THE ASSESSMENT OF GROUNDWATER POLLUTION POTENTIAL RESULTING FROM STORMWATER INFILTRATION BMP'S

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16. ABSTRACT

Washington State has begun a program to dispose of highway runoff in which a priority has been given to the use of infiltration type technologies (e.g. infiltration basins, dry wells, etc.). Heavy metals are the most prevalent priority pollutant in highway runoff. Though traditionally these heavy metals are thought to possess relatively large retardation factors within the subsurface, previous studies have indicated a possibility of their transport being facilitated through complexation with natural organic matter (NOM). If ignored this form of transport may pose serious errors in the prediction of metal(s) breakthrough times and mass loadings to underlying groundwaters. In addressing this issue, soil columns were tested under loading conditions similar to actual infiltration BMP's to assess the performance of these facilities in removing heavy metals (Cd, Cu, Pb, Zn) from infiltrating water. Experiments were performed investigating the effects of high and low concentrations of NOM on metals attenuation by field soils. Results show that high concentrations of NOM actually improved soil column performance. The data revealed that metals speciation and background metals present in the soil are important factors to consider, because they can affect expected metals removal rates of soils. The hydraulics of the system played a secondary role to the geochemistry. Results suggest that infiltration can be a viable alternative in disposing of runoff at low metals concentrations. Modifications to guidelines were discussed to improve the long-term performance of infiltration facilities.

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The Assessment of Groundwater Pollution Potential
Resulting from Stormwater Infiltration BMP's

THE ASSESSMENT OF GROUNDWATER POLLUTION POTENTIAL RESULTING FROM STORMWATER INFILTRATION BMP'S

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

EXECUTIVE SUMMARY

In conjunction with a statewide policy, the Washington State Department of Transportation (WSDOT) has placed an emphasis on the use of infiltration technologies as the best management practice (BMP's) for the treatment of highway stormwater runoff (Ecology, 1991). With many of these waters containing trace quantities of heavy metals and various hydrocarbon residues, the environmental concern is one of preventing the long-term contamination to underlying groundwaters. Although under traditional application the unsaturated zone is commonly thought of as a "treatment column" through which the pollutants are removed or degraded, the actual mechanisms of fate and transport within this subsurface region are poorly understood. One recent example of new discovery is that of "facilitated transport." Here, the introduction of natural organic matter (NOM) present in all stormwater runoff is thought to react with various heavy metal and residual hydrocarbon contaminants derived from any roadway surface. This reaction, in turn, produces intricate physical/chemical complexes which potentially exhibit unusually rapid (or enhanced) transport characteristics. The potential effects are those of greatly reduced travel times during the infiltration process and the increased chance of significant groundwater contamination over a much shorter than expected time of operation. Such effects are, however, unaccounted for in the current design criteria.

In response, this research was conducted to assess the potential for degrading the quality of underlying groundwater resources as they relate to trace heavy metal concentrations associated with the infiltration of highway stormwater runoff. A focus was placed on identifying the applicability of existing design standards in meeting the State's "anti-degradation" policy for existing groundwaters. The primary interest was to examine the environmental performance of a typical infiltration basin under the framework of the possible presence of facilitated heavy metal-NOM transport mechanisms. The goal was to

1

establish revised guidelines (if necessary) for the design of an environmentally compliant infiltration facility.

In order to achieve project objectives, the investigation was divided into two phases. The first phase examined the controlled transport behavior of a single metal constituent (lead) with a laboratory-scale column, wherein focusing on the intricate details of metal-NOM interaction. The second phase, representing full-field (vertical) scale conditions, examined the complete multi-component (lead, cadmium, zinc, and copper) transport problem within a large-scale laboratory column setting. The two phases were designed and executed as a joint study on both small- and large-scale transport behavior. In each case, efforts were made to employ real-lived conditions, using both actual field soils from various locations across the State and naturally derived organic material. The goal was to produce and study quasi-field conditions within the laboratory, wherein observing the environmental performance of various scales of transport behavior.

In the small-scale studies, dissolved organic matter (DOM) was shown to enhance the transport of lead in the bench scale column breakthrough studies via NOM-metal complexation. The uncomplexed form of lead (Pb) exhibited a retardation factor of about 1,100. By contrast, the NOM-complexed form had a retardation factor approximately 4-7 times lower. The results also showed that Pb breakthrough lagged the breakthrough of DOM. This suggested the existence of two possible mechanisms. First, a less-sorbable DOM fraction having no Pb bound to it eluted from the column prior to a more-sorbable Pb-DOM complex. Second, the soil may have "cleansed" lead–DOM complexes as they traveled through the column, resulting in an initial breakthrough of "Pb–cleansed" DOM, followed by a later breakthrough of Pb–DOM complex as the soil became increasingly saturated with DOM. It was unknown whether or not size exclusion played a significant role in the cotransport of lead with DOM. In general, the results suggested that Pb complexation to soluble DOM controlled metal mobility, whereas Pb partitioning to sorbed DOM played a lesser role.

Moreover, the results from the small-scale experiments revealed that existing models of colloid facilitated transport were inadequate in their predictability of transport outcomes. These noted shortcoming were the direct result of errors introduced by the models under the assumptions that the relevant partitioning mechanisms followed linear, equilibrium sorption kinetics. Consequently, the use of simple models invoking these assumptions would be inappropriate to describe the complexity of the behavior observed in this study.

In contrast to the small column studies, the resulting data from the second phase of large-scale experiments showed that increased concentrations of NOM yielded improved metal attenuation by the soils tested. The tendency for the metals, primarily copper and zinc, to form organo-metallic complexes at high organics concentrations was hypothesized to be the cause. Yet, the complexity of the system made it difficult to attribute this effect to a specific mechanism. The data also revealed that background (existing) metal concentrations within the soils tended to be an important consideration, since metals displacement (primarily copper) occurred as a result of the competitive adsorption/exchange and or dissolution effects posed by the multi-component system.

The results of these latter tests further suggest that infiltration can be a viable alternative in disposing of runoff at low metals concentrations. This statement is, however, qualified by the need for revised siting criteria. In particular, the presence of background metals in the soil should be identified. Moreover, the organic content of the soil is likely a better indicator of potential metal retention, and as such should be included as a siting condition along with CEC and silt and clay content. Finally, serious consideration should be given to extending the minimum depth to groundwater from the existing value of 3 feet to 10 feet or more, particularly in those areas in which background metals are present. Here, geochemical controls are thought to produce effluents beneath the infiltration basins which may lead to detectable quantities (particularly for copper and zinc) within underlying

groundwaters, wherein creating a situation that may violate the anti-degradation laws for existing State groundwater resources.

INTRODUCTION AND RESEARCH APPROACH

THE PROBLEM

The United States Environmental Protection Agency (EPA) began a "zero-discharge" campaign in the mid-1970's, with federal legislative backing under the original Clean Water Restoration Act (CWA) of 1966 and the Federal Water Pollution Control Amendments (FWPCA) of 1972. Born out of these efforts was a strict enforcement scheme known as the National Pollutant Discharge Elimination System (NPDES), wherein permits would be granted for (point) effluents on a facility-by-facility basis subject to both quality criteria and compliance scheduling (Krenkel and Novotny, 1980).

Strengthened by further Amendments to the CWA in 1987, the NPDES now regulates municipal (over 100,000 capita) and industrial stormwater discharges, forcing private and public entities to consider land application (or soil infiltration) for waste disposal. An example of that prioritization comes in the removal and treatment of urban highway stormwater runoff. Many States, like Washington, have established infiltration basins as a primary Best Management Practice (BMP) for these discharges. It is believed that current understanding of the soil treatment process makes land application a viable and effective disposal practice.

To its credit, infiltration effectively addresses the hydraulic demands posed by the large and temporally generated volumes of water from rainfall events. In finding economic and practical means of meeting the environmental demands, land-based technologies are also thought to provide adequate removal of contaminants by degradation and attenuation as the contaminated water passes through the unsaturated zone. Yet, there seems to be a natural trade-off between hydraulic efficiency and the expected environmental performance. The greater the ability a soil has to discharge water, it seems the more likely it is to be poor in pollutant removal characteristics.

With such uncertainty, the technology to date is still considered experimental, owing to the lack of consistent information verifying the in-field effectiveness in terms of water quantity and quality control performance. Brown and Caldwell (1991) performed a study for the Washington State Department of Ecology on subsurface stormwater disposal facilities, including infiltration basins and trenches, and found metals concentrations above background levels in water samples taken beneath the facilities. A study by Ku and Simmons (1986) measured concentrations of pollutants in groundwater below a recharge basin receiving stormwater runoff from a neighboring highway and found no significant adverse effects on groundwater quality. Furthermore, Schiffer (1989) concluded that infiltration basins are effective in removing metals before reaching groundwater, while Schueler (1991) reports metals removal efficiencies of over 90%. On the other hand, Wigington (1983) found that the quantities and rates of accumulation in basin soils are highly variable and dependent on the land use, soil type, and residence times of runoff in the basin.

With some encouraging early conclusions, the popularity of infiltration practices continues. Yet, there remain several points of scientific concern, along with various operational difficulties. Longevity problems due to clogging failures are common. A survey by Schueler (1991) found that in Maryland less than 50% of the surveyed structures were operating properly after 5 years, and about one-third showed signs of chronic clogging. Though construction practices and lack of maintenance were cited as most responsible for the failures, it may also be due to the simplistic approach taken in designing the facilities, especially with respect to the hydraulics involved. Furthermore, the exchange capacity and sorption process are by no means permanent. The dynamics of adsorption are very dependent on soil and solution conditions. For example, an increase in solution pH increases solubility of metals and leads to the desorption of bound metals back into solution. Moreover, the notion that infiltration is a "treatment" process is misleading. The

application of pollutants, particularly heavy metals, must satisfy mass conservation. Any mass removed from solution must either remain stored within the soil profile or be leached.

Owing to the lack of accurate information verifying the in-field effectiveness of infiltration facilities in "treating" runoff in terms of the quantity and quality of water handled, the adequacy of current design criteria for such systems is not well understood. Present design criteria address the issues of infiltration rates, soil exchange capacity, and depth to groundwater or impermeable barrier. Yet, fundamental and potentially influential processes such as metal complexation with dissolved natural organic matter (NOM) and their impacts on the transport of these pollutants have not been fully investigated. For example, McCarthy and Zachara (1989) and Corapcioglu and Jiang (1993) note the significance of colloid facilitated transport of pollutants in underestimating concentrations reaching observed boundaries. Moreover, the effects produced under unsteady hydraulics due to the repetitive infiltration and drainage cycles of infiltration is not well understood. Behind these factors lie the additional problems associated with the variability in soil characteristics and the competition and attenuation of sorbing solutes owed to background metals already in the soil. In addition, Washington State has one of the strictest groundwater quality laws in the United States. The "Anti-degradation Policy" (WAC-173-200-030) states that no mass is allowed to reach groundwater which results in concentrations of any pollutant exceeding those that currently exist.

By all accounts, the study of the corresponding processes, both individually and collectively, constitute an enormous scientific endeavor. Recognizing this fact, the basic approach taken here is one of an "impulse-response" type investigation. The soils are "loaded" and observations are then made of the resulting transport. With the data gathered, an attempt is made to explain as much of the "physics" as is known regarding the outcomes in response to changes in soil types and pollutant loads. The crux of those investigations is to evaluate the importance and impacts imposed on trace metal transport in the presence (or absence) of humic/fulvic acids in the source. Fundamentally, an attempt is made to

address the role dissolved NOM may have in enhancing the transport of heavy metals. The overall guidance of the work is directed at evaluating the corresponding performance of infiltration basins in removing metals for stormwater treatment and to assess the groundwater pollution potential raised by the use of infiltration technologies based on design criteria established by the Washington State Department of Ecology.

RESEARCH OBJECTIVES

The objective of this study is to evaluate the effects of heavy metals mobility in three Washington State soils as influenced by the concentrations of dissolved NOM. Since long-term field studies are difficult and costly, the methods developed here are intended to simulate the hydraulic field conditions of infiltration basins under more controlled and less expensive laboratory conditions. The results are extended to assess the relative potential for groundwater pollution in the form of heavy metal contamination resulting from infiltration of highway stormwater runoff. This study is not intended to predict the actual breakthrough times or concentrations of the heavy metals themselves, but to provide an evaluation of the effects of dissolved NOM on the transport of metals in a multi-component system as applied to infiltration practices.

The specific objectives of this project are to:

1. Compare the effectiveness of near-surface field soils which have characteristics acceptable for infiltration basins to study which soil characteristics are most important in metals removal from solution. The comparison is based on particle size distribution, organic content, infiltration rate, and soil cation exchange capacity using the minimum guidelines of the Washington State Department of Ecology (WSDoE) as the controlling features of the laboratory experiments.

2. Compare the performance of the same soils under conditions of high and low dissolved NOM in an attempt to assess the effect of metal-NOM complexation on a

soil's ability to attenuate metals. In an attempt to gain a better understanding of facilitated transport, quantify the effects on the retardation of lead by fulvic and humic acids

3. Study the competition effects of several metals on the adsorption behavior of the soils.

The results of this study can be applied in the verification or alteration of present design criteria of infiltration basins and provide a better understanding of NOM-metals interaction in soil solution.

BACKGROUND

Design of Infiltration Basins. Design guidelines and minimum requirements in this study were based on Washington State Departments of Ecology and Transportation requirements as published in the Stormwater Management Manual for the Puget Sound Basin (Ecology, 1992), hereto referred as the Manual. Many of the guidelines outlined here are similar to other requirements found nationwide (refer to Table 1). The Manual is a cooperative product put forth by the State's Departments of Ecology (WSDOE) and Transportation (WSDOT). The current standards for the State of Washington with respect to infiltration basin design are those defined in the Manual.

In many instances, infiltration is the preferred BMP due to "...its ability to both effectively treat runoff and control streambank erosion" (Ecology, 1992). Some advantages of infiltration basins include: (1) the ability to preserve the natural water balance of the site while serving larger developments; (2) its usefulness as sediment and erosion control; and (3) its relative cost effectiveness compared to other BMPs. Some disadvantages, however, include a relatively high rate of failure due to unsuitable soils and the need for frequent maintenance (MWCOG, 1985).

By construct, infiltration basins are very similar in appearance to conventional dry ponds. The primary element is an impoundment formed by excavation or by construction

of an embankment (see Figure 1). The impoundment stores a designed quantity of runoff and promotes infiltration of the storage through the soil of the basin floor. In that process, the soil is thought to remove contaminants by degradation, attenuation, and/or filtration. Although in concept infiltration basins are simple, they do present some practical problems from a design viewpoint. The Manual lists the following as primary causes of failure: i) inadequate soil investigation, and ii) improper construction practices, especially in soil compaction, and iii) siltation which clogs soils.

Recognizing these facts, infiltration BMPs are not suitable for every site. Their feasibility depends on both the nature of the soils and the need to protect groundwater quality. As such, the location and depth to bedrock or the water table can preclude the use of infiltration. Other concerns include the proximity to drinking/irrigation wells and drainfields. The Manual lists other "general limitations" which control the physical suitability of the site, including:

(i)   the soil infiltration rate should be between 1.27 and 6.10 cm/hr.;

(ii)   runoff must infiltrate through at least 46 cm of soil possessing a minimum cation exchange capacity (CEC) of 5 milliequivalents per 100 grams of soil;

(iii)   soils with 30 percent or greater clay or 40 percent or greater silt/clay cannot be used;

(iv)   fill material cannot be used;

(v)   aerobic conditions are to be maintained wherein the basin must drain the design storm in 24 hours or less.

Although in extensive use, at least three feet must be maintained between the seasonal high water mark, bedrock or impermeable barrier and the basin floor. The soil infiltration rate, CEC, silt and clay content, and depth to groundwater criteria were used directly for quantifying soil properties, and developing the methodology in this study. Other limitations were related to physical siting and were not considered.

Table 1. Typical Infiltration Basin Design Criteria

Agency	Depth to Grnd.Wtr.	Infiltration Rate	Time to infiltrate	CEC	Clay Content
WSDOE	3 ft.	>0.5 in/hr	24 hrs.	5 meq/100g	< 30-40%
VDOT[†]	4 ft.	>0.27 in/hr	48 hrs.	none noted	none noted
FHWA[‡]	2-10 ft.	>0.3 in/hr	72 hrs.	none noted	none noted
MWCOG[*]	2-4 ft.	>0.27 in/hr	72 hrs.	none noted	none noted

[†] Virginia Department of Transportation
[‡] Federal Highway Administration
[*] Metropolitan Washington Council of Governments

11

Top View

Inlet from Pre-treatment BMP

Flat Basin Floor
withDense Grass

RiprapOutfall
Protection

Riprap

Overflow Spillway

Embankment

Ouflow/Overflow Pipe

Side View

Vegetated Basin Floor

3:1 Maximum Slope
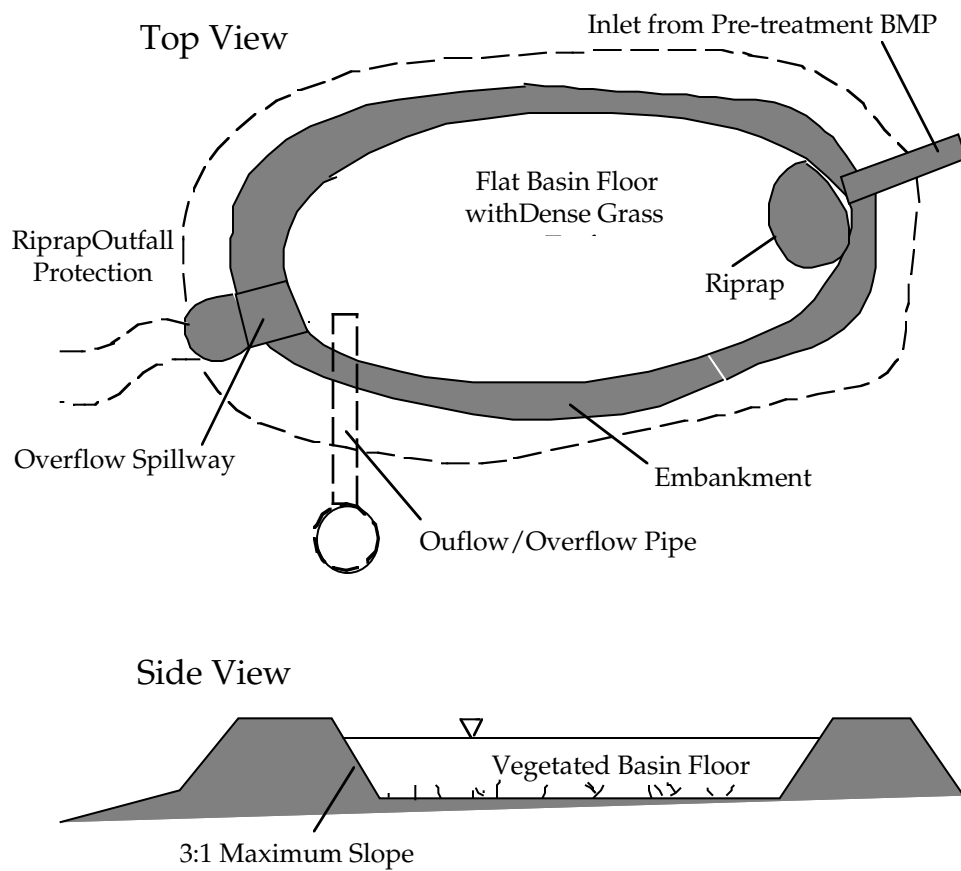
Figure 1. Layout of a Typical Infiltration Basin

Runoff Characteristics. The pollutants of primary concern generated via urban highway runoff include oxygen consuming organic materials, nutrients, toxic organics, oils and greases, and toxic metals. The pollutants under consideration in this study were those of heavy metals, namely cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) which originate from material decomposition associated with vehicular traffic, pavement aging, and wind-blown dusts (Ferguson, 1994). The EPA's Nationwide Urban Runoff Program (NURP) of 1983 concluded that heavy metals are the most prevalent Priority Pollutants detected in urban runoff. Each of the target metals were detected in at least 50% of the samples. Leading the list were lead, zinc, and copper, each being detected in over 90% of the samples collected.

A study sponsored by the Federal Highway Administration (Driscoll, et.al., 1990), provides extensive monitoring of roadway runoff quality of 993 storm events at 31 sites in 11 states (Table 2). Though vast quantities of data were collected in the study, the authors of the report emphasize that the most reliable estimates of a site's average pollutant concentration comes from local monitoring data at the site itself. Fortunately, of the sites included in the study, eight were from the State of Washington. From the Driscoll study, the average concentrations for cooper, lead, zinc and TOC were used in defining the synthetic stormwater quality used in this experimental investigation, with cadmium levels being assumed to be approximately 0.030 mg/l .

Environmental impacts from pollutants, especially metals, are often dependent on the speciation or form in which the pollutant occurs. Mobility and adsorption characteristics vary depending on whether the metal is dissolved or suspended via attachment to particulates. Estimates of soluble fraction for a site based on urban runoff developed under EPA's NURP study suggest 40% or less of detected metals concentrations are soluble. However, since concentrations are in the order of parts per billion, a conservative approach was taken and the metals concentrations reported were considered to be in the completely soluble state for this study.

13

Table 2. Total Metals Concentrations in Washington State Highway Runoff

Study Site	TOC (mg/l)	Cu (mg/l)	Pb (mg/l)	Zn (mg/l)
Montesano SR-12	3	0.036	0.175	0.100
Pasco SR-12	10	0.025	0.101	0.325
Pullman SR-270E	17	0.026	0.130	0.099
Seattle I-5	13	0.037	0.451	0.382
Snoqualmie Pass I-90	33	0.072	1.065	0.280
Spokane I-90	10	0.041	0.173	2.892
Vancouver I-205	7	0.017	0.046	0.040
Average	**11.9**	**0.035**	**0.276**	**0.524**

Infiltration and Unsaturated Water flow. As a means of introducing important transport considerations for metal solutes, this section provides a brief review of the basic transport processes in the unsaturated zone. The study of groundwater flow is based on Darcy's Law which states that the flux of water through soil is proportional to the gradient of the soil water potential. In unsaturated flow, the hydraulic conductivity is dependent on the soil water suction, and hence water content, since the two are directly related through capillarity. This relationship is often represented by water retention or water characteristic curves, i.e. water content versus matric potential or saturation versus capillary pressure. The general form of Darcy's Law for unsaturated flow is the following, with the hydraulic conductivity now a function of the matric suction head or water content:

$$\mathbf{q} = -\mathbf{K}(\psi)\nabla\phi \qquad\qquad \text{(Eqn-1)}$$

where $\mathbf{q}$ is the volumetric flux of water, $\mathbf{K}(\psi)$ is the matric head ($\psi = -p_w/\gamma$) dependent hydraulic conductivity, p_w is the soil water tension (i.e. negative gage pressure), γ is the unit weight of water, and $\nabla\phi$ is the gradient of the total soil water potential: $\phi = \psi + z$, where z is the elevation head above a given datum.

