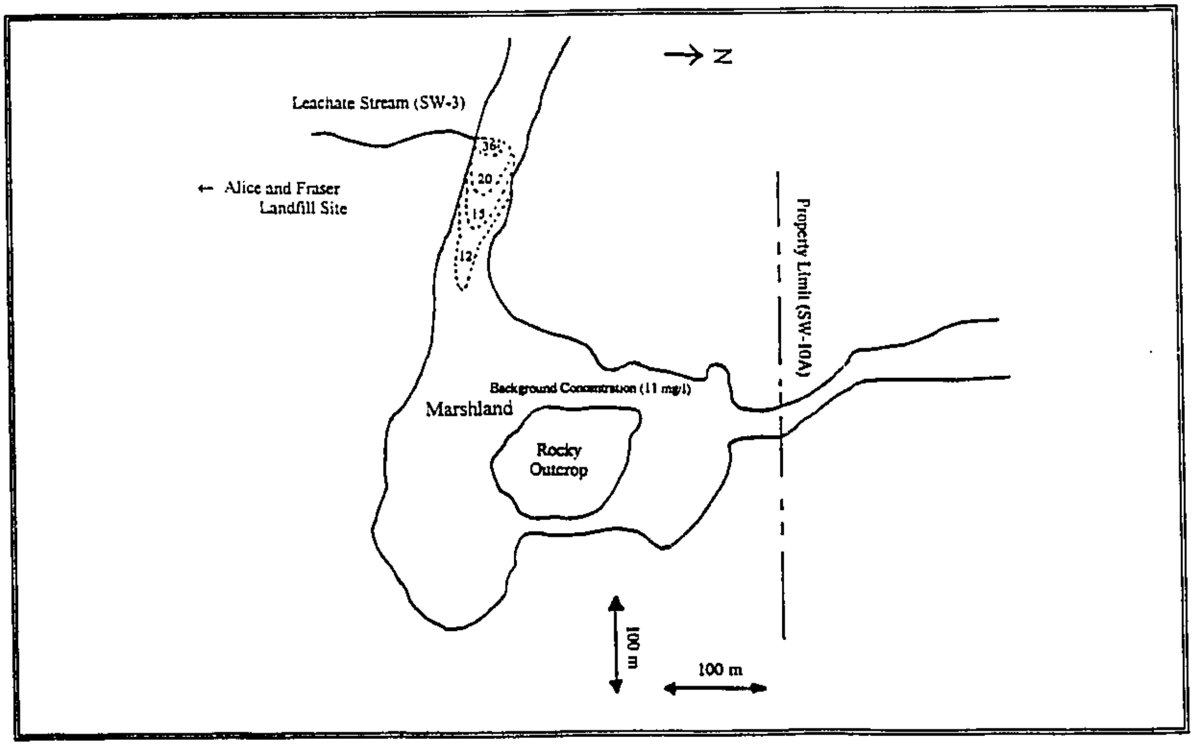

Figure 6.11: Concentration Contours (mg/l) for Chloride after 50 Years

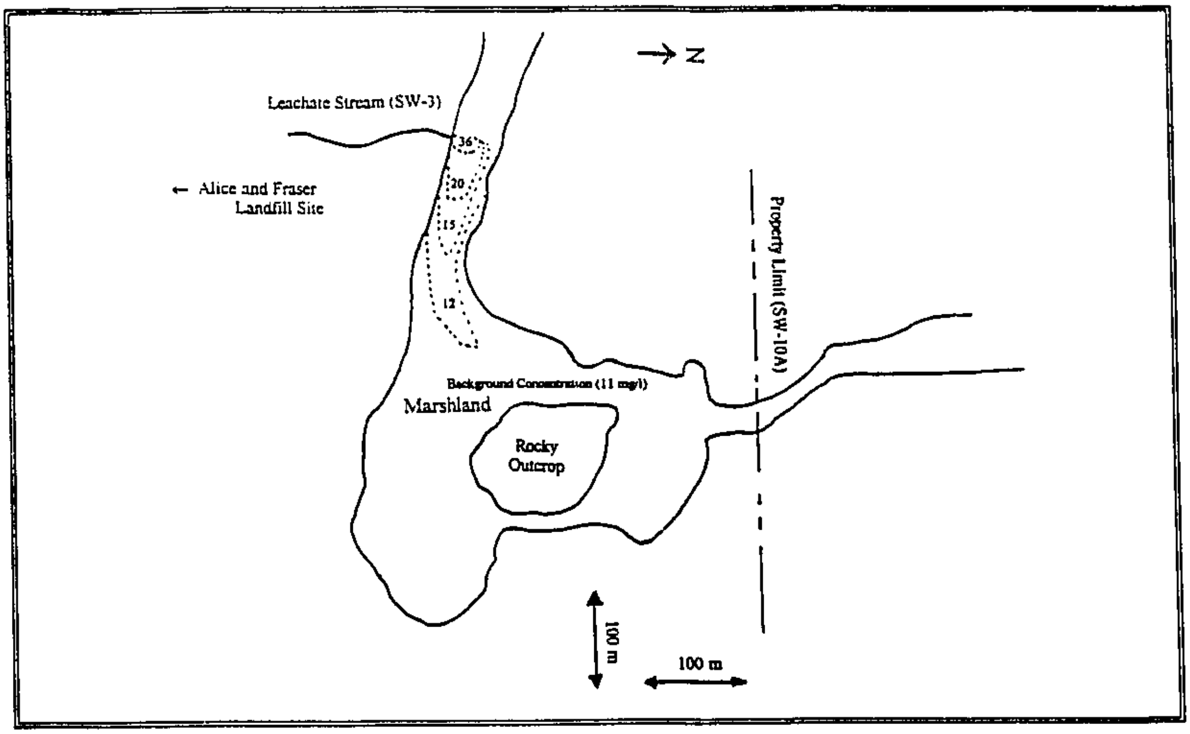

Figure 6.12: **Concentration Contours (mg/l) for Chloride after 100 Years**

The concentration contours for calcium and sodium for a time period of 100 years is presented in Figures 6.13 and 6.14 respectively. As can be seen in these figures, the migration potential is somewhat inferior to that of chloride. As previously detailed, a respective retardation factor of 1.2 and 2 was used to model calcium and sodium.

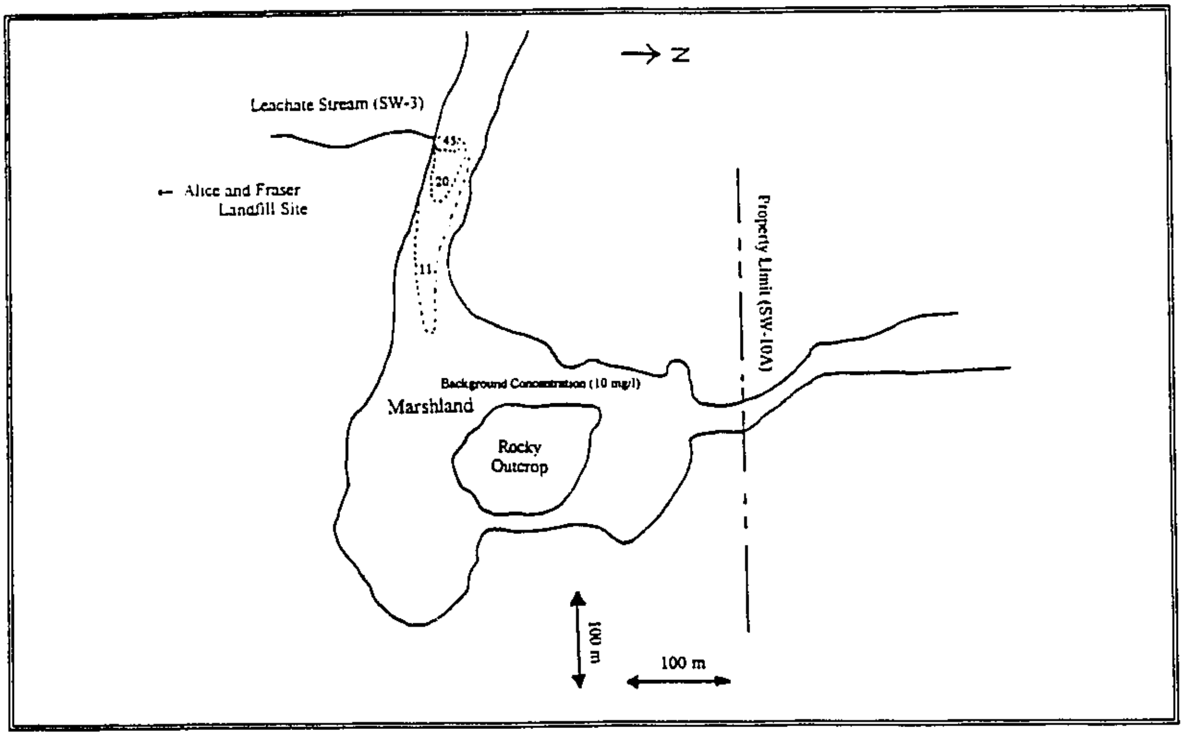

Figure 6.13: Concentration Contours (mg/l) for Calcium after 100 Years

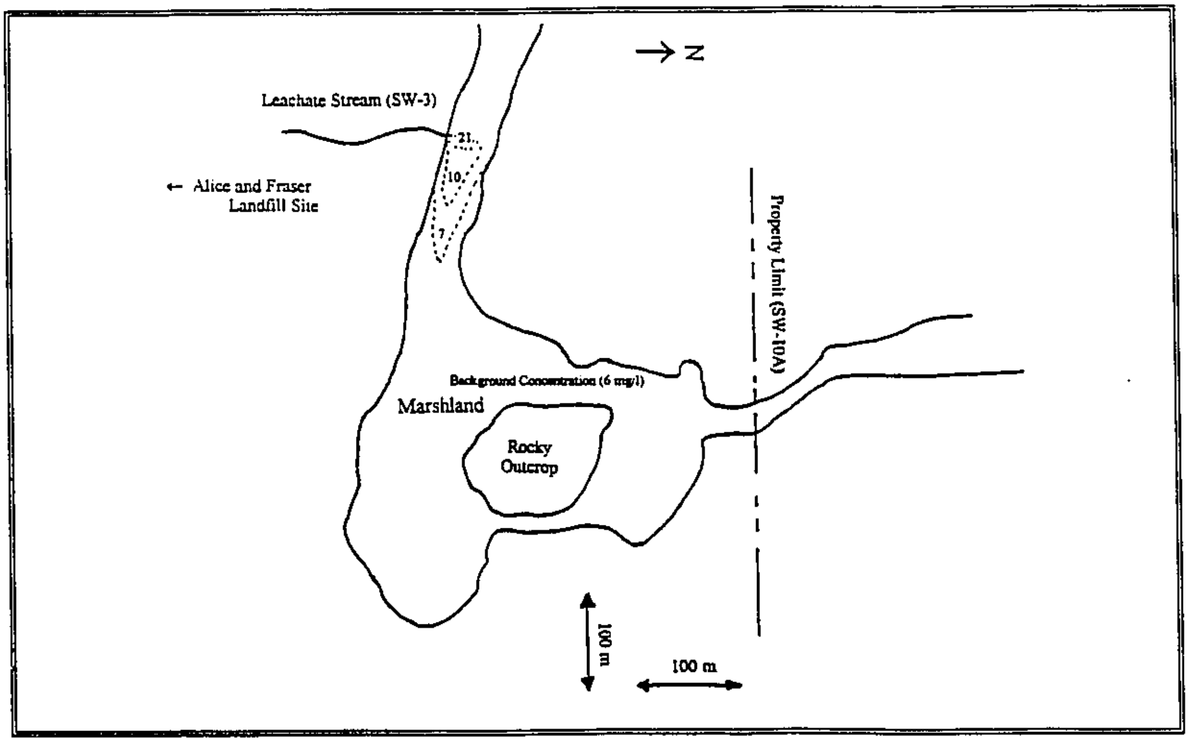

Figure 6.14: Concentration Contours (mg/l) for Sodium after 100 Years

Modelling results gathered for pentachlorophenol, zinc and lead indicate that these contaminant would be almost immobile within the water saturated phase of the organic soil. The high retardation factors of these contaminants associated with the low natural velocity of the subsurface water phase highly restrict their mobility to fractions of a metre per year.

The importance of the adsorption process in contaminant transport is clearly highlighted in Figures 6.10 to 6.14. In comparing the relative mobility of the contaminants investigated it is obvious that the attenuation capacity of a marshland soil is highly variable depending on the targeted contaminants. Referring to the same Figures, it may be concluded that the adsorption process could account for the observed contamination migration at the Locksley Marshland site.

6.4 SUMMARY

The two dimensional contaminant transport model DID2XY has been used to predict the mobility of chloride, calcium, sodium and pentachlorophenol in the Locksley Marshland system. The input data required for the predictions are detailed as is the methodology used. The results of the numerical model have been shown in the form of contour lines after 1, 10, 50 and 100 years of migration.

Results clearly indicates that the low velocity of the subsurface flow associated with the relatively high attenuation capacity of marshland soil effectively reduces the migration potential of several landfill based contaminants.

CHAPTER 7

CONCLUDING REMARKS AND SUGGESTION FOR FURTHER STUDIES

7.1 Conclusion

As the practice of using natural marshland systems, in remote locations, for the treatment of contaminated water increases in popularity, the need to fully understand the pollution attenuation processes and migration potential of these pollutants is becoming primordial. But the complex interactions between soil, plants and biological activity of such environment associated with an often ill defined hydrology severely challenges engineers and scientists in adequately forecasting the attenuation potential of natural marshlands. In recent year's, several mathematical model have been advanced to simulate contaminant migration within marshland systems, but they tend to be quite site specific and they rarely incorporate all possible flow paths endemic to marshland (groundwater, overland and channel flow).

This research focused on the Locksley marshland system, which is located near the city of Pembroke, in Eastern Ontario. Since the early 1980's, leachate originating from the Alice and Fraser municipal landfill has been discharging in a natural marshland system located some 300 meters downgradient from the waste disposal site. However, monitoring of the water quality within the marshland indicates that the contaminant level has not yet surpassed background concentration downstream from the main impact area. A mathematical model was developed in an attempt to predict the mobility of several contaminants species within the marshland environment. Parameters needed for the predictive model were gathered based on the physical configuration of the landfill and marshland associated with laboratory derived data on the attenuation capacity of the marshland soil matrix.

The behaviour, transport and ultimate fate of contaminants in organic soil is greatly affected by their participation in sorption reactions. The adsorption potential of lead, zinc, calcium, sodium and pentachlorophenol by marshland soil was evaluated in the laboratory through both, batch and column experiments. Most contaminants were found to fit either the Freundlich or Langmuir isotherm models. High retardation factors, exceeding 2000 for lead and approaching 100 for both zinc and PCP were measured, while a respective retardation factor of 1, 1.2 and 2.2 were observed for chloride, calcium and sodium. However, desorption experiments indicate that the adsorption process for certain compounds, such as PCP, can be partly reversible.

A two-dimensional finite-difference model based on the Advection-Dispersion Equation was used to predict the migration of the above mentioned contaminants. The model was adapted to the hydrologic characteristics of the marshland, emphasizing subsurface flow, dilution as well as the adsorption capacity of the organic soil. Initial modelling results indicate that marshland soil has the capacity to substantially retard the migration of several contaminant species typically found in landfill leachate. The predictive capacity of the model will eventually be evaluated based on the contaminant migration plume observed at the actual marshland site. Calibration of the model will undoubtedly be necessary to better reflect the complex reactions associated with marshland system.

7.2 Suggestion for Further Research

The following suggestions can be considered to extend the model in order to more adequately reflect the particular setting of the Locksley marshland.

1- The Locksley marshland is a dynamic system where 3 main flow paths (groundwater, overland and channel flow) act simultaneously and where each flow path vary in importance during the course of the year. A more detailed investigation of the Locksley marshland, where the surface hydrology could be quantified in greater detail would be required. Only when the system has been fully understood and that adequate water balance is available, one can contemplate the construction of an integrated model where all flow paths could be simultaneously modelled.

2- The hydrocarbon biodegredation potential of the marsh as well as plant uptake of various contaminants should be investigated by laboratory analysis, and the results should be incorporated in the above mentioned model.

3- Site evaluation of the hydraulic conductivity and effective porosity should be undertaken using tracer testing at the Locksley marshland.

4- Long term monitoring of the Alice and Fraser Landfill Site should be implemented to investigate any adverse effect on the fauna and biota of this marshland environment.

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APPENDIX A

BASIC GROUNDWATER EQUATION

A.1 Darcy's velocity

In order to properly evaluate the migration potential of contaminants at a particular site it is essential to properly understand the mathematical relationships that exist between the soil, water and contaminants phases.

Groundwater flow prediction began in a systematic way with Darcy's law in 1857. Darcy studied the movement of water through sand beds and found the flow rate to be proportional to the difference in head between the two ends of the bed. Darcy law is generally expressed as follows:

$$V = \frac{-K}{\theta_e}\left(\frac{\partial h}{\partial l}\right) \tag{A.1}$$

where: V = Pore velocity of groundwater (m/s)
K = Hydraulic conductivity (m/s)
θ_e = Effective porosity (unitless)
$\left(\frac{\partial h}{\partial l}\right)$ = Hydraulic gradient (m/m)

The negative sign in Darcy's law indicates that the flow is in the direction of decreasing hydraulic head. In equation (A.1) the hydraulic conductivity parameter (K) is a function of both the porous medium and the fluid passing through it. Tchobanoglous and Schroder (1987) expressed the hydraulic conductivity as follows:

$$K = Cd^2\left(\frac{\rho g}{\mu}\right) \tag{A.2}$$

where:
C = Pore space shape factor (unitless)
d = Mean pore diameter (m)
ρ = Density of the fluid (kg/m^3)
g = Acceleration of gravity (m/s^2)
μ = Dynamic viscosity of the fluid (kg/m·s)

The hydraulic conductivity can be measured in a variety of ways, including field and laboratory analysis and by empirical methods. Common field method for determining K include pumping test and single well response test, while laboratory measurement are usually conducted with permeameters. Based on a multitude of laboratory measurements of K, numerous attempts were made to relate the hydraulic conductivity to various properties of the porous medium, resulting in several empirical methods evaluating the hydraulic conductivity (Domenico and Schwartz, 1990).

The effective porosity (θ_e) described in equation (A.1), is the porosity available for fluid flow. In a porous media, not all pores will be available to transmit water, there may be both non-interconnected pores as well as dead-end pores, that will limit the groundwater flow. The effective porosity can be defined by the following equation (Fetter, 1988):

$$n_e = n \times epf \qquad \text{(A.3)}$$

where:
n = total porosity (unitless)
epf = Ratio of porosity available to flow to the total porosity

The Darcy velocity as expressed in equation (A.1) is a useful mean of obtaining an estimate of the rate of movement of a solute in flowing groundwater.

A.2 Contaminant migration within the groundwater

The movement of pollutants in the groundwater environment will be controlled primarily by the bulk motion of the fluid (advection) and by the hydrodynamic dispersion.

Advection is defined as the process by which moving groundwater carries with it dissolved solutes. In the absence of any other processes the migration of the contaminant will be equal to the average groundwater velocity as expressed by the Darcy velocity (Equation (A-1)).

In a homogeneous, isotropic aquifer, advection transport may be the dominant mechanism of migration if the velocity field is due to large gradient. The natural groundwater velocity in aquifers can vary over about five orders of magnitude, from a few centimetres per years to several thousands of meters per year based on the hydraulic gradient and the hydraulic conductivity of the aquifer. Clearly, a knowledge of the advective velocities is a critical factor in evaluation contaminant transport in groundwater (Ram et al., 1990).

For systems where the concentration may be changing with time, but where flow is at steady-state, the following differential equation may be applied:

$$\frac{\delta C}{\delta t} = -V_x \frac{\delta C}{\delta x} \tag{A.4}$$

A.3 Hydrodynamic dispersion

Dispersion is an irreversible process that causes a contaminant to occupy a larger volume of the porous medium than would be expected as a result of advection alone. As a contaminant zone is transported in a groundwater flow domain, the zone gradually spreads, occupying an ever increasing portion of the flow system with ever decreasing peak concentrations (Sudicky et al., 1983). This spreading phenomenon, called hydrodynamic dispersion, is caused by mechanical dispersion within the void spaces of the porous medium and by molecular diffusion that results from concentration gradient.

Mechanical dispersion is caused by fluid velocity variation along the tortuous interstitial flow path in the void space of the porous media. The mixing that occurs along the streamline of fluid flow is called longitudinal dispersion while lateral dispersions is caused by mixing that occurs normal to the pathway of fluid flow. Fetter (1988) identifies three basic causes of longitudinal dispersion as shown on Figure A.1.

(1) A fluid move faster through the centre of the pore than along the edges.

(2) The travel path length of the fluid will vary within the soil.

(3) Fluid will travel at a faster rate through larger pores.

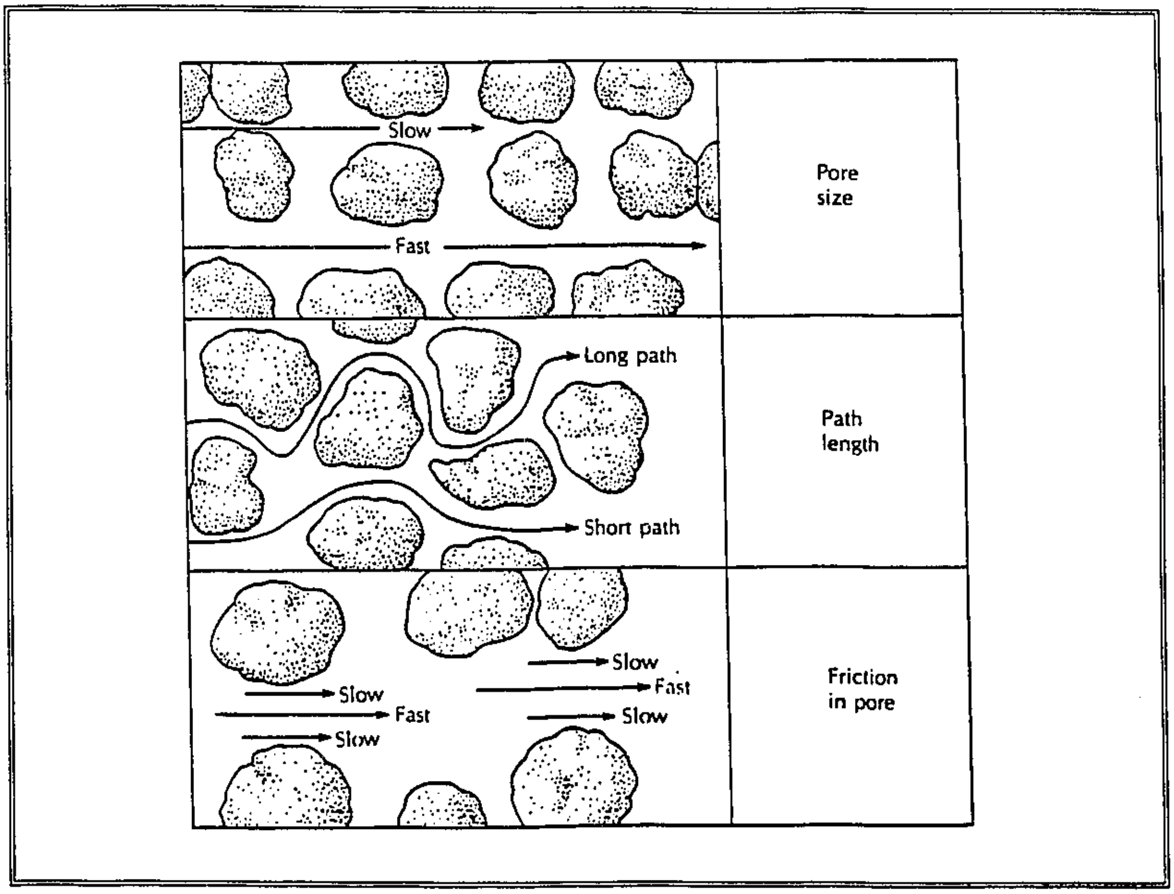


Figure A.1: **Factors Causing Longitudinal Dispersion**

Lateral dispersion is caused by the splitting and branching out of the contaminated fluid through a porous medium as presented in Figure A.2.

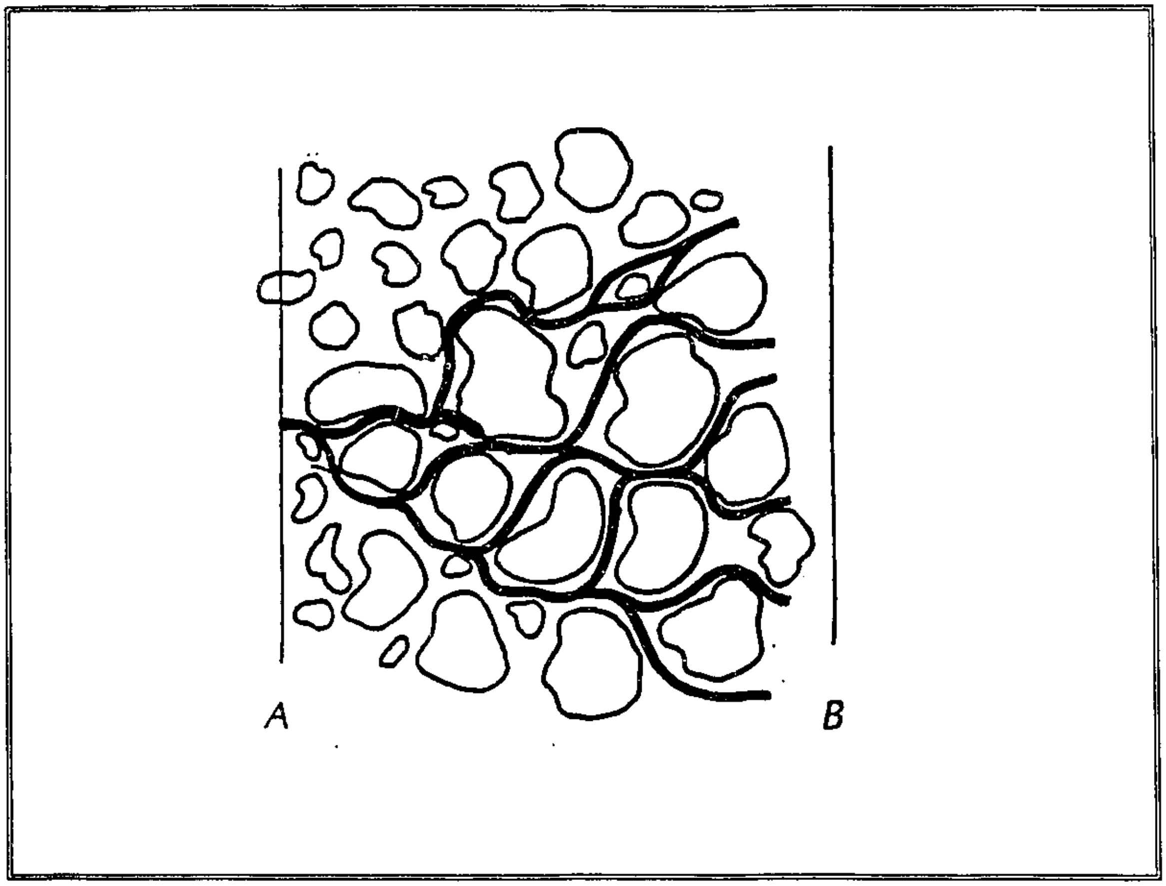


Figure A.2: **Lateral Hydrodynamic Dispersion**

The mechanical dispersion due to the above mentioned factors can be expressed as follows:

$$\text{mechanical dispersion} = a_L V_x \tag{A.5}$$

Where : a_L = Dynamic dispersivity coefficient (m)
V_x = Average linear groundwater velocity (m/s)

Molecular diffusion on the other hand is a physico-chemical phenomenon by which ionic and molecular species dissolved in water move from areas of higher concentration to areas of lower concentration. The movement of contaminant by diffusion through water is generally described by Fick's law:

$$F = -D\frac{\delta C}{\delta x} \tag{A.6}$$

Where :

F = Mass flux of solute per unit area per unit of time
D = Diffusion coefficient (area/time)
C = Solute concentration (mass/volume)
$\frac{\delta C}{\delta x}$ = Concentration gradient (mass/volume/distance)

In porous media, diffusion cannot proceed as fast as it can in water because the ions must follow longer pathways as they travel around mineral grains (Fetter, 1988). In order to incorporate this phenomena, several authors (Fetter, 1988; Domenico and Schwartz, 1990) use an effective diffusion coefficient defined as D^*.

$$D^* = w \times D \tag{A.7}$$

Where :

w = Empirical coefficient (unitless)
D = Diffusion coefficient of species in water only (m^2/s)

In flowing groundwater the processes of molecular diffusion and mechanical dispersion cannot be separated. It is therefore necessary to introduce an inclusive factor called the coefficient of hydrodynamic dispersion D_L. The coefficient of hydrodynamic dispersion D_L is represented by combining equation (A.6) and (A.7), giving:

$$D_L = a_L V_x + D^* \tag{A.8}$$

A.4 The Advection-Dispersion Equation (ADE)

In the previous sub-sections, both phenomena of advection and hydrodynamic dispersion have been introduced to better understand the migration process of contaminant within groundwater system. Both processes are known to act simultaneously to transport and spread the contaminants. Superimposing the dispersion process to the advection equation produces the well known Advection-Dispersion Equation for one-dimensional groundwater flow and solute transport in a homogeneous isotropic medium:

$$\frac{\delta C}{\delta t} = D_L \frac{\delta^2 C}{\delta x^2} - V_x \frac{\delta C}{\delta x} \tag{A.9}$$

It is apparent that at very low velocities, the mixing process is dominated by molecular diffusion, while at high velocities the mixing is dominated by mechanical dispersion processes.

