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Wayne C. Huber

A spreadsheet-based transport model was developed in Microsoft Excel™ as part of a six-year National Cooperative Highway Research Program project conducted at Oregon State University. The model simulated the leaching, transport, removal, and retardation processes that occur in the surface and subsurface pathways of the near highway environment. For all construction and repair materials tested as part of this study sorption was the dominant removal mechanism.

This thesis presents the development of a simple algorithm used for the solution of the advection-dispersion equation incorporating advection, reversible equilibrium sorption, dispersion, and biodegradation. Algorithm results are compared to analytical solutions of the advection-dispersion equation, to column studies conducted as part of this research project, and to results from column studies of cadmium and pesticide (picloram) transport conducted by other researchers.

A Model for Simulation of Subsurface Transport of Highway-Related Water Quality Constituents

by
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APPROVED:

Redacted for Privacy

Major Professor, representing Civil Engineering

Redacted for Privacy

Chair of Department of Civil, Construction, & Environmental Engineering

Redacted for Privacy

Dean of the Graduate School

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Edwin Todd Hesse, Author

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A Model for Simulation of Subsurface Transport of Highway-Related Water Quality Constituents

1 INTRODUCTION

1.1 Problem Statement

The viability and integrity of our highway system depends upon continual rehabilitation and maintenance. In such activities, a wide variety of materials, including Portland cement, asphalt cement, petroleum-base sealants, wood preservatives, and additives are used. During the wet seasons, there is a potential for leaching of the chemical constituents in these materials and the possibility of transport to adjacent surface and subsurface water bodies. Toxic chemicals from these materials could result in adverse environmental effects on the ecological health of the streams, ponds, wetlands, and groundwater systems. If such water bodies are used as a source of potable water, adverse human health effects could also occur.

The National Cooperative Highway Research Program (NCHRP) funded a six-year study at Oregon State University to identify materials capable of producing potentially toxic leachate, to identify the components responsible for toxicity, and to characterize the transport and fate of toxic solutes in the near-highway environment.

Contaminants released from a highway construction and repair (C&R) site migrate with the flow of water or move with water as it infiltrates the soil. Contaminants are advected and diffused (Fischer et al., 1979; Huber, 1993) as they are entrained in the moving surface or subsurface water. They are also subject to several removal, reduction, and retardation (RRR) processes that greatly affect their ultimate mass flux and concentration distribution in space and time. Given a certain contaminant load originating at a highway construction site, the mass entering a receiving water body or groundwater body will depend heavily upon the factors that affect removal, reduction, and retardation (Eldin et al. 2000). Factors considered in the model include sorption, biodegradation, photolysis, and volatilization. Special tests were conducted during this study using three soils to determine the sorptive characteristics of limited samples. Hydrolysis is a process not included in the model that typically results in very slow degradation and is thus not considered further. In flowing streams, sedimentation may also be important for solid particles, but not for highway runoff.

Biodegradation, volatilization, photodegradation, and sorption have been identified during the NCHRP project as the primary removal mechanisms for solutes leached from highway construction materials. Of these removal mechanisms only biodegradation and sorption play a major role in the removal of material (and the associated toxicity) from leachate flowing in the subsurface zone. While photodegradation and volatilization can play important roles in the removal of solutes from surface flows, they have played only minor roles in the reduction of

the toxicity (discussed in the following paragraph) of leachates from the materials tested as part of the NCHRP study. The chemical species responsible for toxicity of the leachates from the materials that have been tested are primarily heavy metals, with some toxicity also attributed to organic compounds. The organic chemicals found in leachates have not been shown to be susceptible to photodegradation and only volatilize slowly. Biodegradation has also played a limited role in the removal of toxicity. The toxic nature of the leachates of interest inhibits biodegradation. The heavy metals found in many of the leachates are not biodegradable, but may be removed in very limited quantities through biological uptake. Thus, soil sorption is the dominant removal mechanism and as such has the greatest impact on the sub-surface transport of solute leached from the highway environment.

Toxicity is the capacity of the solute material to cause adverse effects to living organisms. The assessment of toxicity of a material is expressed as the amount or concentration necessary to cause a measurable response in the test organism. The measurable response can range from a physical impairment, such as the inability to reproduce, to mortality of the organism, the most common indicator of toxicity. The two standard types of toxicity testing are chronic and acute; chronic testing measures the effects due to long-term exposure of a material, while acute testing examines effects from short-term exposure.

1.2 Statement of Purpose

One of the objectives of the NCHRP study was the development of a model capable of predicting toxicological effects from the leachate produced from highway construction and repair materials. This empirical model, developed by Quigley (1998), uses the data derived from the extensive laboratory testing conducted as part of this project. Many refinements have been made to the model since 1998 (Nelson et al., 2000a) and can be found in Nelson et al. (2000b). One refinement in particular had the greatest impact on modeling the transport of material leached from construction materials tested for this project: the development of a new algorithm for the solution of the advection-dispersion equation. The algorithm incorporates advection, reversible sorption, dispersion, and first order biological decay. The focus of this thesis is the development of the algorithm and verification of the algorithm through comparison to analytical solutions, column study results conducted at Oregon State University as part of this project, and to two other column studies found in the literature.

2 BACKGROUND AND LITERATURE REVIEW

2.1 NCHRP Project Summary

Highway construction and repair materials have been identified as a potential source of non-point pollution. Constituents of highway materials can migrate from roadways to the surrounding environment and present a potential pollution source. The primary transport mechanism involves leaching of toxic constituents and their ultimate transport to surface or ground waters.

The use of highway construction and repair (C & R) materials recently has increased in type, volume, and chemical complexity. Increased utilization of solid waste materials has raised concerns leading to a search for a unified approach to evaluate the potential for environmental contamination of leachates from highway C&R materials. There is a clear need to integrate and unify testing and evaluation approaches that will allow greater understanding of the fundamental leaching behavior of such materials and allow for modeling of the transport and fate processes.

A research program, funded by National Cooperative Highway Research Program (NCHRP, affiliated with the National Research Council), was designed to evaluate the potential aquatic toxicity (organism sensitivity) of common highway C&R materials and to determine the fate and transport of their soluble constituents while still in the highway environment. The program was planned in three phases.

Phase I focused on a broad screening of common C&R materials to identify the extent of the problem and to guide the succeeding phases. The deliverables of Phase I were a comprehensive list of the most commonly used C&R materials with their toxicity assessment, a protocol for toxicity measurement and assessment, a preliminary description of a conceptual analytical model to predict the fate and transport of soluble toxicants in the soil-water matrix, and the description of an overall evaluation methodology to be used for additional/future C&R materials.

Phase II focused on analysis of leaching characteristics of C&R materials, full development of a predictive computer model, and the validation of the overall evaluation methodology. Validation of the methodology was achieved by evaluating a number of C&R materials and by broadening the evaluation criteria to include leaching kinetics, reference environments, and impact interpretation.

Phase III focused on additional laboratory testing to validate modeling assumptions, to expand the current database, and to compare laboratory testing and leaching methodologies with conventional EPA procedures. The predictive model itself was enhanced and documented.

Results from all phases of the NCHRP study are published in a series of final reports (Nelson et al. 2000a, Eldin et al. 2000, Nelson et al. 2000b, Nelson et al. 2000c, Hesse et al. 2000).

2.2 Model Description

The computer model IMPACT, developed as part of the NCHRP project, consists of two components: data retrieval and transport model. Data retrieval includes all summary data (e.g., toxicity data, chemistry samples) collected during Phases I, II, and III of the project. Figure 2.2.1 provides an overview of the physical environment simulated by the transport and fate portion of the model.

The model utilizes the laboratory findings to numerically approximate applicable phenomena such as leaching, photodegradation, or sorption. These approximations are supported by the extensive database of laboratory data collected as part of this project. The results are included with the model in a summarized tabular form in an Excel™ spreadsheet format. The data are the main support for the modeling effort and are presented in such a way that they are easily searchable by C&R material tested and by the tests run.

The following discussion provides a brief overview of the functioning of the transport model. For detailed explanations of the workings of the model the reader is referred to the series of reports previously mentioned. Eldin et al. (2000) contains the theoretical development of the model. Nelson et al. (2000b) contains information on model enhancements and an appendix detailing model calculations. Hesse et al. (2000) is an operations manual for IMPACT.

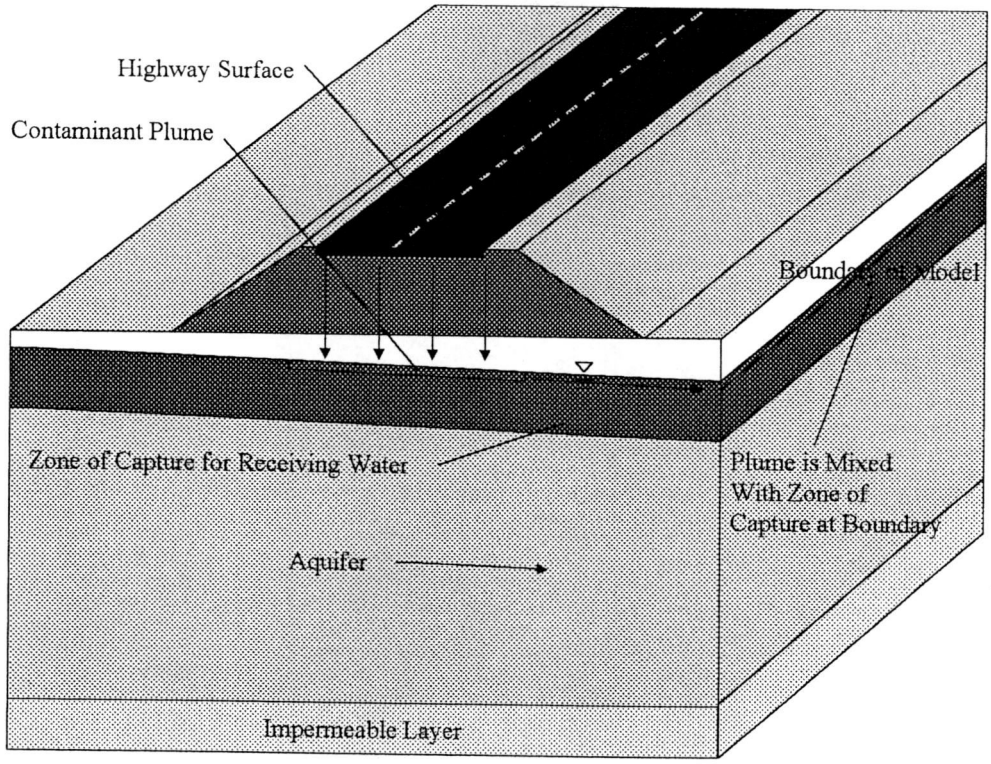

Figure 2.2.1 Physical environment simulated by the fate and transport model IMPACT

The fate and transport model is constructed to simulate one of six reference environments shown in Figure 2.2.2. In addition to these six reference environments, lateral transport of a solute may be simulated, as shown in the bottom of Figure 2.2.1.

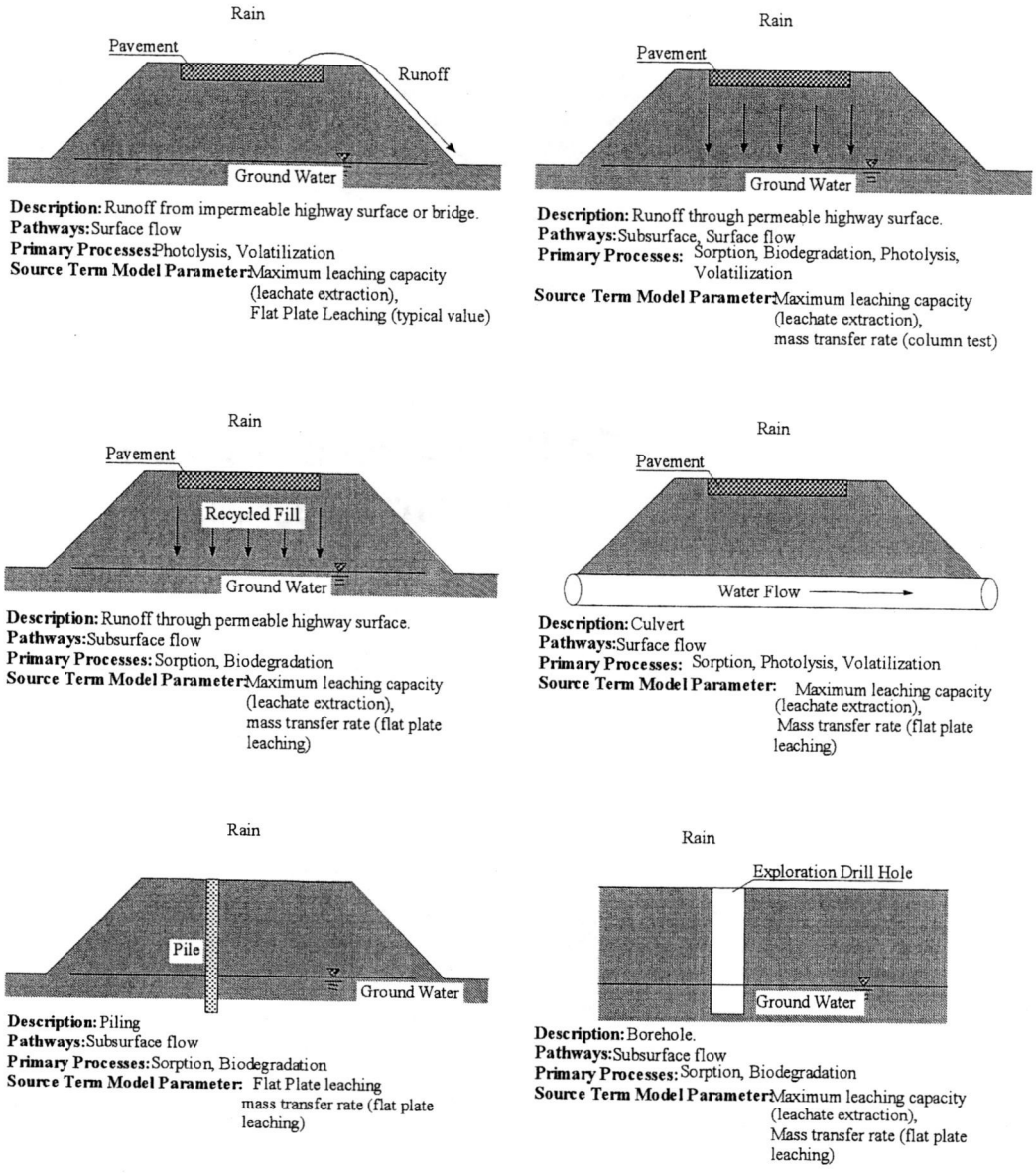

Figure 2.2.2 Reference environments simulated by the fate and transport model IMPACT

After the model user selects a combination of reference environment and C&R material, the model first calculates the source-strength (leaching) rates for generation of constituents transported into the removal, reduction, and retardation (RRR)

model section. Flow equations for the selected reference environment are used to calculate the seepage velocity of the infiltrating water and the resulting contact time of the water with the selected construction material. The types of flow equations that are used in the model are listed in Table 2.2.1 and can be found in Nelson et al. (2000b). A brief description follows.

Table 2.2.1 Type of Flow in Contact with Construction and Repair Materials

Reference Environment	**Type of Flow**				
	Crack	**Darcy**	**Near Pile**	**Pipe**	**Surface**
Bore Hole		X	X		
Culvert		X		X	
Fill		X			
Impermeable					X
Permeable	X				X
Piling		X	X		

Crack — Infiltration through cracks in the pavement surface.

Darcy — Darcy's Law flow through soil surrounding a bore hole, culvert, or piling or through the fill material.

Near Pile — Estimates the area of effect for leaching as a function of the infiltration rate.

Pipe — Used to calculate the flow depth in the culvert environment.

Surface — Used to calculate the time for runoff to leave the pavement surface.

The volume of leachate is calculated from the seepage velocity and the cross sectional area of infiltration. The time the water is in contact with the C&R material is used to calculate the concentration of leachate infiltrating into the soil. The laboratory leaching data are fit using the equation

$$\text{Concentration (mg or mmol /L)} = a \times \text{Time (hrs)}^{\,b} \qquad (2.2.1)$$

The a coefficient of the leaching function has units of mg or mmol / (L $\times$ hr^b), while the b parameter is dimensionless. The curve generated is used to estimate a decrease in the concentration of leachate with time. The term "time increment" refers to a short period of time (15 minutes or one hour) during the model run over which the leachate concentration is assumed constant. The concentration of the leachate for the nth time increment is equal to the change in concentration on the curve (Figure 2.2.3) between the leaching time prior to the nth time increment and the leaching time including the nth increment.

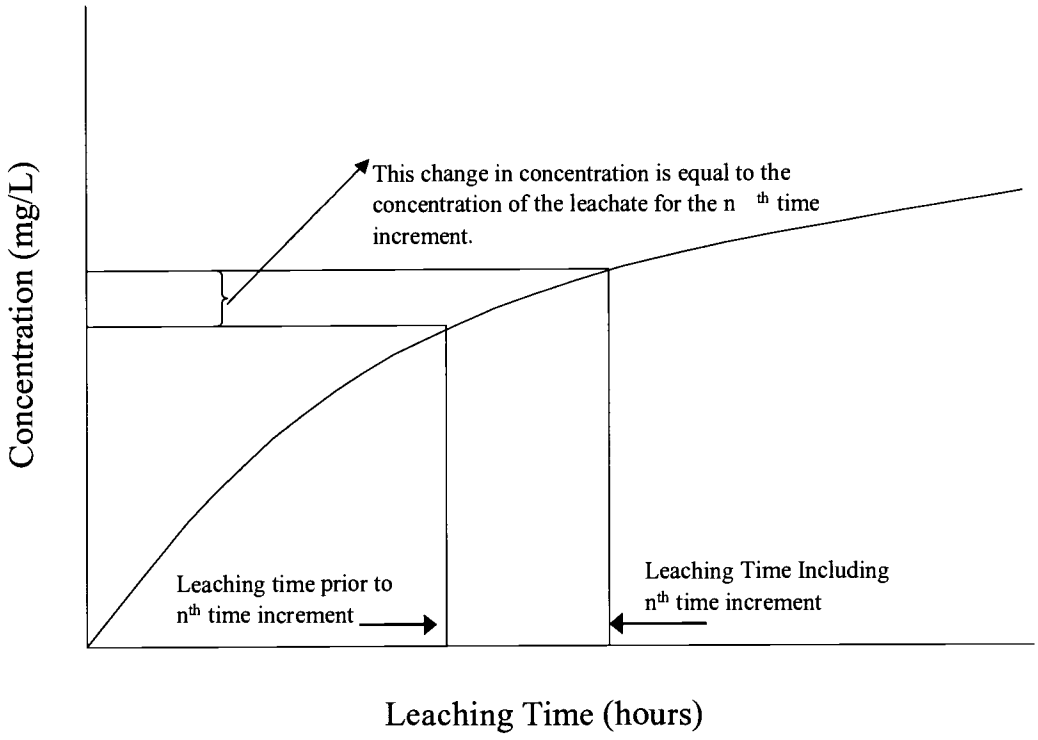

Figure 2.2.3 Points for concentration calculations for n^{th} increment.

The volume of leachate generated in the laboratory is normalized to the volume of leachate generated in the model and the surface area for leaching in the model is normalized with the surface area of material in the laboratory experiments as shown in Equation 2.2.2.

$$C_{adj} = C \times \frac{V_{lab}}{V_{model}} \times \frac{A_{model}}{A_{lab}} \qquad (2.2.2)$$

where:

C = The concentration calculated from the leaching time (mg/L)

V_{lab} = Volume of leachate generated in the laboratory (L)

V_{model} = Volume of leachate generated in the model (L)

A_{lab} = Area for leaching in laboratory (m^2)

A_{model} = Area for leaching in the model (m^2)

C_{adj} = The adjusted concentration used in the model (mg/L)

Larger leaching volumes calculated in the model result in a lower adjusted concentration due to the larger volume for dilution of the solute. Larger leaching areas in the model result in a higher adjusted concentration due to the larger area for leaching of solute.

The result is two series of data (volume and concentration) for the leachate that will infiltrate into the soil. The data define the input boundary condition for the algorithm used to solve the advection dispersion equation. Algorithm development and the boundary conditions are discussed further in Section 3.

Primary model output consists of concentrations and loads into the underlying aquifer for the simulated reference environment. Flow rates, water volumes, and toxicity estimates are also provided. If the surface or subsurface runoff is the primary water volume of interest, then the concentration is of principal concern. If the surface or subsurface runoff will mix with adjacent receiving waters, e.g., in a roadside ditch or stream or in an aquifer, then loads are of primary concern. Elementary mixing (dilution) computations may be performed with the groundwater transport option to carry the impact analysis further. The output from this model may be used as input to a more sophisticated receiving water model.

A model may be defined as a simplified representation of a real world system that attempts to simulate the relevant excitation-response relations of the real-world system. Due to the complexity of real-world systems there is a need for simplification. Simplification is introduced as a set of assumptions that expresses the nature of the system and the features that are relevant to the problem under investigation. This includes the geometry of the investigated domain, the way heterogeneities will be smoothed out, the nature of the porous medium (e.g., its homogeneity, isotropy), the properties of the fluid (or fluids) involved, and the type of flow regime under investigation among other factors (Bear et al., 1992). In the model IMPACT several assumptions are made in the use of the laboratory data for modeling purposes and about the physical environment being simulated. Due to the simplicity of the model there are limitations as to the phenomena that the model can simulate. These assumptions and limitations are listed below.

Key Assumptions of the Model

- The effects of leaching and individual environmental effects, which are tested independently, can be superimposed.
- Dominant environmental effects are taken into account. Laboratory experiments conducted cover most of the realm of possible environmental situations.
- The sorbed and dissolved solutes are in equilibrium. Sorption phenomena are not rate-limited and sorption is reversible.
- The soil is homogeneous.
- The flow is assumed to be uniform and unidirectional (downward within the reference environment).

- Soil moisture is assumed to be constant over the course of a model run.
- The removal mechanisms in the soils are assumed to be sorption and biodegradation.

Key Limitations

- The model cannot simulate heterogeneous or structured soils, except for layering.
- The model cannot simulate preferential flow.
- The model does not simulate changes in the soil moisture content.
- The model cannot simulate chemical reactions (other than sorption and biodegradation), such as precipitation or formation of complexes.
- Leaching rates for large highway surfaces are extrapolated from small (76 cm^2) flat plate studies in the laboratory. Similar extrapolation occurs for column studies of fill materials.

Several recent features enhance the functionality of the model:

- the option of using long-term hydrologic data,
- a decrease in the source term concentration with time,
- the ability to simulate multiple soil layers with multiple model runs, and
- additional forms providing help menus and access to all laboratory parameters used in the model.

For a more detailed description of the model development the reader is referred to Eldin et al. (2000) and Nelson et al. (2000c). For guidance on the operation of the model the reader is referred to Hesse et al. (2000).

2.3 Theoretical Considerations

2.3.1 Introduction

The majority of the discussion of theoretical considerations is reproduced from Appendix F of Eldin et al. (2000).

Soil is a very complex system composed of solid, liquid, and gaseous phases, and each of these phases possesses organic and inorganic constituents as well as inert and active compounds. The heterogeneous character of the environment strongly affects the physical and chemical properties of the soil, thereby having a direct effect on solute transport and sorption in soil. The problems of modeling the soil-water complex can be divided into two categories: (1) the advective-dispersive transport of solutes through soil, and (2) the physical or chemical transformations of the solute during transport (Travis and Etnier, 1981). Several RRR processes that greatly affect the ultimate mass flux and concentration distribution in space and time are indicated in Table 2.3.1.

Table 2.3.1.1 Physical, chemical and biological processes included in the fate and transport model that affect the degradation of water quality constituents from a highway environment (Eldin et al. 2000)

Process	**Nature**	**First Order?**	**Comments**
Sorption	Chemical-physical	No	Adsorption on sediment. Sediment transport governs constituent transport in surface waters, retardation in subsurface waters.
Volatilization	Chemical-physical	Yes	Governed by fluid turbulence and/or atmospheric mass transfer. Henry's law constant is key parameter.
Biodegradation	Biological	Usually	Decay through microbial decomposition. Mineralization is a breakdown of organic matter to CO_2, N_2 and H_2O.
Photolysis	Chemical-physical	Usually	Photolysis rate is a complex function of light absorbency properties of compound.

The processes listed in Table 2.3.1.1 summarize the methods by which a contaminant can be degraded or transformed as it moves along a surface water pathway in the fate and transport model of this project. Subsurface processes from this table include only sorption and biodegradation. Additional processes affecting subsurface contaminant transport include immobilization, ion exchange, dissolution/precipitation, complexation and redox reactions (Charbeneau and

Daniel, 1993; Mercer and Waddell, 1993). A full explanation is beyond the scope of this document, but it is useful to note that several of the degradation processes can be represented by a first-order reaction.

2.3.2 Transport

Advection and diffusion are physical processes that govern the motion of contaminant particles traveling in a water pathway. Advection is transport by the mean fluid velocity, while diffusion is transport away from the region of high concentration. Hydrodynamic dispersion is an additional diffusive-type mixing mechanism in both surface and subsurface transport (Huber, 1993; Mercer and Waddell, 1993).

Mathematically, advective flux is defined as

$$F_a = v\,C \qquad (2.3.2.1)$$

where

F_a = advective flux (mass/area-time);

v = average velocity (length/time); and

C = concentration (mass/volume).

