MODELING OF NATURAL ATTENUATION AT A CONTAMINATED SITE:
A CASE STUDY

MARION E. ORGAN

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by

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Abstract

A petroleum hydrocarbon contaminated site was evaluated using computer software (SEVIEW) in this study. Using a design of experiment approach, the model was calibrated and verified and a sensitivity analysis was completed. Based on the results of the experimental analysis it was found that the computer model adequately estimated the fate and transport of contaminants under conditions of natural attenuation. The estimated results were in reasonable agreement with the actual field measurements. The sensitivity analysis concluded the model was sensitive to chemical properties (K_{oc}), soil properties (soil pore disconnectedness index, intrinsic permeability, effective porosity, f_{oc} and the Freundlich Exponent) and aquifer properties (hydraulic conductivity, longitudinal dispersivity and transverse dispersivity). The calibrated model was then used to predict the time required for natural attenuation to remediate the site within acceptable risk values. The model was also used to predict the fate and transport of petroleum hydrocarbons in the groundwater. The model predicted that the concentration of petroleum hydrocarbons in the soil would be within regulatory guidelines in 16 to 17 years under natural attenuation. Additional remediation would be required for groundwater as the concentrations of petroleum hydrocarbons posed a risk to a down stream receptor (a small stream that was a tributary for a pond) in the future. The model predicted that the plume would reach a tributary, located downstream, in four years. The concentration would reach a maximum value at fifteen years and the stream would be considered impacted from year 10 onwards.

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List of Abbreviations and Symbols

$\overline{\overline{K}}$ = Retarded dispersion tensor
$\dot{M}$ = Contaminant source release rate
$\vec{n}$ = Unit vector normal to S2
λ = Radioactive decay constant
∇ = Gradient (Del operator with respect to x, y, and z)
τ = Duration of the contaminant release
θ = soil water content (ml/ml)
Φ = Hydraulic head
ψ = Stream function
α_L = Longitudinal Dispersivity
α_T = Transverse Dispersivity
α_V = Vertical Dispersivity
ρ_b = Bulk density of the soil
ANOVA = Analysis of Variance
B = Width of the aquifer
BTEX = Benzene, Toluene, Ethyl Benzene, Xylene
B1 = Starting coordinate of the source in the y-direction
B2 = Ending coordinate of the source in the y-direction
C = Dissolved contaminant concentration
C1 = Concentration on the boundary S1
CEC = cation exchange capacity of the soil (meg/100 g of dry weight soil)
C_i = Initial contaminant concentration
CoC = Chemical of Concern
CONC = The concentration sorbed to the soil in μg /g
C_s = Adsorbed contaminant concentration
D = Contaminant depth
$\overline{\overline{D}}$ =Hydraulic Dispersion Coefficient Tensor
d.f. = degrees of freedom
EBS = Environmental Baseline Study
EPA = Environmental Protection Agency3
ESA = Environmental Site Assessment
ESRI = Environmental Systems Research Institute
f_a = $f - \theta$ = air-filled porosity (ml/ml)
f_{oc} = Fraction of organic carbon
G = Green's function
H = Depth of the aquifer
H = Henry's Law Constant (m3 atm/mol)
HHRA = Human health and risk assessment
H1 = Starting coordinate of the source in the z-direction
H2 = Ending coordinate of the source in the z-direction
J_w = water velocity (cm/s)
$J_{w,z}$ = infiltration rate at depth z, which will be the boundary between two major layers (cm/s)
k = number of factors
K = Chemical degradation rate
K_d = Chemical distribution coefficient (μg/g)/(μg/ml)
K_{oc} = Organic carbon adsorption coefficient
K_d = Distribution coefficient
L1 = Starting coordinate of the source in the x-direction
L2 = Ending coordinate of the source in the x-direction
L_p = Plume length

MNA = Monitored Natural Attenuation
MS = Mean Square
MSDS = Material Safety Data Sheet
NAPLs = Non Aqueous Phase Liquids
n = number of replications
n_e = effective porosity
Oral Rat, LD_{50}= Lethal Oral Dose for Rats
PAH = Polycyclic aromatic hydrocarbons
PCB = Polychlorinated Biphenyl
PIRI = Partnership in RBCA Implementation
POLIN = the contaminant load to apply in μg /cm^2/month
q_2 = The contaminant flux across the boundary at a given function of time and location on S2
q_3 = Contaminant flux across the boundary at a given function of time and location on S3
R = A region with respect to x, y, and z (region modeled)
R = Gas Constant (8.2 E 10-5 m^3 atm/(mol ^{o}K)
RBCA = Risk Based Corrective Action
R_d = Retardation factor
R_o = A region with respect to ε, η and ς
RS = The soil bulk density of the soil in g/cm^3
S = The boundary of the region modeled R
S1 =A portion of S
S2 = A portion of S
S3 = A portion of S
S_o = The boundary of the region modeled R
SS = Sum of Squares
t = Time
T = Soil temperature (^{o}C)
TPH = Total Petroleum Hydrocarbons
t_c = Advection time (s)
UST = Underground Storage Tank
USGS = United States Geological Survey
$\vec{v}$ = Retarded Seepage velocity vector
x = Longitudinal coordinate
y = Transverse coordinate
y = Overall Total
y_{ij} = Each value of treatment
z = Vertical coordinate

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Chapter 1: Introduction

1.1 Background

The field of environmental evaluation and clean up is a rapidly evolving field that has faced many challenges throughout its short history.

The first awareness of environmental contamination and the magnitude of this issue began in the 1970s, with hazardous waste sites such as Love Canal. As time progressed, environmental engineering grew to encompass a large number of major military and industrial waste disposal sites, leaking underground fuel tanks and the unique challenge of non-aqueous phase liquids (NAPLs) (Bedient et al., 1999). Presently, there are thousands of contaminated sites identified throughout North America alone.

As more contaminated sites were uncovered and remediation systems installed, environmental professionals became aware of inefficiencies in the approach for the clean-up and remediation of many sites. The sites and contaminants involved became increasingly complex and the remediation measures in place often failed to meet clean-up goals (Bedient et al., 1999). In a 1994 review, one study concluded that traditional clean up treatment systems had only reached clean-up standards in 8 of 77 sites (MacDonald, 2000). In addition, increased public awareness and stringent legislation had artificially inflated these, already unattainable, clean-up goals (Khan and Husain, 2003).

However, environmental professionals have endeavored to overcome these roadblocks. Within the past decade the study of fate and transport of contaminants in the soil and groundwater has been undertaken. The improved understanding of fate and transport processes has been applied by environmental professionals to more complex problems and a better understanding of the processes occurring within contaminated sites has been gained. Improved remediation technologies have been developed and accepted remediation approaches now encompasses a number of options, including monitored natural attenuation (MNA) (Atlantic PIRI, 2003). In conjunction with the use of natural attenuation a new remediation strategy has evolved in the form of risk-based corrective action (RBCA). Risk assessment is the determination of total risk to humans and the environment based on toxicity of the chemical, the receptor, and the exposure to the chemical. RBCA has now become a standard approach to risk assessment (Khan and Husain, 2002).

Environmental professionals agree that the risks associated with soil and groundwater contamination are significant (Khan and Husain, 2002). However, this risk has been exaggerated in recent years and in turn the cost and effort required for clean-up have been exaggerated (Khan and Husain, 2002). Sites have even been left undeveloped because the cost for clean-up exceeds the value of the land (MacDonald, 2000). By using a risk assessment approach sites that present an actual risk to humans and ecological receptors can be identified and treatment systems implemented. However, some contaminated sites, based on a careful risk assessment process, are candidates for MNA.

Natural attenuation is a term used for the naturally occurring processes in soil and groundwater that act without human intervention to reduce the mass, volume, concentration or toxicity of contaminants (Odencrantz et al., 2003). In MNA these processes are used in place of traditional remediation technologies, however the site is carefully monitored to ensure no risk is posed to humans and the environment. This allows much needed funds and resources to be used on the sites that pose an actual risk.

However, this leads to another challenge for environmental professionals. In order to apply a MNA approach the site-specific processes and fate and transport mechanisms must be well understood and documented. Long-term modeling is an integral part of the natural attenuation remediation process (Surampalli et al, 2002). In order to facilitate environmental modeling several computer models have been developed as tools for professionals involved in remediation projects. Increasingly, computer aided modeling has become an invaluable tool for studying contaminated sites.

As with much of the technology developed in the environmental field, computer modeling has created additional challenges. As with any evolving field, much discussion has been presented regarding the advantages and disadvantages of modeling. Opponents argue that computer modeling requires too much data. As well, they argue that there is always uncertainty in the data that is available, since given the variable nature of soils and subsurface conditions many values are difficult to determine. Both of these factors may lead to a time-consuming and costly analysis. As well, some argue that the model can never be proven to be correct, resulting in a lack of confidence in the model output.

Several studies have been presented in recent years that address these concerns. In a study by Chen et al. (2001) an integrated approach for environmental risk assessment of subsurface contamination was proposed. The fate and transport of pollutants in heterogeneous, porous media was studied and the distribution of pollutants under natural attenuation was determined. The study concluded that reasonable outputs were generated in the computer model. In another actual field investigation a site with a limited number of available monitor wells was studied to determine if natural attenuation was occurring. Only 12 monitor wells were available and based on these monitor wells, field scale mass fluxes and first-order natural attenuation rate constants of benzene, toluene, ethyl benzene and xylenes (BTEX) and polycyclic aromatic hydrocarbons (PAHs) were estimated. The results indicated that, even at a heterogeneous site with a sparse monitoring network, reliable information could be obtained on field scale natural attenuation rates if a dependable flow model was available (Bockelmann, et al., 2003).

The objective of this study was to utilize computer-aided modeling to determine whether MNA was a viable remediation alternative for a petroleum hydrocarbon contaminated site and to further address the issues related to the use of computer modeling in environmental fate and transport. Firstly, by using a design of experiment approach the issue of data requirements was addressed as well as concerns related to uncertainty in the data. This approach resulted in time and cost efficient modeling practices. In addition, the model was calibrated and verified, resulting in an improved confidence in the model and the model output. The significance and approach of this study are outlined in detail in the following sections.

1.2 Significance of Study

There were several objectives for this study. Specifically for the site studied, the first objective was to apply the use of computer aided modeling to model natural attenuation at a petroleum hydrocarbon contaminated site. Based on the modeling process it was determined whether or not MNA was a viable remediation option for the soil and groundwater on the site and whether additional remediation strategies were required for the site selected. By using SEVIEW to model the site contaminated with petroleum hydrocarbons, the modeling process was able to prioritize the site in terms of the risk presented to humans and the environment. As well, once the model had determined that additional remediation measures were required, a timeline to implement the remediation could be established. The model was also able to quantify the risk to humans and the environment and this allowed the principals involved to use resources and funds effectively in the future.

Secondly, the study was significant in that a computer model was applied to an actual site with sufficient data for verification. Often on actual sites additional data is not available for verification since funding is usually not available for additional investigation. Often times the site can only be modeled and calibrated. This is one of the issues previously discussed that some claim is a drawback of computer modeling. The model was verified for the site studied, as an additional data set was available. Often time models cannot be verified since a third data set is not available. Through verification the study has increased confidence in the model output. In the future, when similar sites are modeled, without data for verification, there will be an increased confidence in the model output.

Thirdly, this study was also significant in that it addressed several other issues related to implementing computer models. As previously discussed problems related to implementing computer models included the amount of data and time required and the cost involved. As well there is considerable uncertainty in the data input and therefore the output is uncertain. These issues were addressed throughout the course of implementing the model. The use of a design of experiments approach is unique in studies of this type and its use demonstrates an effective modeling practice that will lead to a reduction of time and effort to implement modeling for other sites in the future when the same models are used. A sensitivity analysis was preformed as part of the design of experiment approach, which quantified the uncertainty in the model output and identified which factors influence the model output.

Finally, although there are thousands of contaminated sites in Newfoundland, there have been no previous studies of the application of computer aided modeling in a unique Newfoundland setting. Although environmental professionals have used computer modeling its accuracy has not been formally studied. Modeling studies have been completed in other areas, however Newfoundland sites are unique in many aspects, such high groundwater tables and dense soil conditions, and this study provides a comprehensive investigation of computer modeling on a site located in Newfoundland.

The approach used to achieve these results is outlined in the following sections.

1.3 Approach

In the following study the background of computer modeling was reviewed. Several sites were considered for analysis in the study and based on the site characteristics the most appropriate site was selected. Following selection, the site underwent a detailed review. The detailed review included the site history, physical properties of the site and the contaminants present.

The most appropriate modeling software for the site was selected and the computer model for the site was developed. Using Design Expert Software the model was calibrated and verified. The results of the modeling process were then considered and discussed. The experimental methodology used is presented in Figure 1.1.

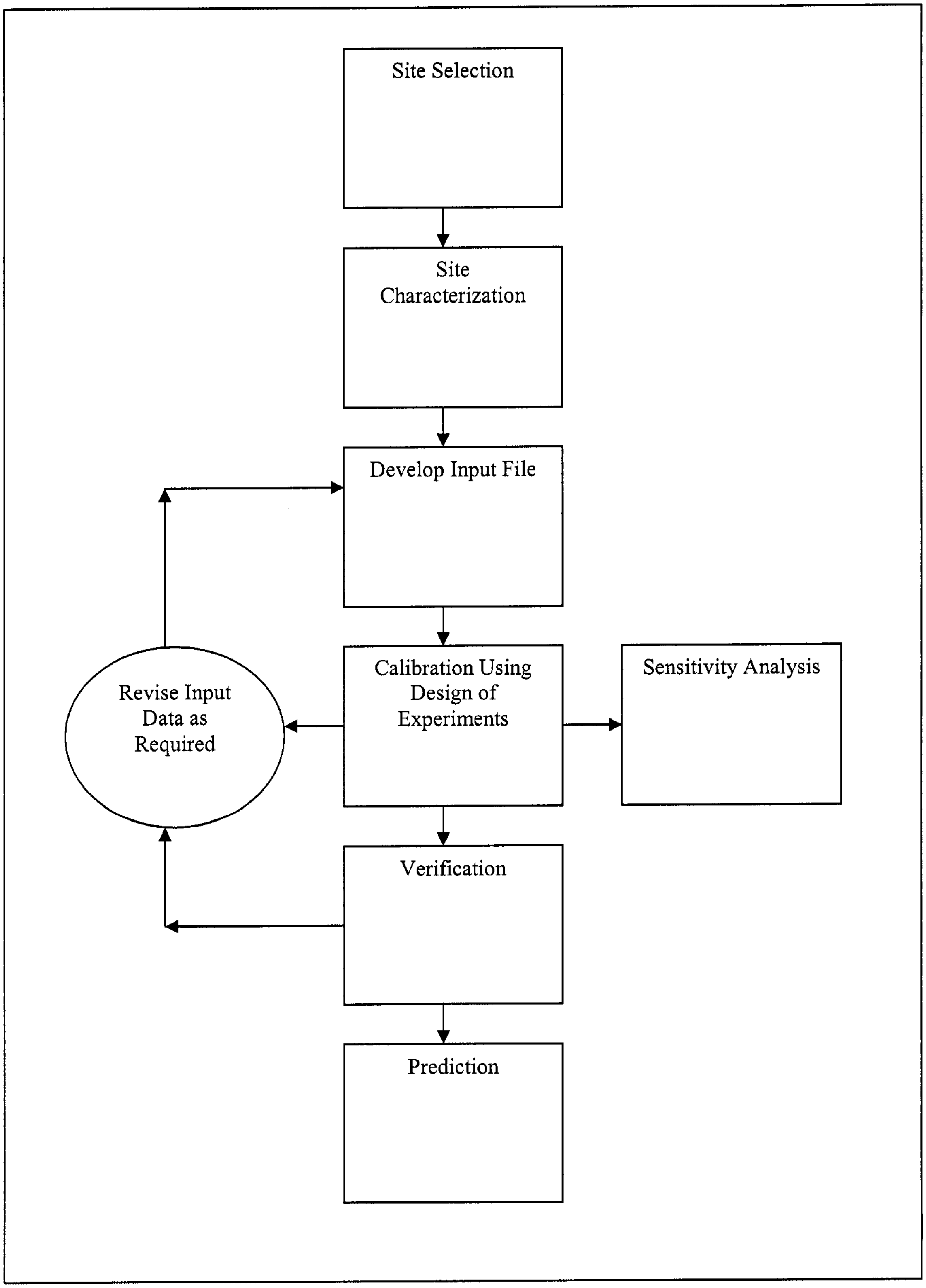

Figure 1.1: Experimental Methodology

The above information is covered in the following chapters as follows:

Chapter 1 provides an introduction to the study. The purpose and significance of the study is outlined and the study approach is presented. Chapter 2 is a literature review of the subject. Included in the literature review is a discussion of MNA, modeling and types of models. Computer models are reviewed and the models specific to this study are discussed. Finally, a discussion on developing a computer model is presented. Following the literature review, in Chapter 3 the site selection is presented. Once the site had been selected a conceptual model of the site was developed. In Chapter 4 the development of the conceptual model of the site is presented. The site-specific data are outlined and the contaminants of concern are defined. Based on the information gathered a computer model input file was completed.

In Chapter 5 the input file complied, based on the site-specific data, is presented. Input files are outlined for climate, chemical properties, soil properties and erosion (washload). The application and preliminary execution of input files are also outlined. For the groundwater model the aquifer properties and points of interest are also presented. Once a preliminary input file was presented the simulation runs are outlined. In Chapter 6 the simulations methodology is discussed and the approach to simulation is outlined. The design of experiments approach, used to simulate fate and transport of the contaminants, is described. In Chapter 7 the simulation results are discussed, including calibration, verification and the sensitivity analysis. Once the model had been calibrated and verified, the results were used for prediction. The model was used to predict the future fate and transport of petroleum hydrocarbons in the soil and groundwater and the results are presented in Chapter 7. The concentration of petroleum hydrocarbons located at a downstream receptor is also predicted and these results are also provided in Chapter 7. The results and significance of the prediction exercise is then discussed.

In Chapter 8 the results of the computer modeling exercise, calibration, sensitivity analysis and verification are concluded. The discussion addresses the applicability of MNA on the site and the risk to a downstream receptor.

Chapter 2: Review of Literature

2.1 Risk-Based Corrective Action and Monitored Natural Attenuation

As previously discussed the introduction of petroleum hydrocarbons into the environment presents a risk to both humans and the environment. However, the growing awareness of the environmental issues related to petroleum hydrocarbons has led to strict remediation guidelines (Husain, 2004). This has resulted in an increase in the time and effort required to remediate sites and in some cases the site may be left undeveloped. Given the large number of contaminated sites this may also lead to a shortage of resources for high-risk sites. In risk-based corrective action each site is evaluated on a case-by-case basis. Where risk is present remediation technologies can be implemented. However, if there is no risk present, MNA can be applied. This allows a more cost-effective approach to remediating contaminated sites (Khan and Husain, 2002). By using modeling, a site can be evaluated on a case by case basis to determine whether human intervention is necessary, and the most effective remediation strategies can be determined.

Surampalli, et al. (2002) emphasized, however, that there is a need to monitor the migration of contaminants in the groundwater to evaluate the extent to which natural attenuation is occurring and that a contingency plan should be in place to protect down-gradient receptors. This is the focus of this study. Natural attenuation is a valid treatment but only should be used where the mechanisms responsible are well understood and documented (MacDonald, 2000).

When a contaminant is released into the environment, the chemicals of concern can partition into one of three phases; air, water or soil; depending upon the chemical properties of the contaminant released and the receiving environment. Once present in each phase the chemical will be broken down by naturally occurring mechanisms. These mechanisms make up the natural attenuation processes (Atlantic PIRI, 2003).

Natural attenuation is a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility or concentration of contaminants in soil and groundwater (Atlantic PIRI, 2003). Natural attenuation processes can be non-destructive, such as dispersion, sorption, dilution and volatilization or destructive, such as biodegradation and abiotic reactions (hydrolysis). MNA is the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site clean-up approach) to achieve site-specific remediation objectives within a time that is reasonable (Atlantic PIRI, 2003).

As previously mentioned, over the past number of years MNA has been increasingly considered as a remediation technology, due to the cost and inefficiencies of other remediation systems (MacDonald, 2000). The combination of the inability of traditional technologies to reach remediation standards and the increased ability to adequately model sites undergoing natural attenuation has lead to an increased use of non-intervention on contaminated sites.

Several studies have been undertaken which have illustrated the effectiveness of MNA. In a recent case study by Khan and Husain (2003), an industrial complex with a residential facility was located 400 metres from a fuel oil contaminated site. The study explored the feasibility and efficiency of natural attenuation in remediation of the site. The analysis indicated that, while there was an initial high risk to workers from benzene and toluene, MNA was effective. After 15 years the plume was diluted and degraded and risk was reduced to acceptable levels. Pennington et al. (2001), concluded that natural attenuation was also a viable remediation option for sites contaminated with explosives.

Rifai, et al. (2000), used BIOPLUM III as a natural attenuation model to simulates aerobic and anaerobic biodegradation of fuel hydrocarbons. The model simulations indicated that natural attenuation was a viable remedy for the site. Skubal et al. (2001), used field biogeochemical characterization and laboratory microsm studies to access the potential for future biotransformation of trichloroethylene (TCE) and toluene in a plume containing petroleum hydrocarbons and chlorinated solvents. The study also concluded that natural attenuation was applicable for this site. Clement et al. (2002), assessed natural attenuation data from a Super Fund Site. The analysis indicated that the site had potential for natural attenuation. A detailed conceptual model was developed to determine exposure pathways and exposure points and study if determined plumes would degrade and attenuate within 1000 feet down gradient before reaching the exposure point. Using the BIOCHLOR (Aziz et al., 1999) model the researchers concluded that natural attenuation was a feasible remediation alternative (Clement et al., 2002).

Natural attenuation of low molecular weight PAHs also appears to be promising for sites investigated (Roger et al., 2002). Seagren et al. (2002), stated that MNA had been accepted as a remediation technology and that a large number of sites contaminated with BTEX had been naturally attenuated.

In all of the studies outlined above, site characterization was an integral part of the implementation of natural attenuation. Site characterization, reactive fate and transport modeling and long-term monitoring are required to implement MNA as a remedial measure (Khan and Husain, 2002). Site characterization determines the extent of contamination, soil properties and aquifer properties. This information is used in a reactive transport model to predict the fate of the contaminants and their transport to receptors. Long-term monitoring assesses concentrations by fate-and-transport modeling of the contaminants and these concentrations are later compared against the observed values.

The ultimate objective of natural attenuation modeling is to reproduce effectively the chemical and physical behaviour of the site from a fundamental understanding of the processes so that long-term behaviour of the plume might be confidently predicted (Husain, 2004).

2.2 Modeling Natural Attenuation at Contaminated Sites

A model can be defined in various ways. Boulding (2002) defines a model as:

" ...a simplified description of an existing physical system or an assembly of concepts in the form of mathematical equations that portrays understanding of a natural phenomena."

Natural attenuation modeling methods, such as those used in this study, predict natural attenuation and are tools designed to represent a simplified version of a real field site. They are an attempt to take physical, chemical and biological processes and translate them into mathematical terms. The resulting model is only as good as the conceptual understanding of the processes. The goal of the modeling exercise is to predict the concentration distribution of a given chemical in the soil and groundwater over a given time period and distance (Boulding, 2002).

2.3 Types of Models

Several classifications exist for contaminant models and several types of models have been developed for modeling the fate and transport of contaminants in the subsurface. The number of dimensions modeled also varies from model to model. Models can also be considered deterministic or stochastic. A deterministic model assumes the occurrence of a given set of events results in a unique solution (Boulding, 2002). A stochastic model assumes that factors contributing to an outcome are uncertain. The model calculates the probability within a desired level of confidence of a specific value occurring at any point (Boulding, 2002). The governing equations for both deterministic and stochastic models can be solved either analytically or numerically. The applicable model types for this study are outlined in the following sections.

2.4 Dimensional Classification of Models

2.4.1 One Dimensional Models

There are a limited number of relatively simple 1-D problems for which analytical solutions exist (Bedient et al., 1999). A 1D model assumes that the chemical is ideal with a constant density and viscosity; the fluid is not compressible; the medium is homogenous and isotropic; and, only saturated flow is considered.

The model used in the computer program SESOIL for vadose zone transport, which was selected for this study, is an example on a one-dimensional model. The model in SESOIL models transports in one direction only since it only considers vertical transport of contaminants. Vertical transport of the contaminant is determined by the following equation:

$$\boxed{D = \frac{J_w t_c}{\theta + \rho_b K_d + \frac{f_a H}{R(T+273)}}}$$

Equation 2.1 (Scheiker, 2000)

Where:

D = contaminant depth
J_w = water velocity (cm/s)
t_c = advection time (s)
θ = soil water content (cm^3/cm^3)
ρ_b = soil bulk density (g/cm^3)
K_d = Chemical distribution coefficient (µg/g)/(µg/ml)
$f_a = f-\theta$ = the air filled porosity (ml/ml)
H = Henry's Law constant (m^3 atm/mol)
R = Gas Constant [8.2×10^{-5} m^3 atm/mol °K]
T = Soil temperature (°C)

2.4.2 Multidimensional Models

Multidimensional methods consider longitudinal, transverse and vertical dispersion along with advection in one dimension. The governing equation is altered to include only velocity in the x direction, and a first order decay term can be added.

A computer program that uses three-dimensional modeling was selected to model the transport of contaminants in groundwater for the site selected for this study. AT123D uses a three-dimensional modeling domain.

The AT123D model is based on the advection-dispersion equation that was used in this study to determine the contaminant distribution in groundwater. Assuming incompressible flow the advection-dispersion equation is:

$$\boxed{\frac{\partial(n_e C)}{\partial t} = \nabla * (n_e \overline{\overline{D}} \nabla * C\vec{q} + \dot{M} - K n_e C - \left(\frac{\partial(\rho_b C_s)}{\partial t}\right) + \lambda \rho_b C_s}$$

Equation 2.2 (Scheiker, 2000)

Where:

C = Dissolved contaminant concentration

C_s = Adsorbed contaminant concentration

$\overline{\overline{D}}$ = Hydraulic dispersion coefficient tensor

K = Chemical degradation rate

$\dot{M}$ = Contaminant source release rate

n_e = effective porosity

$\vec{q}$ = Darcy's velocity vector

t = Time

∇ = Gradient (Del operator with respect to x, y, and z)

λ = Radioactive decay constant

ρ_b = Bulk density of the soil

By definition the ∇ is:

$$\boxed{\nabla = \left(\vec{i}\frac{\partial}{\partial x} + \vec{j}\frac{\partial}{\partial y} + \vec{k}\frac{\partial}{\partial z}\right)}$$

Equation 2.3 (Scheiker, 2000)

The term on the left side of advection-dispersion equation represents the time rate of change of dissolved contaminant mass per unit volume of the aquifer. The first term on the right side of the equation represents the combined effects of hydraulic dispersion and molecular diffusion. The second term on the right side represents the advection of the contaminant. The third term represents the contaminant source load to the aquifer system. The fourth term on the right side of the equation accounts for the chemical and biological degradation of the contaminant, while the fifth term represents radioactive decay. The last two terms of the equation represent the effects of ion exchange and sorption.

The initial condition for the equation is:

$\boxed{C = C_i(x, y, z, t = 0) in R}$ Equation 2.4 (Scheiker, 2000)

Where:

C = Dissolved contaminant concentration
C_i = Initial contaminant concentration
R = A region with respect to x, y, and z (the region modeled)
t = Time
x = Longitudinal coordinate
y = Transverse coordinate
z = Vertical coordinate

This initial condition requires that the background concentration of the contaminant be known before the load is released into the aquifer.

The solution to the 3D model in AT123D for the site under consideration is given by the equation:

$$C(x,y,z,t) = \int_0^t \int_R \frac{\dot{M}}{n_e R_d} G dR_o d\tau + \int_R (GC_i)\tau = 0^{dR_o} - \int_0^t \int_{S_1} \overline{\overline{K}} \nabla G \vec{n} C_1 dS_o d\tau - \int_0^t \int_{S_2} \frac{Gq_2}{n_e R_d} dS_0 d\tau$$

$$- \int_0^t \int_{S_3} \frac{Gq_3}{n_e R_d} dS_0 d\tau$$

Equation 2.5 (Scheiker, 2000)

Where:

C = Dissolved contaminant concentration
C_i = Initial contaminant concentration
C_1 = Concentration on the boundary S_1
G = Green's function (**see** Scheiker, 2000)
$\overline{\overline{K}}$ = Retarded dispersion tensor
$\dot{M}$ = Contaminant source release rate
n_e = Effective porosity
$\vec{n}$ = Unit vector normal to S2
q_2 = The contaminant flux across the boundary at a given function of time and location on S_2
q_3 = Contaminant flux across the boundary at a given function of time and location on S_3
R = A region with respect to x, y, and z (region modeled)
R_o = A region with respect to ε, η and ς
S = Boundary of Region R
S_1 = A portion of S
S_2 = A portion of S
S_3 = A portion of S
S_o = The initial boundary of the region modeled R
t = Time
x = Longitudinal coordinate
y = Transverse coordinate
z = Vertical coordinate
∇ = Gradient (Del operator with respect to x, y, and z)
τ = Duration of the contaminant release

2.5 Mathematical Classification of Models

Mathematical models are usually described by the number of dimensions simulated (as previously discussed); and, the mathematical approaches used, which include analytical or numerical methods. SESOIL and AT123D employ both numerical and analytical, iterative techniques.

2.5.1 Analytical Techniques

Analytical models are useful for defining the magnitude of a contaminant problem. If data is limited or the hydrogeological conditions are simple, an analytical model can simulate contaminant fate and transport (Khan and Husain, 2002). Analytical methods use exact closed form solutions for the appropriate differential equations. The solution is continuous in space and time and employs many simplifying assumptions concerning the system. Analytical models are based on steady-state, isotropic and homogeneous conditions and data needs are moderate.

2.5.2 Numerical Techniques

Numerical methods are used in the solution of partial differential equations and auxiliary conditions. Numerical techniques are more complex than analytical solutions and use less simplifying assumptions than analytical models and are capable of addressing more complicated problems.

In order to facilitate the use of analytical and numerical methods several computer programs, such as those used in this study have been developed. A computer program that implements the analytical and numerical model is referred to as a computer code or computer model.

2.6 Computer Models

The development of an accurate contaminated site computer model was a critical step in modeling natural attenuation at the subject site. In order to comply with regulations and to be cost-effective a scientific and systematic approach must be used to access the site (Husain, 2004). A methodology proposed by Anderson and Woessner (1992) was reviewed and used to develop the computer model.

2.6.1 Selection of Governing Equation and Computer Code

The selection of a model for the site was based on the assumptions used, features, input data required, accuracy, flexibility and validation history (Husain, 2004). Two models were needed, one for the vadose zone and one for the groundwater zone.

Several studies were reviewed to establish the criteria used to select the computer program. The first consideration is that the model must fully account for all the various interactions between pollutants and soil fractions (Odencrantz, 1992).

Secondly, the equations of flow and transport must be capable of incorporating all factors involved in the spill migration in the environment (Geotrans, 1988).