The ADE has been used to predict concentration profiles, C(x) for given t; or curves, C(t) for given x; in a multitude of laboratory and field experiments. The experimental results and predictions of the model were generally in good agreement where the targeted contaminant was conservative.

Contaminants can be considered in two broad classes; conservative and reactive. Solutes that do not react with the soil and/or native groundwater are categorized as being conservative. On the other hand reactive substances can undergo chemical, physical, biological or radioactive change that will tend to reduce the overall concentration of the solute.

The ADE model as described in Equation (A.9) has been found to overestimate the migration potential of reactive substances. To better reflect the particular transformation occurring during the transport process a sink term was introduced in the ADE:

$$\frac{\delta C}{\delta t} = \frac{\delta}{\delta x}\left\{ D_L \frac{\delta C}{\delta x} \right\} - V_x \frac{\delta C}{\delta x} - G \tag{A.10}$$

where : G: Represent the sink term

The overall consequence of the sink term is to account for retardation of the contaminant compared to the groundwater flow. This retardation phenomenon is described in greater details in section 2.3.2.

APPENDIX B

DATA FROM BATCH ADSORPTION EXPERIMENTS

B-1: HEAVY METALS

B-2:CATIONS AND ANIONS

B-3: PENTACHLOROPHENOL

APPENDIX B-1

HEAVY METALS

LEAD AND ZINC

ADSORPTION ISOTERM ANALYSIS
HEAVY METAL SOLUTION

DATE	MASS OF ORGANIC SOIL	TIME OF CONTACT	ICP TEST (PPM)							
									Average	
			Ca	Mg	Mn	Na	Pb	Zn	Pb	Zn
Aug-91	0.5 gr	1 hour	23.9	3.3	0.4	2.1	8.9	81.7	7.65	78.4
	0.5 gr (Duplicate)	1 hour	25.1	3.4	0.4	2.7	6.4	75.1		
	1 gr	1 hour	36.2	6.0	0.7	1.8	2.3	55.6	1.8	53.8
	1gr (Duplicate)	1 hour	36.4	6	0.7	3.4	1.8	53.3		
	1 gr	24 hours	38.2	6.2	0.8	2	1.3	52.5		
	2 gr	1 hour	47.1	9.6	0.9	2.5	0.9	29.3	0.76	29.9
	2gr (Duplicate)	1 hour	44.1	9	0.9	2.4	0.9	34.2		
	2gr	24 hours	49.6	10.1	1	2.2	0.5	26.3		
	4 gr	1 hour	52.2	13.5	1	4	1.3	12.8	0.7	12.3
	4gr (Duplicate)	1 hour	56.3	14.4	1.2	4.1	0.5	13.8		
	4 gr	24 hours	54.2	14.1	1	3.3	0.3	10.4		
	Control solution	1 hour	1	0.1	0	0.9	91.3	96.1	95	97.8
	Heavy Metal Solution		0.3	0.1	0	0.8	98.6	99.4		

ADSORPTION PARAMETERS FOR THE FREUNDLICK AND LANGMUIR ISOTHERMS

LEAD ANALYSIS

Co (mg/l)	Ce (mg/l)	x (mg/l)	x (mg)	m (g)	(x/m) (mg/g)	Ce/(x/m) (g/l)
95	7.65	87.35	8.735	0.5	17.1	0.438
95	1.8	93.2	9.32	1	9.1	0.193
95	0.76	94.24	9.424	2	5.1	0.161
95	0.7	94.3	9.43	4	2.1	0.297

Where: Co = Initial concentration in solution (ppm)
Ce = Concentration of material being adsorbed remaining in solution at equilibrium (mg/l)
x = Mass of material adsorbed on solid phase (mg/l)
m = Mass of solid on which adsorption is taking place (g)

FREUNDLICH ISOTHERM COEFFICIENT

1/N=SLOPE = (log10.1 - log1.1)/(log3 - log.13) = 0.706 When X/M = 1.1 mg/g, Ce = 0.13 mg/l

Kf = (x/m)/CeY(1/n) = 1.1/(0.13 Y(.706)= 4.65

(x/m)=4.65 Ce Y(0.706)

LANGMUIR ISOTHERM COEFFICIENT

1/a = slope = (0.45-0.15) / (7.3-0) = 0.041 a = 24.3

1/(ab)=0.124 b = 0.332

(x/m) = abCe/(1+bCe)

ADSORPTION PARAMETERS FOR THE FREUNDLICK AND LANGMUIR ISOTHERMS

ZINC ANALYSIS

Co (mg/l)	Ce (mg/l)	x (mg/l)	x (mg)	m (g)	(x/m) (mg/g)	Ce/(x/m) (g/l)
97.8	78.4	19.4	1.94	0.50	3.88	20.206
97.8	53.8	44	4.4	1.00	4.40	12.227
97.8	29.9	67.9	6.79	2.00	3.40	8.807
97.8	12.3	85.5	8.55	4.00	2.14	5.754

Where: Co = Initial concentration in solution (ppm)
Ce = Concentration of material being adsorbed remaining in solution at equilibrium (mg/l)
x = Mass of material adsorbed on solid phase (mg/l)
m = Mass of solid on which adsorption is taking place (g)

FREUNDLICH ISOTHERM COEFFICIENT

1/N=SLOPE = (log5.1 - log1.1)/(log80 - log2.4) = 0.437

When X/M = 1.1 mg/g, Ce = 2.4 mg/

Kf = (x/m)/CeY(1/n) = 1.1/2.4Y(0.437) = 0.75

(x/m)=0.75 CeY(0.437)

LANGMUIR ISOTHERM COEFFICIENT

1/a = slope = (18-3) / (80-0) = 0.1875

a = 5.33

1/(ab) = 3.6

b = 0.052

(x/m) = abCe/(1+bCe)

APPENDIX B-2

CATIONS AND ANIONS

CALCIUM, SODIUM AND CHLORIDE

ADSORPTION ISOTERM ANALYSIS CHLORIDE SOLUTION (Na AND Ca)

DATE	MASS OF ORGANIC SOIL	TIME OF CONTACT	ICP TEST (PPM)							
									Average	
			Ca	Mg	Mn	Na	Pb	Zn	Ca	Na
Aug-91	0.5 gr	1 hour	90.2	3.1	0.4	92.8	0.1	0.2	91.1	94.7
	0.5 gr (Duplicate)	1 hour	91.9	3.2	0.4	96.6	0.1	0.1		
	1 gr	1 hour	87.5	5.5	0.6	91.4	0.1	0.7	88.2	92.5
	1gr (Duplicate)	1 hour	89.8	5.7	0.6	93	0.1	0.1		
	1 gr	24 hours	87.4	5.6	0.6	93	0.1	0.1		
	2 gr	1 hour	87	9.5	0.8	92.9	0.1	0.1	87.2	94.6
	2gr (Duplicate)	1 hour	89.2	9.6	0.8	93.9	0.1	0.1		
	2gr	24 hours	85.5	9.6	0.8	97	0.1	0.1		
	4 gr	1 hour	85.3	14.5	1	93.2	0.1	0.1	84.9	93.9
	4gr (Duplicate)	1 hour	86.1	14.6	1	94	0.1	0.1		
	4 gr	24 hours	83.5	14.5	1	94.4	0.1	0.1		
	Control solution	1 hour	97.1	0.1	0	99	0	0	98.1	98.7
	Chloride solution		99.1	0	0	98.3	0.1	0.1		

ADSORPTION PARAMETERS FOR THE FREUNDLICK AND LANGMUIR ISOTHERMS

CALCIUM ANALYSIS

Co (mg/l)	Ce (mg/l)	x (mg/l)	x (mg)	m (g)	(x/m) (mg/g)	Ce/(x/m) (g/l)
98.1	91.1	7	0.70	0.50	1.40	65.071
98.1	88.2	9.9	0.99	1.00	0.99	89.091
98.1	87.2	10.9	1.09	2.00	0.55	160.000
98.1	84.9	13.2	1.32	4.00	0.33	257.273

Where: Co = Initial concentration in solution (ppm)
Ce = Concentration of material being adsorbed remaining in solution at equilibrium (mg/l)
x = Mass of material adsorbed on solid phase (mg/l)
m = Mass of solid on which adsorption is taking place (g)

FREUNDLICH ISOTHERM COEFFICIENT

1/N=SLOPE = (log1.4 - log0.33)/(log91-log84.9) = 20.5 When X/M = 0.1 mg/g, Ce = 80 mg/l

Kf = (x/m)/CeY(1/n) = 0.1/80Y(20.5) = 9.5 E -41

(x/m) = 9.5 E -41 Ce Y(20.5)

LANGMUIR ISOTHERM COEFFICIENT

Slope is negative so the langmuir isotherm is inappropriate.

ADSORPTION PARAMETERS FOR THE FREUNDLICK AND LANGMUIR ISOTHERMS

SODIUM ANALYSIS

Co (mg/l)	Ce (mg/l)	x (mg/l)	x (mg)	m (g)	(x/m) (mg/g)	Ce/(x/m) (g/l)
98.7	94.7	4	0.40	0.50	0.80	118.375
98.7	92.5	6.2	0.62	1.00	0.62	149.194
98.7	94.6	4.1	0.41	2.00	0.21	461.463
98.7	93.9	4.8	0.48	4.00	0.12	782.500

Where: Co = Initial concentration in solution (ppm)
Ce = Concentration of material being adsorbed remaining in solution at equilibrium (mg/l)
x = Mass of material adsorbed on solid phase (mg/l)
m = Mass of solid on which adsorption is taking place (g)

FREUNDLICH ISOTHERM COEFFICIENT

1/N=SLOPE (log.8 - log.12)/(log94.7 - log93.9) = 223 When X/M = 0.1 mg/g, Ce = 90 mg/l

Kf = (x/m)/CeY(1/n) = 0.1/90Y(223) = K tends to 0

LANGMUIR ISOTHERM COEFFICIENT

Slope is negative so the langmuir isotherm is inappropriate.

APPENDIX B-3

PENTACHLOROPHENOL

ADSORPTION ISOTERM ANALYSIS

PENTACHLOROPHENOL SOLUTION

DATE	MASS OF ORGANIC SOIL	TIME OF CONTACT	pH	HPLC ANALYSYS PENTACHLOROPHENOL CONCENTRATION (ppm)	
				readings	average
Jan-92	0.5 gr	1 hour	6.6	5.7	5.5
	0.5 gr	1 hour	7.5*	5.6	
	0.5 gr (Duplicate)	1 hour	6.6	5.5	
	0.5 gr	24 hours		5.3	
Jan-92	1 gr	1 hour		2.4	2.7
	1gr (Duplicate)	1 hour		3.2	
	1 gr	24 hours		2.6	
Jan-92	2 gr	1 hour		1.3	1.2
	2gr (Duplicate)	1 hour		1.3	
	2gr	24 hours		0.9	
Jan-92	4 gr	1 hour		0.5	0.45
	4gr (Duplicate)	1 hour		0.4	
	4 gr	24 hours		--	
Jan-92	8 gr	1 hour		--	--
	8 gr (Duplicate)	1 hour		--	
	8 gr	24 hours		--	
Jan-92	Control Solution	1 hour		9.5	9.7
	Control Solution	24 hours		10.4	
	Pentachl. Solution			9.3	

Note: * pH adjusted chemically

-- Concentration in the vecinity of 0 ppm

ADSORPTION ISOTERM ANALYSIS

PENTACHLOROPHENOL SOLUTION

DATE	MASS OF ORGANIC SOIL	TIME OF CONTACT	pH	HPLC ANALYSYS PENTACHLOROPHENOL CONCENTRATION (ppm)	
				readings	average
Mar-92	0.25 gr	24 hours		5.78	6.015
	0.25 gr (duplicate)	24 hours		6.25	
	0.5 gr	24 hours		4.73	4.825
	0.5 gr (Duplicate)	24 hours		4.92	
	1 gr	1 hour		3.34	2.475
	1 gr	12		2.6	
	1 gr	24 hours		2.47	
	1gr (Duplicate)	24 hours		2.48	
	1 gr	36		2.43	
	1 gr	48 hours		2.4	
	2 gr	24 hours		1.21	1.185
	2gr (Duplicate)	24 hours		1.16	
	4 gr	24 hours		0.37	0.395
	4gr (Duplicate)	24 hours		0.42	
	Control Solution	24 hours		8.03	8.11
	Pentachl. Solution			8.19	

ADSORPTION PARAMETERS FOR THE FREUNDLICK AND LANGMUIR ISOTHERMS

PENTACHLOROPHENOL ANALYSIS

Co (mg/l)	Ce (mg/l)	x (mg/l)	x (mg)	m (g)	(x/m) (mg/g)	Ce/(x/m) (g/l)
8.11	6.015	2.095	0.2095	0.25	0.838	7.178
8.11	4.83	3.28	0.328	0.5	0.656	7.363
8.11	2.48	5.63	0.563	1	0.563	4.405
8.11	1.19	6.92	0.692	2	0.346	3.439
8.11	0.4	7.71	0.771	4	0.193	2.075

Where: Co = Initial concentration in solution (ppm)
Ce = Concentration of material being adsorbed remaining in solution at equilibrium (mg/l)
x = Mass of material adsorbed on solid phase (mg/l)
m = Mass of solid on which adsorption is taking place (g)

FREUNDLICH ISOTHERM COEFFICIENT

1/N=SLOPE = (log1 - log.1)/(log9 - log0.09) = 0.5 When X/M = 0.1 mg/g, Ce = 0.09 mg/l

Kf = (x/m)/CeY(1/n) = 0.1/0.09Y(0.5) = 0.333

(x/m)=0.333 CeY(0.5)

LANGMUIR ISOTHERM COEFFICIENT

1/a = slope = (8-1.8) / (5.5-0) = 1.127 a = 0.887

1/(ab) = 1.8 b = 0.626

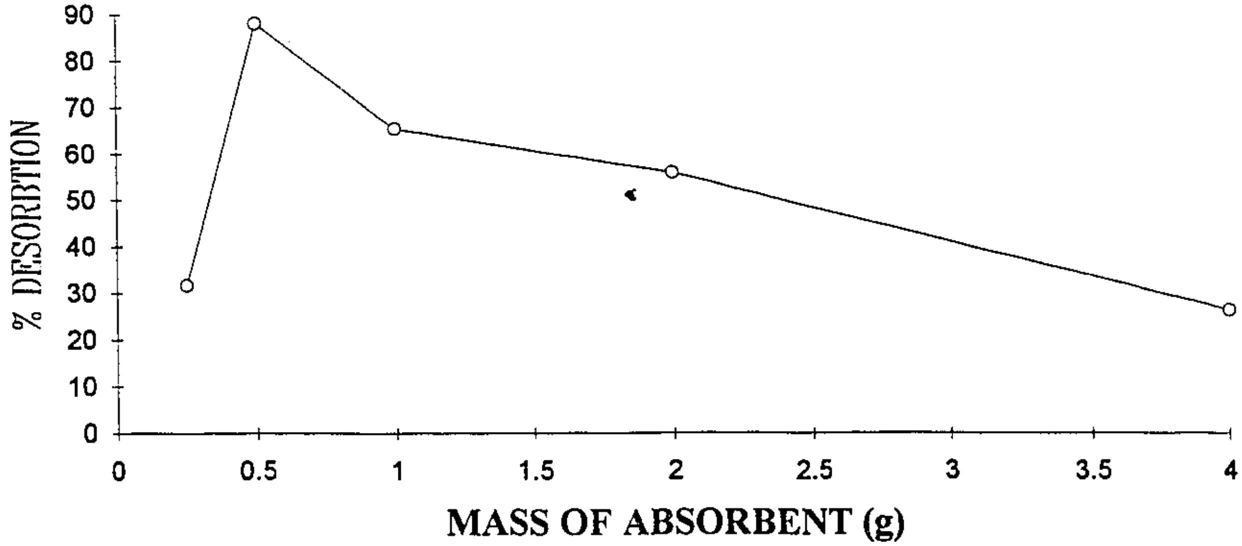
(x/m) = abCe/(1+bCe)

DESORPTION ISOTERM ANALYSIS

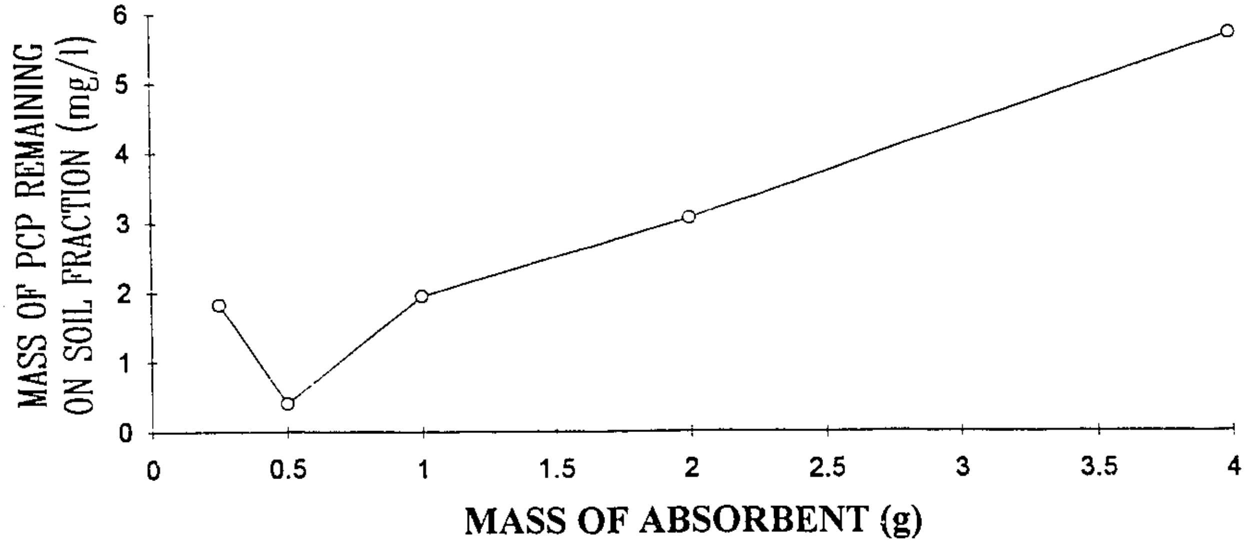
PENTACHLOROPHENOL SOLUTION

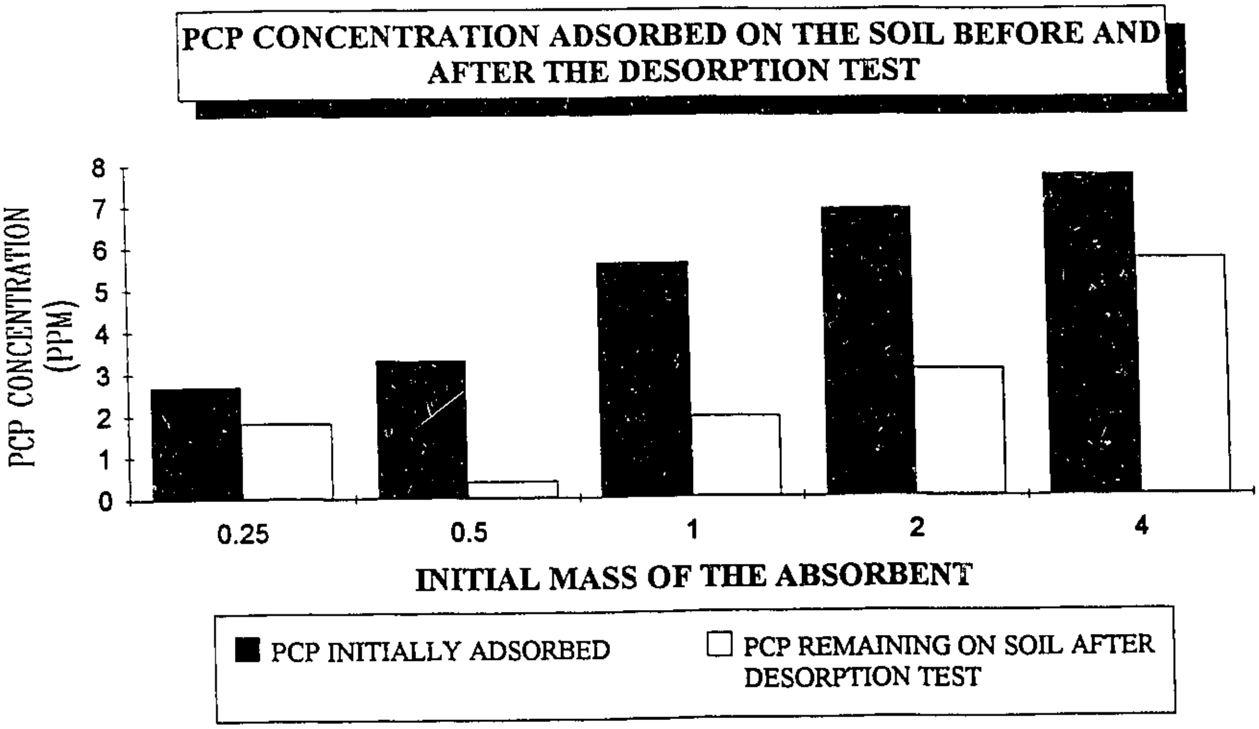
DATE	MASS OF ORGANIC SOIL	AMOUNT INITIALY ADSORBED (PPM)		DESORPTION						
				FIRST STAGE		SECOND. STAGE		REMAINING		% DESORBED
Mar-92	0.25 gr	2.33		0.45		0		1.88		19.31
	0.25 gr (duplicate)	3.14		1.38		0		1.76		43.95
	0.5 gr	3.38		2.31		0.59		0.48		85.80
	0.5 gr (Duplicate)	3.19		2.25		0.62		0.32		89.97
	1 gr	5.64		2.73		1.32		1.59		71.81
	1gr (Duplicate)	5.63		3.02		0.31		2.30		59.15
	2 gr	6.9		2.28		1.7		2.92		57.68
	2gr (Duplicate)	6.95		2.1		1.66		3.19		54.10
	4 gr	7.74		0.86		1.1		5.78		25.32
	4gr (Duplicate)	7.69		0.88		1.22		5.59		27.31

PLOT OF THE % DESORBTION OF PCP VERSUS MASS OF ABSORBENT



PLOT OF THE MASS OF PCP REMAINING OF THE SOIL VERSUS THE MASS OF ABSORBENT





PCP CONCENTRATION ADSORBED ON THE SOIL BEFORE AND AFTER THE DESORPTION TEST

APPENDIX C

CALCULATION OF THE MINIMUM DETECTION LIMIT AND THE ERROR ON "S" FOR THE SORPTION ISOTHERM EXPERIMENTS

C.1 General

For the sorption experiments (Beaudet, 1994) the amount of contaminant sorbed to the marshland soil was calculated from the difference between the initial and the equilibrium concentrations according to :

$$S = \frac{(C_o - C_e) \times V}{M} \tag{C-1}$$

where: C_o = Initial contaminant concentration
C_e = Final equilibrium contaminant concentration
V = Volume of solution in hypovials
M = Mass of marshland soil

Since S is calculated from a combination of variables, each with a different error, the error on S must also be calculated from a combination of the errors on the variables that comprise S. The variances can be combined according to the rules described by Kretz (1985). If, for example, a variable y is a function of three variables, x1, x2 and x3 then the variance of y can be calculated by:

$$\mathrm{var}(y) = \mathrm{var}(x1)(\partial y/\partial x2)^2 + \mathrm{var}(x2)(\partial y/\partial x2)^2 + \mathrm{var}(x3)(\partial y/\partial x3)^2 \tag{C-2}$$

Applying these rules to S, with the additional rule that:

$$\mathrm{var}(A \pm B) = \mathrm{var}(A) + \mathrm{var}(B), \tag{C-3}$$

we get (C-4):

$$\mathrm{var}(\mathrm{S}) = \left(\mathrm{var}(\mathrm{C_o}) + \mathrm{var}(\mathrm{C_e})\right)(V/M)^2 + \left((C_o - C_e)/M^2\right)\mathrm{var}(V) + \left((C_o - C_e)/M^4\right)\mathrm{var}(M)$$

and assuming a constant coefficient of variability (cv) for the concentration measurements, we have:

$$\mathrm{var}(\mathrm{C_o}) = (C_o \times cv)^2 \text{ and } \mathrm{var}(\mathrm{C_e}) = (C_e \times cv)^2 \qquad \text{(C-5)}$$

hence:

$$\mathrm{var}(\mathrm{S}) = \left(C_o^2 + C_e^2\right)cv^2(V/M) + (C_o - C_e)/M^2\ \mathrm{var}(V) + (C_o - C_e)/M^4\ \mathrm{var}(M) \qquad \text{(C-6)}$$

The variances of the hypovial volume and of the mass of marshland soil are small relative to that of the squared concentrations, and therefore the first term dominates the equation. Based on the first term, it is clear that the variance of S is proportional to the sum of the squared concentrations (assuming a constant cv) and therefore the variance or the error on S increases rapidly with concentration.

Since S is based on the difference between two concentrations, these two concentrations have to be significantly different from one another for S to be significantly different than zero. The value of S where, C_e is significantly different from C_o at the 95% confidence level, is significantly different than zero when:

$$C_o - C_e \geq 2\left(\sigma_{C_o} + \sigma_{C_e}\right) \qquad \text{(C-7)}$$

or:

$$S = (C_o - C_e)V/M \geq 2\left(\sigma_{C_o} + \sigma_{C_e}\right)V/M \qquad \text{(C-8)}$$

If the coefficient of variability is constant over the range of $C_o - C_e$, then:

$$\sigma_{C_o} = cv \times C_o \text{ and } \sigma_{C_e} = cv \times C_e \qquad \text{(C-9)}$$

and therefore, S is significantly different than zero when:

$$S \geq 2cv(C_o - C_e)V/M \tag{C-10}$$

The cv, Co and V were more of less constant during the experiments; only m and Ce varied. It is clear from this formula that when m decreases and/or Ce increases the detection limit on S increases. In the sorption experiments, when the mass of marshland soil in the hypovials was small, little contaminants was sorbed and therefore Ce remained high and close to Co. The combined effect of the small mass M and the high equilibrium concentration, Ce, resulted in high detection limits.

Calculations of the coefficient of variability (cv) for ead, zinc, calcium, sodium and pentachlorophenol isotherms are presented in the following pages, associated with the calculations for the minimum detection limit for S. These calculations are graphically presented at the end of this appendix.