Of course, appropriate symbols may be used to indicate velocity and flux in a given direction, since flux is a vector quantity. Here, the velocity v may be assumed to be in the x-direction, or more generally, in the flow direction.

Diffusive and dispersive flux is proportional to the gradient of concentration,

$$F_d = -D_l \, dC/dz \qquad (2.3.2.2)$$

where

F_d = diffusive/dispersive flux (mass/area-time);

dC/dz = concentration gradient in z-direction (mass/length^4); and

D_l = diffusion/dispersion coefficient (length^2/time).

The negative sign indicates a positive flux in the direction of decreasing concentration. Diffusive-type flux can originate from any of three mechanisms: molecular diffusion, turbulent diffusion, and laminar or turbulent hydrodynamic dispersion. Molecular diffusion is important only very near boundaries and in three-dimensional groundwater studies. Turbulent diffusion governs three-dimensional surface water transport, while hydrodynamic dispersion usually dominates one- or two-dimensional surface water transport and unidirectional groundwater transport.

Hydrodynamic dispersion results from a spatial averaging of a concentration profile across a region of varying velocity, e.g., across a stream cross-section or across a collection of solids and voids in a porous medium. It applies only when such an averaging is employed to define the concentration (i.e., the spatial average concentration at a location). Macroscopic dispersion in soils, which is evidenced at the field scale, is generally believed to have its roots in the variation of hydraulic

conductivity within the soil (Abriola, 1987). In such instances, dispersion is almost always the most dominant diffusive-type mechanism.

In practice dispersion is used as an empirical parameter that includes all the solute spreading mechanisms that are not directly included in the advection-dispersion equation (Nielson et al., 1986). The conceptual model of dispersion accounts for the additive phenomena of molecular diffusion and mechanical dispersion. In a one-dimensional system the dispersion coefficient D_l (length^2/time) is written as (Charbeneau and Daniel, 1993)

$$D_l = \tau D_m + \alpha_d \left| V_p \right|^m \qquad (2.3.2.3)$$

where

$V_p = q/\theta$ = pore water velocity (length/time);

q = Darcy velocity or specific discharge (length/time or volume/area time);

θ = volumetric water content (volume/volume);

D_m = molecular diffusion coefficient (length^2/time);

τ = tortuosity factor (length/length);

α_d = empirical constant (dispersivity, length); and

m = empirical constant (unitless).

Under saturated conditions (as assumed in the model) θ is equal to the porosity (η) of the soil. The tortuosity factor depends on the water content, but not on the pore water velocity. When applied to a homogenous, saturated soil, the exponent m is approximately unity, and the parameter α_d is the dispersivity. Chemical transport in

geologic media is strongly influenced by spatial variations in hydraulic conductivity. The variations produce fluctuations in the groundwater velocity, which cause dissolved chemicals to spread at rates considerably greater than those observed in laboratory column experiments (Neuman, 1990). For unsaturated soils, α ranges from about 0.5 cm or less for laboratory-scale experiments to about 10 cm or more for field-scale experiments (Charbeneau and Daniel, 1993). The diffusion coefficient for a solute in the soil environment is much smaller than in water. The soil matrix causes the solute to follow a more tortuous (and therefore longer) path, and adsorption of the solute by the soil contributes to the lower observed values of dispersion (Freeze and Cherry, 1979).

To estimate the lower limits of hydrodynamic dispersion for vertical infiltration, let us assume a rate of 0.1 inches (2.54 mm) per hour. Applying a dispersivity of 5 mm, characteristic of larger laboratory experiments (but lower than field scale dispersivities, which are more appropriate to the model), would give a rate of dispersion of 12.7 mm^2/hour. This result is compared to values for dispersion given by Tchobanoglous and Schroeder (1985) in Table 2.3.1.1.

Table 2.3.2.1 Comparison of Model and Typical Field Values of Coefficients of Molecular Diffusion

Material	**Coefficient of**	
	Molecular Diffusion (mm^2/hr)	**Hydrodynamic Dispersion (mm^2/hr)**
fine grained clay materials	0.036 to 0.36	
course grained material	≤ 7	
model estimate		≥ 12.7

While hydrodynamic dispersion could be lower with lower flow velocities or dispersivity, typical values in simulations of field conditions will be larger than the example of 12.7 mm^2/hour. This is nearly twice as large as the upper limits of dispersion due to molecular diffusion. As rates of molecular diffusion increase in more porous materials, pore velocities are likely to increase as well. Dispersion due to mechanical dispersion will generally be several times larger than dispersion due to molecular diffusion for field situations simulated by the model (infiltration of rainfall) because pore velocities will typically be large and limited only by the hydraulic conductivity of the soil and rainfall intensity. For this reason dispersion in the model is limited to mechanical dispersion.

When conservation of mass is defined for a control volume subject to advection and diffusion/dispersion, the governing equation that results is known as

the advective-diffusion (or advective-dispersion) equation and defines the variation of concentration in space and time, C(x,y,z,t) (Huber, 1993; Mercer and Waddell, 1993). Solution of this equation is well documented in the literature and is the core of many numerical models. The numerical solution used in IMPACT is developed in Section 3.1

2.3.3 Sorption / Desorption

A sorption "isotherm" is the relationship between a constituent in its dissolved and sorbed form. The term sorption refers to the selective uptake and storage of dissolved solute species by soil. Adsorption is the process whereby solutes adhere to the surface of soil particles, while absorption refers to solute accumulating within the soil matrix as in chemisorption and ion exchange. Sorption is an inclusive term used to describe both surface (adsorption) and subsurface (absorption) reactions of solute with soil particles (Ghadiri and Rose, 1992). The sorptive capacity of a solid for a solute tends to increase as the fluid phase solute concentration increases. The term "adsorption isotherm" is generally used to include all of the processes acting to establish equilibrium between dissolved and sorbed solute. This is particularly true in the case of empirical sorptive relationships, which may include other processes in addition to adsorption (Travis and Etnier, 1981). Generally, sorption experiments are not able to differentiate the mechanisms responsible for the removal of solute.

Soil sorption isotherms can be highly dependant on pH. Weak acids are more readily sorbed when in the free acid form at low pH, while weak bases are more readily sorbed at high pH when in the free base form. Substances in the soil matrix (e.g., organic matter) have a higher tendency to form complexes with heavy metals as the pH value increases. At higher pH values the chemical structures that can complex with metals are more likely to be deprotonated and able to interact (complex) with metallic cations. Therefore, the mobility of metal ions is highly dependant upon pH. All column studies conducted as part of the NCHRP project have been conducted at constant pH values, as have the soil sorption studies. When estimating sorption parameters for modeling purposes, it is important to account for the potential effects of variation in pH between the laboratory and site conditions. The characteristics of the soil at the site to be modeled (e.g., organic content, buffering capacity, etc.) will have the largest influence on the pH to which the solute material will be exposed.

In a general sense, this sorption reaction can be either kinetic, where the relative amount of solute in the soil solution and in the soil matrix is changing with time, or it can be an equilibrium situation in which the sorbed and dissolved concentrations are attained rapidly and remain constant thereafter. An equilibrium situation can be defined more precisely as circumstances in which the rate of sorption between the soil solution and the solid phase is much greater than the rate of change in concentration of solute in the soil solution because of any other cause (Travis and Etnier, 1981). Adsorption reactions considered instantaneous are

described by equilibrium isotherms. These isotherms can be of the linear, Freundlich, or Langmuir type, or of many other functional forms (Nielson et al., 1986). A kinetic situation can then be defined as one for which an equilibrium sorption isotherm cannot be used. For example, the applicability of an equilibrium isotherm can be dependent on the sorptive reaction rate relative to the soil water flux. If the reaction rate is much faster than the flow rate, then the equilibrium assumption may be applicable; however, if the reaction rate is slow in comparison to the flow rate, the reaction kinetics may better describe the situation (Travis and Etnier, 1981).

Sorbed chemicals travel with their associated sediments. Thus, chemicals sorbed in surface waters move with (or are retained by) sediments, whereas chemicals sorbed in groundwater transport are retained or retarded (their appearance or "breakthrough" delayed) due to sorption. Retardation thus delays and may reduce the magnitude of contaminant concentrations through soils and other porous media. Chemicals that are sorbed can subsequently be desorbed upon passage of cleaner water through the soil column. The desorption process may or may not follow the same kinetics as the sorption process; however, it is typically a slower process.

For modeling subsurface contaminant transport, the sorption process is often simplified by assuming instantaneous equilibrium, isotherm linearity, and reversable sorption-desorption. These assumptions simplify transport analysis and

can be adequate for certain conditions (Brusseau et al., 1989). These conditions are considered to describe transport processes adequately for use in the material model IMPACT.

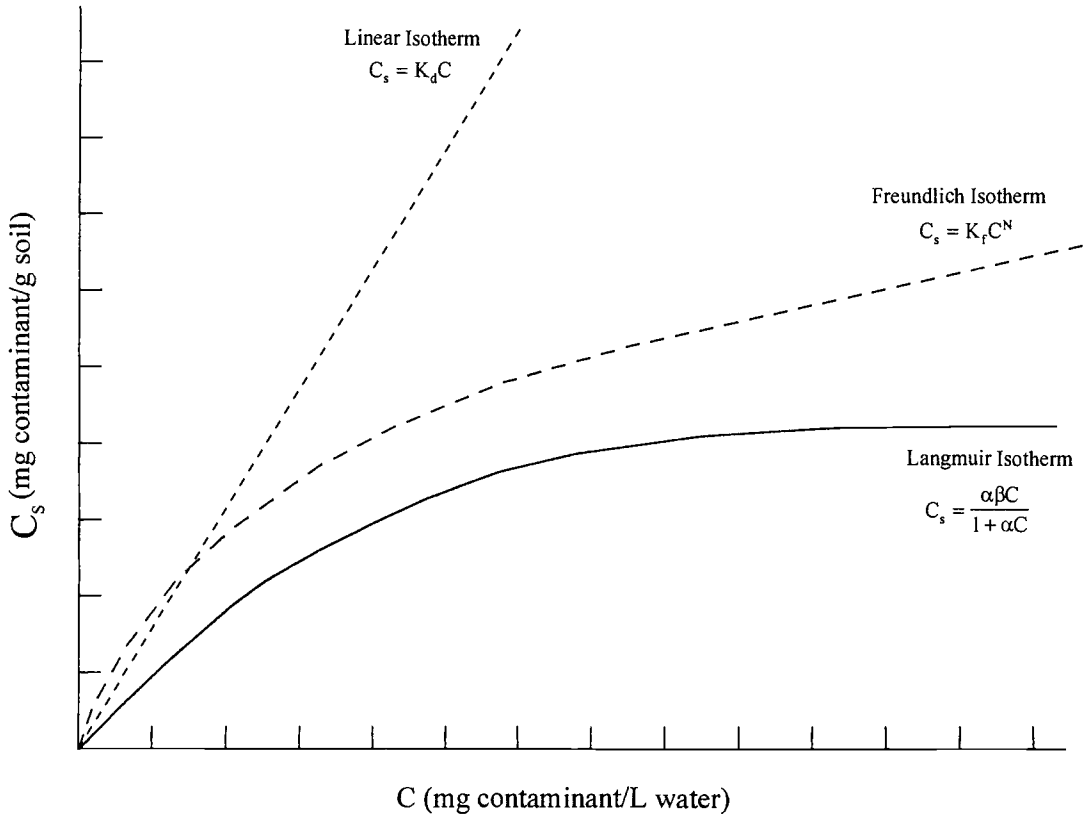

Figure 2.3.3.1 Shapes of standard soil sorption isotherms (after Mills et al., 1985).

For all three isotherms discussed the dissolved solute concentration (C) is mg/L and the sorbed solute concentration (C_s) is mg/g.

Linear Isotherm

The simplest and most widely used of the equilibrium sorption isotherms is characterized by a linear relationship (Figure 2.3.3.1) (Fetter, 1993).

$$C_s = K_d C \qquad (2.3.3.1)$$

where

C_s = mass of sorbed chemical per mass of sediment (mg/g);

K_d = partition or distribution coefficient (L/g); and

C = concentration in liquid phase (mg/L).

Sorption kinetics are typically rapid (seconds to minutes) and first-order, although not universally so. Most attention is focused on the partition coefficient, K_d. It has a typical range of about 0.1 to 10^4 L/g (Chapra, 1997) and is strongly a function of the organic carbon content of the sediment/soil (Karickhoff et al., 1979; Mills et al., 1985; Schwarzenbach et al., 1993):

$$K_d = K_{oc} [0.2(1-F)x^s_{oc} + Fx^f_{oc}] \qquad (2.3.3.2)$$

where

K_{oc} = partition coefficient expressed on an organic carbon basis (L/g);

F = mass fraction of fine sediments (diameter < 50 um);

x^s_{oc} = organic carbon content of coarse sediment fraction (mass fraction); and

x^f_{oc} = organic carbon content of fine sediment fraction (mass fraction).

The bracketed term in Equation. 2.3.3.2 is sometimes denoted as f_{oc} or the fraction of organic carbon. Thomann and Mueller (1987) indicate a typical range of 0.001 to 0.1 for f_{oc}, although Chapra (1997) points out that the top end could be as high as 0.4 when the carbon content of certain living cells in surface water is accounted for. K_{oc} is the ratio of the concentration of the chemical on organic carbon (mg/g) to the concentration in water (mg/L). This coefficient is in turn related to commonly tabulated values (Verschueren, 1983; Schnoor et al., 1987; Charbeneau and Daniel, 1993; Schwarzenbach et al., 1993) of the octanol-water partition coefficient, K_{ow}, as

$$K_{oc} = 0.00063\ K_{ow} \qquad (2.3.3.3)$$

where K_{ow} = equilibrium concentration of chemical in octanol divided by the concentration of the chemical in water (dimensionless); and the coefficient 0.00063 has units of L/g (often seen in the literature as 0.63 mL/g). K_{oc} may also be related to K_{ow} by various logarithmic relationships (Kollig, 1993; Hemond and Fechner, 1994) as a function of pH and pK_a values and/or to the solubility in water of the chemical in question (Schwarzenbach et al., 1993). (pK_a is the negative logarithm of the acid dissociation or ionization constant.)

Linear sorption is not always appropriate, and other models may be used (Mills et al., 1985). Without delving into the theoretical background, functional forms for two common non-linear isotherms (Freundlich and Langmuir) are shown in Figure 2.3.3.1.

Freundlich Isotherm

The empirical Freundlich isotherm (Fetter, 1993) is

$$C_s = K_f C^N \tag{2.3.3.4}$$

where

C = concentration in liquid phase (mg/L);

C_s = sorbed concentration in solid phase (mg/g); and

K_f, N = coefficients found by regression.

A partition coefficient is the slope of the solid vs. liquid concentration relationship. For the Freundlich isotherm,

$$dC_s/dC = K_f N C^{N-1} \tag{2.3.3.5}$$

and it clearly depends on concentration.

The Freundlich isotherms are derived from the sorption data by plotting the sorbed concentration (mg/g) versus the concentration of material remaining in solution (mg/L). The coefficient and the exponent of a power fit of the plotted data points correspond directly to the Freundlich coefficient (K_f) and exponent (N) used in the Freundlich isotherm shown in Equation 2.3.3.4. When C_s and C are plotted on log scales, parameters N and K_f may be determined from the slope and intercept respectively.

This is the oldest of the nonlinear isotherms and has been used widely to describe the sorption of solutes by soils. It should be kept in mind that the flexibility of the two constants N and K_f allow for easy curve fitting but does not guarantee accuracy if the data are extrapolated beyond the experimental points. One limitation of the Freundlich isotherm, similar to the linear isotherm model, is that it does not imply a maximum quantity for sorption.

Langmuir Isotherm

Langmuir (1918) developed an adsorption isotherm to describe the adsorption of gases by solids. Langmuir assumed that the surface of a solid possesses a finite number of adsorption sites (Travis and Etnier, 1981). This model is based upon the idea of an upper limit of adsorption. The maximum amount of adsorption (or sorption) occurs when the surface of the solid is covered with a closely packed adsorbed layer of gas molecules.

The standard form of the Langmuir isotherm is (Fetter, 1993)

$$C_s = \alpha\beta C/(1 + \alpha C) \qquad (2.3.3.6)$$

where

α = measure of the bond strength holding the sorbed solute on the soil surface (L/g)

β = the maximum amount of solute that can be adsorbed by the soil matrix (mg/g)

C = dissolved solute concentration (g/L)

C_S = sorbed solute concentration (mg/g).

Parameters for the Langmuir isotherm (Equation 2.3.3.6) are obtained by plotting C/C_s versus C, as shown in Figure 2.3.3.2. The slope is equal to $1/\beta$ and the intercept is equal to $1/\alpha\beta$ (Fetter, 1993).

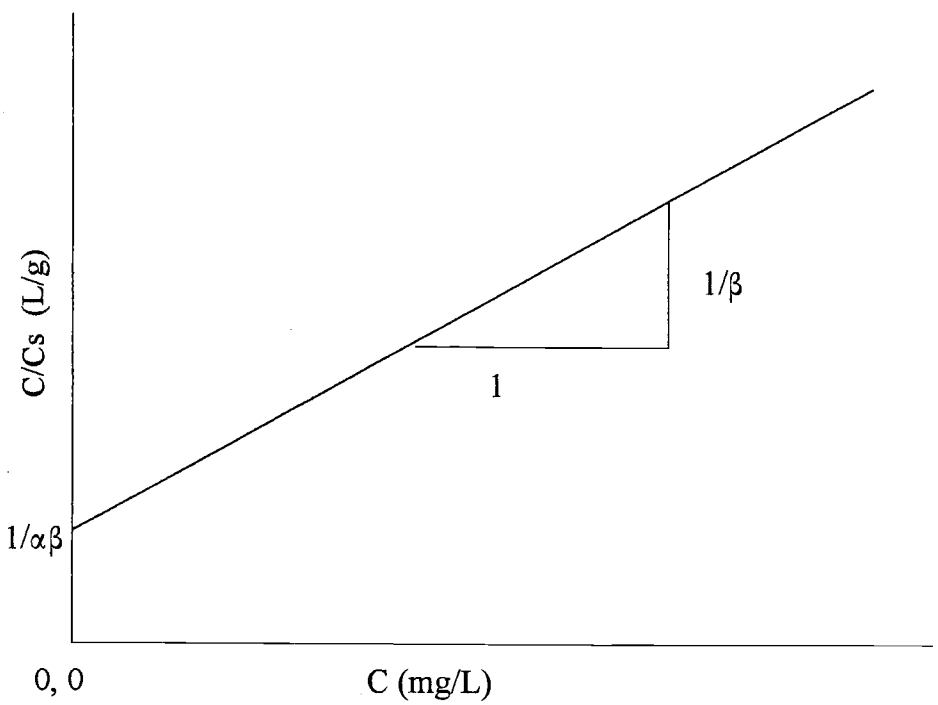

Figure 2.3.3.2 Data analysis for Langmuir isotherm

Surface Water Relationship

In surface water the equilibrium concentration of a constituent in water that is attached to sediment is related by (Mills et al., 1985; Chapra, 1997):

$$C = C_T/(1+K_dS) \qquad (2.3.3.7)$$

where

C = concentration in water (mg/L);

C_T = $C + S\,C_S$ = total concentration, water plus sediment (mg/L);

C_S = $K_d\,C$ = concentration in sediment form (mg/g);

S = suspended sediment concentration (g/L); and

K_d = partition coefficient (L/g).

Partition coefficients range from 1 to 10^4 L/g. For low values nearly all the constituent is present in a dissolved form as is also true when suspended sediment concentrations are very low. When partition coefficients and suspended sediment concentrations are high simultaneously, most of the constituent is present in a sorbed form.

2.3.4 Biodegradation

Biodegradation refers to biologically mediated processes that chemically change a solute. Primary biodegradation refers to any biologically induced structural modification in the parent compound that changes its molecular integrity. Microorganisms are responsible for biodegradation. Reactions take place in both the presence and in the absence of oxygen. Reactions in the presence of oxygen are aerobic, whereas those in the absence of oxygen are anaerobic (Srinivasan and Mercer, 1988).

Organic constituents in a leachate may be subject to biodegradation. In this project this was usually tested by examining the loss of total organic carbon (TOC, serving as a surrogate for toxic organic compounds) in a leachate over time after addition of a mixed culture of aerobic bacteria. The results are generally well represented by a first-order decay process with first-order decay coefficient k_b.

$$dC/dt = - k_b C \tag{2.3.4.1}$$

$$C(t) = C_o e^{-k_b t} \tag{2.3.4.2}$$

where

k_b = first order biodegradation constant ($time^{-1}$),

t = time,

C = concentration,

C_o = initial concentration at time $t = 0$.

The decay term (Equation 2.3.4.1) is added to the conservation equation being used, and the latter is solved numerically. Note that the exponential decay of Equation 2.3.4.2 is true for all first-order processes including biodegradation, volatilization, and photolysis with the use of appropriate rate constants.

2.3.5 Hydraulic Conductivity

The hydraulic conductivity decreases sharply with decreasing water content in unsaturated soils. In unsaturated soils the pore water is under negative pressure

potential caused by surface tension and is referred to as the capillary potential, ψ. The capillary potential is a function of the water content of the soil, θ. As the water content of the soil decreases so do the values of the capillary potential and the wetted cross sectional area, which results in the remaining water having a reduced potential for flow (Fetter, 1993). These factors contribute to the complex relationship between the soil moisture content and hydraulic conductivity, K, of the soil. Water content is related to soil-water tension through the soil-water retention curve, and the hydraulic conductivity is often shown as a function of soil-water tension.

The soil water retention and hydraulic conductivity functions are the crucial parameters for predicting unsaturated flow, but their theoretical description and measurement can be a frustrating challenge for hydrologists and scientists. Direct field measurements to determine the unsaturated hydraulic conductivity are time consuming, expensive, and usually subject to simplifying assumptions (Nielson et al., 1986). Measurements or description of the soil water retention and hydraulic conductivity for disturbed soils can only be more challenging. By necessity the highway environment overlies highly disturbed soils that undergo compaction for structural stability. This compaction results in soils with less porosity and, therefore, less soil water content, which in turn must decrease the hydraulic conductivity. Unless field measurements are conducted after compaction but prior to construction of the road surface, access for any measurement of the physical properties of the soils is likely to be nonexistent.

A study by Wierenga (1977) showed that an average pore water velocity taken as a constant could be used effectively instead of the more complicated transient condition. This suggests that the simpler models based on steady state flow can at times provide realistic predictions in the field. This is particularly true if one is primarily interested in long-term rates and amounts of solute leaving the upper part of the vadose zone, neglecting short-term and dynamic oscillations near the soil surface (Nielson et al., 1986). This simplification in the model is represented by the assumption that flow occurs only when infiltration is occurring due to rainfall. The model neglects the drainage of soil moisture to the water table during dry periods. The result is the overestimation of the time required for solute to reach the underlying aquifer. Although this results in some temporal inaccuracy in the short term, mass loadings to the aquifer, which are the emphasis of this model, are the same regardless of the assumption of a constant seepage velocity.

It is highly unlikely that information on the soil water retention curve will be available for the highly disturbed soils underlying the highway grade. Instead, a simplifying assumption must be applied. The model assumes that water flow in the downward direction through the soil occurs at a constant water content at saturation of the soil pore space. The Darcy velocity can be described by Darcy's Law

$$Q/A = q = -K\ \Delta h/\Delta l \qquad (2.3.5.1)$$

where

Q = flow rate (length^3/time)

A = cross sectional area through which flow occurs (length^2)

q = specific discharge (length/time)

K = saturated hydraulic conductivity (length/time)

$\Delta h/\Delta l$ = hydraulic gradient (length/length).

The maximum specific discharge in the soil is the saturated hydraulic conductivity. If the infiltration rate (from available precipitation) is less than the saturated hydraulic conductivity in the model, then the specific discharge is set equal to the infiltration rate (L/T). The actual seepage velocity of water (V_p) in the soil is related to the specific discharge by the equation

$$V_p = q / \eta \qquad (2.3.5.2)$$

where

η = the porosity of the soil (unitless).

Under saturated flow conditions the soil water content, θ, is equal to the soil porosity, η. The specific discharge in the model is assumed to be the minimum of the infiltration rate or the saturated hydraulic conductivity, K.

2.4 Modeling Options

Prior to the development of IMPACT consideration was given to the use of existing models for incorporation of results from the NCHRP project. Numerous transport models exist, such as Aqua 3D and Sesoil from the Scientific Software Group; MODFLOWT from GeoTrans; GMS (Groundwater Modeling System) and PRINCE from Boss International; Migrate from GAEA Environmental Engineering Ltd.; and RAND3D and TARGET from International Ground Water Modeling Center. Some models such as Aqua 3D, GMS, and MODFLOWT simulate contaminant transport in three dimensions and are more suited to modeling transport in groundwater flow rather than infiltration of leachate through the vadose zone. Other models such as Sesoil and Migrate are capable of simulating one-dimensional infiltration from a surface source; however, all of the aforementioned models are proprietary. This precluded the use of any of these models for the NCHRP project as they would not be able to be modified to include a database containing the extensive laboratory data generated from the project or to simulate the desired highway reference environments. Summary information about these proprietary models and additional proprietary and non-proprietary models is available at the Oklahoma State University web site http://geotech.civen.okstate.edu/ejge/ppr9601/contam3d.htm.