According to Odencrantz (1992) the vadose zone transport model must, at a minimum be:

- A one-dimensional vertical model that can be separated into at least three layers, with varying soil properties and chemical loading concentrations by layers;
- Capable of representing one mobile chemical component in three phases (adsorbed, aqueous, and gaseous)
- Capable of representing biodegradation, volatilization, and gaseous diffusion; and,
- Capable of representing the variable effects of local climate (precipitation, temperature, etc.)

Several vadose zone models for soil modeling were reviewed for the study to determine which were most appropriate for the site selected and are summarized in Table 2.1.

Table 2.1: Comparison of Vadose Zone Models

Model	Description	Comments	Source
CMLS – Chemical Movement in Layered Soils	• calculates the movement and dissipation of non-polar chemicals in soil in response to water application, evapotranspiration, soil properties, plant rooting depth and properties of the chemical chosen	• can deal with soils with up to 20 layers or horizons • enables the user to enter partition coefficients for each horizon in the soil • enables the user to simulate movement of the chemical for up to 15 years	Nofziger and Hornsby, 1987
MOFAT – Multiphase Organic Flow and Transport	• two-dimensional, finite element modeling code • can represent the transport of up to five components between four phases allows for up to ten soil layers of differing properties • considers interphase mass transfer and compositional dependence of phase densities	• complicated and not easy to use	ESRI, 1990
V Leach (Vadose Zone Leaching Model)	• one- dimensional finite difference model • simulates leaching of an organic contaminant through the vadose zone	• Liquid phase dispersion is neglected; • No free product can be present; • The contaminant is not subject to in-situ biodegradation; • Volatilization from the surface is either completely unimpeded or completely restricted.	Ohio EPA, 1996
CHEM FLO (Chemical Flow Model)	• one-dimensional model to simulate water and chemical movement in unsaturated soils	• Predictions are sensitive to the specified boundary conditions • Assumes soil and chemical properties to be homogenous with depth and ignores partitioning and movement of chemicals in the vapour or gaseous phase • Some input parameters utilized could be extremely difficult to measure in field	Ohio EPA, 1996
SESOIL (Seasonal Soil Compartment Model)	one-dimensional vertical transport model for the unsaturated soil zone simultaneously models water transport, sediment transport and pollutant fate includes soil erosion algorithms and is designed to perform "long-term" simulations of chemical transport and transformations in soil can represent the transport of one chemical component through three phases (aqueous, gaseous and adsorbed), with a fourth "pure chemical phase" representative as an immobile storage phase	utilizes less soil, chemical and meteorological values as input than most other similar models • allows the soil profile to be discretized into a maximum of four layers with varying soil properties and chemical loading concentrations	Scheiker, 2000

Due to ease of use and wide acceptance SESOIL was selected, as the most efficient vadose zone model software. The Council for Health and Environmental Safety of Soils' (CHESS) Analysis and Environmental Fate Committee also reviewed several existing environmental fate models and recommended the SESOIL model for further consideration as a tool to aid the risk assessment process (Calabrese and Kostecki, 1992). Brar (1996) also selected SESOIL as the governing computer code. More recently, Khan and Husain (2002) evaluated available models for vadose zone modeling and also concluded that SESOIL was the most appropriate.

Once the vadose zone has been modeled the simulated mass flux rates at the bottom of the vadose zone must be routed into a groundwater transport model to estimate resulting groundwater concentrations. For ease of implementation the groundwater model should interface directly with the vadose zone model. The groundwater transport model should also handle variable-size areas and be capable of representing biodegradation, adsorption and advective dispersive transport (Odencrantz, 1992).

Although there are numerous groundwater transport models only a fraction of these are capable of representing both chemical retardation and degradation. Of those models with these required capabilities only a few are publicly available, well-documented, PC compatible and accepted by the scientific and regulatory communities (Odencrantz, 1992).

Groundwater transport models that generally meet the above minimum requirements have been evaluated for their usefulness in solving the subject problem and are summarized in Table 2.2.

Table 2.2: Comparison of Groundwater Transport Models

Model	Description	Comments	Source
AQUA3D (3-D Groundwater Flow and Contaminant Transport Model)	• 3-d groundwater flow and contaminant transport model • uses the Galerkin finite element method	• developed to solve 3D-groundwater flow and transport problems using the Galerkin finite-element method • solves transient groundwater flow with inhomogeneous and anisotropic flow conditions	Vatnaskil Consulting Engineers, 1998
BIOF&T 2D/3D(Biodegradation, Flow and Transport in the Saturated/Unsaturated Zones)	• models biodegradation flow and transport in the saturated and unsaturated zones in two or three dimensions in heterogeneous, anisotropic porous media or fractured media	• models convection, dispersion, diffusion, desorption and microbial processes	Scientific Software Group, 1998
ChemFlux (Finite Element Mass Transport Model)	• finite-element, contaminant transport modeling software.	• predicts the movement of contaminant plumes through the processes of advection, diffusion, adsorption and decay	Soil Vision Systems Ltd, 2004
FLONET/TRANS (2-D cross-sectional groundwater flow and contaminant transport modeling)	• 2-D cross-sectional groundwater flow and contaminant transport modeling	• simulates advective-dispersive contaminant transport problems with spatially-variable retardation and multiple source terms	Molson and Frind, 2002
FLOWPATH (2-D Groundwater Flow, Remediation, and Wellhead Protection Model)	• 2-D groundwater flow and contaminant transport	• models unconfined, confined and leaky aquifers with heterogeneous properties, multiple pumping wells and complex boundary conditions	Scientific Software Group, 1998
GFLOW (Analytic Element Model with Conjunctive Surface Water and Groundwater Flow and a MODFLOW Model Extract Feature)	• based on the analytic element method • models steady-state flow in a single heterogeneous aquifer	• particularly suitable for modeling regional horizontal flow • supports conjunctive surface water and groundwater modeling using stream networks with calculated baseflow	Gay and Gloski (1984)
MOC (2-D Solute Transport and Dispersion in Groundwater)	• 2-D solute transport in flowing groundwater and one- or two-dimensional problems involving steady state or transient flow • aquifer may be heterogeneous and/or anisotropic • incorporates first-order irreversible rate-reaction; reversible equilibrium controlled sorption with linear, Freundlich, or Langmuir isotherms; and reversible equilibrium-controlled ion exchange for monovalent or divalent ions	• assumes that gradients of fluid density, viscosity and temperature do not affect the velocity distribution	Konikow and Bredehoeft (1988)

MT3D (A Modular 3D Solute Transport Model)	• three-dimensional numerical model for simulating solute transport in complex hydrogeologic settings	• has a modular design that permits simulation of transport processes independently or jointly • capable of modeling advection in complex steady state and transient flow fields, anisotropic dispersion, first-order decay and production reactions, and linear and nonlinear sorption	Zheng,C. (1990)
POLLUTE (Finite-Layer Contaminant Migration Model - Landfill Design)	• used for contaminant migration analysis • "1½-dimensional" solution to the advection-dispersion equation	• does the numerical stability problems of alternate approaches • in addition to advective-dispersive transport, can consider adsorption, radioactive and biological decay, phase changes, and transport through fractures	Scientific Software Group, 1998
VAM2D (2-D Variably-Saturated Groundwater Analysis Model)	• two-dimensional finite-element groundwater model that simulates transient or steady state groundwater flow and contaminant transport in porous media	• contaminant transport option can account for advection, hydrodynamic dispersion, equilibrium sorption, and first-order degradation	Huyakorn et al. (1991)
WinTran (Groundwater Flow and Finite-Element Contaminant Transport Model)	• finite-element simulator	• contaminant mass may be injected or extracted using any of the analytic elements including wells, ponds, and line sinks • transport model includes the effects of dispersion, linear sorption (retardation), and first-order decay	Scientific Software Group, 1998
AT123D	• three-dimensional groundwater transport and fate model • developed to simulate contaminant transport under one-dimensional groundwater flow • results can be used to estimate how far a contaminant plume will migrate and can be compared to groundwater standards to evaluate risk at specific location and times • mechanisms simulated include advection, dispersion, sorption and biological decay	• linked to SESOIL by the SEVIEW interface program	Scheiker, 2000
BIOSCREEN	• screening level groundwater transport model that simulates the natural attenuation of dissolved hydrocarbons • based on the Domenico analytical contaminant transport model • can simulate natural attenuation based on advection, dispersion, adsorption and biological decay	• linked to SESOIL by the SEVIEW interface program	Scheiker, 2000

Most of the models are numerical and are more difficult to use and much more computationally demanding than AT123D, so they should be considered for use only where needed (Odencrantz, 1992). BIOSCREEN, while less complicated than AT123D, cannot handle the level of complexity required for the modeling process. AT123D is also very flexible and user friendly. Thus, AT123D is most useful for the subject problem. Khan and Husain (2002) also selected AT123D as the governing computer code, due to its analytical capability, simplicity and precision.

Based on the above SESOIL and AT123D were selected for modeling the site. SEVIEW was selected as the modeling software since it provides an interface between the two programs. SEVIEW is Windows based menu-driven, integrated contaminant transport and fate modeling system. The code was written by Scheiker (1993) to create a program that extracted the contaminant mass that volatilized to the atmosphere and the concentrations that leached to the groundwater. BIOSCREEN is also incorporated into SEVIEW but was not utilized in the modeling exercises undertaken. A schematic of the computer model is presented in Figure 2.1.

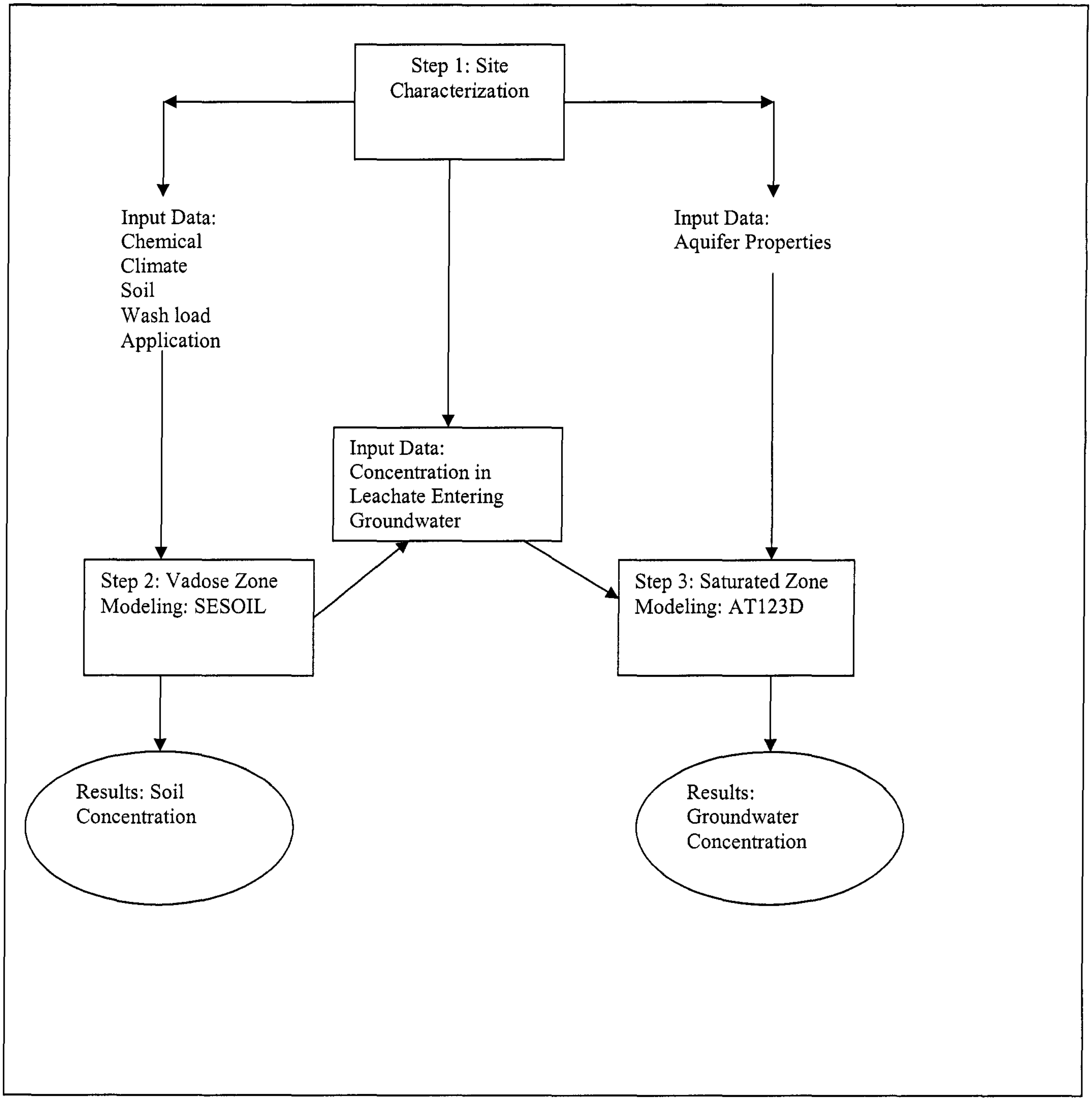

Figure 2.1: Summary of SEVIEW Model

2.6.2 SESOIL

Scheiker (2000) provides a description and governing equations for SESOIL in the user manual for SEVIEW. Bonazountas and Wagner (1981) developed SESOIL for the EPA's Office of Water and the Office of Toxic Substances. SESOIL is a seasonal compartment model that simulates long-term pollutant fate and migration in the unsaturated zone. The model computes pollutant masses in water, soil and air phases. It simulates remediation through natural attenuation based on diffusion, adsorption, volatilization, biodegradation and hydrolysis and is designed to simultaneously model contaminant, soil water and sediment transport in the soil. SESOIL can consider only one chemical at a time and the model is based on mass balance and equilibrium partitioning of the chemical between different phases (dissolved, sorbed, vapour and pure). There are five input files in SESOIL; chemical; climate; soil; washload (sediment transport); and, application. SESOIL estimates the contaminant mass entering groundwater, however, the saturated zone is not modeled. The output from SESOIL can be used for generating input values for groundwater transport models to simulate chemical movement in the saturated zone (Scheiker, 2000).

Figure 2.2 illustrates the process involved in SESOIL.

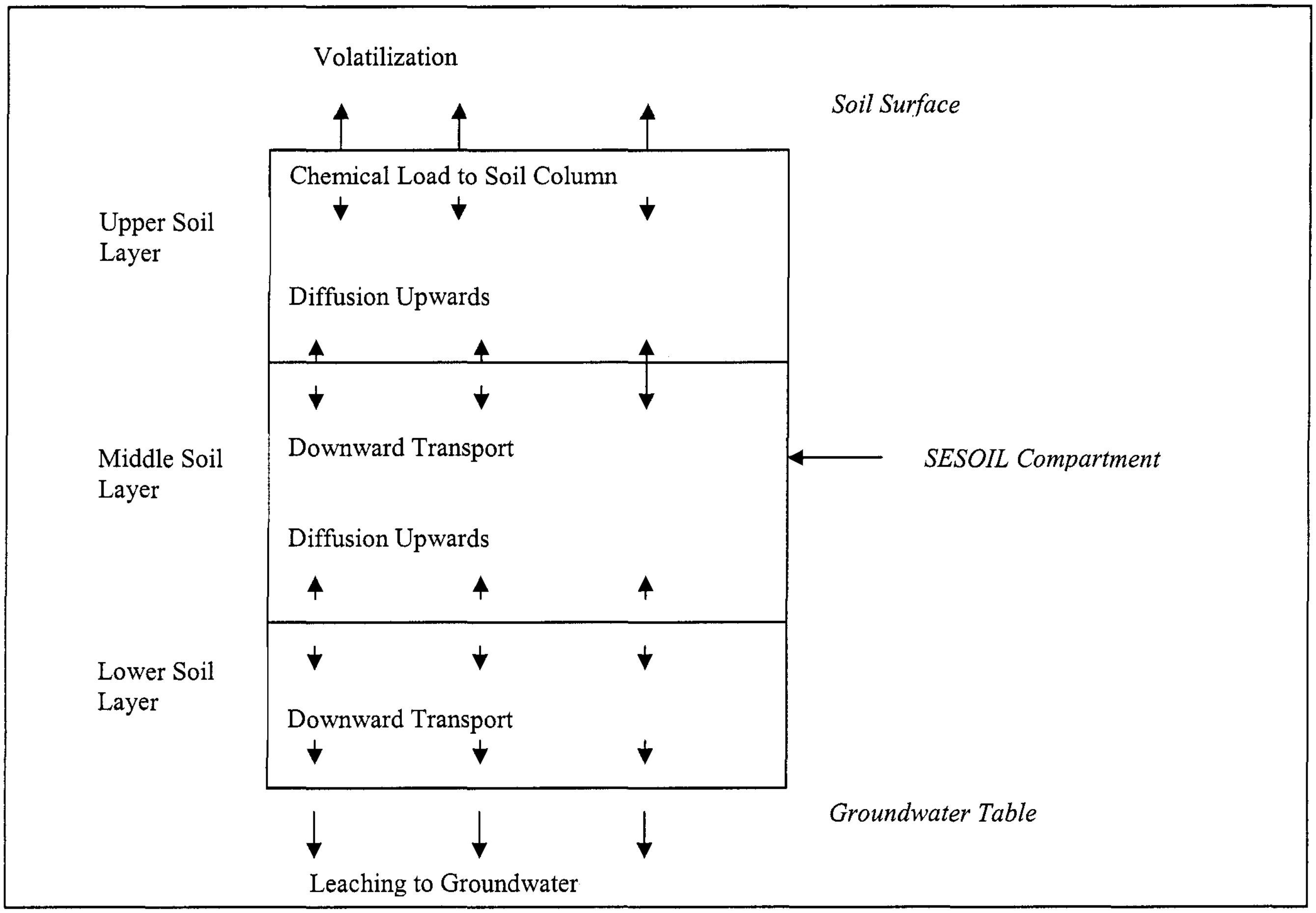

Figure 2.2: Schematic of SESOIL (adapted from Scheiker, 2000)

The SESOIL model is based on three assumptions (Brar, 1996):

- Pollutant concentrations in all phases and in all compartments of the soil system are at equilibrium at all times;
- The law of mass conservation determines the equilibrium concentration of chemical species over a series of monthly or yearly steps; and,
- Pollutant transport takes place in the unsaturated soil zone.

There are several advantages to using the SESOIL modeling software (Brar, 1996):

- Data requirements are not extensive;

- The compartmental module lets many users run the model for specific data sets or site conditions;
- Periodically, SESOIL is improved and modified by the Oak Ridge National Laboratory;
- The scientific community engaged in chemical fate modeling has accepted and recognized the SESOIL model;
- The model is structured to simulate chemical transport for more than a month. SESOIL accommodates physical, chemical and biological changes in the contaminant leaked into the soil system;
- The sensitivity analysis was conducted on adsorption and volatilization for different soil types and in different climates;
- SESOIL's hydrologic cycle has been found to be a good long-term predictor for groundwater and surface runoff, evapotranspiration and infiltration; and,
- Uncertainty analysis is introduced into the hydrological cycle with probability density functions, which produces probability distributions of water balance and yields long-term seasonal averages of the water balance.

Along with its benefits SESOIL also has several drawbacks (Brar, 1996):

- The present code for SESOIL uses a single homogeneous soil column for the hydrological cycle. As a result, SESOIL will not work at sites having large vertical variations in soil properties.
- The use of SESOIL is limited because it requires site-specific data for calibration. When input data are not available, the model user must use complex calculations to generate an input file. The user needs the expertise to select the appropriate equations required for developing input data. In a situation where site-specific data are not available, using data

published in the literature or default values might simulate results that are inaccurate by orders of magnitude.

- The model does not address the free product movement in the vadose zone. The model accommodates the migration of a single solute in an aqueous phase rather than a nonaqueous phase. The model's inability to distinguish between the NAPL phase and the water phase (dominant transport carrier) can create significant errors in simulations.
- Simulations with SESOIL are very poor when run with laboratory-generated input data.
- SESOIL does not address the soil-water spatial variability and water flow in each compartment. Therefore, chemical transport and distribution in the soil column could be affected because the retardation coefficients and volatilization fluxes of certain chemicals are water-sensitive.

2.6.3 AT123D

AT123D is an acronym for Analytical Transient 1-, 2-, and 3-Dimensional Simulation of Waste Transport in the Aquifer System. It is a generalized three-dimensional groundwater model developed by G. T. Yeh (1981) at Oak Ridge National Laboratory. Significant modifications were made in 1982, 1984 and, 1986 of the University of Wisconsin-Madison. Robert A. Scheiker at Environmental Software Consultants, Inc further modified AT123D in 1997.

The model was developed to estimate concentrations of contaminants transported, dispersed, degraded and sorbed in one-dimensional groundwater flow. The transport mechanisms simulated by AT123D include advection, dispersion, sorption, decay/biodegradation and heat losses to the atmosphere. Model results can be used to estimate how far a contaminant plume will migrate and can be compared to groundwater standards to evaluate risks at specific locations and times (Scheiker, 2000).

2.6.4 Application

SESOIL and AT123D have been applied in numerous modeling studies. Odencrantz (1992) incorporated SESOIL and AT123D in a study to determine soil clean up levels for leaking underground fuel tanks in California. The study noted that SESOIL and AT123D were appropriate models in determining soil clean-up levels that were protective of water quality. Sanders (1995) utilized SESOIL, along with four other vadose zone models, to predict leaching of volatile organic compounds from the soil to groundwater.

Brar (1996) used SESOIl to assess leaching of benzene in Alaska. Brar concluded that SESOIL was a well-developed vadose zone model. Peng et al. (1996) utilized SESOIL to estimate pentachlorophenol concentrations in the soil leachate, prior to the leachate entering the groundwater table. AT123D was utilized by Klinchun (1997) to evaluate the fate and transport of BTEX from residual crude oil. By using AT123D the study was able to conclude that MNA was the most favorable able and cost-effective mechanism to remediate BTEX. Sullivan (1997) incorporated SESOIL in the modeling of the fate and transport of diesel fuel.

Husain (2002) also incorporated the SESOIL and AT123D models in the development of a risk-based corrective action computer model. Khan and Husain (2002) utilized SESOIL and AT123D to evaluate natural attenuation of a petroleum hydrocarbon contaminated site.

2.6.5 Design of Model

Following the methodology of Anderson and Woessner (1992) once the appropriate model was selected the model design could then be developed. This step included the selection of a grid design, time parameters, initial and boundary conditions and developing estimates of model parameters. Model design involved data collection, analysis from the field and site characterization.

2.6.6 Calibration

Once the model has been selected and the input file developed model calibration is required. Calibration refers to the process of determining a set of model input parameters that approximate field measured heads, flows and/or concentrations. The purpose of calibration is to establish that the model can reproduce field-measured values of the unknown variable. It was noted in several studies (Odencrantz, 1992) that calibration was quite subjective and in many cases did not yield a unique set of parameters that reproduced field conditions.

Several studies were available on the calibration of vadose zone models. Calibration of unsaturated soil zone models can be uncertain and difficult because climate soil moisture, soil infiltration and percolation are strongly interrelated parameters that are difficult to measure in the field (Scheiker, 2000). However, if at all possible input parameters for any unsaturated soil zone model should be calibrated so that hydrological predictions agree with observations (Eagleson, 1978; Eagleson and Tellars, 1982).

As suggested by Anderson and Woesner (1992) the results of the calibration were evaluated relative to the measured values both qualitatively and quantitatively. To date, there is no standard protocol for evaluating model calibrations. A qualitative evaluation of the calibration involves comparing trends in the simulated results to those observed from the measured data (Scheiker, 2000).

Intrinsic permeability, soil disconnectedness index, and effective porosity have been found to be sensitive parameters in SESOIL (Scheiker, 2000). It was recommended that these values be varied to calibrate results to field data at the site (Scheiker, 2000). In SESOIL, parameters required for the hydrologic cycle can also be difficult to determine. The soil pore disconnectedness index, for example, which is defined as the exponent relating the "wetting" or "drying" time dependent permeability of a soil to its saturated permeability (Eagleson, 1978; Eagleson and Tellars, 1982) is not commonly found in the literature. Default values for the soil pore disconnectedness index suggested by Eagleson (1978) and Bonazountas and Wagner (1981, 1984) are; clay 12; silty clay loam 10; clay loam 7.5; silt loam 5.5; sandy loam 6; sandy clay loam 4; and sand 3.7. Other sensitive parameters for the hydrologic cycle are the effective porosity and the intrinsic permeability.

Bonazountas and Kallidromitou (1993) report that the model must be calibrated for site-specific variables such as biodegradation rate, soil organic carbon content, local climate and depth to the water table.

Ladwig et al. (1993) tested the SESOIL model for benzene, ethylbenzene, toluene, xylene and 1,2-dichloroethane under Wisconsin conditions and discovered that the model was most sensitive to soil type, biodegradation rate, residual concentration, residual layer thickness and organic carbon content of the soil. The model was least sensitive to climate, soil disconnectedness index, pH and depth of contaminant burial. Furthermore, the model was highly sensitive to intrinsic permeability for benzene in sand. However, it was insensitive to intrinsic permeability for treatment of benzene in till.

Hetrick et al. (1993) recommended that the user conduct sensitivity analyses or evaluate results obtained by assigning distributions to the input parameters (O'Neil et al. 1982, Gardner 1984, Hetrick et al. 1991).

Oregon State regulator Anderson (1992) tested the SESOIL model to simulate transport of organic contaminants through the vadose zone. He also used the MINTEQA1 model (USEPA 1987) to simulate inorganic speciation and concentrations under specified field conditions. Sensitivity analyses were performed on organic contaminants—benzene, carbon tetrachloride, ethylbenzene, methyl chloride, naphthalene, perchloroethylene, toluene, 1,1,1-trichloroethane, 1,1,2-trichloro-ethylene and o-xylene. The results of the tests indicated that the most important parameters controlling organic contaminant transport in the SESOIL/AT123D models were the thickness of the contaminated zone, depth from the contaminated zone to groundwater, hydraulic conductivity and gradient, and the fraction of the organic carbon in the soil.

2.6.7 Sensitivity Analysis

The next step in the development of the model is to determine the effects of uncertainty on model runs. This is sometimes referred to as a sensitivity analysis. Sensitivity is a measure of the degree to which model results are affected by changes in selected input parameters such as hydraulic properties. The model parameters are varied individually within a range of possible values, and the effect on model results is evaluated (Odencrantz, 1992).

The purpose of a sensitivity analysis was to quantify the effects of uncertainty in the estimates of model parameters on model results. In a study conducted by Schneiker (1997) 530 model scenarios were used in SESOIL to predict groundwater contamination concentrations. Four parameters were considered for the sensitivity analysis; soil disconnectedness index; soil permeability; air diffusion coefficient; and, soil organic content. High and low values were selected for each parameter. For each sensitivity analysis model run a single parameter was varied. Secondary effects of the parameters were not considered. The highest variation occurred when permeability was reduced. The lowest flux occurred when the fraction of organic carbon was reduced.

2.6.8 Verification

This step involves testing the model's ability to reproduce another set of field measurements using the model parameters that are developed in the calibration process. Because of uncertainties in parameter estimation for a given site, the calibrated model parameters may not accurately represent the system under a different set of boundary conditions or hydrological stresses. In the verification exercise, values of parameters and hydrologic stresses determined during calibration are used to simulate a transient response for which a set of field data exists.

2.6.9 Prediction

Prediction is the estimation of results based on the calibrated model (Anderson and Woesner, 1992). Prediction is one of the more common motivations for modeling. In the predictive simulation, the parameters determined during calibration are used to predict future conditions or the response of the system to future events.

To assess SESOIL's predictive capabilities for contaminant movement, a contaminant transport and validation study was performed by Arthur D, Little, Inc. under contract to EPA (Bonazountas et al., 1982). The application/validation study was conducted on two field sites, one in Kansas and one in Montana. SESOIL results were compared to data for the metals chromium, copper, nickel, and sodium at the Kansas site and the organics naphthalene and anthracene at the Montana site. Results showed reasonable agreement between predictions and measurements, although the concentrations of the metals were consistently underestimated, and the rate of metal movement at the Kansas site was consistently overestimated. At the Montana site, the concentrations of the organics were overestimated by SESOIL.

Bonazountas et al. (1982) stated that the over estimations for the organics were probably due to the fact that biodegradation was not considered in the simulations. Hetrick et al. (1989) compared predictions of the improved version of SESOIL with empirical data from a laboratory study involving six organic chemicals (Melancon et al., 1986). They also compared values from three different field studies invoking the application of aldicarb to two field plots (Homsby et al., 1983; R. L. Jones, 1986; Jones et al., 1983, 1985) and atrazine to a single-field watershed (Smith et al., 1978). Results for several measures of contaminant transport were compared including the location of chemical peak vs. time, the time-dependent amount of contaminant leached to groundwater, the depth distribution of the contaminant at various times, the mass of the chemical degraded, and the amount of contaminant in surface runoff. This study showed that SESOIL predictions were in good agreement with observed data for both the laboratory study and the field studies. SESOIL correctly predicted the leading edge of the chemical profile (Hetrick et al., 1989), due mainly to the improvement of the contaminant depth algorithm to include the chemical sorption characteristics. Also, when a split-sample calibration/validation procedure was used on 3 years of data from the single-field watershed, SESOIL correctly predicted the amount of chemical in the runoff.

The model is less effective in predicting actual concentration profiles; the simulated concentrations near the soil surface under estimate the measurements in most cases. One explanation is that SESOIL does not consider the potential upward movement of the chemical with the upward movement of water due to soil evaporation losses.

Care should be taken when applying SESOIL to sites with large vertical variations in soil properties since the hydrologic cycle assumes a homogeneous soil profile. Only one value for the soil moisture content is computed for the entire soil column. If different permeabilities are input for each soil layer, the soil moisture content calculated in the hydrologic cycle using the vertically averaged permeability might not be valid for the entire soil column Schneiker (2000).

Chapter 3: Site Selection

The first task in the study was to gather information on a number of potential sites to model. Based on the site characteristics and available data one site was selected for further analysis. Initial sites considered are summarized in Table 3.1 and are outlined in further detail in Section 3.1 through Section 3.4.

Table 3.1: Summary of Potential Sites

Site	Area	Type	Contaminants of Concern
Site 1	5200 m^2	Petroleum Retail Outlet	Petroleum Hydrocarbons in the fuel oil range and benzene
Site2	1590 m^2	Petroleum Retail Outlet	Petroleum Hydrocarbons in the gasoline range
Site 3	2030 m^2	Petroleum Retail Outlet	Petroleum Hydrocarbons in the fuel oil and lube oil range
Site 4	633 hectares	Industrial Fire Training Area	Petroleum Hydrocarbons in the fuel oil range and free phase petroleum product

3.1 Site 1: Petroleum Retail outlet

The site building was 100 m^2 and was operated as a gas bar and convenience store. Petroleum storage and distribution equipment consisted of four 22,700 litre underground storage tanks (USTs) located to the north of the site building and two 25,000 litre USTs located to the west of the site building.