CALCULATION OF THE COEFFICIENT OF VARIABILITY (CV) BETWEEN ANALYSES

Lead

Mass of soil	Measured Standards (mg/L)	Average (mg/L)	(xi-X)^2	Sum (xi-X)^2/n-1	Std Deviation	CV (%)
0.5	8.9	7.650	1.563	3.125	1.768	23.108
0.5	6.4		1.563			
1	2.3	1.800	0.250	0.250	0.500	27.778
1	1.8		0.000			
1	1.3		0.250			
2	0.9	0.767	0.018	0.053	0.231	30.123
2	0.9		0.018			
2	0.5		0.071			
4	1.3	0.700	0.360	0.280	0.529	75.593
4	0.5		0.040			
4	0.3		0.160			
cont.	91.3	94.950	13.322	26.645	5.162	5.436
cont	98.6		13.323			

Average CV= **32.41**

Zinc

Mass of soil	Measured Standards (mg/L)	Average (mg/L)	(xi-X)^2	Sum (xi-X)^2/n-1	Std Deviation	CV (%)
0.5	81.7	78.400	10.890	21.780	4.667	5.953
0.5	75.1		10.890			
1	55.6	53.800	3.240	2.590	1.609	2.991
1	53.3		0.250			
1	52.5		1.690			
2	29.3	29.933	0.401	15.903	3.988	13.323
2	34.2		18.204			
2	26.3		13.201			
4	12.8	12.333	0.218	3.053	1.747	14.168
4	13.8		2.151			
4	10.4		3.738			
cont.	96.1	97.750	2.723	5.445	2.333	2.387
cont	99.4		2.723			

Average CV= **7.76**

CALCULATION OF THE COEFFICIENT OF VARIABILITY (CV) BETWEEN ANALYSES

Na

Mass of soil	Measured Standards (mg/L)	Average (mg/L)	(xi-X)^2	Sum (xi-X)^2/n-1	Std Deviation	CV (%)
0.5	92.8	94.700	3.610	7.220	2.687	2.837
0.5	96.6		3.610			
1	91.4	92.467	1.138	0.853	0.924	0.999
1	93		0.284			
1	93		0.284			
2	92.9	94.600	2.890	4.570	2.138	2.260
2	93.9		0.490			
2	97		5.760			
4	93.2	93.867	0.444	0.373	0.611	0.651
4	94		0.018			
4	94.4		0.284			
cont.	99	98.650	0.122	0.245	0.495	0.502
cont	98.3		0.123			

Average CV= **1.45**

Ca

Mass of soil	Measured Standards (mg/L)	Average (mg/L)	(xi-X)^2	Sum (xi-X)^2/n-1	Std Deviation	CV (%)
0.5	90.2	91.050	0.723	1.445	1.202	1.320
0.5	91.9		0.722			
1	87.5	88.233	0.538	1.843	1.358	1.539
1	89.8		2.454			
1	87.4		0.694			
2	87	87.233	0.054	3.463	1.861	2.133
2	89.2		3.868			
2	85.5		3.004			
4	85.3	84.967	0.111	1.773	1.332	1.567
4	86.1		1.284			
4	83.5		2.151			
cont.	97.1	98.100	1.000	2.000	1.414	1.442
cont	99.1		1.000			

Average CV= **1.60**

CALCULATION OF THE COEFFICIENT OF VARIABILITY (CV) BETWEEN ANALYSES

PCP

Mass of soil	Measured Standards (mg/L)	Average (mg/L)	(xi-X)^2	Sum (xi-X)^2/n-1	Std Deviation	CV (%)
0.25	5.78	6.015	0.055	0.1105	0.332	5.525
0.25	6.25		0.055			
0.5	4.73	4.825	0.009	0.0090	0.095	1.969
0.5	4.92		0.009			
1	2.47	2.445	0.001	0.0014	0.037	1.512
1	2.48		0.001			
1	2.43		0.000			
1	2.4		0.002			
2	1.21	1.185	0.001	0.0013	0.035	2.984
2	1.16		0.001			
4	0.37	0.395	0.001	0.0013	0.035	8.951
4	0.42		0.001			
cont	8.03	8.110	0.006	0.0128	0.113	1.395
cont	8.19		0.006			

Average CV= **3.72**

CALCULATION OF THE MINIMUM DETECTION LIMIT

Lead Stock solution: 94.95 mg/L

Sample	Measured Solution (L)	Mass of Soil (g)	Remaining Concent. (mg/L)	CV	S (mg/g)	Minimum Det. Limit (mg/g)
0.5	0.1	0.50	7.65	0.324	17.46	13.301
1	0.1	1.00	1.8	0.324	9.315	6.271
2	0.1	2.00	0.767	0.324	4.70915	3.102
4	0.1	4.00	0.7	0.324	2.35625	1.550

Zinc Stock solution: 97.75 mg/L

Sample	Measured Solution (L)	Mass of Soil (g)	Remaining Concent. (mg/L)	CV	S (mg/g)	Minimum Det. Limit (mg/g)
0.5	0.1	0.50	78.4	0.078	3.87	5.468
1	0.1	1.00	53.8	0.078	4.395	2.352
2	0.1	2.00	29.93	0.078	3.391	0.991
4	0.1	4.00	12.33	0.078	2.1355	0.427

Na Stock solution: 98.65 mg/L

Sample	Measured Solution (L)	Mass of Soil (g)	Remaining Concent. (mg/L)	CV	S (mg/g)	Minimum Det. Limit (mg/g)
0.5	0.1	0.50	94.7	0.015	0.79	1.121
1	0.1	1.00	92.47	0.015	0.618	0.554
2	0.1	2.00	94.6	0.015	0.2025	0.280
4	0.1	4.00	93.87	0.015	0.1195	0.140

Ca Stock solution: 98.1 mg/L

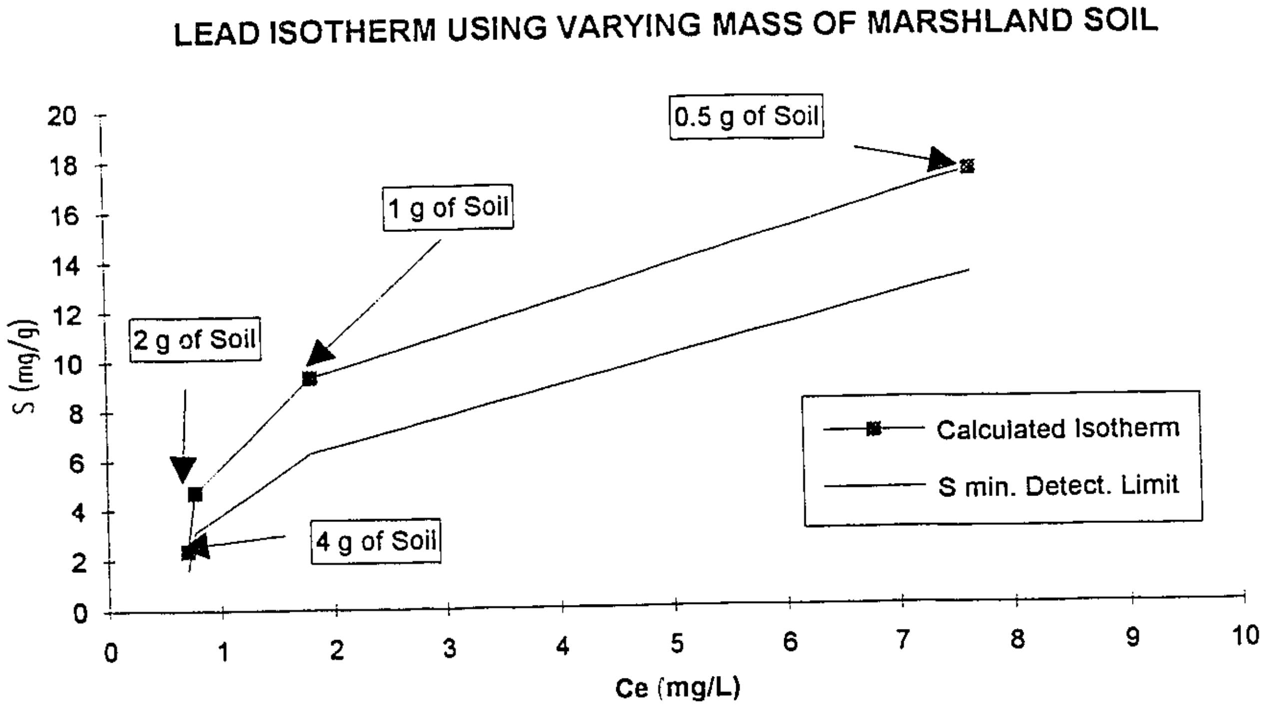
Sample	Measured Solution (L)	Mass of Soil (g)	Remaining Concent. (mg/L)	CV	S (mg/g)	Minimum Det. Limit (mg/g)
0.5	0.1	0.50	91.05	0.016	1.41	1.211
1	0.1	1.00	88.23	0.016	0.987	0.596
2	0.1	2.00	87.23	0.016	0.5435	0.297
4	0.1	4.00	84.97	0.016	0.32825	0.146

CALCULATION OF THE MINIMUM DETECTION LIMIT

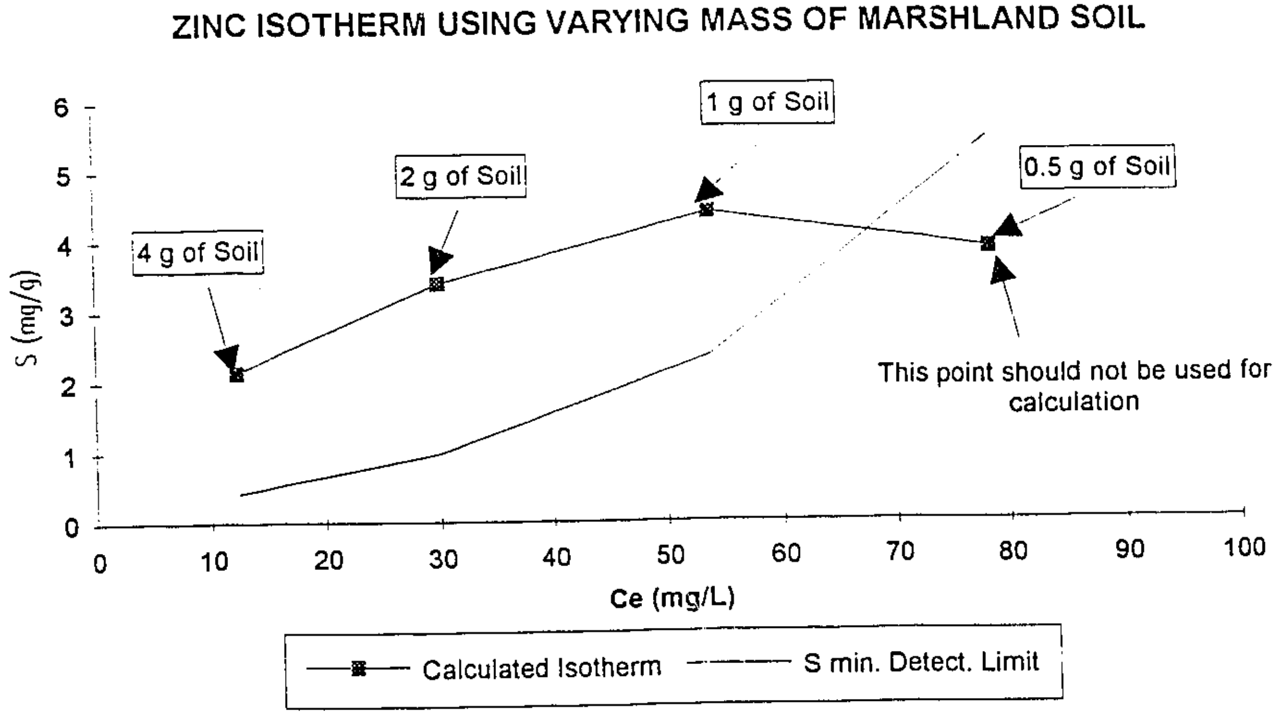
PCP

Stock solution: 8.11 mg/L

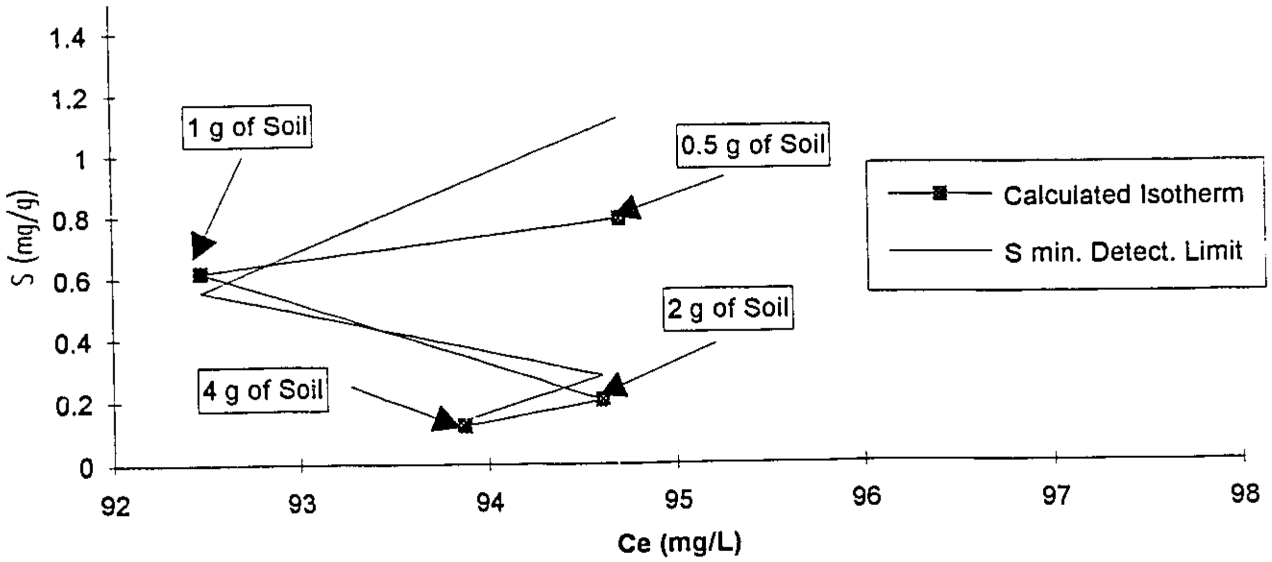
Sample	Measured Solution (L)	Mass of Soil (g)	Remaining Concent. (mg/L)	CV	S (mg/g)	Minimum Det. Limit (mg/g)
0.25	0.1	0.25	6.015	0.037	0.838	0.420
0.5	0.1	0.5	4.825	0.037	0.657	0.192
1	0.1	1	2.445	0.037	0.5665	0.079
2	0.1	2	1.185	0.037	0.34625	0.035
4	0.1	4	0.395	0.037	0.192875	0.016



LEAD ISOTHERM USING VARYING MASS OF MARSHLAND SOIL


ZINC ISOTHERM USING VARYING MASS OF MARSHLAND SOIL
S (mg/g)
6
5
4
3
2
1
0
0
10
20
30
40
50
60
70
80
90
100
Ce (mg/L)
4 g of Soil
2 g of Soil
1 g of Soil
0.5 g of Soil
This point should not be used for calculation
Calculated Isotherm
S min. Detect. Limit

SODIUM ISOTHERM USING VARYING MASS OF MARSHLAND SOIL



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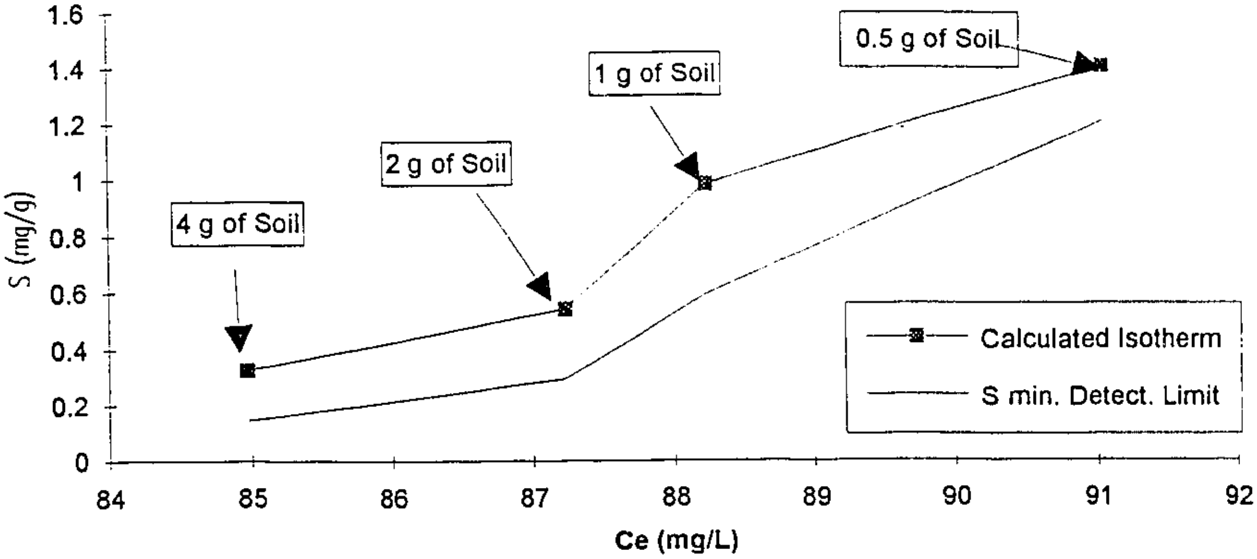

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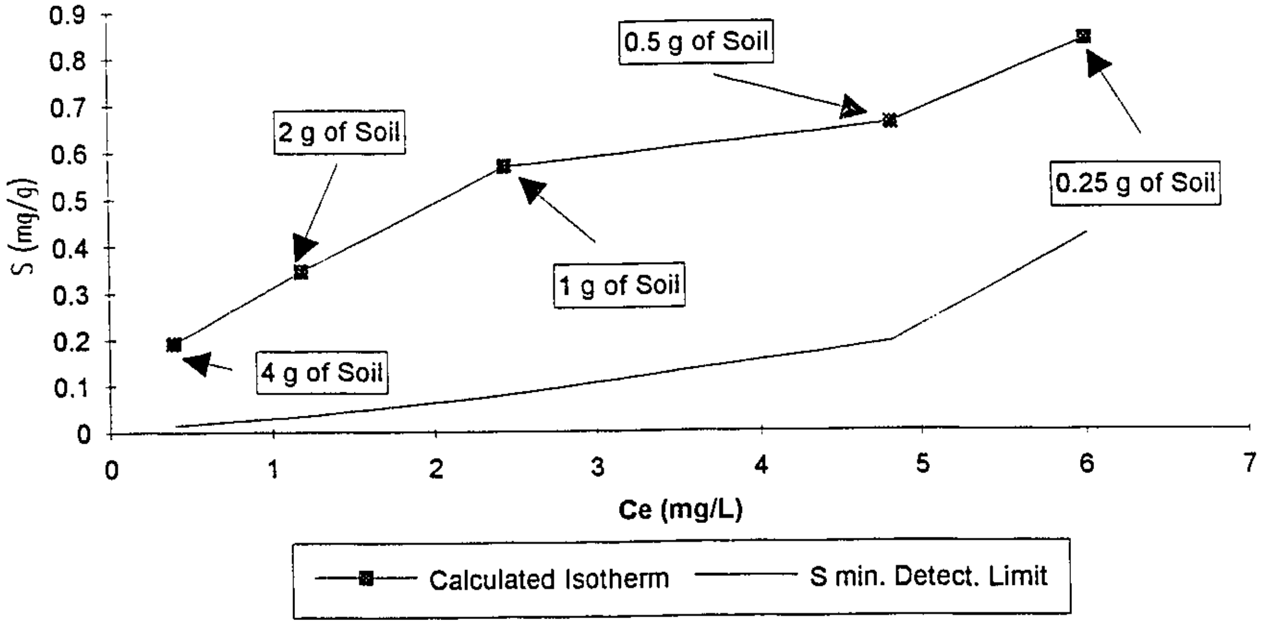


APPENDIX D

DATA FROM COLUMN LEACHING EXPERIMENTS

D-1: HEAVY METALS

D-2:CATIONS AND ANIONS

D-3: PENTACHLOROPHENOL

APPENDIX D-1

HEAVY METALS

LEAD AND ZINC

CELL 1 ANALYSIS

Date Collected	Volume Collected (ml)	Total Volume Collected (ml)	Approximate Pore Volume	Hydraulic Conductivity (cm/sec)	ICP TEST (PPM)							
					Ba	Ca	Cu	Mg	Mn	Pb	Sr	Zn
June 18	123.4	123.4	0.2	1.2E-5	0.2	17.2	0.0	4.0	0.3	0.0	0.1	0.3
June 19	65.1	188.5	0.3	6.6E-6	0.0	14.8	0.0	4.3	0.2	0.0	0.0	0.2
June 20	48.7	237.2	0.4	4.9E-6	0.0	14.1	0.0	4.6	0.3	0.0	0.1	0.0
June 22	68	305.2	0.5	3.4E-6	0.1	19.2	0.0	6.1	0.4	0.0	0.1	0.0
June 24	67	372.2	0.6	3.4E-6	0.1	18.3	0.0	6.0	0.4	0.0	0.1	0.0
June 26	67	439.2	0.7	3.4E-6	0.1	18.8	0.0	6.1	0.4	0.0	0.1	0.0
June 28	60.7	499.9	0.8	4.3E-6	0.1	19.0	0.0	6.1	0.4	0.0	0.1	0.0
June 30	106.7	606.6	0.9	4.1E-6	0.1	21.1	0.0	7.2	0.4	0.0	0.1	0.0
July 3	90.8	697.4	1.1	4.2E-6	0.1	22.8	0.0	7.7	0.5	0.0	0.1	0.1
July 6	104.5	801.9	1.2	3.5E-6	0.1	25.4	0.0	8.7	0.3	0.0	0.1	0.1
July 9	213.6	1015.5	1.6	5.8E-6	0.2	29.3	0.0	9.9	0.7	0.0	0.2	0.0
July 12	197.6	1213.1	1.9	7.2E-6	0.2	31.9	0.0	10.8	0.7	0.0	0.2	0.0
July 15	138.5	1351.6	2.1	4.7E-6	0.2	27.0	0.0	9.0	0.5	0.0	0.2	0.1

July19	161	1512.6	2.3	3.7E-6								
July 23	108.8	1621.4	2.5	3.0E-6								
July 30	397.4	2018.8	3.1	5.5E-6	0.1	22.5	6.0	7.3	0.3	0.0	0.1	0.1
Aug 10	384.6	2403.4	3.7	3.6E-6								
Aug 15	97	2500.4	3.8	2.0E-6	0.1	15.5	0.0	4.3	0.5	0.2	0.1	0.3
Aug 24	390	2890.4	4.4	4.5E-6	0.1	17.8	0.1	4.2	0.3	0.2	0.1	0.7
Sept 3	633	3523.4	5.4	6.4E-6								

CELL 2 ANALYSIS

Date Collected	Total Volume Collected (ml)	Total Volume Collected (ml)	Approximate Pore Volume	Hydraulic Conductivity (cm/sec)	ICP TEST (PPM)							
					Ba	Ca	Cu	Mg	Mn	Pb	Sr	Zn
June 18	472.9	472.9	0.7	7.6E-5	0.1	9.6	0.0	2.3	0.1	0.0	0.0	0.1
June 19	366.4	839.3	1.3	3.7E-5	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0
June 20	256.7	1096	1.7	2.6E-5	0.0	10.2	0.0	3.4	0.1	0.0	0.1	0.0
June 22	500	1596	2.5	2.5E-5	0.1	12.6	0.0	3.9	0.2	0.0	0.1	0.0
June 24	416.6	2012.6	3.1	2.1E-5	0.1	13.5	0.0	4.5	0.1	0.0	0.1	0.0
June 26	236.7	2249.3	3.5	1.2E-5	0.1	14.2	0.0	4.8	0.1	0.0	0.1	0.0
June 28	238	2487.3	3.8	1.2E-5	0.1	16.6	0.0	5.4	0.4	0.0	0.1	0.0
June 30	189.4	2676.7	4.1	9.6E-6	0.1	16.8	0.0	5.6	0.2	0.0	0.1	0.2
July 3	278	2954.7	4.5	9.4E-6	0.1	15.8	0.0	5.6	0.1	0.0	0.1	0.3
July 4	90	3044.7	4.7	1.1E-5	0.1	17.3	0.0	6.0	0.0	0.0	0.1	0.1

Cell no 5 was taken out of service on July 4 1991

A total of 90 ml of percolate was obtained immediatly after stopage

July 4	90 ml	residual			0.1	9.6	0.0	3.6	0.1	0.0	0.1	0.1
		pore										
		percolate										

CELL 3 ANALYSIS

Date Collected	Total Volume Collected (ml)	Total Volume Collected (ml)	Approximate Pore Volume	Hydraulic Conductivity (cm/sec)	ICP TEST (PPM)							
					Ba	Ca	Cu	Mg	Mn	Pb	Sr	Zn
June 18	295.6	295.6	0.5	3.0E-5	0.3	9.4	0.0	2.6	0.3	0.0	0.1	0.1
June 19	204.2	499.8	0.8	2.1E-5	0.0	8.8	0.0	2.7	0.2	0.0	0.0	0.0
June 20	216.4	716.2	1.1	2.2E-5	0.4	8.2	0.0	2.7	0.1	0.0	0.0	0.0
June 22	290.8	1007	1.5	1.5E-5	0.1	10.3	0.0	3.4	0.1	0.0	0.1	0.0
June 24	261.4	1268.4	2.0	1.3E-5	0.1	12.8	0.0	4.4	0.1	0.0	0.1	0.0
June 26	165	1433.4	2.2	8.4E-6	0.1	14.8	0.0	5.1	0.2	0.0	0.1	0.0
June 28	154	1587.4	2.4	7.8E-6	0.1	17.3	0.0	5.9	0.2	0.0	0.1	0.0
June 30	148.2	1735.6	2.7	7.5E-6	0.1	19.9	0.0	6.9	0.2	0.0	0.1	0.2
July 3	205.4	1941	3.0	7.0E-6	0.1	20.1	0.0	7.3	0.3	0.0	0.1	0.0
July 6	260.1	2201.1	3.4	8.8E-6	0.1	20.1	0.0	7.0	0.3	0.0	0.1	0.0
July 9	172	2373.1	3.7	5.8E-6	0.1	19.2	0.0	6.7	0.0	0.0	0.1	0.0
July 12	200.3	2573.4	4.0	7.3E-6	0.1	19.9	0.0	6.7	0.3	0.0	0.1	0.0
July 15	146.1	2719.5	4.2	4.9E-6								

July19	148	2867.5	4.4	3.4E-6								
July 23	121.4	2988.9	4.6	3.4E-6								
July 30	217.7	3206.6	4.9	3.0E-6	0.1	25.5	0.0	9.0	0.3	0.0	0.2	0.1
Aug 10	343.8	3550.4	5.5	3.3E-6								
Aug 15	145.6	3696	5.7	3.0E-6	0.1	18.2	0.1	6.2	0.2	0.1	0.1	0.1
Aug 24	557	4253	6.5	6.4E-6	0.1	18.1	0.1	5.8	0.3	0.1	0.1	0.3
Sept 3	405.1	4658.1	7.2	4.1E-6								

CELL 4 ANALYSIS

Date Collected	Total Volume Collected (ml)	Total Volume Collected (ml)	Approximate Pore Volume	Hydraulic Conductivity (cm/sec)	ICP TEST (PPM)							
					Ba	Ca	Cu	Mg	Mn	Pb	Sr	Zn
June 18	394.8	394.8	0.6	4.0E-5	0.1	7.9	0.0	2.0	0.1	0.0	0.0	0.0
June 19	291.3	686.1	1.1	3.0E-5	0.0	0.2	0.0	0.1	0.0	0.0	0.0	0.0
June 20	296.6	982.7	1.5	3.0E-5	0.1	19.0	0.0	6.5	0.4	0.0	0.1	0.0
June 22	485.3	1468	2.3	2.5E-5	0.1	10.4	0.0	3.4	0.2	0.0	0.1	0.0
June 24	268.4	1736.4	2.7	1.4E-5	0.1	11.9	0.0	4.0	0.2	0.0	0.1	0.0
June 26	173.6	1910	2.9	8.8E-6	0.0	14.2	0.0	4.8	0.2	0.0	0.1	0.0
June 28	118	2028	3.1	6.0E-6	0.1	16.8	0.0	5.8	0.1	0.0	0.1	0.1
June 30	80.1	2108.1	3.2	4.1E-6	0.1	19.9	0.0	6.9	0.0	0.0	0.1	0.2
July 3	121.8	2229.9	3.4	4.1E-6	0.1	24.0	0.0	8.4	0.0	0.0	0.1	0.0
July 6	158.1	2388	3.7	5.3E-6	0.1	29.0	0.0	9.7	0.2	0.0	0.2	0.0
July 9	175.1	2563.1	3.9	6.0E-6	0.2	30.2	0.0	10.4	0.0	0.0	0.2	0.0
July 12	173.7	2736.8	4.2	6.4E-6	0.2	29.7	0.0	10.0	0.3	0.0	0.2	0.0
July 15	332.2	3069	4.7	1.1E-5	0.1	[illegible]	0.0	7.9	0.2	0.0	0.1	0.1

July19	486.8	3555.8	5.5	1.1E-5								
July 23	351.3	3907.1	6.0	9.7E-6								
July 30	590.2	4497.3	6.9	8.2E-6	0.0	15.8	0.0	5.6	0.0	0.0	0.1	0.0
Aug-10	548.6	5045.9	7.8	5.2E-6		14.9	0.1	5.0	0.1	0.0	0.1	0.0