During infiltration (under ponded conditions) four zones exist within the soil profile: (i) a *saturated zone* directly beneath the ponded water; (ii) a continuously extending, less than saturated *transmission zone* with uniform wetness; (iii) a steeply decreasing soil wetness region called the *wetting zone*; and (iv) the *wetting front* where the moisture gradient is greatest. The saturated zone lengthens continuously over time, while the wetting zone and wetting front continue to move down at a decreasing rate due to the decreasing moisture gradient. Downward infiltration generally occurs under the influences of both soil matric tension and gravity gradients. As the wetted zone lengthens, the average matric tension gradient decreases since the difference in pressure head is taken along an increased length. As the water penetrates deeper, this tension gradient in the upper profile

becomes negligible and the flow becomes gravity dominated. Here, the flux approaches the saturated hydraulic conductivity and the water content nears the porosity. Though in general these descriptors apply in three dimensions, the experiments and resulting discussion are developed as a one-dimensional model of the process.

Solute Transport Processes in the Unsaturated Zone. As in the discussion on water movement in the unsaturated zone, solute transport processes are developed first in the saturated case and then extended to apply under unsaturated conditions. The traditional approach describing solute transport in the subsurface assumes the total one-dimensional flux is due to advection, diffusion and hydrodynamic dispersion. By combining the flux equation with mass conservation, several authors have derived this fundamental mass transport equation for the unsaturated zone (Fetter, 1993), (Bear and Verruijt, 1987), (Charbeneau, 1992):

$$\frac{\partial\left(B_d C^*\right)}{\partial t} + \frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left(D_s \theta \frac{\partial C}{\partial z} - qC\right) + \sum_i \gamma_i \qquad \text{(Eqn-2)}$$

where B_d = soil bulk density, C' = concentration of solute adsorbed to soil matrix, θ = volumetric water content, D_S = dispersion coefficient, C = solute aqueous phase concentration, and γ = other sources or sinks.

Besides advection and hydrodynamic dispersion, processes such as solute interactions with the soil matrix, chemical and biological reactions, and decay can cause changes in the solution concentration of a solute. The first term on the left side of Eqn. (2-2) expresses the concentration of solute adsorbed on the soil, while the last term on the right accounts for the other chemical/biological processes.

Characterization and Environmental Significance of Colloids. Colloids can be classified as nonsettleable particles having a nominal diameter between 1 and 1000 nm (Mills *et al.*, 1991). Their extremely high surface area–to–mass ratio provides a high specific concentration of contaminant binding sites, which could result in significant

contaminant scavenging in competition with immobile solids. In addition, repulsive forces (most commonly electrostatic) between colloidal particles are often greater than both gravitational and attractive forces acting on the particles, preventing both their sedimentation from solution or coagulation to form settleable floc. Their stability in suspension allows them to be readily transported as a result of their inability to be immobilized by conventional means that require transport of the particle to a collector surface, such as physical or chemical sorption. Thus, a stable dispersion is less susceptible to physical and chemical retardation mechanisms such as accumulation at immobile surfaces and precipitation (Puls and Powell, 1992).

In some systems, colloids have even been known to be transported faster than a nonreactive solute as a result of size exclusion from pores smaller than those of the colloid (Enfield and Bengtsson, 1988; Harvey *et al.*, 1989; Smith *et al.*, 1985). However, like any reactive constituent, colloids are also susceptible to retardation by sorption, precipitation, complexation, and other mechanisms (Jardine *et al.*, 1989). Thus, for colloids to enhance contaminant transport in the subsurface, two criteria must be met (Magee *et al.*, 1991):

  a) The colloidal phase must be able to effectively compete for contaminant binding with the immobile solid phase, and

  b) The colloid–contaminant complex must be less retarded than the contaminant in solution (in the absence of the colloid).

Criterion (b) is intuitively apparent when considering the inherent character of a stable colloidal dispersion, and is met in many cases in which mobile colloids are present with hydrophobic contaminants. Criterion (a), however, is more difficult to predict. Mills *et al.* (1991), in model predictions of colloid–assisted transport of metals, showed that colloids influenced transport relatively little when the contaminant partitioning coefficients between the colloidal phase and the solid medium were quantitatively similar. This was particularly true over very long travel distances, where solutes are rapidly desorbed from

colloids (and subsequently adsorbed to the solid matrix) as they approached a "clean" portion of the aquifer, and the colloids continued migrating with relatively little contaminant attached (this "cleansing" behavior was observed in the current study). In the same study, it was consequently shown that as the partition coefficient between the solute and the media decreased, the presence of colloids decreased the travel time by up to two or more orders of magnitude.

Colloids are ubiquitous in the natural subsurface environment. Organic colloids include bacterial cells and organic macromolecules such as natural organic matter (humic and fulvic acids). Inorganic colloids include clay particles or mobilized subsurface mineral constituents resulting from the geochemical/physical response to a changing subsurface environment (e.g., land application of waste, groundwater recharge, underground detonation, or well–drilling). Particular attention must be paid to the influence of natural organic matter (NOM) upon contaminant cotransport because of its affinity for a variety of contaminants and its significant mobility in the aqueous phase under a wide range of geochemical conditions. Further, the difficulty in removing NOM by conventional treatment processes may contribute to the failure in removing bound contaminants in drinking water treatment (Yeh and Huang, 1994).

Natural Organic Matter Colloids. Natural organic matter (NOM) includes living and senescent organisms, exocellular polymeric substances, and residual detritus resulting from the partial or extensive decomposition of plants and animals, and can exist in either a particulate form (POM) or a dissolved form (DOM) (Aiken and Cotsaris, 1995). One operational definition of NOM components includes subdivisions based upon their pH–dependent solubility. These components are humic acids (soluble in base), fulvic acids (soluble in acid or base), and (insoluble) humin. Because of their solubility at pH ranges commonly found in groundwater systems, the humic and fulvic acid DOM fractions are the primary contributors to enhancing contaminant cotransport. Alternatively, DOM subcomponents can be classified in terms of their hydrophobicity (Leenheer, 1981), where

18

fulvic acids tend be more hydrophilic than humic acids because of their higher density of acidic functional groups.

Because of the complexity and variability in their chemical structures, humic and fulvic acids are most commonly characterized as a heterogeneous group of organic macromolecular chains. They commonly contain as their primary reactive sites, functional groups such as hydroxyl, carboxyl, phenolic, and carbonyl substitutions. Furthermore, two or more classes (strengths and capacities) of binding sites can often be modeled (Langford *et al.*, 1983; Perdue, 1989; Perdue and Lytle, 1983) by fitting contaminant binding data with multi–site mixed ligand models. DOM usually contains between 35% and 60% carbon (Thurman and Malcolm, 1983) and has molecular weights ranging from approximately 500 to 30,000 (Amy *et al.*, 1992). It can be characterized in terms of its hydrophobicity; both humic and fulvic acids are known to contain both hydrophilic and hydrophobic components (Leenheer, 1981). Thus, DOM has the potential to enhance the transport of hydrophobic pollutants such as heavy metals, hydrocarbons, and pesticides. In summary, the heterogeneous nature of DOM and the operational basis upon which its chemical classification and reactive structure are defined could introduce significant uncertainty when predicting the cotransport of contaminants. Discrete structures of humic molecules have so eluded researchers that NOM structure has even been successfully modeled using fractal geometry (Rice and Lin, 1993) to describe its heterogeneity.

Humic and fulvic acids have the potential to influence the speciation of many different types of hazardous substances, including polycyclic aromatic hydrocarbons (Schlautman and Morgan, 1993), organohalides, soluble oxidants, iron and aluminum compounds, strong acids and bases (Manahan, 1989), and radionuclides. An extensive amount of research has also examined the binding of DOM with heavy metals in aqueous systems (Alberts and Giesy, 1983; Langford *et al.*, 1983; Perdue, 1989; Pettersson *et al.*, 1993; Stevenson, 1976). The speciation of heavy metals in surface and groundwater is becoming increasingly important with more stringent maximum contaminant levels of

heavy metals in drinking water. Furthermore, their resistance to biological and chemical degradation in both the subsurface and in conventional treatment processes allows some metals to persist for very long times in toxic forms. Thus, resulting from the previous discussion, an obvious scenario having important implications for groundwater quality is the cotransport of heavy metals by DOM, the focus of this study.

Nonideal Transport Behavior of DOM. Transport of DOM has been observed on both the field (Jardine *et al.*, 1989; McCarthy *et al.*, 1993) and laboratory scales. Often, DOM is highly mobile, eluting simultaneously (or closely associated) with a nonreactive tracer (Jardine *et al.*, 1992; Dunnivant *et al.*, 1992). Thus, it has been recognized as a significant transport–reaction component that should be considered when evaluating contaminant transport (Jardine *et al.*, 1992).

Breakthrough curves of DOM are seldom characterized by the Guassian distributions predicted by the Convection-dispersion equation (CDE). They often exhibit sharp breakthrough fronts and extensive tailing, indicative of a number of mechanisms, including chemical and physical nonequilibrium and sorption isotherm nonlinearity (Brusseau, 1995; Dunnivant *et al.*, 1992). Chemical nonequilibrium (CNE) occurs when the sorption reaction between the DOM and the surface site is slow relative to the rate of transport. Physical nonequilibrium (PNE) occurs when the relatively rapid transport of the solute through the primary porosity is coupled with the diffusion–limited transfer of the solute into a secondary porosity. Pore scale PNE can include diffusion across a boundary layer (film diffusion) or into the microporosity of a particle (intraparticle diffusion). PNE on the local scale typically involves diffusion into aggregated particles. Finally, field and regional scale PNE can occur in formations where solute diffusion into low–permeability clay lenses or binary inclusions are significant. Analogous to diffusion–limited PNE at the field scale is the presence of preferential flow paths, which result in a velocity field distribution which cannot be modeled by a Guassian distribution as in the CDE.

The macromolecular size of DOM may complicate the assessment of PNE. A common method for evaluating PNE at both the laboratory and the field scale is by generating a breakthrough profile of a nonreactive tracer, which commonly includes small, nonsorbing molecules such as tritiated water (^3H_2O) or chloride (Cl^-). Because of its large size, DOM will diffuse in water slower than these solutes, amplifying the effects of PNE. In addition, size exclusion of the DOM molecule could prevent DOM from reaching binding sites in the solid which may be accessible by a traditional nonreactive tracer or other contaminants, dampening the effects of PNE. Brusseau (1993) presents an excellent discussion of pore and local scale PNE of nonreactive solutes of different sizes and the relative contributions of film diffusion, intraparticle diffusion, and pore water velocity.

It is clear that the study of processes affecting the nonideal transport behavior of a reactive solute is a complicated arena. Coupled with the particular characteristics of DOM, including its large size and its ability to complex other contaminants, delineation of these processes becomes a monumental task. However, the ability to assess the influence of chemical and physical nonequilibrium and isotherm nonlinearity upon contaminant transport would be of great value to the predictive utility of a cotransport model.

Cotransport of Contaminants with DOM. This discussion, representative of the majority of research in this area, has focused upon reinforcing criteria (a) and (b) (see *Characterization and Environmental Significance of Colloids*, above) for contaminant cotransport. Although the reactivity of DOM with contaminants and its mobility in porous media have been addressed, relatively little research has focused upon the cotransport of contaminants with DOM. The enhanced breakthrough of organic contaminants was observed in the presence of mobile macromolecules functionally similar to DOM (Kan and Tomson, 1990). Retardation factors were reduced by factors of 2, 26, and 1,000 for naphthalene, phenanthrene, and DDT, respectively, in the presence of the mobile colloid. Magee *et al.* (1991) observed that the retardation of phenanthrene in porous media was significantly reduced (by a factor of 1.8) in the presence of mobile DOM. These studies

reinforce the hypothesis by Enfield and Bengtsson (1988) that the relative mobility of slightly mobile (or more hydrophobic) compounds should be higher than the relative mobility of highly mobile (or more hydrophilic) compounds in the presence of dissolved macromolecules. Thus, it follows that the potential for enhanced macromolecular transport of heavy metals, which can be highly retarded, may be significant in certain soil systems.

Newman *et al.* (1993) reported the enhanced mobility of Cd, Cu, Cr, and Pb in laboratory soil columns by complexation with organic and inorganic hazardous waste ligands, as well as sorption to mobile, turbidity–causing colloids. In another study, both enhanced and inhibited transport of Cu occurred, influenced by the nature (i.e., character of binding sites) of the DOM, a function of its source (Oden *et al.*, 1993). Inhibited Cu transport may have resulted from the formation of a Cu–DOM complex that was more sorbable than Cu alone. In addition, this study illustrated the influence of the contaminant upon the mobility of the DOM, noting that DOM mobility was decreased in the presence of the metal.

Convection–Dispersion Modeling of Cotransport. The aforementioned results confirm that facilitated transport does not necessarily occur in all systems where mobile colloids were present. Moreover, consideration of the criteria outlined above is necessary when evaluating the potential for facilitated transport. Unfortunately, the availability of models to evaluate that criteria and successfully predict contaminant–colloid transport is limited to some basic derivatives of the convection–dispersion equation with simple kinetics or equilibrium sorption parameters (a summary of which can be found in Corapcioglu and Jiang (1993)). A few selections highlighting some key issues are presented in Appendix E.
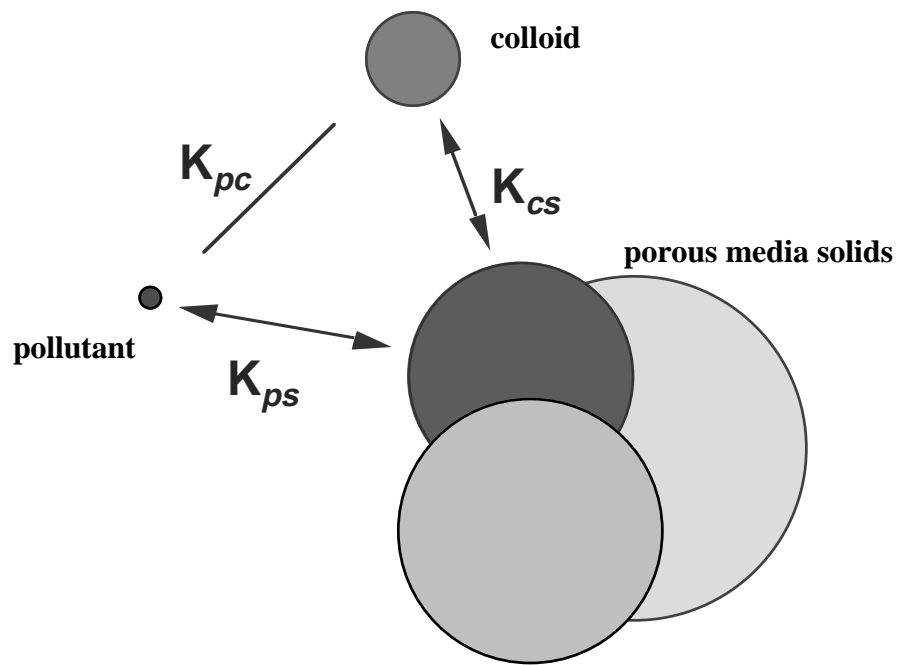
FIGURE 2. Simple Reactions Between Colloids, Contaminants, and Soil.
This figure illustrates the primary, independent reactions between colloids, contaminants
and soil in the subsurface. K_{ij} describes the linear partitioning coefficient between two
constituents, i and j. The porous media solids are assumed to be immobile, while the
pollutants and colloids can be transported with the bulk flow through the porous media.

Contaminant-Colloid Transport Summary. This review has emphasized the importance of several mechanisms affecting the speciation and transport of contaminants and colloids in porous media. When evaluating colloid–contaminant reactions in the subsurface, it is important to realize that colloids can either enhance or inhibit the transport of contaminants. This degree of influence will depend upon the complex processes that govern the reactions of contaminants, colloids, and contaminant–colloid "complexes" with subsurface media. Although conventional modeling approaches have not accounted for a colloidal phase, more recent models have incorporated the colloid as a mobile competitor for contaminant binding. However, the evolution of cotransport modeling has yet to account for the processes that govern speciation and transport in the field, including nonlinear and rate–limited sorption coupled with the reactions of colloid–contaminant complexes with the media.

Although the focus of the experimental study presented here is not upon the modeling of cotransport, the modeling discussion is useful for highlighting and understanding the impacts of some of the processes that are possible in relatively simple systems. This experimental research emphasizes the speciation and transport of lead with dissolved natural organic matter. Some of the processes affecting transport found in this study disqualified existing models based upon their limited applicability. These processes included nonlinear and rate–limited sorption, selective partitioning of DOM into media intraparticle porosity (size exclusion), selective uptake of preferred DOM fractions (i.e., as a result of DOM heterogeneity), and the complex physical and chemical surface heterogeneity of the media.

Consequently, the primary focus of the experiments in phase one contained herein is to illustrate the complexity of one type of colloid–contaminant–media system to emphasize the need to verify and update existing models to better account for system complexity. A secondary objective is to utilize observations in well–controlled batch speciation studies to explain behavior in column transport experiments.

Subsurface Interaction Chemistry Relevant To Metals Attenuation.
Chemical reactions of solutes, such as metals, play a key role in determining the solutes' speciation, bioavailability, e.g. uptake by plants and aquatic life, and their ultimate fate and transport characteristics in the subsurface. Several processes affect the solute movement in soils including adsorption, complex formation, and precipitation/dissolution. For example, attenuation of metals on soils reduces their mobility and bioavailability by reducing the mass in solution. Complexation of metals with other species in solution can alter their solubilities and sorbing characteristics.

Sorption Processes. Sorption refers to the removal of a solute (sorbate) from the solution phase by the solid phase (sorbent). The two basic categories of sorption, absorption and adsorption, are distinguished by the extent to which the sorbate interacts with the sorbent. In *adsorption*, the solute is restricted to the sorbent surface or interface between the sorbate and sorbent, whereas the solute penetrates the sorbent phase by several nanometers in *absorption* processes (Weber, 1990). The distribution of the solute between phases is due to the relative affinity it has for solvent and sorbent phases. This affinity is directly related to the forces, broadly categorized as physical, chemical, and electrostatic, which exist between the phases.

One important process responsible for the sorption of cations is ion exchange. The negative charge on soil colloids, clay, and organic matter on soil surfaces makes ion exchange one of the most important reactions influencing transport of cations in soils (Gaston and Selim, 1990). Ion exchange involves the sorption of one or more species of ions accompanied by the desorption of the previously sorbed species equivalent in total ionic charge. Soils often have surfaces with a net negative charge due to, for example, isomorphic substitution of ions in a clay lattice structure. An electrostatic double-layer is formed when the negative surface charge is counter-balanced by cations which accumulate on the surface of the particle forming an electrostatic double-layer. This double-layer provides the ability of the matrix to attract ions and eventually attenuate them.

Three broad categories affecting the attenuation behavior of a solute include the properties of the solute, the chemical properties of the soil solution, and the physical and chemical properties of the soil. In terms of the solute, such chemical properties as solubility, charge or valency, precipitation chemistry, and size are important characteristics in determining the affinity of a solute to be in solution. Directly related to the sorbent is the relative affinity it has for particular species called its selectivity. In general, higher valency cations are more strongly sorbed, and heavy metals are preferred over alkaline earth/alkali cations (e.g. Ca^{2+}, Na^+, K^+) on hydrous oxides. However, the selectivity and competition among species is strongly dependent on solution characteristics such as pH.

The pH of the soil solution and soil surface is strongly related to sorption (Bodek, 1988). According to some studies, the attenuation of most cations increases with pH since the surfaces become more negatively charged. Also, at high pH metal ions tend to form hydroxy complexes which are preferred over free ions as sorbed species (MacCarthy and Perdue, 1991), (Bodek, 1988). Both at high and low pH, metal complexation is hindered because the hydrogen and hydroxide ions compete with metal ions and ligands in complexation reactions, what McCarthy and Perdue (1991) refer to as side reactions.

The soil physical properties are important in that they influence the rate of movement of water flow, as well as dictate the surface area of soil available to the solute. The composition of the soil, e.g. organic content, mineral content, and metal oxides, which provide the majority of sorption sites, indicates the ability of the soil to sorb solutes. A fundamental indicator of this ability is expressed by the specific area, which is related to the particle size and pore size distributions. Generally, the more clayey a soil, the higher the specific surface and the greater surface area for sorption. The cation exchange capacity (CEC) of a soil is a property related to ion exchange which measures the excess of counter-ions adjacent to the charged layer which can be exchanged for other ions. It is normally expressed as the milliequivalents of cations that can be exchanged in a dry sample of 100 grams soil.

The affinity of the sorbent to adsorb a cation is measured by the sorbent's selectivity coefficient. It is a measure of the competitiveness among various species of cations for the exchange sites on a soil. The selectivity is dependent on the soil, cations, and soil solution as demonstrated by the mass action exchange reaction:

$$Ax + B^+ \Leftrightarrow Bx + A^+ \qquad\qquad \text{(Eqn-3)}$$

$$K_{AB} = \frac{[A^+][Bx]}{[B^+][Ax]} \qquad\qquad \text{(Eqn-4)}$$

where $[Ax]$ and $[Bx]$ are the activities of the B^+ and A^+ cations on the solid; and $[A^+]$ and $[B^+]$ are the activities of the ions in solution; and K_{AB} is the selectivity coefficient. Generally, the selectivity coefficient compares two cations only. Little work has been done on exchange of more than two different cations, which is necessary in multi-component systems.

Further discussions on adsorption to metal oxides, aluminum silicates, and organic matter can be found in several texts (Drever, 1982), (Fetter, 1993), (Freeze and Cherry, 1979). Sposito (1983) provides a thermodynamic discussion of sorption processes.