In May, 1993 six monitor wells were completed as part of the site investigation. Petroleum hydrocarbon contamination was found in the soil and groundwater located on the site. In October and November 1993 site remediation was carried out. The site was excavated and backfill was placed on the site. A total of about 8500 m^3 of impacted soil was excavated and disposed of. Following the remediation elevated levels of TPH remained in the subsurface soils at the north building foundation and a partial barrier wall was installed along the east site boundary.

In July 1994, a soil and groundwater characterization of the site was conducted. Groundwater was found to be impacted with benzene and petroleum impacted soils were also present on the site. In October 1995, an environmental site assessment was carried out on the site. Gasoline range impacts were present in the groundwater. In 2002 and 2003 groundwater modeling was carried out on six existing monitor wells. Following the groundwater-monitoring event, four boreholes were completed and one groundwater monitoring well was installed. Soil and groundwater samples were collected for the analysis of petroleum hydrocarbons. Gasoline range impacts were present in the groundwater.

3.2 Site 2: Petroleum Retail Outlet

The site building was 170 m^2 and consisted of a service station, gasoline retail outlet, and a former car wash. Petroleum storage and distribution equipment consisted of five underground gasoline storage tanks, two pump islands, one underground fuel tank, one underground used oil tank and associated underground pipes.

In July 1994, a soil and groundwater characterization of the site was conducted. One water sample was impacted with metals, however no detectable levels of petroleum hydrocarbon concentrations were reported for any of the groundwater samples tested. Benzene, toluene, ethyl benzene and xylenes (BTEX) and total petroleum hydrocarbons were not detected in any of the soil samples tested.

In October 1995 an environmental site assessment was carried out on the site to compare 1995 groundwater quality with data collected in 1994. There were no detectable petroleum hydrocarbon indicator parameters at any of the monitor wells.

In 2002 and 2003 a groundwater monitoring event was carried out on six existing groundwater monitor wells. Following the groundwater monitoring event three boreholes were completed and four groundwater-monitoring wells were installed. Four additional site wells were then installed and soil and groundwater samples were collected for the analyses of petroleum hydrocarbons. Petroleum hydrocarbon impacts were found to be present in the soil and groundwater.

3.3 Site 3: Petroleum Retail Outlet

The site building was 200 m^2 and consisted of a gasoline retail outlet and convenience store. Petroleum storage and distribution equipment consisted of three underground gasoline storage tanks and two pump islands and associated underground pipes.

In July 1994 soil and groundwater characterization of the site was conducted. Only one groundwater sample contained elevated levels of benzene, however petroleum hydrocarbon impacts were detected. In October 1995 an environmental site assessment was carried out on the site to compare 1995 groundwater quality with data collected in 1994. There was strong gasoline range contamination detected in 1994. These high concentrations of BTEX compounds and TPH represented a saturated condition of soluble petroleum hydrocarbon species in groundwater. In 1995 the TPH levels had disappeared.

In 1996/1997 due to the observations and chemical analysis of groundwater samples in 1994 and 1995 the existing USTs and associated gasoline installations were replaced. During the replacement 4300 tonnes of petroleum hydrocarbon contaminated soil and rock were removed. The remaining contamination underneath the service station was isolated by the installation of a cut-off wall. A TPH concentration of 13,013 mg/kg was encountered in one soil sample collected from below the southwest corner of the building.

After the completion of the site remediation, eleven monitor wells were installed on the site and three wells were installed off-site.

Prior to remediation, free product was present in two monitor wells. Following site remediation groundwater samples from remediated areas did not contain BTEX components in detectable quantities. Some remaining TPH was detected on the site, primarily in the former oil contaminated area in the front of the workshop.

Contamination (mainly waste oil) remained underneath the service station building and under the eastern pump island canopy foundation (gasoline). Contamination may also have been present at the northern pump island apron adjacent to the building.

Unremediated gasoline contamination extended off-site to the south. The extent of any off-site impacts was not known. Groundwater from two out of three off-site monitor wells contained BTEX components. The BTEX impacted wells were located down gradient of the former gasoline contaminated area. All three off-site wells contained TPH components.

In 2002 and 2003 a groundwater monitoring event was carried out on six groundwater monitor wells. Following the groundwater monitoring event six new on-site groundwater monitor wells were installed, followed by an additional four off-site monitor wells. Soil and groundwater samples were collected for the analysis of petroleum hydrocarbons. BTEX impacted wells were again present down gradient of the former gasoline contaminated area and all three off-site wells contained TPH components.

3.4 Site 4: Industrial Fire Training Area

The property was situated about 140 meters above sea level. This site was inactive and was formerly used for fire training exercises. A former scrap vehicle storage site and a former operations area bound it on the west and northwest. A disposal site borders the area to the immediate east and to some extent covered part of the fire training area. The property to the south and southeast was treed with a mixture of moderate to full growth softwood.

The site was active during the 1980s and use was discontinued in the mid 1980s. Potential contaminants of concern included petroleum hydrocarbon components, PAH compounds and trace metals associated with the handling, storage and combustion of fuel products as part of the training exercise.

The former fire training area, disposal sites, former scrap vehicle area and former bulk storage area were investigated during an environmental baseline study (EBS) carried out in 1997 and 1998. The EBS identified the fire tire area as being heavily impacted. The disposal sites and the former bulk storage area had minor metal impacts.

In 2001/2002 a Phase III Environmental Site Assessment (ESA) was conducted. This study was initiated because the EBS did not fully delineate and characterize the area of concern at the fire training area.

In 2003 a Human Health and Ecological Risk Assessment (HHRA) was conducted on the fire training site and also concluded that contamination above applicable guidelines had been identified for soils, groundwater, stream surface water and stream sediments. Contaminants of concern included metals and dissolved phase petroleum hydrocarbons (monocyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons).

In 2003 an existing information review was conducted and a site characterization was completed which included the installation of eleven groundwater monitor wells, three test pits and a hydrogeological study.

3.5 Site Selection

Several factors were considered for site selection and included:

- Availability of data;
- Type of contaminants and reliability of the source input;
- Less uncertainty in data;
- Consistency in sampling;
- Applicability of model for the site; and,
- Site history.

Based on the data available and the level of site characterization Site 4 was selected as the study area. The site had undergone extensive investigation and data over several years was available.

The previous environmental assessment reports were available and the site had been consistently sampled and monitored over a number of years. SESOIL and AT123D modeling could be applied to the site since the site subsurface was undisturbed and no prior remediation activities had been carried out on site. As well, additional data was available for the site such as a detailed hydrogeological study and a quality human health and ecological risk assessment that had been completed on the site.

A detailed discussion of the site is presented in Section 4.0.

Chapter 4: Site Characteristics

Site characterization included identification of the subsurface geology, history of contamination, and water quality at the site. The stratigraphy was determined using soil borings, well logs and test pit results. The subsurface geological data was interpreted into values of the hydraulic conductivity and porosity, which was used as input to the model. The elevation of the water table was interpreted by constructing water level contours to determine the general direction of groundwater flow.

Water quality data collected at specified time intervals from monitoring wells were analyzed to determine the trends in the spatial and temporal distributions of chemicals at the site. The collected water quality data for a specific chemical were contoured to determine the extent of the plume of contamination.

Following site selection available information for the site was compiled and is outlined in the following sections.

4.1 Site Characterization

The first step in the site characterization process was an existing information review. In the previous work on the site the area was sub-divided into four regions, A, B, C and D, which are indicated by the monitor well prefixes. Following the existing review additional site investigations were carried out.

Based on the findings of the previous work, the scope of work for the fieldwork consisted of the following:

- Three test pits were excavated and three groundwater monitor wells were installed in the area south of the fire training area to determine the presence or absence of petroleum hydrocarbons, metals, PAH and PCBs in the soil and groundwater (see Figure 4.1 – Site Plan); and,
- Eight groundwater monitor wells were installed to carry out a hydrogeological study.

4.2 Soil Properties

The site is underlain by Precambrian, Protorozoic III sandstone. The majority of soils encountered during test pitting consisted of very dense, brown silty sand and gravel with numerous cobbles and boulders. The majority of soils encountered during the drilling program consisted of loose to very dense, grey-green brown, silty sand, clay and gravel with numerous cobbles and boulders.

In the 2002 site investigation program, bedrock was encountered from 1.5 metres to 3.0 metres below ground level.

General Notes

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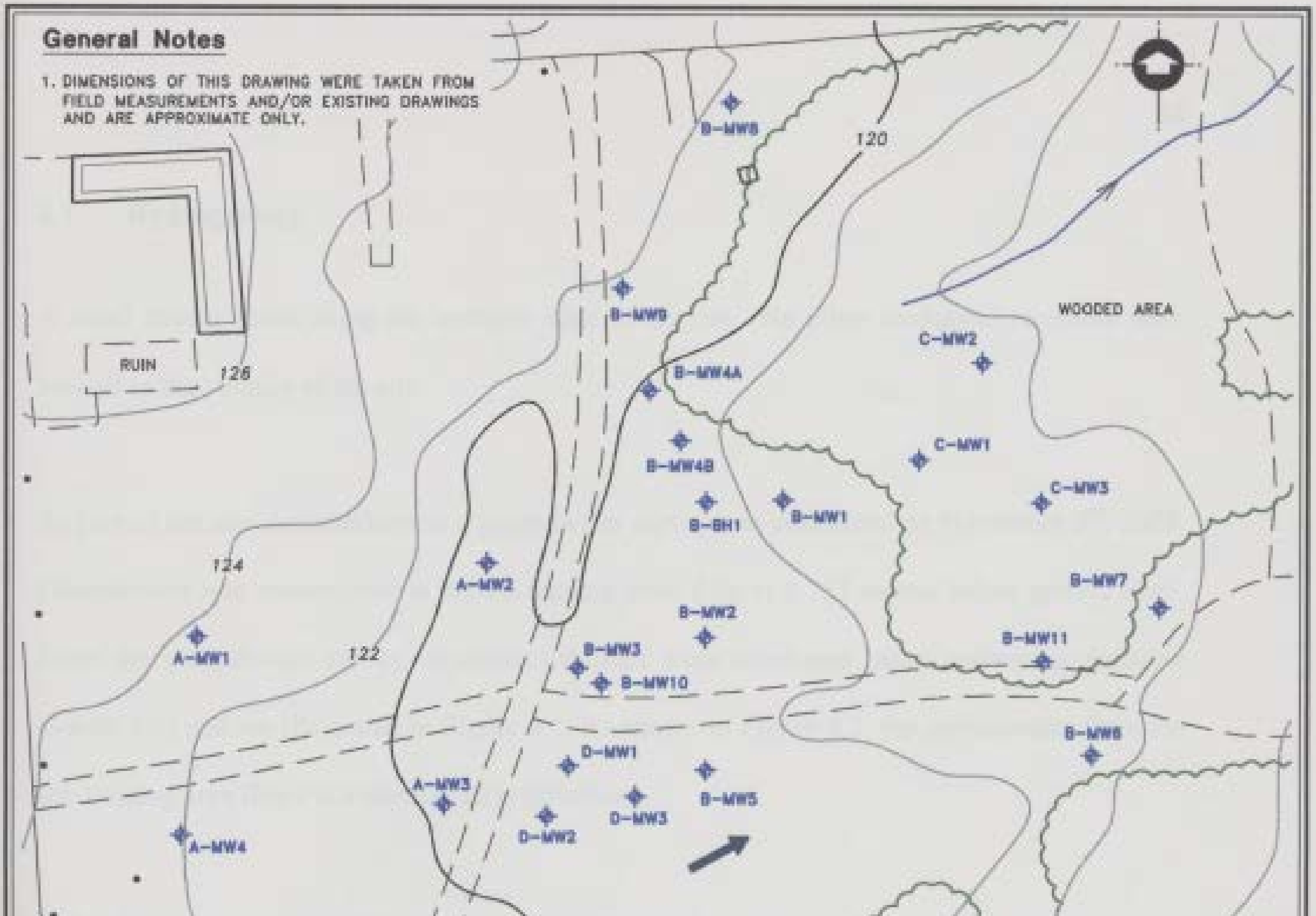

TITLE **Site Plan**	SCALE 1:1500	FIGURE NO. 4.1
PROJECT **Computer Modelling of a Petroleum Hydrocarbon Contaminated Site**	DATE June 2004	

4.3 Hydrogeology

A small stream flows along the northern edge of the site. No other ecological receptors were located in the vicinity of the site.

As part of the site characterization a groundwater survey was conducted on November 3rd, 2003. Groundwater was encountered at depths ranging from 0.96 to 5.757 metres below ground level. From the groundwater survey, equipotential lines were developed using contouring software (Surfer 6.0) and are illustrated in Figure 4.2. As shown in Figure 4.2, the groundwater from the fire training area flows in a northeasterly direction.

Following the groundwater survey, hydraulic conductivity testing was conducted on six groundwater-monitoring wells (D-MW1, D-MW3, DMW4, D-MW6, B-MW10 and B-MW11). Data from two of the wells could be interpreted from the single well response tests using the Hvorslev method (D-MW1 and D-MW4). This method assumes that the aquifer medium is homogeneous, isotropic, infinite in extent and incompressible. The hydraulic conductivities determined from the bail down test from D-MW1 and D-MW4 were 5.9×10^{-4} cm/s and 4.3×10^{-4} cm/s; respectively.

General Notes

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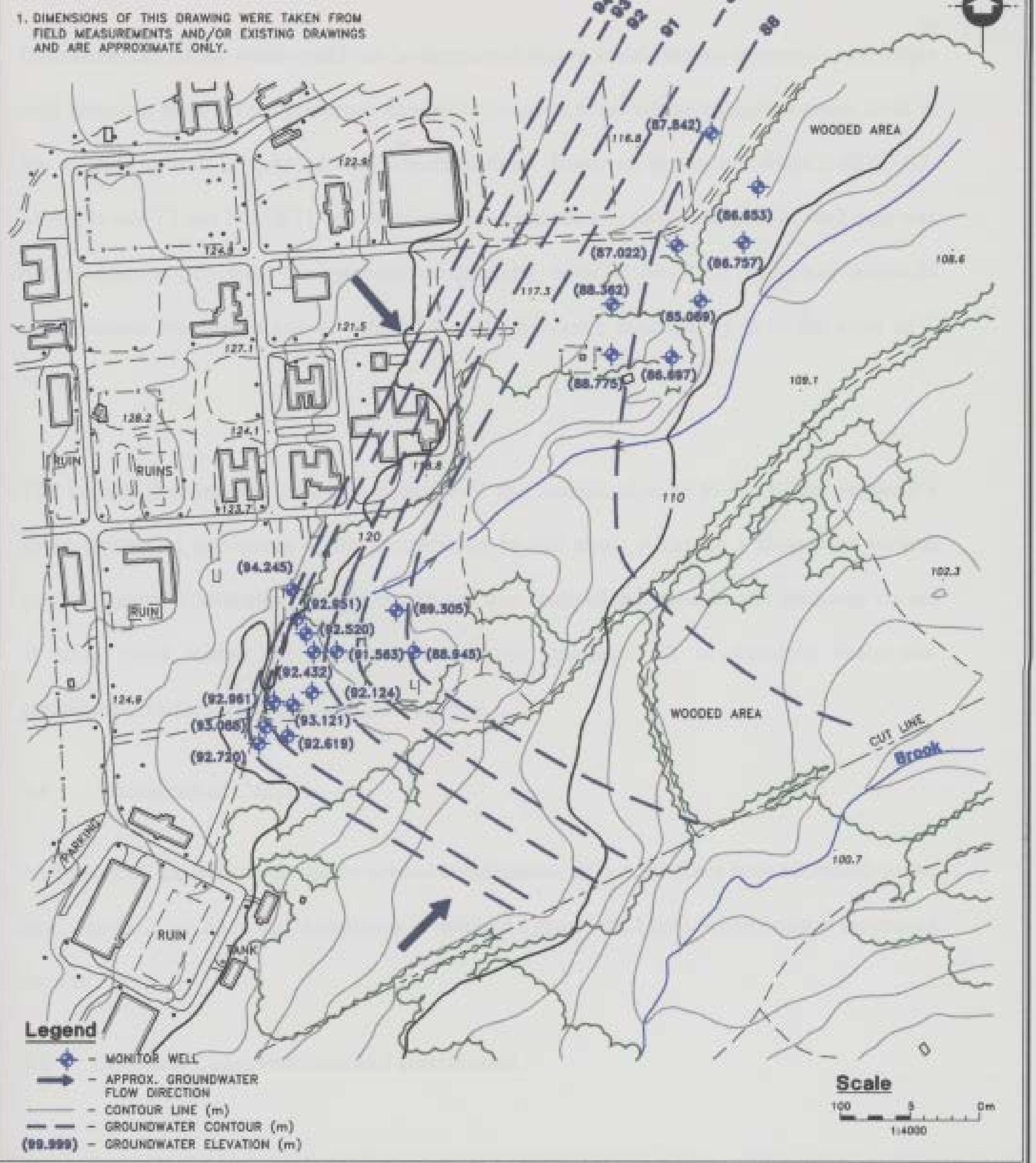


Legend

- ⌖ – MONITOR WELL
- ➡ – APPROX. GROUNDWATER FLOW DIRECTION
- —— – CONTOUR LINE (m)
- — — – GROUNDWATER CONTOUR (m)
- (99.999) – GROUNDWATER ELEVATION (m)

TITLE	SCALE	FIGURE NO.
Groundwater Flow Direction	1:4000	**4.2**
PROJECT **Computer Modelling of a Petroleum Hydrocarbon Contaminated Site**	DATE June 2004	

Data from four of the wells could not be interpreted due to instantaneous recovery. In a single well response when an instantaneous amount of water is removed the change in water level in the monitoring well is recorded with respect to time. However, in monitor wells D-MW3, D-MW6, B-MW10 and B-MW11 the water levels instantaneously recovered and the well data was not adequate to determine the hydraulic conductivity, however based on field observations of instantaneous recovery it can be inferred that the hydraulic conductivity is in the order of 1 cm/sec.

The vertical gradient measured at a nested well site located adjacent to the stream suggests a slight downward movement of the groundwater in this area. Although a downward vertical gradient generally indicates recharge conditions, it is assumed that groundwater discharge occurs at some point within the stream located down gradient. It is therefore likely that groundwater/surface water interaction is ongoing.

4.4 Chemicals of Concern

As a result of the field investigation several contaminants of concern have been identified on the site. The focus of the model, however is to model the petroleum hydrocarbon impacts present on the site.

4.5 Chemical Concentrations and Distribution

The results of the field investigations for concentrations of benzene, toluene, ethyl benzene and xylenes (BTEX) and total petroleum hydrocarbons (TPH) in soil and groundwater are provided in the following tables. It should be noted that the petroleum hydrocarbons present on the site were identified as weathered fuel oil, based on laboratory analysis.

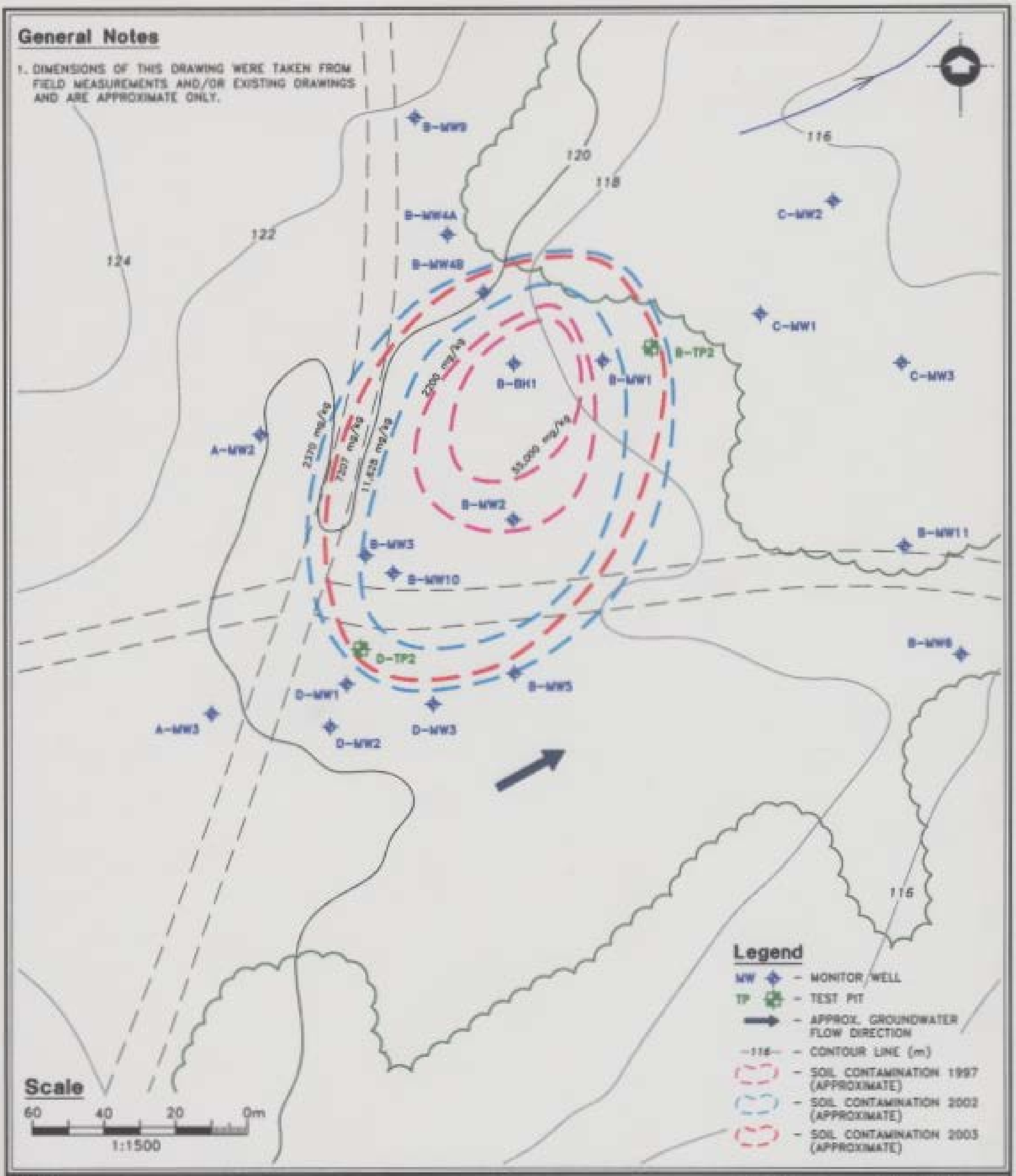
Table 4.1: Summary of Soil Analytical Results – Total Petroleum Hydrocarbons (mg/kg)

Sample Location	Depth	Date Sampled	Benzene	Toluene	Ethyl Benzene	Xylenes	Total Petroleum Hydrocarbons	Comments
A-BH1	0.0-0.6	June 1997	<	<	<	<	29	-
A-BH2	0.0-0.6	June 1997	<	<	<	<	44	-
A-MW1	4.6-5.0	July 1997	<	<	<	<	9.2	-
A-MW2	3.8-4.3	July 1997	<	<	<	<	83	-
A-MW3	0.0-0.6	July 1997	<	<	<	<	22	-
B-BH2	1.8-1.96	Feb 1998	<	<	<	<	22	-
B-MW2	0.0-0.6	June 1997	<	<	<	<	2200	-
B-MW3	0.0-0.6	Oct 1997	<	<	<	<	56	-
B-MW4	0.0-0.6	Oct 1997	<	<	<	<	95	-
B-MW5	0.6-1.2	Feb 1998	<	<	<	<	<	-
B-MW6	0.6-1.2	Feb 1998	<	<	<	<	<	-
B-MW7	0.0-0.6	Feb 1998	<	<	<	<	<	-
B-MW8	2.44-2.6	Feb 1998	<	<	<	<	<	-
B-BH1	0.8-1.4	June 1997	<	<	0.68	3.4	55000	Fuel Oil Range
B-MW9-SS1	1.5-2.1	July 2002	<	<	<	<	<	-
B-MW9-SS5	3.1-3.7	July 2002	<	<	<	<	<	-
B-MW10-SS2	0.8-1.4	July 2002	0.05	0.383	0.84	6.82	11628	Fuel Oil Range
B-MW10-SS4	2.3-2.9	July 2002	<	<	<	<	177	-
B-MW11-SS2	0.8-1.1	July 2002	<	<	<	<	<	-
B-TP1-SS1	0.0-1.0	July 2002	<	<	<	<	255	-
B-TP1-SS3	2.0-3.0	July 2002	<	<	<	<	36	-
B-TP2-SS1	0.0-1.0	July 2002	<	<	<	<	2370	Fuel Oil Range
B-TP3-SS1	0.0-1.0	July 2002	<	<	<	<	<	-
B-TP3-SS2	1.0-1.5	July 2002	<	<	<	<	<	-
C-MW1	0.0-0.6	June 1997	<	<	<	<	<	-
D-TP1-SS1	0.0-1.0	Oct 2003	<	<	<	<	<	-
D-TP1-SS3	2.0-3.0	Oct 2003	<	<	<	<	<	-
D-TP2-SS1	0.0-1.0	Oct 2003	<	<	<	<	102	-
D-TP2-SS3	2.0-3.0	Oct 2003	<	<	<	<	<	-
D-TP3-SS1	0.0-1.0	Oct 2003	<	<	<	<	<	-
D-TP3-SS3	2.0-3.0	Oct 2003	<	<	<	<	<	-
D-MW1-SS1	0.3-0.6	Oct 2003	<	<	<	<	44	-
D-MW1-SS4	2.7-2.9	Oct 2003	<	<	<	<	<	-
D-MW2-SS1	0.3-0.9	Oct 2003	<	<	<	<	7207	Fuel Oil Fraction
D-MW2-SS4	2.7-3.3	Oct 2003	<	<	<	<	<	
D-MW3-SS1	0.3-0.9	Oct 2003	<	<	<	<	<	
D-MW3-SS4	2.7-3.0	Oct 2003	<	<	<	<	19	

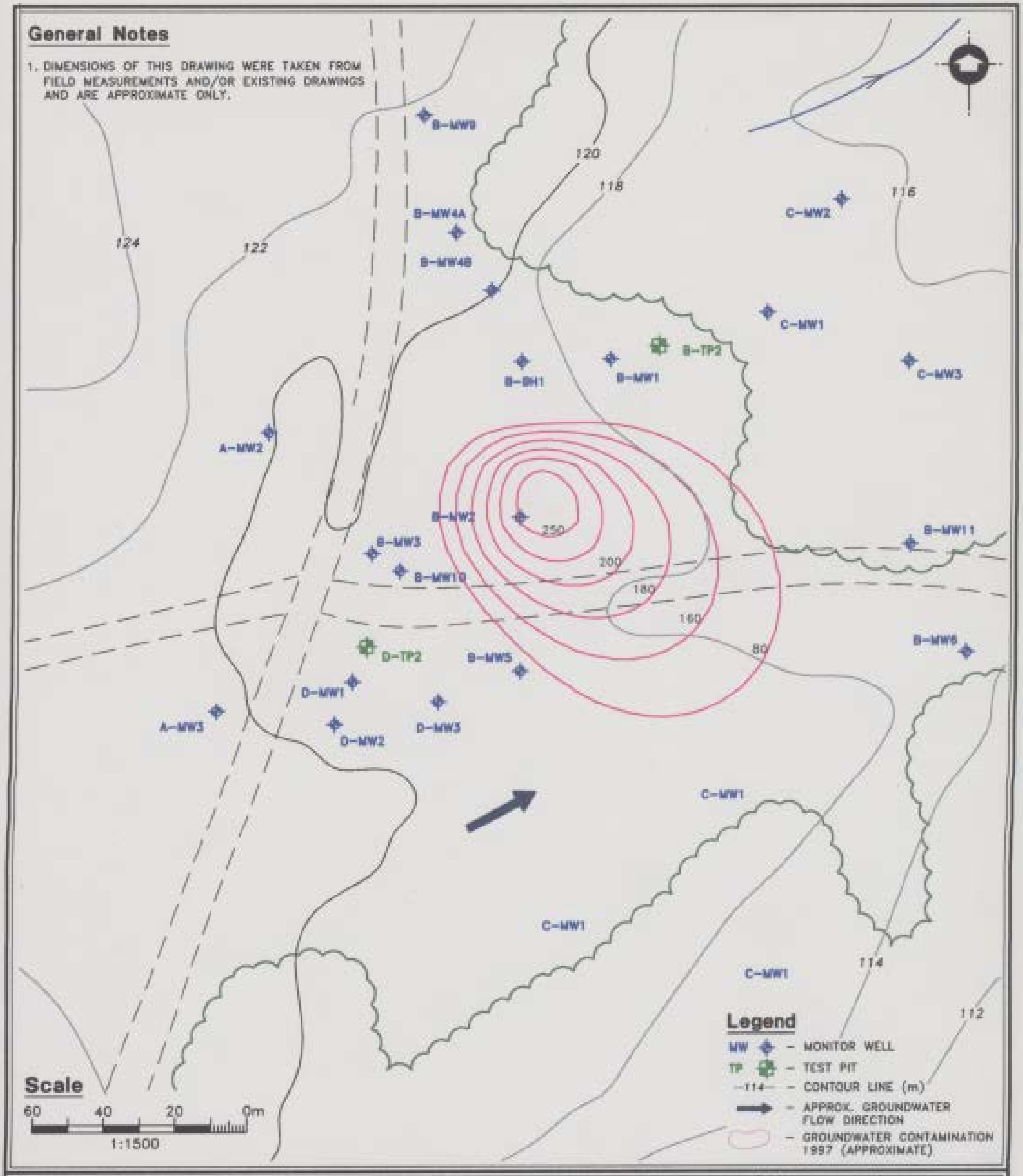
Table 4.2: Summary of Groundwater Analytical Results – Total Petroleum Hydrocarbons (mg/L)

Sample Location	Date Sampled	Benzene	Toluene	Ethyl Benzene	Xylenes	Total Petroleum Hydrocarbons	Comments
A-MW1	1997	<	<	<	<	0.39	-
A-MW2	1997	<	<	<	<	<	-
A-MW3	1997	<	<	<	<	0.29	-
A-MW4	1997	<	<	<	<	0.24	-
C-MW1	2002	<	<	<	<	<	-
C-MW2	2002	<	<	<	<	<	-
C-MW3	2002	<	<	<	<	<	-
D-MW1	2003	<	<	<	<	0.06	-
D-MW2	2003	<	<	<	<	0.18	-
D-MW3	2003	<	<	<	<	<	-
B-BH1	1997	0.21	0.0079	0.036	0.352	17.22	-
B-MW1	1997	<	<	<	<	0.61	-
B-MW2	1997	0.35	0.0016	0.025	0.147	252	Weathered Fuel Oil
B-MW2	1997	0.33	<	0.011	0.154	350	Weathered Fuel Oil
B-MW3	1997	<	<	<	<	1.30	-
B-MW4A	1997	<	<	<	<	<	-
B-MW4B	1997	<	<	<	<	<	-
B-MW5	1997	<	<	<	<	<	-
B-MW6	1997	<	<	<	<	<	-
B-MW7	1997	<	<	<	<	<	-
B-MW8	1997	<	<	<	<	<	-
B-BH1	2002	0.033	<	<	<	52.8	Weathered Fuel Oil
B-MW1	2002	<	<	<	<	0.16	-
B-MW3	2002	<	<	<	<	0.13	-
B-MW4A	2002	<	<	<	<	<	-
B-MW4B	2002	<	<	<	<	<	-
B-MW9	2002	<	<	<	<	0.09	-
B-MW10	2002	<	1	<	4	25.5	Weathered Fuel Oil
B-MW11	2002	<	<	<	<	<	-

The extent of soil contamination is illustrated in Figure 4.3. The extent of groundwater contamination (including contour lines) is illustrated in Figure 4.4 and Figure 4.5.