CELL 5 ANALYSIS

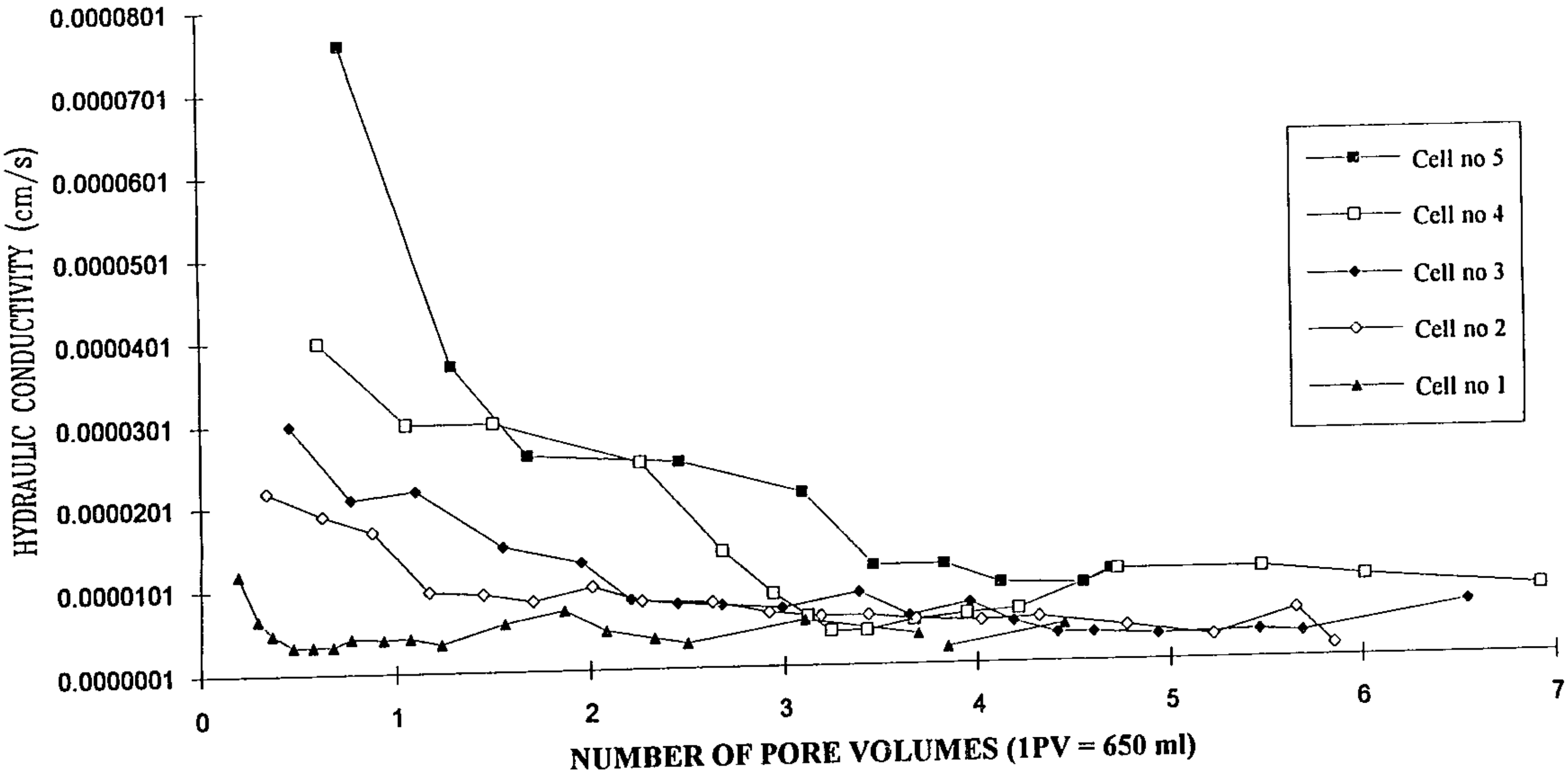
Date Collected	Total Volume Collected (ml)	Total Volume Collected (ml)	Approximate Pore Volume	Hydraulic Conductivity (cm/sec)	ICP TEST (PPM)							
					Ba	Ca	Cu	Mg	Mn	Pb	Sr	Zn
June 18	218.4	218.4	0.3	2.2E-5	0.5	15.1	0.0	3.4	0.2	0.1	0.1	0.5
June 19	186.3	404.7	0.6	1.9E-5	0.1	12.1	0.0	3.4	0.2	0.0	0.1	0.0
June 20	163.4	568.1	0.9	1.7E-5	0.1	10.0	0.0	3.1	0.2	0.0	0.1	0.0
June 22	192	760.1	1.2	9.7E-6	0.1	11.6	0.0	3.6	0.2	0.0	0.1	0.0
June 24	184.3	944.4	1.5	9.4E-6	0.1	13.7	0.0	4.4	0.1	0.0	0.1	0.0
June 26	164.5	1108.9	1.7	8.4E-6	0.0	15.6	0.0	5.0	0.1	0.0	0.1	0.0
June 28	198.3	1307.2	2.0	1.0E-5	0.1	17.5	0.0	5.5	0.4	0.0	0.1	0.0
June 30	162	1469.2	2.3	8.2E-6	0.1	18.0	0.0	5.8	0.3	0.0	0.1	0.2
July 3	234.3	1703.5	2.6	7.9E-6	0.1	18.3	0.0	6.1	0.3	0.0	0.1	0.0
July 6	190.8	1894.3	2.9	6.5E-6	0.1	20.3	0.0	6.3	0.2	0.0	0.1	0.1
July 9	176.8	2071.1	3.2	6.0E-6	0.1	20.9	0.0	6.8	0.0	0.0	0.1	0.0
July 12	162.5	2233.6	3.4	6.0E-6	0.1	22.0	0.0	7.1	0.3	0.0	0.1	0.0
July 15	160.5	2394.1	3.7	5.4E-6	0.1	27.4	0.0	7.4	0.2	0.0	0.1	0.0

July19	217.4	2611.5	4.0	5.1E-6								
July 23	193.8	2805.3	4.3	5.4E-6								
July 30	294.8	3100.1	4.8	4.1E-6	0.1	22.1	0.0	7.2	0.0	0.0	0.1	
Aug 10	292.8	3392.9	5.2	2.8E-6								
Aug 15	281.3	3674.2	5.7	5.8E-6	0.1	16.7	0.1	4.9	0.3	0.0	0.1	0.1
Aug 24	130.5	3804.7	5.9	1.5E-6	0.1	15.1	0.1	4.5	0.3	0.1	0.1	0.2
Sept 3	89.9	3894.6	6.0	9.1E-6								

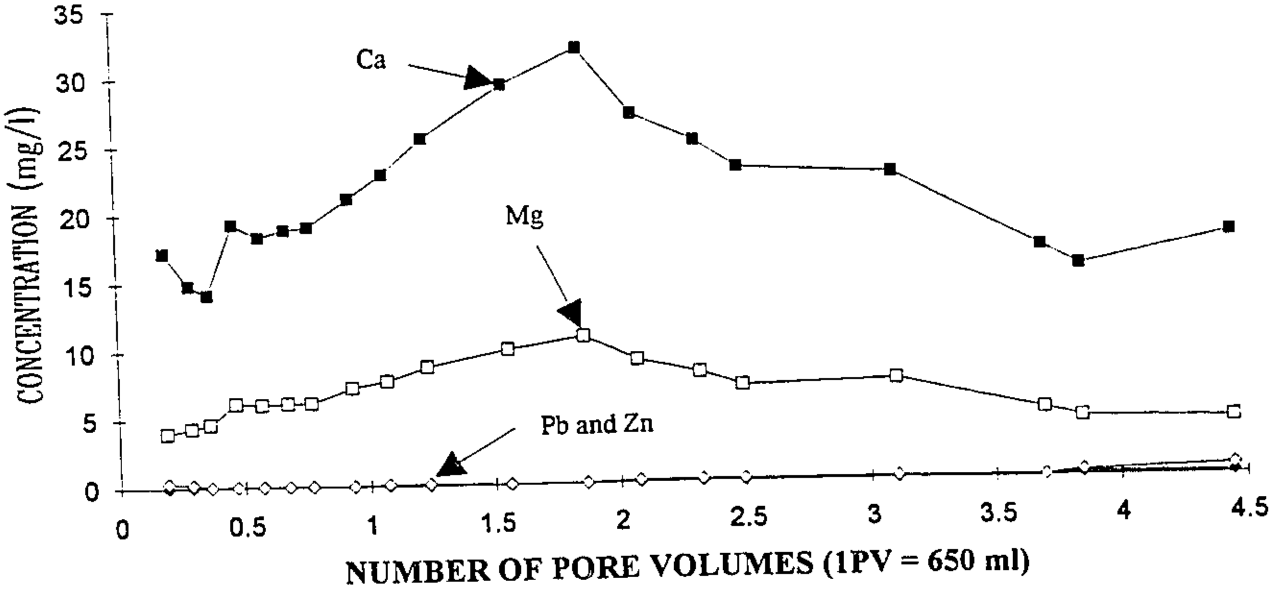
INFLUENT ANALYSIS

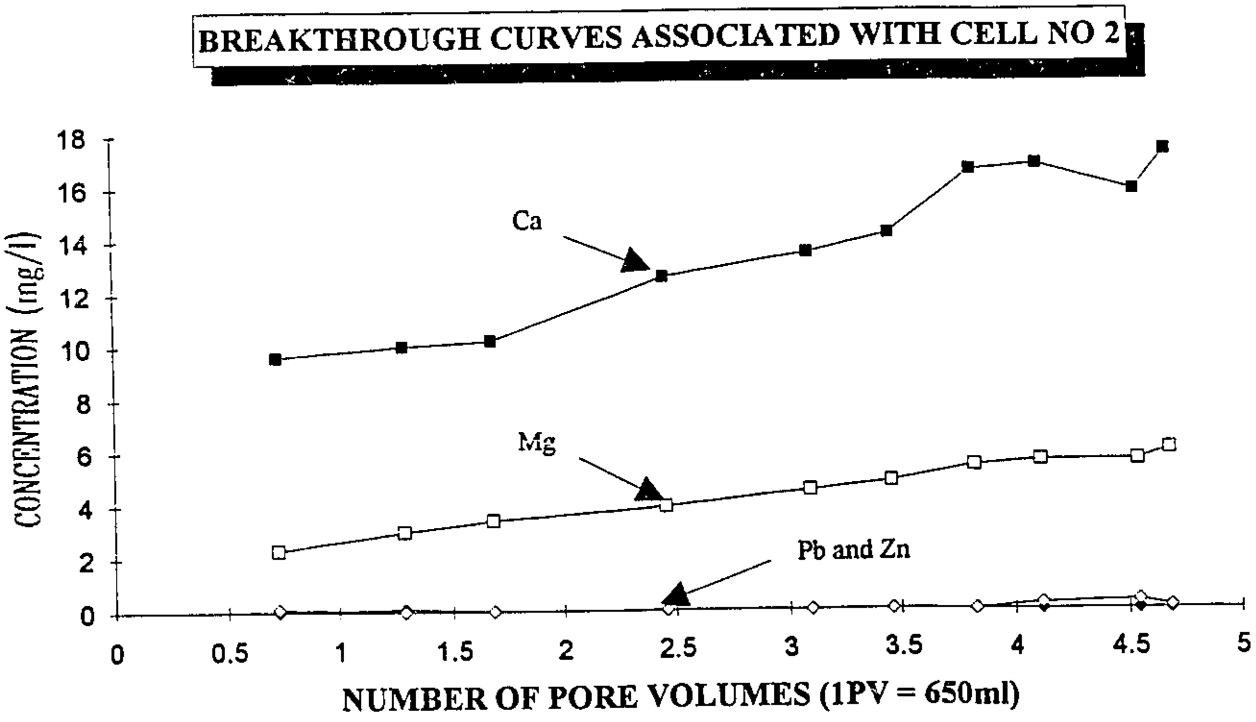
Total Volume Collected (ml)	Hydraulic Conductivity (cm/sec)		Ba	Ca	Mn	Pb	Sr	Zn
-	-	0	0.0	0.0	0.0	115.0	0.0	106.0
-	-	0	0.0	0.0	0.0	106.0	0.0	91.0
-	-	0	0.0	0.4	0.0	105.0	0.0	91.1
-	-		0.0	1.0	0.0	105.0	0.0	91.7
-	-		0.0	0.2	0.0	120.0	0.0	114.0

PERMEABILITY VARIATION OF CELL NO 1 TO 5

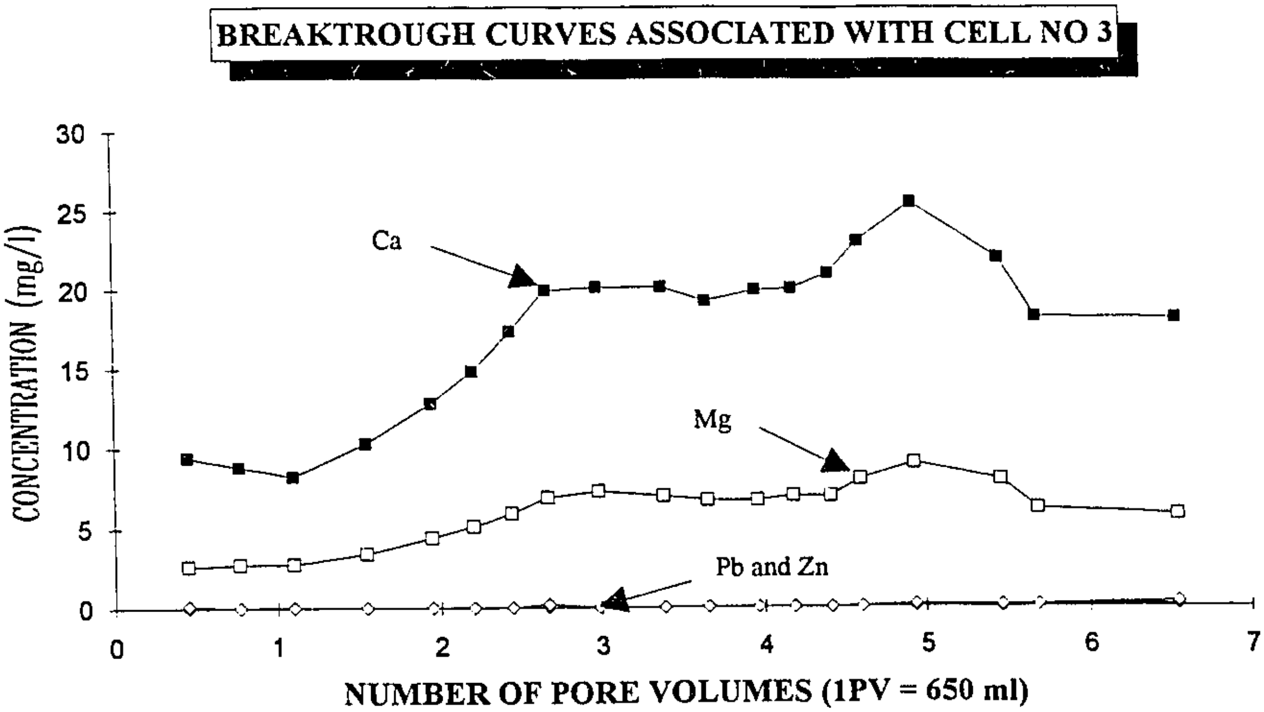


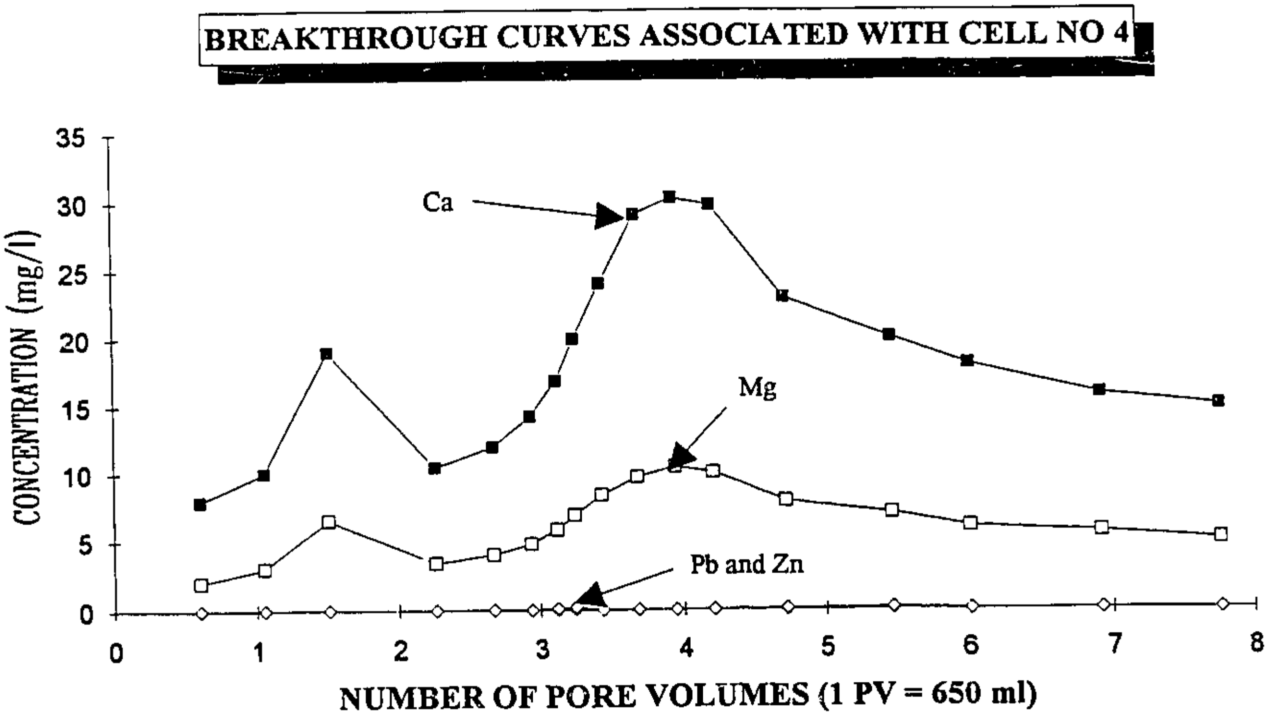
BREAKTROUGH CURVES ASSOCIATED WITH CELL NO 1

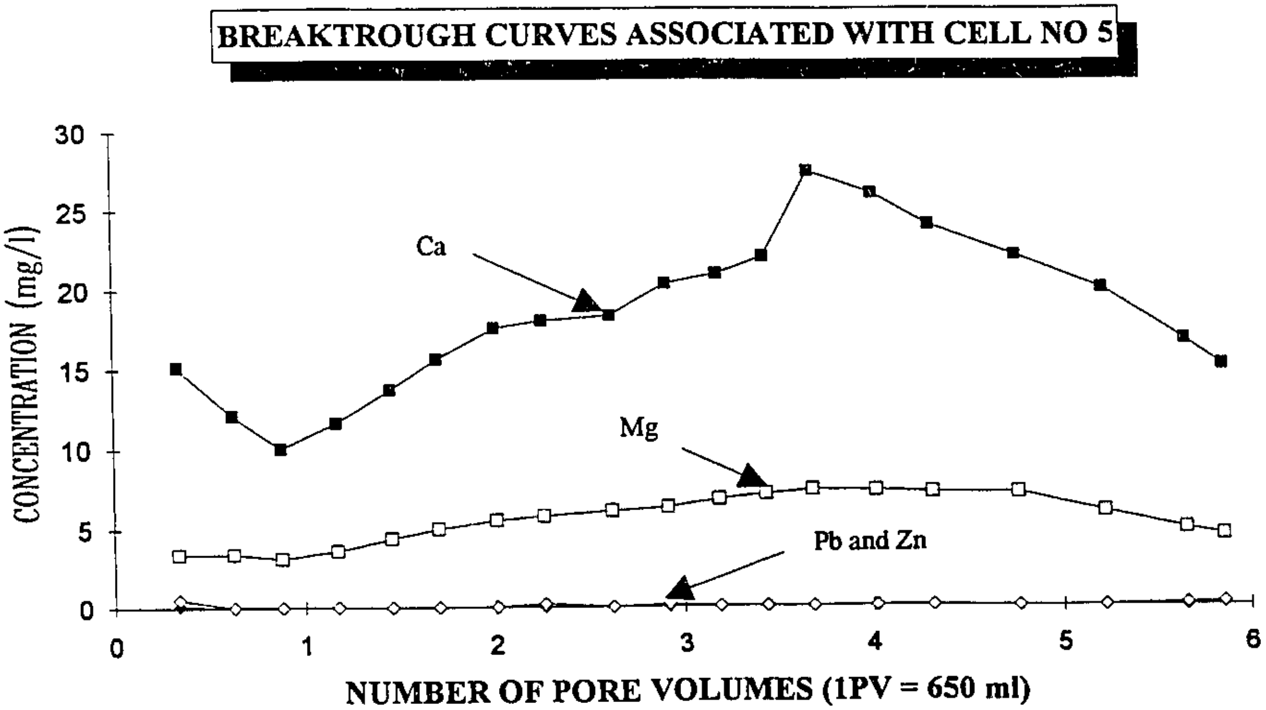




BREAKTHROUGH CURVES ASSOCIATED WITH CELL NO 2


BREAKTROUGH CURVES ASSOCIATED WITH CELL NO 3
CONCENTRATION (mg/l)
30
25
20
15
10
5
0
Ca
Mg
Pb and Zn
0
1
2
3
4
5
6
7
NUMBER OF PORE VOLUMES (1PV = 650 ml)


BREAKTHROUGH CURVES ASSOCIATED WITH CELL NO 4
Ca
Mg
Pb and Zn
CONCENTRATION (mg/l)
NUMBER OF PORE VOLUMES (1 PV = 650 ml)
0
5
10
15
20
25
30
35
0
1
2
3
4
5
6
7
8


BREAKTROUGH CURVES ASSOCIATED WITH CELL NO 5
CONCENTRATION (mg/l)
30
25
20
15
10
5
0
Ca
Mg
Pb and Zn
0
1
2
3
4
5
6
NUMBER OF PORE VOLUMES (1PV = 650 ml)

RESIDUAL PORE WATER CELL NO 4

DATE	PORTION OF THE CELL	ICP TEST (PPM)					
		Ca	Mg	Mn	Na	Pb	Zn
Aug-91	TOP	25.8	1.4	0.6	9.7	0.1	58.9
	2 - 4 CM	38.6	3.8	0.6	13.5	0.0	5.0
	4 - 6 CM	20.5	5.5	0.2	16.7	0.0	0.2
	6 - 8 CM	10.3	3.1	0.0	20.0	0.0	0.2
	BOTTOM	8.3	2.4	0.0	20.3	0.0	0.1

RESIDUAL PORE WATER CELL NO 5

DATE	PORTION OF THE CELL	ICP TEST (PPM)					
		Ca	Mg	Mn	Na	Pb	Zn
Aug-91	TOP	58.8	9.3	1.3	30.2	0.1	25.1
	2.5 - 5 CM	48.9	14.2	0.8	12.0	0.0	2.1
	5 - 7.5 CM	36.0	11.5	0.5	11.4	0.1	0.7
	BOTTOM	30.5	9.5	0.4	12.8	0.1	1.2

HEAVY METAL MIGRATION PROFILE

CELL NO 4

(7.8 pore volume)

DATE	PORTION OF THE CELL	ICP TEST (PPM)					
		% Ca	Mg	Mn	Na	Pb	Zn
Apr-92	TOP	0.7	2400.0	190.0	8000.0	6557.0	1960.0
	2 - 4 CM	1.1	2445.0	281.0	8000.0	27.5	1132.0
	4 - 6 CM	1.1	2673.0	289.0	9000.0	11.0	52.1
	6 - 8 CM	1.1	2808.0	276.0	9200.0	15.1	48.5
	BOTTOM	1.1	2639.0	256.0	9824.0	14.8	47.3
	Natural soil	1.2	2500.0	277.0	13000.0	10.0	45.0

HEAVY METAL MIGRATION PROFILE

CELL NO 5 2

(4.7 pore volume)

DATE	PORTION OF THE CELL	ICP TEST (PPM)					
		% Ca	Mg	Mn	Na	Pb	Zn
Apr-92	TOP	>0.5	2200.0	212.0	11500.0	2450.0	940.0
	2.5 - 5	>0.5	2440.0	250.0	12000.0	27.0	190.0
	5 - 7.5	>0.5	2430.0	244.0	13000.0	13.0	80.0
	BOTTOM	>0.5	2380.0	233.0	12800.0	25.0	91.0
	Natural soil	1.2	2500.0	277.0	13000.0	10.0	45.0

APPENDIX D-2

CATIONS AND ANIONS

CALCIUM, SODIUM AND CHLORIDE

CELL 6 ANALYSIS

Date Collected	Hour	Volume Collected (ml)	Total Volume Collected (ml)	Hydraulic Conductivity (cm/sec)	Approximate Pore Volume	ICP TEST (PPM)				HPLC (PPM)		
						Ca	Na	Mg	Mn		Cl	
July 15	3:00 PM	363.2	-	7.7E-5	0.0	5.9	0.4	1.8	0.1		0.0	
July 16	3:00 AM	354.7	354.7	7.6E-5	0.5	9.4	0.4	3.1	0.2		0.0	
July 16	3:00 PM	403.5	758.2	8.6E-5	1.2	50.9	7.8	17.8	1.0		110.0	
July 17	3:00 AM	420.9	1179.1	9.0E-5	1.8	88.3	36.5	30.7	1.6		217.0	
July 17	3:00 PM	402.5	1581.6	8.6E-5	2.4	85.8	69.8	29.1	1.6		244.6	
July 18	3:00 AM	426.5	2008.1	9.1E-5	3.1	75.3	96.2	25.4	1.4		245.0	
July 19	3:00 AM	822	2830.1	8.9E-5	4.4	70.6	107.2	23.8	1.3		247.5	
July 19	3:00 PM	407	3237.1	8.7E-5	5.0	70.3	115.0	23.5	1.3		250.0	
July 20	3:00 PM	891	4128.1	9.5E-5	6.4	71.7	118.7	23.3	1.3		268.0	
July 21	3:00 PM	870.5	4998.6	9.2E-5	7.7	73.4	116.9	21.5	1.3		251.0	
July 22	3:00 PM	817.5	5816.1	8.7E-5	8.9	74.7	115.0	19.4	1.3		249.0	
July 23	3:00 PM	816.8	6632.9	8.7E-5	10.2	78.0	114.3	17.0	1.4		251.0	
July 24	3:00 PM	800	7432.9	8.5E-5	11.4	81.2	113.8	15.1	1.4		256.0	
July 25	3:00 PM	860	8292.9	9.2E-5	12.8	83.8	114.2	13.5	1.4		254.5	
July 26	3:00 PM	1000	9292.9	1.1E-4	14.3	86.3	114.5	11.8	1.4		253.0	

July 27	3:00 AM	526.2	9819.1	1.1E-4	15.1	90.0	114.3	9.2	1.4		251.5	
July 28	3:00 PM	1752.6	11571.7	1.3E-4	17.8	93.7	114.0	6.6	1.4		250.0	
July 30	3:00 PM	3212.2	14783.9	1.8E-4	22.7	102.0	117.6	4.4	1.4		247.5	
July 31	3:00 PM	1821.2	16605.1	1.9E-4	25.5						250.0	
Aug 1	3:00 PM	2110	18715.1	2.2E-4	28.8						249.0	
Aug 2	3:00 AM	1200	19915.1	2.6E-4	30.6						251.0	
Aug 3	3:00 AM	2400	22315.1	2.5E-4	34.3						250.0	
Aug 4	3:00 AM	2410	24725.1	2.6E-4	38.0							
Aug 5	11:00 AM	4450	29175.1	3.7E-4	44.9	91.2	96.9	0.3	1.0			

Cell no 6 was taken out of service on Aug 5 1991

CELL 7 ANALYSIS

Date Collected	Hour	Volume Collected (ml)	Total Volume Collected (ml)	Hydraulic Conductivity (cm/sec)	Approximate Pore Volume	ICP TEST (PPM)				HPLC (PPM)		
						Ca	Na	Mg	Mn		Cl	
July 15	9:00 PM	263.9	-	5.6E-5	0.0	7.2	0.2	1.9	0.1		0.0	
July 16	9:00 AM	262.9	262.9	5.6E-5	0.4	6.8	0.2	1.9	0.1		0.0	
July 16	9:00 PM	265.9	528.8	5.7E-5	0.8	13.5	0.2	4.2	0.3		6.0	
July 17	9:00 AM	287.7	816.5	6.1E-5	1.3	78.4	2.0	21.5	1.1		144.3	
July 17	9:00 PM	306	1122.5	6.5E-5	1.7	95.6	20.4	30.1	1.8		215.2	
July 18	9:00 AM	298.3	1420.8	6.4E-5	2.2	86.3	60.6	27.9	1.7		232.0	
July 18	9:00 PM	292.5	1713.3	6.2E-5	2.6	77.1	88.4	24.4	1.5		245.1	
July 19	9:00 PM	607	2320.3	6.7E-5	3.6	61.4	97.4	20.0	1.2			
July 20	9:00 PM	617	2937.3	6.6E-5	4.5	61.0	99.2	20.2	1.2			
July 21	9:00 PM	592	3529.3	6.3E-5	5.4	62.0	101.8	20.1	1.3			
July 22	9:00 PM	556.2	4085.5	5.9E-5	6.3	61.1	99.8	19.8	1.2			
July 23	9:00 PM	528.2	4613.7	5.6E-5	7.1	69.2	115.0	22.3	1.4			
July 24	9:00 PM	532	5145.7	5.7E-5	7.9	73.9	120.7	23.3	1.5			
July 25	9:00 PM	540	5685.7	5.7E-5	8.7							
July 26	9:00 PM	525	6210.7	5.6E-5	9.6	73.9	119.5	22.3	1.5			
July 27	9:00 AM	257.1	6467.8	5.5E-5	10.0							

July 28	9:00 PM	772.6	7240.4	5.5E-5	11.1	78.0	123.7	21.8	1.5			
July 30	9:00 PM	996.8	8237.2	5.0E-5	12.7	85.5	129.1	20.8	1.7			
July 31	9:00 PM	443	8680.2	4.7E-5	13.4							
Aug 1	9:00 PM	460	9140.2	4.9E-5	14.1							
Aug 2	9:00 AM	448	9588.2	4.8E-5	14.8							
Aug 3	9:00 PM	440	10028.2	4.7E-5	15.4							
Aug 4	9:00 PM	430	10458.2	4.6E-5	16.1							
Aug 5	9:00 PM	400	10858.2	4.3E-5	16.7							
Aug 6	9:00 PM	400	11258.2	4.3E-5	17.3	80.4	98.0	8.3	1.5			
Aug 7	9:00 PM	400	11658.2	4.3E-5	17.9							
Aug 8	9:00 PM	400	12058.2	4.3E-5	18.6							
Aug 9	9:00 PM	400	12458.2	4.3E-5	19.2							
Aug 10	9:00 PM	400	12858.2	4.3E-5	19.8	111	132.7	5.7	2			