Numerous public domain models also exist, but the majority of the available models simulate groundwater, not unsaturated zone flow. The most promising model for adaptation for use with the NCHRP project, CHEMFLO, was developed

by the U.S. Environmental Protection Agency and is available through several US suppliers at a nominal cost. It can also be downloaded from the EP web site http://www.epa.gov/ada/ csmos/models/chemflo.html with support documentation (Nofziger et al., 1989).

CHEMFLO is a DOS-based one-dimensional Fortran finite difference screening level model for simulation of the movement of water and chemicals in unsaturated soils. Water movement is solved using Richard's equation. The equation describing the movement of chemicals includes advective and dispersive transport, first-order decay in the liquid and solid phase, zero-order production or decay, and linear equilibrium adsorption (using a retardation coefficient). While it was desired to use a one-dimensional finite difference screening level model, the level of sophistication of CHEMFLO is well beyond the level of data available to support the modeling in the NCHRP project. Furthermore, the ability to simulate reversible sorption using either the linear, Freundlich, or Langmuir isotherms was a desired trait for a model to be used as part of the NCHRP project, thus precluding use of CHEMFLO. Another shortcoming of CHEMFLO for use in the NCHRP project was the DOS-based format and Fortran language, as this would make it difficult to link the model with the voluminous Excel™ laboratory database.

It is likely that there are models possessing many of the capabilities desired in a model for use in conjunction with the NCHRP project. However, it is highly unlikely that any existing model possesses all of the desired characteristics. Of primary importance to the modeling effort were the incorporation of the unique

laboratory leaching and toxicity data and the ability to simulate different highway reference environments. Many models allow for the simulation of complicated source conditions, but none of the models reviewed provided the necessary flexibility to simulate flow through the six highway reference environments included in IMPACT. None of the models would allow the relatively easy inclusion of extensive laboratory leaching data to be used in conjunction with the reference environments to determine solute source conditions. Secondary to the modeling effort was the ability to easily distribute the model and database to Departments of Transportation in a form that could be easily maintained and upgraded in the future. The Excel™ format allows for easy distribution because this Microsoft software program is widely distributed and readily available. The programming language Visual Basic for Applications (VBA) is incorporated into Microsoft Excel™ and therefore allows for easy maintenance of the program, as the programming language is already present in the software required to run the model. In addition, VBA is a simple programming language that is easily understood by the novice programmer, further increasing the accessibility of the model code for maintenance and further refinements. The desired functionality of the model, ease of distribution, development of further refinements, and inclusion of laboratory data in a model database determined that development of a computer model in the Excel™ software environment was the preferred solution to the modeling needs of the project.

3 ALGORITHM DEVELOPMENT AND MODEL CALCULATIONS

3.1 Solution for Mass at a Node

One function of the model is simulation of the vertical infiltration of leachate from the highway construction and repair material environment. To do this, the advection-dispersion equation is solved in one dimension. The equation is shown below (Bedient et al., 1999).

$$\frac{\partial C}{\partial t} = \overbrace{D_l \frac{\partial^2 C}{\partial z^2}}^{\text{dispersion}} - \overbrace{V_p \frac{\partial C}{\partial z}}^{\text{advection}} - \overbrace{\frac{\rho \partial C_s}{\eta \partial t}}^{\text{sorption}} + \overbrace{\left.\frac{\partial C}{\partial t}\right|_{rxn}}^{\text{reaction}} \qquad (3.1.1)$$

where

C = concentration (mass/volume)

D_l = longitudinal dispersion coefficient (length^2/time)

V_p = pore velocity in soil (length/time) (Darcy velocity/ porosity)

C_s = sorption (mass sorbed/mass soil)

ρ = bulk density of soil (mass/volume)

η = porosity of soil (fraction of pore space)

t = time

rxn = biological or chemical reaction other than sorption ($r = -k\ \delta C/\delta t$)

z = unit of length in the vertical direction.

The solution method for the advection-dispersion (AD) equation needs to be computationally efficient to allow long-term runs (using real hydrologic data) on

home or office personal computers. Two numerical options, finite elements and finite differences, were considered for its solution. Finite element methods divide the overall spatial domain into a series of smaller finite domains termed finite elements, with the unknown function, C(z,t), represented by an interpolating polynomial which is continuous with its derivatives within the specified element (Lapidus and Pinder, 1982). Finite element methods are more flexible in representing two- and three-dimensional geometries but hold no particular advantage over finite difference methods for one-dimensional systems. Finite difference methods represent the domain of interest by a set of evenly-spaced points (nodes) with the derivatives of the AD equation simulated as difference equations. Different options for the difference representations can be derived by expansion of the derivatives using a Taylor series (Lapidus and Pinder, 1982). Generally, finite difference formulations are straightforward representations of the governing partial differential equation. One of the simplifying assumptions of the model is that flow is solely in the z dimension (vertical infiltration). As finite difference methods are much easier to implement and there are no distinct advantages to finite element methods when applied in one dimension, a finite difference scheme is used in the model.

When the sorption term in the AD equation is a nonlinear function of the concentration (often represented by the Freundlich or Langmuir sorption isotherms), finite difference approximations of the AD equation cannot be solved by direct algebraic methods. The change in concentration, $\delta C/\delta t$, depends upon the

change in sorption $\delta C_S/\delta t$, which in turn depends upon the change in concentration. An iterative method is required to solve the AD equation in this form.

Often the equation is rearranged so the change in sorption and concentration with time are on the same side of the equation. This allows the separation of the sorption term into a term involving the retardation factor as follows:

Rearranging Equation 3.1.1,

$$\frac{\partial C}{\partial t}\left[1+\frac{\rho\,\partial C_s}{\eta\,\partial C}\right]=\frac{D_l\partial^2 C}{\partial z^2}-\frac{V_p\partial C}{\partial z}+\left.\frac{\partial C}{\partial t}\right|_{rxn} \tag{3.1.2}$$

where R_d (retardation coefficient) is given by

$$R_d=\left[1+\frac{\rho\,\partial C_s}{\eta\,\partial C}\right] \tag{3.1.3}$$

The AD equation becomes

$$\frac{\partial C}{\partial t}=\frac{\dfrac{D_l\partial^2 C}{\partial z^2}-\dfrac{V_p\partial C}{\partial z}+\left.\dfrac{\partial C}{\partial t}\right|_{rxn}}{R_d} \tag{3.1.4}$$

The R_d term can be calculated based on the derivative (δC_S / δC) of the isotherm used to fit the sorption data. (e.g., Equations 2.3.3.4 and 2.3.3.5). This works well to account for the movement of dissolved solute but does not provide sufficient information to track the sorbed mass. Instead of utilizing the retardation

coefficient and iterative methods, an alternate rearrangement of the AD equation allows a more direct solution.

In order to solve for the change in mass sorbed to the soil, ($\partial C_S/\partial t$), it is necessary to keep track of mass sorbed in the soil at each node. It is easy enough to calculate the change in mass in a node and the resulting changes in the dissolved and sorbed concentrations, which eliminates the need to calculate the retardation coefficient. Thus, taking the AD equation with time-dependent changes in sorption and concentration on the same side of Equation 3.1.2 and multiplying each side of the equation by the porosity, η, and the volume of a representative node, V_{node}, used in the finite difference approximations results in equation 3.1.5.

$$V_{node}\left[\eta\,\partial C + \rho\,\partial C_s\right] = V_{node}\,\eta\left[\underbrace{\frac{D_l\partial^2 C}{\partial z^2}}_{\text{dispersion}} - \underbrace{\frac{V_p\partial C}{\partial z}}_{\text{advection}} + \underbrace{\left.\frac{\partial C}{\partial t}\right|_{rxn}}_{\text{reaction}}\right]\partial t = \Delta Mass_{node} \quad (3.1.5)$$

where

$\Delta Mass_{node}$ = the change in mass at a node over a time step

The other variables are as defined for Equation 3.1.1.

The terms on the left-hand side of the equation represent the change in mass at a node with respect to time. The change in mass at a node depends only on dispersion, advection, reaction of the solute, and the physical parameters of the node, volume, and porosity.

Backwards-difference approximations for $\delta C/\delta z$ are used because the change in concentration at a node due to advection is a function of the concentration in solution at the node and the concentration in solution at the adjacent node ("upstream") from which the water is advecting (Smith, 1985). The concentration gradient utilizing node concentrations from the previous time step is given by Equation 3.1.6.

(3.1.6)

where

$C(i)$ = the dissolved concentration of solute at node i

$C(i-1)$ = the dissolved concentration of solute at node i – 1

Δz = the distance between adjacent nodes.

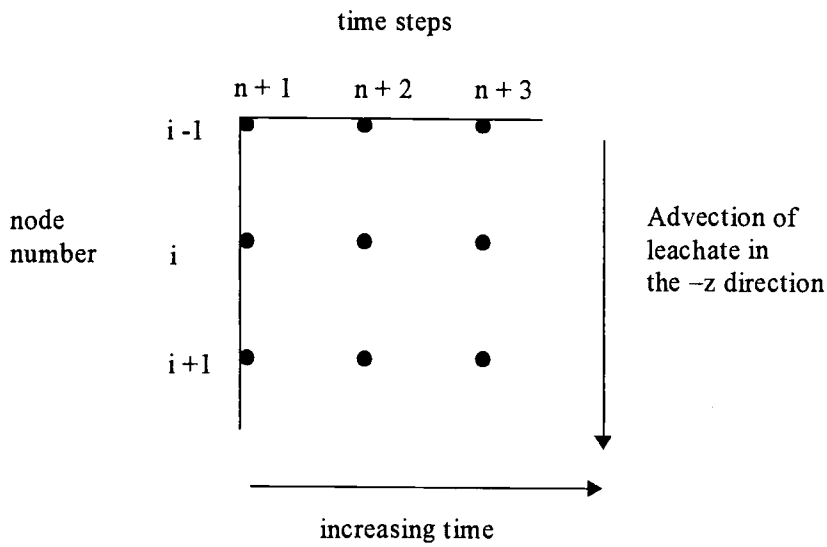

Figure 3.1.1 Schematic of node matrix with time and distance (z direction)

The n values in Figure 3.1.1 represent the iterations for solution of the advection-dispersion equation, where the time of the iteration is given by the summation of the time steps of the previous iterations ($t = \Delta t_1 + \Delta t_2 + \ldots + \Delta t_n$).

The central difference approximation for $\delta^2C/\delta z^2$ is given by (Lapidus and Pinder, 1982; Smith, 1985) as

$$\frac{\partial^2 C}{\partial z^2} \cong \left[\frac{C(i+1) - 2C(i) + C(i-1)}{\Delta z^2}\right] \tag{3.1.7}$$

where variables are as given in Equation 3.1.6 and the concentrations at the node are given by the solution of the previous time step.

Biodegradation reactions are simulated with

$$\left.\frac{\partial C}{\partial t}\right|_{rxn} \cong -K_b\, C(i) \qquad (3.1.8)$$

This allows for the direct solution in the change in mass at a node ($\Delta Mass_{node}$) for a given time step. The substitution of Equations 3.1.6, 3.1.7, and 3.1.8 into Equation 3.1.5 is shown in Equation 3.1.9.

$$\Delta Mass(i)\,\Big|_{n+1} = V_{node}\,\eta\left[\frac{D_l\big(C_n(i+1)-2C_n(i)+C_n(i-1)\big)}{\Delta z^2} - \frac{V_p\big(C_n(i)-C_n(i-1)\big)}{\Delta z} - K_b C_n(i)\right]\Delta t \qquad (3.1.9)$$

where

Δt = duration of the time step (hours)

and other variables are as defined in Equation 3.1.1.

The n subscript signifies that the concentrations used in the solution of Equation 3.1.9 for the n + 1 iteration are given by the solution of the previous (n^{th}) iteration .

Substitution of appropriate units for the parameters in Equation 3.1.9 yields Equation 3.1.10 (note the porosity, η, is unitless).

$$\Delta Mass(i)\,\Big|_{n+1} = L\left[\frac{(mm^2/hr)\times(mg/L)}{mm^2} - \frac{(mm/hr)\times(mg/L)}{mm}\right]\times hr \qquad (3.1.10)$$

Simplification of the units in Equation 3.1.10 results in the change in mass equal to units of milligrams (mg).

The new mass at a node is found from summation of the mass prior to the n + 1 iteration with the change in mass over the time step is shown in Equation 3.1.11.

$$\text{Mass}(i)\,\big|_{n+1} = \text{Mass}(i)_n + \Delta\text{Mass}(i)\,\big|_{n+1} \qquad (3.1.11)$$

Once the mass at a node is known, the left-hand side of Equation 3.1.5 can be evaluated for the sorbed and dissolved concentrations with the selected sorption isotherm. This will be shown in Equation 3.2.1.1.

Once the sorbed and dissolved concentrations are known, the change of mass at the node can be found for the next time step. This process is repeated for the desired duration of the simulation.

This method of solution is in essence an accounting procedure for the mass of solute leached into the soil. The mass at each representative node is tracked for each iteration as changes occur due to advective and or dispersive flux, storage or release via sorption, or decay through biodegradation. An explicit method is used for the solution of the sorbed and dissolved concentrations. All processes affecting the change in mass (and therefore concentration) over a time step are expressed in terms of values derived during the previous iteration. Each iteration begins with the evaluation of the flux boundary condition at the first node and proceeds downward, calculating the new sorbed and dissolved concentrations at each subsequent node.

3.2 Solution of Dissolved and Sorbed Concentrations

3.2.1 Parameters

When using linear or Langmuir isotherms for sorption, the concentrations in solution and sorbed to the soil can be found directly (without iteration) by algebraic manipulation. The Freundlich isotherm requires an iterative procedure to solve for the respective concentrations at the node. Solutions for each isotherm follow.

For all sorption isotherms

C_s = concentration sorbed (mg/kg)

C = concentration in solution (mg/L)

η = porosity

ρ = bulk density of soil (kg/L)

$Mass_{node}$ = Mass of Solute at Node after Time Step

Vol_{node} = Node Volume

The mass at the node is equal to the mass sorbed plus the mass in solution at the node. The mass sorbed is given by: sorbed concentration × the bulk density × Vol_{Node}, while the mass in solution is given by the dissolved concentration × porosity × Vol_{Node}

$$Mass_{node} = V_{node}[C_s\ \rho + C\eta] \qquad (3.2.1.1)$$

3.2.2 Linear isotherm

The linear sorption isotherm is shown in Equation 2.3.3.1. Substituting the linear isotherm for C_s in Equation 3.2.1.1 gives

$$Mass_{node} = V_{node}\left[K_d\, C\ \rho + C\ \eta\right] \tag{3.2.2.1}$$

where

K_d = linear distribution coefficient (L/kg).

Solving for the dissolved concentration results in Equation 3.2.2.2.

$$C = \frac{Mass_{node}}{V_{node}\left[K_d\ \rho + \eta\right]} \tag{3.2.2.2}$$

Then the sorbed concentration can be found from the linear isotherm or from the remaining mass in the node (Equation 2.3.3.1). The latter method is used in the model (see Appendix) in an effort to minimize rounding errors.

3.2.3 Freundlich isotherm

The Freundlich sorption isotherm is shown in Equation 2.3.3.4. Substituting the Freundlich isotherm for C_s in Equation 3.2.1.1 gives

$$Mass_{node} = V_{node}\left[K_f\, C^N\ \rho + C\ \eta\right] \tag{3.2.3.1}$$

where

K_f = Freundlich sorption coefficient (L/kg when N=1), and

N = constant; and

other variables are as defined for all sorption isotherms.

When this formulation is included in Equation 3.2.1.1, an iterative solution is required to solve for C (after which C_s is determined from the remaining mass). A first estimate for C and C_s is found by increasing the estimate for C by a small increment, calculating C_s, and comparing the mass accounted for by the estimate to the known mass at the node. Once the estimates account for an amount of mass equal to or slightly greater than the mass at the node, the Newton-Raphson iterative technique (Chapra and Canale, 1985) is used to solve for the sorbed and dissolved concentration. This is shown in the programming code in the appendix.

3.2.4 Langmuir isotherm

The Langmuir sorption isotherm is shown in Equation 2.3.3.6. Substituting the Langmuir isotherm for C_s in Equation 3.2.1.1 gives Equation 3.2.4.1

$$\text{Mass}_{\text{node}} = V_{\text{node}} \left[\left(\frac{\alpha \beta C}{1 + \alpha C} \right) \rho + C \eta \right] \qquad (3.2.4.1)$$

where

α = absorption constant related to binding energy (L/mg), and

β = maximum amount of solute that can be absorbed by the soil (mg/g); and

other variables are as defined for all sorption isotherms.

Equation 3.2.4.1 can be rearranged as follows:

$$\eta\ \alpha C^2 + C(\eta + \alpha\beta\rho - \alpha\ C_{mass}) - C_{mass} = 0 \qquad (3.2.4.2)$$

where

C_{mass} is the 'bulk' concentration at the node given by Mass $_{node}$ / Vol $_{Node}$.

Then the quadratic equation (Equation 3.2.4.2) can be solved for C, using the quadratic formula (Equation 3.2.4.3) with

$a = \eta\ \alpha$

$b = (\eta + \alpha\ \beta\ \rho - \alpha\ C_{mass})$

$c = -\ C_{mass}$

$$C = \frac{-b + (b^2 - 4ac)^{0.5}}{2a} \qquad (3.2.4.3)$$

The solution for the concentration is given by

$$C = \frac{-(\eta + \alpha\beta\varrho - \alpha C_{mass}) + \left[(\eta + \alpha\beta\varrho - \alpha C_{mass})^2 - 4\eta\alpha - C_{mass}\right]^{0.5}}{2\eta\alpha} \qquad (3.2.4.4)$$

The sorbed concentration can then be found using the Langmuir isotherm or the remaining mass.

3.3 Boundary Conditions and Mass Balance Calculations

The boundary condition at the model source/soil interface is a flux boundary condition. This is a function of the source concentration for each rain increment, the concentration at the boundary node, and the seepage velocity of the infiltrating leachate. The seepage velocity for each increment is found from the flow rate and the node area.

$$V_p = \frac{1000\,Q}{N_A\,\eta} \tag{3.3.1}$$

where

Q = flow rate (m^3/hr)

1000 = conversion factor (mm/m)

N_A = node area (m^2)

η = soil porosity

V_p = seepage velocity (mm/hr).

The mass entering the soil column is described by the following equation

$$M_{soil} = V_p N_A C_{source} \tag{3.3.2}$$

where

C_{source} = concentration of leachate from C&R material (mg/L)

M_{soil} = mass flux into the soil (mg/hr)

V_p and N_A as defined in Equation 3.3.1.

(Note – $1\ mm \times m^2 = 1mm \times m^2 \times \frac{m}{1000mm} \times \frac{1000L}{m^3} = L$).

The boundary for the soil-aquifer interface is also a flux boundary condition. Where the mass flux into and out of the soil environment is only due to advection, and the flux due to dispersion is zero. This is done by setting the second derivative of the concentration gradient ($\partial^2C/\partial z^2$) to zero between the boundary nodes and aquifer or construction and repair leachate source. The mass flux out of the soil column and into the aquifer is described by Equation 3.3.3.

$$M_{Aq} = V_p N_A C_{bn} \tag{3.3.3}$$

where

M_{Aq} = mass flux into the aquifer (or next soil layer for layering option) (mg/hr)

C_{bn} = concentration at boundary node (mg/L)

V_p, and N_A as defined in Equation 3.3.1.

In the model there are variables in the finite difference method that track all the mass leached into the soil and all the mass advected into the aquifer over the course of a model run. At the end of the run the mass in the soil and mass in solution are

calculated by summing the dissolved and sorbed concentrations for each node multiplied by the node volume and porosity (for dissolved concentrations) or bulk density (sorbed concentrations, Equation 3.2.1.1). Four variables track the mass and volume of contaminated water into and out of the soil column. The mass into the aquifer (or the mass into the next soil layer if the layering option is used) is tracked by summing the mass flux from the last node of the model.

$$M_{Aq}(n+1) = M_{Aq}(n) + V_p\ N_A\ \eta\ \Delta t\ C_{bn}(n) \qquad (3.3.4)$$

where

M_{Aq} (n + 1) = sum of mass advected into aquifer after the time step (mg)

M_{Aq} (n) = sum of mass advected into aquifer prior to the time step (mg)

C_{bn} (n) = dissolved concentration at last boundary node prior to time step (mg/L)

Δt = time step (hr)

V_p, N_A, and η as defined in Equation 3.3.1.

The terms to the right of the plus sign in Equation 3.3.4 equal the mass advected into the aquifer over a time step. This is summed with the mass previously advected into the aquifer to give the total mass entering the aquifer after the time step. If the mass is present at the last node, the volume of contaminated water is tracked by Equation 3.3.5.

$$V_{Aq}(n+1) = V_{Aq}(n) + V_p N_A \eta\ \Delta t \qquad (3.3.5)$$

where

V_{Aq} (n + 1) = sum of the volume of contaminated water advected into aquifer after the time step (L)

V_{Aq} (n) = sum of the volume of contaminated water advected into aquifer prior to the time step (L)

V_p, N_A, η, and Δt are as defined for Equations 3.3.1 and 3.3.4.

The current concentration of water entering the aquifer is equal to the concentration at the last node that advects into the aquifer over the time step. The average concentration (mg/L) is found by dividing the total mass input by the total volume of contaminated water reaching the aquifer. Both of these concentrations are tracked over the course of the run for model output.

The mass leached into the soil is the summation of the mass in the leachate entering the soil for each time step during each increment.

$$M_{soil}(n+1) = M_{soil}(n) + V_p N_A \eta \, \Delta t \, C_{source} \tag{3.3.6}$$

where

M_{soil} (n + 1) = sum of mass advected into the soil after the time step (mg)

M_{soil} (n) = sum of mass advected into the soil prior to the time step (mg)

C_{source} = concentration of leachate from C&R material (mg/L)

V_p, N_A, η, and Δt are as defined for Equations 3.3.1 and 3.3.4.

The volume of leachate is tracked in a similar manner.

$$V_{soil}(n+1) = V_{soil} + V_p \, N_A \, \eta \, \Delta t \tag{3.3.7}$$

where

V_{soil} (n + 1) = sum of mass advected into the soil column after time step (mg)

V_{soil} (n) = sum of mass advected into the soil column prior to time step (mg)

V_p, N_A, η, and Δt are as defined for Equations 3.3.1 and 3.3.4.

3.4 Model Stability and Sensitivity

3.4.1 Model Stability

The stability criterion for the magnitude of the time step used in the explicit finite difference scheme in the model is a function of the node spacing, dispersion coefficient, and seepage velocity (Roache, 1972).

$$\Delta t \leq \frac{1}{\frac{2D_l}{\Delta z^2} + \frac{V_p}{\Delta z \times R_d}} \qquad (3.4.1.1)$$

where

D_l = dispersion (mm^2/hr)

Δz = node spacing (mm)

V_p = seepage velocity (mm/hr)

Δt = time step (hr)

R_d = retardation coefficient (unitless) (Equation 3.1.3).

The Courant number is defined as the ratio of the distance solute is advected over the time step to the node spacing as shown in Equation 3.4.1.2. For model stability this ratio must be equal to or less than one, with a Courant number of 1.0 the desired value for the minimization of numerical dispersion (Roache, 1972).

$$\text{Courant number} = \frac{\Delta t \times V_p}{\Delta z \times R_d} \leq 1 \qquad (3.4.1.2)$$

If the dispersion coefficient in the model is set to zero (through selection of the dispersivity), the stability criterion can be reduced to an equation that is only a function of the seepage velocity and node spacing. For this condition the stability criteria (Equation 3.4.1) reduces to Equation 3.4.1.3.

$$\Delta t \leq \frac{\Delta z \times R_d}{V_p} \qquad (3.4.1.3)$$

The time step is optimized for the advective flux of contaminants for this condition, resulting in a Courant number of 1.0. The one exception is that the time step is limited so that it does not exceed the time increment of the hydrologic data used for the model run (15 minutes or one hour).

Model runs utilizing the dispersion coefficient do not allow for this simplification. The model calculates the dispersion coefficient from the dispersivity (entered by the model user) and the seepage velocity (Equation 2.3.2.3).

Substituting this into Equation 3.4.1.1, the stability criterion becomes

$$\Delta t \leq \frac{1}{\dfrac{2 \times V_p \times \alpha_d}{\Delta z^2} + \dfrac{V_p}{\Delta z \times R_d}} \qquad (3.4.1.4)$$

where

α_d is the dispersivity (mm).

Assuming the modeler wishes to simulate a certain storm intensity or use specific hydrologic data, the seepage velocity then depends upon the infiltration rate and soil properties. Therefore, the seepage velocity is not a parameter that can be modified to influence the stability criteria of the model. Operating under another assumption, that a certain level of dispersion is desired, the node spacing is the only remaining parameter to adjust to optimize model runs. The node spacing is controlled through the selection of the number of nodes.

In order to examine the effect of changes in node spacing, time steps were calculated (Equation 3.4.1.4) for variations in the node spacing relative to the dispersivity for several retardation coefficient values. Arbitrary values have been selected for dispersivity (10 mm) and seepage velocity (10mm/hr). Results for the variation in the time step are presented in Table 3.4.1.1 and the resulting Courant number is presented in Table 3.4.1.2.