Metal Complexation. Metals generally exist as complexes in aqueous systems and in most cases water molecules occupy most of the ligand positions available in the coordination spheres (aquated metal ion). Metal ions also form complexes with neutral molecules, and monatomic or polyatomic anions known as ligands. Other potential ligands can replace the water molecules to alter such properties as solubility, toxicity, and attenuation behavior of the central ion. Soluble metal complexes often reduce metal adsorption compared with the absence of these dissolved complexes. This is due to the reduced affinity of the metal complexes for sorption sites as their surface charges are reduced (Bodek, 1988).

Complexation can also occur among solutes and surface materials. The difference between aqueous complexation and surface complexation is that the sorbed solutes become immobile in surface complexation. Sources of charged surfaces able to complex metal ions include soil organic matter, metal oxides, and layer silicate minerals. Charges on the surfaces of these materials result from surface protonation or deprotonation reactions. In soil organic matter, surface carboxyl and hydroxyl functional groups can coordinate with metal ions when these surface ligands replace water molecules in the coordination spheres of the metal ion (Aiken, et.al., 1985).

The strength of a complex is usually defined by its stability constant. The greater the constant, the more stable the complex. This apparent stability constant becomes difficult, if not impossible, to quantify with complicated, heterogeneous ligands such as when macromolecular organics are considered. In general inorganic/organic complexes become more stable with increasing valency and less stable with decreasing ionic radius. However, exchange reactions are generally very fast kinetically and can be dominant in periods immediately following the input of dissolved trace elements into the soil.

Multi-component Mass Transport. In practical situations, several metals are often present in the elluent. The resulting competition may reduce adsorption of a weakly adsorbed ion causing enhanced mobility (Riemsdijk and Hiemstra, 1993). However, to apply the models developed for multi-component adsorption on heterogeneous surfaces would be intangible, at best, since a significant amount of experimental data would need to be collected to satisfy the parameter requirements, as explained below.

The competitive adsorption which results from the multi-components is based on mass action equations involving an equilibrium constant for each component's adsorption reaction. This can be written as:

$$K_{si} = \frac{s_i}{c_i x_s} \qquad \text{(Eqn-5)}$$

where x_s is the chemical formula for the solid site, c_i is the concentration of solute i in solution, s_i is the chemical formula for the sorbed component of i and K_{si} is the equilibrium constant for the reaction. It is assumed that the number of adsorption sites are constant and that the sorbed concentration of component i can be expressed in general as a function of the concentration of each component in solution, e.g. in Langmuir or Freundlich terms:

$$s_i = f_i\,(c_1, c_2, c_3, \ldots, c_n) \quad \text{for} \quad i = 1, \ldots, n \qquad \text{(Eqn-6)}$$

With this model it is easy to see how encompassing attempts to model multi-component transport can become. For example, equilibrium constants for each component and for each sorption site must be known, as well as the functional form of the sorbed concentration based on the aqueous concentrations of each component.

Complex Soil Systems. In order to provide an accurate mass balance of a complicated system, such as when studying field soils, the storage term must be quantified because changes in solid phase composition strongly influence solute interactions with the solid matrix. The question arises of how to deal with this complexity. The most common approach to quantify the metals within soils is through extraction procedures. By performing sequential extractions by using extracting agents of increasing "strength" one obtains the various metals fractions. This operational approach is often the basis for "defining" the metal speciation.

However as Riemsdijk and Hiemstra (1993) point out, several studies on sequential extraction showed that various phases may not always be identified correctly. Because of this, the definitions based on these procedures given for the speciation of metals is questionable . In effect, the mass of metals extracted, which quantifies the storage term, can be highly variable and dependent on the extraction procedure used. This along with the problem that soils sampled may already contain varying amounts of the adsorbed species of interest, makes an accurate mass balance approach very difficult. Therefore, the extraction

procedure adopted for this study was used only for relative comparisons and evaluating relative changes within the soil after application of the runoff.

Sorption of Cd, Cu, Pb, and Zn to Soils and Sediments. Adsorption on soil and sediments significantly affects the mobility of each of the metals considered in this study. Adsorption of cadmium, for instance, correlates with the CEC of a soil. Calcite and iron and aluminum hydrous oxides have been noted as the most important adsorption sites for cadmium at low concentrations. Clay minerals, carbonate minerals, oxides, and to a lesser extent, organic mater have been noted as adsorbents, as well. Several studies have been done on how organic matter affects cadmium adsorption with conflicting results, i.e. whether increased organics concentrations increase or decrease cadmium sorption (Bodek, 1988). There is strong agreement, however, that removal of cadmium from solution increases greatly as the pH increases through a critical range of 6-8 (Huang, 1977).

The important copper sorption mechanisms include precipitation and co-precipitation, ion exchange, sorption onto clay minerals, iron and manganese oxides, and organic matter. The presence of anions may increase sorption by the formation of copper-ligand bonds that increase free-electron sharing with surface ions. Huang's study (1977) showed that copper sorption is very low at pH below 4 and increases significantly above pH 6, while anions including humic acid increase sorption at pH below 6 with no effect above pH 6.

The important mechanisms for sorption of lead onto soils and sediments include ion exchange and co-precipitation with hydrous oxides. Sorption onto clay minerals, iron and manganese oxides, and organic matter are also important with the extent of sorption increasing with increasing pH (Bodek, 1988). A study by Huang (1977) showed that the addition of humic acids increased the sorption of lead by a Metapeak soil. They theorized that lead-ligand associates were formed followed by sorption through chemical bonds to the soil, or lead ions were sorbed by anionic ligands already sorbed to the soil.

Similar to cadmium and lead, important mechanisms in the sorption of zinc include ion exchange, sorption onto clay minerals, iron and manganese oxides, and organic matter. Zinc sorption is also strongly influenced by pH. As Huang (1977) found 10^{-3} M zinc was completely removed from solution when pH was greater than 8, while little or no zinc was removed when pH was 5. Studies also showed that multivalent anions may enhance zinc sorption by Fe oxides.

Though there are several experimentally derived sorption constants for all of these metals, these values vary over an extremely large range. The reasons for this are the different experimental conditions, type of sorbent, concentrations of solute, and other substances present in the soil or sediment in which it was derived.

Speciation of Cd, Cu, Pb, and Zn. Sophisticated instrumentation, such as atomic absorption spectrometry used here, provides very accurate measurements of total concentrations of metals in solution. However, as many studies have shown (Sposito, 1983), the speciation of trace metals is much more significant than the total concentrations when considering toxicity, bioavailability, and mobility.

Sposito (1983) summarized laboratory methods for determining the speciation of trace metals into sorbed, soluble, free, and labile/non-labile inorganic and organic complexes. However, he stressed that the analytical schemes given, which used filters, voltammetry, and uv radiation provided only an operationally defined set of aqueous species. This somewhat arbitrary definition may not truly be the chemical speciation in the original water samples.

Knowing the chemical speciation of the metals in solution may be necessary when studying the toxicity or bioavailability, but the interest here is simply to determine if any metals mass would be detected below the lower boundary of a basin. The mobility after reaching the groundwater table is not an issue in this case. With this in mind, and the fact that speciation of metals cannot be separated from instrumental techniques by which it is determined, the approach taken was to measure total concentration.

31

The following Table 3 taken from Sposito (1983), shows the principal chemical species in acid and alkaline soil solutions under oxic conditions. In alkaline soils or soils with high carbonate content there is a possibility of metal-carbonate species existing. However, in solutions where the pH is below approximately six, the dominant species are the metal 2+ ions.

Table 3. Metal Speciation in Acid and Alkaline Soils

Metal	Acid Soil Solution	Alkaline Soil Solution
Cd(II)	Cd^{2+}, $CdSO_4^o$, $CdCl^+$	Cd^{2+}, $CdCl^{+,}$ $CdSO_4^o$, $CdHCO_3^o$
Cu(II)	Organic Complexes, Cu^{2+}	$CuCO_3^o$, Organic Complexes, $CuB(OH)_4^+$, $Cu(B(OH)_4)_2^+$
Pb(II)	Pb^{2+}, Organic Complexes, $PbSO_4^o$, $PbHCO_3^+$	$PbCO_2^+$, $PbHCO_3^+$, $Pb(CO_3)_2^{2-}$, $PbOH^+$
Zn(II)	Zn^{2+}, $ZnSO_4^o$	$ZnHCO_3^+$, $ZnCO_3^o$, Zn^{2+}, $ZnSO_4^o$, $ZnB(OH)_4^+$

Experimental Considerations and Related Studies on Metals Mobility. Determination of the aqueous concentrations of all relevant complexing ligands can be of critical importance since they can strongly influence the aqueous activities of the metals. However, the complex mixtures of organic ligands in soil solutions makes such a comprehensive analysis extremely difficult. Besides this, solubility determinations use equilibrium relationships which are often based on practical experimental considerations rather than attainment of some steady-state condition (Logan and Traina, 1993). Because

of the low concentrations typically present, it is difficult to directly obtain the solid phase form of a given trace metal, e.g. by infrared analysis.

Due to limitations in analytical detection limits, experiments on trace metal chemistry are conducted at unrealistically high levels. Complexation studies are difficult because sensitivity is poor at low concentrations such as those used here. In addition, few thermodynamic formation constants are available for these ligands and metals (Logan and Traina, 1993). For these reasons, the approach taken here was to observe in a macroscopic sense the effects of the organics on metals attenuation without characterization of the ligands. Though this gives limited interpretation capability, characterization of the ligands was beyond the scope of the project. To annotate the current understanding of metals leaching and transport characteristics under varying test conditions, several related studies are reviewed below.

Newman, Elzerman, and Looney (1993) examined field soils in small columns to study facilitated transport of metals under hazardous waste concentrations. They found that, for low pH conditions, 50% of the lead, cadmium and copper applied were eluted with mobile colloids (defined as clay fraction turbidity).

Keller and Vedy (1994) studied the distribution of copper and cadmium in forest soils and found that organic matter (and/or Fe/Mn oxides) seemed to immobilize copper, whereas cadmium was exchanged onto the mineral oxide sites. Here, a sequential extraction procedure showed that cadmium seemed to be less strongly bound than copper. More importantly, these authors concluded that organic matter played an important role in the immobilization of copper.

Sawhney, Bigbee, and Stilwell (1994) studied the leaching of source separated municipal solid waste compost. Their results indicated that the transport of heavy metals to underlying aquifers to be negligible, this owed primarily to the ultimate dilution realized after reaching the groundwater. They further concluded the order of leachability for the metals to be: $Cd > Zn > Cu > Pb$, with lead being least mobile.

Finally, Holm and Zhu (1994) presented the results of metal sorption experiments involving landfill leachate-contaminated groundwater. They found that cadmium sorption increased with pH, which they concluded indicated surface complexation. They also found dissolved organic matter (DOM) complexed cadmium very weakly, if at all. Lead showed similar behavior to cadmium. Copper, on the other hand, was strongly complexed by DOM. They also showed DOM increased Cu^{2+} sorption at pH < 6. Davis hypothesized that sorbed organic matter formed ternary surface-ligand-metals complexes at low pH, while at high pH the metal-organic complexes remained dissolved.

RESEARCH APPROACH

The work plan was broken into two main components in order to provide an accurate and justifiable analysis of the fate and transport of the metals. Besides being highly dependent on the initial concentrations present in the stormwater, the partitioning of these pollutants onto any solids present or into solution must be known a priori in order to effectively assess the metals mobility. With this in mind, a series of experiments attempting to charcacterize partitioning among the metals-NOM-soil matrix was developed (Phase 1), as well as a experiments to investigate macro-scale transport behavior of the metals (Phase 2). Phase 1 experiments, due to resource and time constraints, focused on the single solute of lead with humic and fulvic acids, but had greater controls on the geochemistry of the system, e.g. pH, ionic strength; while Phase 2 dealt with multiple metals in the feed and was able to incorporate field hydraulic and soil effects. Details of the procedure are included in Appendices A and B, respectively.

Soils. An important aspect of this study was the use of field soils appropriate for infiltration. A matrix of soil types having cross-characteristics of high/low permeability and high/low organic content were sought. (Note, the use of the terms high or low refer to relative properties amongst those soils likely as candidates for infiltration basin siting. As such, these soils are generally the more permeable of those found within a given region.)

34

In their actual selection, candidate soils were identified in areas supporting relatively large urban centers in the State (King and Spokane Counties). Moreover, soil survey maps were used to confirm their presence along extensive (regional) sections of State and Federal highways.

The final selection of the soils for the study evolved from both preliminary in-house testing and outside laboratory analysis. The candidate for high permeability/low organic content was Springdale sand. Given its character, Springdale became the "control" soil both in terms of pore size distribution (uniform) and organic content (very low). Everett, a loamy sand, became the high permeability, moderate organic content candidate. Everett was also amongst the easiest to work with, not only in terms of physical handling, but also in terms of hydraulic and transport control. Finally, in search of a low permeable/high organic content soil, Garrison sandy loam was investigated.

Phase 1 Experimental Approach. Only soil samples of Everett sand were used in these series of experiments. Background organic matter was removed (without changing the other chemical surface characteristics of the soil) to minimize interferences with the nonindigeneous dissolved organic matter used in the experiments. Further, the larger sand fraction was isolated to better investigate the influence of intraparticle reactions and to allow for the timely breakthrough of strongly–sorbing solutes in the column experiments by decreasing the specific surface area of the media. Finally, removal of fines increased the mean pore diameters in the media, minimizing the possibility of straining or size exclusion of macromolecular organic matter in the bulk soil matrix pores. Peat–extracted humic (PHA) and fulvic (PFA) acids obtained from the International Humic Substances Society (IHSS) comprised the dissolved organic matter (DOM) in this portion of the study.

Phase 1 involved performing Pb-NOM equilibration studies, batch kinetic and equilibrium studies, and finally soil column experiments to characterize how the NOM (both fulvic and humic acids) interacted or complexed Pb and how their interaction affected

the metal's transport behavior. Batch equilibrium sorption studies were performed to generate sorption isotherms for Pb and DOM onto Everett sand. In addition to Pb and DOM individually, isotherms of Pb in the presence of DOM were developed for varying concentrations of DOM.

In the equilibration studies varying concentrations of lead (Pb) were added to flasks containing 75 mL of DOM stock (as 25 mg DOC L^{-1}, corresponding to 8.75 and 47.5 μmol L^{-1} PHA and PFA, respectively) and equilibrated by gentle mixing for 24 hours. The concentration of uncomplexed Pb was measured on the filtrate passing an ultrafiltration membrane. UV absorbance, pH, and Pb concentrations were determined on both filtered and unfiltered samples in the binding studies.

Kinetic sorption was studied in batch systems containing equal soil and solute concentrations. Each experiment consisted of several replicated batches, each analyzed for soluble (Pb or DOM) concentrations over a range of time intervals between 30 seconds and 204 hours. Rate of sorption was observed for Pb and PHA only. Fractional uptakes were measured over time to assess the rate of sorption. All added solutions were unbuffered and adjusted to pH 7.0 with dilute NaOH. The ionic strength of the solute was maintained at a relatively constant value.

After equilibration with the soil, aqueous phase concentrations were determined, as well as the particle size distribution of sorbent in the shaken samples to examine the effects of agitation and reaction upon the release of aggregated or agglomerated secondary particles. The mass of desorbed particles, about 3% of the total soil mass, suggested that the effects of desorbed particles could be neglected in the sorption experiments. Further, preliminary experiments suggested that mixing intensity and the degree of particle desorption did not affect the equilibrium uptake of solute.

The Phase 1 column experiments were performed in 2.5 cm (dia) x 5.7 cm (length) cylindrical soil–packed glass columns. The procedure used minimized the entrainment of air into the column, maximizing water saturation of the total pore volume. DOM in the

column effluent was monitored continuously for UV absorbance at 254 nm. Samples exiting the cell were collected by an automatic fraction collector, acidified to pH < 2, and analyzed for Pb. Flow was monitored at predetermined intervals throughout the solute transport experiments. Upon conditioning the columns (packing and saturation), solute feed solutions were applied as a step input and allowed to continue until complete breakthrough was approached. Various combinations of DOM and Pb in the feed (adjusted to pH 7.0 with dilute NaOH and prepared in a 0.01M KCl matrix) were investigated in separate breakthrough experiments. Experiments involving Pb were ended prior to complete breakthrough because of the significant retardation of Pb in the column. Effluent pH was monitored throughout each transport experiment.

Column homogeneity, dispersion, and channeling were evaluated simultaneously by analyzing the breakthrough curve (BTC) of a nonreactive tracer (^3H_2O). The breakthrough curve was fitted to the convection dispersion equation to determine the dispersion coefficient and pore water velocity. These parameters were fit using nonlinear regression analysis with the program CXTFIT (Parker and van Genuchten, 1984).
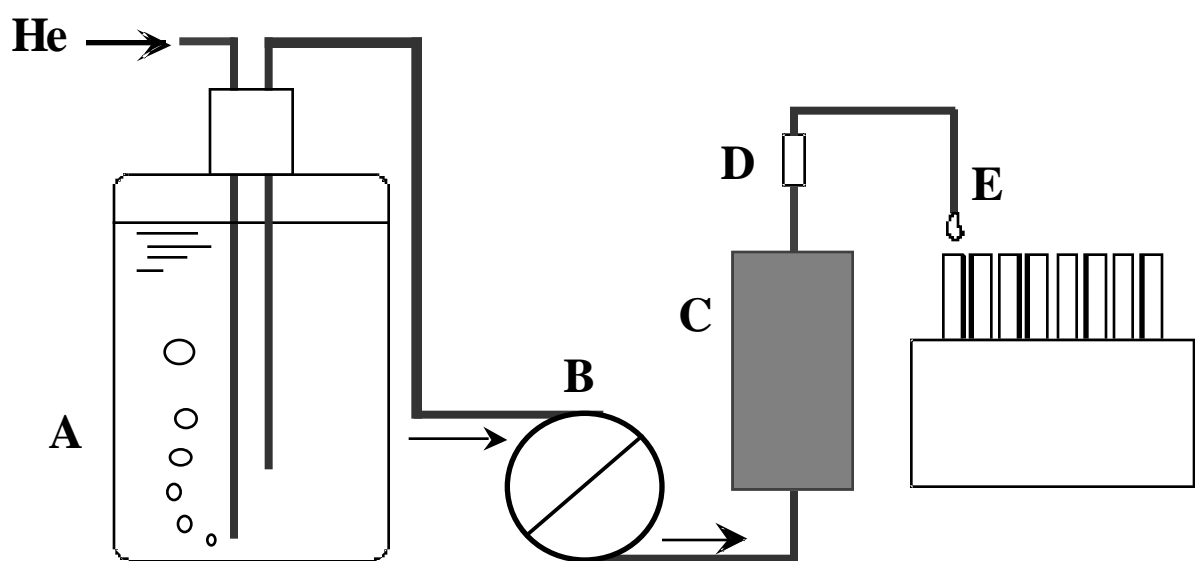
FIGURE 3. Column Apparatus. (A) Feed reservoir, kept under a helium atmosphere; (B) 8-roller peristaltic pump equipped with a microcassette tubing cartridge for small-diameter tubing and low flow rates; (C) Borosilicate glass column housing the soil; (D) 1-mL continuous-flow quartz cell coupled with an ultraviolet absorbance detector; (E) Automatic fraction collector

Phase 2 Soil Column Experiments. The main goal in developing this part of the study was to simulate the field scale hydraulic loading and draining conditions of infiltration basins using appropriate field soils. The sampling scheme and matrix of tests conducted were selected such that adequate data would be available for: (i) comparing performance amongst several soils - performance referring to a soils ability to remove metals from solution, and (ii) evaluating the effects of the inclusion (or exclusion) of dissolved natural organic matter (NOM) in the feed. As guidance, Washington State Department of Ecology (WSDoE) minimum design criteria for infiltration basins were used in defining the physical set-up of the soil column experiments.

To quantify the metals transport through the column, the concentrations of metals applied and eluted from the column were integrated throughout the experimental trials. In addition concentrations of each metal were observed at regularly spaced (30 cm) intervals along the soil column depth, as well as the lower outfall, in an attempt to examine mass fluxes across intermediate boundaries. Moreover, at the conclusion of each loading sequence, the distribution of (stored) mass within the column was measured via samples taken at regularly spaced intervals along the soil column's length. This information was then used to quantify the overall performance of the columns subject to different loadings and soil types.

Each soil tested underwent the four procedures listed in Table 4. First, initial and final bromide tracer tests were conducted for each repacked soil column. Then, the metals-only synthetic stormwater solutions were applied in a sequence of five "storm events." Samples of dissolved metals, total organic carbon (TOC), and pH were taken from each port at designated intervals of depth infiltrated. The soil was then unpacked and soil samples were taken for metals extraction. A new column was packed with the same soil type and a sequence of five metals-NOM storm events were applied.

Table 4. Summary of Procedures

Procedure Number	Description	Analysis	Sampling Port
P1	Bromide Tracer Test	Bromide Concentration	ESP*
	Metals-only solution	metals concentration	ESP/ISP**
P2	Cd, Cu, Pb, Zn	TOC	ESP/ISP
	5 simulated events	pH	ESP/ISP
	Metals-NOM	metals concentration	ESP/ISP
P4	solution on new soil	TOC	ESP/ISP
	5 simulated events	pH	ESP/ISP
P5	Final soil analysis	extractable metals	

* ESP - Exit Sampling Port   ** ISP - Intermediate Sampling Port
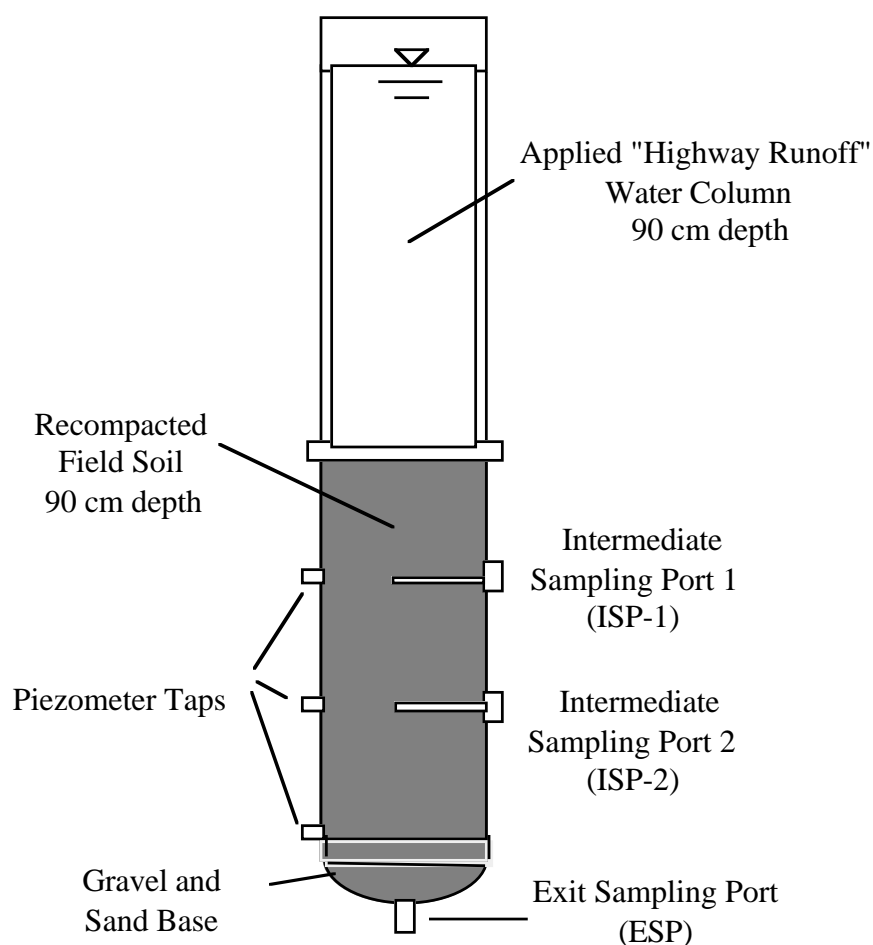
Figure 4. Schematic of Soil Column

FINDINGS AND DISCUSSION

This work consisted of two major components. The first phase entailed performing batch and small scale column experiments on lead and NOM constituents in an attempt to understand metal-organic-soil matrix interactions in a highly controlled, isolated system. The second phase involved performing large scale column experiments on a series of soils to observe the effects of NOM on metals-removal performance under hydraulic conditions similar to actual basins. This section is divided into subsections discussing and summarizing the main findings of the two phases of the study.