CELL 8 ANALYSIS

Date Collected	Hour	Total Volume Collected (ml)	Total Volume Collected (ml)	Hydraulic Conductivity (cm/sec)	Approximate Pore Volume	ICP TEST (PPM)				HPLC (PPM)		
						Ca	Na	Mg	Mn		Cl	
July 15	9:00 PM	398.4	-	8.5E-5	0.0	5.4	0.1	1.5	0.1		0.0	
July 16	9:00 AM	350.5	350.5	7.5E-5	0.5	5.6	0.2	1.6	0.1		0.0	
July 16	9:00 PM	404.9	755.4	8.6E-5	1.2	41.8	0.9	13.9	0.8		111.0	
July 17	9:00 AM	396.7	1152.1	8.4E-5	1.8	102.0	19.7	32.9	2.0		295.0	
July 17	9:00 PM	411.8	1563.9	8.8E-5	2.4	88.4	70.9	28.2	1.7		311.0	
July 18	9:00 AM	395.2	1959.1	8.4E-5	3.0	77.4	105.2	24.4	1.5		323.0	
July 18	9:00 PM	359.7	2318.8	7.6E-5	3.6	80.2	125.3	24.8	1.6		350.0	
July 19	9:00 PM	722	3040.8	7.6E-5	4.7	79.4	127.1	24.3	1.5		331.0	
July 20	9:00 PM	739	3779.8	7.8E-5	5.8	77.0	123.9	24.1	1.5		326.0	
July 21	9:00 PM	692	4471.8	7.4E-5	6.9	78.2	127.0	24.1	1.5		323.0	
July 22	9:00 PM	640.6	5112.4	6.8E-5	7.9	77.5	123.9	24.0	1.5		321.0	
July 23	9:00 PM	624.3	5736.7	6.6E-5	8.8	79.9	127.2	23.7	1.5		351.0	
July 24	9:00 PM	595	6331.7	6.3E-5	9.7	77.0	125.9	23.5	1.5		324.0	
July 25	9:00 PM	618	6949.7	6.6E-5	10.7							
July 26	9:00 PM	610	7559.7	6.5E-5	11.6	80.1	126.5	22.9	1.5		328.0	
July 27	9:00 AM	283.4	7843.1	6.0E-5	12.1							

July 28	9:00 PM	816.1	8659.2	8.0E+0	13.3	79.2	122.8	19.6	1.5		314.0	
July 30	9:00 PM	1050	9709.2	5.5E-5	14.9	83.3	118.8	15.9	1.6		315.0	
July 31	9:00 PM	468	10177.2	5.0E-5	15.7							
Aug 1	9:00 PM	480	10657.2	5.1E-5	16.4							
Aug 2	9:00 PM	472	11129.2	5.1E-5	17.1							
Aug 3	9:00 PM	445	11574.2	4.7E-5	17.8							
Aug 4	9:00 PM	421.8	11996	4.5E-5	18.5							
Aug 5	9:00 PM	400	12396	4.3E-5	19.1							
Aug 6	9:00 PM	400	12796	4.3E-5	19.7	113.0	134.3	4.4	2.0			
Aug 7	9:00 PM	400	13196	4.3E-5	20.3							
Aug 8	9:00 PM	400	13596	4.3E-5	20.9							
Aug 9	9:00 PM	400	13996	4.3E-5	21.5							
Aug 10	9:00 PM	400	14396	4.3E-5	22.1	111.0	127.4	2.0	2.0			

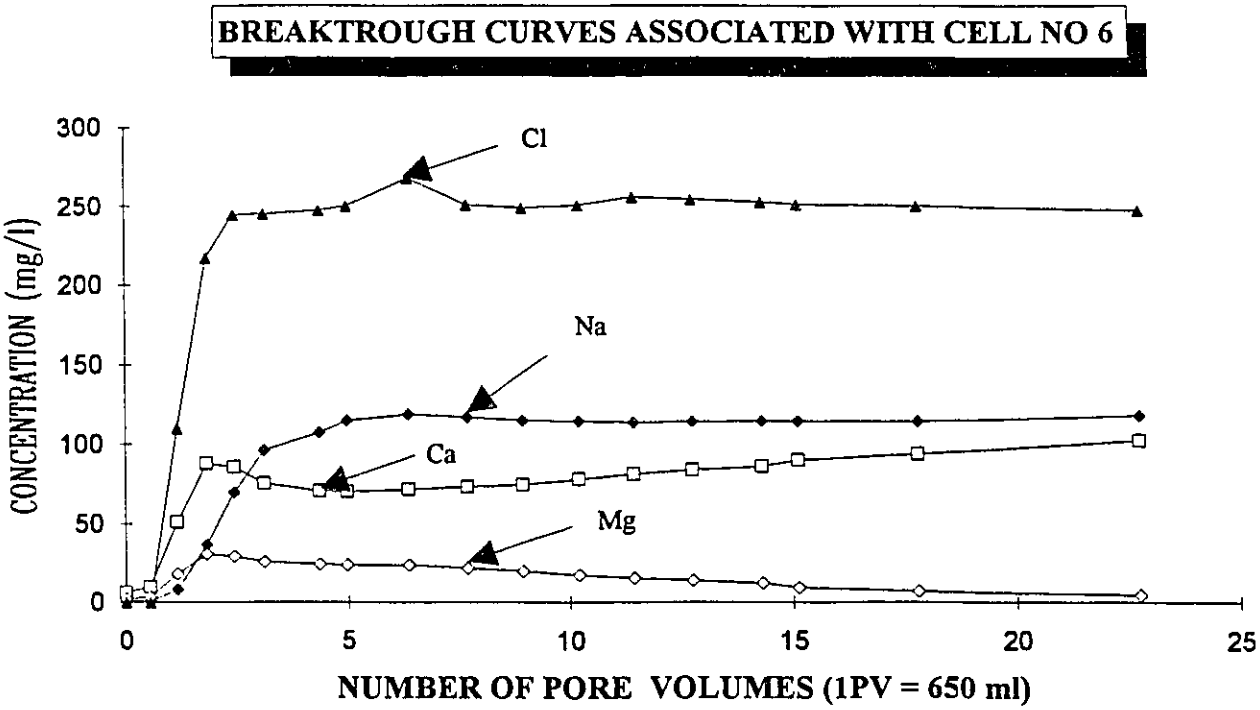
CELL 9 ANALYSIS

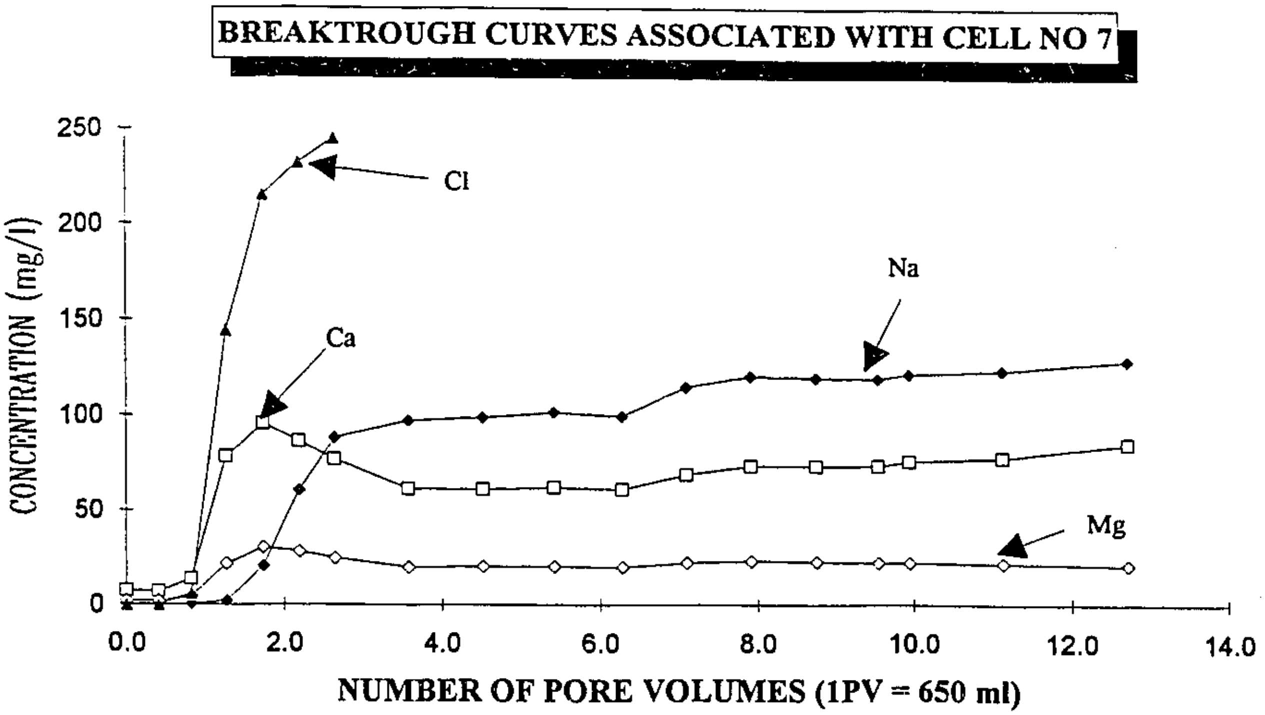
Date Collected	Hour	Total Volume Collected (ml)	Total Volume Collected (ml)	Hydraulic Conductivity (cm/sec)	Approximate Pore Volume	ICP TEST (PPM)				HPLC (PPM)		
						Ca	Na	Cu	Mg		Cl	
July 15	3:00 PM	666.7	-	2.8E-4	-							
July 15	9:00 PM	800	800	3.4E-4	1.2							
July 16	3:00 AM	1042	1842	4.4E-4	2.8							
July 16	9:00 AM	893.8	2735.8	3.8E-4	4.2							
		Excessive percolation in Cell 9.										
		It will be rebuilt.										
		From July 29 to July 30 3 PM water was passed										
July 29	9:00 AM	730.4	-	3.1E-4	-	4.2	0.1	1.2	0.1		0.0	
July 29	3:00 PM	632.7		2.7E-4		4.9	0.1	1.1	0.1		0.0	
July 29	9:00 PM	588.6		2.5E-4		6.5	0.2	1.2	0.1		0.0	
July 30	3:00 AM	617		2.6E-4								
July 30	9:00 AM	632.6		2.7E-4								
July 30	3:00 PM	630		2.7E-4	0.0	5.2	0.2	1.2	0.1		0.0	
July 30	9:00 PM	684.4	684.4	2.9E-4	1.1	6.5	0.4	1.6	0.1		214.0	

July 31	3:00 AM	940	1624.4	4.0E-4	2.5	99.3	35.6	27.4	2.1		253.6	
July 31	9:00 AM	803	2427.4	3.4E-4	3.7	74.9	104.4	20.4	1.6			
July 31	3:00 PM	935	3362.4	4.0E-4	5.2	56.8	85.4	15.5	1.2			
July 31	9:00 PM	945	4307.4	4.0E-4	6.6							
Aug 1	3:00 AM	960	5267.4	4.1E-4	8.1							
Aug 1	9:00 AM	900	6167.4	3.8E-4	9.5	55.5	86.4	15.1	1.2			
Aug 2	3:00 AM	2630	8797.4	3.8E-4	13.5							
Aug 2	3:00 PM	1690	10487.4	3.7E-4	16.1							
Aug 3	3:00 AM	1750	12237.4	3.7E-4	18.8	74.3	87.3	1.0	1.5			
Aug 3	3:00 PM	1690	13927.4	3.6E-4	21.4							
Aug 4	3:00 AM	1680	15607.4	3.6E-4	24.0							
Aug 4	3:00 PM	1620	17227.4	3.5E-4	26.5							
Aug 5	3:00 AM	1700	18927.4	3.6E-4	29.1							
Aug 5	3:00 PM	1800	20727.4	3.8E-4	31.9							
Aug 6	3:00 AM	1900	22627.4	4.0E-4	34.8							
Aug 6	3:00 PM	1850	24477.4	3.9E-4	37.7							
Aug 7	3:00 AM	1850	26327.4	3.9E-4	40.5							
Aug 7	3:00 PM	1820	28147.4	3.9E-4	43.3							
Aug 8	3:00 AM	1770	29917.4	3.8E-4	46.0							
Aug 8	3:00 PM	1740	31657.4	3.7E-4	48.7							
Aug 9	3:00 AM	1670	33327.4	3.5E-4	51.3							
Aug 9	3:00 PM	1660	34987.4	3.5E-4	53.8							
Aug 10	3:00 AM	1600	36587.4	3.4E-4	56.3	83.8	86.6	0	0.3			
Aug 10	3:00 PM	1610	38197.4	3.4E-4	58.8							

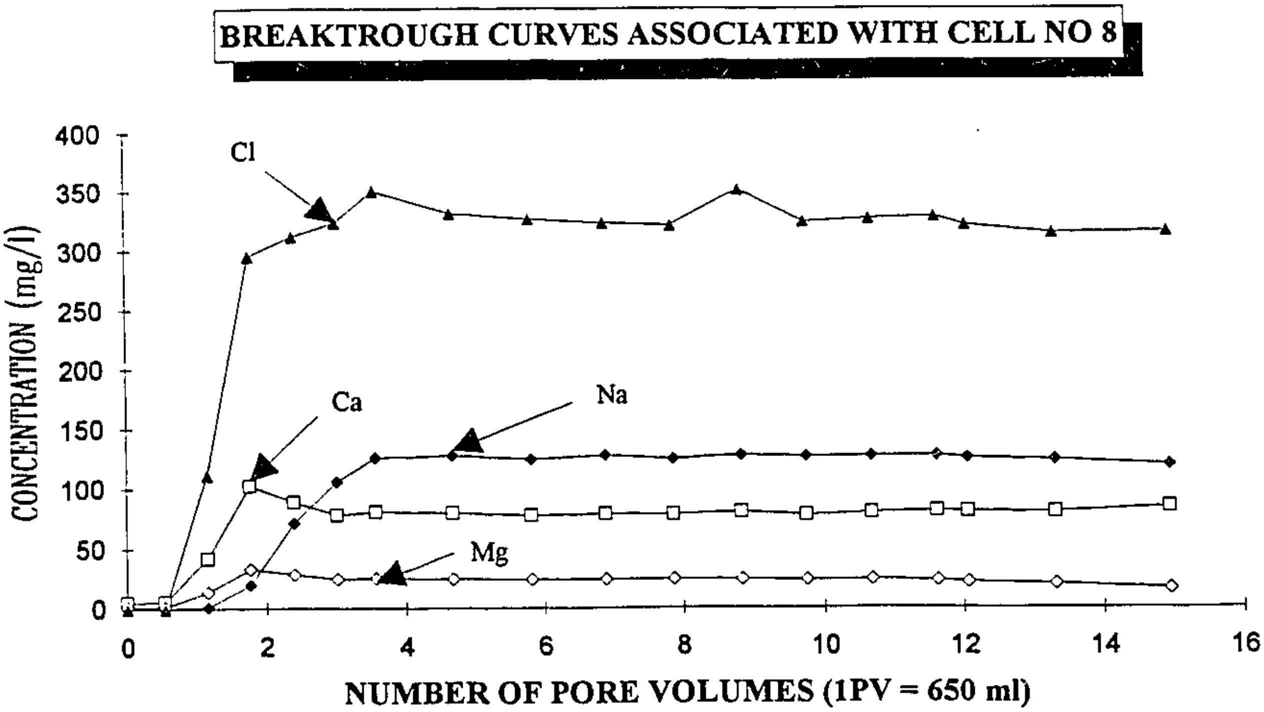
INFLUENT ANALYSIS

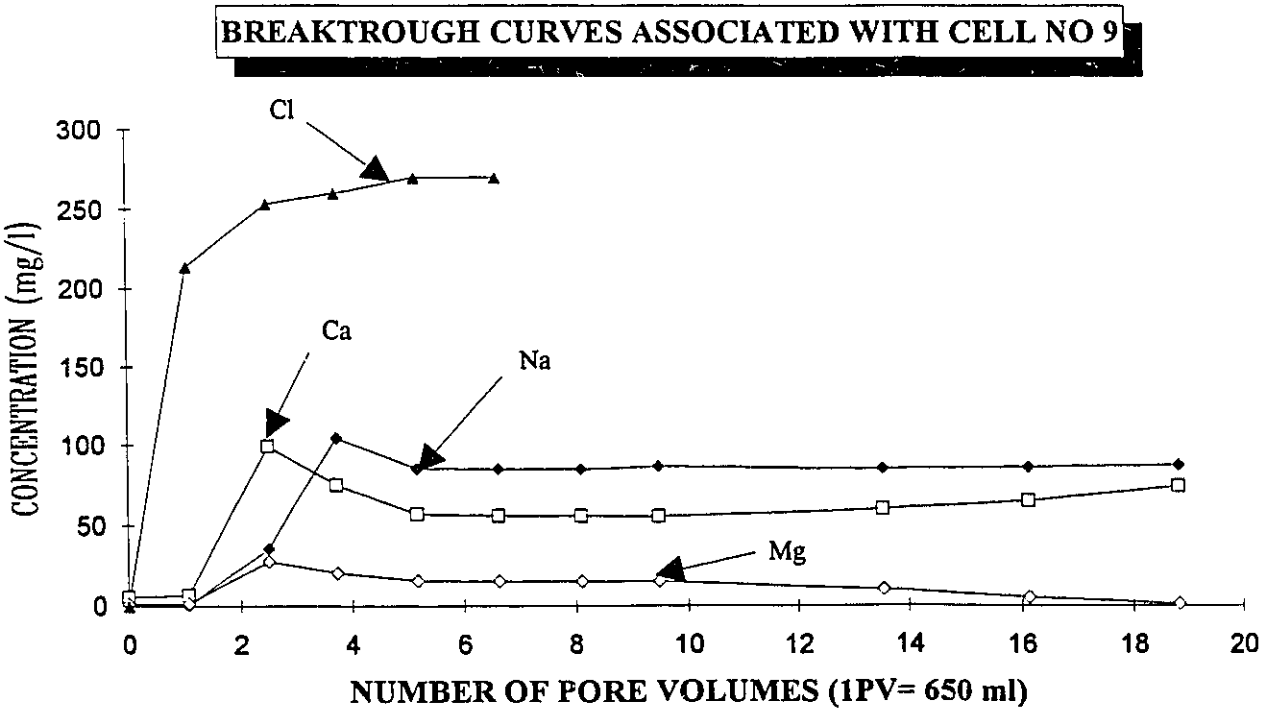
Date Collected	Hour	Total Volume Collected (ml)	Total Volume Collected (ml)	Hydraulic Conductivity (cm/sec)	Approximate Pore Volume	ICP TEST (PPM)				HPLC (PPM)		
						Ca	Na	Mg	Mn		Cl	
July 17						110	114.4	0.1	0		249	
July 30						113	113.4	0.1	0.1		250	


BREAKTROUGH CURVES ASSOCIATED WITH CELL NO 6
CONCENTRATION (mg/l)
300
250
200
150
100
50
0
Cl
Na
Ca
Mg
0
5
10
15
20
25
NUMBER OF PORE VOLUMES (1PV = 650 ml)



BREAKTROUGH CURVES ASSOCIATED WITH CELL NO 7


BREAKTROUGH CURVES ASSOCIATED WITH CELL NO 8
CONCENTRATION (mg/l)
400
350
300
250
200
150
100
50
0
Cl
Ca
Na
Mg
0
2
4
6
8
10
12
14
16
NUMBER OF PORE VOLUMES (1PV = 650 ml)


BREAKTROUGH CURVES ASSOCIATED WITH CELL NO 9
Cl
Ca
Na
Mg
CONCENTRATION (mg/l)
300
250
200
150
100
50
0
0
2
4
6
8
10
12
14
16
18
20
NUMBER OF PORE VOLUMES (1PV= 650 ml)

RESIDUAL PORE WATER

CELL NO 6

DATE	PORTION OF THE CELL	ICP TEST (PPM)					
		Ca	Mg	Mn	Na	Pb	Zn
Aug-91	TOP	81.3	0.6	0.0	94.2	0.0	0.0
	2 - 4 CM	84.7	0.4	0.0	98.3	0.0	0.0
	6 - 8 CM	82.1	0.3	0.2	98.1	0.0	0.0
	BOTTOM	82.7	0.6	0.5	105.4	0.0	0.2

RESIDUAL PORE WATER

CELL NO 7

DATE	PORTION OF THE CELL	ICP TEST (PPM)					
		Ca	Mg	Mn	Na	Pb	Zn
Aug-91	TOP	87.9	0.5	0.0	96.2	0.0	0.2
	2 - 4 CM	84.4	0.3	0.3	98.3	0.0	0.3
	6 - 8 CM	81.1	0.5	0.9	99.8	0.0	0.3
	BOTTOM	82.1	3.3	1.1	104.0	0.0	0.3

RESIDUAL PORE WATER

CELL NO 8

DATE	PORTION OF THE CELL	ICP TEST (PPM)					
		Ca	Mg	Mn	Na	Pb	Zn
Aug-91	TOP	84.7	0.3	0.1	93.7	0.0	0.2
	2.5 - 5 cm	85.6	0.2	0.4	92.1	0.0	0.2
	5 - 7.5 cm	81.9	0.2	1.0	92.5	0.0	0.3
	BOTTOM	80.1	1.5	1.2	92.8	0.0	0.4

RESIDUAL PORE WATER

CELL NO 9

DATE	PORTION OF THE CELL	ICP TEST (PPM)					
		Ca	Mg	Mn	Na	Pb	Zn
Aug-91	TOP	88.2	0.3	0.0	92.1	0.0	0.3
	2.5 - 5 cm	88.7	0.2	0.0	92.1	0.0	0.2
	5 - 7.5 cm	95.9	0.3	0.0	103.3	0.1	0.2
	BOTTOM	96.9	0.3	0.1	103.1	0.1	0.2

SODIUM AND CALCIUM MIGRATION PROFILE

CELL NO 6

(45 pore volume)

DATE	PORTION OF THE CELL	ICP TEST (PPM)					
		% Ca	Mg	Mn	Na	Pb	Zn
Apr-92	TOP	1.23	2124.0	177.0	10390.0	10.0	50.0
	2 - 4 CM	1.31	2037.0	164.0	10440.0	8.0	56.0
	6 - 8 CM	1.34	2100.0	202.0	10440.0	8.0	47.0
	BOTTOM	1.32	2158.0	264.0	10700.0	7.0	47.0
	Natural soil	1.19	2500.0	277.0	13000.0	10.0	45.0

SODIUM AND CALCIUM MIGRATION PROFILE

CELL NO 7

(20 pore volume)

DATE	PORTION OF THE CELL	ICP TEST (PPM)					
		% Ca	Mg	Mn	Na	Pb	Zn
Apr-92	TOP	1.26	2037.0	175.0	10409.0	9.0	63.0
	2 - 4 CM	1.30	2115.0	224.0	10543.0	8.0	47.8
	6 - 8 CM	1.33	2270.0	288.0	11001.0	8.0	49.2
	BOTTOM	1.27	2144.0	278.0	10310.0	8.0	50.4
	Natural soil	1.19	2500.0	277.0	13000.0	10.0	45.0

SODIUM AND CALCIUM MIGRATION PROFILE

CELL NO 9

(59 pore volume)

DATE	PORTION OF THE CELL	ICP TEST (PPM)					
		% Ca	Mg	Mn	Na	Pb	Zn
Apr-92	TOP	1.17	2207.0	191.0	10280.0	9.0	33.0
	2 - 4 CM	1.27	2246.0	183.0	9480.0	8.0	58.0
	6 - 8 CM	1.33	2158.0	187.0	10530.0	8.0	44.0
	BOTTOM	1.26	2200.0	190.0	11000.0	8.0	43.0
	Natural soil	1.19	2500.0	277.0	13000.0	10.0	45.0

APPENDIX D-3

PENTACHLOROPHENOL

CELL 11 ANALYSIS

Date Collected	Hour	Volume Collected (ml)	Total Volume Collected (ml)	Hydraulic Conductivity (cm/sec)	Approximate Pore Volume	HPLC (PPM) PENTACHLOROPHENOL		
Jan. 29	3:10 PM	Start	-	-	-			
Jan. 30	3:55 PM	300	300	3.1E-5	0.4		0	
Jan. 31	3:55 PM	300	600	3.2E-5	0.9			
Feb. 1	12:15 PM	340	940	4.3E-5	1.3			
Feb. 2	1:02 PM	480	1420	4.9E-5	2.0		0	
Feb. 3	3:25 PM	520	1940	5.0E-5	2.8			
Feb. 4	12:50 PM	460	2400	5.5E-5	3.4			
Feb. 5	1:20 PM	500	2900	5.2E-5	4.1		0	
Feb. 6	5:25 PM	540	3440	5.1E-5	4.9			
Feb. 7	3:37 PM	370	3810	4.3E-5	5.4			
Feb. 8	3:20 PM	450	4260	4.9E-5	6.1		0	
Feb. 9	4:20 PM	530	4790	5.4E-5	6.8			
Feb. 10	6:55 PM	500	5290	4.8E-5	7.6			
Feb. 11	2:36 PM	360	5650	4.7E-5	8.1		0	
Feb. 12	10:17 PM	480	6130	3.9E-5	8.8			
Feb. 13	4:23 PM	260	6390	3.7E-5	9.1			
Feb. 14	21:41	410	6800	3.6E-5	9.7			
Feb. 16	7:56 AM	520	7320	3.9E-5	10.5		0	
Feb.17	1:33 PM	410	7730	3.5E-5	11.0			
Feb. 18	6:05 PM	330	8060	3.0E-5	11.5			
Feb. 19	4:11 PM	260	8320	3.0E-5	11.9			
Feb. 20	4:04 PM	260	8580	2.8E-5	12.3			
Feb. 21	4:56 PM	250	8830	2.6E-5	12.6			
Feb. 22	2:16 PM	220	9050	2.6E-5	12.9			
Feb. 23	7:02 PM	270	9320	2.4E-5	13.3		0	
Feb. 24	11:12 AM	140	9460	2.2E-5	13.5			
Feb. 26	1:12 PM	420	9880	2.1E-5	14.1			
Feb. 28	12:07 PM	400	10280	2.2E-5	14.7			
1 Mar.	2:31 PM	370	10650	1.9E-5	15.2		0	
4 Mar.	7:47 PM	550	11200	1.8E-5	16.0			
7 Mar.	11:06 AM	400	11600	1.6E-5	16.6			
10 Mar.	3:10 PM	450	12050	1.5E-5	17.2		0	
14 Mar.	2:48 PM	535	12585	1.4E-5	18.0			
18 Mar.	1:37 PM	540	13125	1.5E-5	18.8			

CELL 11 ANALYSIS

Date Collected	Hour	Volume Collected (ml)	Total Volume Collected (ml)	Hydraulic Conductivity (cm/sec)	Approximate Pore Volume	HPLC (PPM)		
						PENTACHLOROPHENOL		
23 Mar.	1:42 PM	610	13735	1.30E-05	19.6		0	
27 Mar.	1:20 PM	370	14105	9.90E-06	20.2			
1 Apr.	10:50 AM	440	14545	9.60E-06	20.8			
7 Apr.	4:00 PM	470	15015	8.10E-06	21.5		0	
13 Apr.	3:43 PM	390	15405	6.90E-06	22.0			
20 Apr.	1:50 PM	330	15735	5.07E-06	22.5			
28 Apr.	1:50 PM	360	16095	4.80E-06	23.0		0	
1 May.	10:10 AM	340	16435	1.27E-05	23.5			
3 May.	2:50 PM	290	16725	1.40E-05	23.9			
6 May.	11:55 AM	340	17065	1.30E-05	24.4		0	
10 May.	12:42 PM	460	17525	1.20E-05	25.0			
14 May.	1:40 PM	520	18045	1.40E-05	25.8			
19 May.	12:04 PM	720	18765	1.60E-05	26.8			
22 May.	4:39 PM	630	19395	2.10E-05	27.7			
24 May.	1:45 PM	740	20135	4.20E-05	28.8			
25 May.	6:22 PM	570	20705	7.80E-05	29.6			
26 May.	8:22 PM	800	21505	7.80E-05	30.7			
27 May.	1:33 PM	830	22335	1.80E-04	31.9			
28 May.	1:43 PM	1680	24015	1.80E-05	34.3			

Note: Cell no 11 was stop on May 28
due to excessive flow through the column.

CELL 12 ANALYSIS

Date Collected	Hour	Volume Collected (ml)	Total Volume Collected (ml)	Hydraulic Conductivity (cm/sec)	Approximate Pore Volume	HPLC (PPM)		
						PENTACHLOROPHENOL		
Jan. 29	3:10 PM	Start	-	-	-			
Jan. 30	3:55 PM	640	640	6.6E-5	0.9		0	
Jan. 31	3:55 PM	640	1280	6.8E-5	1.8			
Feb. 1	12:15 PM	720	2000	9.0E-5	2.9		0	
Feb. 2	1:02 PM	930	2930	9.6E-5	4.2			
Feb. 3	3:25 PM	1360	4290	1.3E-4	6.1		0	
Feb. 4	12:50 PM	1280	5570	1.5E-4	8.0			
Feb. 5	1:20 PM	2200	7770	2.3E-4	11.1		0	

Note: Cell no 12 was taken out of service due to excessive permeability.