TITLE	SCALE	FIGURE NO.
Soil Contamination	1:1500	**4.3**
PROJECT **Computer Modeling of a Petroleum Hydrocarbon Contaminated Site**	DATE June 2004	



General Notes

1. DIMENSIONS OF THIS DRAWING WERE TAKEN FROM FIELD MEASUREMENTS AND/OR EXISTING DRAWINGS AND ARE APPROXIMATE ONLY.

Legend

MW ✦ – MONITOR WELL
TP ✦ – TEST PIT
–114– – CONTOUR LINE (m)
➡ – APPROX. GROUNDWATER FLOW DIRECTION
◯ – GROUNDWATER CONTAMINATION 1997 (APPROXIMATE)

TITLE	SCALE	FIGURE NO.
Groundwater Contamination (1997)	1:1500	4.4
PROJECT	DATE	
Computer Modelling of a Petroleum Hydrocarbon Contaminated Site	June 2004	

General Notes

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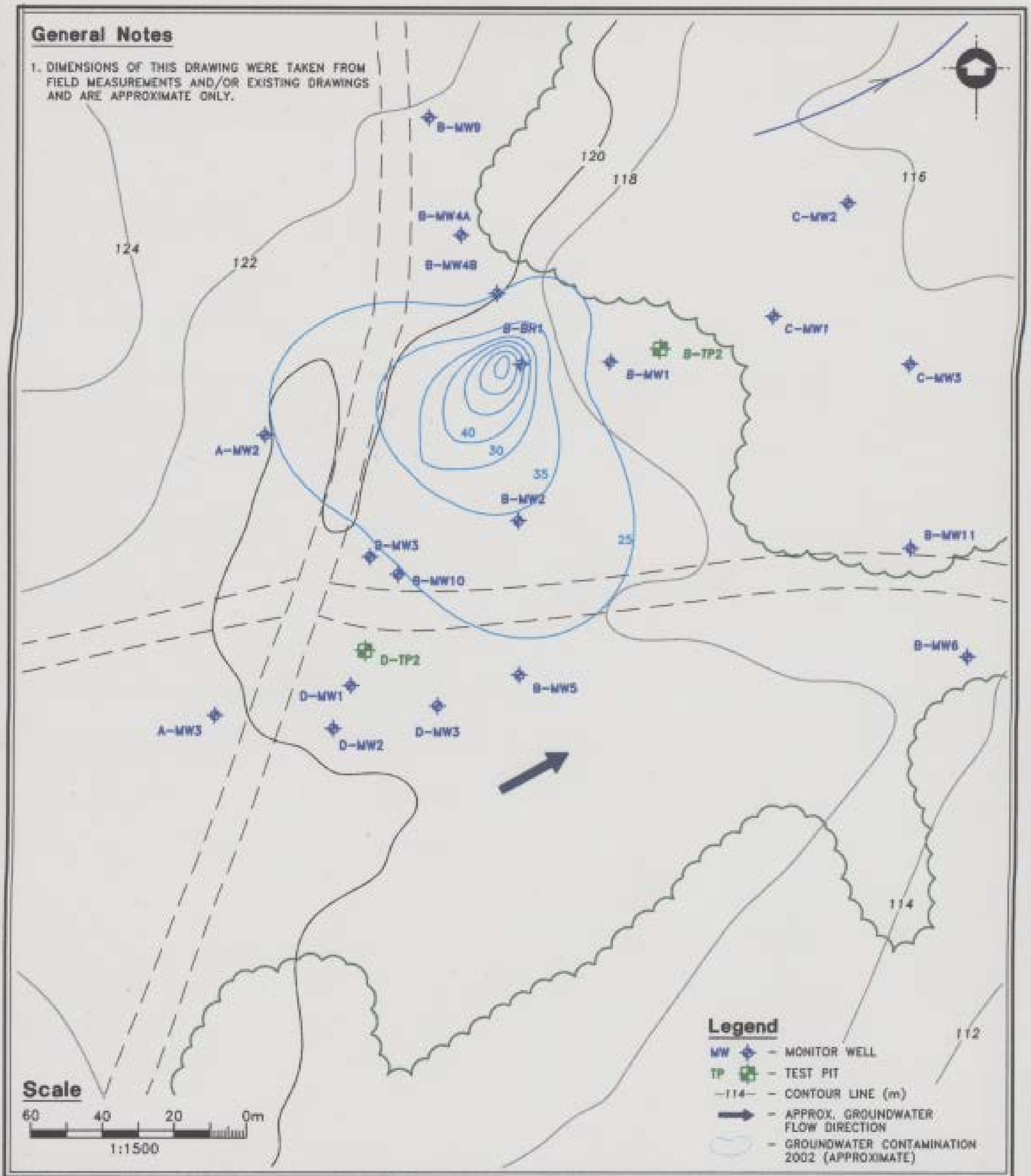

TITLE

Groundwater Contamination (2002)

PROJECT

Computer Modelling of a Petroleum Hydrocarbon Contaminated Site

SCALE

1:1500

DATE

June 2004

FIGURE NO.

4.5

4.6 Toxicity

4.6.1 Human Health

Some aspects of the toxicity of petroleum oils depend on the chemical composition of the oil. Where this has been studied, most toxicity has been found associated with the aromatic compounds in oil (Pierzynski et al., 2000).

Many toxicological effects are related to organic chemicals. The simple alkane, alkene, and alkyne hydrocarbons are volatile gases that cause asphyxial disorders, which are related to insufficient oxygen intake. Hydrocarbon liquids are known to cause dermatitis which is associated with the dissolution of fatty skin tissues and results in inflammation, drying and scaly skin. Other problems associated with some of these substances are irritation, headaches, dizziness and nervous system disorders (Pierzynski et al., 2000).

Fuel oil is derived from crude petroleum and is a mixture of aliphatic (64%), aromatic (35%) and olefinic (1-2%) hydrocarbons (Tripathi, 2001). A summary toxicological information of fuel oil is provided in Table 4.3.

Table 4.3: Summary of Human Toxicity for Fuel Oil

Effect	**Toxicity**	**Source**
Acute Ingestion – respiratory, neurotoxic and gastrointestinal effects Dermal/Inhalation - cardiovascular, hematological, renal effects Chronic Heaviness on chest Eye irritation Dermatosis	Probable effects Level (PEL) = 400 ppm (8 hours/day for 40 hour work week)	Tripathi, 2001
Acute Inhalation – irritation, depress central nervous system, giddiness, headache, vomiting, lack of coordination, narcosis, stupor, coma and unconsciousness Ingestion - irritation, depress central nervous system, giddiness, anesthetic stupor, coma, death Dermal – drying, cracking and defatting dermatitis Chronic Inhalation – dizziness, weakness, weight loss, anemia, nervousness, renal failure, degenerative changes of liver kidneys may occur Ingestion – no data available Dermal – irritation, dermatitis and rash	Oral Rat; LD50 = 14,500 mg/kg (Oral ingestion rate for lab rates at which there is a 50% mortality rate)	Material Safety Data Sheet (MSDS) on #2 Fuel Oil, 2002

4.6.2 Impacts on Plants and Microorganisms

The mechanisms of TPH toxicity are not well studied. Although the inherent toxicity of some compounds is a probable cause, the lack of water and nutrients in oily soils has been found to be a significant factor in an organism's response (Langley et al., 2003). In addition, plant response is determined by the exposure mechanisms (ie atmospheric deposition, spill, water contamination or land application).

Organic chemicals introduced into the environment can have serious impacts on certain organisms. The toxicity of petroleum hydrocarbons in soil has been studied using a range of species, including bacteria, algae, earthworms and plants, and a range of lethal and sub-lethal effects, related to seed germination, root elongation and reproduction (Langley et al., 2003).

Most of the published literature has focused on the whole product toxicity, with the majority using crude oil. Toxic effects have appeared over a large range of TPH concentrations. However, most effect concentrations are >1000 mg/kg (Langley et al., 2003). The lowest EC_{50} (effect concentration for which 50% of the plants are effected) for seed germination studies are in the range of 2000 to 3000 mg/kg (Langley et al., 2003). The low molecular weight aromatic component is likely to be a significant contributor to the toxicity of these mixtures (Langley et al., 2003).

A range of effect concentrations for TPH are presented in Table 4.4.

Table 4.4: Selected Range of Effect Concentration of TPH (Langley et al., 2003)

Product	Age	Endpoint	Value	Comment
Plants				
Fuel Oil –light fraction	Fresh	Seed germination LC_{50}	3000 mg/kg (sand)	Maize
Fuel Oil –heavy fraction	Fresh	Seed germination LC_{50}	60,000 mg/kg (sand)	Maize
Fuel Oil	Fresh	Seed germination LC_{50}	3000 mg/kg-70,000 mg/kg (sand)	7 crops (most sensitive lettuce, least sunflower)
Diesel Fuel	Fresh	Seed germination LC_{50}	25,000 mg/kg (sand)	9 species of grasses
Diesel Fuel	Fresh	Seed germination LC_{50} for 50% of the species	50,000 mg/kg (sand)	22 species of grasses legumes and commercial crops
Light Crude Oil	Fresh	Significantly reduced growth – (20-70%)	4200-26,600 mg/kg	Wheat and oats. More sensitive but more variable than seed germination
Microalgae				
Diesel Oil	Weathered	Biomass and enzyme activity NOEC	<2,120 mg/kg	---
Soil Invertebrates (Earthworms)				
Light Crude Oil	Artificially Weathered	Survival LC_{50}	42-96 mg/kg	Dependent on the organic content of the soil
Crude Oil	Weathered	Survival NOEC	1000 mg/kg	Generally non-toxic above 4000 mg/kg

4.7 Applicable Guidelines

Based on the site's location two sets of guidelines may to apply to the site. The first being the Atlantic Partnership in Risk Based Correction Risk-Based Screening Levels. Under the Atlantic PIRI classifications system the site would be classified as a commercial site with coarse-grained soil and non-potable groundwater. Also considered were the federal guidelines for commercial, non-sensitive sites, developed by the CCME. These guidelines are summarized in Table 4.5.

Table 4.5: Summary of Applicable Guidelines

Soil (mg/kg)					
Atlantic PIRI Guidelines					
Receptor	Groundwater Use	Soil Type	Exposure Pathway	Compound of Concern	Allowable Concentration
Commercial	Non-Potable	Coarse Grained	Indoor Air	Diesel/#2	7400
			Soil Ingestion		7400
			Soil Leaching		Not Applicable for non-potable scenarios
CCME					
Non-Sensitive				TPH	1000
Groundwater (mg/L)					
Atlantic PIRI Guidelines					
Receptor	Groundwater Use	Soil Type	Exposure Pathway	Compound of Concern	Allowable Concentration
Commercial	Non-potable	Coarse-grained	Indoor Air	Disel/#2	20
			Ingestion		Not Applicable for non-potable scenarios
CCME					
No guideline in place					

For Atlantic PIRI a value of 20 mg/L is applied to any calculated groundwater value that exceeds 20 mg/L as this is considered the upper concentration limit. Concentrations above this value may represent the presence of free product.

Using the above table the target levels were specified as 1000 mg/kg for soil and 20 mg/L for groundwater.

Chapter 5: Model Input File

Based on the information gathered, the site characterization, and the history of the site a SEVIEW input file was created for the site.

5.1 Climate File Input parameters

The SESOIL climate data set contains information describing the specifics of the local climate. This includes; air temperature, cloud cover, relative humidity, short wave albedo, mean evapotranspiration rate, monthly precipitation, mean length of precipitation events, number of precipitation events per month and the distribution of precipitation events throughout the month. The site specific climate file was completed and is summarized in Table 5.1.

Table 5.1: Summary of Climate Input Parameters

Month	Air Temp (°C)[1]	Cloud Cover Fraction[2]	Relative Humidity [1]	Short Wave Albedo	Evapo. Rates	Precip[1] (cm)	Storm Duration (days)	# Storm Events	Length Rainy Season (days)
Jan	-4.8	0.78	0.85	0.7	0	15	0.6	5.91	30.4
Feb	-5.4	0.66	0.76	0.7	0	12.52	0.63	5.05	30.4
March	-2.5	0.62	0.76	0.7	0	13.08	0.62	5.80	30.4
April	1.6	0.51	0.74	0.5	0	12.18	0.6	5.74	30.4
May	6.2	0.62	0.76	0.2	0	10.09	0.54	5.80	30.4
June	10.9	0.47	0.72	0.2	0	10.19	0.39	5.63	30.4
July	15.4	0.52	0.67	0.2	0	8.94	0.32	5.27	30.4
Aug	15.5	0.69	0.72	0.2	0	10.81	0.38	5.16	30.4
Sept	11.8	0.45	0.76	0.2	0	13.09	0.47	4.52	30.4
Oct	6.9	0.56	0.74	0.2	0	16.19	0.58	4.58	30.4
Nov	2.6	0.80	0.84	0.8	0	14.40	0.6	6.13	30.4
Dec	-2.2	0.72	0.87	0.8	0	14.80	0.63	6.16	30.4

1 Environment Canada
2 http://www.geocities.com/meteomode

The air temperature is entered in degrees Celsius. The air temperature is used to determine the monthly evapotranspiration rates and soil temperatures. The air temperature averages were obtained from Environment Canada and are the monthly averages collected from St. John's Airport.

The cloud cover is entered as a fraction. In SESOIL the cloud cover is a dimensional fraction ranging from 0.0 to 1.0 and is used to calculate the evapotranspiration rates. The cloud cover data was obtained from local weather observations of cloud cover.

The fractions were determined by the following values:

Overcast = 1
Cloudy = 0.9
Mostly Cloudy = 0.8
Mainly Cloudy = 0.7
Partly Sunny = 0.6
Variable Clouds = 0.5
Partly Cloudy = 0.4
Mainly Sunny = 0.3
Mostly Sunny = 0.2
A few Clouds = 0.1
Sunny = 0

Relative humidity is also provided as a fraction. It is used to calculate evapotranspiration rates. The relative humidity averages were obtained from Environment Canada and are the monthly averages collected from St. John's Airport.

The short wave albedo is provided as a fraction. In SESOIL the albedo fraction is the ratio of the reflective short wave energy to the incoming energy. An array of the short wave albedo fraction for each month of the year (dimensionless fraction ranging from 0.0 to 1.0) is used to determine the soil temperature, which is used to calculate evapotranspiration rates. Using typical short wave albedo values provided in Table 5.2 and based on the site conditions the short wave albedo fractions for each month of the year were determined and ranged from 0.2 to 0.8.

Table 5.2: Typical Short Wave Albedo Values (Scheiker, 2000)

Surface	Range	Typical Values
Soil and Bedrock		
Dark moist soil with high humus content	0.05-0.15	0.10
Grey moist soil	0.10-0.20	0.15
Dry desert soil	0.20-0.35	0.30
Sand, wet	0.20-0.30	0.25
Sand, light dry	0.30-0.40	0.35
Soil (black, moist)	0.05-0.10	--
Soil (black, dry)	0.10-0.15	--
Desert	0.25-0.40	0.37
Desert, clayey	0.29-0.31	--
Granite	0.12-0.18	--
Rocks in general	0.12-0.15	--
Sand, wet	0.15-0.25	--
Snow		
Fresh dry snow	0.70-0.90	0.80
Old snow	0.60-0.75	0.70
Dirty snow	0.40-0.75	--
Thawing snow	0.35-0.65	0.50
Vegetation		
Grasses	0.15-0.30	0.20
Green grass	0.18-0.27	--
Green vegetation (short)	0.10-0.20	0.17
Grassland parched	0.16-0.30	--
Grassland, dry	0.25-0.30	--
Dry vegetation	0.20-0.30	0.25
Forests	0.05-0.20	--
Coniferous forest	0.10-0.15	0.12
Green deciduous forest	0.15-0.25	0.17
Yellow deciduous forest (autumn)	0.33-0.38	--
Man made Surfaces		
Concrete	0.15-0.35	0.20
Asphalt	0.05-0.10	0.07

The evapotranspiration rates were not available for the area. This value was omitted and was calculated by SEVIEW based on the other input parameters provided.

The precipitation is measured in cm/month. The precipitation averages were obtained from Environment Canada and are monthly averages.

The duration of individual storm events is measured in days. Site-specific values were not available for the site. The values from the SESOIL climate file for Portland, Maine were used since the climate and latitude of the site are similar to the climate and latitude of Portland Maine.

The number of storm events is measured in storm events/month. In SESOIL it is array of the number of storm events per month for each month of the year. Again site-specific values were not available for the site. The values for the SESOIL climate file for Portland, Maine were used since the climate and latitude of the site are similar to the climate and latitude of Portland Maine.

The length of the rainy season is measured in days. The rainy season is defined as the number of days in a given month upon which rain may occur. For most regions of Canada, this parameter should be set to 30.4 for all months, since rain events may occur throughout the entire month. The length of rainy season was entered as 30.4.

5.2 Chemical File Input Parameters

The chemical input file contains information describing the chemical and physical properties of the contaminant released or applied to the soil column. This information includes water solubility, an air diffusion coefficient, Henry's Law constant, an organic carbon adsorption coefficient, a soil partition coefficient, the molecular weight, the valance of the compound, acid, base and neutral hydrolysis rate constants, liquid and solid phase biodegradation rates, a ligand stability constant, the moles ligand per mole of compound and the molecular weight of the ligand. Fuel oil is not a ligand compound and therefore the ligand stability constant, the moles ligand per mole of compound and the molecular weight of the ligand were applicable. A zero value was entered for these three compounds. The remaining chemical input parameters are described in the following paragraphs.

Water solubility is measured in μg/ml. It is the solubility of the compound in water at 25°C. The reported values of water solubility for fuel oil were varied. Sources report values ranging from 3.11×10^{-7} to 535 mg/L (Fitzgerald, 1989). From the available site information, the highest concentration of TPH observed in the groundwater was 350 mg/L, therefore this value was used as the solubility of the TPH compound.

The air diffusion coefficient is measured in cm^2/sec. This parameter is used by SESOIL to calculate volatilization. In a study completed by Sullivan et al. (1997) a value of 0.0463 was used as the air diffusion coefficient for diesel fuel and therefore this value was entered as the air diffusion coefficient in the SESOIL input file.

Henry's Law Constant is measured in M^3-atm/mol and is a dimensional form of Henry's law Constant. Again the Henry's Law Constant for fuel oil is variable. In a study completed by Sullivan et al. (1997) a value of 0.042 was used as the Henry's Law Constant and this value was entered into the SESOIL input file as the Henry's Law Constant.

The organic carbon adsorption coefficient, K_{oc} is a coefficient that describes the distribution of an organic chemical between the aqueous and soil organic matter phases.

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad \text{Equation 5.1}$$

K_{oc} is measured in (μg/g)/(mg/ml). Sullivan et al. (1997) used a K_{oc} value of 1100 and this value was entered into the SESOIL input file as the value for K_{oc}.

The distribution coefficient, K_d is also measured in (μg/g)/(mg/ml). The K_d value defines the distribution of the contaminant between soil solid and solution phases (Pierzynski et al., 2000).

A zero value was entered for the distribution coefficient and SESOIL calculated K_d by multiplying the organic carbon adsorption coefficient (K_{oc}) times the soil organic carbon content, (Organic carbon in the soil input file).

The molecular weight of the soil is measured in g/mol and the molecular weight was based on the value used by Sullivan et al. (1997) and was entered as 226.

The valence of the compound is measured in g/mole and was used to calculate the cation exchange with the soil. The Cation Exchange Capacity algorithm was not used since the adsorption process was being modeled. This parameter was entered as zero.

Hydrolysis involves the chemical transformation between an organic chemical and water that results in the breaking of one bond while forming a new carbon-oxygen bond. Since hydrolysis was not considered a major process for this site the neutral, base and acid hydrolysis rate constants were entered as zero.

The liquid and solid phase biodegradation rates were measured in day^{-1} and are a measure of the biodegradation rates of the compound in the liquid and solid phase; respectively. Again, following the study conducted by Sullivan et al. (1997) the liquid and solid phase biodegradation rates were entered as zero since biodegradation mainly affects the benzene, toluene, xylene and ethyl benzene concentrations and the fresher fuel oil products. Once the product is weathered biodegradation no longer is a major source of natural attenuation for fuel oil (Sullivan et al., 1997).

5.3 Soil File Input Parameters

The soil-input file specifies information describing the soil properties for a SESOIL column. This information includes: soil bulk density, intrinsic permeability, soil disconnectedness index, effective porosity, organic carbon content, cation exchange capacity and Freundlich exponent. The SESOIL programs accounts for vertical variation in the soil column by allowing up to four soil layers. The variation of the soil properties for non-uniform soils is then specified in the application file. The soil-input parameters are provided in the following paragraphs.

Bulk density is measured in g/cm^3. Typical soil bulk density values are provided in Table 5.3.

Table 5.3: Typical Soil Bulk Density Values (Scheiker, 2000)

Soil Type	**Estimated Bulk Density (g/cm3)**
Sand	1.18-1.58
Silt	1.29-1.80
Clay	1.40-2.20

The bulk density for the site was not measured in the field and as a result a range of typical values was considered.

Intrinsic permeability is measured in cm^2. Intrinsic permeability can be estimated by multiplying hydraulic conductivity in units of cm/sec by 1.0×10^{-5} cm sec. Based on the hydraulic conductivity testing carried out (see page 47) on the site the intrinsic permeability ranged from 4.9×10^{-9} to 1.0×10^{-5} cm^2.

A range of values were also considered for the soil pore disconnectedness index. Typical values are provided in Table 5.4.

Table 5.4: Default values for Soil Pore Disconnectedness Index (Bonazoutas and Wagner, 1984)

USDA Textural Soil Class	Soil Pore Disconnectedness Index
Clay (very fine)	12
Clay (medium fine)	12
Clay (fine)	12
Silty Clay	12
Silty clay loam	10
Clay loam	7.5
Loam	6.5
Silt loam	5.5
Silt	12
Sandy Clay	6
Sandy Clay Loam	4
Sandy loam	4
Loamy sand	3.9
Sand	3.7

The effective porosity is a dimensionless ratio of the volume of interconnected voids to the bulk volume of the aquifer matrix. The porosity of the site was estimated as 0.25. However, the actual porosity was not measured. A range of values for effective porosity were considered based on the typical values provided in Table 5.5 and Table 5.6.

Table 5.5: Default Values for Effective Porosity (Bonazoutas and Wagner, 1984)

USDA Textural Soil Class	Effective Porosity
Clay (very fine)	0.20
Clay (medium fine)	0.20
Clay (fine)	0.22
Silty Clay	0.25
Silty clay loam	0.27
Clay loam	0.30
Loam	0.30
Silt loam	0.35
Silt	0.27
Sandy Clay	0.24
Sandy Clay Loam	0.26
Sandy loam	0.25
Loamy sand	0.28
Sand	0.30

Table 5.6: Typical values for Effective Porosity (Domenico et al, 1990)

Soil Type	Effective Porosity
Clay	0.01-0.20
Silt	0.01-0.30
Fine Sand	0.10-0.30
Medium Sand	0.15-0.30
Coarse Sand	0.20-0.35
Gravel	0.10-0.35
Sandstone	0.005-0.10
Unfractured Limestone	0.001-0.05
Fractured Granite	0.00005-0.01

The organic carbon content is measured as a percent and is the organic carbon content of the uppermost soil layer. Since the organic carbon content was not measured in the field a range of organic carbon contents in the soil was considered in the calibration phase of the simulation.

The cation exchange capacity is measured in milliequivalents/100 grams dry soil. Unless the combined effects of cation exchange and sorption are accounted for, these processes should not be used at the same time. Since sorption would dominate the fate and transport process this process was included and the cation exchange capacity was set to zero.

The Freundlich Exponent is dimensionless and is used to establish the chemical sorption for the top soil layer. Values of Freundlich Equation Exponent typically range from 0.9 to 1.4. If the value is not known, the default value of 1.0 is recommended. Since the Freundlich Exponent was not measured in the field, a range of values were considered in the calibration phase of simulation.

5.4 Washload Input File

The washload file contains data used by SESOIL to calculate the washload transport or the removal of the contaminants adsorbed to eroding soil particles.

The washload area is measured in cm^2. The washload area should be equal to or less than the application area of the soil column. The washload area in the model was set to the application area of 1.4×10^7 cm^2.

The silt, sand and clay fractions are the fractions of silt, sand and clay in the washload topsoil and are estimated from site characteristics. An actual grain size analysis was not completed as part of the field work, however based on observations made during test pit and monitor well programs the silt, sand and clay fractions were set to 0.2, 0.66 and 0.14; respectively.

The slope length or length of travel of the representative overland flow profile is measured in cm. The slope length was determined by field measurements and was specified as 6279 cm.

The land slope is measured in cm/cm. The land slope is the average slope over the representative overland flow profile. The land slope was determined by field measurements and was specified as 0.04 cm/cm.

The soil erodibility factor is measured in tons/acre. This value typically ranges from 0.03 to 0.69; the default value is 0.23. The soil erodibility factor was not measured in the field and was specified as the default value of 0.23. The default value was reasonable since the land was not cultivated and had a gentle slope and no erosion control measures were in place.

The soil loss ratio is unitless. The ratio depends on the type of ground cover and land management practices. Typical values range from 0.0001 (well-managed land) to 0.94 (tilled soil). The soil loss ratio was not measured in the field and was specified as the default value of 0.26 since the land was not tilled or cultivated and no erosion control measures were in place.

The contouring factor is a fraction and is used for agricultural land. Typical contouring factors range from 0.1 (extensive practices) to 1.0 (no supporting practice). The contouring factor was not available for the site and was specified as the default value of 1.0 since the land was not cultivated and no agricultural activity was present on the site.

Manning's Coefficient (unitless) for overland flow typically ranges from 0.01 to 0.40; the default value is 0.03. Manning's coefficient was not available for the site and was specified as the default value of 0.03 since the land was vegetated with trees and grass.

5.5 Execution Input File

Within SEVIEW the execution file is used to specify the number of years to be modeled by SESOIL. Years is the only parameter required and between 1 and 999 years can be specified. This value was varied and ranged from six to seven years in the calibration and verification processes and up to 50 years for the prediction process.

5.6 Application Input File

The application file contains information describing the amount of contaminant released or applied to the soil column. The application file also contains specifications regarding the dimensions of the soil column, the thickness of the soil layers, and the additional soil properties beyond those specified in the soil input file.

Application area is measured in cm^2 and is the aerial extent of contaminated soil in the SESOIL column. The application area was specified as 1.4×10^7 cm^2.

The latitude of the site in decimal degrees is used, along with the climate parameters of temperature, relative humidity, short wave albedo and percent cloud cover to calculate evapotranspiration. The latitude was determined and was specified as 47.50 degrees in the SESOIL model.

The spill index is unitless and indicates if a contaminant load is instantaneous or a continuous load over each month. The spill index was set to 1 to model an instantaneous spill occurring at the beginning of the month.

The layer thickness is measured in cm and is the thickness of the SESOIL layers. The number of sublayers in each SESOIL layer was also specified. Upper, second, third and lower layers with thickness' of 5, 5, 125 and 5 cm, respectively, were considered.

The number of sublayers can be set from 0 to 10. SESOIL divides each layer into the appropriate number of sublayers of equal thickness. Each sublayer will have the same properties of the layer in which it resides. In the model the number of sublayers was specified as zero.

5.7 Ratio parameters

Several ratio parameters are specified in the SESOIL model.

The pH of each layer can be specified. The pH parameter is only used if the hydrolysis algorithm is utilized. The pH values for the layers were set to 7 since the hydrolysis algorithm was not utilized.

The intrinsic permeability for each SESOIL layer can also be specified. The intrinsic permeability for individual soil layers was not specified and the intrinsic permeability was taken as the overall value specified.

Several ratio parameters are included in the SESOIL application file and include; ratio of liquid phase biodegradation to upper layer biodegradation; ratio of solid phase biodegradation to upper layer biodegradation; organic carbon ratio to upper layer organic carbon; cation exchange ratios to upper layer cation exchange; Freundlich exponent ratio to upper layer Freundlich; and, adsorption coefficient ratio to upper layer adsorption coefficient. For all model runs 1.0 was used for the layer ratios.

5.8 Soil Layer Input File

The soil layer values include the contaminant load, mass of contaminant transformed/removed, ligand load, volatilization/diffusion index, index of contaminant transport in surface runoff; and ratio of contaminant concentration in rainwater. These parameters are summarized in the following paragraphs.

The contaminant load (POLIN) is measured in $\mu g/cm^2/month$ and is a measure of the monthly contaminant load (mass per unit area) entering the top of each soil layer. The contaminant load is calculated using the following equation:

$$\text{POLIN} = \text{CONC} \times \text{D} \times \text{RS} \qquad \text{Equation 5.2}$$

Where:

POLIN = the contaminant load to apply in $\mu g/cm^2/month$
CONC = The concentration sorbed to the soil in $\mu g/g$
D = the thickness of the layer in centimeters to which the contaminant is applied
RS = The soil bulk density of the soil in g/cm^3

The POLIN values were based on the highest measured concentration of petroleum hydrocarbon present within the soil layer, the layer thickness and a soil bulk density of 2.2 g/cm^3. Contaminant loads of 2.1×10^4 $\mu g/cm^2/month$, 2.1×10^4 $\mu g/cm^2/month$, 1.7×10^7 $\mu g/cm^2/month$ and 5.3×10^5 $\mu g/cm^2/month$ were applied to soil layers 1, 2, 3 and 4; respectively.

The mass of contaminant transformed is measured in μg /cm^2/month and is a measure the monthly mass of contaminant removed from each layer by a process not otherwise included in SESOIL. The value was specified as zero.

The ligand load is measured in μg /cm^2/month and is the monthly ligand load input into each layer. The ligand load was specified as zero.

The volatilization is measured as a fraction and is the index of volatilization/diffusion upward from a soil layer. Values range from 0.0 to 1.0. A volatilization index of 0.0 means there would be no volatilization/diffusion upward from the soil layer. A volatilization index of 1.0 means 100 percent of the estimated volatilization/diffusion is modeled for the soil layer. The volatilization index was set to 1.0 for each soil layer.

The index for contaminant transport in surface runoff may range from 0.0 to 1.0. The index of contaminant transport in surface runoff was specified as 0.0.

The ratio of contaminant concentration in rain to water is measured as a fraction and is a measure of the contaminant load contained in the monthly precipitation. This value was specified as 0.0.

5.9 AT123 Aquifer Input File

The AT123D aquifer parameters describe the soil characteristics and aquifer geometry and this includes hydraulic conductivity, hydraulic gradient, effective porosity, soil bulk density, longitudinal, transverse and vertical dispersivities and aquifer width and depth. The input file also contains information on the number of eigenvalues and the model steady state tolerance factor.