PHASE 1 DISCUSSION

DOM Kinetics. Figures associated with this discussion are included in Appendix C. It is clear that upon addition of PHA to a mixture of soil and water, significant liberation of free hydrogen ions occurred, resulting possibly from hydrolysis of the PHA. This resulted in a sharp drop in pH and corresponding "uptake" (precipitation) of PHA. An inverse correlation can be observed between pH and PHA uptake, resulting from the stability of the DOM colloids. In samples having a pH less than 4, pinfloc particles of PHA could be observed by the naked eye. This is not surprising, since it is well known that the solubility of humic acid decreases with pH. After approximately 0.1 days, the electrostatic reactions tended to stabilize, after which uptake kinetics could be observed. However, the limited number of data points collected once electrostatic equilibrium had occurred and the lack of available data at short times precluded the use of the kinetic models that were applied in the study of lead uptake kinetics. Uptake equilibrium was finally attained after about 50 hours. This apparently erratic behavior was not observed in the monitoring of effluent pH in the column studies. It is unknown whether or not electrostatic dynamics controlled speciation of DOM on a more localized scale (e.g., on a pore scale).

DOM Mobility. Since a more aromatic humic material should sorb more strongly to a sorbent dominated by mineral surfaces (Oden *et al.*, 1993), such as Everett sand, there is little reason to believe that PHA should not be more retarded than PFA in the column experiments and more strongly sorbed than PFA in the batch equilibrium sorption experiments. However, this expected behavior was not observed. Thus, it is suspected that size exclusion of PHA from intraparticle pores is resulting in the earlier breakthrough of PHA relative to PFA and in the ability of PHA to enhance the cotransport of Pb relative to PFA. A methodological argument for size exclusion follows.

First, it is known that humic acids are, in general, more reactive than fulvic acids. Not only is this general trend reported in the literature (Oden *et al.,* 1993; Murphy *et al.,* 1990), it can be suspected from the density of the aromatic carbon functional groups of PHA and PFA. Murphy et al. (1990) even reported the stronger sorption of humic acid over fulvic acid onto clays with the same DOM materials used in this study. Furthermore, the Pb-DOM aqueous binding studies indicate that PHA can bind much higher concentrations of Pb than PFA, resulting from the more hydrophobic nature of PHA and its higher binding site molar density. It would follow that PHA should sorb more strongly to the soil than PFA.

Examination of the sorption isotherms between PHA and PFA indicates that the Everett soil has a higher affinity for PFA than for PHA over a range of equivalent molar concentrations. In addition, the column experiments show that PHA breakthrough occurs prior to PFA breakthrough, consistent with the results from the sorption isotherms. These results are contrary to suspected behavior based upon the relative hydrophobicities between the two compound mixtures.

It has also been shown that sorptive uptake of solute by the media can be successfully modeled using a diffusion kinetic model for Pb uptake. SEM microscopy and measurement of the surface area of the soil strongly suggest the presence of a significant intraparticle porous structure. Thus, size exclusion of the larger PHA molecules from

smaller intraparticle pores (and failure of the PHA to access intraparticle binding sites which are accessible by smaller solutes) could be enhancing PHA transport in the breakthrough studies (and inhibiting sorptive uptake of PHA in the batch experiments) to such a degree that size exclusion "overcomes" PHA hydrophobicity and allows its transport to be enhanced relative to PFA.

Relative Mobility of Pb in the Presence of PHA and PFA. Predicting Pb mobility in the presence of DOM requires collective consideration of the results from the batch experiments. The Pb-DOM aqueous binding study (Figure C.7) suggests that PHA has a higher affinity for Pb than PFA. Since PFA has a higher affinity for the soil than PHA in the DOM–only batch equilibrium sorption experiments, it would follow that Pb mobility should be enhanced in the presence of PHA relative to PFA. This is consistent with the results of the Pb-DOM column studies (Figure C.10). Of course, this prediction is based upon the assumption that *soluble DOM controls Pb speciation*. If Pb speciation was controlled by sorbed phase DOM, then Pb may be less soluble in the presence of PHA relative to PFA.

The results of the Pb-DOM sorption experiments (Figure C.6) suggest some interesting mechanisms that are in competition with each other. First, Pb solubility was enhanced in the presence of DOM relative to Pb solubility in the absence of DOM, indicating that soluble DOM is complexing sufficient Pb to prevent its sorption to the soil. (Alternatively, DOM and DOM-Pb complexes may be outcompeting Pb for non-specific sorption sites on the soil.) However, it was noted that Pb solubility at high equilibrium Pb concentrations was inhibited in the presence of low concentrations of PHA (see the point *A'* in Figure C.6) relative to the case where no DOM was added. This behavior suggests that at low Pb concentrations, soluble PHA controls Pb speciation, keeping Pb in a more soluble species than in the "No DOM" case. Further, at higher Pb concentrations, the complexation capacity of the soluble PHA is approached, and Pb binds with sorbed PHA. If sorption of PHA to the soil increased the soil's affinity for Pb, then it is not surprising

43

that Pb sorption would actually be inhibited at higher Pb concentrations if the soil was coated with PHA.

The second general trend is that PFA enhances Pb solubility better than PHA. This would suggest that sorbed DOM is the controlling mechanism affecting relative Pb speciation when comparing DOM types, since it was observed in the aqueous binding experiments that Pb has a higher affinity for PHA than for PFA. However, this trend is reversed at low Pb concentrations. At low concentrations, Pb solubility is greater in the presence of PHA than in the presence of PFA, suggesting that soluble DOM is controlling relative speciation. The points labeled B' simply indicate the equilibrium concentration at which the complexing capacity of soluble DOM is being approached and Pb binding by sorbed DOM begins to define the relative speciation of Pb.

Therefore, to predict column behavior, Pb speciation over expected pore water concentration ranges must be considered. The feed solution to the column was about 6 μmol Pb L^{-1}. Careful examination of Figure C.6 reveals that at this equilibrium concentration, the apparent solubility of Pb (in the presence of Low DOM, which approximates the DOM concentrations in the feed solution) was actually higher in the presence of PHA relative to PFA. This behavior would seem to occur at all Pb concentrations lower than this critical value (B'_{low}), which should be representative of the pore water concentrations in the column experiment. Thus, Pb binding to aqueous DOM would dominate speciation, and Pb would be more soluble in the presence of the DOM type which has a higher affinity for Pb. Consequently, since PHA has a higher affinity for Pb than PFA, then Pb mobility should be greater in the presence of PHA than in the presence of PFA. Also, since PHA is more mobile than PFA, this relative behavior is further emphasized. Indeed, this is what occurs in the column studies, as shown in Figure C.10.

It should be noted that above the critical concentration (B'), as the DOM became saturated with Pb, Pb binding to sorbed DOM (and other sorption sites) would control speciation. Again, Pb would tend to favor binding to the DOM type which has a higher

affinity for Pb (PHA). Consequently, Pb would be more mobile in the presence of PFA relative to PHA (assuming both PFA and PHA had equivalent sorption affinities for the soil). However, the higher affinity of PFA than PHA for the soil will introduce an effect that will compete. The strength of this competition cannot be qualitatively evaluated from the batch experiments discussed above.

"Cleansing" Mechanisms. Although it cannot be confirmed with the data presented here, size exclusion may also be playing a role in the cleansing phenomena observed in the breakthrough of Pb-DOM feeds. A possible scenario illustrating this begins when a Pb-DOM complex is transported to a pore larger than the DOM molecule. At the pore, if the energy for lead to diffuse through the pore (in either the solid or aqueous phase) overcomes the energy of binding between the Pb-DOM complex, then Pb may detach from the DOM molecule and continue through the pore to a desirable sorption site, leaving behind a "cleansed" DOM molecule.

Of course, another likely mechanism for cleansing could simply be competitive sorption of Pb onto an easily accessible surface site and the subsequent detachment of the DOM molecule. Regardless of the exact mechanism, cleansing is a likely process influencing cotransport in this study. Pb would tend to detach from a DOM molecule and sorb to the media as a Pb-DOM complex approached a "clean" (Pb-deficient) portion of the column to maintain equilibrium distribution relationships. This behavior was predicted in a sensitivity analysis of the colloid-metal transport model COMET by Mills *et al.* (1991) and observed in the simultaneous breakthrough of copper and fulvic acid by Oden *et al*. (1993).

Other Considerations. An alternative to the cleansing theory for explaining the breakthrough of DOM prior to Pb is the possibility of decreased mobility of the Pb-DOM complex relative to DOM alone. The results from the Pb-DOM aqueous binding study suggest that the amount of Pb in the complexed state in the PHA-Pb feed solution in the column experiments comprises at least 50% of the total Pb. Thus, if the dominant mechanism was preferential sorption of Pb-DOM complexes, then differences in

breakthrough characteristics of DOM with and without Pb should be observable in the column studies. However, upon careful comparison of Figures C.9 and C.10, one can see that DOM breakthrough between experiments 1H/1F and 3H/3F cannot be significantly distinguished. Thus, the change in sorption character of DOM upon binding to Pb is not likely to be a dominant mechanism.

Finally, since preferential sorption of individual components of DOM within each fraction may be occurring, the elution of UV-absorbing components which do not bind Pb may be occurring prior to the breakthrough of those fractions which do not bind Pb. However, Figure C.10 shows that the relative concentration of DOM had reached 0.6 and 0.75 for PHA and PFA, respectively, when Pb breakthrough began. These relatively high DOM concentrations suggest that components with a substantial aromatic character, which would tend to bind Pb, are eluting. This is supported by noting that the mass fraction of [DOM eluted:total DOM applied to the column] when Pb begins breakthrough is significant (approximately 28% and 38%, for PHA and PFA, respectively). Thus, we would expect Pb to begin eluting earlier, as the aromaticity of the effluent began to significantly increase. This cannot be confirmed, however, without knowledge of the absorptivity (absorbance per gram of carbon) breakthrough of the effluent, which would indicate the degree of "specific" (normalized to mass of carbon) aromaticity of the effluent.

Main Results of Phase 1.

- The column experiments show that PHA breakthrough occurs prior to PFA breakthrough, consistent with the results from the sorption isotherms.

- Size exclusion of the larger PHA molecules from smaller intraparticle pores (and failure of the PHA to access intraparticle binding sites which are accessible by smaller solutes) could be enhancing PHA transport in the breakthrough studies (and inhibiting sorptive uptake of PHA in the batch experiments) to such a degree that

46

size exclusion "overcomes" PHA hydrophobicity and allows its transport to be enhanced relative to PFA.

- Pb solubility was enhanced in the presence of DOM relative to Pb solubility in the absence of DOM, indicating that soluble DOM is complexing sufficient Pb to prevent its sorption to the soil. At low Pb concentrations, soluble PHA controls Pb speciation, keeping Pb in a more soluble species than in the "No DOM" case. Further, at higher Pb concentrations, the complexation capacity of the soluble PHA is approached, and Pb binds with sorbed PHA. If sorption of PHA to the soil increased the soil's affinity for Pb, then it is not surprising that Pb sorption would actually be inhibited at higher Pb concentrations if the soil was coated with PHA.

- PFA enhances Pb solubility better than PHA. At low concentrations, Pb solubility is greater in the presence of PHA than in the presence of PFA, suggesting that soluble DOM is controlling relative speciation.

- To predict column behavior, Pb speciation over expected pore water concentration ranges must be considered. Pb binding to aqueous DOM would dominate speciation, and Pb would be more soluble in the presence of the DOM type which has a higher affinity for Pb.

- Although it cannot be confirmed with the data presented here, size exclusion may also be playing a role in the cleansing phenomena observed in the breakthrough of Pb-DOM feeds. Another likely mechanism for cleansing could simply be competitive sorption of Pb onto an easily accessible surface site and the subsequent detachment of the DOM molecule.

PHASE 2 DISCUSSION

Phase 2 of the study involved performing the large scale column experiments on three near surface soils sampled across the State having a range of soil properties adequate for infiltration as required by the Manual. Detailed discussion and summary plots are included in Appendix D. As a prologue to the following discussion, a summary of the findings from Phase 2 are presented.

Hydraulics. The variability of infiltration rates among the different soil columns was undoubtedly due to differences in compaction effort and the physical and structural differences of the soils. Moreover, infiltration rates varied (at times significantly) among the individual runs of the same soil. Varying drainage periods between runs may have had an effect on soil pore configuration, caused air entrapment, and/or varied the initial water content of the soil at the wetting front. Though all of these factors can potentially change the hydraulic conductivity, air entrapment was likely to have caused the most unpredictability in these column experiments. Such effects probably play minor roles in the field, however, other processes such as siltation and desiccation may be significant in producing varying infiltration rates in the field (Note dessication cracking is discussed further in Appendix E).

Soil Analysis and Performance. The three soils considered in this study included a sand (Springdale), a loamy sand (Everett), and a sandy loam (Garrison), each with varying silt and clay content, CEC, and organic content. Although higher CEC corresponded with greater metal attenuation, the soil organic content seemed to control, more directly, the attenuation of copper and zinc. To support this, first consider that the metals-only runs resulted in poor copper attenuation for the loamy sand, while the sandy loam had almost twice the removal rate. The most notable difference between these two soils was not their CEC, which differed by 25%, but rather their percent organic content, which differed by an order of magnitude. This finding suggests that soil organic content is as good a measure of soil metals attenuation, if not better, than CEC alone for copper and

zinc. In the case of cadmium and lead the organics seemed to play a minor role in their transport behavior. Secondly, when the NOM was added to the feed solution, the removal efficiencies for copper and zinc drastically improved. That is, if organics are present in high enough concentrations, it can control the transport behavior of copper and zinc because of the effects organic complexing may have in metals sorption characteristics. The mineral content of the soils may have also played a role if dissolution was indeed occurring and was the cause for the increased copper and zinc concentrations.

Effects of Competition and Background Metals. Interesting results were observed concerning competition effects among the four metals. Most notably, desorption/dissolution of copper, and zinc to some extent, was observed within the upper reaches of all of the soil columns. At the same time, the majority of cadmium and lead concentrations were observed to be greatly reduced near the surface. This suggested that either copper and zinc were displaced by cadmium and/or lead within this top region of the soil column, or dissolution occurred by the fact that concentrations of copper and zinc were low relative to their solubilities. Because cadmium is generally thought to have a lower affinity than copper for soils, the latter explanation is more likely.

The order of potential mobility for the experiments performed here are listed in Table 5. This ordering is based on the calculated removal efficiencies from each soil. But again, speciation of the metals may have determined this order, since prior studies have determined that cadmium and lead generally have lower affinities for soils than copper or zinc in the free ion state. Inorganic complexation and the trace concentrations used made dissolution of the metals a likely cause for the observed order.

Studies evaluating metals mobility often do so under varying aqueous conditions (i.e. varying pH and ionic strength), but rarely over multi-component solutions. Although in most instances cadmium was determined to be more mobile than copper, the results here did not agree. In terms of greatest mobility, the order was Cu > Zn > Pb > Cd. The mobility or affinity of metals for a soil are strongly dependent on the conditions of the test,

49

e.g. here, much larger columns packed with "unwashed" field soils and the much smaller concentrations were used.

Table 5. Order of Relative " Mobility" for Soil Columns

Soil	Metals-only Runs	Metals-NOM Runs
Everett (loamy sand)	Cu > Zn > Pb = Cd	Cu > Zn > Pb = Cd
Springdale (sand)	Cu > Zn > Cd > Pb	Zn > Cu > Pb = Cd
Garrison (sandy loam)	Cu > Zn > Pb = Cd	Cu > Zn > Cd > Pb

Effects of NOM. All soils considered showed greater attenuation of metals to varying degrees when NOM was added to the feed solution. Based on metals mass removal efficiency, improvements in the attenuation of cadmium and lead due to the addition of NOM were minimal, since their affinities for the soil were already high. Generally, improvements for these two metals were less than 10%. For the sand (Springdale) and loamy sand (Everett) with low and moderate organic content, the addition of NOM improved copper and zinc attenuation by as much as over 40%.

The NOM applied to the column, instead of facilitating metals transport, actually hindered it. The observations made during the present study suggest a possible explanation. The organic ligands may have decreased mobility of the metals by themselves sorbing onto the soil matrix from physical straining of the NOMs due to their large macromolecular nature providing additional sorption sites for the metals. It is hypothesized that as a result of the loading conditions (the impulse release approaching a continuous

50

release), an accumulation of NOM's in the near surface soils resulted. This "web" of organics near the surface provided additional sites for copper and zinc binding. Another possibility is that the high concentrations of organics allowed metal-NOM complexes to form in solution which had greater affinity for the soil than free, hydrated or inorganically complexed metals. In any case there was definite NOM removal from solution when the NOM was added. The sandy loam with naturally high organic content showed elevated metals removal ability without the additional NOM. This supports the idea that organic content is a viable gauge with which to rate soils for copper and zinc removal during infiltration.

"Metals-Only" Stormwater Applications Discussion. Generally speaking, cadmium and lead are thought to have lower affinity for exchange sites than copper and zinc (Sawhney, et.al., 1994), (Bodek, 1988), (Amoozegar-Fard, et.al., 1984). Hence, a pure exchange dominated system could not have explained the observed desorption of copper and zinc. To do so, the speciation and complexation of the metals must also be addressed. Unfortunately, since only total metal concentrations were measured, speciation could not be determined directly (nor was adequate water quality data taken on other dominant ions). Nevertheless, pH values may be employed as indicators of likely forms in solution. Noting that the pH of the samples ranged between 6.0 to 6.5, the free (or aquated) metal ion species probably dominated, i.e. Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}. For these forms, traditional cation exchange likely controlled the transport. In Springdale and Everett, where organic carbon contents were small, this exchange was probably dominated by attachment with mineral (Fe/Mn) oxide sites on the soil. While for Garrison, the exchange was likely controlled via resident organic matter. The greater removal efficiency observed for increased CEC would tend to validate these ideas.

These assumptions, however, do not fully explain the observed mobility of copper and zinc. Recall, that deionized water was used in the columns, producing an early condition in the feed water that was undersaturated with respect to the metal ions,

particularly for zinc and copper, which can exist at much higher aqueous concentrations. Once added and placed onto the soil, some of the dissolved metals likely formed inorganic complexes with either carbonate (CO_3^{2-}) or sulfate (SO_4^{2-}). Under this framework, the solubility of the individual inorganic complexes may have controlled the observed concentrations throughout the column. For lead and cadmium, the amount added may have been large enough to satisfy various solubility limits at concentrations which were below detection limits. On the other hand, for copper and zinc, the amount added was likely less than the soluble capacity and, as such, existing mass was "stripped" from the soil to satisfy equilibrium conditions. The result was concentrations in the effluent which exceeded those added.

To shed further light, the speciation of the metals may have also contributed to the controls of the system. For example, if the metals and other ions from the soil were complexed with other inorganic ligands such as sulfates and carbonates, the concentrations of these ligands in solution could have limited the dissolution of the heavy metals due to the common ion effect. In addition, the speciation of these metals may have been such that their affinity for the soil was greatly reduced, i.e. an inorganic complex has a reduced or zero valency.

"**Metals-NOM" Stormwater Applications Discussion.** With the addition of NOM in the feed solution, eluted copper continued to exceed the initial feed concentrations, while cadmium and lead remained strongly bound for each of the soils. The data revealed repetitive behavior (i.e. similar to that found in the metals-only experiments) for the pairs: cadmium-lead and copper-zinc. Notwithstanding, the overall aqueous phase concentrations throughout the column decreased as compared with the metals-only experiments.

If solute metal-organic coordination occurred, any organics attached to the soil matrix would likely lead to an increase in metal sorption. On the other hand, if organics leaching is increased, then more of the metals would be eluted. This would be the case if

the metals had no preference for coordinating to bound or mobile organic matter. However, even though higher concentrations of TOC were observed from each port due to the addition of NOM, the concentrations eluted from the column were consistently less than half of the feed TOC values, and there was no corresponding increase in metals concentration. Increased metals concentrations would be the expected outcome had preference for complexation with mobile dissolved or particulate organic matter been the case. This leaves the two possibilities: i) mobile phase organic complexes formed, but had a high affinity for the soil matrix, and ii) the metals had a higher affinity towards the bound organics which were removed from the elluent.

The data collected did not allow determination of which of these processes was dominant. It was likely that both of these phenomena occurred. In any case, the results showed that as the TOC (organics) was transported it left a NOM-rich region in its wake from which minimal metals mass migrated beyond. The organics that did attach themselves to the upper portion of the soil column appeared to have provided increased metal sorption. The organo-metallic complexes formed in solution may have been such that their affinity for the soil was greater than the inorganic complex species of metals present in the metals-only experiments. Especially in the case of copper, it appears the organic ligands out-competed the inorganic ligands for complexation with copper to form organic complexes with a greater affinity for the soil matrix, thus leading to the much lower aqueous concentrations. However, with enough applications of NOM loaded runoff, the migration of this NOM-rich region may eventually breakthrough to the water table. As a result, the sorption sites would then be "in contact" with the groundwater, which may allow transport of the metals.