Table 3.4.1.1 Variation in Time Step (hours) with Node Spacing

Node Spacing/ Dispersivity	Retardation Coefficient				
	1	5	25	100	500
0.1	0.004762	0.004951	0.004990	0.004998	0.005000
0.5	0.1000	0.1190	0.1238	0.1247	0.1249
1	0.3333	0.4545	0.4902	0.4975	0.4995
5	3.571	8.333	11.36	12.20	12.44
10	8.333	25.00	41.67	47.62	49.50
25	23.15	89.29	208.3	277.8	304.9
50	48.08	208.3	625.0	1000	1190

Table 3.4.1.2 Variation in Courant Number with Node Spacing

Node Spacing/ Dispersivity	Retardation Coefficient				
	1	5	25	100	500
0.1	0.0476	0.00990	0.00200	0.000500	9.99E-05
0.5	0.200	0.0476	0.00990	0.00249	0.000500
1	0.333	0.0909	0.0196	0.00498	0.000999
5	0.714	0.333	0.0909	0.0243	0.00498
10	0.833	0.500	0.167	0.0476	0.00990
25	0.926	0.714	0.333	0.111	0.02444
50	0.962	0.833	0.500	0.200	0.0476

Examination of the resulting time step values in Table 3.4.1.1 reveals that when the node spacing is small relative to the dispersivity, the left hand term in the denominator of equation 3.4.1.4 dominates; therefore, increases in the retardation

coefficient affect the resulting time step very little. When the node spacing is large relative to the dispersivity, the advective term in the stability criterion dominates, and the dispersion influences the time step very little. Increasing the node spacing results in increased time steps and Courant numbers closer to one (Table 3.4.1.2), which indicates a decrease in numerical dispersion. When selecting the node spacing, it is important to remember that the upper limit of the time increments in the model is one hour, so node spacing that is relatively large in comparison to the dispersivity (giving time steps >> 1 hour) will not provide improved model performance, but only serve to reduce the resolution of the infiltration of the solute. If the dispersivity (and therefore dispersion) is equal to zero, the Courant number becomes 1.0 for all scenarios (providing the time step is one hour or less).

Due to the limitations on the time step in the model, node spacing on the order of the dispersivity results in a time step approaching, but less than, one hour (which is, of course, also a function of the seepage velocity and retardation coefficient). Larger node spacing will help to minimize numerical dispersion at the expense of reduced resolution.

3.4.2 Model Sensitivity

Sensitivity analysis was conducted through multiple model runs using the parameters listed in Tables 3.4.2.1a and 3.4.2.1b.

Table 3.4.2.1a Model Parameters for Dispersion Sensitivity Analysis

Parameter	Units	Value
Model Depth	mm	500
Seepage Velocity	mm/hr	10
Source Conc	mg/L	10
Distribution Coefficient	L/g	0.001
Soil Porosity		0.50
Bulk Density of Soil	g/ml	2.0
Number of Nodes		51
Node Spacing	mm	10
Retardation Coefficient		5

Table 3.4.2.1b Dispersion and Time Step for Dispersivities

Dispersivity (mm)	Dispersion (mm^2/hour)	Time Step (hour)
0	0	1.00 (5.00)
25	250	0.1923
50	500	0.0980
75	750	0.0658
100	1000	0.0495
150	1500	0.0331

Model results for the six runs are presented in Figure 3.4.2.1. Results are plotted by the resulting dispersivity (α_d) in the model runs.

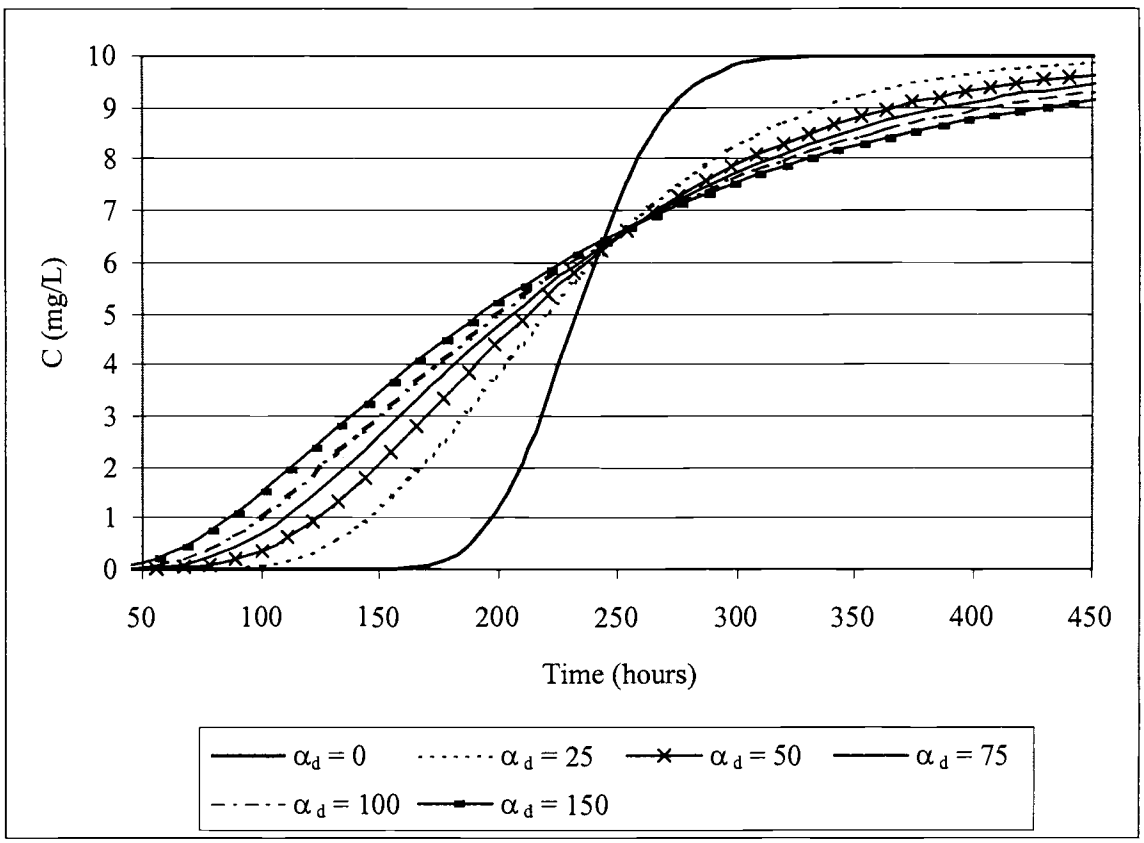

Figure 3.4.2.1 Model Results for Dispersion Sensitivity Analysis

As one would expect, increases in the dispersivity (and thereby increases in dispersion) in the model runs simply result in an increase in the spread of the solute front. In addition, there is numerical dispersion that results from utilizing a dispersion coefficient in the model runs. If dispersion is set to zero, the time step can be set to a value giving a Courant number of 1.0 (Equation 3.4.1.1), preventing numerical dispersion. However, when dispersion is included in the model runs, the Courant number will necessarily be less than one (Table 3.4.1.1), resulting in some numerical dispersion. Results in Figure 3.4.2.1 shows the influence of dispersion

on the breakthrough curve for model runs incorporating sorption. Table 3.4.2.1b lists the time step calculated from the stability criterion as 5 hours in parenthesis for the run with dispersivity set equal to zero. The run with the dispersivity (and therefore dispersion) set to zero should not have the spreading of the solute front, but this numerical dispersion results from the limit of one hour on the time steps in the model. Adjusting the seepage velocity from 10 to 50 mm/hr for the model parameters in Table 3.4.2.1a results in a time step of one hour. The time step of one hour in combination with a dispersivity of zero results in a Courant number of one as previously discussed. The model results for a run with the same model parameters in Table 3.4.2.1a, except for the 50 mm/hr seepage velocity, is shown in Figure 3.4.2.2.

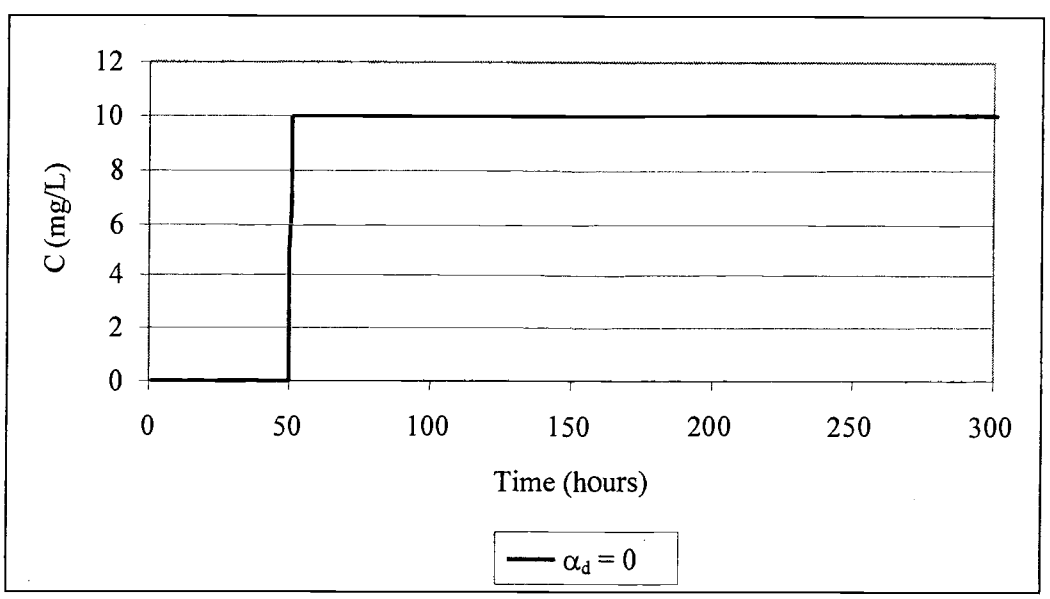

Figure 3.4.2.2 Model Results for Zero Dispersion with Courant Number of One

The difference in the shape of the breakthrough curves for the model runs without dispersion in Figures 3.4.2.1 and 3.4.2.2 illustrates the potential effect of numerical dispersion on model runs. For most model runs utilizing dispersion and having appreciable sorption the resulting Courant number will be less than 1.0, which will result in some unavoidable numerical dispersion.

Another series of model runs was conducted to examine model sensitivity with the selection of node spacing. Results from these runs are presented in Section 3.5, as the analytical solution was used to examine the effects of changes in node spacing on the accuracy of the solution.

3.5 Comparison to Analytical Solution Incorporating Advection, Dispersion, and Linear Sorption

Analytical solutions to various formulations of the advection-dispersion equation began to appear commonly in the 1960s. As the modeling of solute transport became more sophisticated during the 1970s and 1980s, so did the analytical solutions incorporating phenomena such as mobile-immobile pore regions (van Genuchten and Wierenga, 1976), rate-limited sorption (Lassey, 1988), and two-site competitive sorption (van Genuchten and Wagnet, 1989). The simple algorithm developed here does not require this level of sophistication in the analytical solution for comparison to model results. The analytical solution used for comparison is presented by Lindstrom et al. (1967).

Lindstrom et al. solved the advection-dispersion equation equivalent to

$$\frac{\partial C}{\partial t} = D_l \frac{\partial^2 C}{\partial z^2} - V_p \frac{\partial C}{\partial z} - \frac{\rho \partial S}{\eta \partial t} \tag{3.5.1}$$

with variables as defined for Equation 3.1.1.

The solution was subject to the boundary conditions describing initial saturated flow of fluid concentration C = 0. At t = 0 the concentration of the plane source is changed to

$C = C_0.$

$C(0, t) = C_0 \; ; t \geq 0$

$C(x, 0) = 0 \; ; x \geq 0$

$C(\infty, t) = 0 \; ; t \geq 0$

The analytical solution given by Lindstrom et al. uses the transformation variables shown in Equations 3.5.2 and 3.5.3.

$$U = \frac{V_p}{1 + K_d \times \frac{\rho}{\eta}} \tag{3.5.2}$$

$$Y = \frac{D_l}{1 + K_d \times \frac{\rho}{\eta}} \tag{3.5.3}$$

where

K_d = linear sorption coefficient (L/g)

and other variables are as defined for Equation 3.1.1.

The solution to Equation 3.5.1 is given by Lindstrom et al. as

$$\frac{C(z,t)}{C_0} = \frac{1}{2}\{L(z,t) + M(z,t) + N(z,t)\} \tag{3.5.3}$$

where

$$L(z,t) = \mathrm{erfc}\left(\frac{z}{2\sqrt{Yt}} - \frac{U}{2}\sqrt{\frac{t}{Y}}\right) \tag{3.5.4}$$

$$M(z,t) = \left(\frac{4U^2t}{Y\pi}\right)^{\frac{1}{2}} \exp\left(-\left(\frac{z}{2\sqrt{Yt}} - \frac{U}{2}\sqrt{\frac{t}{Y}}\right)^2\right) \tag{3.5.5}$$

$$N(z,t) = -\frac{U}{Y}\left(z + Ut + \frac{Y}{U}\right) \times \exp\left[\frac{zU}{Y}\right] \bullet \mathrm{erfc}\left(\frac{z}{2\sqrt{Yt}} + \frac{U}{2}\sqrt{\frac{t}{Y}}\right) \tag{3.5.6}$$

In Equations 3.5.4 and 3.5.6, erfc is the complementary error function (Abramowitz and Stegun, 1964).

Arbitrary values were selected for the variables used in the solution of the AD equation.

Table 3.5.1 Values Used for Analytical Solution of the Advection Dispersion Equation

Parameter	**Units**	**Values**
C (leachate conc)	mg/L	10
V_p (seepage velocity)	mm/hr	10
D_l (dispersion coefficient)	mm^2/hr	200
z (model depth)	mm	200
K_d (distribution coeff.)	L/g	0.005
bulk density	g/L	2500
porosity		0.5
R (retardation factor)		26

Model parameters used for comparison with the analytical solution are given in Table 3.5.2.

Table 3.5.2 Values Used for Numerical Solution of the Advection Dispersion Equation

Parameter	**Units**	**Values**
C (leachate conc)	mg/L	10
V_p (seepage velocity)	mm/hr	10
α_d (dispersivity)	mm	20
z (model depth)	mm	200
K_d (distribution coeff.)	L/g	0.005
bulk density	g/L	2500
porosity		0.5
number of nodes		11
node spacing	mm	20
Resulting		
D_l (dispersion coefficient)	mm^2/hr	200
Time Step	hour	0.95

The model depth was set equal to 200 mm (z in Table 3.5.1) with 11 nodes so the resulting node spacing of 20 mm would be equal to the magnitude of the dispersivity (as recommended in Section 3.4.1). The resulting time step is 0.98 hours and the Courant number for the given parameters is 0.49 (Table 3.4.1.1).

The values from Tables 3.5.1 and 3.5.2 substituted into the analytical and numerical solutions respectively, give the results shown in Figure 3.5.1.

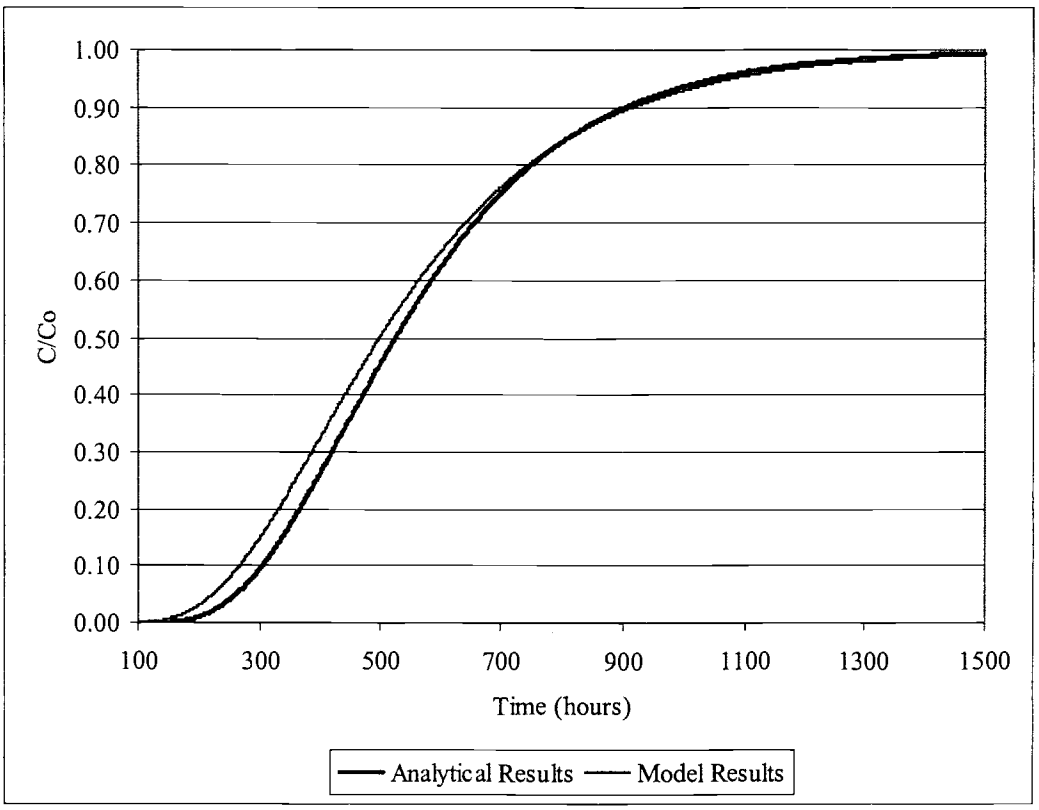

Figure 3.5.1 Analytical and numerical results for solution of the advection-dispersion Equation (3.5.1).

As can be seen in Figure 3.5.1, the results from the numerical algorithm compare favorably with the analytical solution. The small discrepancy in the arrival times between the breakthrough curves for the analytical and numerical solutions results from the application of the stability criteria.

For the numerical solution of the advection-dispersion equation the selected parameters result in a Courant number of 0.333 (as mentioned following Table 3.5.2). The stability criterion results in the advection of solute 1/3 of the distance between the nodes during each time step. The numerical methods employed in the

model are not capable of distinguishing concentration gradients within a node, and each node is considered to be homogeneous with respect to the sorbed and dissolved concentrations within the node. When mass reaches a given node (node n), it is advected 1/3 of the way into that node during the time step. During the next time step, mass is considered to advect from node n into the next node (node n + 1) because of the assumption that mass is uniformly distributed in the nodes. The result is that mass is advected ahead of the solute front, which is the phenomenon termed numerical dispersion. Figure 3.5.2 helps to illustrate this concept.

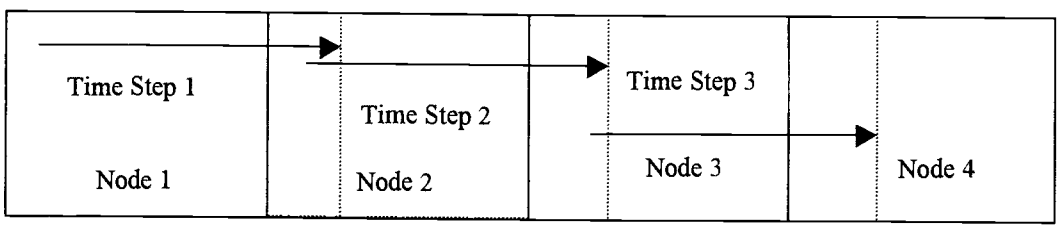

Figure 3.5.2 Numerical Dispersion Resulting from Time Step Limitations

This limit on the length of the time step is necessary for model stability, although it causes numerical dispersion. If the time step were not limited and the Courant number was 1.0, all of the mass in solution would advect from node n into node n + 1. Over this time step mass is also dispersed from node n to node n + 1 (assuming the concentration at node n + 1 is lower). The mass advected and dispersed into node n + 1 for this condition would exceed the available mass in solution at node n, violating the conservation of mass. Although numerical

dispersion can result from the limit on the length of the time step imposed by a stability criterion, it is more desirable than the violation of continuity that can occur without the stability criterion. Furthermore, it only alters the timing, not the total mass, of the leachate migrating through the soil column.

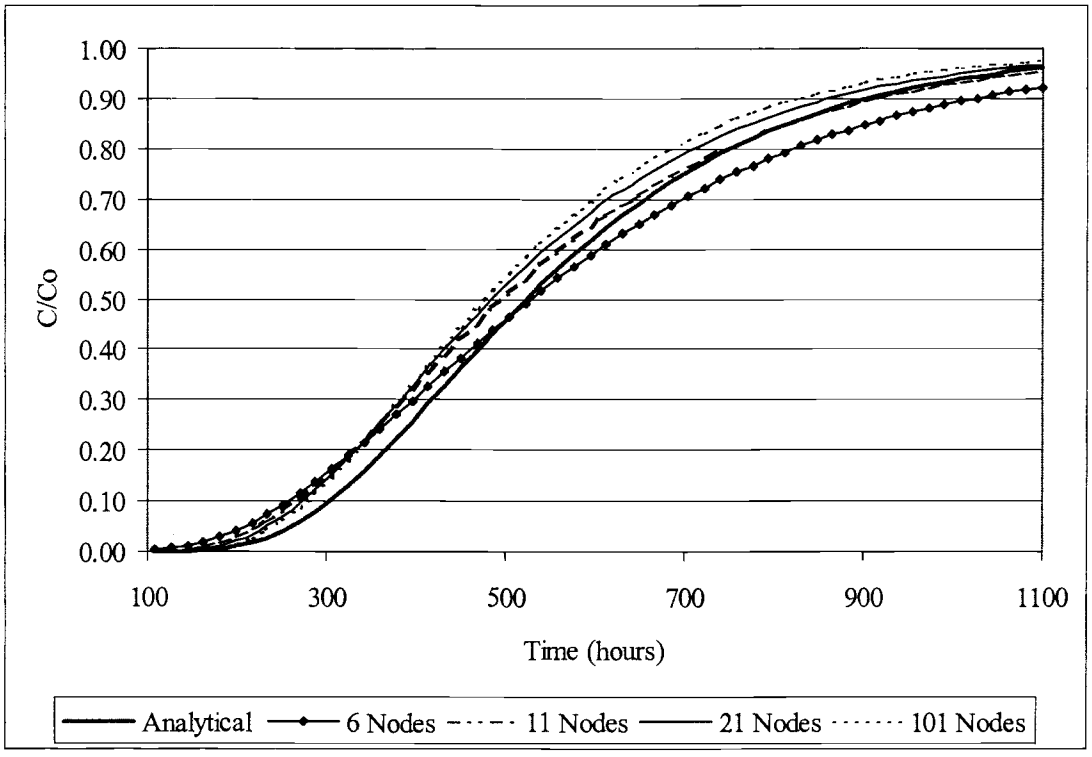

Figure 3.5.3 Model Results for Node Spacing Sensitivity Analysis

Figure 3.5.3 displays the results for four model runs. The node spacing and resulting time step are given in Table 3.5.3 for the runs.

Table 3.5.3 Number of Nodes, Node Spacing, and Time Steps for Model Runs

Number of Nodes	Node Spacing (mm)	Time Step (hours)
6	40	1.00 (3.63)
11	20	0.952
21	10	0.244
101	2	0.00995

The model has an upper limit of one hour for a time step to correspond to changes (decay) in the source concentration for model runs utilizing C&R materials. The time step in parenthesis for the run with 6 nodes is the value given by the stability criterion. Figure 3.5.3 supports the conclusions on the optimal number of node in Section 3.4.1.1. The best results are for the model run with the node spacing (11 nodes) equal to the magnitude of the dispersivity. Model runs with more nodes and a smaller node spacing provide acceptable results, but the offset between the analytical solution and model results gradually increases due to numerical dispersion as the number of nodes increases. Using a node spacing (6 nodes) equal to twice the magnitude of the dispersivity (giving a Courant number of ½) results in poor agreement with the analytical solution through much of the breakthrough curve due to numerical dispersion.

Run times are sufficiently short (less than a minute for the 101 node run on a 670 MHz personal computer) that the number of nodes does not need to be limited to provide practical run times when using the linear (or Langmuir) isotherm. However, long-term runs utilizing the Freundlich isotherm can take on the order of

an hour to complete due to the necessity for the iterative technique for solution of the advection-dispersion equation. While the model run with 11 nodes provides the best results compared to the analytical solution, a larger number of nodes provides better vertical resolution giving the best definition of vertical penetration. Ideally, the selection of the number of nodes should represent a compromise between the two considerations.

4 MODEL VERIFICATION

The intent of model verification is to demonstrate that the model gives a reasonable approximation to the results obtained from actual leachate transport through soil. This is a test of the numerical methods employed in the model, the modeling parameters obtained from laboratory testing, and the assumptions of the model.

4.1 Available Column Studies

In NCHRP Phase III Task 1, Confirmation of Phase II Methodology, AZCA and 2,4,6-TCP leachates were used in column studies with Sagehill and Woodburn soils. Not all of the individual metal species (Cu and Zn) reached a breakthrough concentration high enough in all of the column studies to be useful for comparison with model results. Although arsenic was available for model comparisons in the 50 mm Woodburn soil column, it was not run because studies utilizing longer columns were available. The column studies used for comparison with the breakthrough curves predicted by the model are listed in Table 4.1.1.

Table 4.1.1 Column Studies Used for Comparison with Model Results

ACZA Column Comparisons				TCP Column Comparisons	
Sagehill	Arsenic	Copper	Zinc	Sagehill	
50 mm	X	X	X	110 mm	X
110 mm	X				
Woodburn				Woodburn	
50 mm		X	X	50 mm	X
110 mm	X				
200 mm	X				

4.2 Modeling Parameters

For meaningful comparison of model outputs to data from column studies, the parameters used in a model run must reflect the actual conditions in the column as closely as possible. Modeling parameters for the soil sorption isotherms were obtained from analyzing laboratory sorption data for arsenic, copper, and zinc. The remaining modeling parameters used reflect the physical parameters of the soil columns and the physical properties of the soils as closely as possible.