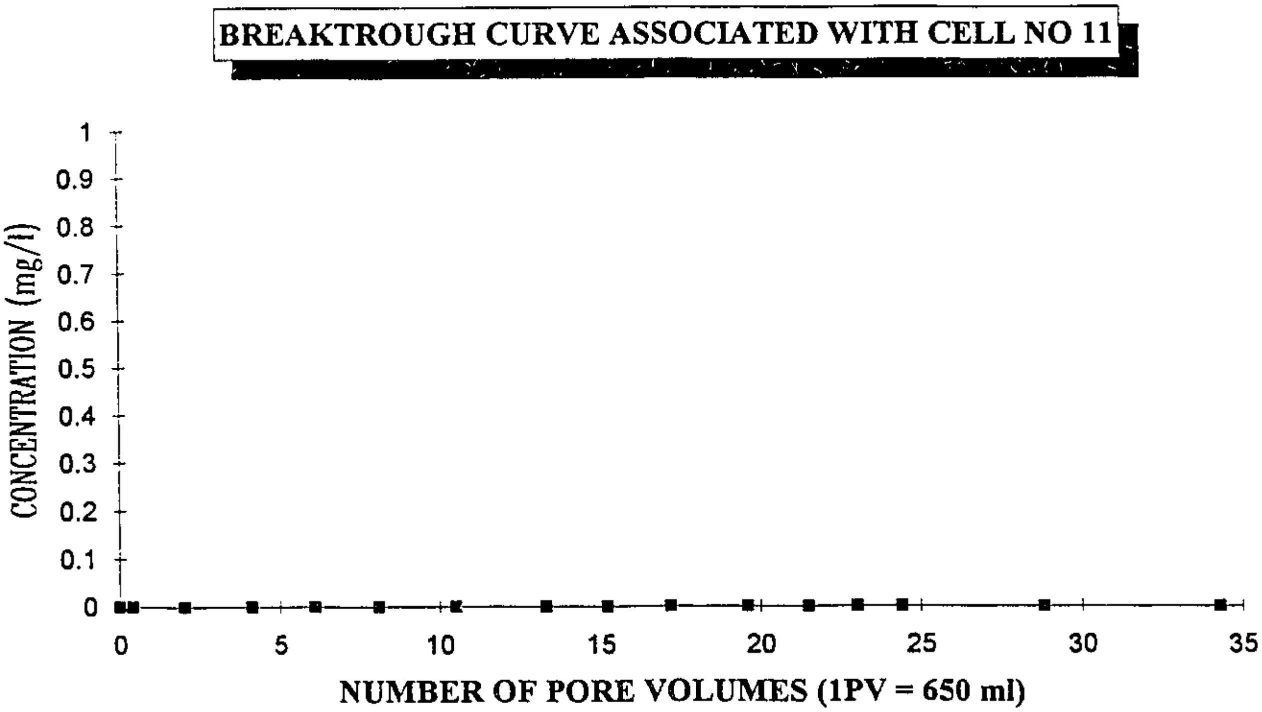
CELL 13 ANALYSIS

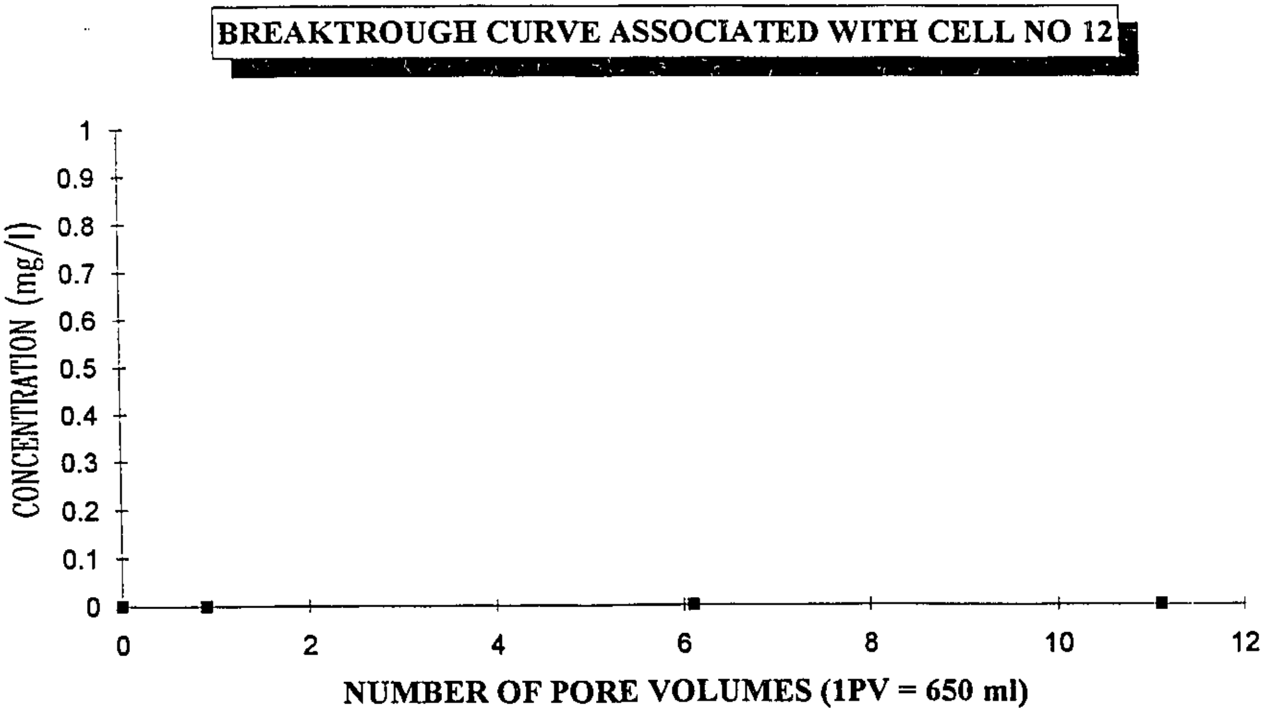
Date Collected	Hour	Volume Collected (ml)	Total Volume Collected (ml)	Hydraulic Conductivity (cm/sec)	Approximate Pore Volume	HPLC (PPM) PENTACHLOROPHENOL		
Jan. 29	3:10 PM	Start	-	-	-		0	
Jan. 30	3:55 PM	530	530	5.5E-5	0.8			
Jan. 31	3:55 PM	440	970	4.7E-5	1.4			
Feb. 1	12:15 PM	380	1350	4.8E-5	1.9		0	
Feb. 2	1:02 PM	530	1880	5.5E-5	2.7			
Feb. 3	3:25 PM	560	2440	5.4E-5	3.5			
Feb. 4	12:50 PM	540	2980	6.4E-5	4.3		0	
Feb. 5	1:20 PM	630	3610	6.6E-5	5.2			
Feb. 6	5:25 PM	670	4280	6.3E-5	6.1			
Feb. 7	3:37 PM	490	4770	5.6E-5	6.8		0	
Feb. 8	3:20 PM	570	5340	6.1E-5	7.6			
Feb. 9	4:20 PM	840	6180	8.6E-5	8.8			
Feb. 9	6:10 PM	160	6340	2.2E-4	9.1		0	

Note: Cell no 13 was taken out of operation due to excessive permeability.

INFLUENT ANALYSIS

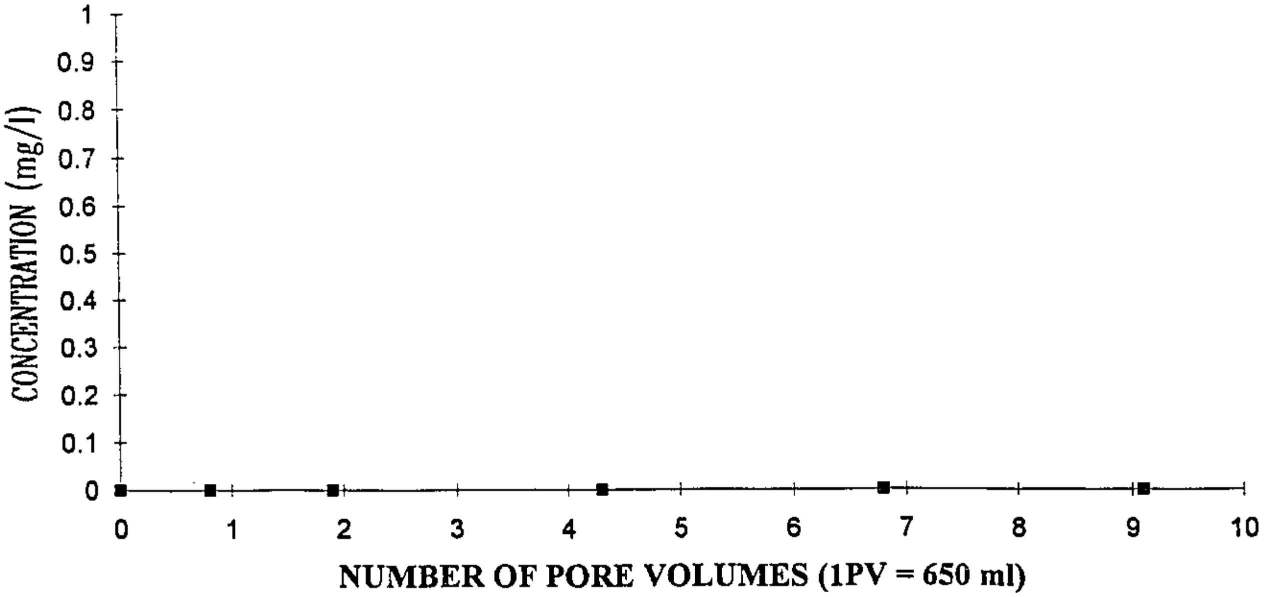
Date Collected	Hour	Total Volume Collected (ml)	Total Volume Collected (ml)	Hydraulic Conductivity (cm/sec)	Approximate Pore Volume	HPLC (PPM)		
						PENTACHLOROPHENOL		
Jan.30							8.4	
Feb. 4							8.7	
Feb. 16							5.1	
Feb.24							4.3	
Mar. 10							6.2	
Mar. 11							8.2	
Mar. 25							8.4	
Apr. 20							8.3	
May 6							8.1	


BREAKTROUGH CURVE ASSOCIATED WITH CELL NO 11
CONCENTRATION (mg/l)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
30
35
NUMBER OF PORE VOLUMES (1PV = 650 ml)



BREAKTROUGH CURVE ASSOCIATED WITH CELL NO 12

BREAKTROUGH CURVE ASSOCIATED WITH CELL NO 13



RESIDUAL PORE WATER

CELL NO 11

34 PORE VOLUMES

DATE	PORTION OF THE CELL	HPLC (PPM)		
		PENTACHLOROPHENOL		
Oct. 92	TOP		7.4	
	2.0 - 4.0 cm		4.3	
	4.0 - 6.0 cm		3.7	
	6.0 - 8.0 cm		2.5	
	BOTTOM		1.4	

RESIDUAL PORE WATER

CELL NO 12

11 PORE VOLUMES

DATE	PORTION OF THE CELL	HPLC (PPM)		
		PENTACHLOROPHENOL		
Feb. 92	TOP		1.2	
	2.0 - 4.0 cm		0.9	
	4.0 - 6.0 cm		0.0	
	6.0 - 8.0 cm		0.0	
	BOTTOM		0.0	

RESIDUAL PORE WATER

CELL NO 13

9 PORE VOLUMES

DATE	PORTION OF THE CELL	HPLC (PPM)		
		PENTACHLOROPHENOL		
Feb. 92	TOP		0.7	
	2.0 - 4.0 cm		0.0	
	4.0 - 6.0 cm		0.0	
	6.0 - 8.0 cm		0.0	
	BOTTOM		0.0	

PCP EXTRATION FROM CELL NO 11

Sample	Cell Portion	Area	Wet Soil Mass (g)	Hexane volume (ml)	PCP in hexane (mg/l)	Mass of dry soil *	PC P concentration mg/g of dry soil	Average
F-1	Top	1086409	3.13	10	50.46	1.16	0.44	
F-2	Top		1.47	5	23	0.54	0.21	
F-3	Top	539729	1.42	5	26	0.52	0.25	0.30
F-4	2 - 4	259755	1.24	5	13.5	0.48	0.14	
F-5	2 - 4	178432	1.24	5	9.9	0.48	0.10	0.12
F-6	4 - 6	330009	1.61	5	16.65	0.64	0.13	
F-7	4 - 6	135023	1.44	5	7.94	0.58	0.07	0.10
F-8	6 - 8	182069	1.3	5	10.04	0.55	0.09	
F-9	6 - 8	82165	1.6	5	5.58	0.67	0.04	0.07
F-10	Bottom		1.61	5	0	0.64	0.00	
F-11	Bottom	49168	1.29	5	4.1	0.52	0.04	0.02
F-12	Top	977956		5	#DIV/0!	0.7459	#DIV/0!	
F-13	2 - 4	854552		5	#DIV/0!	0.5705	#DIV/0!	
F-14	4 - 6	582645		5	#DIV/0!	0.5071	#DIV/0!	
F-15	6 - 8	367138		5	#DIV/0!	0.5803	#DIV/0!	
F-16	Bottom	84070		5	#DIV/0!	0.46805	#DIV/0!	
F-17	Bottom			10	0	0.5375	0.00	
A	Top	0		10	0	0.312	0.00	
B	2 - 4	262473		10	#DIV/0!	0.3501	#DIV/0!	
C	4 - 6	40283		10	#DIV/0!	0.371	#DIV/0!	
D	6 - 8	60622		10	#DIV/0!	0.3371	#DIV/0!	
E	Bottom	0		10	0	0.3103	0.00	

APPENDIX E

MASS BALANCE ANALYSES

E.1 General

Mass balance analyses were carried out in order to establish the validity of the methodology used in the column study investigation. This was achieved by comparing the total influx of contaminants entering the cell, with the mass of contaminants detected in the effluent, pore fluids and soil matrix. These calculations were done for each of the targeted contaminants as described in the following pages.

Total recovery varying between 74.7 and 94.9% was achieved for lead while a recovery of between 44.7 and 53.4% was achieved for zinc. The total recovery of pentachlorophenol was limited to 35%. No mass balance were undertaken for calcium and sodium in view of the very low adsorption capacity of those compounds.

The relatively low recovery for zinc and pentachlorophenol can be explained by the strong variability of the contaminant concentration as a function of the cell depth. As can be seen in the following tables a substantial decrease in concentration is observed between the top portion of the cell and the underlying soil matrix. Based on this observation, it can now be reasoned that the soil sampling procedure for soil digestion will greatly influence the estimate of the total recovery. Since most of the contaminants are being retained in the top portion of the cell, sampling of this portion should be greatly increased. Layering the cell at an interval of 5 mm instead of the 20 or 25 mm would have greatly improved the percentage of recovery.

It is also important to stress that pentachlorophenol is a very reactive contaminants which has been found to adsorb quite easily on a multitude of different surfaces. Therefore it is recommended that any further attempt to replicate the column study with pentachlorophenol be done with a non reactive cell, such as glass and that the storage of sample been done using either glass, acrylic or Teflon containers in order to limit any outside interference.

MASS BALANCE
ANALYSES

Lead

Cell No 2

A - Mass of contaminant inputed:

Average con. of Stock Solution (mg/L):	110.2
Total Volume of Solution (4.7 PV) (L):	3.055

Total mass of contaminant (mg): 336.66

B - Mass of contaminant recovered:

Average mass in the effluent (mg): 0

Average vol. of water per soil layer (L):	0.162
Average mass of soil per layer (kg)	0.1

Mass of Contaminant in the Pore Fluids			Mass of Contaminant in the Soil Matrix		
Depth (cm)	Measured Concent. (mg/L)	Mass of Cont. (mg)	Depth (cm)	Measured Concent. (mg/kg)	Mass of Cont. (mg)
0 - 2.5	0.1	0.02	0 - 2	2450	245
2.5 - 5	0	0.00	2 - 4	27	2.7
5 - 7.5	0.1	0.02	4 - 6	13	1.3
7.5 - 10	0.1	0.02	8 - 10	25	2.5

Total Mass:	0.0486	Total Mass:	251.5

Total mass of soil recovered (mg): 251.55

C - Mass Balance Calculation:

$$\textbf{Total recovery} = \frac{\text{Total Recovery Mass}}{\text{Total Mass of Contaminant}} \times 100$$

Total recovery = **74.72**

Lead

Cell No 4

A - Mass of contaminant inputed:

Average con. of Stock Solution (mg/L): 110.2

Total Volume of Solution (7.8 PV) (L): 5.07

Total mass of contaminant (mg): 558.714

B - Mass of contaminant recovered:

Average mass in the effluent (mg): 0

Average vol. of water per soil layer (L): 0.13

Average mass of soil per layer (kg) 0.08

Mass of Contaminant in the Pore Fluids			Mass of Contaminant in the Soil Matrix		
Depth (cm)	Measured Concent. (mg/L)	Mass of Cont. (mg)	Depth (cm)	Measured Concent. (mg/kg)	Mass of Cont. (mg)
0 - 2	0.1	0.01	0 - 2	6557	524.56
2 - 4	0	0.00	2 - 4	27.5	2.2
4 - 6	0	0.00	4 - 6	11	0.88
6 - 8	0	0.00	6 - 8	15.1	1.208
8 - 10	0	0.00	8 - 10	14.8	1.184

Total Mass: 0.013 Total Mass: 530.03

Total mass of soil recovered (mg): 530.05

C - Mass Balance Calculation:

$$\textbf{Total recovery} = \frac{\text{Total Recovery Mass}}{\text{Total Mass of Contaminant}} \times 100$$

Total recovery = 94.87

MASS BALANCE
ANALYSES

Zinc

Cell No 2

A - Mass of contaminant inputed:

Average con. of Stock Solution (mg/L): 98.8
Total Volume of Solution (4.7 PV) (L): 3.055

Total mass of contaminant (mg): 301.834

B - Mass of contaminant recovered:

Average mass in the effluent (mg): 0

Average vol. of water per soil layer (L): 0.162
Average mass of soil per layer (kg) 0.1

Mass of Contaminant in the Pore Fluids			Mass of Contaminant in the Soil Matrix		
Depth (cm)	**Measured Concent. (mg/L)**	**Mass of Cont. (mg)**	**Depth (cm)**	**Measured Concent. (mg/kg)**	**Mass of Cont. (mg)**
0 - 2.5	25.1	4.07	0 - 2	940	94
2.5 - 5	2.1	0.34	2 - 4	190	19
5 - 7.5	0.7	0.11	4 - 6	80	8
7.5 - 10	1.2	0.19	8 - 10	91	9.1

Total Mass: 4.7142 Total Mass: 130.1

Total mass of soil recovered (mg): 134.81

C - Mass Balance Calculation:

Total recovery = Total Recovery Mass X 100
Total Mass of Contaminant

Total recovery = 44.67

MASS BALANCE
ANALYSES

Zinc

Cell No 4

A - Mass of contaminant inputed:

Average con. of Stock Solution (mg/L):	98.8
Total Volume of Solution (7.8 PV) (L):	5.07

Total mass of contaminant (mg): 500.916

B - Mass of contaminant recovered:

Average mass in the effluent (mg): 0

Average vol. of water per soil layer (L):	0.13
Average mass of soil per layer (kg)	0.08

Mass of Contaminant in the Pore Fluids			Mass of Contaminant in the Soil Matrix		
Depth (cm)	Measured Concent. (mg/L)	Mass of Cont. (mg)	Depth (cm)	Measured Concent. (mg/kg)	Mass of Cont. (mg)
0 - 2	58.9	7.66	0 - 2	1960	156.8
2 - 4	5	0.65	2 - 4	1132	90.56
4 - 6	0.2	0.03	4 - 6	52.1	4.168
6 - 8	0.2	0.03	6 - 8	48.5	3.88
8 - 10	0.1	0.01	8 - 10	47.3	3.784

Total Mass: 8.372 Total Mass: 259.19

Total mass of soil recovered (mg): 267.56

C - Mass Balance Calculation:

Total recovery = $\frac{\text{Total Recovery Mass}}{\text{Total Mass of Contaminant}}$ X 100

Total recovery = 53.41

MASS BALANCE ANALYSES

PCP

Cell No 11

A - Mass of contaminant inputed:

Average con. of Stock Solution (mg/L):	8
Total Volume of Solution (34.3 PV) (L):	22.29

Total mass of contaminant (mg): 178.32

B - Mass of contaminant recovered:

Average mass in the effluent (mg): 0

Average vol. of water per soil layer (L):	0.13
Average mass of soil per layer (kg)	0.08

Mass of Contaminant in the Pore Fluids			Mass of Contaminant in the Soil Matrix		
Depth (cm)	Measured Concent. (mg/L)	Mass of Cont. (mg)	Depth (cm)	Measured Concent. (mg/kg)	Mass of Cont. (mg)
0 - 2	7.4	0.96	0 - 2	440	35.2
2 - 4	4.3	0.56	2 - 4	120	9.6
4 - 6	3.7	0.48	4 - 6	100	8
6 - 8	2.5	0.33	6 - 8	70	5.6
8 - 10	1.4	0.18	8 - 10	20	1.6

Total Mass: 2.509

Total Mass: 60

Total mass of soil recovered (mg): 62.51

C - Mass Balance Calculation:

Total recovery = $\frac{\text{Total Recovery Mass}}{\text{Total Mass of Contaminant}}$ X 100

Total recovery = 35.05

APPENDIX F

NUMERICAL ADAPTATION OF THE ADVECTION DISPERSION EQUATION WITH SORPTION USING FINITE DIFFERENCE APPROXIMATION (IMPLICIT SCHEME)

F.1 Mathematical Background

It is possible to estimate the retardation factor of contaminants by investigating their migration pattern during the leaching cell test as described in section 4.4. Knowing the contaminant distribution through space and time it is possible, using a numerical model, to back-calculate the retardation factor (R_F) characteristic of each contaminant species.

By adapting the Advection-Dispersion-Equation (ADE) with sorption, as detailed in section 2.3.4, to a spreadsheet layout it is feasible to numerically approximate the contaminant distribution profiles obtained in the laboratory column experiments. The ADE with sorption was previously defined as:

$$\frac{\delta C}{\delta t}=\frac{\delta}{\delta x}\left\{\frac{D_L}{R_F}\frac{\delta C}{\delta x}\right\}-\frac{V_x}{R_F}\frac{\delta C}{\delta x} \qquad (2.11)$$

This equation can be approximated using finite differences (implicit scheme) as follows:

$$\frac{\left(U_{i,j}-U_{i,j-1}\right)}{\Delta t}=\left({}^{D_L}\!/_{R_F}\right)\left[\frac{\left(U_{i-1,j}-2U_{i,j}+U_{i+1,j}\right)}{\Delta x^2}\right]-\left({}^{V_x}\!/_{R_F}\right)\left[\frac{\left(U_{i,j}-U_{i-1,j}\right)}{\Delta x}\right] \qquad (F\text{-}1)$$

where: U is the unknown, in this case concentration
Δt is the time increment between time steps
Δx is the space increment
i is the nodal index in space
j is the nodal index in time

if: $\alpha = 1/\Delta t$
$\beta = D_L / R_F \Delta x^2$
$\varepsilon = V_x / R_F \Delta x$

then: $$\alpha U_{i,j} - \alpha U_{i,j-1} = \beta U_{i-1,j} - 2\beta U_{i,j} + \beta U_{i+1,j} - \varepsilon U_{i,j} + \varepsilon U_{i-1,j} \qquad \text{(F-2)}$$

Equation (F-2) is centere on Ui,j, with the j^{th} time level being unknown and j-1 being known. Now by putting the known value $(j-1)$ on the right side of the equation, the following is obtained:

$$(-\beta - \varepsilon)U_{i-1,j} + (\alpha + 2\beta + \varepsilon)U_{i,j} - \beta U_{i+1,j} = \alpha U_{i,j-1} \qquad \text{(F-3)}$$

So for the following cell disposition in which time progresses downward :

	A	
B	C	D

The resulting equation will be:

$$(-\beta - \varepsilon)B + (\alpha + 2\beta + \varepsilon)C - \beta D = \alpha A \qquad \text{(F-4)}$$

So the central cell can be approximated by:

$$Cell\ \mathrm{C} = \frac{(\beta + \varepsilon)B + \beta D + \alpha A}{(\alpha + 2\beta + \varepsilon)} \qquad \text{(F-5)}$$

The above mentioned equation can be solved using a spreadsheet program (such as Excel). The problem is solved iteratively until convergence is achieved. In the following subsections, the initial input parameters for each contaminant studied, as obtained during the soil column leaching tests, are presented as well as the results of the spreadsheet simulation. A copy of the spreadsheet analysis for zinc (cell no 5) is presented at the end of this appendix.

F.2 Leaching Cell Simulation

F.2.1 Chloride Migration

The migration profile data obtained during the leaching column experiment for chloride is presented in Table F-1.

TABLE F-1
Migration Data for Chloride

Cell 6	
Time :	1 day
C_o :	250 mg/l
$C_{(10cm)}$:	110 mg/l
V :	12.1 cm/day
R_F :	1
D_L :	?

Cell 8	
Time :	1 day
C_o :	250 mg/l
$C_{(10cm)}$:	111 mg/l
V :	12.4 cm/day
R_F :	1
D_L :	?

Since chloride is a non-reactive contaminant, it is assumed that the retardation factor (R_F) is equal to 1. Any variation of the breakthrough curve of chloride is thus attributable solely to the effects of the dispersion coefficient (D_L) as reported in section 2.3.

By imputing the data presented in Table F-1 into the spreadsheet program and varying only the dispersion coefficient (D_L) it was possible to mathematically simulate the migration profile of chloride by trial and error. Results of this analysis indicate a D_L of 1.5 cm^2/day for cell 6 and of 0.7 cm^2/day for cell 8. An average D_L of 1 cm²/day will therefore be assumed for all the remaining contaminants for the retardation factor (R_F) estimation.

F.2.2 Lead Migration

The migration profile data obtained during the leaching column experiment for lead is presented in Table F-2

TABLE F-2

Migration Data for Lead

Cell 5	
Time :	16 day
C_o :	110 mg/l
$C_{(1cm)}$:	0.1 mg/l
V :	3.19 cm/day
R_F :	?
D_L :	1 cm²/day

Cell 4	
Time :	53 day
C_o :	110 mg/l
$C_{(1cm)}$:	0.1 mg/l
V :	1.52 cm/day
R_F :	?
D_L :	1 cm²/day

Results from the numerical approximation using the spreadsheet program indicate a R_F in excess of 2000. It however to be noticed that the very low concentration level observed within the pore water of the cell, does not lend itself to precise evaluation. One can only conclude that lead is extremely adsorbed by the marshland soil.

F.2.3 Zinc Migration

The migration profile data obtained during the leaching column experiment for zinc is presented in Table F-3.

TABLE F-3

Migration Data for Zinc

Cell 5	
Time :	16 day
C_o :	99 mg/l
$C_{(1.25cm)}$	25.1 mg/l
V :	3.19 cm/day
R_F :	?
D_L :	1 cm^2/day

Cell 4	
Time :	53 day
C_o :	99 mg/l
$C_{(1cm)}$:	58.9 mg/l
V :	1.52 cm/day
R_F :	?
D_L :	1 cm^2/day

Results from the numerical approximation using the spreadsheet program indicate a R_F of 84 and 105 for cell 5 and 4 respectively.

F.2.4 Sodium Migration

The migration profile data obtained during the leaching column experiment for sodium is presented in Table F-4.

TABLE F-4

Migration Data for Sodium

Cell 6	
Time :	48 hours
C_o :	113 mg/l
$C_{(10cm)}$	70 mg/l
V :	12.7 cm/day
R_F :	?
D_L :	1 cm^2/day

Cell 7	
Time :	60 hours
C_o :	113 mg/l
$C_{(10cm)}$:	61 mg/l
V :	9.1 cm/day
R_F :	?
D_L :	1 cm^2/day

Results from the numerical approximation using the spreadsheet program indicate a R_F of 1.9 and 2.4 for cell 6 and 7 respectively.

F.2.5 Calcium Migration

The migration profile data obtained during the leaching column experiment for calcium is presented in Table F-5.

TABLE F-5

Migration Data for Calcium

Cell 6	
Time :	24 hours
C_o :	111 mg/l
$C_{(10cm)}$	51 mg/l
V :	12.1cm/day
R_F :	?
D_L :	1 cm^2/day

Cell 7	
Time :	36 hours
C_o :	111 mg/l
$C_{(10cm)}$:	78 mg/l
V :	8.8 cm/day
R_F :	?
D_L :	1 cm^2/day

Results from the numerical approximation using the spreadsheet program indicate a R_F of 1.0 and 1.25 for cell 6 and 7 respectively.

F.2.6 Pentachlorophenol Migration

The migration profile data obtained during the leaching column experiment for pentachlorophenol is presented in Table F-6.

TABLE F-6

Migration Data for Pentachlorophenol

Cell 11	
Time :	117 days
C_o :	8.0 mg/l
$C_{(1cm)}$	7.4 mg/l
V :	3.17cm/day
R_F :	?
D_L :	1 cm^2/day

Cell 11	
Time :	117 days
C_o :	8.0 mg/l
$C_{(5cm)}$:	3.7 mg/l
V :	3.17 cm/day
R_F :	?
D_L :	1 cm^2/day

Results from the numerical approximation using the spreadsheet program indicate a R_F varying from 93 to 150 for cell no 11.