The results observed indicate that at high NOM concentrations, sorption processes can be dominated by the organics in solution and on the matrix. For example, Everett, whose sorbent properties were dominated by mineral surfaces, as determined in a related study (Jordan, 1995), showed much greater sorption ability in the presence of higher

concentrations of NOM. This effect was even more prominent in Springdale, which had an even lower organic content and CEC. Unfortunately, the extent of the enhancement or decline of metals attenuation with soils already high in organic content could not be compared.

Mass Removal Efficiency. Table 6 shows that, in general, Garrison soil performed better than Everett, which in turn, performed better than Springdale. This order corresponds to the soils' decreasing CEC and organic content, and confirms the important role quantification of CEC has in predicting metals attenuation ability of a soil. More importantly, the organic content of the soil seemed to strongly control the attenuation of copper and zinc. Although the addition of NOM enhanced the attenuation of all four metals, the improvements for each metal differed. Lead and cadmium were significantly removed from solution by each of the soils, even without the addition of NOM (i.e. over 90% removal efficiency for each case with the exception of Springdale). With the addition of NOM, cadmium and lead were nearly completely attenuated. It is apparent that copper and zinc (to a lesser extent) were desorbed from the soils in the upper third of the column, while cadmium and lead were significantly adsorbed. By the exit port, however, there was a net removal of copper and zinc.

When NOM was added to the stormwater, copper and zinc attenuation was drastically improved for Springdale. Copper improved from almost no net attenuation to almost 70% removal, while zinc attenuation had close to 40% improvement. For Everett, copper attenuation improved by 40%, as well, while zinc removal increased by 50%. These results indicate copper and zinc coordinated with the organics to a much greater degree than cadmium or lead.

Table 6. Percent of Metals Mass Attenuated

Cadmium	Everett	Springdale	Garrison
Metals-only	96	82	99
Metals-NOM	99	99	87*

Copper	Everett	Springdale	Garrison
Metals-only	41	2	72
Metals-NOM	82	69	-22*

Lead	Everett	Springdale	Garrison
Metals-only	95	91	99
Metals-NOM	99	97	99*

Zinc	Everett	Springdale	Garrison
Metals-only	42	24	97
Metals-NOM	92	62	42*

*Garrison Metals-NOM runs formed a near impermeable barrier layer yielding unreliable data

Dominant Transport Mechanisms. The speciation of the metals would indicate their affinity for sorption sites on the soil matrix, e.g. whether they have a charge imbalance which needs to be satisfied, and therefore a greater tendency for sorption. The pH of the soil and corresponding pore water is one important factor determining the species of the metals. In acidic soils the free ion and metal sulfates predominate, as do organic complexes for copper. In alkaline soils, the carbonate and bicarbonate complexes are important. Unfortunately, no measurements were made to determine the metals' speciation, since measurements made on the atomic absorption spectrometer measured total concentrations only. Data taken of solution pH and soil carbonate contents suggest, however, the likely species of the metals were those of the free metal ion along with sulfate complexes for cadmium, lead and zinc (refer to Table 7). For the more alkaline solutions in the Springdale metals-NOM experiment, carbonate complexes may also be important.

Although a rigorous equilibrium speciation study of the metals could not be performed due to the absence of relevant anion and cation concentrations, a simple comparison of reaction constants may provide some insight to the observed results. If the measured concentrations of total metals were controlled by elution of copper and zinc, the solubility products and stability constants of three common anions with the four metals considered may provide an explanation. Note, from Table 8, that the log K_{sp} for copper and zinc are much higher than cadmium or lead for the three common minerals, i.e. the minerals with copper and zinc will tend towards dissolution to a greater extent than those with cadmium or lead. Moreover, because the feed concentrations for copper and zinc were relatively low, there may have been a tendency for those metals to go into solution.

Table 7. Range of Soil Solution pH from Columns[*]

Experiment	Soil Solution pH
Springdale Metals-only	6.0 - 6.5
Springdale Metals-NOM	7.2 - 7.7
Everett Metals-only	6.0 - 6.5
Everett Metals-NOM	5.2 - 5.8
Garrison Metals-only	6.1 - 6.9
Garrison Metal-NOM	7.1 - 7.6

[*] pH generally increased with depth

Table 8. Logarithms of Solubility Products for Common Minerals (log K_{sp})[*]

Metal	SO_4^{2-}	Cl^-	CO_3^{2-}
Cd	-0.10	-0.68	-12.1
Pb	-7.79	-4.77	-13.1
Zn	3.01	7.03	-10.0
Cu	3.01	3.73	-9.63

$$K_{sp} = \left[M^{2+}\right]\left[A^{n-}\right]^{2/n}$$

[*] Data taken from Ball and Nordstrom (1991)

Table 9. Logarithms of Complexation Stability Constants for Common Ligands (log K_{sc})[*]

Metal	SO_4^{2-}	Cl^-	CO_3^{2-}
Cd	-2.46	-2.60	N/A
Pb	-2.75	-1.80	-7.24
Zn	-2.37	-0.45	N/A
Cu	-2.31	-0.16	-6.73

$$K_{sc} = \frac{\left[M^{2+}\right]\left[L^{n-}\right]^{2/n}}{[ML]}$$

Solubility controls cannot completely account for the results, otherwise the concentrations should have been the same throughout the column due to equilibrium considerations. The observed reduction in copper and zinc concentrations with depth may be explained in terms of complexation. Table 9 shows the stability constants of metal-inorganic complexes with common ligands. Note that the smaller log K_{SC} possessed by cadmium and lead implies a lower natural tendency for these two cations to form inorganic complexes with these anions than copper or zinc. The (neutral) inorganic complex species of copper and zinc have a reduced tendency to sorb to charged surfaces and are more mobile.

The addition of NOMs increased the organics concentration available for organic complexation of copper and zinc. The organic complexes formed could have had a higher affinity for the soil matrix, because of the physical "straining" of the NOMs due to their macromolecular structure, or the greater potential of the vast surface functional groups in sorbing metals due to clay-metal-humate coordination. Therefore, it is postulated that the addition of the organics had a three-fold effect causing increased copper and zinc attenuation: i) the organics competed with inorganic ligands in solution resulting in decreased inorganic complexation, and hence a reduction in neutral inorganic complex formation (which possesses a lower sorption affinity), ii) organic-complexes formed with a much higher affinity for the soil matrix than the inorganic complexes resulting in increased attenuation, iii) the attenuated organics (matrix bound) provided increased sorption sites for copper and zinc. This illustrates that copper and zinc transport can be strongly influenced by organics in solution and in the soil.

The minimal improvements in cadmium and lead concentration reductions with the addition of NOM demonstrates that these two metals' transport behavior are unlikely organics controlled. In fact, the sorption of the two metals are likely controlled by mineral exchange sites as demonstrated in the similar attenuation rates in both Everett and Garrison.

Recall that the much higher organic content Garrison soil showed no greater cadmium or lead removal than Everett. However, their CECs were the same.

To illustrate the points above, copper is considered further. Free copper was the primary species at the measured pH range. The free copper ion was strongly bound to the exchange sites in the upper reaches of the column. At the same time, since copper concentrations were so low, copper in the form of inorganic complexes were solubilized because the reactions tended towards producing more copper in the aqueous state. This would explain the measured concentrations exceeding the feed values in the upper reaches. That is, dissolution of copper in the form of inorganic complexes in addition to the free copper brought the measured concentrations above the feed, but then an observed reduction in concentration was measured at the ESP because the free copper was adsorbed leaving only the inorganic complexes in solution at the ESP. Whatever copper was measured at that point was in the form of complexes (carbonate, sulfates, chlorides) and was controlled by the solubility products of each of those constituents. When the NOM was added, organo-metallic complexes formed in solution, possibly even before infiltration (while in the ponded water). In addition, the organics in solution competed with inorganic ligands for complexation with copper, and those organic complexes were attenuated by the soil. This reduced the aqueous inorganic complexes, i.e. $CuSO_4^0$, $CuCO_3^0$, etc., and hence the total measured concentrations.

Review of Results. Although the intent of this study was to determine the effects of NOM on metals attenuation under quasi-field scale conditions, there were still obvious distinctions between the model and field conditions in this study. Most notable of these distinctions was the use of repacked soil columns. Although "unwashed" natural field soils were used, it was obvious that actual field soil structure and placement could not be achieved. The NOM used, though arguably more "realistic" than using manufactured humic or fulvic acids, was still not what actually occurs in nature. Certain information such as redox conditions, alkalinity, hardness, and soil water contents were also lacking

which may have provided a clearer explanation for the developments in this study. The observations, nonetheless, provide important insights into the effectiveness of infiltration in disposing of stormwater, the primary goal of the study.

From the results, several conclusions could be made concerning the objectives outlined. Although, the final removal rates were relatively high, several other factors were found to be of potential significance in considering stormwater disposal via infiltration. The following highlights specific findings in this study:

- CEC and silt and clay contents are effective indicators of a soil's ability to attenuate metals - at least on the short term. However, organic properties of the soil seem to be better measures of a soil's direct ability to attenuate copper and zinc, since copper and zinc seem to coordinate with organics readily. Mineral exchange sites seem to control to a greater extent the attenuation of cadmium and lead.

- Soil properties (organics leachability, infiltration rates, attenuated metals) can change with relatively few pore volumes eluted. The "washing" effect of the organics from the soil can lead to changing exchange capacity and sorption characteristics over time. As shown in these experiments as little as five "storm events" were produced the changes. This suggests siting decisions should involve consideration of evolving site conditions within the design life of the basin.

- The hydraulics of the system can be highly variable due to the intermittence of loading associated with infiltration practices, but this variability was not shown to directly affect a soil's ability to attenuate metals. The infiltration rate plays a secondary role when considering metals removal at these concentrations.

However, this is an important factor in how well a site can dispose of its design storm in the long-term.

- Speciation and background metals present in the soil are important factors to consider, because they can affect expected metals removal rates of soils. It was hypothesized that the trace concentrations of the metals resulted in some mineral dissolution and formation of inorganic-metal complexes resulting in increased copper and zinc concentrations. The existing copper and zinc which was leached from the soils can be an unaccounted source of heavy metal pollution and is not currently considered by design guidelines. Therefore, mineral content and background metals may be important parameters to quantify.

- An increase in NOM in the feed solution resulted in increased attenuation of metals by the soils tested. The greatest improvements in attenuation occurred near the surface, especially for the case of copper and zinc. The results indicate that increases in NOM concentration in solution can increase a soil's ability to attenuate metals by either the forming organic complexes with greater affinity for the soil, or by the sorbed organics providing more sorption sites for the metals.

- As far as the three soils tested, the sandy loam is considered a poor soil for infiltration because of potential hydraulic problems; though hydraulically the sand is probably the most stable, zinc and copper were not effectively attenuated by Springdale soil; the loamy sand shows the most potential, both hydraulically and in terms of metals removal characteristics, as an infiltration soil.

CONCLUSIONS

The underlying goal of this research was to evaluate how heavy metals attenuation in soils is influenced by high and low concentrations of dissolved NOM in solution. The methods employed in this study were intended to simulate field hydraulic conditions under more easily controlled laboratory conditions. The primary application for this research is to evaluate whether current minimum guidelines for infiltration basins are adequate in removing metals mass to acceptable concentrations before reaching groundwater. In a broader perspective, the results of this work can be used to gain a better understanding of metal-organic interactions in the subsurface and metals transport in the vadose zone.

This research has illustrated the complex problem of delineating the process-level mechanisms which influence contaminant cotransport. Clearly, the system studied involved a wide range of competing process that contributed to non ideal behavior in breakthrough experiments. These processes may have included:

- nonlinear equilibrium sorption over the concentration range studied;
- non equilibrium sorption kinetics during transport resulting from diffusion into intraparticle porosity;
- size exclusion of organic macromolecules; and
- complexation dynamics occurring during transport.

Existing colloid facilitated contaminant transport models were disqualified from application to the data set presented in this study by the nature of their simplifying assumptions. The important assumptions which were not consistent with the results include linear, equilibrium sorption and/or first-order sorption kinetics. There is enough evidence at the laboratory scale and an overwhelming body of evidence at the field scale that non ideal solute breakthrough (i.e., long tailing and sharp initial wave fronts) is a normal consequence of natural porous media. The mechanisms affecting nonideality are even well characterized and can be illustrated using simple models. However, the relative

sensitivity of breakthrough behavior to these mechanisms is not well understood, making it extremely difficult to delineate their respective influence upon observed nonideality. Consequently, the use of simple models invoking the assumptions stated above would be inappropriate to describe the complexity of the behavior observed in this study.

It was an objective of this research to contribute some insight into the mechanisms affecting the cotransport of metal contaminants with natural organic matter. This research shows that even a simple, three-component, well-controlled system, is an inherently complex collection of competing mechanisms.

Thus, only by examining isolated components of these complex systems can we truly begin to appreciate the magnitude of the problem of groundwater contamination and its impact upon the field of remediation engineering. In addition, experimental observation of these specialized systems, coupled with the development of models to efficiently describe the systems in response to sensitive variations in parameters, can this problem even begin to be approached.

Foresight on the part of state agencies to recognize the importance of soil sorptive properties (e.g. CEC, silt and clay content) is commendable. However results of this study suggest that further soil characterization is necessary. Background metals in the soil should be accounted for when siting facilities. Moreover, results here show organic content of the soil can be a better indicator of how well a soil will retain metals, and as such should be included as a siting condition along with CEC and silt and clay content. Soils with high clay and silt content, though providing greater CEC, should be avoided since they may prove to be troublesome as the wetting and drying of these soils can vary significantly from expected infiltration rates.

In our quest to find the balance between environmental and economic demands, we can become confused about the means to this end. In particular, infiltration practice is considered a "treatment" technology. However, this point of view is mistaken, because over the lifetime of a basin the attenuated metals would accumulate. Any changes in the

water quality infiltrating a site can potentially change the geochemical conditions, leading to the possible release of the sorbed mass on the soil. Therefore, it is stressed here that infiltration is merely a mass storage technology when considering metals and should be thought of as such. Serious consideration of this point should be made before any long-term management decisions concerning land disposal of runoff are made.

The question needs to be answered: are land application technologies, such as infiltration of runoff, a "safe" practice? In view of the results obtained in this study, concentrations would arguably be very minor when considering the dilution effects of the groundwater. The long-term accumulation effects may eventually lead to concentrations approaching or surpassing present groundwater and drinking water standards. But at the same time, technology pushes detection limits ever lower, which in effect allows regulators to require stricter standards. However, lower standards do not necessarily produce significant reductions in risk to human health or in the deterioration rate of the environment. It is up to the public, and everyone personally, to decide how to balance their ardor for sustaining a healthy environment with a realistic view of risk and the economics involved with tipping this balance too far in either direction. In the case of infiltration, the technology can work as long as the soil-water system's assimilative capacity is not taken for granted, and the technology is not considered an appropriate disposal means for any and all wastes, much as landfills and streams were treated in the past.

IMPLEMENTATION

<u>RECOMMENDATIONS</u>

The findings of this research suggests the following recommendations be followed by WSDOT for the design of infiltration basins:

1. An assessment should be made of the metal concentrations existing within the soil at all newly proposed sites. Here, grab samples of soil extending down to (at least) 1 meter in depth should be analyzed for various heavy metals, including lead, copper, cadmium, and zinc. Soils containing concentrations in excess of 20 µg/g for lead, 20 µg/g for copper, 1µg/g cadmium, and 50 µg/g zinc should be avoided.

2. The fraction of soil organic carbon should exceed 0.3% to improve metals attenuation, but should not exceed 1.5% (by weight) for hydraulic effectiveness to a depth of (at least) 1 meter.

3. The silt/clay content upper limits should be reduced to 20% silt and 10% clay to improve/maintain hydraulic performance.

4. The minimum depth to underlying unconfined aquifers should be extended to (at least) 3 meters.

5. The post-constructed basin should be monitored (or checked) on a regular basis for poor hydraulic performance due to sedimentation/siltation. Those basins not draining within the originally specified 24 hour period should be renovated via silt removal. Unfortunately, due to the great variability in the stormwater runoff events from one location to another, an exact maintenance schedule cannot be defined. It is clear, however, that only

a few (2-4) centimeters of fine silt can severely degrade the hydraulic and environmental performance of these basins.

6. The basins should also be monitored (visually) for the presence of significant cracks (i.e. those extending beyond 10 cm in depth) formed in the bottom soils during periods of extended drying. These cracks should be removed via tillage, raking or other acceptable physical means.

Note: these recommendations should be viewed as additional points of design consideration amongst those already defined under the Puget Sound Stormwater Management Manual.

SUGGESTIONS FOR FUTURE RESEARCH

Large scale soil column experiments such as the ones used here provide a convenient intermediate scale on which to conduct long-term studies. Results can, arguably, be more directly applied to field scale performance studies than smaller columns, but without the difficulties involved in operating and maintaining field studies. However, several improvements or modifications could be implemented to this study. For example, lacking water content profiles to monitor the movement of water was limiting in terms of transport description. Secondly, excavated soil pedons may be "inserted" into the columns and used rather than repacked soils. Thirdly, "activated" granular material can be easily tested on the scale used here to assess their feasibility in enhancing metals removal from infiltrating water. As for improving the design of infiltration facilities, further work needs to be done on quantifying background metals, measuring geochemical parameters to develop a better capability for speciation studies, and quantitatively determining the organic contents for use in design guidelines.

In order to provide a long-term evaluation of infiltration as an effective disposal practice, computer simulations of ion transport can be developed which consider multi-

component (solutes and ligands), unsteady hydraulics, and perhaps even structured soils. The results of this study are planned for incorporation into computer simulations using single and multi-component models, and using speciation models such as PHREEQE or GEOCHEM to determine whether speciation did indeed control the mobility of these metals. Further data analysis techniques can also be investigated to analyze the immense quantity of data collected here in a more rigorous and quantitative manner.

This study has suggested some possibly significant mechanisms affecting solute transport in groundwater. These include:

- size exclusion of organic macromolecules;
- the influence of intraparticle porosity and solute diffusion upon transport;
- complexation dynamics and pH effects in soil-water systems;
- reactive characteristics of colloid-contaminant complexes; and
- the complexity of natural organic matter.

Thus, future research is proposed based upon the findings in this study:

1. Determination of the reactive characteristics of natural organic matter complexes (vs. NOM alone) of heavy metals with subsurface media.

2. Investigation of the potential for size exclusion to enhance NOM transport.

3. Delineation of the processes affecting the kinetic and equilibrium dynamics in multicomponent solute systems where the components can react with each other (i.e., colloids and contaminants).

4. Model development and experimental verification (at laboratory and field scales) of models that investigate collections of mechanisms that influence non ideal transport of a solute.

This research conducted for WSDOT has implications far beyond transportation considerations. The points listed above should not be limited to identifying future, specific transportation research projects, rather they could be incorporated into the way contaminant hydrology problems are generally investigated. The utility of the convection dispersion

equation, the local equilibrium assumption, and first-order kinetic models has been shown to be highly questionable in the solution of this complex problem.

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Appendix A

EXPERIMENTAL PROCEDURES AND METHODS

MATERIALS FOR PHASE 1

Soil. Bulk soil samples of Everett sand were obtained from a site near Stillwater, WA. Soil was air–dried at 20 ˚C for two weeks prior to preparation. Removal of background organic matter (without changing the other chemical surface characteristics of the soil) was desired to minimize interferences with the nonindigeneous dissolved organic matter used in the experiments. Further, isolation of a larger sand fraction was desired to better investigate the influence of intraparticle reactions (which are controlled by particle diameter, the diffusion path length) and to allow for the timely breakthrough of strongly–sorbing solutes in the column experiments by decreasing the specific surface area of the media. Finally, removal of fines increased the mean pore diameters in the media, minimizing the possibility of straining or size exclusion of macromolecular organic matter in the bulk soil matrix pores. Thus, particles were descretized in a muller–grinder for 30 minutes, washed in deionized water to remove fine particles and low–density (organic) litter, and dried at 40 ˚C for 48 h. The 0.425–0.850 mm (mean particle diameter) size fraction was isolated in a graded sieve stack on a hammer–type shaker for 30 minutes. Soil was stored at 20 ˚C under desiccated conditions. Table A.1 outlines selected chemical and physical properties of the soil. Scanning electron microscopy (SEM) coupled with energy dispersive x–ray (EDX) analysis was performed on the prepared soil to qualitatively characterize physical and chemical surface properties and to investigate the existence of intraparticle porosity. Figure A.1 is an SEM micrograph of a representative grain emphasizing the intraparticle porosity at the surface.

Primary mineral constituents of the soil included (in decreasing order of peak energy absorbed) Si, Fe, Al, and Mn. Less prominent energy–absorbing peaks in the EDX survey included Cu, Cr, Ca, and Mg. A soil washing procedure (acidification to pH < 2) resulted in > 75% decrease in peak energy of Cu, Ca, and Mg, indicating that most of these metals are probably in an easily exchangeable phase. However, little change was observed in the

energy absorbed by Si, Fe, Al, Mn, and Cr, suggesting the presence of more strongly bound forms of these metals, such as in mineral oxides

Dissolved Organic Matter. Peat–extracted humic (PHA) and fulvic (PFA) acids obtained from the International Humic Substances Society (IHSS) comprised the dissolved organic matter (DOM) in this study. Stock solutions were prepared by adding 100 mg DOM L^{-1} HPLC–grade deionized water and adjusted to pH 7.0 with dilute sodium hydroxide (NaOH). Stock solutions were stored at 4 ˚C and monitored frequently for dissolved organic carbon (DOC) stability. No detectable microbial growth (evidenced by no significant change in DOC concentrations) in the stock solution was observed during its storage life (< 2 weeks). Stock solution concentrations were approximately 50 mg DOC L^{-1}. Table A.2 outlines the distribution of carbon functional groups in each of the IHSS materials.

All other chemicals used in the study were of reagent grade or better. All water used in the study had a UV absorbance at 254 nm < 0.002 and DOC < 0.5 mg L^{-1}.

TABLE A.1   Selected Properties of Everett Sand, 20–40 Mesh Isolate.