The sorption data were analyzed to give Freundlich and Langmuir soil sorption isotherms for ACZA leachate in both Sagehill and Woodburn soils. Individual isotherms for arsenic, copper, and zinc were obtained. The data analysis for the sorption isotherms and leachate concentration for the model verification were done in units of milligrams rather than millimoles for ease of comparison with the

column study data. The units of the isotherm constants were then changed when incorporated into the final version of the model.

All but one of the isotherm analyses gave reasonable data fits. The only problem was the Langmuir isotherm for zinc in the Woodburn soil. In an effort to obtain usable parameters for α and β in the Langmuir isotherm, the following rationale was employed. The constant β represents the maximum sorption capacity of the soil, so mass balance data from the column study just prior to switching to deionized water (i.e., just prior to the desorption phase of the experiment) were used for the following calculation. The mass influx to the column was known from the volume of infiltrating leachate multiplied by the concentration. The mass of zinc out of the column was estimated from analysis of the effluent and by extrapolating between the concentrations between the samples taken at certain time intervals. From these values the mass remaining in the soil column could be estimated. The average concentration in solution in the soil column was estimated by averaging the influent and effluent concentrations at the time the mass balance data were used. This estimated concentration multiplied by the pore volume gave the mass in solution, which, when subtracted, left an estimate of the mass sorbed to the soil. Dividing this quantity by the mass of soil in the column gave an estimate for β (mg solute / g soil). Plotting points near the origin (assuming that $1 >> \alpha \times C$ for these points) gives a slope of $\alpha \times \beta$. Dividing this value by the estimate for β gave an estimate for α. These estimated parameters are listed in Table 4.2.1 along with parameters for all model runs simulating OSU column studies.

No additional sorption data were available for 2,4,6-TCP. The isotherm parameters used in the model runs are the parameters from Section 4.14 of the Phase II report (Eldin et al., 2000).

Power (i.e., Freundlich) plots of the sorption data for arsenic, copper, and zinc for Sagehill and Woodburn soils are shown in Figures 4.2.1 – 4.2.6. Each figure also displays the equation derived from an analysis of the data using the Langmuir isotherm. Sorption data are obtained in the laboratory by mixing different amounts of soil and water and by observing equilibrium concentrations. In two cases data points obtained by mixing 10 grams soil per liter of solution were omitted. These omissions were made for the Langmuir fit of arsenic data in the Sagehill soil (Figure 4.2.1) and for the Langmuir fit of copper data in the Woodburn soil (Figure 4.2.6) in order to get a better fit of the data ($R^2 \approx 0.6 - 0.7$ rather than $0.1 - 0.2$).

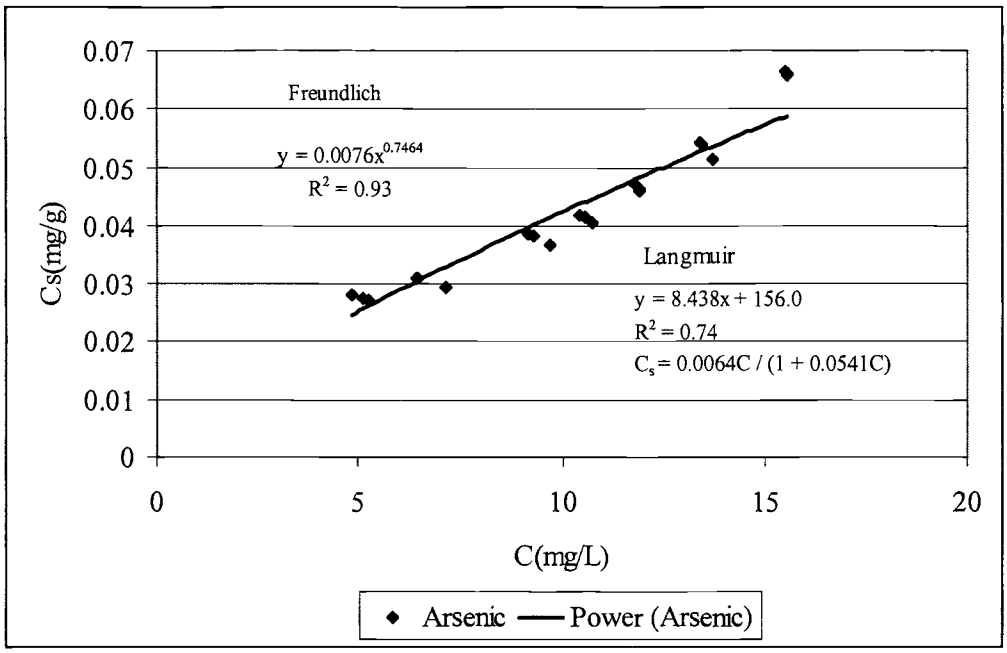

Figure 4.2.1 Arsenic Sorption Data for Sagehill Soil

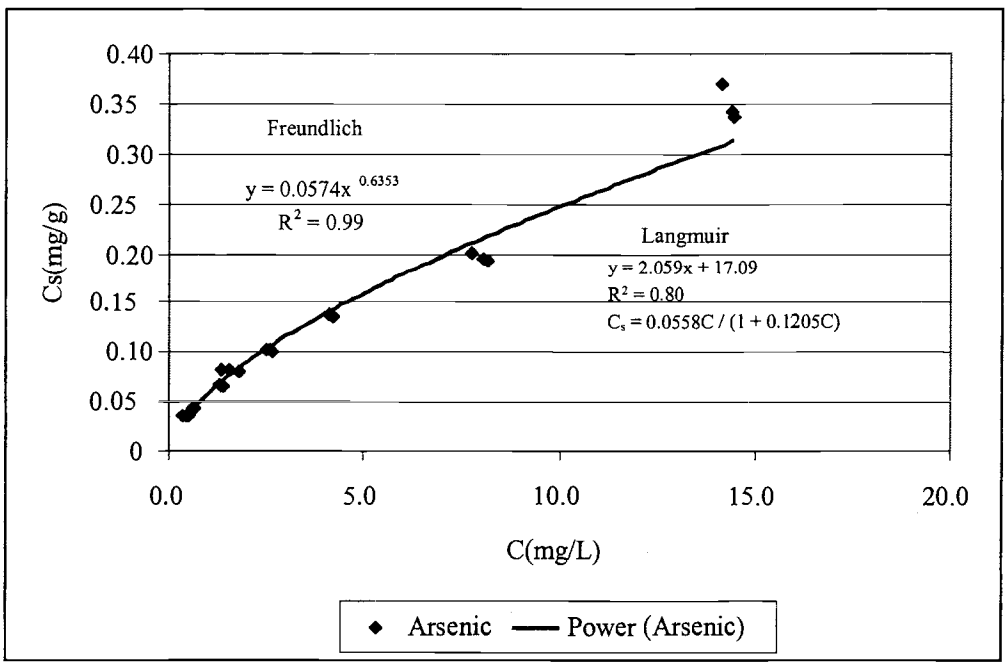

Figure 4.2.2 Arsenic Sorption Data for Woodburn Soil

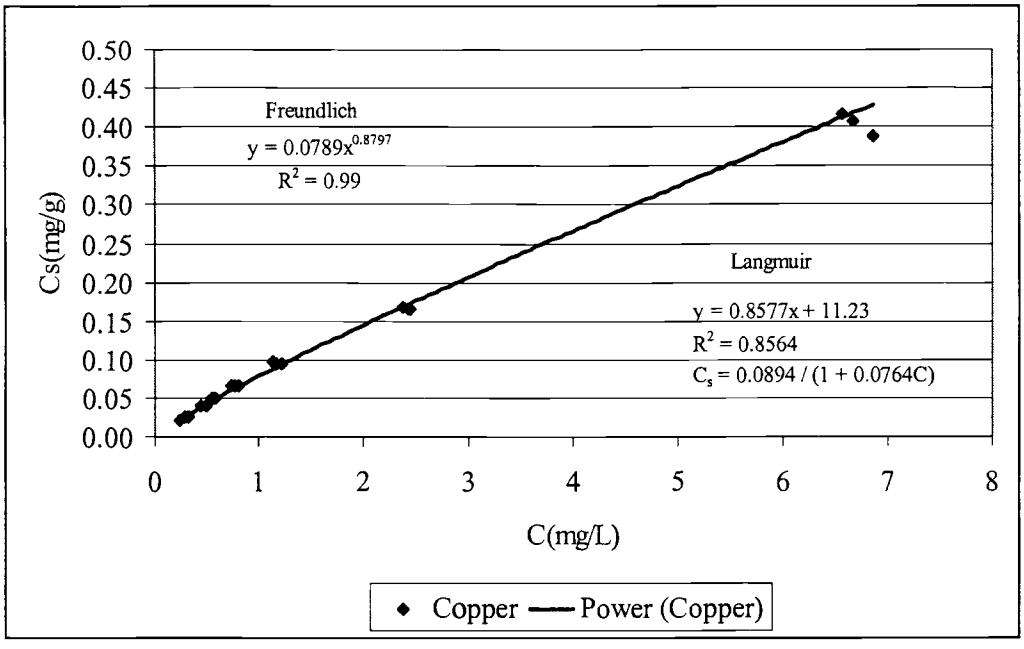

Figure 4.2.3 Copper Sorption Data for Sagehill Soil

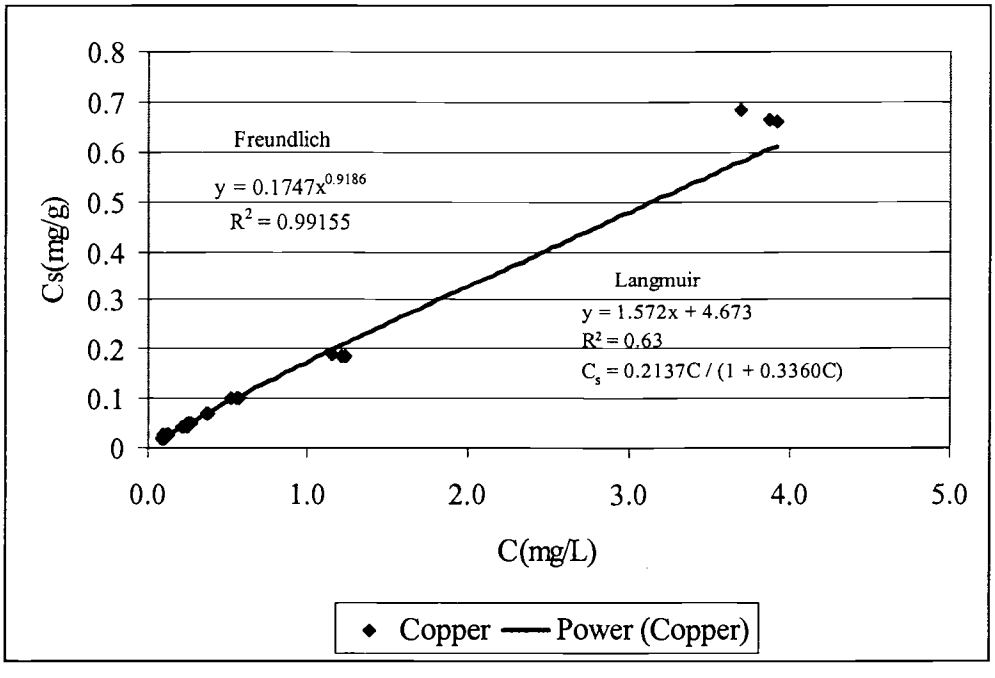

Figure 4.2.4 Copper Sorption Data for Woodburn Soil

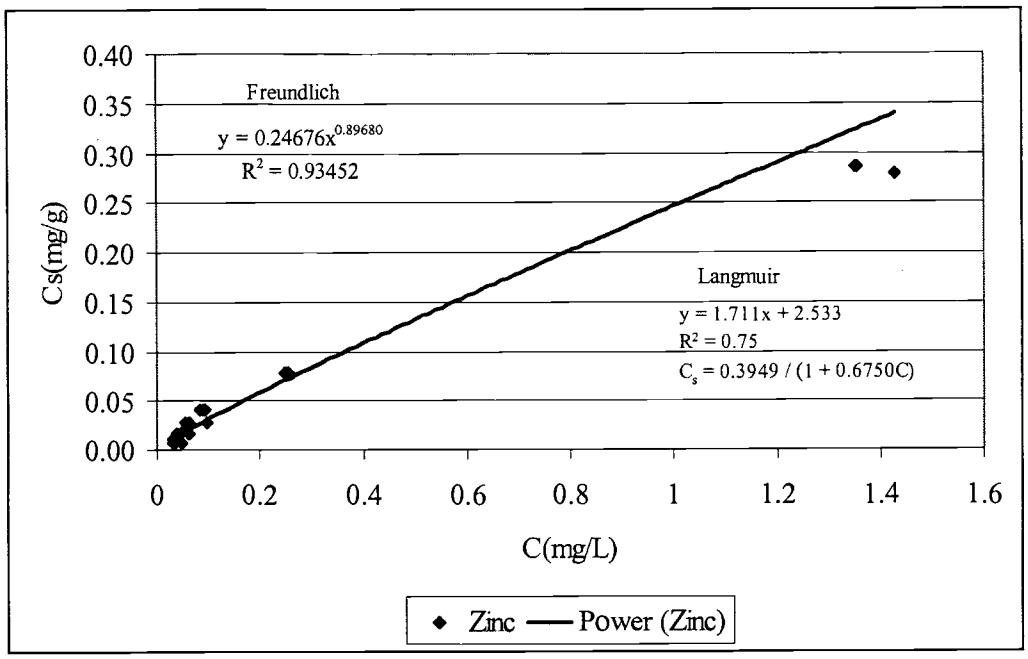

Figure 4.2.5 Zinc Sorption Data for Sagehill Soil

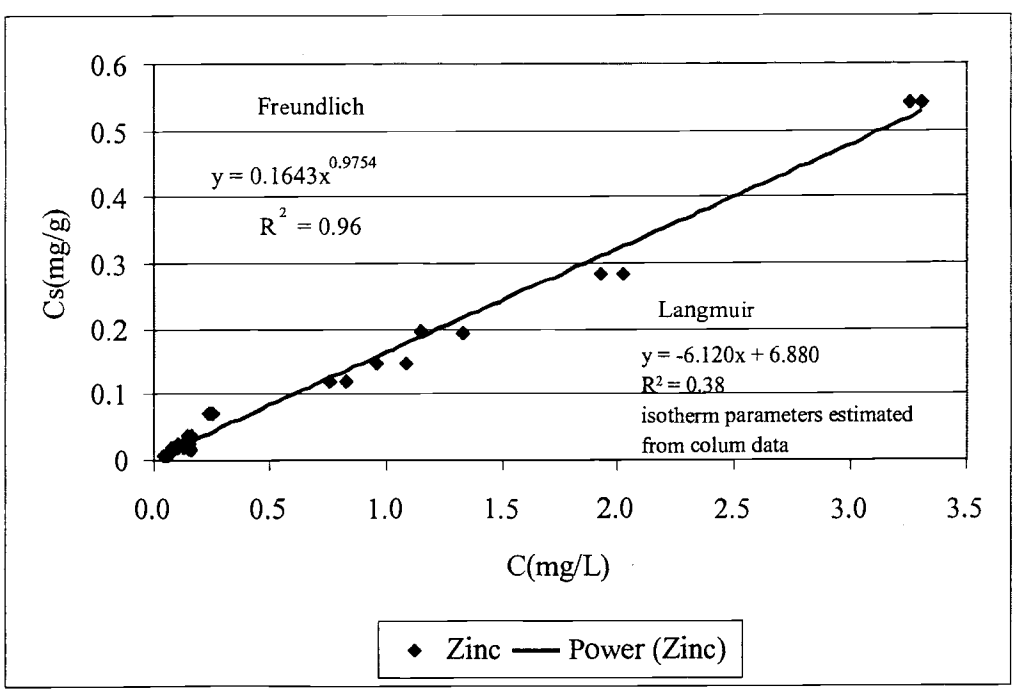

Figure 4.2.6 Zinc Sorption Data for Woodburn Soil

Table 4.2.1 Modeling Parameters Used for Column Comparisons

	ACZA Column Studies					TCP Column Studies	
Soil Data	**Sagehill**		**Woodburn**			**Sagehill**	**Woodburn**
porosity	0.37	0.37	0.49	0.52	0.43	0.50	0.40
bulk density	1.66	1.67	1.59	1.24	1.50	1.33	1.58
Column Data							
Length (mm)	50	110	50	110	200	110	50
Area (mm^2)	49.1	49.1	49.1	49.1	49.1	49.1	49.1
Volume (mL)	24.6	54.0	24.6	54.0	98.1	54.0	24.6
Pore Volume (mL)	9.1	20.1	12.1	28.7	42.7	27.0	9.8
Flow Rate (mL/hr)	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Seepage Velocity (mm/hr)	55.1	54.6	41.3	38.3	46.8	40.7	51.0
Duration of Run (hr)	500	460	320	480	650	58	150
Time to D.I. Water (hr)	337.3	402.5	264	307.9	597.2	52.7	103
Leachate Conc. (mg/L)							
Arsenic	27.65	27.65	27.65	29.74	29.74	-	-
Copper	26.43	26.43	26.43	23.00	23.00	-	-
Zinc	10.46	10.46	10.46	9.87	9.87	-	-
TCP	-	-	-	-	-	2	2

Isotherm Parameters	**Sagehill**		**Woodburn**	
Freundlich	Kf	N	Kf	N
Arsenic	0.0076	0.7464	0.0547	0.635
Copper	0.0788	0.880	0.175	0.919
Zinc	0.247	0.897	0.164	0.975
TCP	0.00071	0.794	0.0226	0.583
Langmuir	α (L/mg)	β (mg/g)	α (L/mg)	β (mg/g)
Arsenic	0.0541	0.119	0.121	0.486
Copper	0.0764	1.17	0.336	0.636
Zinc	0.675	0.585	2.86	0.324
TCP	0.290	0.0032	1.66	0.035

Finally, parameters used in the model runs are shown in Table 4.2.1. The values in this table are the measured values of soil properties, solute concentrations

in the leachate used for the study, physical parameters of the columns, and isotherm parameters from the sorption data analysis.

In all of the column studies a leachate of constant concentration (the leachate data in Table 4.2.1) is pumped into the soil column at a flow rate of 10 mL/hr. After the breakthrough concentrations reach a significant level, the influent is switched to deionized water for the desorption phase of the column study, shown by "Time to D.I. Water" in Table 4.2.1.

The seepage velocities for the columns were calculated by dividing the column length (mm) by [pore volume (mL) / flow rate (mL/hr)]. This is equivalent to the column length divided by the time required for complete replacement of the fluid in the pore volume.

4.3 Model Verification Runs

The code of the IMPACT model was adapted to mimic the column studies. The solute concentrations, duration of the model run, seepage velocity, and the time at which the influent concentration was changed to zero were set equal to the times of the actual column studies. The contact time in the model was set to zero so that the time of the model outputs would coincide with the time of the column studies. The model depth was set equal to the length of the columns. The soil physical parameters were entered in the Soil Parameters form, and the isotherm parameters were entered using the Parameters Input form. The dispersivity was set to one tenth the lengths of the columns being modeled as suggested in the dispersivity help

form. After entering all the parameters for the Task 1 column study being duplicated, the model was run. Each scenario was run twice, once using Freundlich isotherm parameters and once with the Langmuir parameters. The model results are not calibrated further.

The data in the Aquifer Inputs sheet (part of the model output) were used for comparison with the column data. The data in the column entitled "Concentration of Water Entering Aquifer (mg/L)" (in the Aquifer Input shet) were divided by the influent concentration to give (C/Co), a value ranging from zero to one. The values from the real column studies were plotted along with the data from both model runs.

4.3.1 Model Verification Results

The graphs of the results for all ten column comparisons (4 As, 2 Cu, 2 Zn, 2 TCP) between model results and column study data are shown in Figures 4.3.1.1 – 4.3.1.10.