Hydraulic Conductivity is measured in m/hour and is a measure of the horizontal hydraulic conductivity of the saturated porous medium. The hydraulic conductivity was based on the intrinsic permeability value in the SESOIL input file.

The hydraulic gradient is measured in meters/meter and is the slope of the potentiometric surface. In unconfined aquifers this is equivalent to the slope of the water table. It is assumed to be along the longitudinal direction. Typical values range from 0.0001 – 0.05 m/m. The hydraulic gradient of the site was not measured in the field and a range of values from 0.003 m/m to 0.04 m/m were considered.

As previously discussed the effective porosity is a dimensionless ratio of the volume of interconnected voids to the bulk volume of the aquifer matrix. Typical values are provided in Table 5.5 and Table 5.6.

The soil bulk density is measured in kilograms/m^3 and is the bulk density of the aquifer matrix. Typical values are provided in Table 5.7. The bulk density at the site was estimated to be 1690 kg/m^3 however a wide variation was present. As a result, a range of typical values were considered.

Table 5.7: Typical Values of Soil Bulk Density (Scheiker, 2000)

Soil Type	**Bulk density (kg/m^3)**
Clay	1400-2200
Silt	1290-1800
Sand	1180-1580

Longitudinal/Transverse/Vertical Dispersivity are measured in meters and are a measure of the process whereby the plume will spread out in a longitudinal direction (along the direction of groundwater flow), transversely (perpendicular to groundwater flow), and vertically downwards due to mechanical mixing in the aquifer and chemical diffusion.

Selection of dispersivity values is a difficult process, given the impracticability of measuring dispersion in the field. These values were estimated based on site characteristics. Methods to establish dispersivities in feet based on contaminant plume length (L_p) are presented below.

Longitudinal Dispersivity:

$$\alpha_L = 1.13 \times \{\log_{10}(L_p/3.28)\} \qquad \text{Equation 5.3}$$

(Scheiker, 2000)

Note L_p is in feet

Transverse Dispersivity

$$\alpha_T = 0.10\alpha_L \text{ (Scheiker, 2000)} \qquad \text{Equation 5.4}$$

Vertical Dispersivity

$$\alpha_v = \text{very low (i.e. } 1 \times 10^{-99} \text{ ft) Scheiker, 2000} \qquad \text{Equation 5.5}$$

Based on the above equations the values for longitudinal, transverse and vertical dispersivity were calculated and converted to meters. A range of values were considered for dispersivities.

The aquifer width is measured in meters and measures the width of the aquifer in the y-direction. The aquifer width was specified as infinite.

The aquifer depth is measured in meters and is a measure of the aquifer depth in the z-direction. The depth can also be set to an infinite value. In this model, however the aquifer depth was specified as 0.2 since the average depth to bedrock was 2.0 metres below the ground surface and the average depth to the groundwater table was 1.8 metres below the ground surface.

The number of eigenvalues establishes the maximum number of terms that will be calculated for a series solution before truncation occurs. The default value of 500 was specified.

Model error tolerance is the error tolerance if a steady state solution is desired. The default value is 0.001. The default value of 0.001 was specified.

5.9.1 AT123D Input File Parameters

The AT123D input parameters contains information describing the geometry of the source release and the contaminant properties. Input parameters include the starting and ending coordinates of the release, the chemical distribution coefficient, water diffusion coefficient and the first order decay coefficient.

Starting and ending coordinates of the source in the X/Y/Z-Directions are measured in meters and provide the starting and ending coordinates of the source in the x/y/z direction. The starting and ending coordinates of the source were specified as the SESOIL column.

The distribution coefficient, K_d, as previously discussed, is measured in meters^3/kilogram and is a chemical specific partition coefficient. The air diffusion coefficient for the chemical is calculated by multiplying the water diffusion coefficient by the tortuosity. The values were based on the SESOIL input file.

5.9.2 AT123D Output Parameters

The AT123 output parameters contain information that specified contaminant concentrations at specific times and coordinates. Output parameters include the starting and ending points in time and the size of the time step. The output parameters also include information on the coordinates where the concentration would be determined in the x,y and z directions. The starting time step is provided in months and is the first month for which a solution is desired. The ending time step is also provided in months and is the final month for which a solution is desired. The time step is measured in months and is the number of months between results presented in the AT123D output file. These values were based on the SESOIL input values in the execution file.

The X, Y and Z axis coordinates are measured in meters and are the coordinates in the x, y and z-direction (direction of flow) where the concentration is desired. The total distance in the x, y and z direction was set to be slightly larger than down gradient point of concern.

These coordinates were modified based on the desired output locations.

Chapter 6: Simulation Runs

Following site selection and the selection and development of the computer model the simulation analysis was completed. In the design process the model was calibrated, verified and predictions were made. In each step of this process a statistical analysis was carried out which included a sensitivity analysis, a determination of statistical significance and calculation of the confidence intervals.

6.1 Methodology

Based on the site characterization study three data sets are available for modeling. The first set of data from 1997 was used to establish the initial concentration of petroleum hydrocarbons in the soil. The second set of data from 2002 was used to calibrate the model and the third set of data from 2002 was used to verify the model.

The first step in experimentation is calibration. Calibration is the process of adjusting selected model parameters within an accepted range until the differences between model predictions and field observations are within selected criteria of performance.

A design of experiment (DOE) approach was used for the calibration exercise as opposed to varying various factors. DOE was chosen since it is a systematic approach that incorporates the use of statistics in the experimental design and calibration process.

The statistical design of experiments is defined as the:

"...process of planning the experiment so that the appropriate data will be collected which may be analyzed by statistical methods resulting in valid and objective conclusions." (Montgomery, 2001).

DOE incorporates a factorial approach to experimentation. The alternative to DOE is a one factor at a time approach. One factor at a time experiments are regarded as easier to implement, more easily understood and more economical than factorial experiments. These assumptions however are incorrect. As well, there are two other key reasons why one factor at a time experiments should not be conducted, firstly it does not provide adequate information on interactions and secondly it does not provide estimates of the effects of factors.

The first step in DOE is to define the objective of the experiment and to state the problem. The second step in DOE is to choose the factors involved and the levels over which the factors will be varied. The third step is to select the response variables and then an experiment design can be chosen. Following this step the experiment is performed and the data is analyzed.

In data analysis the following procedure is followed (Montgomery, 2001):

- the effects of the factors are estimated;
- the significance of the effects is determined through normal probability plots, the analysis of variance (ANOVA) and comparison to standard error;
- the residuals are analyzed to check for normality and equality of variance;
- prediction of response using model if all tests (i.e. normality and equality of variance) are okay;
- confirmation of model; and,
- interpretation of effects.

6.1.1 Two Factorial Approach

Factorial designs are widely used in experiments involving several factors. In a two factorial design k factors are varied over two levels only, a high value and a low value, and 2^k experiments are performed for the analysis (Montgomery, 2001). Say for example if four factors are studied then 2^4 or 16 experiments (or runs in a computer model) will be completed. All combinations of highs and lows are run.

To estimate the effect, the contrast associated with each effect must be calculated. The contrast is determined as follows:

$$Contrast_{AB} = (a \pm 1)(b \pm 1)....(k \pm 1)$$ Equation 6.1 (Montgomery, 2001)

When expanded the sign in each set of parentheses is negative if the factor is included in the effect and positive if the factor is not included. For example in a 2^3 factorial the contrast of factor AB (the interactive effect of A and B) would be:

$$Contrast_{AB} = (a-1)(b-1)(c+1) = abc + ab + c + (1) - ac - bc - a - b$$

Equation 6.2 (Montgomery, 2001)

Once the contrast for the effect has been determined the effect can be estimated as:

$$AB...K = \frac{2}{n2^k}(Constrast_{A,B,...K})$$ Equation 6.3 (Montgomery, 2001)

Where:

A,B,...K = Effect

k = Number of Factors

n = Number of Replications

6.1.2 Sensitivity Analysis and Statistical Analysis

The purpose of the sensitivity analysis is to examine how sensitive the output parameters (in this case the concentrations of petroleum hydrocarbons in the soil and groundwater) are to changes in various input parameters. Preliminary runs were made to narrow down the parameters considered since there were many variables. A DOE approach to calibration automatically incorporates a sensitivity analysis since the variables are changed over high and low values. However, less runs are required, as well the degree of sensitivity is quantified since the magnitude of the effect of each factor is provided. Lastly in DOE the statistical significance of the result is quantified.

The statistical significance of the effects includes which effects are most important and which effects can be dropped. Statistical or sensitivity analysis focuses on the relative impact each parameter or term has on the model output, in order to determine the effect of data quality on output reliability. Uncertainty analysis seeks to quantify the uncertainty in the model output as a function of uncertainty in both model input and model operations (Box et al., 1978).

Several statistical methods were included in the experimental design. The first method was based on the normal probability plot of the effects. When the effects are plotted on a normal probability plot effects that fall along a straight line are considered noise and outlying values are significant. The visual method is especially important when there is no replication, hence no pure error estimates, as is the case in computer modeling. In unreplicated design the effects that are not found to be significant can be used as a measure of error (Montgomery, 2001).

The second statistical method employed was an analysis of variance or an ANOVA. In the ANOVA approach a significance level of 5% was chosen. The sum of squares was calculated by:

$$SS_{AB...K} = \frac{1}{n2^k}(Contrast_{AB..K})^2$$ Equation 6.4 (Montgomery, 2001)

The mean square was calculated by:

$$MS_{AB...K} = \frac{SS_{AB...K}}{d.f.}$$ Equation 6.5 (Montgomery, 2001)

Where:

MS = Mean Square

SS = Sum of Squares

d.f. = degrees of freedom

The estimate of experimental error (SSE) was obtained by subtraction:

$$SSE = SST - Sum\ of\ SS\ of\ effects$$ Equation 6.6 (Montgomery, 2001)

and SST is calculated by:

$$SST = \sum\sum y_{ij}^2 - \frac{y^2}{n2^k}$$ Equation 6.7 (Montgomery, 2001)

Where:

y_{ij} = each value of treatment

y = overall total

With only a single replicate of the 2^k factorial it was not possible to determine the experimental error or the mean square error. In order to analyze the unreplicated design less significant factors (usually higher order interactions) were assumed to be negligible and combined to estimate experimental error (Box et al., 1978).

The standard error of effects was used as a guide or confidence interval with a 5% significance level. If the confidence interval includes zero the effect is not significant since they were no different than zero (Montgomery, 2001).

Based on the sum of squares and the mean square error the test statistic for each factor was determined by:

$$F_0 = \frac{MS_A}{MSE}$$ Equation 6.8 (Montgomery, 2001)

F_0 was then compared to the 5% F-table (See Appendix A) using one degree of freedom and $2^k(n-1)$ (in this analysis n was one).

From the initial model, regression equations were developed for prediction. Only significant effects were used. Once the regression had been completed the assumptions of the regression were checked, which were as follows (Box et al., 1978):

- Residuals must be normally distributed (Residual = observed value – predicted value)
- Check whether or not the residuals have a constant variance

6.2 Experimental Design

As previously stated the first step in the experiment was to establish the initial concentration of the soil. This was done using the initial data collected in 1997.

The second process involved model calibration. As previously stated, calibration is the process of adjusting selected model parameters within an accepted range until the differences between model predictions and field observations are within selected criteria of performance (Donnigan and Dean, 1985). Data from 2002 was used to calibrate the model. Only one set of data was available from 2002 to calibrate the model for concentrations of petroleum hydrocarbon concentrations in 2002. Two points were available from 2002 to calibrate the model for petroleum hydrocarbon concentrations in the groundwater. Insufficient data was available to further calibrate the model.

Based on a DOE approach the problem of calibration can be stated as the development of the required input values in order to achieve the required output. It is also desired that the calibration be carried out in a systematic manner so that the data can statistically analyzed. In order to facilitate the DOE approach the computer program, Stat Ease, was utilized.

A number of factors were considered over two levels, a low and high. By varying selected parameters their effect was estimated and this information was used to calibrate the model.

Initially all factors and their interactions were considered. As the data were analyzed the terms that were not significant were removed and the model was refined.

Three parameters were of interest in the model calibration. The first parameter required was the initial concentration in the soil, the second was the concentration in the soil in 2002. The final parameter of interest was the groundwater concentration in 2002. As previously discussed, the calibration of a soil and groundwater model can be a complex process. Given the nature of soil and the variability of the contaminant many unknowns existed in the model, which influenced the parameters of interest. A systematic and simplified approach was developed to obtain an appropriate model for the site. This approach was as follows:

- <u>Establish the initial concentration of petroleum hydrocarbons in the soil:</u> Preliminary runs were made to determine which values affected the initial soil concentrations. The effective porosity, bulk density, soil pore disconnectedness value, the fraction of organic carbon, and the Freundlich exponent for soil were varied in the SESOIL model. The climate file was varied, in addition to the chemical parameters such as water solubility, Koc, Henry's Law Constant, air diffusion coefficient and molecular weight. After setting the water solubility to a fixed value, the factors that had influenced the initial soil concentration were varied within a two factorial design framework. Once the desired value had been established the influencing parameters were fixed and considered constants for the remainder of the calibration process.

- <u>Establish the concentration of petroleum hydrocarbons in the soil in 2002</u>: In the next step of the calibration process the concentration of petroleum hydrocarbons in the soil in 2002 was established. Preliminary trial and error runs were made to determine which values influenced the soil concentration in 2002. Chemical parameters such as the air diffusion coefficient and Henry's Law constant were varied along with soil parameters such as bulk density, intrinsic permeability, soil pore disconnectedness index and porosity. Of the six proceeding factors, intrinsic permeability, soil pore disconnectedness and porosity were the most influential on the soil concentrations. This is in agreement with the SEVIEW manual and with other published work on calibrating SESOIL. These three parameters were then varied within a two factorial framework and the desired concentration was established. These parameters were then set as constants for the final step in the calibration process.

- Establish the groundwater concentration: In the final step of the calibration process input parameters in the AT123D input file were varied to establish the concentration in the groundwater in 2002. The parameters were varied within a two factorial design framework and included the hydraulic gradient, longitudinal dispersivity, transverse dispersivity and vertical dispersivity.

Following the calibration of the model, washload input parameters were varied since default values were assumed in the initial calibration exercise since field data was not available. In the sensitivity analysis the values for soil erodibility, soil loss ratio, contouring factor and Manning's n were varied individually to determine if any of the parameters affected the concentrations of petroleum hydrocarbons. The parameters were varied over three intervals, the minimum value, the default value and the maximum value.

Soil and groundwater petroleum hydrocarbon concentrations from 2003 were then used to verify the model.

Chapter 7: Results

Following the methodology specified in Chapter 6 the simulation results were obtained. The results are outlined in the following sections.

7.1 Calibration Results

In the first calibration exercise the initial concentration in the soil was established. Based on the field measurements the initial concentration required was approximately 55,000 mg/kg. Three parameters were considered; K_{oc}, the Freundlich Exponent and the fraction of organic carbon. A high and low value was selected for each parameter, and they are outlined in Table 7.1.

Table 7.1: Input Parameter Ranges: Initial Soil Concentration

Parameter	Low Value	High Values
K_{oc}	1100	2000
Freundlich Exponent	0.9	1.0
f_{oc}	1	3

In a two factorial design, with three factors, 2^3 (8) experimental runs were required. Summaries of the results of the model runs are outlined in Table 7.2.

Table 7.2: 2-Factorial Design – Initial Soil Concentration

Run	K_{oc}	Freundlich Exponent	f_{oc}	Initial Concentration in Soil
1	1100	0.9	1	7404
2	2000	0.9	3	40180
3	1100	1	3	11580
4	1100	0.9	3	22210
5	2000	1	3	21060
6	2000	0.9	1	13460
7	2000	1	1	7019
8	1100	1	1	3860

The percent contribution of each factor is summarized in Table 7.3.

Table 7.3: Percent Contribution of Factors to Initial Soil Concentration

Factor	**% Contribution**
K_{oc}	17.96
Freundlich Exponent	21.31
f_{oc}	60.74
K_{oc} - Freundlich Exponent	9.6×10^{-5}
K_{oc} - f_{oc}	7.0×10^{-5}
Freundlich Exponent - f_{oc}	8.5×10^{-5}
K_{oc} - Freundlich Exponent - f_{oc}	7.9×10^{-5}

The effect of each factor was plotted on a normal probability plot (See Figure 7.1), and based on visual observation the main factors were considered significant while the interactions were not considered.

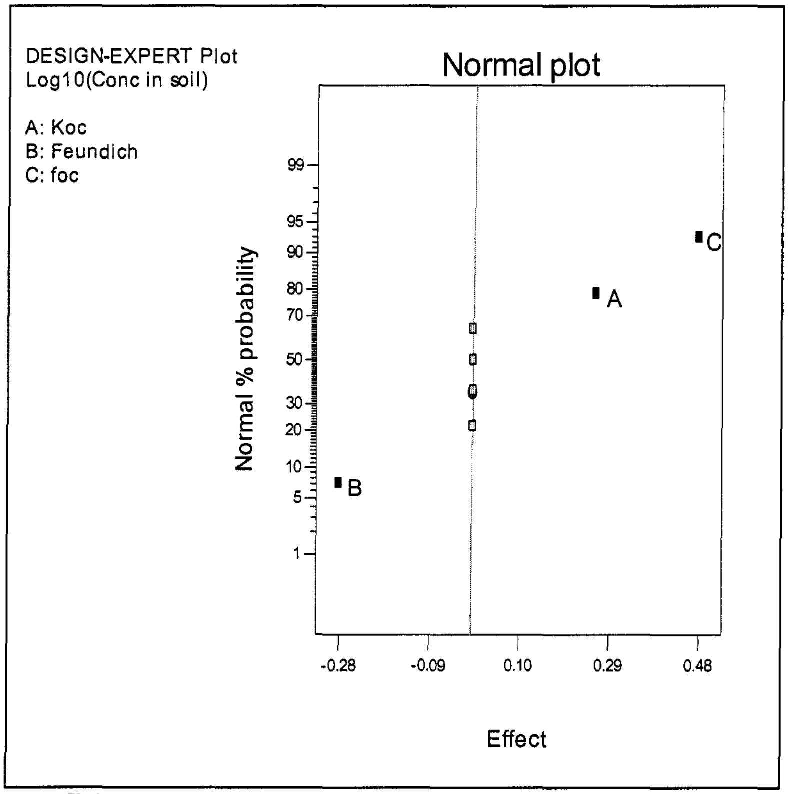

Figure 7.1: Normal Probability Plot of Initial Soil Concentration Effects

An ANOVA was then completed for initial soil concentration results, which confirmed the assumptions of the normal probability plot. The initial ANOVA results are presented in Table 7.4.

Table 7.4: ANOVA - Initial Soil Concentration

Source of Variation	Sum Squares	Degrees of Freedom	Mean Squares	F_0	p-value
K_{oc}	0.13	1	0.13	$2.3x10^5$	0.0013
Freundlich Exponent	0.16	1	0.16	$2.7x10^5$	0.0012
f_{oc}	0.45	1	0.45	$2.6x10^5$	0.0007
K_{oc} - Freundlich Exponent	$7.2x10^{-7}$	1	$7.2x10^{-7}$	1.21	0.4696
K_{oc} - f_{oc}	$5.3 \text{ x } 10^{-7}$	1	$5.3 \text{ x } 10^{-7}$	0.89	0.5186
Freundlich Exponent - f_{oc}	$6.4x10^{-7}$	1	$6.4x10^{-7}$	1.07	0.4888
K_{oc} - Freundlich Exponent - f_{oc}	$5.9x\ 10^{-7}$	1	5.9x 10-7		

The model was then refined to only include the significant terms. The refined ANOVA is summarized in Table 7.5:

Table 7.5: Refined ANOVA - Initial Soil Concentration

Source of Variation	Sum Squares	Degrees of Freedom	Mean Squares	F_0	p-value
K_{oc}	0.13	1	0.13	$4.0 \text{ X } 10^5$	<0.0001
Freundlich Exponent	0.16	1	0.16	$2.2 \text{ x } 10^5$	<0.0001
f_{oc}	0.45	1	0.45	$2.6 \text{ x } 10^5$	<0.0001
Residual	$2.5 \text{ x } 10^{-6}$	4	$6.2 \text{ x } 10^{-7}$		

The assumptions of the factorial design were then checked. The residuals plotted as a straight line on a normal plot (See Figure 7.2).

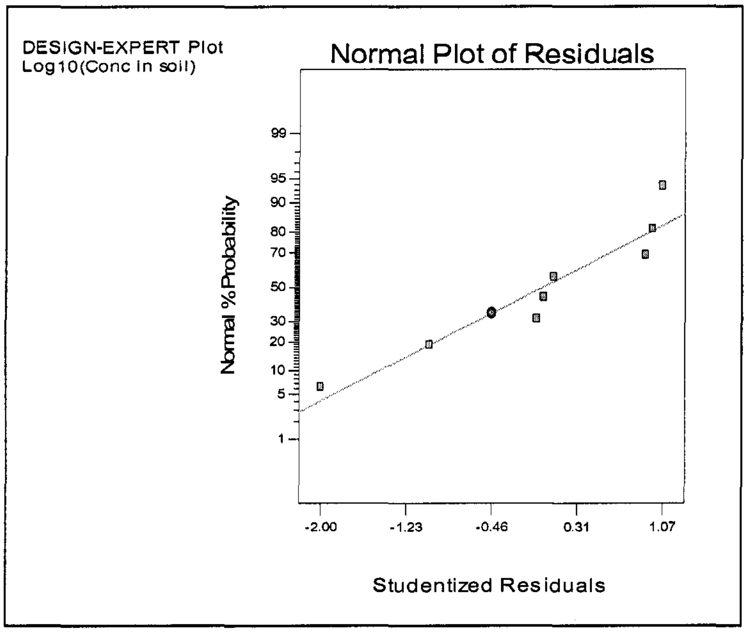

Figure 7.2: Initial Soil Concentration Residual Normal Probability Plot

Next the residuals were checked for constant variance. A plot was made for the residuals versus the variance (See Figure 7.3). A detailed sensitivity analysis is provided in Appendix C.

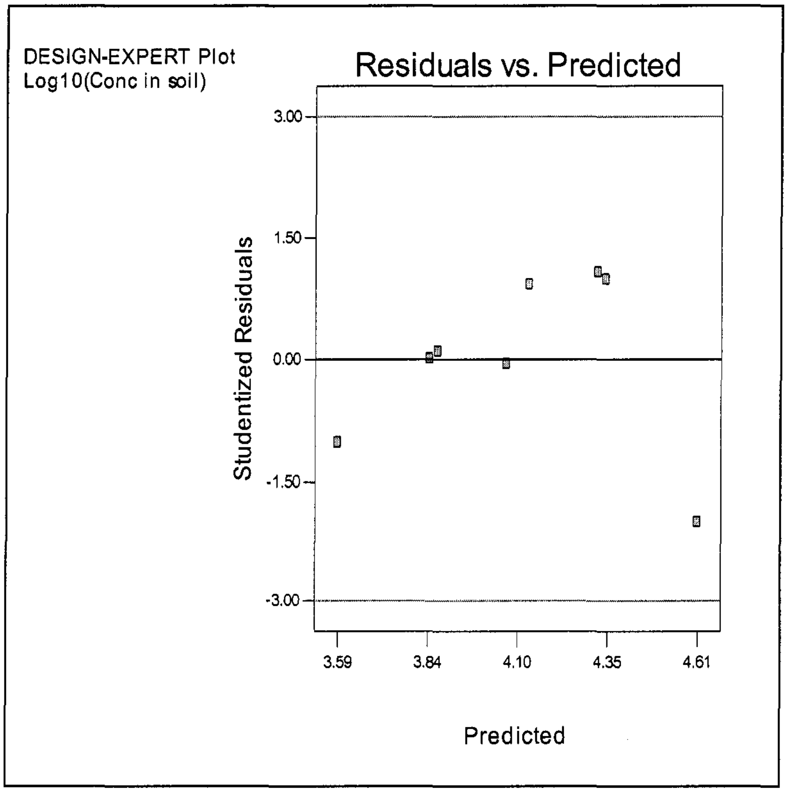

Figure 7.3: Initial Soil Concentration: Predicted vs Residuals

Based on the above results K_{oc} was set to 2000, the Freundlich Exponent was set to 0.9 and the f_{oc} was set to 3%. The resulting soil concentration was 40,180 mg/kg which is in reasonable agreement with the actual field conditions of 55,000 mg/kg. The output of the calibrated run is provided in Appendix B

In the second calibration exercise the final concentration in the soil was established. Based on the field measurements the final concentration required was approximately 11,000 mg/kg. Four parameters were considered; bulk density, intrinsic permeability, soil pore disconnectedness index and effective porosity. A high and low value was selected for each parameter, and they are outlined in Table 7.6.

Table 7.6: Input Parameter Ranges: Final Soil Concentration

Parameter	Low Value	High Values
Bulk Density	1.69	2.20
Intrinsic Permeability	4.3×10^{-9}	0.00001
Soil Pore Disconnectedness Index	3.7	12
Effective Porosity	0.20	0.30

In a two factorial design, with four factors, 2^4 (16) experimental runs were required. A summary of the results of the model runs is outlined in Table 7.7.

Table 7.7: 2-Factorial Design – Final Soil Concentration

Run	Bulk Density	Intrinsic Permeability	Soil Pore Disconnectedness Index	Effective Porosity	Final Concentration in Soil
1	1.69	4.3E-09	3.70	0.20	40380
2	2.20	0.00001	12.00	0.20	40380
3	2.20	4.3E-09	3.70	0.30	34040
4	2.20	0.00001	3.70	0.30	14440
5	1.69	4.3E-09	12.00	0.20	40380
6	1.69	0.00001	3.70	0.20	28010
7	1.69	0.00001	12.00	0.20	40380
8	2.20	4.3E-09	12.00	0.20	40380
9	2.20	0.00001	12.00	0.30	35840
10	1.69	0.00001	12.00	0.30	40380
11	1.69	0.00001	3.70	0.30	14480
12	2.20	4.3E-09	3.70	0.20	39560
13	1.69	4.3E-09	3.70	0.30	40380
14	1.69	4.3E-09	12.00	0.30	40380
15	2.20	4.3E-09	12.00	0.30	40380
16	2.20	0.00001	3.70	0.20	24070

The percent contribution of each factor is summarized in Table 7.8.

Table 7.8: Percent Contribution of Factors to Final Soil Concentration

Factor	% Contribution
Bulk Density	2.15
Intrinsic Permeability	30.84
Soil Pore Disconnectedness Index	36.97
Effective Porosity	3.78
Bulk Density - Intrinsic Permeability	1.413×10^{-3}
Bulk Density - Soil Pore Disconnectedness Index	0.24
Bulk Density - Effective Porosity	0.68
Intrinsic Permeability - Soil Pore Disconnectedness Index	20.93
Intrinsic Permeability - Effective Porosity	0.68
Soil Pore Disconnectedness Index - Effective Porosity	0.93
Bulk Density - Intrinsic Permeability - Soil Pore Disconnectedness Index	1.03
Bulk Density - Intrinsic Permeability - Effective Porosity	0.088
Bulk Density - Soil Pore Disconnectedness Index - Effective Porosity	0.23
Intrinsic Permeability - Soil Pore Disconnectedness Index - Effective Porosity	0.024
Bulk Density - Intrinsic Permeability - Soil Pore Disconnectedness Index - Effective Porosity	1.62

The effect of each factor was plotted on a normal probability plot (See Figure 7.4), and based on visual observation the intrinsic permeability, soil pore disconnectedness index, effective porosity and the interaction effect between intrinsic permeability and the soil pore disconnectedness were considered significant. The bulk density was not considered a significant factor (ie the soil concentration was not sensitivity to bulk density).

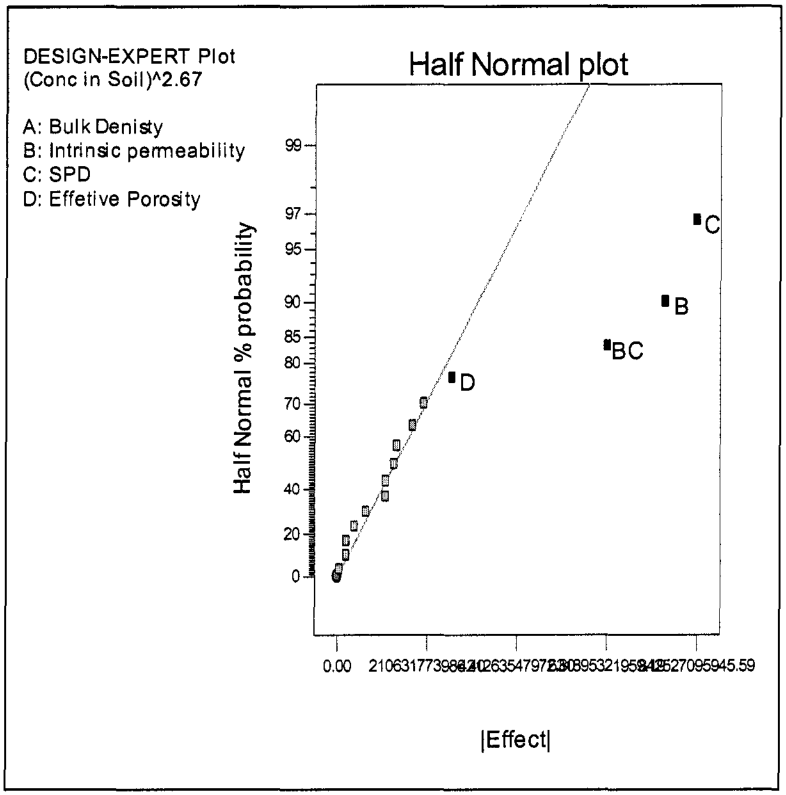

Figure 7.4: Normal Probability Plot of Final Soil Concentration Effects

An ANOVA was then completed for final soil concentration results, which confirmed the assumptions of the normal probability plot. The initial ANOVA results are presented in Table 7.9.

Table 7.9: ANOVA - Final Soil Concentration

Source of Variation	**Sum Squares**	**Degrees of Freedom**	**Mean Squares**	**F_0**	**p-value**
Bulk Density	1.653E+023	1	1.653E+023	3.86	0.1068
Intrinsic Permeability	2.369E+024	1	2.369E+024	55.26	0.0007
Soil Pore Disconnectedness Index	2.839E+024	1	2.839E+024	66.24	0.0005
Effective Porosity	2.906E+023	1	2.906E+023	6.78	0.0480
Bulk Density - Intrinsic Permeability	1.085E+020	1	1.085E+020	2.532E-003	0.9618
Bulk Density - Soil Pore Disconnectedness Index	1.836E+022	1	1.836E+022	0.43	0.5417
Bulk Density - Effective Porosity	5.245E+022	1	5.245E+022	1.22	0.3190
Intrinsic Permeability - Soil Pore Disconnectedness Index	1.608E+024	1	1.608E+024	37.51	0.0017
Intrinsic Permeability - Effective Porosity	5.200E+022	1	5.200E+022	1.21	0.3209
Soil Pore Disconnectedness Index - Effective Porosity	7.180E+022	1	7.180E+022	1.67	0.2521

The model was then refined to only include the significant terms. The refined ANOVA is summarized in Table 7.10.