[a]indigenous exchangeable Pb, $\mu g\ g^{-1}$	2.5
[b]organic matter, % wt.	0.12
[b]organic carbon, % wt.	0.07
[b]cation exchange capacity, $cmol(+)\ kg^{-1}$	3.0
[c]surface area, $m^2\ g^{-1}$	3.54 ± 0.09
[d]specific gravity, $g\ cm^{-3}$	2.48 ± 0.02
[e]pH	6.8 ± 0.2

[a]Determined by extraction with 1N HNO_3 for 1 hr. [b]Analytical Sciences Laboratory, University of Idaho. [c]Measured by ten-point N_2 (g) adsorption and calculated using the BET equation (Department of Earth Sciences, University of Waterloo). [d]Measured by water displacement and vacuum air evacuation in a volumetric flask. [e]Measured in a 1:1 (v/v) soil:water slurry after 24 hours of gentle agitation on a wrist-action shaker.

TABLE A.2   Carbon Function Group Distributions of IHSS Humic Materials.

	peat humic acid[a]	peat fulvic acid[a]
[b]aromatic C	47	34
[b]aliphatic C	24	29
[b]carboxyl C	20	28

[a]These and other properties of listed IHSS reference materials can be found in Murphy *et al.* (1990). [b]Distribution of carbon functional groups are expressed as % distribution of total carbon.
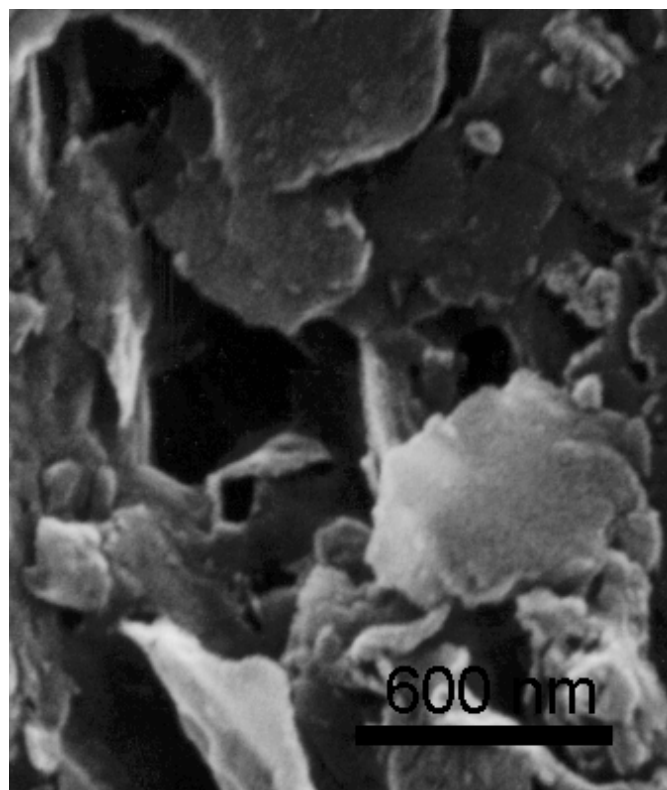
FIGURE A.1 SEM Micrograph of Everett Sand, 50 000 X. This photo of the sand surface shows evidence of an intraparticle pore structure. The pores visible at the surface are typically between 100 and 500 nm in diameter, easily large enough to accommodate large macromolecules such as humic and fulvic acids. However, constriction of the pores towards the center of the particle may be excluding large humic acid molecules and affecting their transport relative to fulvic acids (see *Chapter Four, Results and Discussion*).

METHODS FOR PHASE 1

Pb–DOM Equilibration Studies. Varying concentrations of lead (Pb) were added to borosilicate glass reaction flasks containing 75 mL of DOM stock (as 25 mg DOC L^{-1}, corresponding to 8.75 and 47.5 µmol L^{-1} PHA and PFA, respectively) and equilibrated by gentle mixing for 24 hours. The solution was adjusted to pH 7.0 with dilute NaOH. The concentration of uncomplexed Pb was measured on the filtrate passing a 1,000 molecular weight cut–off (MWCO) ultrafiltration membrane (Amicon YM–1000). Membranes were pretreated with several rinses of deionized water to remove residual UV–absorbing material and sodium azide (a filter preservative) and soaked in 5% sodium chloride (NaCl) to neutralize the charge on the membrane surface. Filters treated in this manner contributed negligible amounts of UV absorbance when soaked in deionized water overnight. Further, they absorbed < 5% of UV–absorbing material after being soaked in a solution of 5 mg DOC L^{-1} (1.75 and 9.5 µmol L^{-1} PHA and PFA, respectively) for 24 hours. Filter membranes (1,000 MWCO) retained approximately 95% and 70% of UV–absorbing material upon filtration of stock solutions of PHA and PFA, respectively. UV absorbance, pH, and Pb concentrations were determined on both filtered and unfiltered samples in the binding studies.

Batch Kinetics Studies. Kinetic sorption was studied in batch systems containing equal soil and solute concentrations. Each experiment consisted of several replicated batches, each analyzed for soluble (Pb or DOM) concentrations over a range of time intervals between 30 seconds and 204 hours. Phases were separated by filtration through a 0.45–mm glass fiber filter (DOM) or a 0.45–mm PTFE membrane (Pb) to minimize solute sorption to the filter. Filtration was selected over centrifugation (used in the equilibrium sorption studies), since the delay time between cessation of mixing and aqueous phase sampling after centrifugation (~25 minutes) would have introduced significant uncertainty in evaluating the solid–water contact time in the short–term samples. As such, the "lag" time for the filtration process was less than 30 seconds, and provides

significant interference only for samples evaluated at contact times of less than five minutes.

Pb sorption kinetic studies were performed in 125–mL LDPE bottles, while DOM studies were performed in 40–mL borosilicate glass vials to minimize unintentional sorption of the solute onto the bottle material. Rate of sorption was observed for Pb and PHA only. Fractional uptakes were measured over time to assess the rate of sorption.

Equilibrium Sorption Studies. Batch equilibrium sorption studies were performed to generate sorption isotherms for Pb and DOM onto Everett sand. In addition to Pb and DOM individually, isotherms of Pb in the presence of DOM were developed for varying concentrations of DOM. All isotherms were developed at a constant soil concentration and varying solute concentration in 125–mL LDPE bottles. Control experiments were performed to assess the degree of sorption of Pb and DOM onto the bottle material. Separate aqueous (no soil) 100 mL solutions (pH = 7.5) with original concentrations 0.24 mmol Pb L^{-1} and 5 mg DOC L^{-1} were brought to equilibrium on a wrist-action shaker for 48 hours. Solute concentrations in aqueous phase samples were > 95% of the original concentration, indicating that solute sorption onto the bottle walls was negligible. Table 2.3 outlines each of the sorption isotherm experiments. All bottle points were replicated at least twice.

Samples were preconditioned for 24 hours with 50 mL of water (as 0.01M KCl) to hydrate the soil prior to spiking with a stock solute solution. All samples were brought to equilibrium by gentle agitation on a wrist–action shaker for 48 h. Kinetics studies showed that this time was sufficient for sorption to reach 95% of equilibrium for both Pb and DOM. All added solutions were unbuffered and adjusted to pH 7.0 with dilute NaOH. The buffer capacity of the soil resulted in a final equilibrium pH of 6.8 ± 0.2 units. The ionic strength of the solute was maintained at a relatively constant value; all solutions were prepared in a matrix of 0.01M KCl.

After equilibration with the soil, aqueous phase concentrations were determined on the centrate of a sample that had been centrifuged at 3,000g for 20 min. In addition, the particle size distribution of sorbent in the shaken samples was determined (with a particle size distribution analyzer) to examine the effects of agitation and reaction upon the release of aggregated or agglomerated secondary particles. These results indicated that mixing in the batch studies resulted in the release of plate–shaped clays and layer silicates having a mean particle diameter of 1.5 mm. These were suspected to result from the release of attached particles from the larger grains as opposed to primary particle attrition, confirmed by SEM microscopy (Figure A.2). The mass of desorbed particles, about 3% of the total soil mass, suggested that the effects of desorbed particles could be neglected in the sorption experiments. Further, preliminary experiments suggested that mixing intensity and the degree of particle desorption did not affect the equilibrium uptake of solute.

Column Experiments. Transport experiments were performed in 2.5 cm (dia) x 5.7 cm (length) cylindrical soil–packed glass columns. The columns were equipped with fritted glass end plates (to uniformly distribute the solute as it entered the column) clamped with Viton o–ring seals in a glass end cap. Feed was delivered by a peristaltic pump at 1.0 mL min^{-1} ($\pm$0.1 mL min^{-1}) through a short section of nondegradable, nonreactive tubing (Viton). Remaining tubing in the apparatus was PTFE. All feed solutions were pre–purged with helium for 24 hours; during delivery of the feed, the feed reservoir was maintained under a slight helium atmosphere. This procedure prevented the entrainment of air into the column, maximizing water saturation of the total pore volume. DOM in the column effluent was monitored continuously for UV absorbance at 254 nm (UV$_{254}$) in a 1 mL quartz flow–through cell. Samples exiting the cell were collected by an automatic fraction collector in polycarbonate vials, acidified to pH < 2, and analyzed for Pb. Flow was monitored at predetermined intervals throughout the solute transport experiments.

Soil was packed dry in the column in 2 cm lifts, vibrating the column between lifts to ensure consolidation of the material. This packing technique produced reproducible soil

bulk densities of 1.68 ± 0.02 g/cm^3. Dry columns were conditioned for 48 hours by feeding 0.01M KCl (adjusted to pH 7.0 with dilute NaOH) to allow the column to saturate and the effluent to achieve a stable pH and UV absorbance. Upon conditioning, solute feed solutions were applied as a step input and allowed to continue until complete breakthrough was approached. Various combinations of DOM and Pb in the feed (adjusted to pH 7.0 with dilute NaOH and prepared in a 0.01M KCl matrix) were investigated in separate breakthrough experiments (Table A.4). Experiments involving Pb were ended prior to complete breakthrough because of the significant retardation of Pb in the column. In addition, after several days, fatigue of the tubing through the peristaltic pump made flow control very difficult, resulting in unsteady flow through the column or tubing rupture. Only data collected prior to tubing failure will be discussed. Effluent pH was monitored throughout each transport experiment.

Column homogeneity, dispersion, and channeling were evaluated simultaneously by analyzing the breakthrough curve (BTC) of a nonreactive tracer (^{3}H$_2$0). The breakthrough curve was fitted to the convection dispersion equation to determine the dispersion coefficient and pore water velocity. These parameters were fit using nonlinear regression analysis with the program CXTFIT (Parker and van Genuchten, 1984).

Analytical Methods. Pb samples were acidified to pH < 2 with concentrated HNO$_3$ prior to analysis by furnace atomic absorption spectroscopy. The influence of acidified DOM (especially slightly coagulated PHAs) upon analytical measurements of Pb was insignificant (determined by the use of standard additions) if appropriate care was taken to ensure sample homogeneity (by vigorous mixing, to disperse slightly flocculated DOM) prior to injection of the sample in the graphite tube atomizer.

DOM was analyzed by measuring ultraviolet (UV) absorbance at 254 nm. UV absorbance was selected over dissolved organic carbon (DOC) as an indicator of DOM because unpredictable concentrations of indigenous DOC readily desorbed from the soil upon contact with water. This precluded the use of a background correction factor. Initial

81

calibration showed that UV_{254} absorbance was a reliable indicator of DOC concentrations for aqueous solutions of humic material; furthermore, there was a linear relationship between DOC and UV absorbance for the concentrations of DOC used in this study. However, because of the probability of preferential sorption of DOM components upon contact with the soil and the desorption of indigenous DOC from the soil, the correlation cannot necessarily be extended to quantifying DOC in samples that have been in contact with the soil. Since the desorbed indigenous DOC from the Everett sand exhibited a very low UV_{254} absorbance, UV_{254} absorbance is reliable as an indicator of the DOM used in this study, albeit an operational definition.

In addition to UV_{254} absorbance, absorbance at 330 nm and 450 nm was monitored in the DOM isotherm experiments to examine the potential for preferential sorption of different DOM components that exhibit varying absorbance characteristics. Results showed that UV_{254} subcomponents tended to sorb more strongly than those at higher wavelengths. However, because of the much lower sensitivity of DOM quantification at these wavelengths for low concentrations, the relative strengths between sorption of preferential components could not be quantified. Consequently, their detailed results are not discussed in this paper. Since UV_{254} absorbance can be an indicator of aromatic carbon compounds, one would suspect that PHA, having a higher aromatic carbon content than PFA (Table 2.2) would have an absorptivity (absorbance per gram of carbon) higher than that for FAc. Furthermore, preferential sorption of UV_{254} relative to 330 nm and 450 nm may be stronger in PHA than in PFA. Both hypotheses were confirmed in the study of the sorption of preferential components, indicating that PHA is structurally, more "reactive" than PFA. This is consistent with the literature (cf. Chapter One).

Tritium (^{3}H) concentrations were quantified by liquid scintillation counting to a precision of $2s < 5\%$ (i.e., the magnitude of the confidence interval bracketed by 2 standard deviations was less than 5% of the mean measured value).

TABLE A.3   Summary of Batch Equilibrium Sorption Experiments.

sorbate	soil conc.	initial solute concentration
Pb	10 g L^{-1}	$4.8 - 57.9 \text{ } \mu\text{mol Pb L}^{-1}$
PHA	200 g L^{-1}	$0.35 - 8.75 \text{ } \mu\text{mol DOM L}^{-1}$
PFA	200 g L^{-1}	$1.9 - 47.5 \text{ } \mu\text{mol DOM L}^{-1}$
Pb + PHA	10 g L^{-1}	$19.2, 57.9 \text{ } \mu\text{mol Pb L}^{-1}$ x 1.75, 8.75 $\mu\text{mol DOM L}^{-1}$
Pb + PFA	10 g L^{-1}	$19.2, 57.9 \text{ } \mu\text{mol Pb L}^{-1}$ x 9.5, 57.9 $\mu\text{mol DOM L}^{-1}$

TABLE A.4   Summary of Column Breakthrough Experiments.

Experiment	Feed Characteristics	
	$\mu\text{mol Pb L}^{-1}$	$\mu\text{mol DOM L}^{-1}$
1H	0	1.76 (PHA)
1F	0	9.81 (PFA)
2	7.19	0
3H	6.13	1.79 (PHA)
3F	5.74	9.90 (PFA)
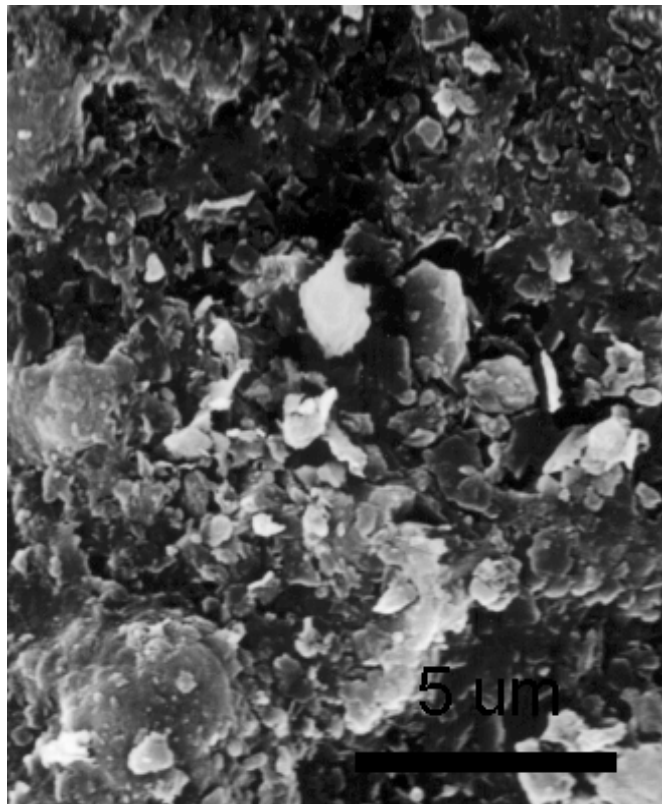
FIGURE A.2 SEM Micrograph of Everett Sand, 3 000 X. This photo of the sand surface shows evidence of plate-shaped particles attached to the surface of the larger sand grains. During batch sorption experiments, these particles appeared to be released, evidenced by a cloudy appearance in the liquid phase following agitation of the sample. A particle size distribution analysis of the particles showed that they had a mean diameter of about 1.5 mm, the approximate size of many of the attached particles shown in this photo. Although the release of the particles did not appear to introduce significant error during the batch sorption studies, their release in the subsurface may contribute to enhanced contaminant migration if they bind contaminants. It is unknown whether or not their release played a role in the column transport experiments performed in this study. However, no evidence of particle release from the column was observed by the naked eye.

MATERIALS AND METHODS FOR PHASE 2

An important aspect of this study was the use of field soils appropriate for infiltration. A matrix of soil types having cross-characteristics of high/low permeability and high/low organic content were sought. (Note, the use of the terms high or low refer to relative properties amongst those soils likely as candidates for infiltration basin siting. As such, these soils are generally the more permeable of those found within a given region.) In their actual selection, candidate soils were identified in areas supporting relatively large urban centers in the State (King and Spokane Counties). Moreover, soil survey maps were used to confirm their presence along extensive (regional) sections of State and Federal highways. Ultimately, it was the availability and ease of access to sites that dictated which soil candidates were actually sampled. Table A.5 lists the soils which were sampled and their matrix category.

Table A.5 Soils Utilized for the Study

Soil Name	Matrix Category	Sampling Location
Everett	high permeability/moderate organic content	Stillwater, WA
Garrison	low permeability/high organic content	Spokane, WA
Springdale	high permeability/low organic content	Spokane, WA

The final selection of the soils for study evolved from both preliminary in-house testing and outside laboratory analysis (Table A.6). The candidate for high permeability/low organic content was Springdale. Moreover, given its character,

85

Springdale became the "control" soil both in terms of pore size distribution (uniform) and organic content (very low). Everett, a loamy sand, became the high permeability, moderate organic content candidate. Everett was also amongst the easiest to work with, not only in terms of physical handling, but also in terms of hydraulic and transport control. Finally, in search of a low permeable/high organic content soil, Garrison was investigated.

Table A.6a. Soil Analysis Results

Soil	%Organic Content	CEC*	% Sand	% Silt	% Clay	% Inorganic carbon (CO_3)	Texture (USDA)
Springdale	0.13	3.2	93.8	4.0	2.2	0.7	Sand
Everett	0.35	17.4	83.2	12.0	4.8	0.01	Loamy Sand
Garrison	3.22	20.6	53.6	40.0	6.4	0.11	Sandy Loam

* CEC in units of cmol(+)/kg

Table A.6b. Soil Analysis - Alkalinity

Soil	SO_4^- (s) (ug/g) (ug/g)	CO_3^{2-} mmol(-)/L	HCO_3^- mmol(-)/L	Cl^- mmol(-)/L
Springdale	4	< 0.2	0.8	0.8
Everett	3	< 0.2	0.5	0.8
Garrison	24	< 0.2	1.7	1.1

Table A.6c. Soil Analysis - Soluble Cations

Soil	Ca (mmol(+)/L	Mg mmol(+)/L	Na mmol(+)/L	K mmol(+)/L
Springdale	1.46	0.14	0.26	0.09
Everett	0.32	0.10	1.35	0.05
Garrison	3.10	1.37	0.78	0.20

Table A.6c. Soil Analysis

Soil	Saturated Paste pH	$CaCO_3$ Equivalent (%)
Springdale	8.3	2.5
Everett	6.1	< 0.7
Garrison	7.0	< 0.7

Soil Column Design.   The soil column structures were designed and constructed with the intention of modeling one-dimensional infiltration of water through approximately 1 meter (3 feet) of soil, the minimum guideline established under the Manual.   Since metals were to be measured, the use of any metal material in the apparatus was avoided as much as possible. Stainless steel was used in cases when no other material was available, e.g. various fittings, needles.   All other materials were made of PVC, polypropylene, polyethylene, glass, or Teflon, which have a no tendency to leach metals and also have a relatively low affinity for the metals. The column was constructed of one foot diameter PVC pipe with two sampling ports placed at 30 cm intervals along the length of the column with an exit sampling port at the bottom of the column.

The columns consisted of two sections. The lower section allowed approximately 90 cm of soil to be packed. A pipe cap containing coarse gravel and sand was placed at the bottom to act as the base and screen to prevent washing out the soil. The upper section of the column stored the "storm runoff" equivalent to 90 cm (3 ft.) of water to be infiltrated. This depth was chosen as a typical design depth of infiltration basins.   It also gave a convenient piezometric head gradient of two during constant head infiltration. A 55 gallon HDPE mixing tank mixed the synthetic stormwater and a pump delivered the water to the top of the soil column. Circulation lines were provided from the top of the column to the mixing tank when tracer tests were performed.

Water Quality And Soil Parameters Tested. Piezometer taps were placed at one-third depth intervals to allow reading heads (pressure) during near-saturated conditions. It also provided an indication of whether soil packing was uniform throughout the depth by showing headlosses along the soil profile. Soil-water quality data consisted of

87

the aqueous concentrations of the four metals (Cd, Cu, Pb, Zn), solution total organic carbon (TOC) concentrations, and solution pH of samples extracted from the two intermediate sampling ports and the bottom exit port. As mentioned earlier, soil extractable metals were analyzed before and after metals were applied for each soil tested. Finally, an analysis of soil cation exchange capacity, organic matter and organic content, and particle size distribution was performed by an outside laboratory on grab samples of the six soils sampled (University of Idaho Analytical Laboratory, Holm Center, University of Idaho, Moscow, ID 83843).

Column Packing And Tracer Test. The columns were packed in separate (5-7 cm) lifts and tamped with a 7 kg rod (7 cm dia.) dropped approximately 10 cm using a technique similar to that described under ASTM D-1557. This tamping pattern was repeated three times for each lift placed.

The packed columns were then checked for hydraulic integrity by performing a bromide (breakthrough) tracer test to establish the presence (or absence) of short-circuiting due to faulty packing of soil along the column walls. The bromide breakthrough curve also provided an estimate of the porosity of the soil columns since standard weighing techniques were difficult with these large columns. To minimize entrapped air, the columns were initially back-filled with water under low pressures via the effluent port with feed from a raised carboy. A solution of 20 mg/l bromide (Br^-) was then applied (to the top of the column) under constant head conditions with breakthrough effluent samples taken at regular volumetric intervals (2500 ml) while the time elapsed was recorded. Approximately three pore volumes were applied for each tracer test, producing 30 samples. These samples were then analyzed with an Orion bromide ion selective electrode to determine the bromide concentration. The results were used to generate breakthrough curves (BTC) from which evidence was sought for the presence (or absence) of side-wall flow (early peaks), preferential flow (breaks in the BTC) , or uneven packing.