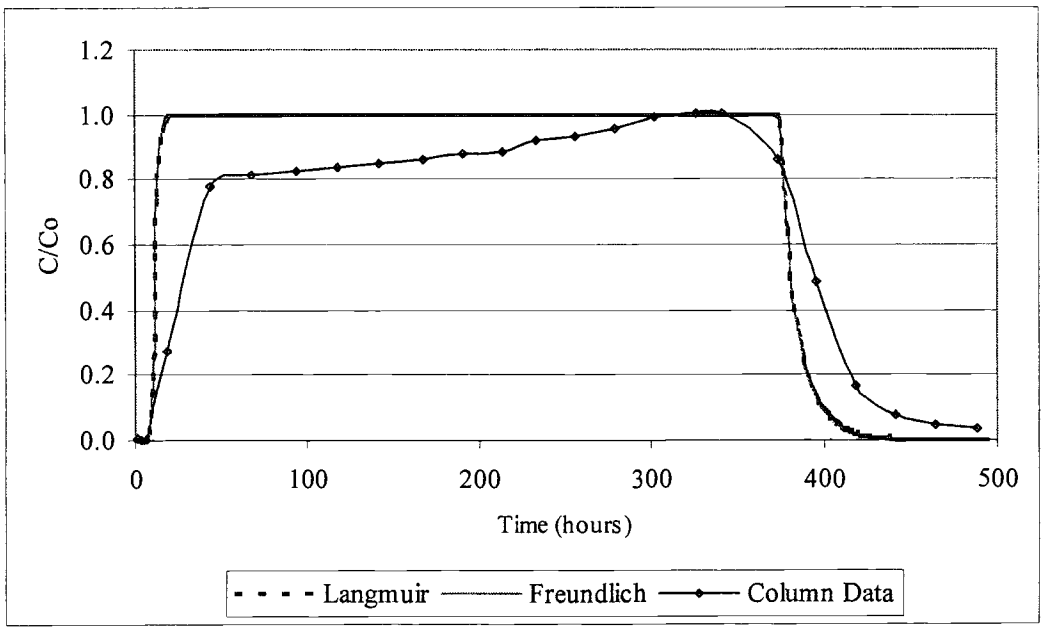

Figure 4.3.1.1 Data for 50mm Column Comparison Arsenic in Sagehill Soil

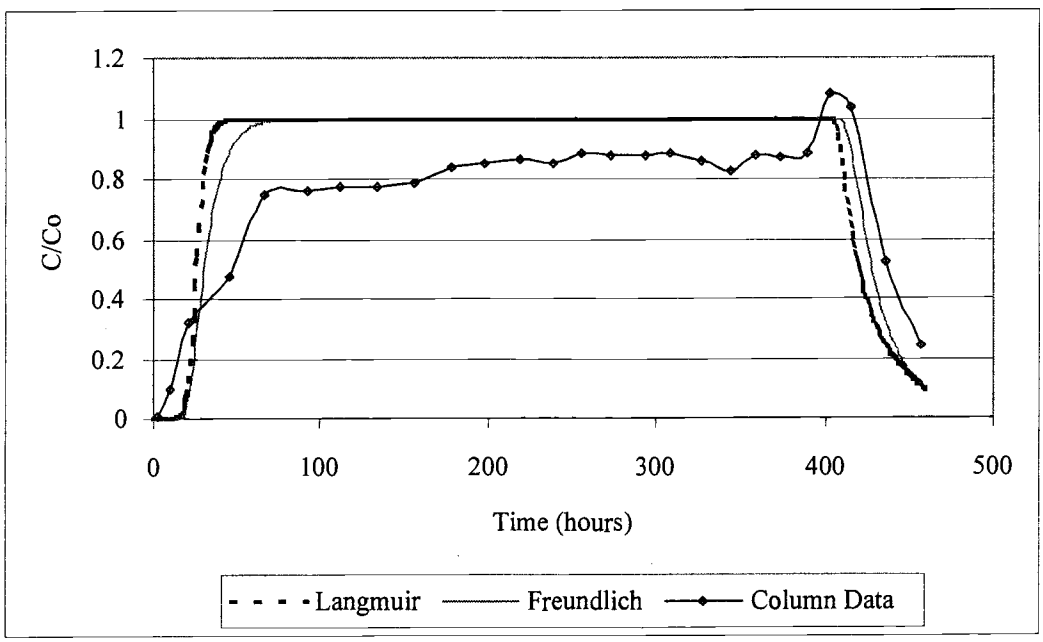

Figure 4.3.1.2 Data for 110mm Column Comparison Arsenic in Sagehill Soil

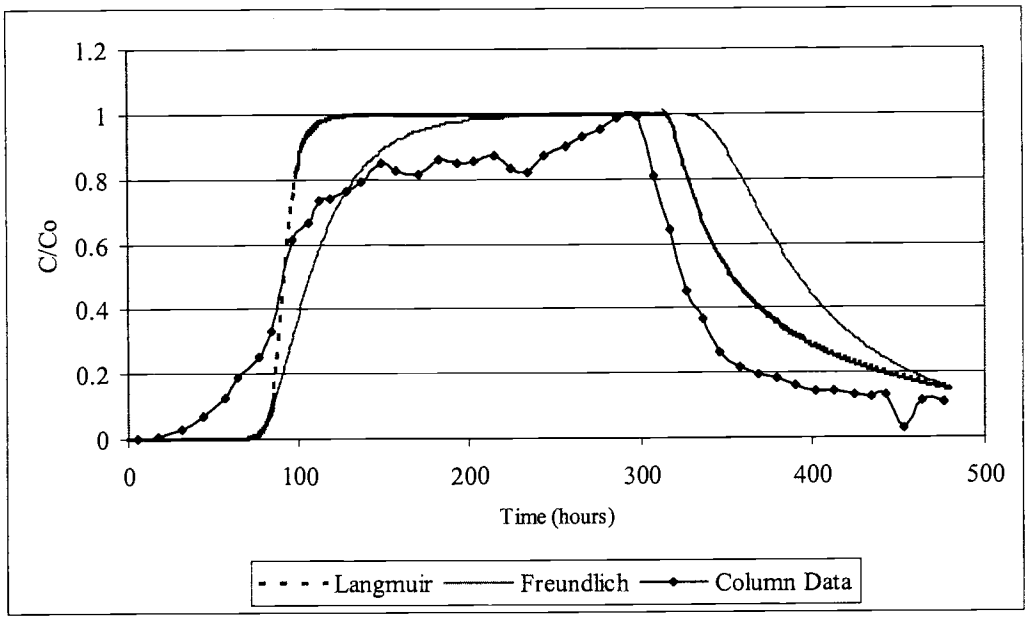

Figure 4.3.1.3 Data for 110mm Column Comparison Arsenic in Woodburn Soil

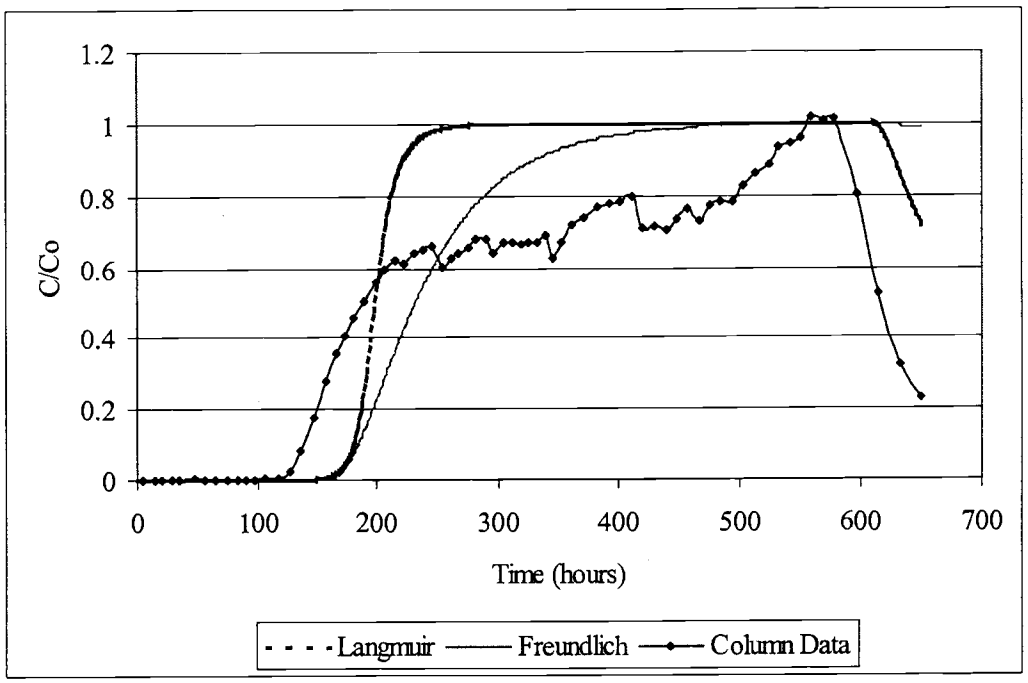

Figure 4.3.1.4 Data for 200mm Column Comparison Arsenic in Woodburn Soil

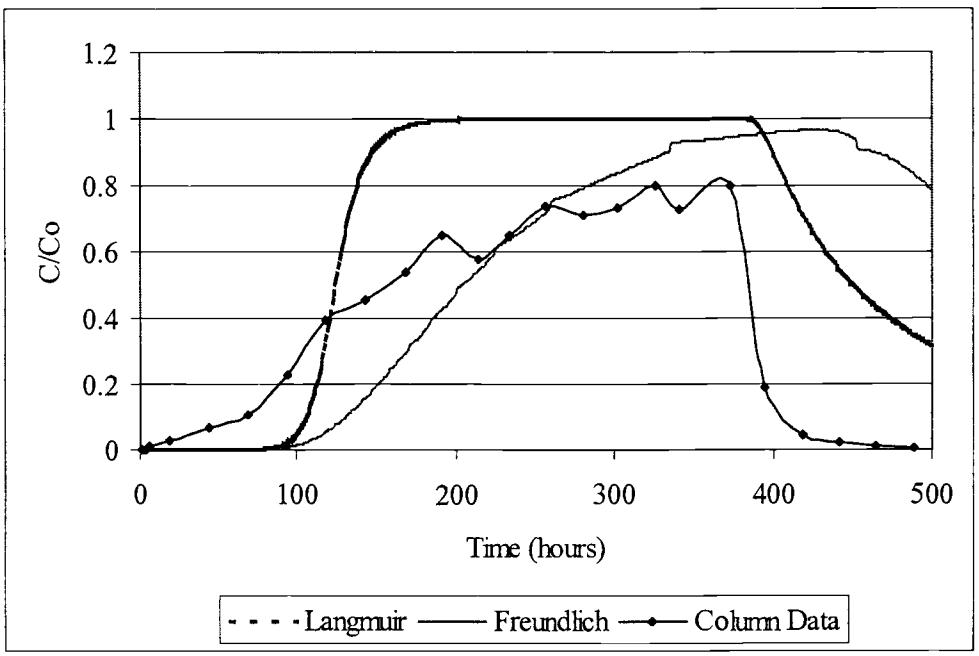

Figure 4.3.1.5 Data for 50mm Column Comparison Copper in Sagehill Soil

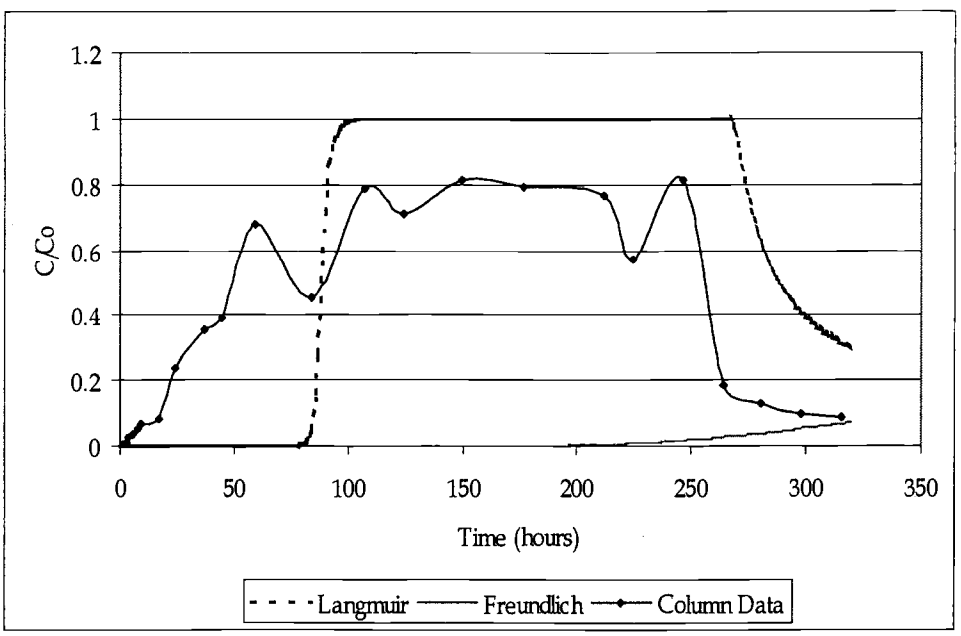

Figure 4.3.1.6 Data for 50mm Column Comparison Copper in Woodburn Soil

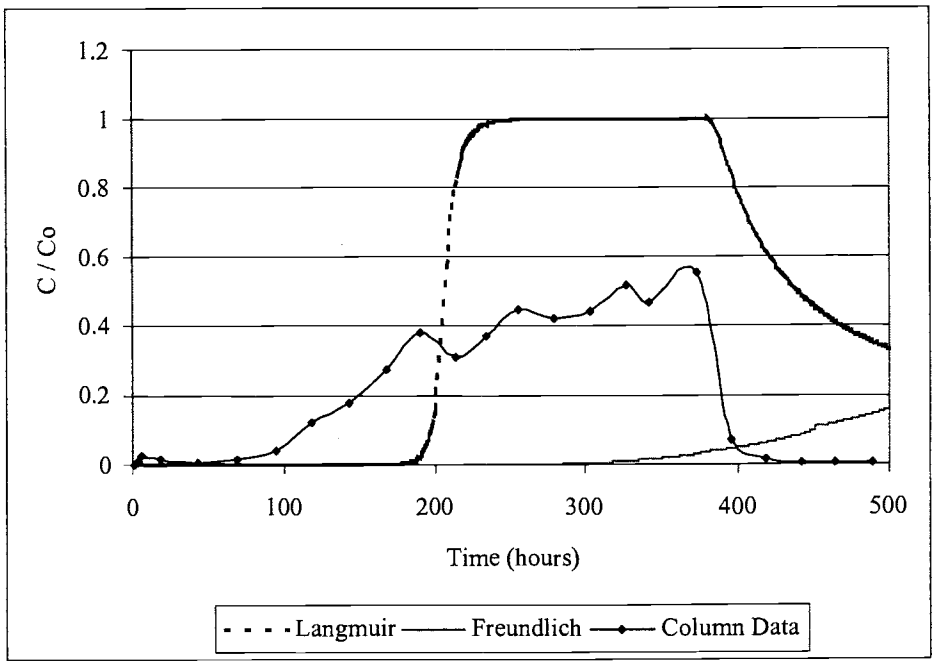

Figure 4.3.1.7 Data for 50mm Column Comparison Zinc in Sagehill Soil

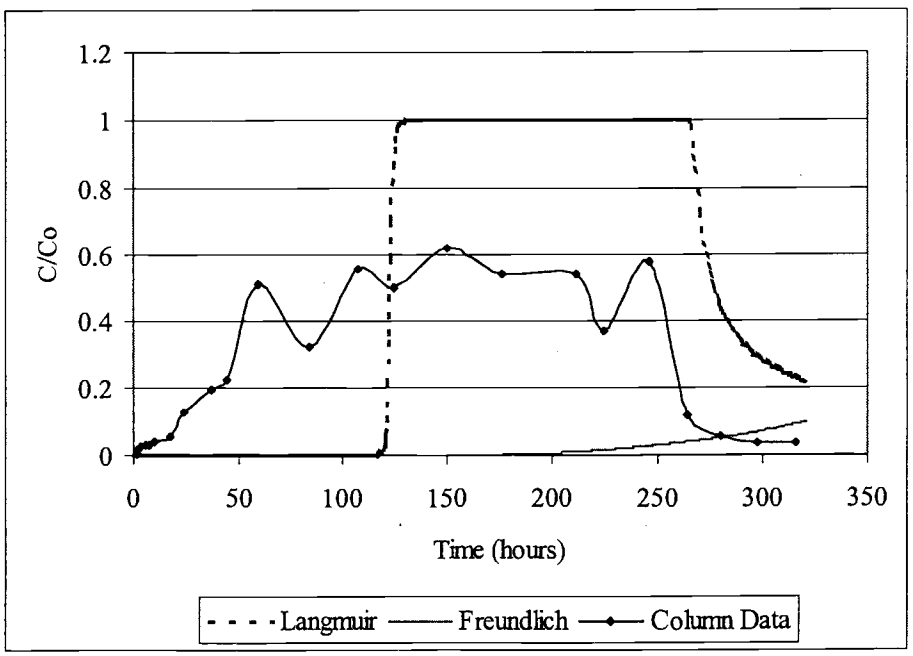

Figure 4.3.1.8 Data for 50mm Column Comparison Zinc in Woodburn Soil

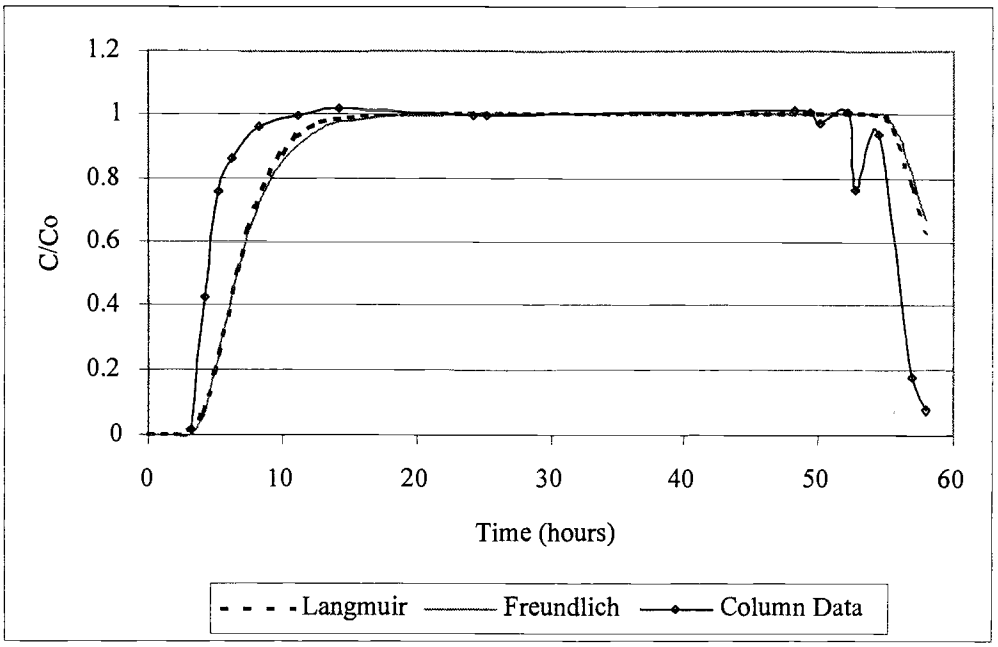

Figure 4.3.1.9 Data for 50mm Column Comparison TCP in Sagehill Soil

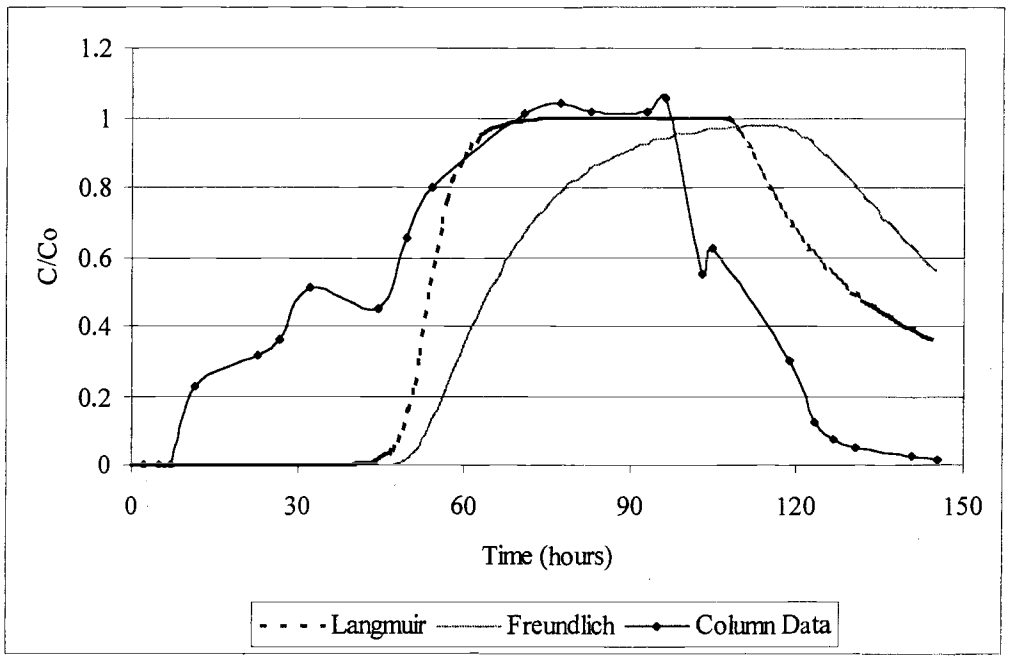

Figure 4.3.1.10 Data for 50mm Column Comparison TCP in Woodburn Soil

Table 4.3.1.1 Numerical Results from Sagehill Soil Model Runs

		Arsenic Sagehill 50		Arsenic Sagehill 110		Arsenic Woodburn 110		Arsenic Woodburn 200	
Row		Langmuir	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich
1	Retardation factor	225.85	109.55	27.36	31.34	103.30	92.73	73.35	62.17
2	% Reduction in Mass Due to Sorption	8.65	0.01	0.60	0.74	8.16	6.77	25.84	32.81
3	Total Mass Leached for Event (mg)	103.20	103.20	110.23	110.23	89.58	89.58	175.43	175.43
4	(mass input in column study)	103.22	103.22	111.29	111.29	91.57	91.57	177.61	177.61
5	Mass Sorbed at End of Run (mg)	8.9300	0.0089	0.6622	0.8201	7.3114	6.0691	45.3356	57.5640
6	Mass in Solution at End of Run (mg)	0.0397	0.0001	0.0251	0.0270	0.0715	0.0662	0.6266	0.9411
7	Mass into Aquifer During Run (mg)	94.5303	103.1860	109.5720	109.4265	82.4103	83.6294	130.5102	118.3286
8	Sum of Mass at End of Run (mg)	103.5001	103.1950	110.2593	110.2736	89.7931	89.7647	176.4724	176.8337
9	Percent Change	0.29%	0.00%	0.03%	0.04%	0.23%	0.20%	0.59%	0.80%
10	Number of Nodes	21	21	21	21	21	21	21	21
11	Node Spacing	2.50	2.50	5.24	5.24	5.24	5.24	10.00	10.00
12	Time Step	0.0109	0.0113	0.0219	0.0224	0.0319	0.0323	0.0522	0.0531

		Copper Sagehill 50		Copper Woodburn 50		Zinc Sagehill 50		Zinc Wooburn 50	
Row		Langmuir	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich
1	Retardation factor	280.78	259.03	244.43	450.66	679.29	925.29	536.72	501.48
2	% Reduction in Mass Due to Sorption	12.68	27.67	22.66	97.90	36.81	97.39	38.51	98.34
3	Total Mass Leached for Event (mg)	98.70	98.70	69.32	69.32	39.05	39.05	27.44	27.44
4	(mass input in column study)	98.66	98.66	69.78	69.78	39.05	39.05	27.61	27.61
5	Mass Sorbed at End of Run (mg)	12.5161	27.3156	15.7087	67.8629	14.3740	38.0266	10.5685	26.9857
6	Mass in Solution at End of Run (mg)	0.0447	0.1059	0.0645	0.1509	0.0212	0.0411	0.0197	0.0539
7	Mass into Aquifer During Run (mg)	86.4762	72.1739	53.8993	1.7484	24.9779	1.2895	17.0660	0.5271
8	Sum of Mass at End of Run (mg)	99.0370	99.5954	69.6725	69.7622	39.3731	39.3573	27.6542	27.5667
9	Percent Change	0.34%	0.90%	0.51%	0.64%	0.84%	0.80%	0.77%	0.46%
10	Number of Nodes	21	21	21	21	21	21	21	21
11	Node Spacing	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
12	Time Step	0.0113	0.0113	0.0150	0.0151	0.0112	0.0113	0.0150	0.0151

		TCP Sagehill 110		TCP Woodburn 50	
Row		Langmuir	Freundlich	Langmuir	Freundlich
1	Retardation factor	2.97	2.97	131.70	111.68
2	% Reduction in Mass Due to Sorption	3.43	3.55	25.59	29.21
3	Total Mass Leached for Event (mg)	1.06	1.06	2.06	2.06
4	(mass input in column study)	1.05	1.05	2.06	2.06
5	Mass Sorbed at End of Run (mg)	0.0363	0.0376	0.5281	0.6027
6	Mass in Solution at End of Run (mg)	0.0184	0.0191	0.0040	0.0054
7	Mass into Aquifer During Run (mg)	1.0063	1.0044	1.5454	1.4728
8	Sum of Mass at End of Run (mg)	1.0610	1.0611	2.0775	2.0809
9	Percent Change	0.18%	0.19%	0.67%	100.84%
10	Number of Nodes	21	21	21	21
11	Node Spacing	5.24	5.24	2.50	2.50
12	Time Step	0.0274	0.0278	0.0120	0.0122

4.3.2 Discussion of Model Verification Results

Table 4.3.1.1 displays the results from the model runs simulating the column studies conducted as part of the NCHRP project. The results include mass balance results and comparisons and the node spacing and time step used in the finite difference scheme. The number of nodes, resulting node spacing, and the time step used in the model runs are displayed in rows 10 to 12 of the table. The time step for model runs utilizing nonlinear sorption isotherms is a function of the concentration. The time step is constant for the sorption phase of these verification runs because of the constant influent solute concentration. During the desorption phase the time steps would be different from those listed in row 12 of Table 4.3.1.1. The results in rows 1 and 2 in Table 4.3.1.1 display the retardation factor calculated by the model and the percent of mass sorbed to the soil at the end of the model run. Row 3 displays the mass predicted by the model reaching the soil column, while row 4 is the estimated mass used in the column study. Rows 5 and 6 display model results for the sorbed and dissolved mass remaining in the soil at the end of the model run. Row 7 is equivalent to the mass eluted from the soil column over the model run. Finally, rows 8 and 9 evaluate the conservation of mass over the model run. Row 8 is the summation of mass remaining in the soil and the mass eluted during the model run. Row 9 compares the result of row 8 (mass output) to row 3 (mass input). The difference displayed in row 9 is the result of small cumulative errors in the model run.

The solution of the algorithm for the sorbed and dissolved concentrations for each node and each time step can have small rounding errors. These errors accumulate over the course of a model run causing the "drift" in the mass accounted for by the model. The majority of model runs for simulating the column studies are run for several hundred hours, which is equivalent to nearly half a year's rainfall data based on rainfall analysis for a National Climatic Data Center rain gauge in Eugene, Oregon (data analyzed from 1949 to 1983 with average annual rainfall 49 inches and average of 978 hours of rainfall data collected annually). The error in the conservation of mass is less than one percent (row 9) for all of these relatively long model runs. This small error is negligible compared to the errors in the estimation of model parameters and, therefore, does not significantly contribute to differences between model predictions and real world results. The model results compared well with the column data for arsenic and 2,4,6-TCP in Sagehill soil (Figures 4.3.1.1, 4.3.1.2, and 4.3.1.9), while the results for arsenic and 2,4,6-TCP in the Woodburn soil (Figures 4.3.1.3, 4.3.1.4, and 4.3.1.10) are not as favorable. The results in the remaining column studies for copper and zinc (Figures 3.4.1.5, 4.3.1.6, 4.3.1.7, 4.3.1.8) were very poor. The model results using the Langmuir isotherm for copper gave C/Co estimates that were around 20% higher than actual breakthrough concentrations for both soils. The model runs for copper with the Freundlich isotherm produced mixed results. The fit for the Sagehill soil was mediocre (Figure 4.3.1.5). The time of arrival of the solute front was delayed by about 80%, and the decrease in concentration was even more delayed. The

results for copper using the Freundlich isotherm with the Woodburn soil were extremely poor (Figure 4.3.1.6). Results using the Freundlich isotherm and the Langmuir isotherm for zinc were poor for both soils (Figures 4.3.1.7 and 4.3.1.8). The time to breakthrough for both runs was much longer than the column study, and both model runs overestimated the concentration by about 50%.

The difficulties in modeling copper and zinc are due (at least) to the limited sorption data and the complexities of chemical interactions between metallic species and the soil. The available concentration data for analysis of the sorption isotherms are much lower than the concentrations that were modeled. Both copper and zinc sorb very strongly to the Woodburn and Sagehill soils. When testing for sorption in the laboratory, even a small amount of soil added to ACZA leachate removes the majority of the copper and zinc from solution. The modeled concentrations and available concentrations in the sorption data are compared in Table 4.3.2.1.

Table 4.3.2.1 Comparison of Modeled Leachate Concentrations with Available Concentrations in the Sorption Data

Compound or Element Modeled	**Maximum Concentration in Solution of Sorption Data Points – Sagehill Soil (mg/L)**	**Maximum Concentration in Solution of Sorption Data Points – Woodburn Soil (mg/L)**	**Concentration of Leachate Modeled in Column Comparisons (mg/L)**
TCP	1.43	0.76	10.46
Arsenic	1.90	1.00	2.00
Copper	18.24	14.48	29.74
Zinc	6.86	3.92	23.00

The lack of sorption data in the range of concentrations being modeled appears to result in high estimates of the parameters used in the sorption isotherms for copper and zinc, which, in turn, result in high estimates of the mass of material being sorbed by the soil. The high estimates of the sorption parameters account for the delay in the time for the solute front to arrive in the model calculations. This results in a somewhat delayed time of arrival for model runs using the Langmuir isotherm and the extremely delayed times with the Freundlich isotherm. Figures 4.3.2.1 and 4.3.2.2 help illustrate the differences observed in model runs with the different sorption isotherms.