Table 7.10: Refined ANOVA - Final Soil Concentration

Source of Variation	**Sum Squares**	**Degrees of Freedom**	**Mean Squares**	**F_0**	**p-value**
Intrinsic Permeability	2.369E+024	1	2.369E+024	45.37	< 0.0001
Soil Pore Disconnectedness Index	2.839E+024	1	2.839E+024	54.38	< 0.0001
Effective Porosity	2.906E+023	1	2.906E+023	5.57	0.0379
Intrinsic Permeability - Soil Pore Disconnectedness Index	1.608E+024	1	1.608E+024	30.79	0.0002
Residual	5.744E+023	11	5.222E+022		

The assumptions of the factorial design were then checked. The residuals plotted as a straight line on a normal plot (See Figure 7.5).

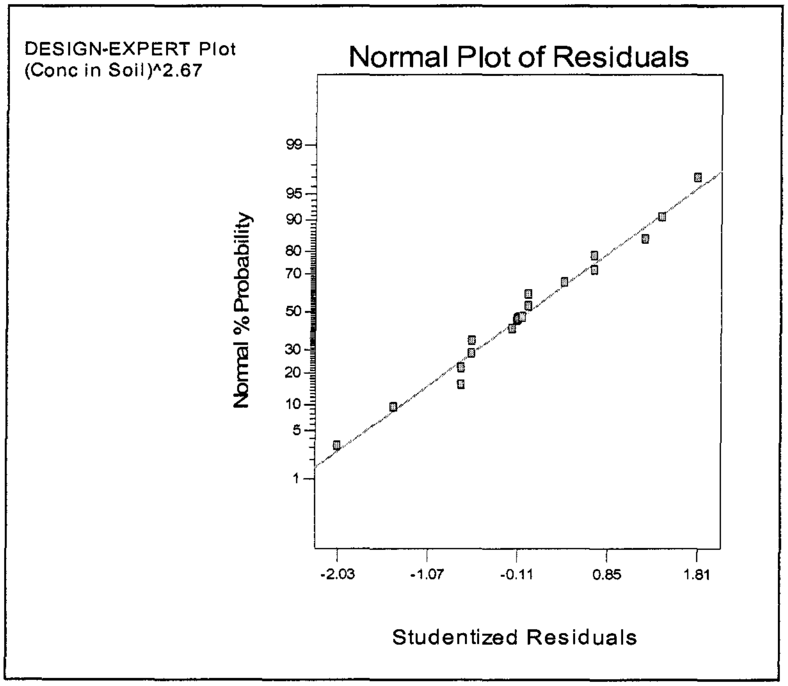

Figure 7.5: Final Soil Concentration Residual Normal Probability Plot

Next the residuals were checked for constant variance. A plot was made for the residuals versus the variance (See Figure 7.6).

A detailed sensitivity analysis is provided in Appendix E.

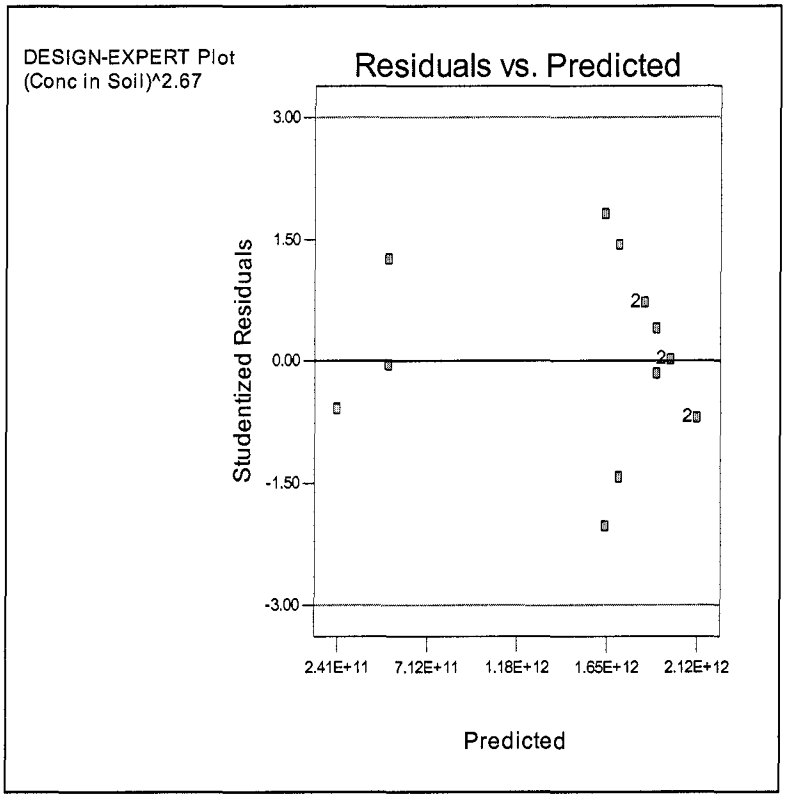

Figure 7.6: Final Soil Concentration: Predicted vs Residuals

Based on the above results bulk density was set to 2.20, intrinsic permeability was set to 0.00001, the soil pore disconnectedness index was set to 3.7 and the effective porosity was set to 0.30. The resulting soil concentration was 14,440 mg/kg which is in reasonable agreement with the actual field conditions of 11,000 mg/kg. The calibrated output run is provided in Appendix D.

In the final calibration exercise the groundwater concentration was established. Based on the field measurements the final concentration required was approximately 25.5 mg/L. Four parameters were considered; hydraulic gradient, longitudinal dispersivity, transverse dispersivity and vertical dispersivity. A high and low value was selected for each parameter, and they are outlined in Table 7.11.

Table 7.11: Input Parameter Ranges: Groundwater Concentration

Parameter	Low Value	High Values
Hydraulic Gradient	0.003	0.04
Longitudinal Dispersivity	2.00	10.0
Transverse Dispersivity	0.20	1.00
Vertical Dispersivity	0.05	0.24

In a two factorial design, with four factors, 2^4 (16) experimental runs were required. A summary of the results of the model runs is outlined in Table 7.12.

Table 7.12: 2-Factorial Design – Groundwater Concentration

Run	Hydraulic Gradient	Longitudinal Dispersivity	Transverse Dispersivity	Vertical Dispersivity	Groundwater Concentration
1	0.04	2.00	1.00	0.24	1.13
2	0.04	2.00	1.00	0.05	1.13
3	0.003	2.00	1.00	0.05	21.8
4	0.003	10.00	1.00	0.24	21
5	0.003	2.00	1.00	0.24	21.8
6	0.003	10.00	1.00	0.05	21
7	0.04	10.00	1.00	0.05	1.46
8	0.04	10.00	0.20	0.05	1.56
9	0.003	2.00	0.20	0.05	21.9
10	0.04	2.00	0.20	0.05	1.13
11	0.003	10.00	0.20	0.24	21.2
12	0.003	2.00	0.20	0.24	21.9
13	0.04	2.00	0.20	0.24	1.13
14	0.04	10.00	1.00	0.24	1.46
15	0.003	10.00	0.20	0.05	21.2
16	0.04	10.00	0.20	0.24	1.56

The percent contribution of each factor is summarized in Table 7.13.

Table 7.13: Percent Contribution of Factors to Groundwater Concentration

Factor	**% Contribution**
Hydraulic Gradient	99.86
Longitudinal Dispersivity	0.015
Transverse Dispersivity	2.746×10^{-3}
Vertical Dispersivity	0
Hydraulic Gradient - Longitudinal Dispersivity	0.12
Hydraulic Gradient - Transverse Dispersivity	3.47×10^{-5}
Hydraulic Gradient - Transverse Dispersivity	0
Longitudinal Dispersivity - Transverse Dispersivity	1.375×10^{-3}
Longitudinal Dispersivity - Transverse Dispersivity	0
Transverse Dispersivity - Transverse Dispersivity	0
Hydraulic Gradient - Longitudinal Dispersivity - Transverse Dispersivity	4.5×10^{-4}
Hydraulic Gradient - Longitudinal Dispersivity - Transverse Dispersivity	0
Hydraulic Gradient - Transverse Dispersivity - Transverse Dispersivity	0
Longitudinal Dispersivity - Transverse Dispersivity - Transverse Dispersivity	0
Hydraulic Gradient - Longitudinal Dispersivity - Transverse Dispersivity - Transverse Dispersivity	0

The effect of each factor was plotted on a normal probability plot (See Figure 7.7), and based on visual observation the hydraulic gradient and the transverse and longitudinal dispersivities (and the two and three level interactions of these factors) were considered significant. The hydraulic gradient however had the highest effect level, or in other words had the highest sensitivity. The vertical dispersivity and its interactions were not considered significant factors (ie the groundwater concentration was not sensitive to vertical dispersivities).

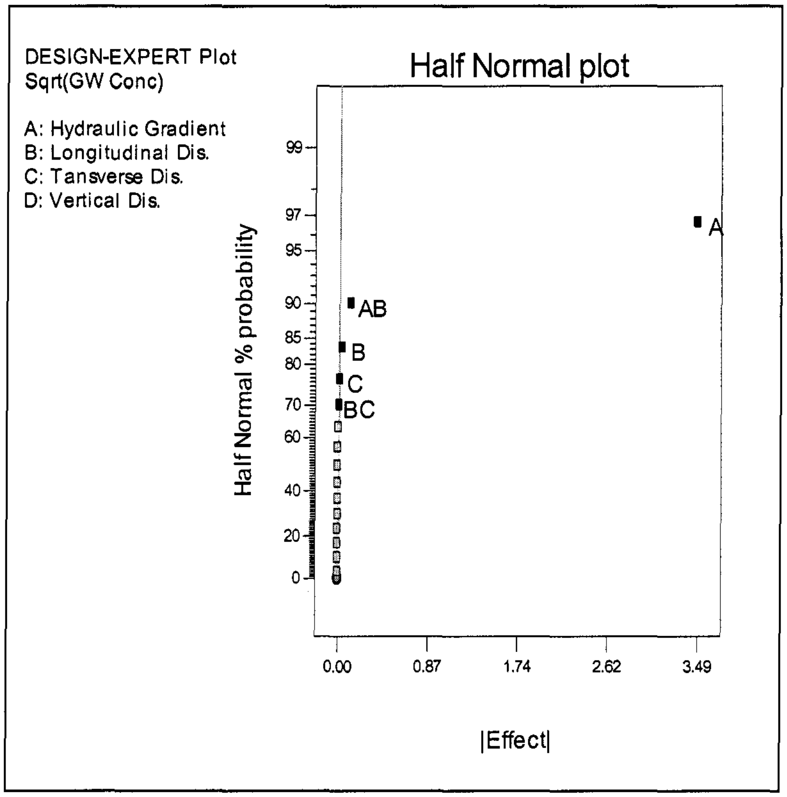

Figure 7.7: Normal Probability Plot of Groundwater Concentration Effects

An ANOVA was then completed for groundwater concentration results, which confirmed the assumptions of the normal probability plot. The initial ANOVA results are presented in Table 7.14.

Table 7.14: ANOVA - Groundwater Concentration

Source of Variation	**Sum Squares**	**Degrees of Freedom**	**Mean Squares**	**F_0**	**p-value**
Hydraulic Gradient	48.67	1	48.67	6.366E+007	< 0.0001
Longitudinal Dispersivity	7.175E-003	1	7.175E-003	6.366E+007	< 0.0001
Transverse Dispersivity	1.338E-003	1	1.338E-003	6.366E+007	< 0.0001
Vertical Dispersivity	0.000	1	0.000	-	-
Hydraulic Gradient - Longitudinal Dispersivity	0.061	1	0.061	6.366E+007	< 0.0001
Hydraulic Gradient - Transverse Dispersivity	1.693E-005	1	1.693E-005	6.366E+007	< 0.0001
Hydraulic Gradient - Vertical Dispersivity	0.000	1	0.000	-	-
Longitudinal Dispersivity - Transverse Dispersivity	6.700E-004	1	6.700E-004	6.366E+007	< 0.0001
Longitudinal Dispersivity - Vertical Dispersivity	0.000	1	0.000	-	-
Transverse Dispersivity - Vertical Dispersivity	0.000	1	0.000	-	-
Hydraulic Gradient - Longitudinal Dispersivity - Transverse Dispersivity	2.194E-004	1	2.194E-004	6.366E+007	< 0.0001
Hydraulic Gradient - Longitudinal Dispersivity - Vertical Dispersivity	0.000	1	0.000	-	-
Hydraulic Gradient - Transverse Dispersivity - Vertical Dispersivity	0.000	1	0.000	-	-
Longitudinal Dispersivity - Transverse Dispersivity - Vertical Dispersivity	0.000	1	0.000	-	-

The model was then refined to only include the significant terms. The refined ANOVA is summarized in Table 7.15.

Table 7.15: Refined ANOVA - Final Soil Concentration

Source of Variation	**Sum Squares**	**Degrees of Freedom**	**Mean Squares**	**F_0**	**p-value**
Hydraulic Gradient	48.67	1	48.67	6.366E+007	< 0.0001
Longitudinal Dispersivity	7.175E-003	1	7.175E-003	6.366E+007	< 0.0001
Transverse Dispersivity	1.338E-003	1	1.338E-003	6.366E+007	< 0.0001
Hydraulic Gradient - Longitudinal Dispersivity	0.061	1	0.061	6.366E+007	< 0.0001
Hydraulic Gradient - Transverse Dispersivity	1.693E-005	1	1.693E-005	6.366E+007	< 0.0001
Longitudinal Dispersivity - Transverse Dispersivity	6.700E-004	1	6.700E-004	6.366E+007	< 0.0001
Hydraulic Gradient - Longitudinal Dispersivity - Transverse Dispersivity	2.194E-004	1	2.194E-004	6.366E+007	< 0.0001

The assumptions of the factorial design were then checked. The residuals plotted as a straight line on a normal plot (See Figure 7.8).

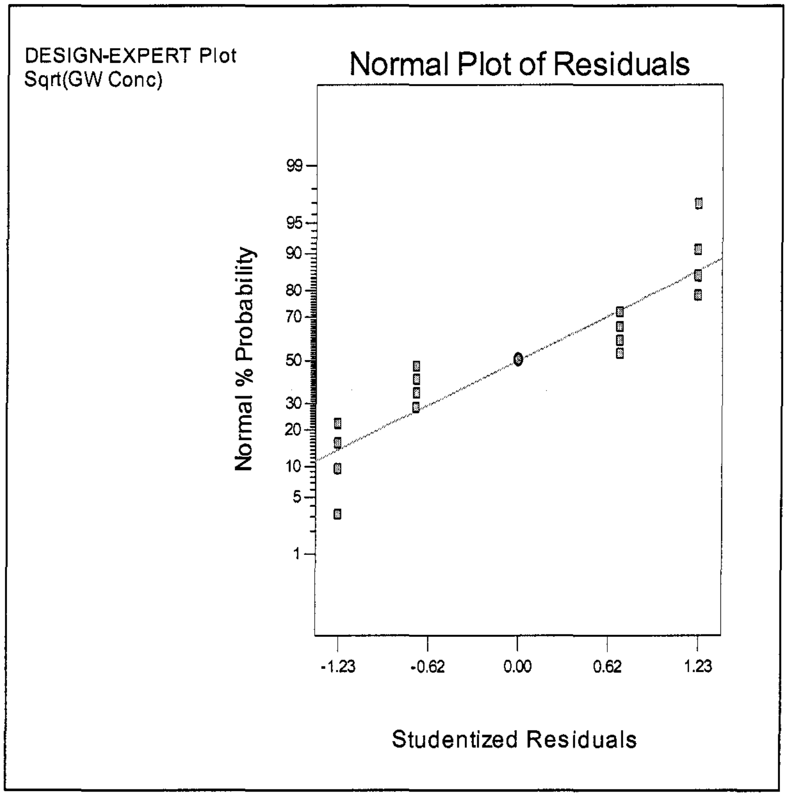

Figure 7.8: Groundwater Concentration Residual Normal Probability Plot

Next the residuals were checked for constant variance. A plot was made for the residuals versus the variance (See Figure 7.9).

A detailed sensitivity analysis is provided in Appendix G.

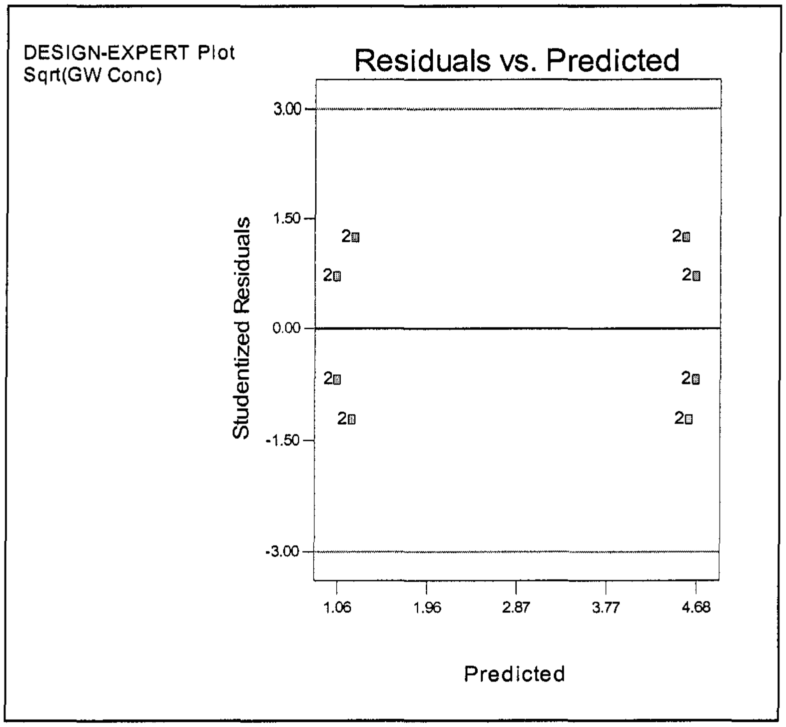

Figure 7.9: Groundwater Concentration: Predicted vs Residuals

Based on the above results hydraulic gradient was set to 0.003, longitudinal dispersivity was set to 2.0, transverse dispersivity was set to 0.20 and vertical dispersivity was set to 0.24. The resulting groundwater concentration was 39.7 mg/L and 29.8 mg/L in B-BH1 and B-MW10, which is in reasonable agreement with the actually field conditions of 52.8 mg/L and 25.5 mg/L. The calibrated output run is provided in Appendix F.

As previously discussed, following the calibration of the model, washload input parameters were varied since default values were assumed in the initial calibration exercise since field data was not available. The parameters were varied over three intervals, the minimum value, the default value and the maximum value. The washload file input parameters however did not have any significant effect on the initial concentration of petroleum hydrocarbon in the soil, the final concentration of petroleum hydrocarbon in the soil and the final concentration of petroleum hydrocarbon in groundwater.

7.2 Verification Results

Verification establishes that results from each of the algorithms of the model are correct and compares measured with predicted results. It includes analysis of the theoretical foundations of the model, focusing on the model's performance in simulating actual behavior of the chemical in the environment under study.

The final concentration was verified by soil concentration measurements from 2003. The final model parameters chosen were inputted and a simulation period of seven years was selected. The soil concentration after seven years was estimated as 11,410 mg/kg (Appendix H). The actual soil concentration measured in the field was 7207 mg/kg. The relative percent difference between the field measurements and the predicted value was 58%.

Given the variable nature of the soil and the contaminant being considered this is an acceptable level of agreement. As well, although there was only one set of data available, in this particular instance the model did overestimate the actual concentrations of hydrocarbons in the soil, as opposed to under estimating the concentration.

As determined in the calibration exercise the final concentration will be sensitive to the parameters chosen. These values include; K_{oc}, f_{oc}, and the Freundlich Exponent; and, soil parameters such as the intrinsic permeability, the soil pore disconnectedness index and effective porosity.

7.3 Prediction Results

Once the model had been calibrated and the model had been verified the results were applied to predict contaminant behaviour on the subject site. First, the model was used to predict the time required for the concentration of petroleum hydrocarbons to be naturally attenuated to acceptable levels. Next the model was used to predict when concentrations of petroleum hydrocarbons in the groundwater would reach the downstream receptor (located approximately 70 metres down gradient), and the concentration of petroleum hydrocarbons present.

7.3.1 Soil

The acceptable level of petroleum hydrocarbons on the subject site was based on the Canadian Council of Ministers of the Environment (CCME) soil quality guidelines (2001) for the protection of human health and the environment. The site is not considered sensitive since the site was commercial and there were no residential properties in the surrounding area. A summary of the SESOIL run is provided in Appendix H. The results are plotted in Figure 7.10.

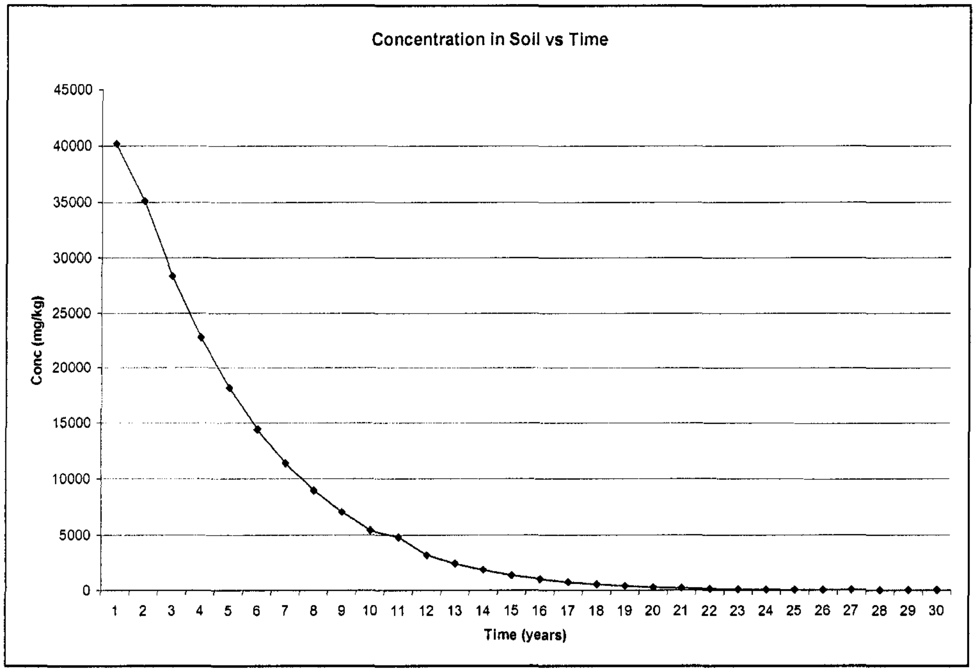

Figure 7.10: Concentration in Soil vs Time

As shown in Figure 7.1, the model predicts that concentration of petroleum hydrocarbons in the soil will be within regulatory guidelines (1000 mg/kg) in between 16 and 17 years. Again, for this site, based on the data set available, the model is conservative and the actual time to reach regulatory values may be shorter. The model also predicts that the concentration of petroleum concentrations will be entirely naturally attenuated within approximately 30 years.

7.3.2 Groundwater

Following the prediction of the concentration of petroleum hydrocarbons in the soil the model was used to predict the fate and transport of petroleum hydrocarbons in the groundwater. The model was used to determine if and when petroleum hydrocarbons would reach a downstream receptor and the concentration of petroleum hydrocarbons present at the downstream receptor. Based on the AT123D model run (See Appendix J), the petroleum hydrocarbon plume moves down gradient over time. The petroleum hydrocarbons reach the stream located 80 metres downstream after a four-year period, at a low concentration of 1.02 x 10^{-5} mg/L. The concentration of petroleum hydrocarbons increases to a maximum of 39.6 mg/L at year 15. The concentration then steadily declines. The results of the groundwater modeling are summarized in Figure 7.11.

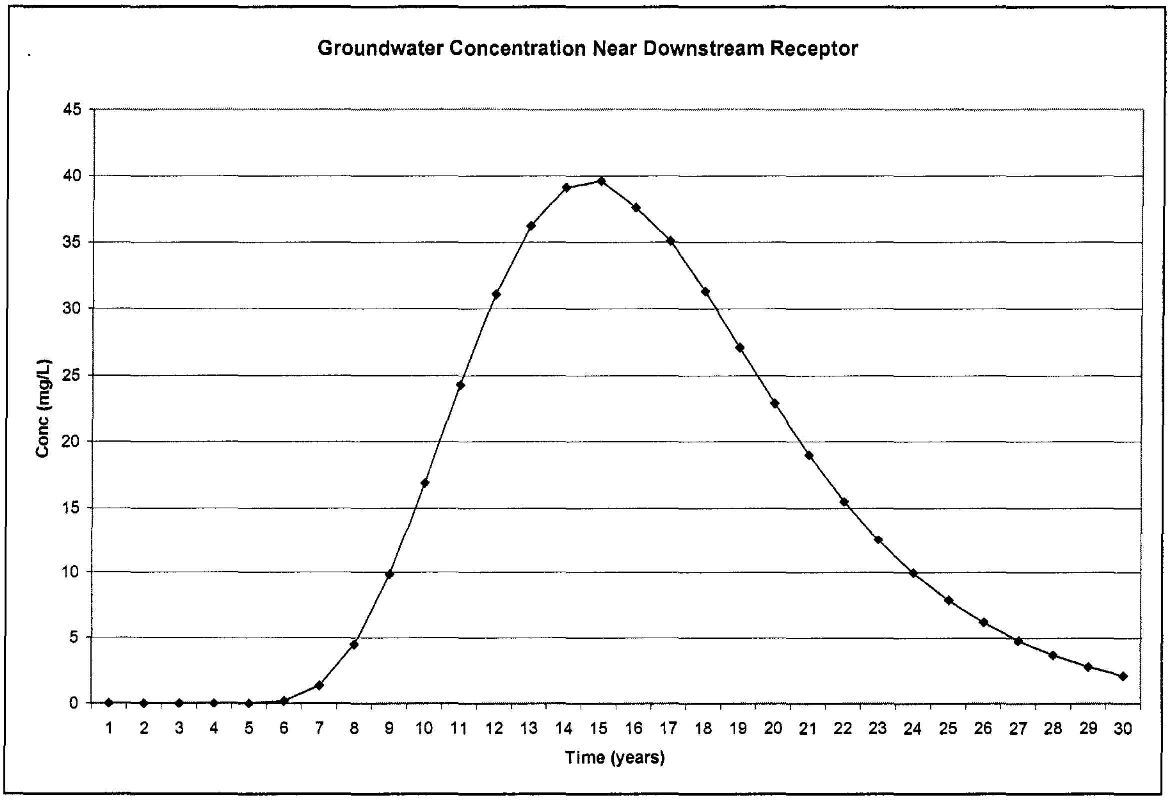

Figure 7.11: Groundwater Concentration Near Downstream Receptor

Chapter 8: Conclusions

Based on the modeling exercises conducted the following conclusions were derived:

1. The results of the model calibration and verification exercise have demonstrated that the model can be calibrated to reproduce the field measurements. During the calibration exercise the initial concentration measured in the field was 55,000 mg/kg while the results of the computer model indicted an initial soil concentration of 40,180 mg/kg. This represents a relative percent difference of approximately 27%.

2. The soil concentration after six years was measured in the field as 11,000 mg/kg. After six years, the computer model predicted the concentration of petroleum hydrocarbons in the soil as 14,440 mg/kg. This represented a relative percent difference of approximately 31%.

3. The concentration of petroleum hydrocarbons in the groundwater was measured in the field as 52.8 mg/L in B-BH1 and 25.5 mg/L in B-MW10. After six years the computer model predicted the concentration of petroleum hydrocarbons in the groundwater as 39.7 mg/L and 29.8 mg/L in B-BH1 and B-MW10; respectively. This represented an average relative percent difference of approximately 20%.

4. In the verification exercise the model estimated that the concentration of petroleum hydrocarbons in the soil was 11,410 mg/kg while the actual field measurement was 7207 mg/kg. This represented a relative percent difference of approximately 58%.

5. The sensitivity analysis was completed in conjunction with the calibration exercise. Preliminary runs indicated that the initial soil concentration established was not sensitive to effective porosity, bulk density, soil pore disconnectedness values, climate variations and to the chemical parameters such as Henry's Law Constant, air diffusion coefficient and molecular weight. The initial concentration of petroleum hydrocarbons in the soil was, however, sensitive to K_{oc}, f_{oc} and the Freundlich exponent. The model was found to have the highest sensitivity to f_{oc}, followed by the Freundlich exponent and K_{oc}. As previously discussed, following the calibration of the model, washload input parameters were varied since default values were assumed in the initial calibration exercise since field data was not available. In a follow-up sensitivity analysis the values for soil erodibility, soil loss ratio, contouring factor and Manning's n did not have any significant effect on the initial concentration of petroleum hydrocarbon in the soil, the final concentration of petroleum hydrocarbon in the soil and the final concentration of petroleum hydrocarbon in groundwater.

6. For the final concentration of petroleum hydrocarbons in the soil, preliminary runs indicated that chemical parameters such as the air diffusion coefficient and Henry's Law constant did not influence the final concentration of petroleum hydrocarbons in the soil. A sensitivity analysis of soil parameters such as bulk density, intrinsic permeability, soil pore disconnectedness index and porosity indicated that, while the concentration of petroleum hydrocarbons was not sensitive to bulk density, the concentration was sensitive to intrinsic permeability, soil pore disconnectedness and porosity. The model was most sensitive to the soil pore disconnectedness index and the intrinsic permeability and the interaction between these two parameters. The model was also sensitive to the effective porosity, but to a much lesser extent.

7. The sensitivity analysis indicated that the hydraulic gradient, longitudinal dispersivity and transverse dispersivity influenced the concentration of petroleum hydrocarbons in groundwater. However, the model was not sensitive to vertical dispersivity. Due to the shallow water table vertical dispersivity did not influence the concentrations of petroleum hydrocarbons in groundwater. The hydraulic gradient had the greatest influence on the concentration of petroleum hydrocarbons in groundwater. The model was sensitive to longitudinal and transverse dispersivities, but to a much lesser extent.

8. Following the calibration and verification exercises the model was used to predict the future fate and transport of petroleum hydrocarbons in the soil and groundwater. The model predicts that the concentration of petroleum hydrocarbons in the soil will be within regulatory guidelines between 16 and 17 years. The actual time to reach regulatory values could be shorter since the model was conservative and over estimated the actual concentration of petroleum hydrocarbons in the soil. The model also predicted that the concentration of petroleum concentrations would be entirely naturally attenuated within approximately 30 years.

9. The presence of an ecological receptor, located down gradient, was of significant interest when determining the fate and transport of petroleum hydrocarbons in the groundwater. Based on the AT123D model run the petroleum hydrocarbon plume reached the stream, located 80 metres down gradient, after a four-year period, at a low concentration of 1.02×10^{-5} mg/L. The concentration of petroleum hydrocarbons increased to a maximum of 39.6 mg/L at year 15. The concentration then steadily declined. Based on a regulatory guideline of 20 mg/L (Atlantic PIRI, 2002), the stream would be potentially impacted from year 10 to year 20.