Stormwater Applications To Soil Columns.   After determining the soil column to be performing properly, the metals-only synthetic stormwater was applied. The soil was allowed to drain before applying the stormwater, and so was run initially unsaturated before each application. A metals stock solution was prepared by dissolving metal salts ($CdCl_2$, $CuCl_2$, $PbNO_3$, $ZnCl_2$) in a 1 N HNO_3 solution. A measured volume of the stock was mixed with deionized water in the mixing tank to obtain a feed concentration of metals (Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}) approximating the average stormwater concentrations. The initial pH of the feed was measured, and then the solution was applied to the soil column to a depth of 90 cm or a volume of approximately 67 liters and allowed to infiltrate as a slug. Table A.7 shows the stock solution proportions used. Samples were taken at designated intervals of infiltration at the three sampling ports. A minimum of two days and a maximum of one week was allowed between subsequent tests for a total of five applications of metals-only stormwater.

After running the set of metals-only solution trials and repacking the columns with "fresh" soil, the series of five metals-NOM applications were run. The tests were executed in the same manner except a measured volume of NOM stock was added to the mixing tank to produce about 50 mg/l TOC in the applied stormwater. This concentration of TOC was chosen because background TOC concentrations in some of the samples taken from the metals-only trials exceeded 15 mg/l TOC. Enough differentiation in TOC concentrations was desired between the two sets of runs in order to distinguish the effects of high TOC on the metals removal performance and overcome any background fluctuations, while remaining within the same order-of-magnitude as typical highway stormwater TOC concentrations.

The NOM solution was derived by an extraction procedure using standard garden peat. Two liters of peat moss was added to a 0.5 N NaOH solution and mixed for at least six hours. The mixture was centrifuged for one hour and the supernatant was poured off. This supernatant contains a mixture of humic acids, fulvic acids, and humin. No further

characterization of the natural organic matter was made due to time constraints. The total organic carbon concentration was measured and used as a relative measure of the organic matter in the stock.

Soil Water Sampling And Preservation. Soil-water samples were extracted from the two intermediate sampling ports (ISP) and the exit sampling port (ESP). The ISPs consisted of syringes connected to stainless steel needles placed inside kynar tubing. The ESP was also the drainage port and was open to atmosphere. Samples were taken from the bottom exit port every three inches of infiltration, and samples were taken every six inches through the intermediate sampling ports. Thus, a maximum of twelve ESP samples and six samples from each ISP was possible. When sampling through the syringes an attempt was made to apply just enough suction to extract flow equal to the flow entering the sampling tube. This was not always successful as air from the column and any captured from port leaks was at times extracted. Problems also occurred, most often with the center intermediate port, when a vacuum developed preventing any samples from being extracted. The sampling port designs are shown below in Figure A.3.

Standard Methods (Greenberg, et.al., 1992) was referenced for sample preservation methods. Metals samples were stored in polyethylene or polypropylene bottles, and TOC samples were stored in glass scintillation vials. The TOC samples were also used for pH measurements. Metal samples were acidified to 1 N HNO_3 to keep the metals in aqueous form, then filtered through Whatman GF/C filters and refrigerated at 4° C. By acidifying the samples to pH < 2 , any metals attached to any colloids would probably be detached (*Standard Methods* 3010-B and 3030-A). Therefore, the aqueous phase concentrations measured would be higher than what would normally occur. This is acceptable with respect to being conservative in the evaluations. What is sought, afterall, is the total concentration of metal (aquated, free, organic complexes). This method measures total metals, therefore, no speciation determinations could be made. pH measurements were made on the TOC samples and then refrigerated at 4° C until analysis.

Soil Metal Extraction.   An initial and final extractable metals profile was determined for Everett and Garrison soils.   Grab samples of soils were collected at specified intervals as the soil was being packed (depths of 1-2", 3-4", 5-6", 7-8", 9-10", 11-12", 14-16", 20-22", 26-28", and 32-34" from the soil surface).   The extraction procedure was performed on the soils passing the U.S. standard #40 sieve.   Triplicates were measured for each depth sampled. A 1 ml solution of 1 N HNO_3 was added per gram of soil and shaken for 30-40 minutes. The sample was then filtered with a Whatman GF/C filter and analyzed for aqueous concentration of metals.   The same basic procedure was performed after running the series of storm events to produce a final extractable metals profile.

Analytical Methods. The analytical equipment used includes the Varian Atomic Absorption Spectrometer, Shimadzu Total Organic Carbon Analyzer, and Orion Ionalyzer with a Bromide Ion Selective Electrode.

ASTM standards were referenced for each sample type taken (Cu, Pb, Cd, Zn in water, TOC, and pH). These references included : ASTM D1688-90, D3559-90, D3557-90, D1691-90, D3919-85, D1293-84, D2579-85, respectively.

Table A.7 Feed Solution Concentrations of Metals

Metal - Metal Salt	Mass per liter (g)	Volume of Stock per 100 L Feed (ml)	Final Feed Concentration (mg/l)
Cd - $CdCl_2$	0.489	10	0.030
Cu - $CuCl_2$	0.741	10	0.035
Pb - $PbNO_3$	0.441	100	0.276
Zn - $ZnCl_2$	1.092	100	0.524

(Not to Scale)

PVC Column Wall

1/4" NPT Nipple

Pipe Tubing

Drilled holes

1/4" NPT(M) on pipe tube

Pipe Cap
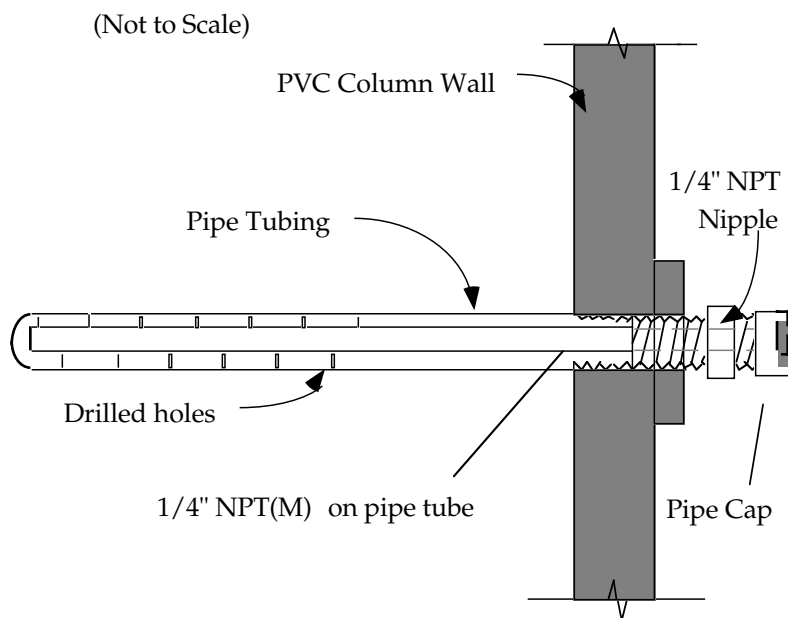
Figure A.3 Illustration of Intermediate Sampling Ports

Atomic Absorption Spectrometer. Atomic absorption is often used for monitoring trace metals in water. The two methods used in this study were: i) direct air-acetylene flame method for the Zn samples, and ii) graphite furnace atomization method for Cd, Cu, and Pb samples. The furnace method was used when greater sensitivity was needed, i.e. lower concentrations to be detected. *Standard Methods* 3111-B was used for flame analysis and *Analytical Methods for Graphite Tube Atomizers* published by Varian was used for furnace analysis.

The following includes some specific details in the AAS procedure used:

- All samples and standards were preserved with 1 N nitric acid;
- Standards were prepared and stored for not more than two weeks when a series of analyses were to be run;
- A check on a new set of standards was run to compare the readings with the old standards;
- Blanks were run to check for contamination from sample bottles, stock solutions, and glassware. Reagents were also checked for levels of metals;
- Blanks and standards were intermittently run among the samples to confirm the consistency in readings;
- All glassware was acid washed in 1:6 to 1:3 nitric bath.

Total Organic Carbon Analyzer. Measuring total organic carbon (TOC) was chosen as the means for quantifying the relative amount of organic matter in solution because it is a convenient and direct expression of total organic content. *Standard Methods* 5310-B (Greenberg, et.al., 1992) was used as a reference. The method used by the Shimadzu analyzes fractions of total carbon (TC) and the inorganic carbon (IC) fraction, i.e. carbonates, bicarbonates, and dissolved carbon dioxide. TOC is defined as all the carbon atoms covalently bonded in organic molecules and is the difference between the two. The TOC was not fractionated into dissolved (DOC), volatile (VOC) and

nonpurgeable (NPOC). Standards were prepared by using potassium bipthylate (KHP-organic carbon) and sodium carbonate (Na_2CO_3-inorganic carbon) dissolved in deionized water. As with the AAS analysis standards were run intermittently between samples to check for consistency.

Bromide Ion Selective Electrode. An Orion Ionalyzer model 801 with a bromide ion selective electrode was used to analyze the bromide samples from the tracer test. Samples of 50 ml volume were collected and 1 ml of standard sodium nitrate ionic strength adjuster was added. The sample was placed on a stirring plate with the bromide and reference electrodes submersed in the solution. A reading which held steady for more than 45 seconds for higher concentration samples and 2 minutes for lower concentration samples was recorded. A calibration curve was prepared and checked intermittently with the samples.

Appendix B

ANALYTICAL METHODOLOGY FOR PHASE 1 EXPERIMENTS

Evaluation of Dissolved Organic Matter Concentrations. Dissolved organic matter (DOM) concentrations were indirectly quantified by UV_{254} absorbance. It was also mentioned that a linear relationship between UV_{254} absorbance and dissolved organic carbon (DOC) concentration was found in solutions prior to contact with soil. Further, preservation of this relationship after the solution had come into contact with the soil was not probable due to preferential sorption of DOM subcomponents having different UV_{254} absorbance characteristics.

Consequently, many studies quantify DOM by a direct measurement of DOC. However, one objective of this study was to compare the behavior of PHA and PFA. Common in much literature evaluating sorption of hydrophobic organic compounds onto soils is comparison of the compounds' behavior using molar concentrations. Thus, all measurements of UV absorbance have been transformed into approximate molar DOM concentrations. Estimated molecular weights for PHA and PFA were 5,000 and 1,000, respectively. These values were arbitrarily selected to emphasize the differences in reactivity of the materials when quantified in terms of molar concentrations, and do not necessarily represent the true molecular weights of the compounds used in this study. However, they are not unreasonable estimates and fall within the published ranges of humic and fulvic acids (cf. reviews: Thurman and Malcom, 1983; MacCarthy and Suffet, 1989). The organic carbon contents of the DOM are well known (Murphy *et al.,* 1990). Thus, since the relationship between UV_{254} absorbance and DOC was quantified in this study, the approximate molar concentrations can be determined. One mg DOC corresponded to 0.35 µmol DOM and 1.9 µmol DOM for solutions containing PHA and PFA, respectively.

It should be noted that most of the experiments where PHA and PFA were compared had approximately equal concentration ranges of DOC. However, because of the different molecular weights of humic and fulvic acids, differences in molar concentrations are quite significant. Like UV_{254} absorbance, this transformation yields only an

operational definition of DOM concentration. Furthermore, since the molecular weights of PHA and PFA are estimated, there is some degree of uncertainty in the absolute values of the molar concentrations. However, the estimates are believed to be conservative and thus accurately represent the data for qualitative comparison of the behavior between humic and fulvic acids. In addition, transformation of the concentrations from UV_{254} absorbance to molar concentrations of DOM did not impact the *qualitative* description of the results in terms of the relative behaviors between the two DOM fractions. Comparisons based upon the transformation of absorbance to DOC concentrations yielded qualitatively similar descriptions.

Sorption Kinetics.

It was assumed that the sorption process proceeded as follows:

1. Transport from the bulk solution to the water boundary layer surrounding the particles;

2. Diffusion through the boundary layer (film diffusion);

3. Sorption to readily available external surface sites;

4. Intraparticle diffusion;

5. Sorption to surface sites within the intraparticle porosity.

It was further assumed that appropriate mixing conditions (Ball and Roberts, 1991) eliminated external mass transfer limitations (steps 1–2). Thus, a dual process approach was used to quantify uptake rates for lead. It was assumed that sorptive uptake could be classified into two types: an instantaneous sorption to readily accessible external sites (step 3, instantaneous), and a rate–limited uptake as a result of chemical reaction kinetics (step 3, rate–limited) and/or intraparticle diffusion (steps 4–5). Thus, only chemical sorption kinetics and intraparticle diffusion were assumed to control sorption in this investigation. It should be noted that the rate–limited portion of the model incorporates diffusion into the particle as well as rate–limited chemical sorption onto internal sites. The dual process kinetic model can take on the general form:

97

$$F_t = F_i + (1-F_i)f(t) \qquad\qquad (B.1)$$

where

F_t t=   fractional uptake of the sorbent over time, defined by

$$F_t = \frac{C_{et} - C_e}{C_e}$$

where

C_{et} =   solute concentration at time t and C_e is the solute concentration at equilibrium;

F_i =   instantaneous fractional uptake of the solute by the sorbent;

$f(t)$ =   a function which depends upon the rate of solute uptake for the remaining

fraction left in solution.

Two approaches were utilized in modeling f(t). The first, a commonly used method for describing sorption rates in transport experiments, is simply a first–order kinetic model, where

$$f(t) = 1-e^{-Kt} \qquad\qquad (B.2)$$

where K is the first–order sorption rate constant having units of $[T^{-1}]$.

The use of this model has seen widespread attention. However, if diffusion is the rate–controlling mechanism, the model is limited in that it does not consider an appropriate length scale for diffusion. Thus, a diffusion model, based upon classical theory of solute diffusion into a sphere from a fixed volume liquid (Crank, 1956), was also employed:

$$\frac{\partial C}{\partial t} = \left(\frac{D_a}{r^2}\right)\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) \qquad\qquad (B.3)$$

where r is the location within the sphere, C is the solute concentration, and D_a is the apparent diffusion coefficient which accounts for tortuosity resulting from the pore

structure and retardation due to internal sorption.

The solution to the diffusion coefficient in radial coordinates (B.3) assumes the following:

1. The concentration of the solute in solution is always uniform, and initially equal to C_0;

2. The solution concentration at the finite outer boundary of the sphere is equal to the concentration in the bulk solution (i.e., the sphere has finite dimensions);

3. The sphere is initially free from solute;

4. The rate of diffusion into the sphere is constant;

5. Chemical sorption within the pores is linear, reversible, and at equilibrium.

An analytical solution can be substituted for f(t) in (B.1) and solved for a single parameter, an apparent diffusion coefficient, D_a $[L^2\ T^{-1}]$. Analytical solutions for this scenario exist where the total solute mass in the sphere after time t is expressed as a fraction of the total mass uptake by the sphere at time $t = \infty$. The solution used in this study was that of Carman and Haul as presented in Crank (1956):

$$f_t = (1+\alpha)\left[\quad 1 - \frac{\gamma_1}{\gamma_1+\gamma_2}eerfc\left\{\frac{3\gamma_1}{\alpha}\left(\frac{D_at}{a^2}\right)^{1/2}\right\} - \frac{\gamma_1}{\gamma_1+\gamma_2}eerfc\left\{\frac{3\gamma_2}{\alpha}\left(\frac{D_at}{a^2}\right)^{1/2}\right\}\right] \qquad (B.4)$$

α is a parameter which accounts for the final fractional uptake of solute by the sphere at equilibrium, γ_1 and γ_2 are functions of α, a is the particle diameter, and $eerfc(z)$ $= \exp(z^2)erfc(z)$, where z is an arbitrary function argument.

The major advantage of the diffusion model is that it considers a length scale for the diffusion process as the diameter, a, of the particle into which the solute is diffusing. Both models were parameterized by nonlinear least squares regression of the observed uptake rate data using two parameters, D_a, the apparent diffusion coefficient, and F_i, the

99

instantaneous fractional uptake. Parameterization involved minimization of the mean weighted squared error (MWSE):

$$MWSE = \frac{1}{v}\sum_{i=1}^{n} w_i(C_{si} - \overline{C}_{si})^2 \qquad (B.5)$$

where C_{si} is the observed solid phase concentration of the solute for sample i, n is the number of sample points, and v is the number of degrees of freedom (defined as n – the number of fitted parameters (2: F_i and either K or D_a) in the experiment). W_i is a weighting factor, an estimator of the square of the inverse variance in C_{si}.

The weighting factor is designed to lend more importance to those values for which variance is small. Ball and Roberts (1991) suggest that if variance in C_s arises only from random fluctuations in C_s resulting from sample heterogeneity, then the variance should be proportional to the magnitude of C_s. Consequently, weighting factors for this nonlinear regression were assigned as $1/C_{si}^2$.

Sorption Isotherms. Equilibrium data was analyzed by fitting Langmuir, Freundlich, and linear isotherm models using linear or nonlinear least squares regression. In addition, a two site Langmuir model was used to describe the Pb isotherm data. Table B.1 highlights the equations and parameters used in each of the models. C_s and C_e in each of the models designate solute concentrations in the solid and solution phases, respectively. Isotherm parameters were selected to minimize the mean weighted square error (MWSE) between observed and predicted values, with a weighting factor of $1/C_{si}^2$ as described above. Comparisons of model fits were made based upon their relative MWSE's.

Failure to include a rational approach for assigning weighting factors in isotherm parameterization reduces the nonlinear regression to a fitting exercise. Preservation of model validity will be enhanced with the use of weighting factors as described above, and

will better highlight model failure. This is illustrated in the results by comparing the fit of one– and two–site Langmuir models to the Pb isotherm data.

Assignment of different weighting factors in nonlinear regression parameterization techniques is appropriate for developing isotherm relationships for which the variance of C_S is nonuniform. It must be noted here that isotherm linearization and linear regression of the transformed data, a common technique for determining isotherm parameters, is valid only when the linearization of the isotherm does not transform the relationship between C_S and its variance (Berthouex and Brown, 1994). In particular, Freundlich isotherms are often plotted on log–log scales to linearize the data, where the corresponding best fit line slope is 1/n. However, this approach is not valid if the variance in C_S over the plotted range is uniform, since the transformed variances plotted on a log–log scale will result in overweighting the isotherm toward higher values of C_S. Linearization of Freundlich isotherm data is valid only when the variance is proportional to the magnitude of C_S. Ideally, nonlinear regression using weighting factors calculated from known variances or a verified relationship between variance and C_S to determine isotherm parameters, is a preferred approach. Thus, caution should be used when using transformations to linearize isotherm data or in applying weighting factors using an unknown relationship, since transformation can change the magnitude of the distribution of the residuals about the mean.

Consequently, all nonlinear regression techniques used in isotherm model parameterization in this study were performed upon original C_e vs. C_S data without the use of linearization techniques or other data transformations.

TABLE B.1   Sorption Isotherm Models and Parameters.

	Model	Parameters
Langmuir	$C_s = \dfrac{QbC_e}{1+bC_e}$	Q, b
2-site Langmuir	$C_s = C_e\left(\dfrac{Q_1b_1}{1+b_1C_e} + \dfrac{Q_2b_2}{1+b_2C_e}\right)$	Q_1, b_1, Q_2, b_2
Freundlich	$C_s = K_fC_e^{1/n}$	K_f, 1/n
Linear	$C_s = K_dC_e$	K_d

Column Experiments. Column dispersion was determined by analyzing the breakthrough curve (BTC) of a nonreactive tracer (^3H_2O). Hydrodynamic dispersion and pore water velocity were calculated by fitting the classic convection dispersion equation (CDE) to the data using nonlinear least squares regression with the program CXTFIT (Parker and van Genuchten, 1984).

The soil occupied a bulk volume in the column apparatus of 28 cm^3. However, the entire column apparatus, including end caps, tubing, and fittings, had a volume of 36 cm^3. The observed breakthrough data used in the nonlinear regression was based upon the residence time of the entire apparatus volume, and not just the soil bulk volume. Thus, the hydrodynamic dispersion number presented in the results is an uncorrected number. This should not significantly impact the interpretation of this study, and would only introduce error if a modeling effort was applied to this data.

Since approximately 20% of the total system volume did not contain soil, the originally fitted velocity represented that of the entire system pore volume. However, this was not the actual pore water velocity. Consequently, a correction technique, described in the results, was applied to the original velocity to account for a decrease in apparent soil bulk volume (resulting from subtraction of the end caps, fittings, and tubing). This corrected velocity is presented in the results and more accurately represents the actual pore water velocity traveling through the column. The porosity and pore volume of the bulk soil volume were calculated using the corrected velocity. It should be noted, however, that BTC's presented in the results section are normalized with respect to time based upon the pore volume of the entire apparatus. Normalization of the BTC's based upon the pore volume of the soil bulk volume only would tend to overestimate breakthrough times.

The form of the CDE and its corresponding solution can be found elsewhere (Freeze and Cherry, 1979). ^3H_2O and PHA BTC's were triplicated. No significant differences in breakthrough behavior among replicates were observed.

In addition, Peclet numbers were calculated to determine the relative strength of advection and dispersion as follows:

$$P_e = \frac{vL}{D} \qquad (B.6)$$

where v = pore water velocity (Q/nA), L = column length, and D = hydrodynamic dispersion coefficient.

All breakthrough curves are presented in terms of normalized time (# of pore volumes) and normalized concentrations (concentration of effluent ÷ concentration of feed). Time–based corrections were made in each breakthrough experiment for variable average flow rates between experiments. Concentration–based corrections were also made in each experiment to account for the variability in preparation of feed solutions. Thus, the average flow velocity and feed concentrations were determined independently in each experiment.

Appendix C

PHASE 1 DETAILED DISCUSSION OF RESULTS

Sorption Kinetics. The data in Figure C.1 show the sorptive uptake of lead over time by the soil in batch sorption kinetics experiments. Table C.1 summarizes the results of the nonlinear regression used to parameterize the kinetic models fitted to observed data. Both models were fitted with a two-parameter (instantaneous uptake fraction and either diffusion coefficient or first-order rate constant) nonlinear regression analysis to minimize the weighted sum of squares.