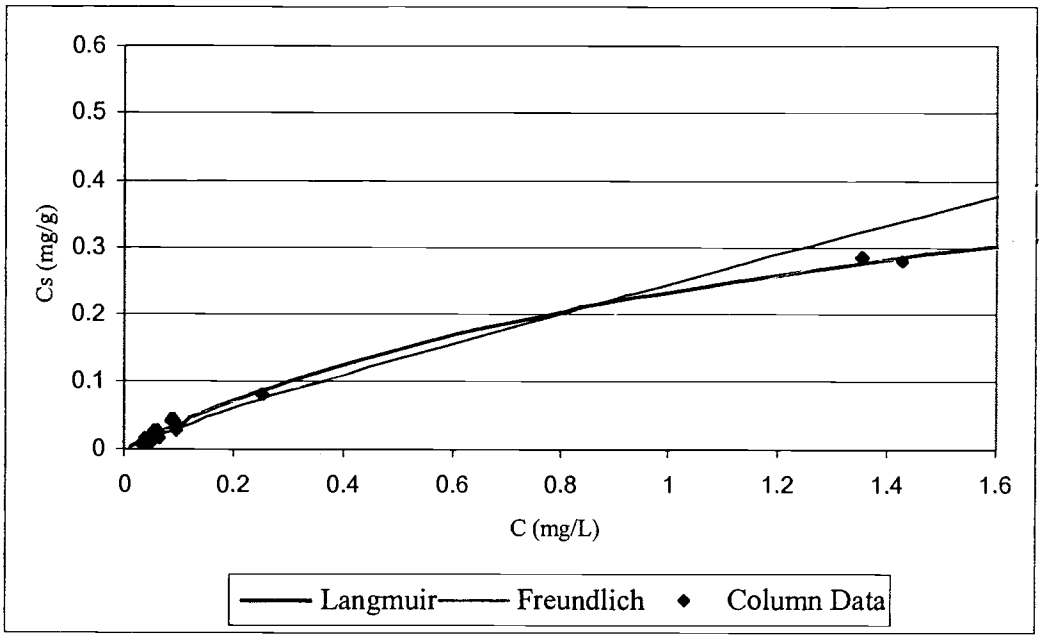

Figure 4.3.2.1 Langmuir and Freundlich Isotherm Comparison with Sorption Data for Zinc in Sagehill Soil

Figure 4.3.2.1 shows the Langmuir and Freundlich isotherms with the sorption data from laboratory experiments used to calculate the isotherms. The highest concentration in solution is 1.4 mg/L after sorption by the soils sample (details of the sorption studies can be found in Nelson et al., 2000c). Due to the nature of the isotherms, the predicted sorbed concentrations begin to diverge near the upper limit of the sorption data; however, the difference is not large. The predicted sorbed concentrations are 0.284 mg/g for the Langmuir isotherm and 0.334 mg/g for the Freundlich isotherm (or 18% higher than the Langmuir isotherm). This difference is not very significant at a dissolved concentration of 1.4 mg/L, but the concentration of zinc in the column study using Sagehill soil was 10.46 mg/L.

Figure 4.3.2.2 expands the x axis to include the concentration of zinc used in the column study. The available sorption data for zinc with the Sagehill soil (from Figure 4.2.5) are shown in Figure 4.3.2.2.

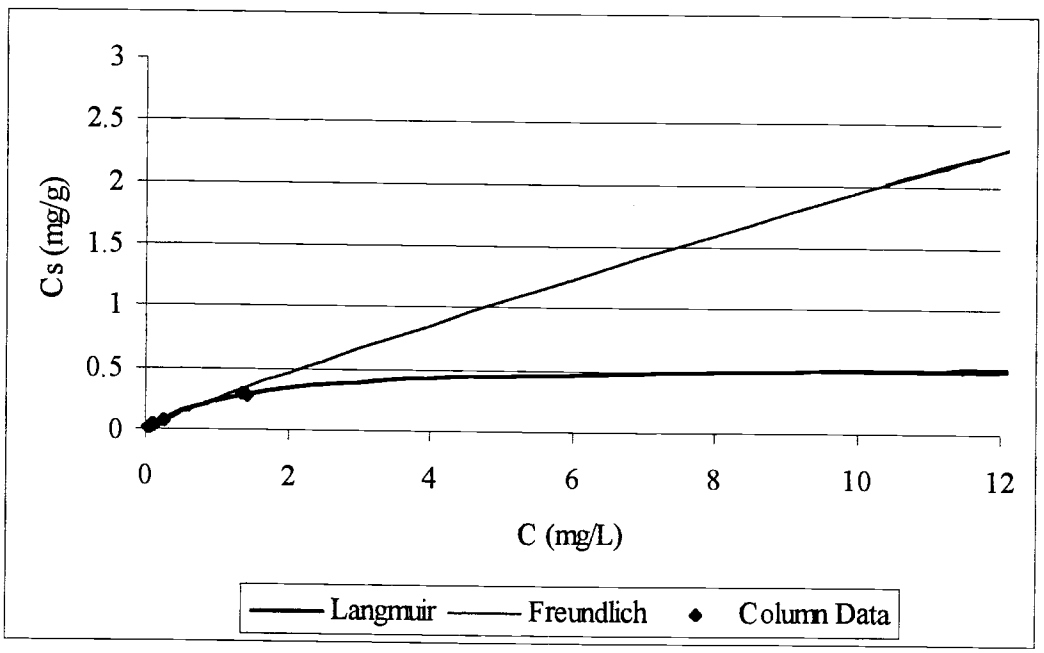

Figure 4.3.2.2 Langmuir and Freundlich Isotherm Comparison with Sorption Data for Zinc in Sagehill Soil (Expanded axes)

At the concentration of 10.46 mg/L used in the column study, the Langmuir isotherm predicts a sorbed concentration of 0.513 mg/g while the Freundlich isotherm predicts 2.04 mg/g of zinc will be sorbed by the soil. This is 398% higher than the sorbed concentration predicted by the Langmuir isotherm. The Langmuir isotherm resulted in a model run that overestimated the time required for the solute front to reach the end of the soil column. The factor of four difference predicted by

the Freundlich isotherm for the sorbed concentration results in the model predicting a drastic difference in the time required for breakthrough of the solute to occur. This same phenomenon applies to the column studies for both copper and zinc transport through the Woodburn soil, which resulted in a drastically delayed time for solute breakthrough. The limited range of concentrations available in the sorption studies contributes to the overestimation of sorbed concentrations with the Freundlich isotherm. The nature of the isotherm itself contributes to the problem as well. The isotherm is a power fit of the sorption data and, therefore, does not reach a maximum sorbed concentration. Sufficiently large concentrations in the sorption data would help attenuate this problem by eliminating the large extrapolation needed to predict sorbed concentrations at the dissolved concentrations used in the column studies. While this may account for the large time delays for the solute front to reach the end of the soil columns when modeling with the Freundlich sorption isotherms, it does not explain the large difference between the C/Co concentrations predicted by model runs with the Langmuir isotherms (e.g., Figures 4.3.1.5, 4.3.1.7, 4.3.1.8).

The other challenge in modeling the transport of copper and zinc is the complex chemical reactions the two metals can undergo. Several different mechanisms can influence the adsorption of metal ions to soils: cation exchange, specific adsorption, co-precipitation, and organic complexation (Alloway, 1995). Heavy metals can be classified into five categories based on accumulation mechanisms in soils: 1) adsorptive and exchangeable, 2) bound to carbonate

phases, 3) bound to reducible phases (Fe and Mn oxides), 4) bound to organic matter and sulfides, and 5) detrital and lattice metals (Ma and Rao, 1997). Four of these possible reaction mechanisms can result in copper and zinc being bound to the soil matrix in a fashion that may not be reversible over the limited duration for desorption in the column studies. Retention and release are influenced by several soil properties including texture, bulk density, pH, organic matter, and the type and amount of clay minerals. Retention-release reactions in the soil solution have been observed to be strongly time dependant for several heavy metals (e.g., Cr, Cu, Zn, Cd, and Hg) (Selim and Amacher, 1997).

Zinc has been found to adsorb reversibly by ion-exchange and irreversibly by lattice penetration in clay minerals. The reversible sorption by ion-exchange has been shown to undergo hysteresis with the adsorption curve in excess of the desorption curve. It was found that the amounts between the adsorption and desorption isotherm may be considered irreversibly fixed to the soil (Alloway, 1995).

Mass balances performed on the influent and effluent in the column studies demonstrate that significant amounts of the zinc and copper remain sorbed to the soil. Estimated amounts of sorbed material remaining in the columns after flushing with deionized water until the effluent concentration approached zero are shown in Table 4.3.2.2. The input values are the total mass of each metal into the column over the time of the test. The mass sorbed is the amount not accounted for in the effluent from the columns.

Table 4.3.2.2 Residual Amounts of Metals in the Soil Columns

Soil	Sagehill			Woodburn		
Solute	**Input (mg)**	**Sorbed (mg)**	**% Retained**	**Input (mg)**	**Sorbed (mg)**	**% Retained**
Arsenic	94.35	16.83	18	60.88	12.41	18
Copper	90.15	48.60	54	64.98	25.39	39
Zinc	35.73	27.06	76	25.75	14.79	57

Regardless of the cause for the majority of copper and zinc to be irreversibly sorbed, the breakthrough of these metals cannot be accurately modeled under the assumption that the sorption isotherms are reversible. It is possible that the copper and zinc are not irreversibly sorbed, but that desorption is rate limited. Rate limited desorption still contradicts the model assumption that the sorbed and dissolved concentrations of a solute are in equilibrium. The result is that the model is conservative in that it computes total desorption in a time span comparable to that required to sorb the material during the hydrologic event when using the Langmuir isotherm. Results when using the Freundlich isotherm severely overestimate the time to breakthrough. Estimations of breakthrough curves in the case of column comparisons, or mass loading to an aquifer in real world simulations, exceed the actual results by a factor of about 20 to 50% for the model runs using the Langmuir isotherm. This discrepancy increases for larger model depths. In reality, some additional desorption will occur with time, but probably not all. That is, especially

for metallic cations, some permanent sorption in the soil matrix is probable as described earlier.

Despite the disappointing results for copper and zinc, the comparisons of model results with column data still support the use of the model as a screening tool. Results for arsenic and TCP were good. In comparisons utilizing the Langmuir isotherm, the model results were good for arsenic and TCP, fair for copper, and poor for zinc. Model results using the Freundlich isotherm were good for arsenic and TCP but extremely poor for copper and zinc. This is likely due in part to the complexities of the sorption of metallic species discussed previously. In addition, the range of concentration data in the sorption studies for arsenic and TCP was relatively close to the concentrations used in the column studies, while the ranges in the copper and zinc sorption studies were much lower than the concentrations in the column studies (Table 4.3.2.1). The lack of sophistication of the model can be offset by a modeler familiar with transport and fate phenomena who is able to make educated deductions about how real-world complexities will affect the results predicted by the model. This short-coming in the model results for copper and zinc is a combination of the model limitations (i.e., reversible equilibrium sorption) and of the limited sorption data.

4.4 Column Study – Cadmium Transport

A column study by Christensen (1985) utilized a loam soil with moderate cation exchange capacity in a small laboratory column. Relative cadmium velocities of 0.0015 to 0.002 observed in the column studies indicated a very limited mobility. The relative velocity is the ratio of the distance traveled by the solute to the distance traveled by the solution. The relative velocity is equivalent to the inverse of the retardation coefficient shown in Equation 3.1.3. Relative velocity values observed in this column study result in a retardation coefficient ranging from 500 to 670. Breakthrough data from two of the soil columns were utilized for comparison with model output. Column and soil parameters are listed in Table 4.4.1 for columns 9 and 11 in the study.

Table 4.4.1 Column Study Parameters for Cadmium Transport

Parameter	Units	Column 9	Column 11
Column Length	mm	20	20
Column Area	mm^2	97	97
Dispersivity	mm	2	2
Soil Porosity		0.33	0.33
Bulk Density	(g/ml)	1.70	1.70
Flow Rate	ml/hr	not given	not given
Seepage Velocity	mm/hour	5	5
Leachate Conc	ug/L	20.0	10.0
Kd	(L/g)	1.05×10^{-5}	1.05×10^{-5}
Number of Nodes		21	21
Node Spacing		1	1
Time Step	hour	0.043	0.043

The model was modified to reflect the constant inlet concentrations of the columns and column length. The soil parameters and linear distribution coefficient were entered in the model input sheets. The flow rate in the column study is not specified so a low seepage velocity of 5 mm/hr was assumed. The column study results were compared with the model results by plotting pore volumes on the x axis in the results rather than the time.

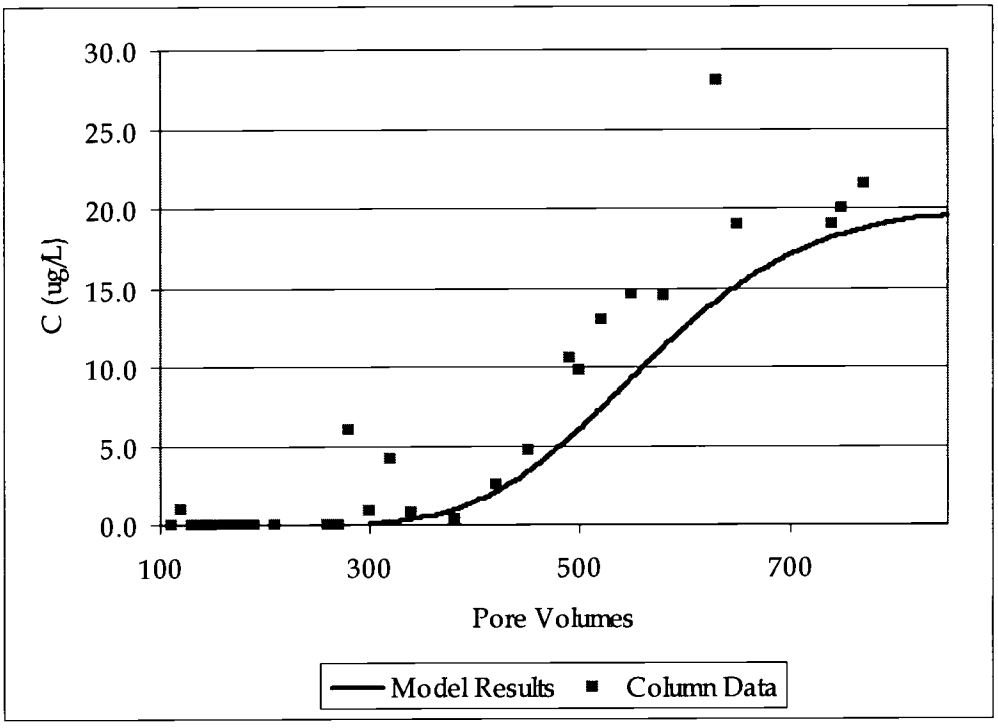

Figure 4.4.1 Model Results and Column Data Column 9

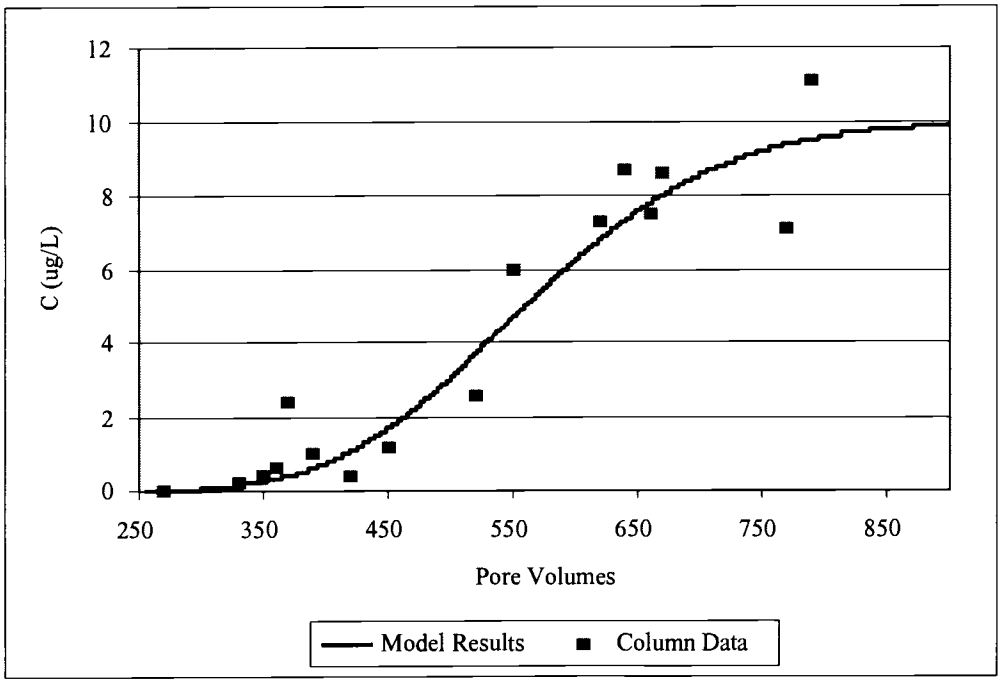

Figure 4.4.2 Model Results and Column Data Column 11.

The low inlet concentrations decrease the propensity for complex chemical reactions to occur as in the Oregon State University column studies with copper and zinc. The cadmium column study results support the conclusion that under the proper circumstances the model is capable of simulating the transport of metals very well.

4.5 Column Study – Pesticide (Picloram) Transport

A study by Kryszowska et al. (1994) examined the movement of the pesticide picloram through a 50-cm column prepared to simulate the A, B1, and B2 soil horizons of the Wyoming soil used in the study. The laboratory soil column was prepared with a 20-cm A soil horizon and 15-cm B1 and B2 soil horizons. Initially 60 mL of water containing 15.9-mg/L picloram were applied to the column. Following the herbicide application, 60 mL of water were applied daily to the column for 28 days. (The study did not specify the method in which the water was applied.) In the model simulation a saturated steady flow rate was assumed. The model was modified to simulate the flow rate and initial source concentration of herbicide applied. The model was also modified to represent the actual physical dimensions of the column used in the laboratory study. This allows for comparison of the calculated amounts of mass flowing into the soil column by the model compared to the mass injected in the column study. The layering option in the model IMPACT was used to simulate the soil layers in the column study. Table 4.5.1 lists the physical parameters of the soil layers. To specify the parameters for

the column cross sectional area, seepage velocity, and the concentration of the solute used in the column study, values must be entered in the program code. The 60-mL volume of solute was simulated in the model by setting the source concentration to 15.9 mg/L for the first 24 hours of the model run at a flow rate of 2.5 mL/hour. All other parameters used for simulation of the column study are entered through the user forms in IMPACT. Soil layers B1 and B2 are simulated using the layering option in IMPACT for simulating additional soil layers below the initial reference environment.

Table 4.5.1 Parameters Used in IMPACT for Simulation of Picloram Column Study

Parameter	Units	Horizon A	Horizon B1	Horizon B2
Column Length	mm	200	150	150
Column Area	mm^2	5542	5542	5542
Dispersivity	mm	20	15	15
Soil Porosity		0.2	0.2	0.2
Bulk Density	(g/mL)	1.34	1.54	1.52
Flow Rate	mL/hr	2.5	2.5	2.5
Seepage Velocity	mm/hour	2.256	2.256	2.256
Leachate Conc	mg/L	15.9	N/A	N/A
K_f	(Freundlich)	7.65×10^{-5}	2.58×10^{-4}	1.0×10^{-7}
N	(Freundlich)	1.064	0.98	0.98
Biodegradation	hr^{-1}	0.00163	0.0163	0.00163
Number of Nodes		21	21	21
Node Spacing		10	7.5	7.5
Time Step	hour	0.962 (initial)	varies	varies

The biodegradation option in the model was used to simulate the degradation rate of 0.039 $days^{-1}$ (0.00163 $hours^{-1}$) fit from the column breakthrough data.

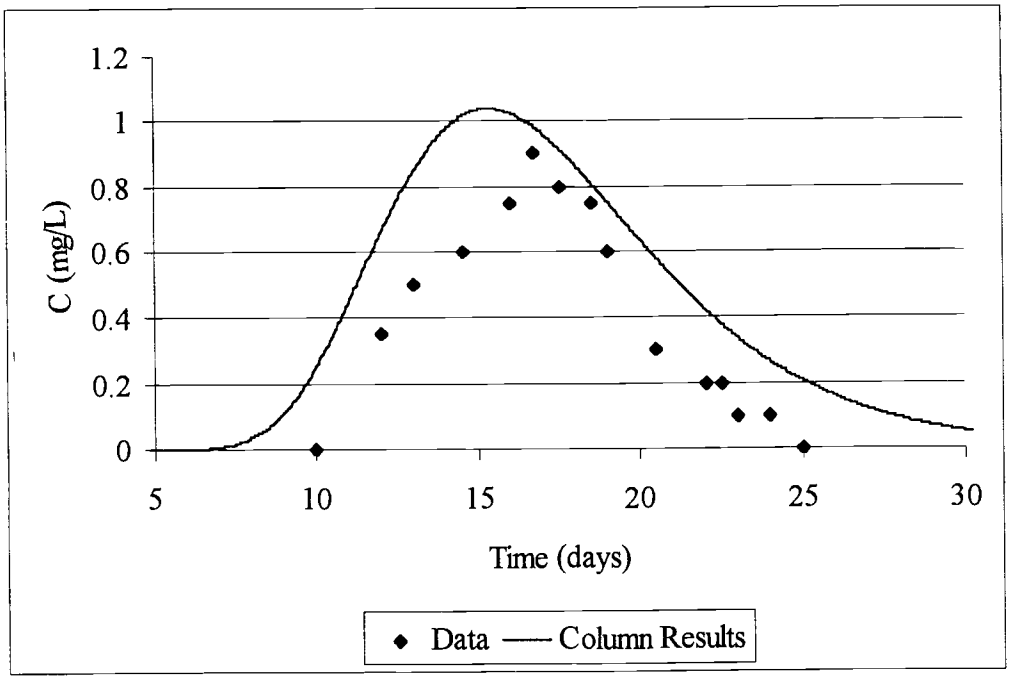

Figure 4.5.1 Model Results and Column Data for Picloram Transport

Table 4.5.2 Model Output for Picloram Simulation

Horizon A	
Retardation factor	1.23
Percent of Mass Sorbed (%)	0.0
Total Mass Leached for Event (mg)	0.954
Mass Sorbed at End of Run (mg)	0.0
Mass in Solution at End of Run (mg)	0.0
Mass into Aquifer During Run (mg)	0.824
1st order biodegradation rate (hr^{-1})	0.00163
Horizon B1	
Retardation factor	3.21
Percent of Mass Sorbed (%)	68.8
Mass Sorbed at End of Run (mg)	0.0
Mass in Solution at End of Run (mg)	0.0
Mass into Aquifer During Run (mg)	0.740
1st order biodegradation rate (hr^{-1})	0.00163
Horizon B2	
Retardation factor	1.00
Percent of Mass Sorbed (%)	0.08
Mass Sorbed at End of Run (mg)	0.0
Mass in Solution at End of Run (mg)	0.0
Mass into Aquifer During Run (mg)	0.660
1st order biodegradation rate (hr^{-1})	0.00163

The mass calculated by the model for input into the soil column for the horizon A simulation is 0.954 mg which is equal to the mass input in the column study 60 mL × 15.9 mg/L = 0.954. In the column study only 51.9% of the picloram was eluted from the column with about 1% of the mass of the picloram remaining sorbed to the soil. The model results predict 0.66 mg of picloram leaving the soil column which is 69.2% of the mass input. This discrepancy accounts for the somewhat higher concentrations calculated by the model compared to the concentrations eluted in the column study as shown in Figure 4.5.1. The somewhat larger spread in the model estimations indicates that a dispersivity set to 10% of the model length overestimates the dispersion in the column study.

The model was run again using a biodegradation rate constant (0.0032 hr^{-1}) that results in 48% of the mass exiting the column (twice the biodegradation rate cited in the study) and a dispersion coefficient set to 5% of the soil horizon lengths. All other parameters for the model run were the same as those shown in Table 4.5.2. Using the adjusted biodegradation rate and dispersion coefficient gave the results sown in Figure 4.5.2 and Table 4.5.3.