10. The results of the model calibration and verification exercise have demonstrated that the model can be calibrated to reproduce the field measurements. The differences in the actual versus the predicted values were well within acceptable limits.

Based on the above conclusion the following items are recommended for the subject site:

- Based on the modeling of the petroleum hydrocarbons in the soil the priority of the site would be considered low. There was no immediate risk to human and other receptors, no buildings were present on site and the impacted soil was below the surface. The soil would be naturally attenuated to regulatory guidelines between 16 and 17 years and within 30 years the petroleum hydrocarbons would be entirely naturally attenuated.

- In terms of the fate and transport of petroleum hydrocarbons in the groundwater, based on the model predictions, the groundwater concentrations would not reach regulatory guidelines through natural attenuation alone. However, it should be noted that the petroleum hydrocarbons did not pose an immediate threat since the groundwater was not potable and the nearest ecological receptor was located 80 metres down gradient. As the stream would not be impacted until year ten the site could be given a medium priority. Within ten years a remedial strategy should be developed and during this period the groundwater should be monitored.

- Using the natural attenuation model as a foundation, additional modeling could be carried out to determine the most appropriate remedial strategy for the site which might include technologies such as bioventing and air stripping.

As well the following recommendations should be incorporated into future modeling exercises for other sites:

- Based on the findings of the modeling exercise the SEVIEW soil can be used with confidence in Newfoundland to model contaminated sites. Three data sets are recommended for calibration of verification, however two data sets would be sufficient for modeling purposes.

- In future site characterization work additional soil data should be collected for future use in a risk-assessment process; such data should include the fraction of organic carbon; grain size analysis; soil bulk density; and, the contaminant properties.

- A design of experiments methodology should be applied to determine the influence of various unknowns and to set their values in the calibration exercise. This methodology will also allow the modeler to perform a sensitivity analysis.

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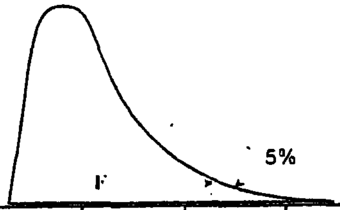
APPENDIX A
5% F-TABLE

F-Table for 5%

Percentage points of the F-distribution: upper 5% points



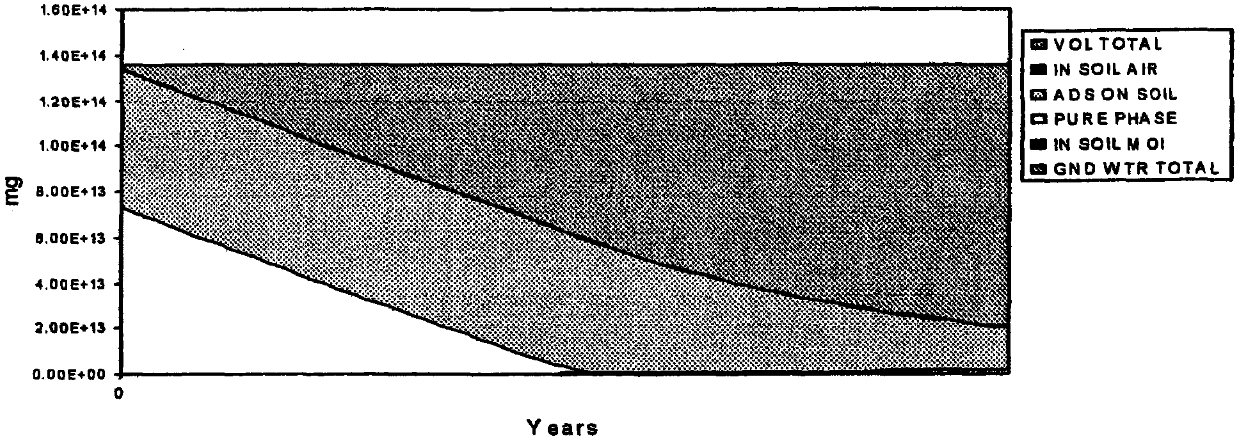
df_{num} df_{den}	1	2	3	4	5	6	7	8	9	10	15	20
1	161.45	199.50	215.71	224.58	230.16	233.99	236.77	238.88	240.54	241.88	245.95	248.01
2	18.513	19.000	19.164	19.247	19.296	19.330	19.353	19.371	19.385	19.396	19.429	19.446
3	10.128	9.552	9.277	9.117	9.013	8.941	8.887	8.845	8.812	8.786	8.703	8.660
4	7.709	6.944	6.591	6.388	6.256	6.163	6.094	6.041	5.999	5.964	5.858	5.803
5	6.608	5.786	5.409	5.192	5.050	4.950	4.876	4.818	4.772	4.735	4.619	4.558
6	5.987	5.143	4.757	4.534	4.387	4.284	4.207	4.147	4.099	4.060	3.938	3.874
7	5.591	4.737	4.347	4.120	3.972	3.866	3.787	3.726	3.677	3.637	3.511	3.445
8	5.318	4.459	4.066	3.838	3.687	3.581	3.500	3.438	3.388	3.347	3.218	3.150
9	5.117	4.256	3.863	3.633	3.482	3.374	3.293	3.230	3.179	3.137	3.006	2.936
10	4.965	4.103	3.708	3.478	3.326	3.217	3.135	3.072	3.020	2.978	2.845	2.774
11	4.844	3.982	3.587	3.357	3.204	3.095	3.012	2.948	2.896	2.854	2.719	2.646
12	4.747	3.885	3.490	3.259	3.106	2.996	2.913	2.849	2.796	2.753	2.617	2.544
13	4.667	3.806	3.411	3.179	3.025	2.915	2.832	2.767	2.714	2.671	2.533	2.459
14	4.600	3.739	3.344	3.112	2.958	2.848	2.764	2.699	2.646	2.602	2.463	2.388
15	4.543	3.682	3.287	3.056	2.901	2.790	2.707	2.641	2.588	2.544	2.403	2.328
16	4.494	3.634	3.239	3.007	2.852	2.741	2.657	2.591	2.538	2.494	2.352	2.276
17	4.451	3.592	3.197	2.965	2.810	2.699	2.614	2.548	2.494	2.450	2.308	2.230
18	4.414	3.555	3.160	2.928	2.773	2.661	2.577	2.510	2.456	2.412	2.269	2.191
19	4.381	3.522	3.127	2.895	2.740	2.628	2.544	2.477	2.423	2.378	2.234	2.155
20	4.351	3.493	3.098	2.866	2.711	2.599	2.514	2.447	2.393	2.348	2.203	2.124
21	4.325	3.467	3.072	2.840	2.685	2.573	2.488	2.420	2.366	2.321	2.176	2.096
22	4.301	3.443	3.049	2.817	2.661	2.549	2.464	2.397	2.342	2.297	2.151	2.071
23	4.279	3.422	3.028	2.796	2.640	2.528	2.442	2.375	2.320	2.275	2.128	2.048
24	4.260	3.403	3.009	2.776	2.621	2.508	2.423	2.355	2.300	2.255	2.108	2.027
25	4.242	3.385	2.991	2.759	2.603	2.490	2.405	2.337	2.282	2.236	2.089	2.007
26	4.225	3.369	2.975	2.743	2.587	2.474	2.388	2.321	2.265	2.220	2.072	1.990
27	4.210	3.354	2.960	2.728	2.572	2.459	2.373	2.305	2.250	2.204	2.056	1.974
28	4.196	3.340	2.947	2.714	2.558	2.445	2.359	2.291	2.236	2.190	2.041	1.959
29	4.183	3.328	2.934	2.701	2.545	2.432	2.346	2.278	2.223	2.177	2.027	1.945
30	4.171	3.316	2.922	2.690	2.534	2.421	2.334	2.266	2.211	2.165	2.015	1.932
40	4.085	3.232	2.839	2.606	2.449	2.336	2.249	2.180	2.124	2.077	1.924	1.839
60	4.001	3.150	2.758	2.525	2.368	2.254	2.167	2.097	2.040	1.993	1.836	1.748
120	3.920	3.072	2.680	2.447	2.290	2.175	2.087	2.016	1.959	1.910	1.750	1.659
100K	3.842	2.996	2.605	2.372	2.214	2.099	2.010	1.939	1.880	1.831	1.666	1.571

K (Multiply this value by 1000)

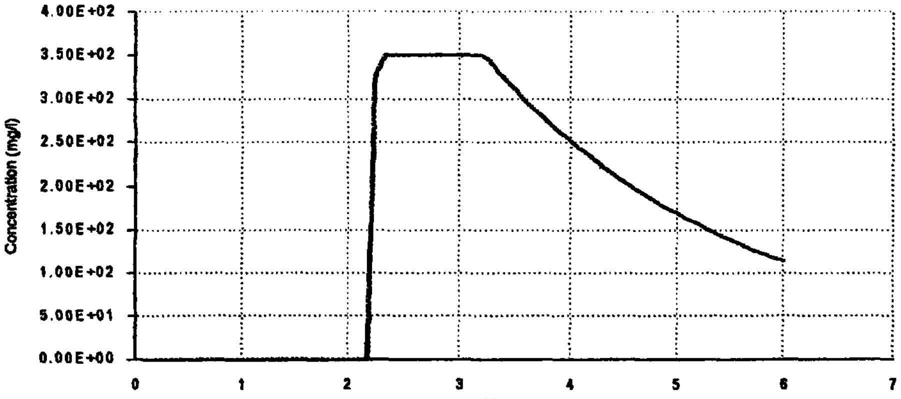
APPENDIX B
CALIBRATION RUNS FOR INITIAL SOIL CONCENTRATION

SESOIL Pollutant Fate Cycle Report for C10-C21 #2 Fuel Oil

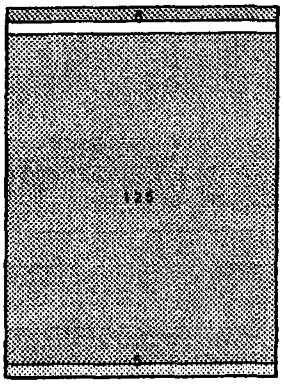
SESOIL Mass Fate



Leachate Concentration



SESOIL Profile (cm)

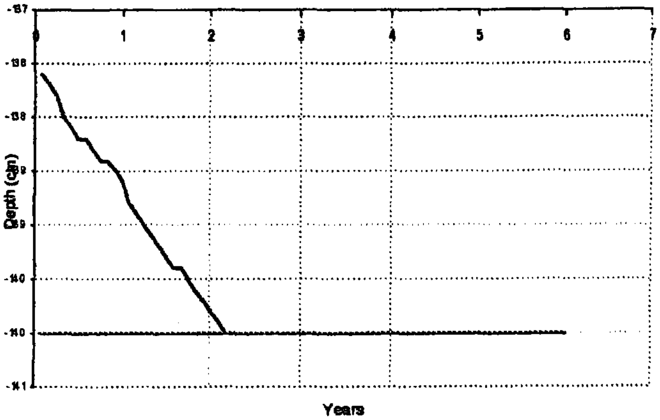


SESOIL Process	Pollutant Mass µg	Percent Input
Volatilized	1.149E+14	84.69
Soil Air	1.481E+11	0.10
Sur. Runoff	0.000E-01	0.00
In Washld	0.000E-01	0.00
Ads On Soil	1.918E+13	14.13
Hydrol Soil	0.000E-01	0.00
Degrad Soil	0.000E-01	0.00
Pure Phase	0.000E-01	0.00
Complexed	0.000E-01	0.00
Immobile CEC	0.000E-01	0.00
Hydrol CEC	0.000E-01	0.00
In Soil Moi	1.724E+09	0.00
Hydrol Mois	0.000E-01	0.00
Degrad Mois	0.000E-01	0.00
Other Trans	0.000E-01	0.00
Other Sinks	0.000E-01	0.00
Gwr. Runoff	1.400E+12	1.03
Total Output	1.356E+14	99.97
Total Input	1.357E+14	
Input - Output	2.773E+10	

Maximum leachate concentration: 3.509E+02 mg/l

Climate: ST. JOHN'S, NL
Chemical: C10-C21 #2 Fuel Oil
Soil: Silty Sand and Gravel
Application: MFA BH1

Starting Depth (cm): 137.60 **Ending Depth (cm):** 140.00
Total Depth (cm): 140.00



C:\SEVIEW\SJMFTA.CLM
C:\SEVIEW\soil1-2.CHM
C:\SEVIEW\soil1-2.SOI
C:\SEVIEW\BASE2.APL
C:\SEVIEW\SITEWASH.WSH
C:\SEVIEW\SOIL1-2.OUT

APPENDIX C
SENSITIVITY ANALYSIS FOR INITIAL SOIL CONCENTRATIONS

Use your mouse to right click on individual cells for definitions.

Response: Conc in soil Transform: Base 10 log Constant: 0

ANOVA for Selected Factorial Model

Analysis of variance table [Partial sum of squares]

Source		**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
Model		0.75	3	0.25	4.025E+005	< 0.0001	significant
	A	*0.13*	*1*	*0.13*	*2.168E+005*	*< 0.0001*	
	B	*0.16*	*1*	*0.16*	*2.573E+005*	*< 0.0001*	
	C	*0.45*	*1*	*0.45*	*7.335E+005*	*< 0.0001*	
Residual		2.477E-006	4	6.193E-007			
Cor Total		0.75	7				

The Model F-value of 402540.62 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, C are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	7.870E-004	R-Squared	1.0000
Mean	4.10	Adj R-Squared	1.0000
C.V.	0.019	Pred R-Square	1.0000
PRESS	9.909E-006	Adeq Precisior	1829.333

The "Pred R-Squared" of 1.0000 is in reasonable agreement with the "Adj R-Squared" of 1.0000.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 1829.333 indicates an adequate signal. This model can be used to navigate the design space.

Factor	**Coefficient Estimate**	**DF**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	4.10	1	2.782E-004	4.10	4.10	
A-Koc	0.13	1	2.782E-004	0.13	0.13	1.00
B-Feundich	-0.14	1	2.782E-004	-0.14	-0.14	1.00
C-foc	0.24	1	2.782E-004	0.24	0.24	1.00

Final Equation in Terms of Coded Factors:

Log_{10}(Conc in soil) =
+4.10
+0.13 * A
-0.14 * B
+0.24 * C

Final Equation in Terms of Actual Factors:

Log_{10}(Conc in soil) =
+5.85476
+2.87910E-004 * Koc
-2.82260 * Feundich
+0.23829 * foc

Diagnostics Case Statistics

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t
1	3.87	3.87	5.257E-005	0.500	0.094	0.002	0.082
2	4.13	4.13	5.118E-004	0.500	0.920	0.211	0.897
3	3.59	3.59	-5.664E-004	0.500	-1.018	0.259	-1.024
4	3.85	3.85	2.078E-006	0.500	0.004	0.000	0.003
5	4.35	4.35	5.469E-004	0.500	0.983	0.241	0.977
6	4.60	4.61	-1.111E-003	0.500	-1.997	0.997	-30.989 *
7	4.06	4.06	-3.301E-005	0.500	-0.059	0.001	-0.051
8	4.32	4.32	5.974E-004	0.500	1.073	0.288	1.102

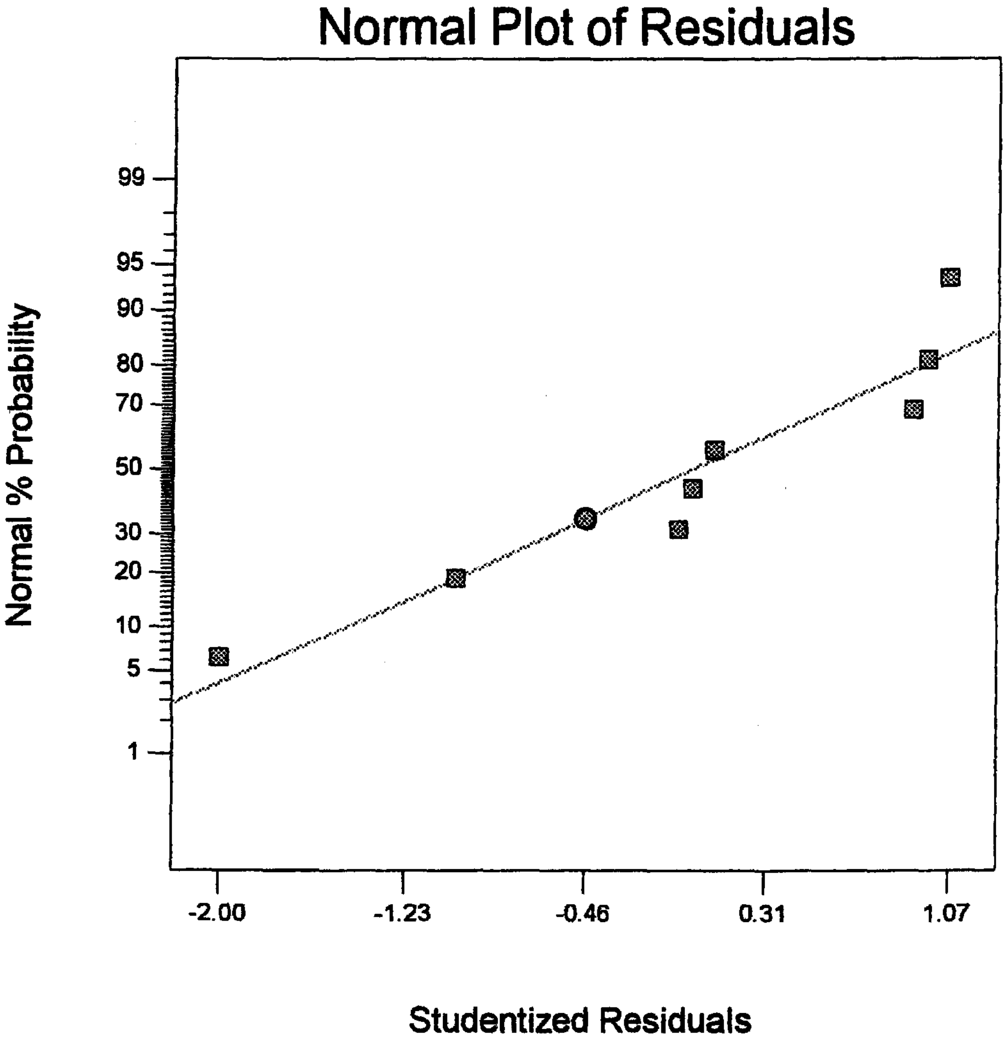
* Case(s) with |Outlier T| > 3.50

Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

1) Normal probability plot of the studentized residuals to check for normality of residuals.
2) Studentized residuals versus predicted values to check for constant error.
3) Outlier t versus run order to look for outliers, i.e., influential values.
4) Box-Cox plot for power transformations.

If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

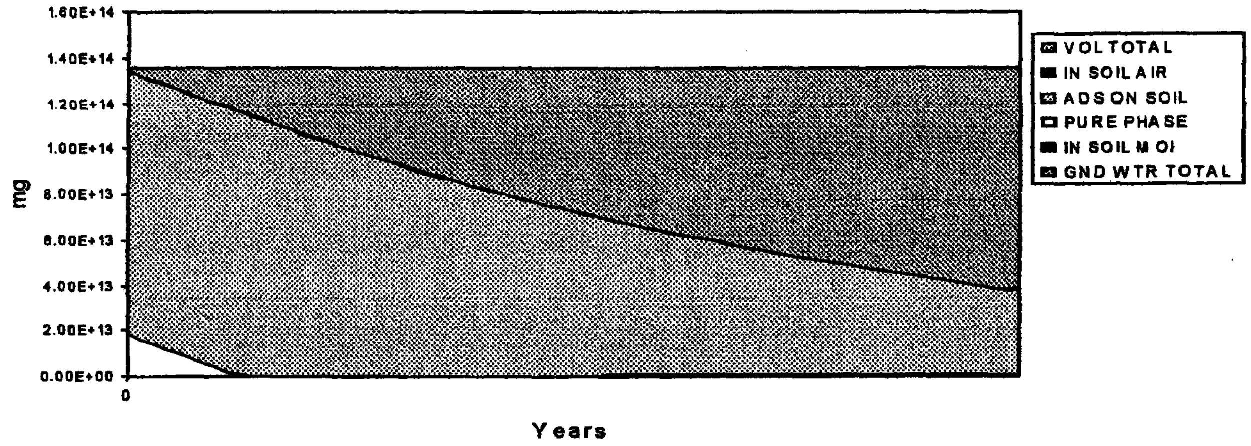
DESIGN-EXPERT Plot
Log10(Conc in soil)



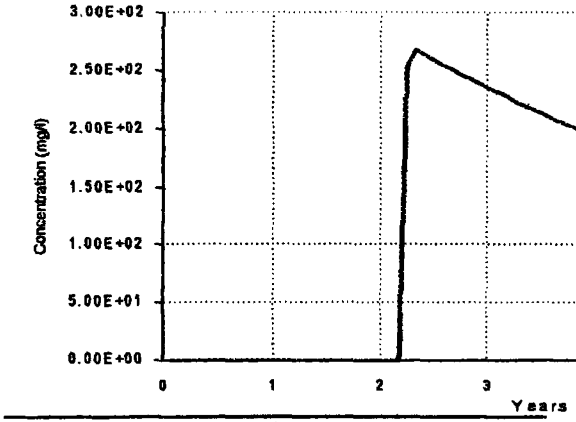
APPENDIX D
CALIBRATION RUNS FOR FINAL SOIL CONCENTRATIONS

SESOIL Pollutant Fate Cycle Report for C10-C21 #2 Fuel Oil

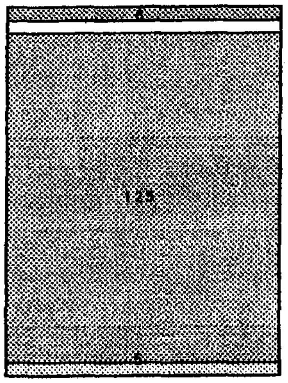
SESOIL Mass Fate



Leachate Concentration



SESOIL Profile (cm)

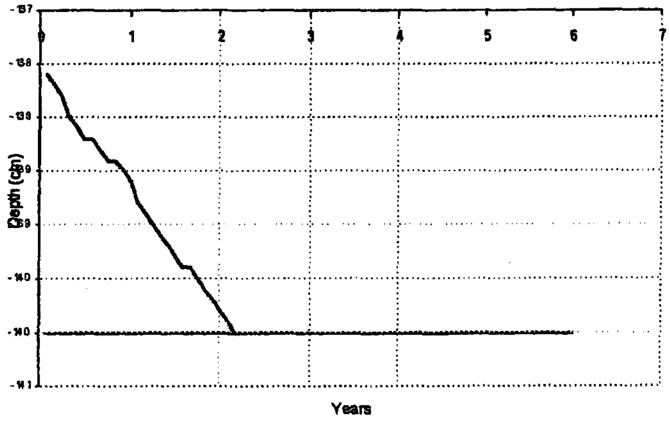


Maximum leachate concentration: 2.675E+02 mg/l

SESOIL Process	Pollutant Mass µg	Percent Input
Volatilized	9.725E+13	71.67
Soil Air	1.675E+11	0.12
Sur. Runoff	0.000E-01	0.00
In Washld	0.000E-01	0.00
Ads On Soil	3.711E+13	27.34
Hydrol Soil	0.000E-01	0.00
Degrad Soil	0.000E-01	0.00
Pure Phase	0.000E-01	0.00
Complexed	0.000E-01	0.00
Immobile CEC	0.000E-01	0.00
Hydrol CEC	0.000E-01	0.00
In Soil Moi	1.951E+09	0.00
Hydrol Mois	0.000E-01	0.00
Degrad Mois	0.000E-01	0.00
Other Trans	0.000E-01	0.00
Other Sinks	0.000E-01	0.00
Gwr. Runoff	1.094E+12	0.80
Total Output	1.356E+14	99.94
Total Input	1.357E+14	
Input - Output	6.810E+10	

Climate: ST. JOHN'S, NL
Chemical: C10-C21 #2 Fuel Oil
Soil: Silty Sand and Gravel
Application: MFA BH1

Starting Depth (cm): 137.60 **Ending Depth (cm):** 140.00
Total Depth (cm): 140.00



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C:\SEVIEW\soil2-4.SOI
C:\SEVIEW\BASE2.APL
C:\SEVIEW\SITEWASH.WSH
C:\SEVIEW\SOIL2-4.OUT

APPENDIX E
SENSITIVITY ANALYSIS FOR FINAL SOIL CONCENTRATION

Use your mouse to right click on individual cells for definitions.

```
Response:   Conc in Soil   Transform:     Power      Lambda:      2.67      Constant:       0
      ANOVA for Selected Factorial Model
Analysis of variance table [Partial sum of squares]
                     Sum of                        Mean             F
Source              Squares          DF          Square         Value      Prob > F
Model             7.107E+024          4      1.777E+024         34.02      < 0.0001     significant
            B     2.369E+024          1      2.369E+024         45.37      < 0.0001
            C     2.839E+024          1      2.839E+024         54.38      < 0.0001
            D     2.906E+023          1      2.906E+023          5.57        0.0379
           BC     1.608E+024          1      1.608E+024         30.79        0.0002
Residual          5.744E+023         11      5.222E+022
Cor Total         7.681E+024         15
```

The Model F-value of 34.02 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case B, C, D, BC are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy),
model reduction may improve your model.

```
Std. Dev.     2.285E+011          R-Squared          0.9252
Mean          1.499E+012          Adj R-Squared      0.8980
C.V.               15.24          Pred R-Square      0.8418
PRESS         1.215E+024          Adeq Precisior     14.730
```

The "Pred R-Squared" of 0.8418 is in reasonable agreement with the "Adj R-Squared" of 0.8980.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 14.730 indicates an adequate signal. This model can be used to navigate the design space.

```
                  Coefficient               Standard        95% CI        95% CI
Factor               Estimate        DF        Error           Low          High          VIF
Intercept          1.499E+012         1   5.713E+010    1.373E+012    1.625E+012
B-Intrinsic permeaBi[illegible]E+011    1   5.713E+010   -5.105E+011   -2.590E+011         1.00
C-SPD              4.213E+011         1   5.713E+010    2.955E+011    5.470E+011          1.00
D-Effetive Porosity348E+011           1   5.713E+010   -2.605E+011   -9.032E+009          1.00
BC                 3.170E+011         1   5.713E+010    1.913E+011    4.427E+011          1.00
```

Final Equation in Terms of Coded Factors:

$(\text{Conc in Soil})^{2.67}$ =
+1.499E+012
-3.848E+011 * B
+4.213E+011 * C
-1.348E+011 * D
+3.170E+011 * B * C

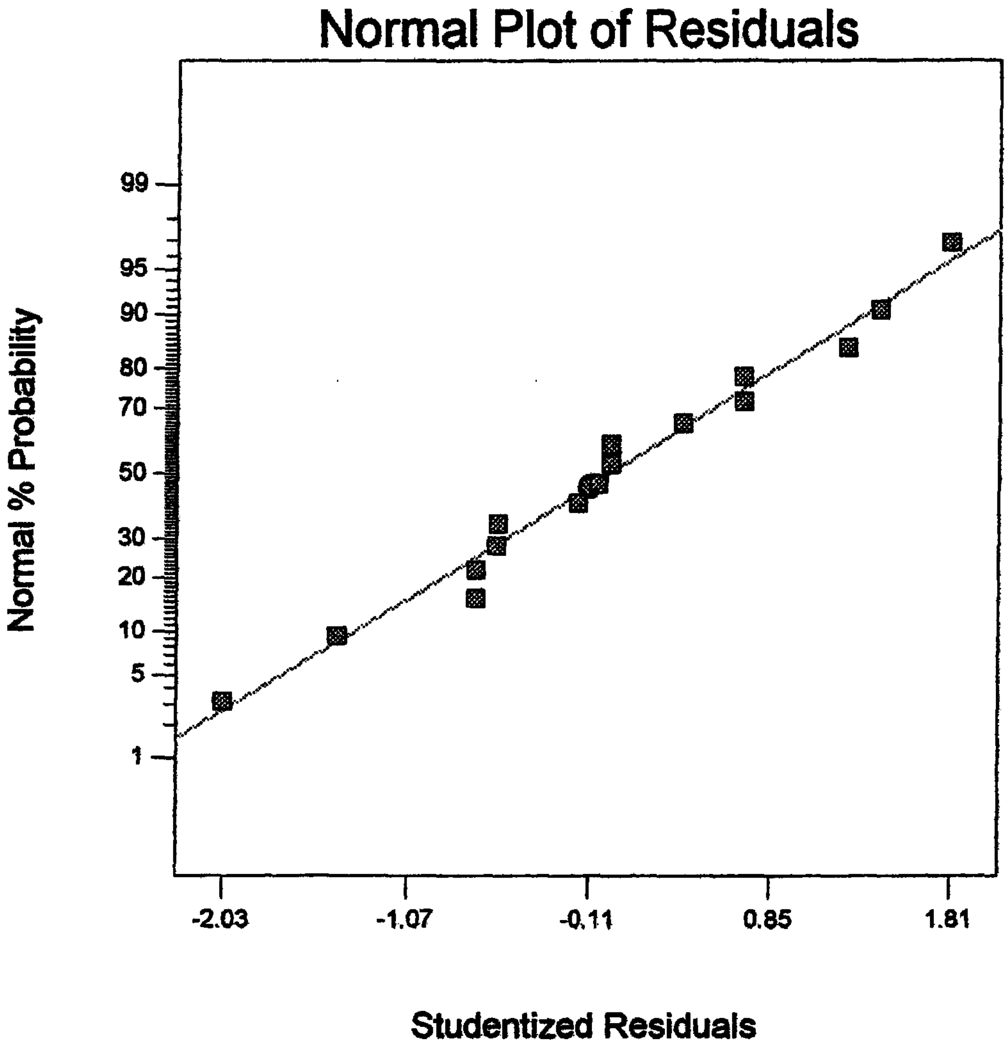
Final Equation in Terms of Actual Factors:

$(\text{Conc in Soil})^{2.67}$ =
+2.36144E+01
-1.96968E+01 * Intrinsic permeability
+2.50571E+01 * SPD
-2.69541E+01 * Effetive Porosity
+1.52839E+01 * Intrinsic permeability * SPD

Diagnostics Case Statistics

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t
1	1.988E+012	1.914E+012	7.375E+010	0.313	0.389	0.014	0.374
2	1.882E+012	1.914E+012	-3.223E+010	0.313	-0.170	0.003	-0.162
3	7.487E+011	5.109E+011	2.378E+011	0.313	1.255	0.143	1.293
4	4.995E+011	5.109E+011	-1.139E+010	0.313	-0.060	0.000	-0.057
5	1.988E+012	2.123E+012	-1.348E+011	0.313	-0.711	0.046	-0.694
6	1.988E+012	2.123E+012	-1.348E+011	0.313	-0.711	0.046	-0.694
7	1.988E+012	1.987E+012	7.886E+008	0.313	0.004	0.000	0.004
8	1.988E+012	1.987E+012	7.886E+008	0.313	0.004	0.000	0.004
9	1.988E+012	1.645E+012	3.433E+011	0.313	1.812	0.298	2.062
10	1.260E+012	1.645E+012	-3.848E+011	0.313	-2.031	0.375	-2.449
11	1.286E+011	2.414E+011	-1.128E+011	0.313	-0.595	0.032	-0.577
12	1.277E+011	2.414E+011	-1.137E+011	0.313	-0.600	0.033	-0.582
13	1.988E+012	1.853E+012	1.348E+011	0.313	0.711	0.046	0.694
14	1.988E+012	1.853E+012	1.348E+011	0.313	0.711	0.046	0.694
15	1.988E+012	1.718E+012	2.703E+011	0.313	1.427	0.185	1.507

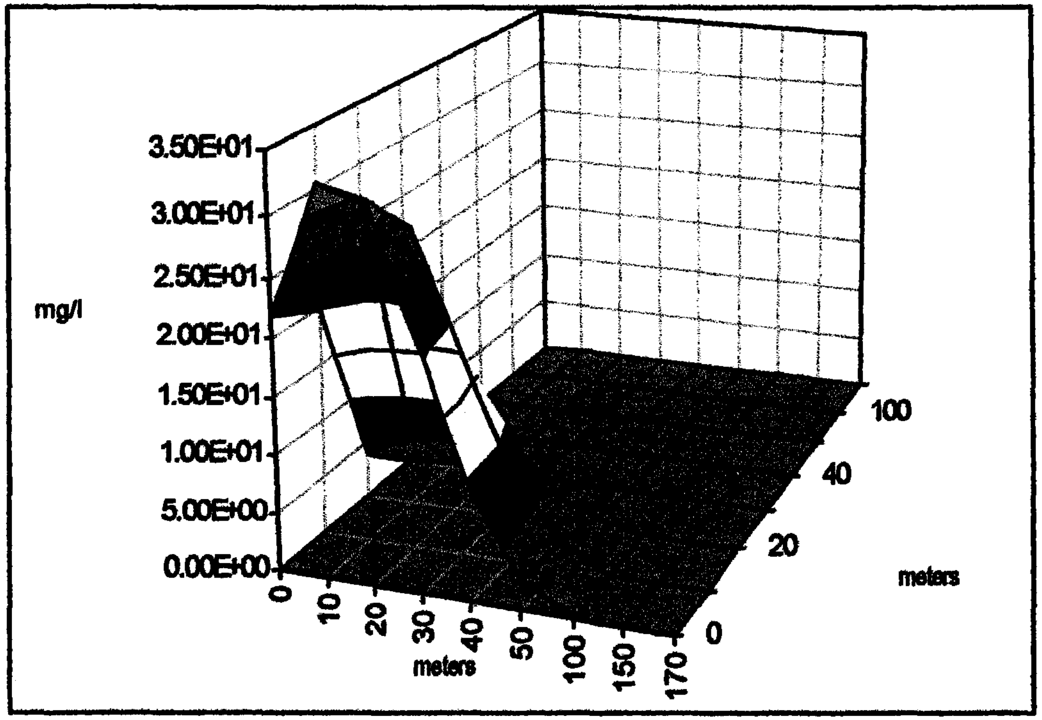
DESIGN-EXPERT Plot
(Conc in Soil)^2.67



page 1 for Diagnostics of Conc in Soil of C:\Program Files\DX6Trial\DATA\soil2.dx6 04:34 PM May 29, 2004

APPENDIX F
CALIBRATION RUNS FOR GROUNDWATER CONCENTRATIOSN

Dissolved Concentrations in Plume



Depth (Z) = 0.00 meters, 0.00 feet.
Distribution in mg/l at 2190.00 days, 6.00 years.
Maximum concentration of 3.290E+01 mg/l (100.00 percent of the maximum concentration of 3.290E+01 mg/l).