ZINC ANALYSIS
USING A SPREADSHEET ADAPTATION OF THE ADVECTION DISPERSION EQUATION WITH SORPTION

Where:
x (cm) = 0.25
t (d) = 1
Dl (cm²/d) 1
V (cm/d) 3.19
Rf = 84 (By trial and error)
Co = 99

a = 1/(t) = 1
ß = Dl/ (Rf x²) = 1.90E-01
e = V/ (Rf x) = 0.151905

SPACE (cm)

DAYS

Time	0	0.25	0.5	0.75	1	1.25	1.5	1.75
1	99	0	0	0	0	0	0	0
2	99	22.76315	5.233949	1.203446	0.276709	0.063624	0.014629	0.003364
3	99	38.51331	12.47684	3.701493	1.042547	0.283736	0.075362	0.019655
4	99	49.74132	20.14591	7.210743	2.38334	0.745247	0.223712	0.065087
5	99	57.98099	27.5076	11.38058	4.283885	1.505439	0.502185	0.160823
6	99	64.1955	34.26057	15.90563	6.669177	2.589428	0.947024	0.330207
7	99	69.00233	40.31741	20.55463	9.438258	3.994258	1.584026	0.595896
8	99	72.80599	45.69143	25.16664	12.48639	5.696346	2.427199	0.977561
9	99	75.87733	50.43887	29.6373	15.7174	7.65918	3.479409	1.490379
10	99	78.40181	54.63005	33.90401	19.04922	9.839807	4.734177	2.144334
11	99	80.50919	58.3357	37.9335	22.41535	12.19366	6.177907	2.944175
12	99	82.29223	61.62098	41.71216	25.76403	14.67781	7.792136	3.889832
13	99	83.81859	64.54343	45.23915	29.05641	17.25293	9.555509	4.977112
14	99	85.13859	67.15267	48.52151	32.26441	19.88425	11.4454	6.19852
15	99	86.29029	69.49105	51.57088	35.3686	22.54198	13.43916	7.544088
16	99	87.30301	71.59447	54.40131	38.35633	25.2011	15.51497	9.002158
17	99	88.19965	73.49334	57.02781	41.22018	27.84113	17.65245	10.56006
18	99	88.99833	75.21343	59.46552	43.95661	30.44559	19.83299	12.20467
19	99	89.71362	76.77662	61.7291	46.56499	33.00154	22.03993	13.92289
20	99	90.35732	78.20155	63.83248	49.0468	35.49901	24.2586	15.70194
21	99	90.93913	79.50418	65.78866	51.40496	37.93059	26.47624	17.52966
22	99	91.46705	80.69819	67.60967	53.64342	40.29097	28.68194	19.39463
23	99	91.9478	81.79537	69.30658	55.76677	42.57656	30.86646	21.28633
24	99	92.387	82.80594	70.8895	57.78	44.78516	33.02211	23.19513
25	99	92.78944	83.73878	72.36765	59.6883	46.91573	35.14252	25.11237
26	99	93.15921	84.60164	73.74942	61.4969	48.96811	37.22258	27.03028
27	99	93.4998	85.4013	75.04247	63.21098	50.94284	39.25819	28.94202
28	99	93.81425	86.14373	76.25374	64.83564	52.84103	41.2462	30.84154
29	99	94.10519	86.8342	77.38955	66.37577	54.66419	43.18423	32.72363
30	99	94.37491	87.47737	78.45564	67.83609	56.41416	45.07057	34.58377
31	99	94.62543	88.07737	79.45726	69.22111	58.093	46.9041	36.41811
32	99	94.85852	88.63791	80.39918	70.53511	59.70292	48.68418	38.22342
33	99	95.07574	89.16227	81.28574	71.78213	61.24626	50.41057	39.99698
34	99	95.27848	89.65342	82.12093	72.96601	62.7254	52.08338	41.73657
35	99	95.46797	90.11401	82.90838	74.09035	64.14274	53.70298	43.44043
36	99	95.64533	90.54644	83.65141	75.15855	65.5007	55.27	45.10713
37	99	95.81154	90.95286	84.35309	76.17381	66.80166	56.78522	46.73561
38	99	95.96748	91.33523	85.01621	77.13912	68.04795	58.24961	48.32512
39	99	96.11396	91.69533	85.64334	78.05731	69.24187	59.66422	49.87513
40	99	96.2517	92.03476	86.23684	78.931	70.38565	61.03023	51.38537
41	99	96.38135	92.355	86.79891	79.76269	71.48145	62.34885	52.85575
42	99	96.50351	92.65739	87.33155	80.5547	72.53135	63.62136	54.28634
43	99	96.61871	92.94316	87.83662	81.30921	73.53737	64.84907	55.67738
44	99	96.72745	93.21342	88.31583	82.02827	74.50144	66.03333	57.02921
45	99	96.83017	93.46921	88.77077	82.7138	75.42542	67.17545	58.34228

APPENDIX G

LISTING OF THE DID2XY
COMPUTER PROGRAM

```
C    DID2  PROGRAM                                                      DID00010
C                                                                       DID00020
C     ::::::::::::::::::::::::::::::::::::::::::::::::::::::::::        DID00030
C     *                                                        *        DID00040
C     *       UNSTEADY TWO DIMENSIONAL SOLUTE                  *        DID00050
C     *                                                        *        DID00060
C     *  AND FLUID TRANSPORT IN CLAY SOILS COMPUTER PROGRAM    *        DID00070
C     *                                                        *        DID00080
C     *       USING THE FINITE DIFFERENCE METHOD               *        DID00090
C     *                                                        *        DID00100
C     *--------------------------------------------------------*        DID00110
C     *                                                        *        DID00120
C     *        DR. BAOLIN CAI                                  *        DID00130
C     *        FRANCOIS LA FORGE (REVISED 1992-1994)           *        DID00140
C     *        OTTAWA UNIVERSITY                               *        DID00150
C     *                                                        *        DID00160
C     *    DEPARTMENT OF CIVIL ENGINEERING                     *        DID00170
C     *                                                        *        DID00180
C     *         OTTAWA, CANADA                                 *        DID00190
C     *         AUGUST , 1990                                  *        DID00200
C     *                                                        *        DID00210
C     *--------------------------------------------------------*        DID00220
C                                                                       DID00230
C////////////////////////////////////////////////////////////////C      DID00240
C----------------------------------------------------------------C      DID00250
C                                                                C      DID00260
C                LIST OF VARIABLES                               C      DID00270
C                                                                C      DID00280
C----------------------------------------------------------------C      DID00290
C                                                                       DID00300
C////////////////////////////////////////////////////////////////C      DID00310
C                                                                       DID00320
C   1-POROS    = POROSITY OF THE SOIL                                   DID00330
C   2-RO       = DRY  DENSITY OF THE SOIL                               DID00340
C   3-KH       = PERMEABILITY  OF THE SOIL                              DID00350
C   4-D        = AA*EXP(BB*C). D IS THE DIFFUSION- DISPERSION           DID00360
C                COEFFICIENT                                            DID00370
C   5-KHC      = OSMOSIS  COEFFICIENT                                   DID00380
C   6-KCH      = ION RESTRICTION COEFFICIENT                            DID00390
C   7-DX       = D COEF. IN X- DIRECTION                                DID00400
C   8-DZ       = D COEF. IN Z- DIRECTION                                DID00410
C   9-DXTDZ    = DX/DY                                                  DID00420
C  10-R        = UNIVERSAL GASES CONSTANT                               DID00430
C  11-T        = ABSOLUTE TEMPERATURE                                   DID00440
C  12-MS       = MOLCULAR WEIGHT OF THE SOLUTE                          DID00450
C  13-GAMAL    = SPECIFIC WEIGHT OF THE SOLVENT                         DID00460
C  14-LEN      = FIELD LENGTH                                           DID00470
C  15-DEF      = DEPTH OF THE CLAY LINER BENEATH THE LANDFILL           DID00480
C  16-LENL     = LENGTH  OF THE LANDFILL                                DID00490
C  17-NLLS     = NUMBER OF LENGTH STEPS OF THE LANDFILL                 DID00500
C  18-NLS      = NUMBER OF LENGTH STEPS OF THE FIELD                    DID00510
C  19-NDEPS    = NUMBER OF LENGTH STEPS OF THE CLAY LINER               DID00520
C  20-NTS      = NUBER OF TIME STEPS                                    DID00530
C  21-DELX     = X-STEP LENGTH                                          DID00540
C  22-DELZ     = Z-STEP LENGTH                                          DID00550
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C 23-DELT      = TIME STEP INTERVAL                                      DID00560
C 24-NXN       = NUMBER OF NODES IN X-DIRECTION OF THE FIELD             DID00570
C 25-NZN       = NUMBER OF NODES IN Z-DIRECTION OF THE CLAY LINER        DID00580
C 26-CO        = UPPER BOUNDARY CONCENTRATION                            DID00590
C 27-HO        = UPPER BOUNDARY HEAD                                     DID00600
C 28-CI        = BACKGROUND CONCENTRATION INTHE PORE FLUID               DID00610
C 29-ITER      = NO. OF ITERATIONS IN FLUID FIELD SOLUTION               DID00620
C                PROGRAM(POISON)                                         DID00630
C 30-ITMAX     = MAXIMUM NUMBER OF ITERATION                             DID00640
C 31-RELAX     = RELAXATION FACTOR IN POISON SUBROUTINE                  DID00650
C                                                                        DID00660
C*****************************************************************C     DID00670
C                                                                        DID00680
C:::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::C     DID00690
C                                                                 C     DID00700
C                          MAIN   PROGRAM                         C     DID00710
C                                                                 C     DID00720
C:::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::C     DID00730
C                                                                        DID00740
      IMPLICIT REAL*8(A-H,O-Z)                                           DID00750
      REAL*4  KH , KCH , KHC , MS , LEN , LENL , LAMBDA                  DID00760
C                                                                        DID00770
C------------------------COMMON BLOCK-----------------------------C     DID00780
C                                                                        DID00790
      COMMON  C(50,51), H(50,51) , HN(50,51)                             DID00800
      COMMON  POROS , RO, KH ,D ,AA ,BB, KHC ,KCH, DX,DZ,DXTDZ,R,        DID00810
     &        T,MS, GAMAL                                                DID00820
      COMMON  LEN, DEP,LENL, NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT           DID00830
      COMMON  NXN, NXLN, NZN,N,ITER,III                                  DID00840
      COMMON  A,B,OSM,ITMAX                                              DID00850
      COMMON  /RE/RELAX,CO,HO,CI,DLAP,DEL2,LAMBDA,RI,TT,ITERC            DID00860
      COMMON /V/ TX(99,9),TZ(99,9)                                       DID00870
C-----------------------------------------------------------------C     DID00880
C                                                                        DID00890
C     OPEN (1,FILE='CHK100.DAT,'STATUS='NEW',FORM='FORMATTED')           DID00900
      CALL INPUT                                                         DID00910
      CALL BOUNDR                                                        DID00920
      KCH=(KHC*POROS)/(R*T)                                              DID00930
      RI=KCH/KH                                                          DID00940
      OSM=KCH*KHC/(2.D0*KH*MS)                                           DID00950
      LAMBDA=(POROS*KHC)/(KH*MS)                                         DID00960
      DEL2=(DELX/DELZ)**2                                                DID00970
C                                                                        DID00980
C     GIVING INITIAL VALUES TO HEADS                                     DID00990
C                                                                        DID01000
CC    NZNM1=NZN-1                                                        DID01010
CC    DO 70 I=1, NXN                                                     DID01020
CC    DO 70 J=2, NZNM1                                                   DID01030
CC    H(I,J)=50.D0                                                       DID01040
CC 70 CONTINUE                                                           DID01050
      ITER = 0                                                           DID01060
      DO 300 N=1,NTS                                                     DID01070
      IF(ITER.GT.1) GOTO 81                                              DID01080
C                                                                        DID01090
C     CALCULATING THE LAPLACIAN OF CONCENTRATIONS                        DID01100
```

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                                                                         DID01110
C                                                                        DID01120
      DO 80 J=2,NDEPS                                                    DID01130
      DO 80 I=1,NXN                                                      DID01140
      IF(I.EQ.NXN.OR.I.EQ.1) GO TO 76                                    DID01150
      D2CX2=(C(I+1,J)-2*C(I,J)+C(I-1,J))/(DELX**2)                       DID01160
      GOTO 77                                                            DID01170
   76 D2CX2=0.0                                                          DID01180
   77 D2CZ2=(C(I,J+1)-2*C(I,J)+C(I,J-1))/(DELZ**2)                       DID01190
      DLAP=D2CX2+D2CZ2                                                   DID01200
   80 CONTINUE                                                           DID01210
   81 ITER = ITER+1                                                      DID01220
CC    III = 3                                                            DID01230
CC 82 CALL POISON                                                        DID01240
C                                                                        DID01250
C     CHECK THE CRITERIA                                                 DID01260
C                                                                        DID01270
CC    IF(ITER.EQ.ITMAX) GOTO 105                                         DID01280
CC    IF(III.EQ.1) GOTO 81                                               DID01290
  105 CALL IMPLT                                                         DID01300
      WRITE(6,111) N,ITER,ITERC                                          DID01310
  111 FORMAT(5X,'TIME STEP=', I5,6X,'ITERATION FOR HEAD=',I5,6X,         DID01320
     &       ITER. FOR CONCENT.=',I5)                                    DID01330
      ITER=0                                                             DID01340
  300 CONTINUE                                                           DID01350
      CALL OUTPUT                                                        DID01360
C     CALL PLOT                                                          DID01370
      STOP                                                               DID01380
      END                                                                DID01390
C***********************************************************************C DID01400
C                                                                       C DID01410
C.......................................................................C DID01420
C                                                                       C DID01430
C                          SUBROUTINES                                  C DID01440
C                                                                       C DID01450
C.......................................................................  DID01460
C-----------------------------------------------------------------------C DID01470
C-----------------------INPUT-------------------------------------------C DID01480
C***********************************************************************C DID01490
C     SUBROUTINE # 1                                                      DID01500
C     IN THIS SUBROUTINE THE MAXIMUM NO. OF ITERATION, SOIL              DID01510
C    & CHARACTERSTICS , CONSTANTS, GEOMETRY OF REGION,                    DID01520
C    & NUMBER OF SPACE AND TIME STEPS, ARE GIVEN                          DID01530
C                                                                         DID01540
      SUBROUTINE INPUT                                                    DID01550
      IMPLICIT REAL*8(A-H,O-Z)                                            DID01560
      REAL*4  KH , KCH , KHC , MS , LEN , LENL , LAMBDA                   DID01570
                          .COMMON BLOCK.________________________________C DID01580
C_________________________________                                        DID01590
C                                                                         DID01600
      COMMON  C(50,51), H(50,51) , HN(50,51)                              DID01610
      COMMON  POROS , RO, KH ,D ,AA ,BB, KHC ,KCH, DX,DZ,DXTDZ,P,         DID01620
     &          T,MS, GAMAL                                               DID01630
      COMMON  LEN, DEF,LENL, NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT            DID01640
      COMMON  NXN, NXLN, NZN,N,ITER,III                                   DID01650
      COMMON  A,B,OSM,ITMAX
```

```
      COMMON  /RE/RELAX,CO,HO,CI,DLAP,DEL2,LAMBDA,RI,TT,ITERC           DID01660
      COMMON /V/ TX(99,9),TZ(99,9)                                      DID01670
                                                                        DID01680
C_____________________________________________________________C         DID01690
C                                                                       DID01700
C     GIVING THE MAXIMUM NUMBER OF ITERATION                            DID01710
C                                                                       DID01720
      ITMAX=300                                                         DID01730
C                                                                       DID01740
C     GIVING OVER RELAXATION FACTOR                                     DID01750
C                                                                       DID01760
      RELAX=1.8D0                                                       DID01770
C                                                                       DID01780
C     SOIL CHARACTERISTICS (GR,CM,DAY)                                  DID01790
C                                                                       DID01800
CC    VALIDATION OF THE DID2XY MODEL                                    DID01810
CC                                                                      DID01820
CC    DZ=15B3 36D0                                                      DID01830
CC    DXTDZ=0.D0                                                        DID01840
CC    CO=1000.0D-6                                                      DID01850
CC    CI=0.0D-6                                                         DID01860
CC    GEOMETRY OF THE REGION                                            DID01870
CC    LEN=10000.D0                                                      DID01880
CC    DEP=20000.D0                                                      DID01890
CC    LENL=2000.D0                                                      DID01900
CC                                                                      DID01910
CC    RET1=1.D0                                                         DID01920
CC    H0=1000.D0                                                        DID01930
C                                                                       DID01940
C     LOCKSLEY MARSHLAND PARAMETER                                      DID01950
C                                                                       DID01960
      POROS=0.30D0                                                      DID01970
      RO=0.45D0                                                         DID01980
      KH=4.32D0                                                         DID01990
      AA=0.23650                                                        DID02000
      BB=0.                                                             DID02010
      A=0.                                                              DID02020
      B=0.                                                              DID02030
      KHC=0                                                             DID02040
      DZ=15E3.36D0                                                      DID02050
      DXTDZ=0.33                                                        DID02060
C     KZ=2200.                                                          DID02070
C     KX=733.3                                                          DID02080
C                                                                       DID02090
C     CONTAMINANT CHARACTERISTICS                                       DID02100
C                                                                       DID02110
C     CHLORIDE                                                          DID02120
C     RET1=1.0                                                          DID02130
C     CI=11.0D-6                                                        DID02140
C     CO=36.D-6                                                         DID02150
C     CALCIUM                                                           DID02160
C     RET1=1.2                                                          DID02170
C     CI=10.0D-6                                                        DID02180
C     CO=42.0D-6                                                        DID02190
C     SODIUM                                                            DID02200
```

```
C       RET1=2.2                                                DID02210
C       CI=6.0D-6                                               DID02220
C       CO=21.4D-6                                              DID02230
C       ZINC                                                    DID02240
C       RET1=100.0                                              DID02250
C       CI=0.01D-6                                              DID02260
C       CO=0.03D-6                                              DID02270
C       PENTACHLOROPHENOL                                       DID02280
C       RET1=90.0                                               DID02290
C       CI=0.003D-6                                             DID02300
C       CO=0.2D-6                                               DID02310
C       LEAD                                                    DID02320
        RET1=2000.0                                             DID02330
        CI=0.00D-6                                              DID02340
        CO=0.001D-6                                             DID02350
C                                                               DID02360
        H0=8530.D0                                              DID02370
C                                                               DID02380
C       CONSTANTS                                               DID02390
C                                                               DID02400
        R=82.0567D0*1034                                        DID02410
        T=273.D0+20.                                            DID02420
        MS=40.                                                  DID02430
        GAMAL=1.D0                                              DID02440
        KCH=(KHC*POROS)/(R*T)                                   DID02450
C                                                               DID02460
C       GEOMETRY OF THE REGION                                  DID02470
C                                                               DID02480
        LEN=8000.D0                                             DID02490
        DEP=60000.D0                                            DID02500
        LENL=2000.D0                                            DID02510
C                                                               DID02520
        NLS=10                                                  DID02530
        NLLS=5                                                  DID02540
        NDEPS=20                                                DID02550
CC ------------------1YR                                        DID02560
        NTS=12                                                  DID02570
CC ------------------10YR                                       DID02580
C       NTS=122                                                 DID02590
CC-------------------50YR                                       DID02600
C       NTS=612                                                 DID02610
CC-------------------100YR                                      DID02620
C       NTS=1220                                                DID02630
C                                                               DID02640
C       NUMBER & TIME STEPS                                     DID02650
C                                                               DID02660
        DELX=(LEN/2.D0)/NLS                                     DID02670
        DELZ=DEP/NDEPS                                          DID02680
        DELT=30.D0                                              DID02690
C                                                               DID02700
C       NUMBER OF SPACE NODES                                   DID02710
C                                                               DID02720
        NXN=NLS+1                                               DID02730
        NXLN=NLLS+1                                             DID02740
        NZN=NDEPS+1                                             DID02750
```

```
                                                                        DID02760
      RETURN                                                            DID02770
      END                                                               DID02780
C*****************************************************************C     DID02790
C------------------------------BOUNDR-----------------------------C     DID02800
C     SUBROUTINE #2                                                     DID02810
C                                                                       DID02820
C     IN THIS SUBROUTINE INITIAL AND BOUNDARY CONDITIONS ARE GIVIN.     DID02830
C                                                                       DID02840
                                                                        DID02850
      SUBROUTINE BOUNDR                                                 DID02860
      IMPLICIT REAL*8(A-H,O-Z)                                          DID02870
      REAL*8 KH , KCH , KHC , MS , LEN , LENL , LAMBDA                  DID02880
C_________________________.COMMON BLOCK.__________________________C     DID02890
C                                                                       DID02900
C                                                                       DID02910
      COMMON  C(50,51), H(50,51) , HN(50,51)                            DID02920
      COMMON  POROS , RO, KH ,D ,AA ,BB, KHC ,KCH, DX,DZ,DXTDZ,R,       DID02930
     &        T,MS, GAMAL                                               DID02940
      COMMON  LEN, DEP,LENL, NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT          DID02950
      COMMON  NXN, NXLN, NZN,N,ITER,III                                 DID02960
      COMMON  A,B,OSM,ITMAX                                             DID02970
      COMMON  /RE/RELAX,CO,HO,CI,DLAP,DEL2,LAMBDA,RI,TT,ITERC           DID02980
      COMMON /V/ TX(99,9),TZ(99,9)                                      DID02990
C-----------------------------------------------------------------C     DID03000
C                                                                       DID03010
C     INITIAL & BOUNDART CONDITIONS                                     DID03020
C                                                                       DID03030
C     UPPER BOUNDARY CONDITION                                          DID03040
C                                                                       DID03050
C     FOR VALIDATION OF THE DID2XY MODEL                                DID03060
C                                                                       DID03070
CC    DO 20 I=1,NXN                                                     DID03080
CC    IF (I.GT.NXLN)GO TO 10                                            DID03090
CC    H(I,1)=H0                                                         DID03100
CC    HN(I,1)=H(I,1)                                                    DID03110
CC    C(I,1)=C0                                                         DID03120
C     GO TO 20                                                          DID03130
C 10  H(I,1)=H0                                                         DID03140
C     HN(I,1)=H(I,1)                                                    DID03150
C     C(I,1)=CI                                                         DID03160
C 20  CONTINUE                                                          DID03170
CC                                                                      DID03180
CC    LOWER BOUNDARY CONDITION                                          DID03190
CC                                                                      DID03200
CC    DO 30 I=1,NXN                                                     DID03210
CC    H(I,NZN)=0.0                                                      DID03220
CC 30 CONTINUE                                                          DID03230
C                                                                       DID03240
C     LOCKSLEY MARSHLAND PARAMETERS                                     DID03250
C                                                                       DID03260
      DO 20 I=1,NXN                                                     DID03270
      IF (I.GT.NXLN) GO TO 10                                           DID03280
      H(I,1)= 8530.D0                                                   DID03290
      H(I,2)= 8495.D0                                                   DID03300
      H(I,3)= 6480.D0
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      H(I,4)= 8468.D0                                                   DID03310
      H(I,5)= 8463.D0                                                   DID03320
      H(I,6)= 8460.D0                                                   DID03330
      H(I,7)= 8458.D0                                                   DID03340
      H(I,8)= 8455.D0                                                   DID03350
      H(I,9)= 8453.D0                                                   DID03360
      H(I,10)= 8450.D0                                                  DID03370
      H(I,11)= 8440.D0                                                  DID03380
      H(I,12)= 8430.D0                                                  DID03390
      H(I,13)= 8420.D0                                                  DID03400
      H(I,14)= 8405.D0                                                  DID03410
      H(I,15)= 8390.D0                                                  DID03420
      H(I,16)= 8370.D0                                                  DID03430
      H(I,17)= 8340.D0                                                  DID03440
      H(I,18)= 8310.D0                                                  DID03450
      H(I,19)= 8290.D0                                                  DID03460
      H(I,20)= 8270.D0                                                  DID03470
      H(I,21)= 8220.D0                                                  DID03480
      C(I,1)=C0                                                         DID03490
      GO TO 20                                                          DID03500
   10 H(I,1)= 8530.D0                                                   DID03510
      H(I,2)= 8495.D0                                                   DID03520
      H(I,3)= 8480.D0                                                   DID03530
      H(I,4)= 8468.D0                                                   DID03540
      H(I,5)= 8463.D0                                                   DID03550
      H(I,6)= 8460.D0                                                   DID03560
      H(I,7)= 8456.D0                                                   DID03570
      H(I,8)= 8455.D0                                                   DID03580
      H(I,9)= 8453.D0                                                   DID03590
      H(I,10)= 8450.D0                                                  DID03600
      H(I,11)= 8440.D0                                                  DID03610
      H(I,12)= 8430.D0                                                  DID03620
      H(I,13)= 8420.D0                                                  DID03630
      H(I,14)= 8405.D0                                                  DID03640
      H(I,15)= 8390.D0                                                  DID03650
      H(I,16)= 8370.D0                                                  DID03660
      H(I,17)= 8340.D0                                                  DID03670
      H(I,18)= 8310.D0                                                  DID03680
      H(I,19)= 8290.D0                                                  DID03690
      H(I,20)= 8270.D0                                                  DID03700
      H(I,21)= 8220.D0                                                  DID03710
      C(I,1)=CI                                                         DID03720
   20 CONTINUE                                                          DID03730
C                                                                       DID03740
C     LOWER BOUNDARY CONDITION                                          DID03750
C                                                                       DID03760
      DO 30 I=1, NXN                                                    DID03770
      H(I,NZN)=82.2                                                     DID03780
   30 CONTINUE                                                          DID03790
C                                                                       DID03800
C     CONCENTRATION INITIAL CONDITION                                   DID03810
C                                                                       DID03820
      DO 50 I=1, NXN                                                    DID03830
      DO 50 J=2, NZN                                                    DID03840
      C(I,J)=CI                                                         DID03850
```

```
   50  CONTINUE                                                         DID03860
       DO 60 I=1,NXN                                                    DID03870
       DO 60 J=1,NZN                                                    DID03880
       HN(I,J)= H(I,J)                                                  DID03890
   60  CONTINUE                                                         DID03900
       RETURN                                                           DID03910
       END                                                              DID03920
C                                                                       DID03930
C**********************************************************************C DID03940
C---------------------------POISON------------------------------------C  DID03950
C      SUBROUTINE #3                                                    DID03960
C                                                                       DID03970
C      IN THIS SUBROUTINE THE HYDRAULIC HEADS ARE CALCULATED BY         DID03980
C    & USING THE GAUSS-SEIDEL OVER RELAXATION METHOD                    DID03990
C                                                                       DID04000
       SUBROUTINE POISON                                                DID04010
       IMPLICIT REAL*8(A-H,O-Z)                                         DID04020
       REAL*8  KH , KCH , KHC , MS , LEN , LENL , LAMBDA                DID04030
C                                                                       DID04040
C_________________________.COMMON BLOCK.______________________________C  DID04050
C                                                                       DID04060
       COMMON  C(50,51), H(50,51) , HN(50,51)                           DID04070
       COMMON  POROS , RO, KH ,D ,AA ,BB, KHC ,KCH, DX,DZ,DXTDZ,R,      DID04080
     &         T,MS, GAMAL                                              DID04090
       COMMON  LEN, DEP,LENL, NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT         DID04100
       COMMON  NXN, NXLN, NZN,N,ITER,III                                DID04110
       COMMON  A,B,OSM,ITMAX                                            DID04120
       COMMON  /RE/RELAX,CO,HO,CI,DLAP,DEL2,LAMBDA,RI,TT,ITERC          DID04130
       COMMON /V/ TX(99,9),TZ(99,9)                                     DID04140
C---------------------------------------------------------------------C DID04150
C                                                                       DID04160
C      OBTAINING HEADS BY ITERATION                                     DID04170
C                                                                       DID04180
   82  DO 90 J=2, NDEPS                                                 DID04190
       DO 90 I=1, NXN                                                   DID04200
C                                                                       DID04210
C      LINE OF SYMMETRY BOUNDARY CONDITIONS                             DID04220
                                                                        DID04230
       IF(I.EQ.1) GO TO 85                                              DID04240
                                                                        DID04250
C      RIGHT HAND BOUNDARY CONDITIONS                                   DID04260
C                                                                       DID04270
       IF(I.EQ.NXN) GO TO 87                                            DID04280
C                                                                       DID04290
C      START ITERATION                                                  DID04300
C                                                                       DID04310
       HN(I,J)=(1.D0-RELAX)*H(I,J)+RELAX*((H(I+1,J)+H(I-1,J)+           DID04320
     &         DEL2*(H(I,J+1)+H(I,J-1))+LAMBDA*(DELX**2)*DLAP)/         DID04330
     &         (2.D0+2.D0*DEL2))                                        DID04340
       GO TO 88                                                         DID04350
   85  HN(I,J)=(1.D0-RELAX)*H(I,J)+RELAX*((2.D0*H(I+1,J)+              DID04360
     &         DEL2*(H(I,J+1)+H(I,J-1))+LAMBDA*(DELX**2)*DLAP)/         DID04370
     &         (2.D0+2.D0*DEL2))                                        DID04380
       GO TO 88                                                         DID04390
   87  HN(I,J)=(1.D0-RELAX)*H(I,J)+RELAX*((2.D0*H(I-1,J)+              DID04400
```