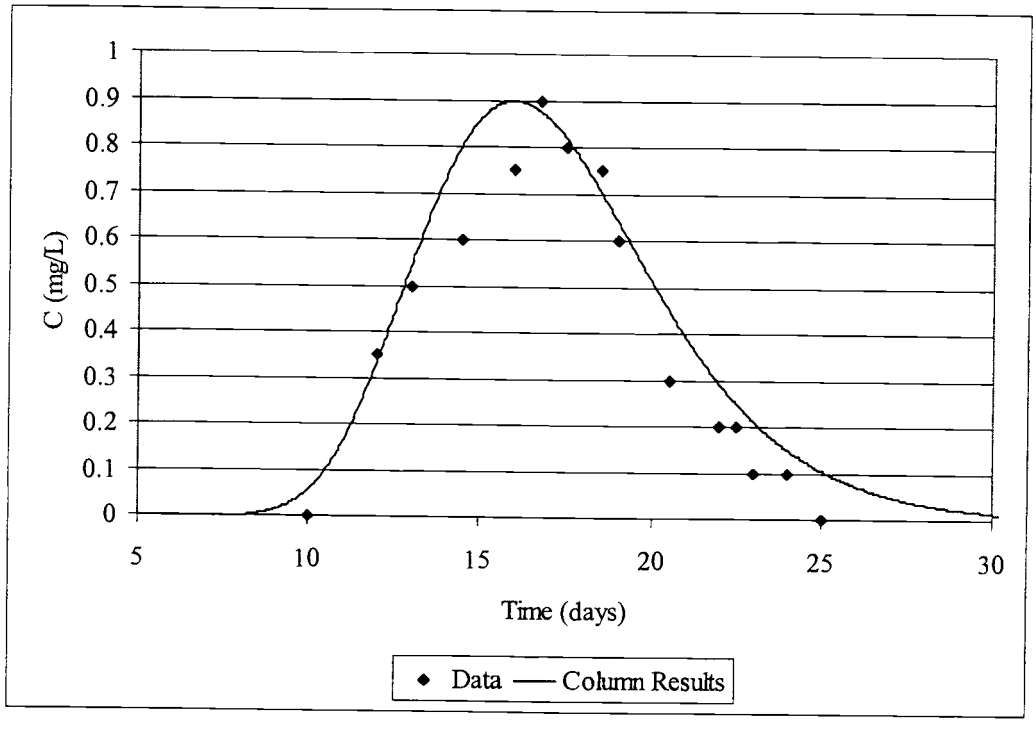

Figure 4.5.2 Model Results with Modified Biodegradation and Dispersion and Column Data for Picloram Transport

Table 4.5.3 Model Output for Picloram Simulation with Adjusted Biodegradation Rate

Horizon A	
Retardation factor	1.12
Percent of Mass Sorbed (%)	0.0
Total Mass Leached for Event (mg)	0.954
Mass Sorbed at End of Run (mg)	0.0
Mass in Solution at End of Run (mg)	0.0
Mass into Aquifer During Run (mg)	0.716
1st order biodegradation rate (hr^{-1})	0.0032
Horizon B1	
Retardation factor	3.3
Percent of Mass Sorbed (%)	69.7
Mass Sorbed at End of Run (mg)	0.0
Mass in Solution at End of Run (mg)	0.0
Mass into Aquifer During Run (mg)	0.580
1st order biodegradation rate (hr^{-1})	0.0032
Horizon B2	
Retardation factor	1.00
Percent of Mass Sorbed (%)	0.08
Mass Sorbed at End of Run (mg)	0.0
Mass in Solution at End of Run (mg)	0.0
Mass into Aquifer During Run (mg)	0.460
1st order biodegradation rate (hr^{-1})	0.0032

The adjustment of the biodegradation and dispersion coefficients results in a good fit of model results to column data as shown in Figure 4.5.2. The modification to the dispersion coefficient does not significantly change the model result, but only narrows the breakthrough curve slightly. The adjustment to the biodegradation rate constant results in a comparable amount of mass eluted in the model predictions as in the column study (48 to 52 percent respectively). These results demonstrate that although some parameters may need to be assumed, IMPACT is flexible enough to fit most data.

5 CONCLUSIONS

5.1 Summary of Results

The reliability of the model is highly dependent on the input parameters. Equally important are the applicability of the model assumptions and limitations and how the model results are interpreted and used. In most instances the combination of solute and soil environment to be modeled will not be well represented by the available data included in the database portion of the model. This will require that the modeler approximate the removal, reduction, and retardation parameters based upon the available data in the model and information in the scientific literature. In these instance the model is best regarded as a screening model; that is, the model is capable of providing a range of possible results that should be based upon multiple model runs reflecting the uncertainties in the model parameters influencing transport, particularly sorption to the soil. When data are available for the specific combination of solute and soil to be simulated, the model is capable of achieving results that are more representative of a predictive model. The ability of the model to simulate solute transport in a predictive sense is also highly dependant on the applicability of the model limitations to the situation to be modeled. For example, the excellent agreement between column and model results for 2,4,6 trichlorophenol indicates that sufficient data are available and model assumptions are accurate enough for this scenario to give accurate predictions of the solute transport (i.e., the model is predictive).

Despite the availability of similar data for copper and zinc, the data and model assumptions are insufficient to make accurate predictions for the transport of these solutes for the reasons previously discussed.

Key Assumptions of the Model

- The effects of leaching and individual environmental effects, which are tested independently, can be superimposed.
- Dominant environmental effects have been taken into account. Laboratory experiments cover most of the realm of possible environmental situations.
- The sorbed and dissolved solute is in equilibrium. Sorption phenomena are not rate-limited and sorption is reversible.
- The soil is homogeneous and isotropic.
- The flow is assumed to be uniform and unidirectional (downward from reference environment).
- Soil moisture is assumed to be constant over the course of a model run.
- The removal mechanisms in the soils are assumed to be sorption and biodegradation.

Key Limitations

- The model cannot simulate heterogeneous or structured soils except for layering.
- The model does not simulate changes in the soil moisture content.
- The model cannot simulate chemical reactions (other than sorption and biodegradation), such as precipitation or complex formation.
- Leaching rates for large highway surfaces are extrapolated from small (76 cm^2) flat plate studies in the laboratory. Similar extrapolation occurs for column studies of fill materials.

Model parameters of particular importance are the sorption isotherm and physical properties of the soil. It is important to remember that the model does not

provide an answer, but only an indication of what may be occurring in the field. Many factors can influence solute transport that the model (in its current development) cannot simulate. An understanding of solute transport and detailed knowledge of the physical site to be modeled are necessary ingredients for the model to be used to its potential as a screening tool for predicting possible environmental impacts as a result of the use of highway construction and repair materials.

The algorithm developed for solution of the advection-dispersion equation conserves mass and incorporates sorption, desorption, and biodegradation reactions. Model results compared favorably with an analytical solution of the advection-dispersion equation, with column studies for arsenic and 2,4,6-trichlorophenol conducted as part of this project, and with column study results for the transport of cadmium and for the transport of the pesticide picloram through three distinct soil layers. These comparisons support the conclusion that the transport and fate model developed during this project is quite capable of simulating the transport of solutes which do not undergo reactions, other than sorption and biodegradation in the soil environment. Model results did not compare well to copper and zinc column studies conducted as part of this project. Part of the difficulty was limitations in the model assumptions and the limited sorption data range, resulting in the overestimation of extrapolated sorption concentrations for model runs using the Freundlich isotherm. Another possible reason for the less than favorable model results for copper and zinc is the inability of the model to simulate

the complex chemical reactions and complexation of metallic cations in the soil environment affecting solute transport. Despite this inability of the model to accurately predict the transport of all solutes in the column studies, the developed algorithm has met the desired objectives of model development as part of the NCHRP project. The model IMPACT can be a useful tool for a modeler with an understanding of the processes at work. The modeler needs to have an understanding of real world complexities, which the model cannot simulate, that differ from the model assumptions and needs to apply her or his experience and good judgment in estimating the effects of these complexities on the results output by the model.

5.2 Recommendations for Future Work

Future efforts to improve the model could begin with the model assumptions and limitations. Incorporating changes into the model to address its limitations will be of little use without accompanying laboratory or field work to provide the necessary information for the new model parameters. For example, addressing preferential flow may not be practical because of the need for characterization of the field conditions where the model is to be applied. Application of the model is intended for highway construction and repair sites which typically have highly disturbed soils. Information on probable changes to soil parameters due to construction is not currently provide in the model. The inclusion of highway related soil parameters in the model database would greatly assist the modeler's ability to

more closely simulate field conditions. In addition, there is the potential to include additional laboratory parameters for removal, retardation, and reduction mechanisms for numerous soil and material combinations.

The Visual Basic for Applications (VBA) code has proven sufficient for the model in its current state of development. Further refinements to the model may be better suited for a more sophisticated programming language that would allow the model to be run independently of a software application such as Excel. Significant additions to the model database would be more suited to storage in a true database format rather than the Excel spreadsheets that are used for storage of laboratory parameters. Due to the similarity of VBA with the Visual Basic programming language, Visual Basic would allow the most direct transfer of the existing code to create a stand-alone computer model.

The best way to improve the range of situations the model is capable of simulating would be to include a rate-limited sorption term that could be used to simulate one or more chemical processes that is not occurring in equilibrium. These include precipitation and solution, co-precipitation, oxidation and reduction, adsorption and desorption, ion exchange, complexation, nuclear decay, and ion filtration (Mercer and Faust, 1980). This term might also be used as a storage parameter for hysteretic effects in the desorption isotherm. This type of improvement to the model will require further laboratory work to provide the necessary information, or, at the very least, some literature review.

The ability to simulate changes in soil moisture content and unsaturated flow, while useful, is not considered to be a high priority. In order to simulate changes in soil moisture content, the soil water retention and hydraulic conductivity functions are needed. Direct field measurements to determine the unsaturated hydraulic conductivity are time consuming and expensive (Nielson et al., 1986). While transport is of vital importance in understanding the motion of contaminant plumes in larger surface or groundwater bodies, the principal issue at a highway C&R site is the total mass flux of contaminant that enters the nearest surface stream, pond, lake, etc., or that enters a subsurface aquifer below the construction area. That is, the temporal distribution, affected by changes in the soil moisture content, is unlikely to be of great importance; rather, the receiving waters will be impacted primarily by the total contaminant mass that enters. While more detailed timing estimates can be made, realistic knowledge of the temporal distribution will relate mainly to the duration of storm events that cause runoff, coupled with the lifetime of the construction site. Thus, total storm event loads can be estimated that do not require intricate knowledge of miniature water pathways but instead use gross runoff characteristics.

The are many possible refinements to IMPACT that could improve the usefulness of the model for simulating contaminant transport in the near highway environment. The best way to reveal the shortcomings (or potential improvements)

to the model would be to have practicing highway engineers test the model's utility. Ideally, additional refinements and research will serve to increase the usefulness of IMPACT for highway engineers.

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APPENDIX

Appendix: Programming Code for the Developed Algorithm

The code for the numerical method is the heart of the program. The code from the Visual Basic for Applications program is explained following the definition of variables; the text in italics explains what each line of code does.

Definition of variables used in example calculations:

Variable in code	Definition of Variable	Units
aAreaNode	cross sectional area of node	m^2
bBulkdensity	bulk density of the soil	g/L
cConcEst	estimate of concentration in iteration	mg or mmol/L
cConcEstCounter	counter used to increase the concentration estimate in the iterative process	no units
cConcMax	maximum concentration if all the mass at a node is in solution	mg or mmol/L
cConcNew	concentration at a node at end of a time step	mg or mmol/L
cConcOld	concentration at a node from previous time step	mg or mmol/L
cConcSorbEst	estimate of sorbed concentration used in iteration	mg or mmol/g
cConcSorbNew	concentration sorbed at a node at end of a time step	mg or mmol/g
cConcSorbOld	conc. sorbed at a node from previous time step	mg or mmol/g
dDataDepth	depth of rainfall of the Nth event	mm
dDataFlowRate	flow rate of leachate of the Nth event	m^3/hr
dDataSourceConc	concentration of leachate of the Nth event	mg or mmol/L
dDegrate	biodegradation rate	hr^{-1}
dDeltaMass	change in mass at a node over a time step	mg or mmol
dDeltaMassAdve	change in conc. at a node due to advection	mg or mmol/L
dDeltaMassDegr	change in conc. at a node due to biodegradation	mg or mmol/L
dDeltaMassDisp	change in conc. at a node due to dispersion	mg or mmol/L
dDeltaT	duration of a time step in finite difference calcs.	hr
dDeltaZ	distance between node in model	mm
dDepthRainTotal	total depth of rain	mm
dDFofcConcEstDC	parameter used in Newton Raphson iteration	no units
dDispersivity	property of soil used to calculate the dispersion	m
fFofcConcEst	parameter used in Newton Raphson iteration	no units
gGroundWaterVel	seepage velocity of flow in aquifer	mm/hr
kKd	linear distribution coefficient	L/g
kKf	coefficient of Freundlich isotherm	L/g (if nN = 1)
lLangAlpha	alpha constant from Langmuir isotherm	L/mg
lLangBeta	beta constant from Langmuir isotherm	mg/g
lLinearDegRate	linear degradation rate	mg or mmol/L
hrmMassIntoAquifer	cumulative mass leached into the aquifer	mg or mmol
mMassIntoSoil	cumulative mass leached into the soil	mg or mmol
mMassNode	mass at node used to calculate dissolved and sorbed concentrations	mg or mmol
mMassNodeEst	estimate of mass at node used in iteration	mg or mmol
mMassNodeNew	mass at node at end of time step	mg or mmol
mMassNodeOld	mass at a node from previous time step	mg or mmol
nNumberofEvents	number of events of rainfall in long term runs or number of hours of single event run	no units
nNumberofNodes	number of nodes used in finite differences method	no units
nNumberofTimes	number of calculation iterations during an event	no units
pPorosity	fraction of pore spaces in the soil	no units

Variable in code	Definition of Variable (concluded)	Units
rRetardation	retardation factor for solute during model run	no units
sSeepageVelocity	seepage velocity of the water through the soil	mm/hr
tTimeIncrement	length of time of long term rainfall data	hr
tTimeStep	length of time for finite difference calculations	hr
tTimetoAquifer	time for solute from leachate to reach aquifer	hr
vVel	seepage velocity for the Nth event	mm/hr
vVolContWaterIntoAquifer	volume of contaminated water into aquifer	L
vVolumeNode	volume of each node	L
vVolumeofLeachate	volume of leachate for the Nth event	m^3

Outer loop is run for each increment.
For K = 1 To nNumberofEvents

Set seepage velocity for the time increment based on depth of rainfall, which has been limited to the amount that can infiltrate.
sSeepageVelocity = (dDataFlowRate(K) / aAreaNode) × 1000 / pPorosity

Define initial Darcy velocity at each node.
```
For I = 1 To (nNumberofNodes + 1)
        vVel (I) = sSeepageVelocity
Next I
```

Begin finite difference procedure.
This loop runs the finite difference procedure for each time step or the rainfall increment duration.
Do Until tTempTime ≥ tTimeIncrement

reset temporary tracking variable
tTemp = 0

Search for the highest concentration to calculate the minimum Retardation coefficient
```
For I = 1 To nNumberofNodes
        If cConcOld(I) > tTemp Then tTemp = cConcOld(I)
Next I
```

Compare with the source concentration to find the highest solute concentration advecting into a node
If dDataSourceConc(K) > tTemp Then tTemp = dDataSourceConc(K)

set concentration to a minimum value to avoid division by zero with Freundlich isotherm
If tTemp < 0.00001 Then tTemp = 0.00001

calculate the retardation coefficient for the selected isotherm
If iIsotherm = "Linear" Then rRd = (1 + (bBulkdensity / pPorosity) × kKd)
If iIsotherm = "Freundlich" Then rRd = (1 + (bBulkdensity / pPorosity) × (kKf × nN × (tTemp ^ (nN - 1))))
If iIsotherm = "Langmuir" Then rRd = (1 + (bBulkdensity / pPorosity) × (lLangAlpha × lLangBeta) × ((1 + lLangAlpha × tTemp) ^ -2))

calculate time step from stability criteria

dDeltaT = (((2 × dDispersivity × 1000 × sSeepageVelocity) / (dDeltaZ ^ 2)) + SeepageVelocity / (rRd × dDeltaZ)) ^ -1

limit time step to no larger than time increment of data
If dDeltaT > tTimeIncrement Then dDeltaT = tTimeIncrement

limit time step to residual time if the end of the time increment
If dDeltaT + tTempTime > tTimeIncrement Then dDeltaT = tTimeIncrement – tTempTime

track cumulative time
tTempTime = tTempTime + dDeltaT

calculate the mass, dissolved concentration, and sorbed concentration at the first node with the flux boundary condition
approximate dC/dZ and d2C/dZ2 using finite difference approximations
dDCDZ = (cConcOld(1) - dDataSourceConc(K)) / (dDeltaZ) ' dC/dZ

limit dispersion to only transport mass between first and second node, no mass dispersed across boundary into first node to maintain conservation of mass
dDDCDDZ = (cConcOld(2) - cConcOld(1)) / (dDeltaZ ^ 2) ' d2C/dZ2

Calculate amount of mass into and out of the node due to different terms in the advection dispersion equation, 1000 to convert dispersivity from meters to mm
dDeltaMassDisp(1) = dDispersivity × 1000 × vVel(1) × dDDCDDZ × dDeltaT
dDeltaMassAdve(1) = -vVel(1) × dDCDZ × dDeltaT
dDeltaMassDegr(1) = (dDegrate × cConcOld(1) + lLinearDegRate) × dDeltaT
dDeltaMass(1) = (dDeltaMassDisp(1) + dDeltaMassAdve(1) + DeltaMassDegr(1)) × vVolumeNode × pPorosity

Find new mass at the first node
mMassNodeNew(1) = mMassNodeOld(1) + dDeltaMass(1)

Use the selected isotherm to find new concentration in solution at node 1 from sorption isotherm
If mMassNodeNew(1) > 0 Then

linear isotherm
If Isotherm = "Linear" Then
    cConcNew(I) = mMassNodeNew (I) / (vVolumeNode × (pPorosity + Kd × bBulkdensity))
    cConcSorbNew(I) = kKd × cConcNew (I)

End If

Freundlich isotherm
If Isotherm = "Freundlich" Then
Find maximum possible concentration in solution, used for beginning estimate.
    cConcMax = mMassNodeNew (I) / (vVolumeNode × pPorosity)
    cConcEstCounter = 0 - *counter for initial estimate*
    mMassNodeEst = 0 - *counter for initial estimate*

    This is to find a good first estimate for the Newton-Raphson iteration below.
    Do Until Mass Node Est > mMassNodeNew (I)
        cConcEstCounter = cConcEstCounter + 0.01
        cConcEst = cConcEstCounter × cConcMax
        cConcSorbEst = kKf × (cConcEst ^{nN})
        mMassNodeEst = vVolumeNode × (pPorosity × cConcEst + bBulkdensity × cConcSorbEst)
    Loop

    Newton-Raphson iteration for estimate of the concentration.
    Do Until 0.9995 × mMassNodeNew (I) < mMassNodeEst < 1.0005 × mMassNodeNew (I)

        FofcConcEst - function of estimated C
        fFofcConcEst = (bBulkdensity × Kf × (cConcEst ^{nN})) + (pPorosity × cConcEst) - (mMassNode(I) / vVolumeNode)

        Df(C)/DC – rate of change of estimate w/ concentration
        dDFofcConcEstDC = (bBulkdensity × kKf × nN × (cConcEst $^{nN-1}$)) + pPorosity
        cConcEst = cConcEst - (fFofcConcEst / dDFofcConcEstDC)
        cConcSorbEst = kKf × (ConcEst ^{nN})
        mMassNodeEst = vVolumeNode × (pPorosity × cConcEst × bBulkdensity × cConcSorbEst)

Loop

Sorbed and dissolved concentration found within 0.05% of equilibrium values, compromise between accuracy and time of solution.

cConcNew (I) = cConcEst

cConcSorbNew(I) = kKf × cConcEst ^nN

End If

Langmuir isotherm

iIsotherm = "Langmuir" Then

a = (pPorosity × lLangAlpha × vVolumeNode)

b = vVolumeNode × pPorosity + lLangAlpha × lLangBeta × bBulkdensity × vVolumeNode - lLangAlpha × mMassNodeNew(I)

c = - mMassNodeNew (I)

cConcNew (I) = $(-b + (b^2 - 4 \times a \times c)^{0.5}) / (2 \times a)$

cConcSorbNew(I) = (lLangAlpha × lLangBeta × cConcNew (I)) / (1 + lLangAlpha × cConcNew (I))

End If

This loop calculates the new sorbed and dissolved concentrations for each node, except the first node,

For I = 2 To nNumberofNodes

if there is not any dissolved mass at the node above, at the node, or at the node below then no mass will enter next node skip to next node to speed upiteration times

If cConcOld(I - 1) = 0 And cConcOld(I) = 0 And cConcOld(I + 1) = 0 Then GoTo 500

Approximate dC/dZ and d^2C/dZ^2 using finite difference approximations.

$\delta C/\delta Z$ = (cConcOld (I) – cConcOld (I - 1)) / (DeltaZ)

$\delta^2C/\delta Z^2$ = (cConcOld (I + 1) - 2 × cConcOld (I) + cConcOld (I - 1)) / (dDeltaZ ^{2})

Mass calculations - amounts of mass into and out of cell due to different terms in the advection dispersion equation. Change in mass due to dispersion

dDeltaMassDisp (I) = dDispersivity × 1000 × vVel(I) × $\delta^2C/\delta Z^2$ × dDeltaT

dDeltaMassAdve (I) = -Vel(I) × $\delta C/\delta Z$ × dDeltaT

dDeltaMassDegr(I) = (dDegrate × cConcOld (I)) × dDeltaT)

dDeltaMass(I) = (dDeltaMassDisp (I) + dDeltaMassAdve (I) + dDeltaMassDegr(I)) × pPorosity × vVolumeNode

mMassNodeNew (I) = mMassNodeOld(I) + dDeltaMass (I)

Use selected isotherm to find new concentration in solution from sorption and soil equilibrium.
If mMassNodeNew (I) > 0 Then

Linear isotherm
If Isotherm = "Linear" Then
    cConcNew(I) = mMassNodeNew (I) / (vVolumeNode × (pPorosity + Kd × bBulkdensity))
    cConcSorbNew(I) = kKd × cConcNew (I)
End If

Freundlich isotherm
If Isotherm = "Freundlich" Then
    Find maximum possible concentration in solution, used for beginning estimate.
    cConcMax = mMassNodeNew (I) / (vVolumeNode × pPorosity)
    cConcEstCounter = 0 - *counter for initial estimate*
    mMassNodeEst = 0 - *counter for initial estimate*

    This is to find a good first estimate for the Newton-Raphson iteration below.
    Do Until Mass Node Est > mMassNodeNew (I)
        cConcEstCounter = cConcEstCounter + 0.01
        cConcEst = cConcEstCounter × cConcMax
        cConcSorbEst = kKf × (cConcEst ^{nN})
        mMassNodeEst = vVolumeNode × (pPorosity × cConcEst + bBulkdensity × cConcSorbEst)
    Loop

    Newton-Raphson iteration for estimate of the concentration.
    Do Until 0.9995 × mMassNodeNew (I) < mMassNodeEst < 1.0005 × mMassNodeNew (I)

        FofcConcEst - function of estimated C
        fFofcConcEst = (bBulkdensity × Kf × (cConcEst ^{nN})) + (pPorosity × cConcEst) - (mMassNode(I) / vVolumeNode)

        Df(C)/DC – rate of change of estimate w/ concentration
        dDFofcConcEstDC = (bBulkdensity × kKf × nN × (cConcEst $^{nN-1}$)) + pPorosity
        cConcEst = cConcEst - (fFofcConcEst / dDFofcConcEstDC)
        cConcSorbEst = kKf × (ConcEst ^{nN})
        mMassNodeEst = vVolumeNode × (pPorosity × cConcEst × bBulkdensity × cConcSorbEst)

Loop

Sorbed and dissolved concentration found within 0.05% of equilibrium values, compromise between accuracy and time of solution.

```
    cConcNew (I) = cConcEst
    cConcSorbNew(I) = kKf × cConcEst ^nN
End If
```

Langmuir isotherm

```
If iIsotherm = "Langmuir" Then
        a = (pPorosity × lLangAlpha × vVolumeNode)
        b = vVolumeNode × pPorosity + lLangAlpha × lLangBeta × bBulkdensity ×
                vVolumeNode - lLangAlpha × mMassNodeNew(I)
        c = - mMassNodeNew (I)
        cConcNew (I) = (-b + (b^2 - 4 × a × c)^0.5) / (2 × a)
        cConcSorbNew(I) = (lLangAlpha × lLangBeta × cConcNew (I)) /
                                (1 + lLangAlpha × cConcNew (I))
End If
```

skip to this point if no mass will reach the node

500:

Next I – *begin calculations for next node number*

The following mass and volume calculations are completed for every time step. Track mass into soil from flux across model boundary, the conversion factors 1m/1000mm x 1000L /1m³ cancels out.

```
mMassIntoSoil = mMassIntoSoil + (sSeepageVelocity × aAreaNode × pPorosity ×
                        dDeltaT × dDataSourceConc (K))
```

Track contaminated water (volume of leachate) for the flow increment.

```
vVolumeofLeachate = vVolumeofLeachate + dDataFlowRate (K) × dDeltaT
```

Track mass introduced into aquifer from flux across model boundary.

```
mMassIntoAquifer = mMassIntoAquifer + (sSeepageVelocity × aAreaNode ×
                        pPorosity × dDeltaT × cConcOld (nNumberofNodes))
```

Track volume of contaminated water into aquifer from flux across boundary.

```
If cConcOld (nNumberofNodes) > 0.000001 Then
 vVolContWaterIntoAquifer = vVolContWaterIntoAquifer + (sSeepageVelocity ×
                                aAreaNode × pPorosity × dDeltaT)
End If
```

Transfer concentration values for next set of calculations.
For I = 2 To (nNumberofNodes + 1)
    cConcOld(I) = cConcNew (I)
    cConcSorbOld(I) = cConcSorbNew(I)
    Mass Node Old(I) = mMassNodeNew (I)
    Track time to reach aquifer - if this occurs during run

    If cConcOld (nNumberofNodes + 1) > 0.000001 And tTimetoAquifer = 0 ...
        ... Then tTimetoAquifer = tTimeStep × dDeltaT + (increment # - 1) × tTimeIncrement
Next I

Iterate through steps for individual increment.
Loop

Track rain depth for retardation calculation.
dDepthRainTotal = dDepthRainTotal + dDataDepth (K)

Calculate retardation factor if solute reaches aquifer. If solute does not reach aquifer the retardation coefficient is calculated from the depth of penetration (not shown here).
If tTimetoAquifer > 0 Then rRetardation = dDepthRainTotal / mModelDepth

Calculations for the output of data to the 'Aquifer Inputs' sheet are performed as explained below in Model Output Calculation. Data are then output to the 'Aquifer Inputs' sheet at the end of every increment, and a concentration profile is output to the 'Model Results' sheet approximately every 10% of the rain increments.

Next K - *iterates through all increments*