AT123D INPUT PARAMETERS

Effective Porosity: 0.300
Hydraulic Gradient: .003000 m/m
Hydraulic Conductivity: 3.600E+01 m/hr 1.000E+0 cm/sec
Soil Bulk Density: 2.200E+03 kg/m3 2.200E+0 g/cm3
Aquifer Width: 0.000E-01 m 0.000E-01 ft
Aquifer Depth: 2.000E-01 m 6.566E-01 ft

Dispersivities	Meters	Feet
Longitudinal:	2.00	6.57
Lateral:	1.00	3.28
Vertical:	0.05	0.16

Distribution Coefficient (Kd): 6.000E-02 m3/kg
Molecular Diffusion Coefficient: 3.528E-06 m2/hr
First-Order Decay Coefficient: 0.000E-01 1/hr

Load	Begin (m)	End (m)	Begin (ft)	End(ft)
X-Direction	-15.810	15.810	-51.910	51.910
Y-Direction	-15.810	15.810	-51.910	51.910
Z-Direction	0.000	0.000	0.000	0.000

INITIAL RESULTS

Retardation Factor: 441.000
Retarded Darcy Velocity: 8.163E-04 m/hr 2.267E-05 cm/sec
Retarded Longitudinal Dispersion Cofficient: 1.633E-03 m2/hr
Retarded Lateral Dispersion Cofficient: 8.164E-04 m2/hr
Retarded Vertical Dispersion Cofficient: 4.084E-05 m2/hr

Meters		0.00	10.00	20.00	30.00	40.00	50.00	100.00	150.00	170.00
	Feet	0.00	32.83	65.67	98.50	131.33	164.17	328.33	492.50	558.17
0.00	0.00	2.180E+01	3.290E+01	3.210E+01	2.080E+01	9.220E+00	2.460E+00	3.100E-06		
10.00	32.83	1.970E+01	2.900E+01	2.760E+01	1.740E+01	7.600E+00	2.020E+00	2.520E-06		
20.00	65.67	3.590E+00	6.350E+00	7.240E+00	5.290E+00	2.490E+00	6.890E-01	9.110E-07		
30.00	98.50	9.980E-02	2.420E-01	3.370E-01	3.040E-01	1.710E-01	5.330E-02	8.570E-08		
40.00	131.33	8.190E-04	2.310E-03	3.570E-03	3.530E-03	2.220E-03	7.740E-04	1.600E-09		
50.00	164.17	5.810E-06	1.580E-05	2.340E-05	2.240E-05	1.340E-05	4.400E-06	8.400E-12		
100.00	328.33									
150.00	492.50									

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C:\SEVIEW\GW5.ATO

APPENDIX G
SENSITVITY ANALYSIS FOR GROUNDWATER CONCENTRATION

Use your mouse to right click on individual cells for definitions.

Response: GW Conc Transform: Square root Constant: 0

ANOVA for Selected Factorial Model

Analysis of variance table [Partial sum of squares]

Source		**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
Model		48.74	5	9.75	4.125E+005	< 0.0001	significant
	A	*48.67*	*1*	*48.67*	*2.060E+006*	*< 0.0001*	
	B	*7.175E-003*	*1*	*7.175E-003*	*303.64*	*< 0.0001*	
	C	*1.338E-003*	*1*	*1.338E-003*	*56.63*	*< 0.0001*	
	AB	*0.061*	*1*	*0.061*	*2573.07*	*< 0.0001*	
	BC	*6.700E-004*	*1*	*6.700E-004*	*28.36*	*0.0003*	
Residual		2.363E-004	10	2.363E-005			
Cor Total		48.74	15				

The Model F-value of 412529.47 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, C, AB, BC are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	4.861E-003	R-Squared	1.0000
Mean	2.89	Adj R-Squared	1.0000
C.V.	0.17	Pred R-Square	1.0000
PRESS	6.049E-004	Adeq Precisior	1215.018

The "Pred R-Squared" of 1.0000 is in reasonable agreement with the "Adj R-Squared" of 1.0000.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 1215.018 indicates an adequate signal. This model can be used to navigate the design space.

Factor	**Coefficient Estimate**	**DF**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	2.89	1	1.215E-003	2.89	2.89	
A-Hydraulic Gradient	-1.74	1	1.215E-003	-1.75	-1.74	1.00
B-Longitudinal Dis.	0.021	1	1.215E-003	0.018	0.024	1.00
C-Tansverse Dis	-9.145E-003	1	1.215E-003	-0.012	-6.438E-003	1.00

AB	0.062	1	1.215E-003	0.059	0.064	1.00
BC	-6.471E-003	1	1.215E-003	-9.179E-003	-3.763E-003	1.00

Final Equation in Terms of Coded Factors:

Sqrt(GW Conc) =
+2.89
-1.74 * A
+0.021 * B
-9.145E-003 * C
+0.062 * A * B
-6.471E-003 * B * C

Final Equation in Terms of Actual Factors:

Sqrt(GW Conc) =
+4.99160
-99.27091 * Hydraulic Gradient
-0.010189 * Longitudinal Dis.
+1.40347E-00 * Tansverse Dis.
+0.83301 * Hydraulic Gradient * Longitudinal Dis.
-4.04441E-003 * Longitudinal Dis. * Tansverse Dis.

Diagnostics Case Statistics

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t
1	4.68	4.68	2.674E-003	0.375	0.696	0.048	0.677
2	1.06	1.07	-2.674E-003	0.375	-0.696	0.048	-0.677
3	4.60	4.61	-4.731E-003	0.375	-1.231	0.152	-1.268
4	1.25	1.24	4.731E-003	0.375	1.231	0.152	1.268
5	4.67	4.67	-2.674E-003	0.375	-0.696	0.048	-0.677
6	1.06	1.06	2.674E-003	0.375	0.696	0.048	0.677
7	4.58	4.58	4.731E-003	0.375	1.231	0.152	1.268
8	1.21	1.21	-4.731E-003	0.375	-1.231	0.152	-1.268
9	4.68	4.68	2.674E-003	0.375	0.696	0.048	0.677
10	1.06	1.07	-2.674E-003	0.375	-0.696	0.048	-0.677
11	4.60	4.61	-4.731E-003	0.375	-1.231	0.152	-1.268

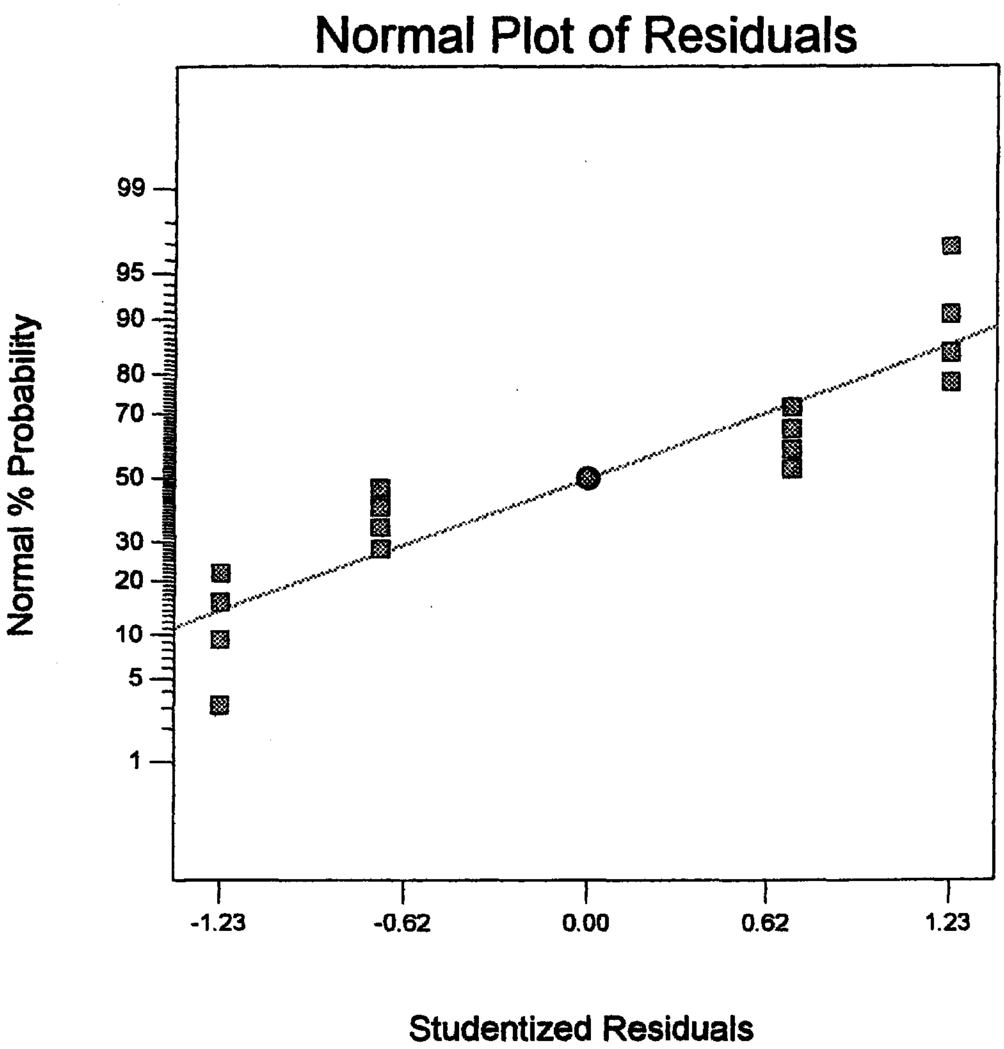
12	1.25	1.24	4.731E-003	0.375	1.231	0.152	1.268
13	4.67	4.67	-2.674E-003	0.375	-0.696	0.048	-0.677
14	1.06	1.06	2.674E-003	0.375	0.696	0.048	0.677
15	4.58	4.58	4.731E-003	0.375	1.231	0.152	1.268
16	1.21	1.21	-4.731E-003	0.375	-1.231	0.152	-1.268

Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

1) Normal probability plot of the studentized residuals to check for normality of residuals.
2) Studentized residuals versus predicted values to check for constant error.
3) Outlier t versus run order to look for outliers, i.e., influential values.
4) Box-Cox plot for power transformations.

If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

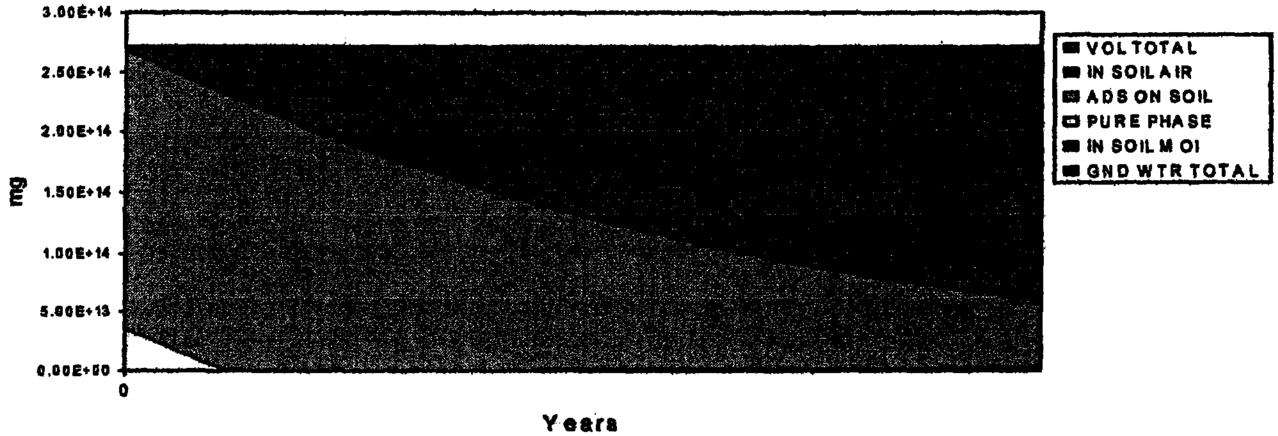
DESIGN-EXPERT Plot
Sqrt(GW Conc)



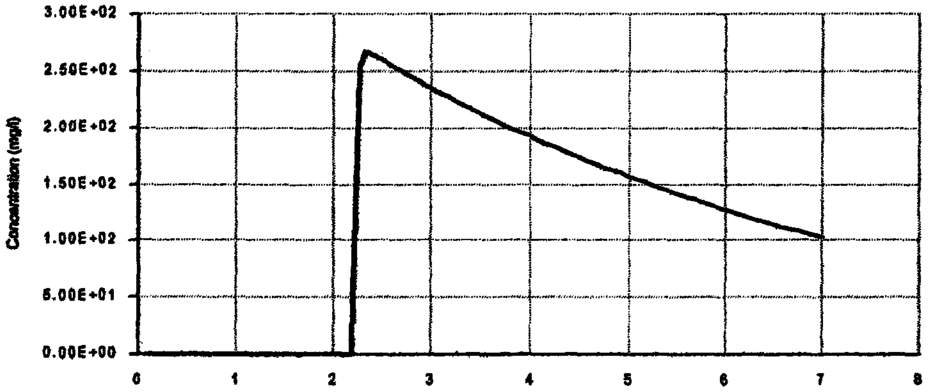
APPENDIX H
MODEL VERIFICATION RUN

SESOIL Pollutant Fate Cycle Report for C10-C21 #2 Fuel Oil

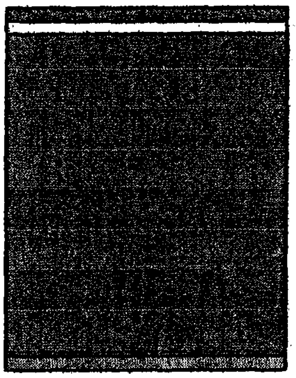
SESOIL Mass Fate



Leachate Concentration



SESOIL Profile (cm)

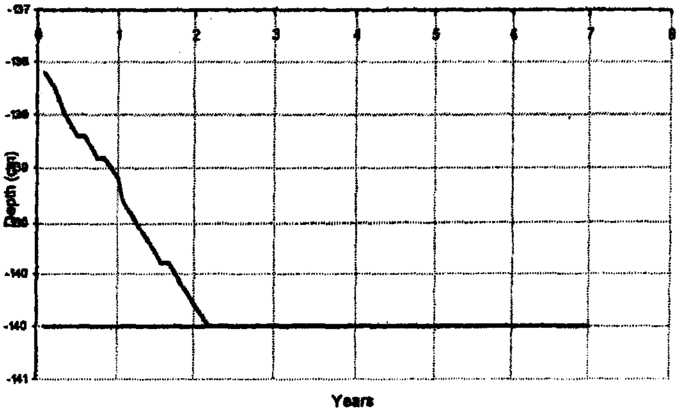


SESOIL Process	Pollutant Mass µg	Percent Input
Volatilized	2.099E+14	77.36
Soil Air	2.705E+11	0.09
Sur. Runoff	0.000E-01	0.00
In Washld	0.000E-01	0.00
Ads On Soil	5.850E+13	21.55
Hydrol Soil	0.000E-01	0.00
Degrad Soil	0.000E-01	0.00
Pure Phase	0.000E-01	0.00
Complexed	0.000E-01	0.00
Immobile CEC	0.000E-01	0.00
Hydrol CEC	0.000E-01	0.00
In Soil Moi	3.150E+09	0.00
Hydrol Mois	0.000E-01	0.00
Degrad Mois	0.000E-01	0.00
Other Trans	0.000E-01	0.00
Other Sinks	0.000E-01	0.00
Gwr. Runoff	2.531E+12	0.93
Total Output	2.712E+14	99.95
Total Input	2.714E+14	
Input - Output	1.128E+11	

Maximum leachate concentration: 2.675E+02 mg/l

Climate: ST. JOHN'S, NL
Chemical: C10-C21 #2 Fuel Oil
Soil: Silty Sand and Gravel
Application: MFA BH1

Starting Depth (cm): 137.60 **Ending Depth (cm):** 140.00
Total Depth (cm): 140.00



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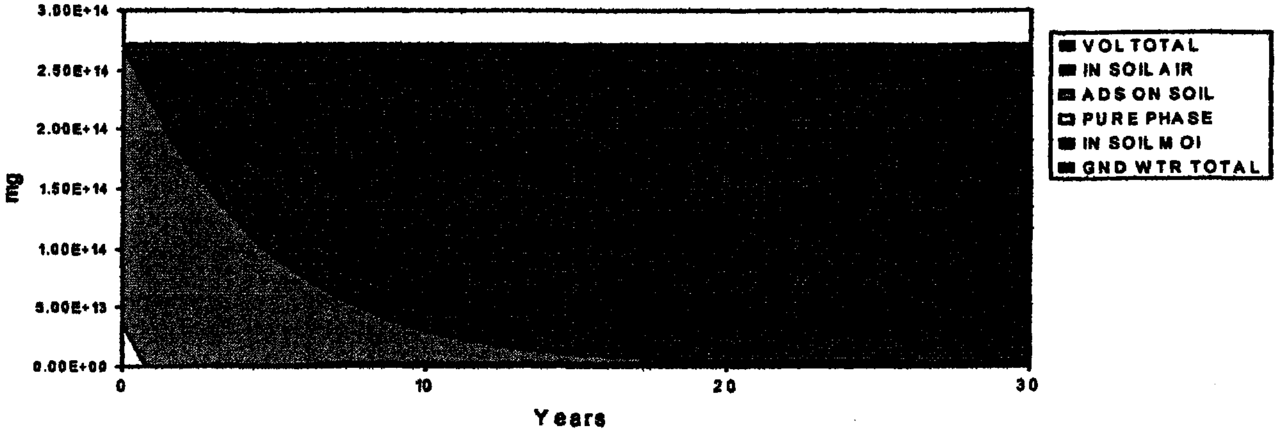
C:\SEVIEW\constant.CHM
C:\SEVIEW\constant.SOI
C:\SEVIEW\BASE3.APL
C:\SEVIEW\SITEWASH.WSH
C:\SEVIEW\VALIDATE.OUT

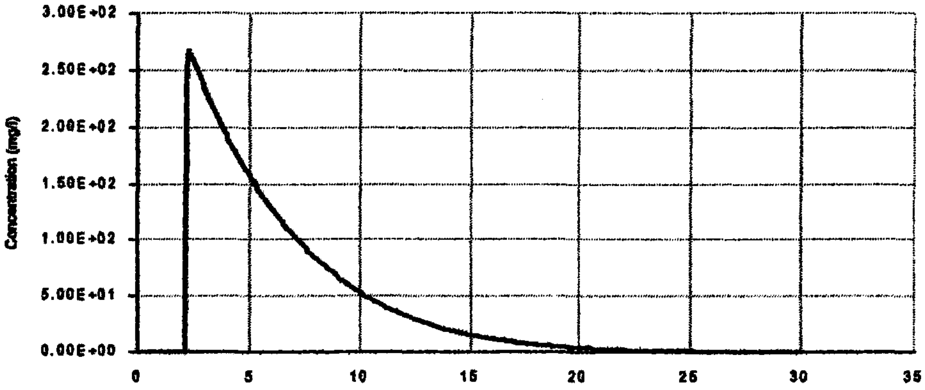
APPENDIX I
MODEL PREDICTION RUN – SOIL

SESOIL Pollutant Fate Cycle Report for C10-C21 #2 Fuel Oil

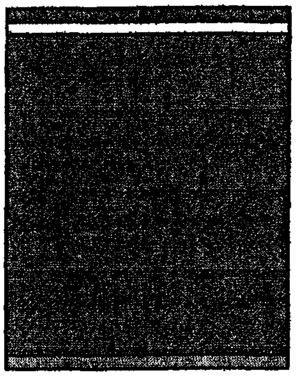
SESOIL Mass Fate



Leachate Concentration



SESOIL Profile (cm)

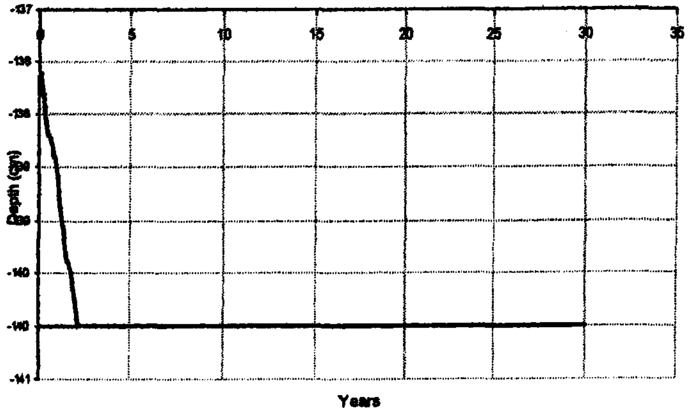


Maximum leachate concentration: 2.675E+02 mg/l

SESOIL Process	Pollutant Mass µg	Percent Input
Volatilized	2.675E+14	98.56
Soil Air	1.948E+08	0.00
Sur. Runoff	0.000E-01	0.00
In Washld	0.000E-01	0.00
Ads On Soil	1.885E+10	0.00
Hydrol Soil	0.000E-01	0.00
Degrad Soil	0.000E-01	0.00
Pure Phase	0.000E-01	0.00
Complexed	0.000E-01	0.00
Immobile CEC	0.000E-01	0.00
Hydrol CEC	0.000E-01	0.00
In Soil Moi	2.267E+06	0.00
Hydrol Mois	0.000E-01	0.00
Degrad Mois	0.000E-01	0.00
Other Trans	0.000E-01	0.00
Other Sinks	0.000E-01	0.00
Gwr. Runoff	3.813E+12	1.40
Total Output	2.713E+14	99.98
Total Input	2.714E+14	
Input - Output	4.982E+10	

Climate: ST. JOHN'S, NL
Chemical: C10-C21 #2 Fuel Oil
Soil: Silty Sand and Gravel
Application: MFA BH1

Starting Depth (cm): 137.60 **Ending Depth (cm):** 140.00
Total Depth (cm): 140.00



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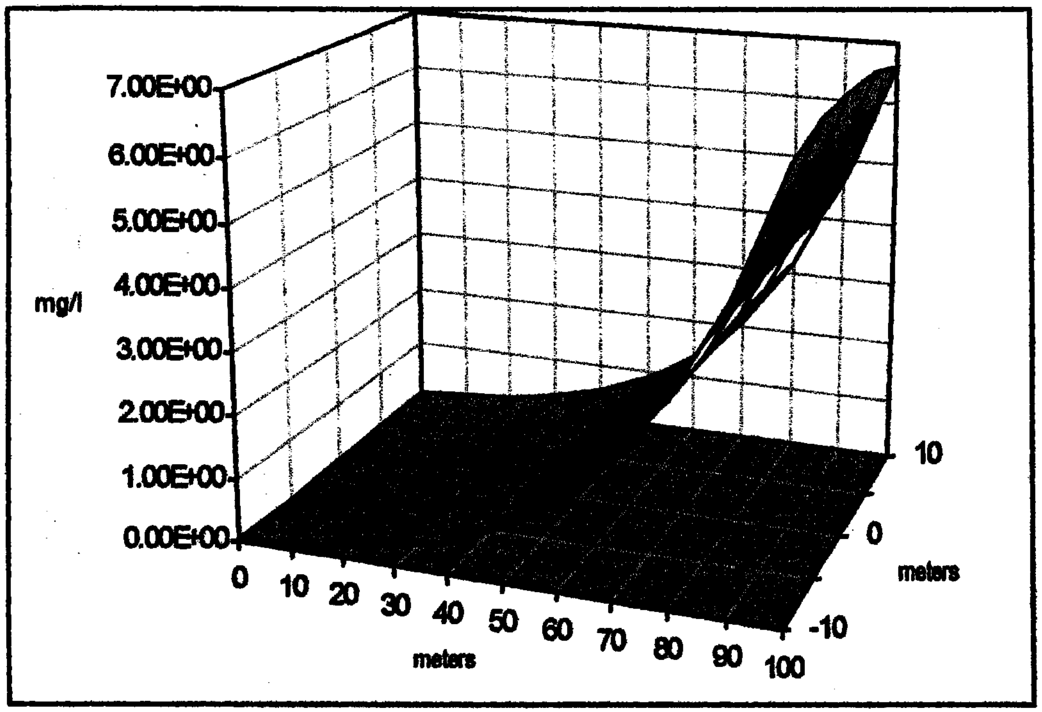
C:\SEVIEW\constant.CHM
C:\SEVIEW\constant.SOI
C:\SEVIEW\BASE3.APL
C:\SEVIEW\SITEWASH.WSH
C:\SEVIEW\PREDICT3.OUT

APPENDIX J
MODEL PREDICTION RUN - GROUNDWATER

Dissolved Concentrations in Plume



AT123D INPUT PARAMETERS

Effective Porosity: 0.300
Hydraulic Gradient: .003000 m/m
Hydraulic Conductivity: 3.600E+01 m/hr 1.000E+0 cm/sec
Soil Bulk Density: 2.200E+03 kg/m3 2.200E+0 g/cm3
Aquifer Width: 0.000E-01 m 0.000E-01 ft
Aquifer Depth: 2.000E-01 m 6.566E-01 ft

Dispersivities	Meters	Feet
Longitudinal:	2.16	7.09
Lateral:	0.20	0.66
Vertical:	0.02	0.07

Distribution Coefficient (Kd): 6.000E-02 m3/kg
Molecular Diffusion Coefficient: 3.528E-06 m2/hr
First-Order Decay Coefficient: 0.000E-01 1/hr

Load	Begin (m)	End (m)	Begin (ft)	End(ft)
X-Direction	-22.360	22.360	-73.415	73.415
Y-Direction	-22.360	22.360	-73.415	73.415
Z-Direction	0.000	0.000	0.000	0.000

INITIAL RESULTS

Retardation Factor: 441.000
Retarded Darcy Velocity: 8.163E-04 m/hr 2.267E-05 cm/sec
Retarded Longitudinal Dispersion Cofficient: 1.763E-03 m2/hr
Retarded Lateral Dispersion Cofficient: 1.633E-04 m2/hr
Retarded Vertical Dispersion Cofficient: 1.635E-05 m2/hr

Depth (Z) = 0.00 meters, 0.00 feet.
Distribution in mg/l at 10950.00 days, 30.00 years.
Maximum concentration of 6.930E+00 mg/l (15.57 percent of the maximum concentration of 4.450E+01 mg/l).

Meters		0.00	10.00	20.00	30.00	40.00	50.00	60.00	70.00	80.00	90.00	100.00
	Feet	0.00	32.83	65.67	98.50	131.33	164.17	197.00	229.83	262.67	295.50	328.33
-10.00	-32.83	4.570E-02	9.550E-02	1.810E-01	3.160E-01	5.300E-01	8.610E-01	1.360E+00	2.090E+00	3.150E+00	4.630E+00	6.650E+00
-5.00	-16.42	4.580E-02	9.570E-02	1.820E-01	3.180E-01	5.350E-01	8.730E-01	1.380E+00	2.140E+00	3.230E+00	4.780E+00	6.880E+00
0.00	0.00	4.580E-02	9.570E-02	1.820E-01	3.180E-01	5.360E-01	8.740E-01	1.390E+00	2.150E+00	3.250E+00	4.800E+00	6.930E+00
5.00	16.42	4.580E-02	9.570E-02	1.820E-01	3.180E-01	5.350E-01	8.730E-01	1.380E+00	2.140E+00	3.230E+00	4.780E+00	6.880E+00
10.00	32.83	4.570E-02	9.550E-02	1.810E-01	3.160E-01	5.300E-01	8.610E-01	1.360E+00	2.090E+00	3.150E+00	4.630E+00	6.650E+00

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