```
     &         DEL2*(H(I,J+1)+H(I,J-1))+LAMBDA*(DELX**2)*DLAP)/          DID04410
     &         (2.D0+2.D0*DEL2))                                         DID04420
   88   CONTINUE                                                         DID04430
        TOL= ABS(HN(I,J)-H(I,J))                                         DID04440
        IF(TOL.GE.0.001D0) III=1                                         DID04450
        H(I,J)=HN(I,J)                                                   DID04460
   90   CONTINUE                                                         DID04470
        RETURN                                                           DID04480
        END                                                              DID04490
C::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::C   DID04500
C---------------------EXPLIT-----------------------------------------C   DID04510
C::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::C   DID04520
C       SUBROUTINE #4                                                    DID04530
C       IN THIS SUBROUTINE THE CONCENTRATION AT ADVANCED TIME STEPS      DID04540
C       ARE CALCULATED BY THE EXPLICIT FINITE DIFFERENCE METHOD          DID04550
C                                                                        DID04560
        SUBROUTINE EXPLIT                                                DID04570
        IMPLICIT REAL*8(A-H,O-Z)                                         DID04580
        REAL*8  KH , KCH , KHC , MS , LEN , LENL , LAMBDA                DID04590
C                                                                        DID04600
C_________________________.COMMON BLOCK._____________________________C   DID04610
C                                                                        DID04620
        COMMON  C(50,51), H(50,51) , HN(50,51)                           DID04630
        COMMON  POROS , RO, KH ,D ,AA ,BB, KHC ,KCH, DX,DZ,DXTDZ,R,      DID04640
     &          T,MS, GAMAL                                              DID04650
        COMMON  LEN, DEP,LENL, NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT         DID04660
        COMMON  NXN, NXLN, NZN,N,ITER,III                                DID04670
        COMMON  A,B,OSM,ITMAX                                            DID04680
        COMMON  /RE/RELAX,CO,HO,CI,DLAP,DEL2,LAMBDA,RI,TT,ITERC          DID04690
        COMMON /V/ TX(99,9),TZ(99,9)                                     DID04700
C-------------------------------------------------------------------C    DID04710
C                                                                        DID04720
        IF(N.LT.NTS) GO TO 100                                           DID04730
        TT=NTS*DELT/365.D0                                               DID04740
        WRITE(6,331) TT                                                  DID04750
  331   FORMAT(5X,'THE TOTAL TIME= ', F10.2,'YEARS')                     DID04760
C                                                                        DID04770
C       DETERMINATION OF VELOCITIES & CONCENTRATIONS                     DID04780
C                                                                        DID04790
  100   DO 120 I=2, NLS                                                  DID04800
        DO 120 J=2, NDEPS-1                                              DID04810
        DCXC=(C(I+1,J)-C(I-1,J))/(2.D0*DELX)                             DID04820
        DCZC=(C(I,J+1)-C(I,J-1))/(2.D0*DELZ)                             DID04830
C                                                                        DID04840
        DHXC=(HN(I+1,J)-HN(I-1,J))/(2.D0*DELX)                           DID04850
        IF(ABS(DHXC).LE.10**8) DHXC=0.                                   DID04860
                                                                         DID04870
        DHZC=(HN(I,J+1)-HN(I,J-1))/(2.D0*DELZ)                           DID04880
        VX=(-KH/POROS)*DHXC-KHC*DCXC                                     DID04890
        VZ=(-KH/POROS)*DHZC-KHC*DCZC                                     DID04900
C       TX(I,J)=VX                                                       DID04910
C       TZ(I,J)=VZ                                                       DID04920
C       IF(N.LT.NTS) GO TO 335                                           DID04930
C       WRITE(6,332) VX,VZ                                               DID04940
C 332   FORMAT(5X,'VX= ',F15.8,10X,'VZ= ',F15.8)                         DID04950
```

```
C 335  RET =A*B*EXP(A*C(I,J))*(RO/POROS)
C
C      USE BACKWARD DIFFERENCE
C
C      USE CENTRAL DIFFERENCE

       DCX=DCXC
       DCZ=DCZC
C
       D2C2X=(C(I+1,J)**2 -2.D0*C(I,J)**2+ C(I-1,J)**2)/(DELX**2)
       D2C2Z=(C(I,J+1)**2 -2.D0*C(I,J)**2+ C(I,J-1)**2)/(DELZ**2)
       DCXD=(C(I+1,J)-C(I-1,J))/(2.D0*DELX)
       DCZD=(C(I,J+1)-C(I,J-1))/(2.D0*DELZ)

       D2CX=(C(I+1,J) -2.D0*C(I,J) +C(I-1,J))/(DELX**2)
       D2CZ=(C(I,J+1) -2.D0*C(I,J) +C(I,J-1))/(DELZ**2)

       ADT=(1+RI)*(VX*DCX+VZ*DCZ)
       OSMT=DSM*(D2C2X+D2C2Z)
       DZ=158.36D0
       DX=DXTDZ*DZ
       DIFTX=BB*DX*(DCXD**2)+DX*D2CX
       DIFTZ=BB*DZ*(DCZD**2)+DZ*D2CZ
       CPLW=C(I,J)
C      WRITE (6,2) D2CZ,CPLW
C   2  FORMAT(5X,'D2Z=',F15.12,10X,'CPLW=',F15.8)
       C(I,J)=CPLW+(DELT/(1+RET))*(-ADT-OSMT + DIFTX + DIFTZ)
  120  CONTINUE
       DO 200 I=1, NXN
       C(I,NZN)=C(I,NZN-1)
  200  CONTINUE
       DO 250 J=2,NZN
       C(1,J)=C(2,J)
       C(NXN,J)=C(NXN-1,J)
  250  CONTINUE
       RETURN
       END
C::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::C
C--------------------IMPLT-------------------------------------------C
C::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::C
C      SUBROUTINE #5
C      IN THIS SUBROUTINE THE CONCENTRATION AT ADVANCED TIME STEPS
C      ARE CALCULATED BY THE IMPLICIT FINITE DIFFERENCE METHOD
C
       SUBROUTINE IMPLT
       IMPLICIT REAL*8(A-H,O-Z)
       REAL*8  KH , KCH , KHC , MS , LEN , LENL , LAMBDA
C                                                                   C
C_____________________________.COMMON BLOCK.________________________C
C
       COMMON  C(50,51), H(50,51) , HN(50,51)
       COMMON  POROS , RO, KH ,D ,AA ,BB, KHC ,KCH, DX,DZ,DXTDZ,R,
     &         T,MS, GAMAL
```

```
      COMMON  LEN, DEP,LENL, NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT          DID05510
      COMMON  NXN, NXLN, NZN,N,ITER,III                                 DID05520
      COMMON  A,B,OSM,ITMAX,VX,VZ,RET1                                  DID05530
      COMMON  /RE/RELAX,CO,HO,CI,DLAP,DEL2,LAMBDA,RI,TT,ITERC           DID05540
      COMMON /V/ TX(99,9),TZ(99,9)                                      DID05550
C-----------------------------------------------------------------------C DID05560
      DIMENSION TEMP(100),AT(100),BT(100),CT(100),DT(100)               DID05570
      DIMENSION X(100),B1(100),G(100),W(100),C1(50,51)                  DID05580
      ITERC=0                                                           DID05590
      IF(N.LT.NTS) GOTO 133                                             DID05600
      TT=NTS*DELT/365.DO                                                DID05610
      WRITE(6,331) TT                                                   DID05620
  331 FORMAT(5X,'THE TOTAL TIME=',F10.2,2X,'YEAR')                      DID05630
C                                                                       DID05640
C     GIVING INITIAL VALUES FOR CONCENTRATIONS                          DID05650
C                                                                       DID05660
  133 DO 88 I=1, NXN                                                    DID05670
      DO 88 J=1, NZN                                                    DID05680
      C1(I,J)=C(I,J)                                                    DID05690
   88 CONTINUE                                                          DID05700
  100 LLL=0                                                             DID05710
      DO 120 J=2,NDEPS                                                  DID05720
      DO 111 I=1,NXN                                                    DID05730
      TEMP(I)=C1(I,J)                                                   DID05740
  111 CONTINUE                                                          DID05750
C                                                                       DID05760
C     DETERMINNATION OF VELOCITY & CONCENTRATIONS                       DID05770
C                                                                       DID05780
  113 DO 120 I=2,NLS                                                    DID05790
      DCXC1=(C1(I+1,J)-C1(I-1,J))/(2.DO*DELX)                           DID05800
      DCZC1=(C1(I,J+1)-C1(I,J-1))/(2.DO*DELZ)                           DID05810
C                                                                       DID05820
      DHXC=(HN(I+1,J)-HN(I-1,J))/(2.DO*DELX)                            DID05830
C                                                                       DID05840
      IF(ABS(DHXC).LE.10**8) DHXC=0.                                    DID05850
      IF(ABS(DCXC1).LE.10**8) DCXC1=0.                                  DID05860
C                                                                       DID05870
      DHZC=(HN(I,J+1)-HN(I,J-1))/(2.DO*DELZ)                            DID05880
      VX=(-KH/POROS)*DHXC-KHC*DCXC1                                     DID05890
      VZ=(-KH/POROS)*DHZC-KHC*DCZC1                                     DID05900
      IF(N.LT.NTS) GOTO 335                                             DID05910
      WRITE (6,332) VX,VZ                                               DID05920
C 332 FORMAT(5X,'VX=',F15.8,10X,'VZ=',F15.8)                            DID05930
  335 RET=-A*B*EXP(A*C1(I,J))*(RO/POROS)                                DID05940
      RET1=RET+1                                                        DID05950
C                                                                       DID05960
C                                                                       DID05970
C     DETERMINATION OF THE RESPECTIVE RETARDATION FACTOR                DID05980
C     CHLORIDE                                                          DID05990
C     RET1=1.0                                                          DID06000
C     CALCIUM                                                           DID06010
C     RET1=1.2                                                          DID06020
C     SODIUM                                                            DID06030
C     RET1=2.2                                                          DID06040
C     PENTACHLOROPHENOL                                                 DID06050
C     RET1=90.0
```

```
C
C     ZINC
C     RET1=100.0
      LEAD
      RET1=2000.0
C     WRITE(6,337) RET1
C 337 FORMAT (/.'RETARDATION = ',F8.2)
C     USE CENTRAL DIFFERENCE
C

      D2C2X1=(C1(I+1,J)**2 -2.D0*C1(I,J)**2+ C1(I-1,J)**2)/((DELX)**2)
      D2C2Z1=(C1(I,J+1)**2 -2.D0*C1(I,J)**2+ C1(I,J-1)**2)/((DELZ)**2)
      DCX1=(C1(I+1,J)-C1(I-1,J))/(2.D0*DELX)
      DCZ1=(C1(I,J+1)-C1(I,J-1))/(2.D0*DELZ)

      D2CX1=(C1(I+1,J) -2.D0*C1(I,J) +C1(I-1,J))/((DELX)**2)
      D2CZ1=(C1(I,J+1) -2.D0*C1(I,J) +C1(I,J-1))/((DELZ)**2)
C
      RI1=(1+RI)
      DZ=1583.36D0
      DX=DXTDZ*DZ
C     DX=0.
C
C     DETERMINING THOMAS COEFFICIENTS AT,BT,CT,DT
C
      AT1=-RI1*VX/(2.D0*DELX)+ (OSM/((DELX)**2))*(C1(I-1,J))
      AT2=-BB*DX*((C1(I-1,J)+C1(I+1,J))/((DELX)**2))-DX/((DELX**2))
      AT(I)=AT1+AT2 .
      BT1=RET1/DELT-(2.D0*OSM/(DELZ)**2)*C1(I,J)
      BT2=-(2.D0*OSM/(DELX)**2)*C1(I,J)
      BT3=2.D0*DZ/((DELZ)**2) +2.D0*DX/((DELX)**2)
      BT(I)=BT1+BT2+BT3
      IF(I.EQ.NXN) GOTO 70
      CT1=RI1*VX/(2.0D0*DELX)+(OSM/(DELX)**2)*(C1(I+1,J))
      CT2=-BB*DX*((C1(I+1,J)+C1(I-1,J))/((DELX)**2))
      CT3=-DX/((DELX)**2)
      CT(I)=CT1+CT2+CT3
   70 DT1=(RET1/DELT)*C(I,J)-RI1*VZ*(DCZ1)
      DT2=-OSM*((C1(I,J+1)**2+ C1(I,J-1)**2)/((DELZ)**2))
      DT4=(BB*DZ)*((DCZ1)**2)
      DT5=DZ*((C1(I,J+1)+C1(I,J-1))/((DELZ)**2))
      DT(I)=DT1+DT2+DT4+DT5
  120 CONTINUE
C
C     THOMAS ALGORITHM
C
C     APPLYING BOUNDARY CONDITIONS
C
C     LEFT HAND SIDE BOUNDARY CONDITIONS
C
C     SINCE C1(1,J)=C1(2,J),SET AT(1)=0. , BT(1)=1.
C                               CT(1)=-1., DT(1)=0.
C

      AT(1)=0.
      BT(1)=1.D0
      CT(1)=-1D0
```

```
      DT(1)=I
      W(1)=BT(1)
      B1(1)=CT(1)/W(1)
      G(1)=DT(1)/W(1)
C
C     RIGHT HAND SIDE BOUNDARY CONDITIONS
C
C      SINCE C1(NXN-1,J)=C1(NXN,J),SET AT(NXN)=1.,  BT(NXN)=-1.
C                                      CT(NXN)=0.,  DT(NXN)=0.
C

      AT(NXN)=1.D0
      BT(NXN)=-1.D0
      CT(NXN)=0.
      DT(NXN)=0.

      DO 90 I=2 ,NXN
      W(I)=BT(I)-AT(I)*B1(I-1)
      B1(I)=CT(I)/W(I)
 89   G(I)=(DT(I)-AT(I)*G(I-1))/W(I)
 90   CONTINUE
      NXNM1=NXN-1
      X(NXN)=G(NXN)
      C1(NXN,J)=X(NXN)
      DO 105 II=1,NXNM1
      KK=NXN-II
      X(KK)=G(KK)-B1(KK)*X(KK+1)
      C1(KK,J)=X(KK)
105   CONTINUE
      DO 109 I=1,NXN
      TOLC=DABS(C1(I,J)-TEMP(I))
      IF(TOLC.GE.1.0D-10) LLL=1
109   CONTINUE
125   CONTINUE
C
C     APPLYING LOWER BOUNDARY CONDITION
C
      DO 140 I=1,NXN
      C1(I,NZN)=C1(I,NDEPS)
140   CONTINUE
      ITERC=ITERC+1
C     WRITE(*,*) ITERC
C
C     CHECKING CRITERIA
C
      IF(ITERC.EQ.300) GOTO 127
      IF(LLL.EQ.1) GOTO 100
      DO 150 I=1,NXN
      DO 150 J=2,NZN
      C(I,J)=C1(I,J)
150   CONTINUE
      GOTO 128
127   WRITE(*,*) 'NO CONVERGENCE'
128   RETURN
      END
```

```
C::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::C    DID07160
C                                                                  C    DID07170
C--------------------OUTPUT----------------------------------------C    DID07180
C                                                                  C    DID07190
C::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::C    DID07200
                                                                        DID07210
C                                                                       DID07220
C      SUBROUTINE #5                                                    DID07230
C      IN THIS SUBROUTINE THE COMPUTED CONCENTRATION AND HEADS          DID07240
C      RESULTS ARE PRINTED                                              DID07250
C                                                                       DID07260
       SUBROUTINE OUTPUT                                                DID07270
                                                                        DID07280
       IMPLICIT REAL*8(A-H,O-Z)                                         DID07290
       REAL*8  KH , KCH , KHC , MS , LEN , LENL , LAMBDA                DID07300
C                                                                  C    DID07310
C_________________________.COMMON BLOCK.___________________________C    DID07320
C                                                                       DID07330
       COMMON  C(50,51), H(50,51) , HN(50,51)                           DID07340
       COMMON  POROS , RO, KH ,D ,AA ,BB, KHC ,KCH, DX,DZ,DXTDZ,R,      DID07350
     &         T,MS, GAMAL                                              DID07360
       COMMON  LEN, DEP,LENL, NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT         DID07370
       COMMON  NXN, NXLN, NZN,N,ITER,III                                DID07380
       COMMON  A,B,OSM,ITMAX,VX,VZ,RET1                                 DID07390
       COMMON  /RE/RELAX,CO,HO,CI,DLAP,DEL2,LAMBDA,RI,TT,ITERC          DID07400
       COMMON /V/ TX(99,9),TZ(99,9)                                     DID07410
       DIMENSION DP(51),HX(51)                                     C    DID07420
C------------------------------------------------------------------     DID07430
C                                                                       DID07440
                                                                        DID07450
C      PRINT INPUT DATA                                                 DID07460
C                                                                       DID07470
C      READ (7,1001) TITLE                                              DID07480
       WRITE(6,2001)                                                    DID07490
       WRITE(6,2002) TT                                                 DID07500
       WRITE(6,2004) LEN                                                DID07510
       WRITE(6,2005) DEP                                                DID07520
       WRITE(6,2012)                                                    DID07530
       WRITE(6,2013) DELX,DELZ,DELT                                     DID07540
       WRITE(6,2014)                                                    DID07550
       WRITE(6,2015) NXN,NZN,NTS                                        DID07560
       WRITE(6,2016)                                                    DID07570
       WRITE(6,2017) DX,DZ                                              DID07580
       WRITE(6,2018)                                                    DID07590
       WRITE(6,2019) VX,VZ,RET1                                         DID07600
       WRITE(6,2111)                                                    DID07610
       WRITE (6,2112)                                                   DID07620
C1001  FORMAT(A60)                                                      DID07630
C-----------------------------------------------------------------      DID07640
 2001  FORMAT (/5X,20(':'),'PENTACHLOROPHENOL MIGRATION IN MARSHLAND')  DID07650
 2002  FORMAT (//1X,'TOTAL TIME (YEARS) =',F8.3,/1X,10('-'))            DID07660
 2004  FORMAT (//1X,'MARSH WIDTH (CM) =     ',F9.3,/1X,10('-'))         DID07670
 2005  FORMAT (//1X,'MARSH LENGTH (CM)  =    ',F9.3,/1X,10('-'))        DID07680
 2012  FORMAT (///5X,10('-'),'THE    SPACE--TIME     DATA        ',     DID07690
     &          10('-'),                                                DID07700
     &        //3X,'DELX (CM)',9X,'DELY (CM)',9X,'DELT (DAY)'
```

```
     &         /3X,9('-'),9X,9('-'),9X,9('-'),/)
 2013  FORMAT (1X,F8.2,12X,F8.2,9X,F8.2)
 2014  FORMAT (///5X,10('-'),'THE NODES NUMBER OF SPACE-TIME    ',
     &          10('-'),
     &         //3X,'NODE-X ',9X,'NODE-Y ',10X,'STEP-T'
     &          /3X,6('-'),10X,6('-'),11X,6('-'),/)
 2015  FORMAT (2X,I5,11X,I5,12X,I5)
 2016  FORMAT (///5X,10('-'),'THE DIFFUSION COEFFICIENTS OF NODE ',
     &          'POINT',10('-'),
     &         //5X,' -DIFFUSION',9X,'Y-DIFFUSION',
     &          /5X,11('-'),9X,11('-'),/)
 2017  FORMAT (5X,F8.2,12X,F8.2)
 2018  FORMAT (//5X,10('-'),' THE GROUNDWATER VELOCITY DATA   ',
     &          10('-'),
     &         //3X,'VELOC. X',9X,'VELOC. Y',9X,'RETARDATION',
     &          /3X,8('-'),9X,8('-'),9X,11('-'),/)
 2019  FORMAT (1X,F8.4,9X,F8.4,10X,F8.4)
C
C      PRINTING RESULTS
C
C2111  FORMAT (1X,70('*'),/1X,'*',68X,'*',/1X,'*',25X,'RESULTS TITLE',
C    &         30X,'*',/1X,'*',68X,'*',/1X,'*',4X,A60,4X,'*',/1X,'*',
C    &          /1X,70('*'))
 2111  FORMAT (/5X,42(':'),'THE RESULTS',41(':'),//)
 2112  FORMAT (/5X,34(':'),'HYDRAULIC HEAD DISTRIBUTION',35(':'),/)
C
C      PRINT HEADS
C
       DO 505 K=0, NZN-1
        DP(K+1) = DELZ*K
  505  CONTINUE
C
       DO 506 K=0,NXN-1
        HX(K+1) = DELX*K
  508  CONTINUE
C
       WRITE (6,597)
  597  FORMAT (/,17X,'|',26('-'),'MARSHLAND WIDTH (CM)',34('-'),'|')
       WRITE (6,598) (HX(I), I=1,NXN)
  598  FORMAT(/,'WIDTH    ',4X, 11F8.2,/1X,100('-'))
       WRITE (6,599)
  599  FORMAT (/,1X,'MARSHLAND')
       WRITE (6,600)
  600  FORMAT (/1X,'LENGTH (CM)')
C
       WRITE (6,1000) (DP(J),(HN(I,J),I=1,NXN),J=1,NZN)
 1000  FORMAT(/,F8.2,4X,11F8.2)
C
C
C     PRINT CONCENTRATIONS
C
        WRITE(6,1500)
 1500   FORMAT(/5X,35(':'),'CONCENTRATIONS DISTRIBUTION',34(':'),/)
        WRITE (6,1505)
```

```
 1505   FORMAT(/,17X,'|',26('-'),'MARSHLAND WIDTH (CM)',34('-'),'|')
       DO 500 I=1, NXN
       DO 500 J=1, NZN
       C(I,J)=C(I,J)*1.0D6
 500   CONTINUE
C
       WRITE (6,603) (HX(I),I=1,NXN)
  603  FORMAT(/,'WIDTH    ',4X,11F8.2,/1X,100('-'))
       WRITE (6,610)
  610  FORMAT(/,1X,'MARSHLAND')
       WRITE(6,700)
  700  FORMAT(/1X,'LENGTH(CM)')
       WRITE(6,2000) (DP(J),(C(I,J),I=1,NXN),J=1,NZN)
 2000  FORMAT(/,F6.2,4X,11F8.2)
       RETURN
       END
```

APPENDIX H

DID2XY OUTPUT FILE FOR CHLORIDE SIMULATION AFTER 1 YEAR

```
FILE: DID2XY   RESULT                         VM/SP CONVERSATIONAL MONITOR SYSTEM                         PAGE 00001

    TIME STEP=     1       ITERATION FOR HEAD=     1       ITER. FOR CONCENT.=     2
    TIME STEP=     2       ITERATION FOR HEAD=     1       ITER. FOR CONCENT.=     2
    TIME STEP=     3       ITERATION FOR HEAD=     1       ITER. FOR CONCENT.=     2
    TIME STEP=     4       ITERATION FOR HEAD=     1       ITER. FOR CONCENT.=     2
    TIME STEP=     5       ITERATION FOR HEAD=     1       ITER. FOR CONCENT.=     2
    TIME STEP=     6       ITERATION FOR HEAD=     1       ITER. FOR CONCENT.=     2
    TIME STEP=     7       ITERATION FOR HEAD=     1       ITER. FOR CONCENT.=     2
    TIME STEP=     8       ITERATION FOR HEAD=     1       ITER. FOR CONCENT.=     2
    TIME STEP=     9       ITERATION FOR HEAD=     1       ITER. FOR CONCENT.=     2
    TIME STEP=    10       ITERATION FOR HEAD=     1       ITER. FOR CONCENT.=     2
    TIME STEP=    11       ITERATION FOR HEAD=     1
    THE TOTAL TIME=        0.99  YEAR
    TIME STEP=    12       ITERATION FOR HEAD=     1       ITER. FOR CONCENT.=     2

    ::::::::::::::::::::CHLORIDE MIGRATION IN MARSHLAND

  TOTAL TIME (YEARS) =   0.986
  ----------

  MARSH WIDTH (CM) =    8000.000
  ----------

  MARSH LENGTH (CM)  =   60000.000
  ----------

    ----------THE SPACE--TIME    DATA      ----------

    DELX (CM)       DELY (CM)        DELT (DAY)
    ---------       ---------        ---------

    400.00           3000.00           30.00

    ----------THE NODES NUMBER OF SPACE-TIME   ----------

    NODE-X          NODE-Y          STEP-T
    ------          ------          ------

      11              21              12

    ----------THE DIFFUSION COEFFICIENTS OF NODE POINT----------

    X-DIFFUSION       Y-DIFFUSION
    -----------       -----------

      522.5[illegible]          1563.36
```

```
FILE: DID2XY   RESULT   *                VM/SP CONVERSATIONAL MONITOR SYSTEM                PAGE 00002

    ---------- THE GROUNDWATER VELOCITY DATA  ----------

   VELOC. X          VELOC. Y          RETARDATION
   --------          --------          -----------

   0.0000           19.6987             1.0000
    ::::::::::::::::::::::::::::::::::::::::::THE RESULTS::::::::::::::::::::::::::::::::::::::::::


    ::::::::::::::::::::::::::::::::::::HYDRAULIC HEAD DISTRIBUTION::::::::::::::::::::::::::::::::::

                     |-------------------------MARSHLAND WIDTH (CM)-----------------------------------|
WIDTH                0.00  400.00  800.00 1200.00 1600.00 2000.00 2400.00 2800.00 3200.00 3600.00 4000.00
------------------------------------------------------------------------------------------------------

 MARSHLAND

 LENGTH (CM)
   0.00       8530.00 8530.00 8530.00 8530.00 8530.00 8530.00 8530.00 8530.00 8530.00 8530.00 8530.00
 3000.00      8495.00 8495.00 8495.00 8495.00 8495.00 8495.00 8495.00 8495.00 8495.00 8495.00 8495.00
 6000.00      8480.00 8480.00 8480.00 8480.00 8480.00 8480.00 8480.00 8480.00 8480.00 8480.00 8480.00
 9000.00      8468.00 8468.00 8468.00 8468.00 8468.00 8468.00 8468.00 8468.00 8468.00 8468.00 8468.00
12000.00      8463.00 8463.00 8463.00 8463.00 8463.00 8463.00 8463.00 8463.00 8463.00 8463.00 8463.00
15000.00      8460.00 8460.00 8460.00 8460.00 8460.00 8460.00 8460.00 8460.00 8460.00 8460.00 8460.00
18000.00      8458.00 8458.00 8458.00 8458.00 8458.00 8458.00 8458.00 8458.00 8458.00 8458.00 8458.00
21000.00      8455.00 8455.00 8455.00 8455.00 8455.00 8455.00 8455.00 8455.00 8455.00 8455.00 8455.00
24000.00      8453.00 8453.00 8453.00 8453.00 8453.00 8453.00 8453.00 8453.00 8453.00 8453.00 8453.00
27000.00      8450.00 8450.00 8450.00 8450.00 8450.00 8450.00 8450.00 8450.00 8450.00 8450.00 8450.00
30000.00      8440.00 8440.00 8440.00 8440.00 8440.00 8440.00 8440.00 8440.00 8440.00 8440.00 8440.00
33000.00      8430.00 8430.00 8430.00 8430.00 8430.00 8430.00 8430.00 8430.00 8430.00 8430.00 8430.00
36000.00      8420.00 8420.00 8420.00 8420.00 8420.00 8420.00 8420.00 8420.00 8420.00 8420.00 8420.00
39000.00      8405.00 8405.00 8405.00 8405.0  8405.00 8405.00 8405.00 8405.00 8405.00 8405.00 8405.00
42000.00      8390.00 8390.00 8390.00 8390.00 8390.00 8390.00 8390.00 8390.00 8390.00 8390.00 8390.00
45000.00      8370.00 8370.00 8370.00 8370.00 8370.00 8370.00 8370.00 8370.00 8370.00 8370.00 8370.00
```

```
FILE: DID2XV   RESULT   *              VM/SP CONVERSATIONAL MONITOR SYSTEM                    PAGE 00003

48000.00      8340.00 8340.00 8340.00 8340.00 8340.00 8340.00 8340.00 8340.00 8340.00 8340.00 8340.00
51000.00      8310.00 8310.00 8310.00 8310.00 8310.00 8310.00 8310.00 8310.00 8310.00 8310.00 8310.00
54000.00      8290.00 8290.00 8290.00 8290.00 8290.00 8290.00 8290.00 8290.00 8290.00 8290.00 8290.00
57000.00      8270.00 8270.00 8270.00 8270.00 8270.00 8270.00 8270.00 8270.00 8270.00 8270.00 8270.00
60000.00        82.20   82.20   82.20   82.20   82.20   82.20   82.20   82.20   82.20   82.20   82.20
     :::::::::::::::::::::::::::::::::::CONCENTRATIONS DISTRIBUTION::::::::::::::::::::::::::::::::::::

                 |-------------------------MARSHLAND WIDTH (CM)----------------------------------|
WIDTH               0.00  400.00  800.00 1200.00 1600.00 2000.00 2400.00 2800.00 3200.00 3600.00 4000.00
------------------------------------------------------------------------------------------------------

 MARSHLAND
 LENGTH(CM)
    0.00         36.00   36.00   36.00   36.00   36.00   36.00   11.00   11.00   11.00   11.00   11.00
 3000.00         12.65   12.65   12.64   12.62   12.53   12.23   11.42   11.12   11.03   11.01   11.01
 6000.00         11.06   11.06   11.06   11.06   11.05   11.04   11.02   11.01   11.00   11.00   11.00
 9000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
12000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
15000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
18000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
21000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
24000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
27000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
30000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
33000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
36000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
39000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
42000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00 [illegible] [illegible] [illegible] [illegible]
45000.00         11.00   11.00 [illegible] 11.00 11.00 [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]
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FILE: DID2XY   RESULT   *               VM/SP CONVERSATIONAL MONITOR SYSTEM                          PAGE 00004

48000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
51000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
54000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
57000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
60000.00         11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00   11.00
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