For the first-order model (Equation B.2) with instantaneous uptake, predicted fractional uptakes are lower than observed values for short times (0.1 hr > t > 1 hr) and higher than observed values for longer times (i.e., the predicted approach to equilibrium faster than that observed). Thus, the first-order model inadequately describes the rate of sorptive uptake. The instantaneous uptake fraction is also overpredicted with respect to the data collected within the first minute of reaction.

The soil used in this study was found to have a BET surface area nearly three orders of magnitude greater than the theoretical surface area calculated by assuming spherical *nonporous* particles having a diameter of 0.63 mm and specific mass weight of 2.48 g/cm^3 . Thus, the existence of *intraparticle* porosity, evidenced by the high specific surface of the soil, is likely affecting the sorptive uptake rate of solute from the solution (since the rate limiting mechanism may be predominantly diffusion, rather than a first-order chemical reaction), resulting in the lack of fit of the first order model. The first-order model underpredicted the value for t_{95} (time required to reach 95% of the equilibrium fractional uptake) as 9 hours. Thus, a model that accounts for solute diffusion into a porous sphere (again, coupled with the instantaneous uptake fraction) was employed (Equation B.4) to quantify the diffusion coefficient of lead into the soil grains. The scale of diffusion is accounted for in the model simply as the diameter of the particle. The results show a much better fit (Figure C.1) than that for the first-order model, with a fitted diffusion coefficient of 0.0014 mm^2 hr^{-1}. In addition, the MWSE for the diffusion model fit was less than half of the MWSE for the kinetic model fit. The diffusion model predicted a more realistic t_{95} of

106

about 30 hours. It should be noted that the diffusion coefficient is not the true diffusion coefficient for lead through the intraparticle porosity, but an apparent coefficient that also accounts for retardation of lead inside the particle as well as tortuosity resulting from the particle's pore structure.

The results indicate that solute uptake kinetics can be modeled adequately using a classic diffusion model. This model has also been successfully applied to describe observed uptake of organic contaminants into aquifer material having a significant intraparticle porosity (Ball and Roberts, 1991). Existing models based upon first-order sorption kinetics may fail to predict transport of contaminants that are significantly affected by intraparticle diffusion. As an illustration, a transport model, coupled with the first-order model used here, would tend to underestimate the evolution of a solute plume (by predicting shorter migration and a lower concentration at a given time), since the t_{95} for the model is nearly half an order of magnitude smaller than the probable "true" t_{95}. This could have significant implications upon the application of generally accepted transport codes to some aquifers. Modeling would thus require replacement of the first order kinetic model with a diffusion-based model that would account for the scale of diffusion in the particle size distribution. A discussion outlining incorporation of a diffusion-controlled rate law into a transport model can be found in Fetter (1993).

Sorption of PHA was governed by electrostatic dynamics at early times. Thus, the data was not amenable to the conventional models described above, which do not account for the electrostatic influences upon sorption resulting from time-dependent solution chemistry. It is unknown how the sorption kinetics of PHA is affected by intraparticle diffusion or size exclusion from intraparticle pores. The results are shown in Figure C.2.
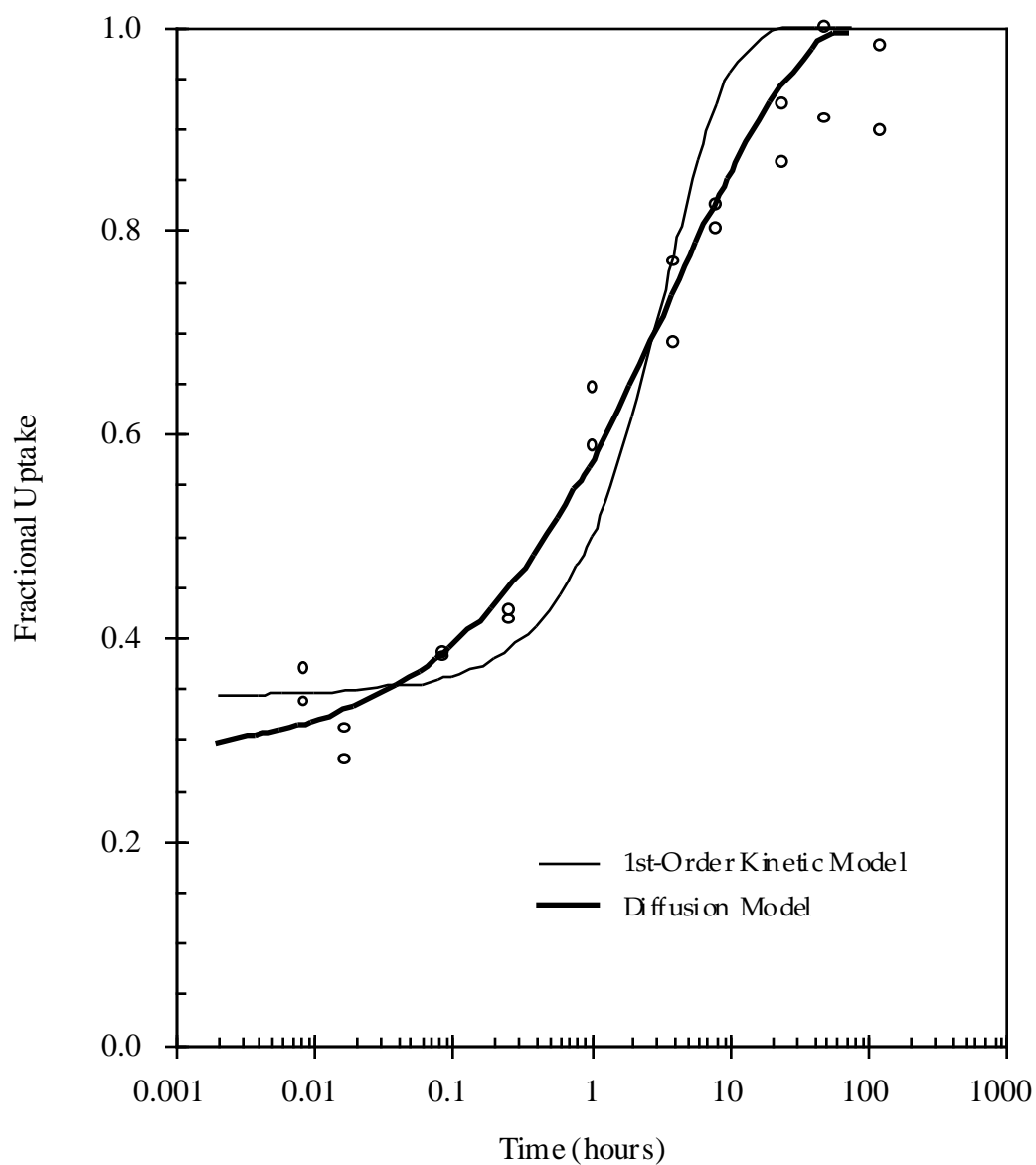
FIGURE C.1   Pb Sorption Kinetics. Fraction uptake represents the normalized fraction of solute sorbed, where a value of 1.0 indicates the amount sorbed at an infinite time (true equilibrium).

TABLE C.1 Pb Sorption Kinetic Model Results. The diffusion coefficient is an "apparent" diffusion coefficient which accounts for tortuosity in the diffusion path, internal solute retardation, etc. Instantaneous uptake fraction represents the fraction sorbed (assumed in the model as an instantaneous reaction) within the time of analysis of the earliest sample (~ 30 seconds). MWSE = mean weighted square error. t_{95} is the time to reach 95% of the total equilibrium uptake.

	diffusion model	first-order model
diffusion coefficient, $mm^2\ hr^{-1}$	0.0014	—
rate constant, hr^{-1}	—	0.27
instantaneous uptake fraction, F_i	0.278	0.344
MWSE	0.00601	0.0154
t_{95}, hr	30	9
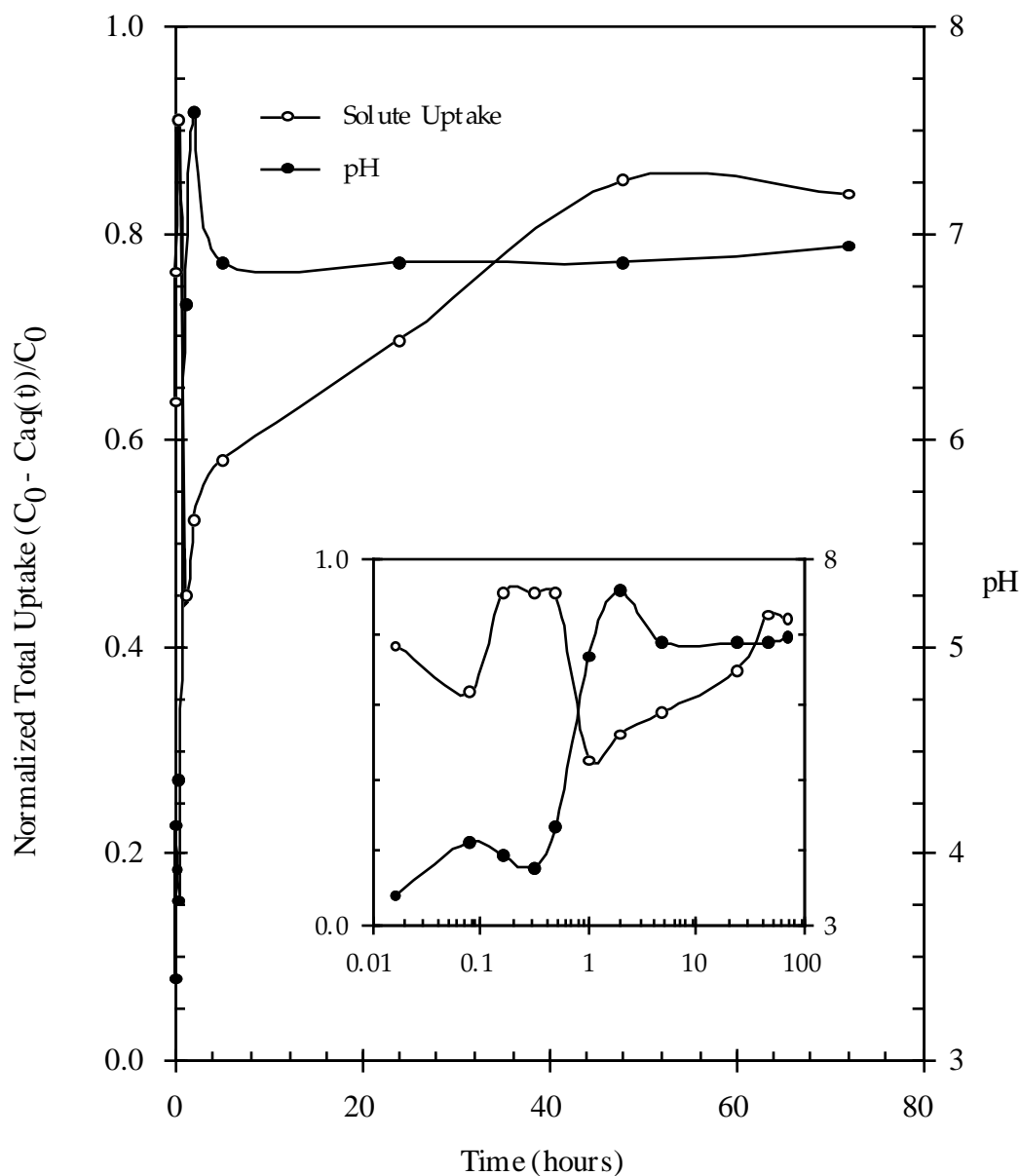
FIGURE 4.2   PHA Sorption Kinetics.   Initial PHA: Soil concentration (C0:S) = 0.029 μmol/g. Normalized total uptake represents the *fraction of total initial* solute sorbed to the soil. $C_{aq(t)}$ represents the aqueous concentration of PHA at time t.   Each point is the average of two or more replicates. The average coefficient of variation (standard deviation mean) in normalized total uptake was 3.6%. Inset shows the same data plotted on a logarithmic scale to emphasize the dynamics occurring during the early times.

Equilibrium Sorption. Linear, Langmuir, and Freundlich isotherm models were fit to each of lead (Pb), humic acid (PHA), and fulvic acid (PFA) isotherms onto Everett sand using linear or nonlinear weighted regression as described in the analytical methodology (Chapter Three). Figures C.3 - C.4 show the isotherm data and best fit model predictions for Pb and PHA/PFA, respectively. Table C.2 compares the results of the regression analyses. The MWSE is presented for each regression as a measure of model fit.

The data in Figures C.3 - C.4 show that isotherms for Pb and PFA are highly nonlinear. The use of a theoretically sound methodology (i.e., assuming that the variance of the measurement is directly proportional to the solid phase concentration and assigning the weighting factors for the residuals accordingly) for nonlinear weighted regression suggests that the single site Langmuir model does not adequately describe the higher liquid phase equilibrium concentrations. Consequently, Pb isotherm data are best described by a two-site Langmuir model. Table C.2 shows that a high energy site (defined by Q_1 and b_1) constitutes about 15% of the total exchange capacity of the soil for Pb, while a lower energy site (defined by Q_2 and b_2) accommodates the remainder of the total capacity. However, the reader should keep in mind that model fitness does not exclusively justify the existence of a two-site mechanism or the behavior of the two sites as described above, since the parameters may not provide a unique solution.

Isotherm nonlinearity is less apparent in Figure C.4 for the PHA isotherm, but examination of the fit of the model parameters in Table C.2 show that a nonlinear Freundlich model fits the data better than a linear model. The equilibrium concentrations in these isotherms were intended to bracket upper and lower values that would be eluting from the column in the transport experiments (i.e., the range of pore water concentrations). Isotherm nonlinearity in the concentration ranges studied precludes the use of most existing cotransport models that account only for linear partitioning. Further, it emphasizes the need to couple nonlinear partitioning with transport models, since the concentrations observed

here are representative of typical levels found in a subsurface environment exposed to lead and/or DOM contamination.

Isotherm nonlinearity introduces a retardation factor (R) dependent upon soluble equilibrium concentration into a transport model. For single-site Langmuir and Freundlich isotherms, respectively, R can be defined as (Fetter, 1993)

$$R_L = 1 + \frac{\rho_b}{\eta}\left(\frac{Qb}{(1+bC_e)^2}\right) \qquad (C.1a)$$

$$R_F = 1 + \frac{\rho_b K_f^{\frac{1}{n}} C_e^{\frac{1}{n}-1}}{\eta} \qquad (C.1b)$$

where the parameters and variables are as defined in Chapter One and Table 3.1

Figure C.5 illustrates the effect of isotherm nonlinearity upon the retardation factor for DOM. The best fit isotherm models were used to predict R using the parameters in Table C.2. It is shown that in the concentration ranges examined, PFA appears to have a stronger affinity for the soil than PHA.
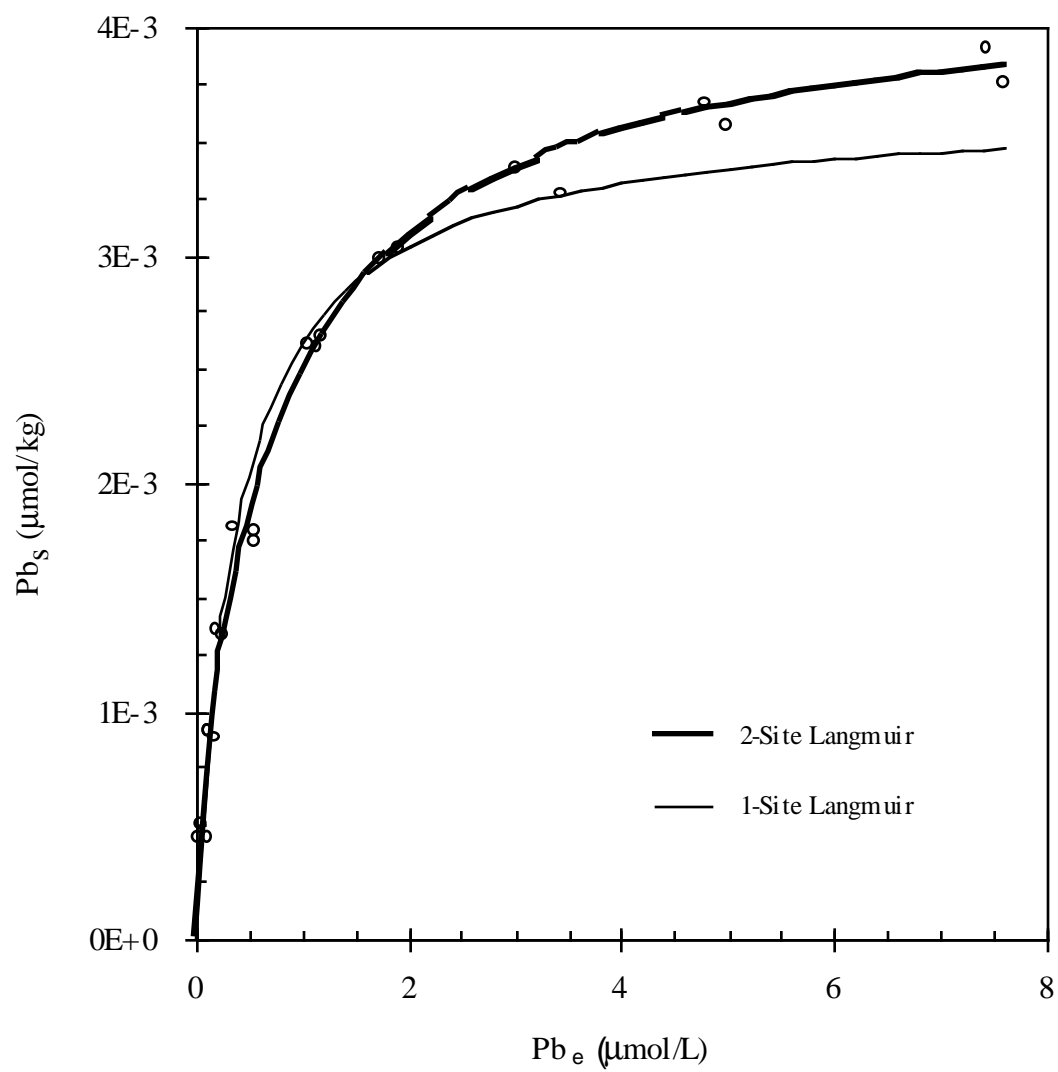
FIGURE C.3 **Pb Sorption Isotherm**. Sorption of Pb onto Everett sand. Pb_e represents soluble Pb concentration. Pb_s represents sorbed Pb concentration per kg of soil.

113
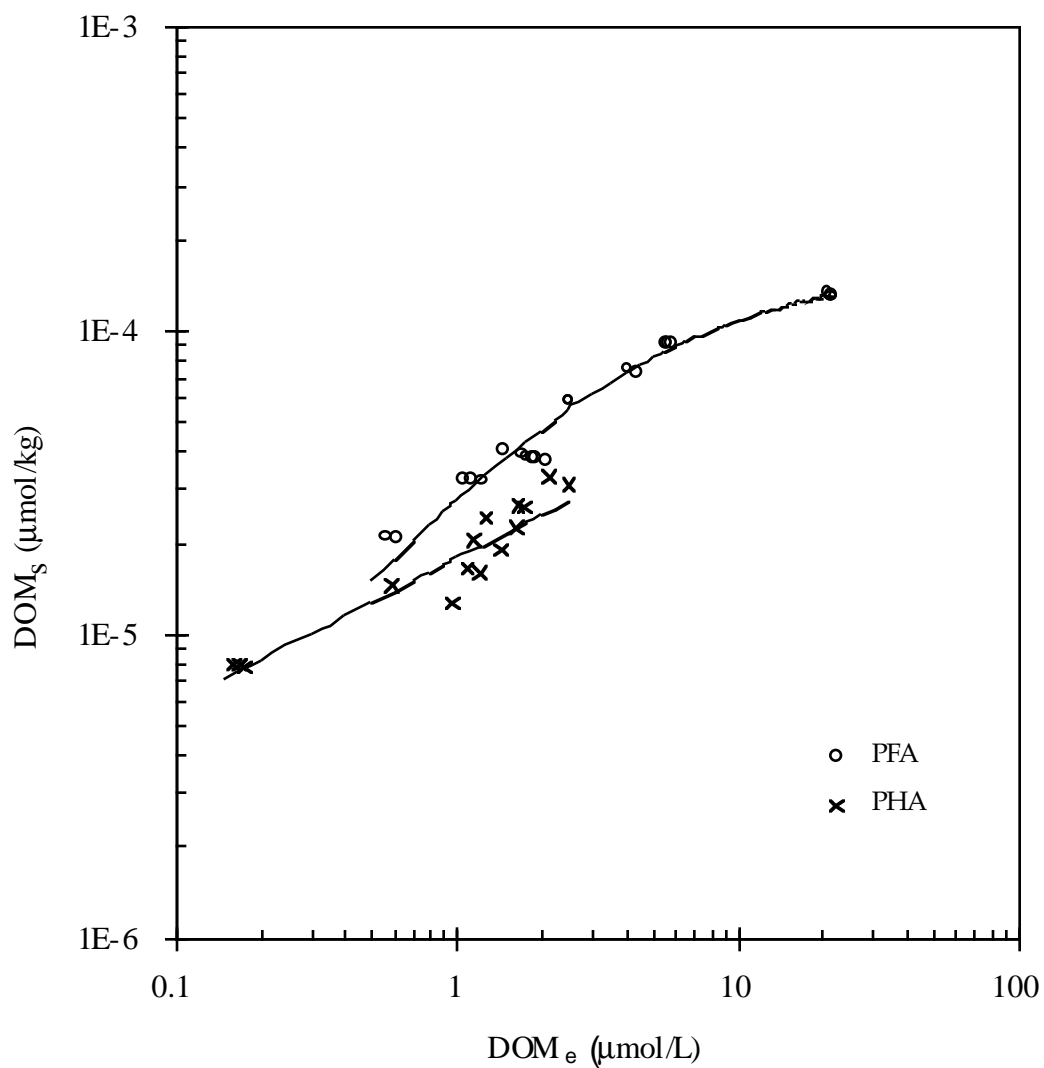
FIGURE C.4 DOM Sorption Isotherms. Sorption Isotherms of DOM fractions onto Everett sand. DOMe represents soluble equilibrium concentration, while DOMs represents sorbed DOM mass per kg of soil.

TABLE C.2 Sorption Isotherm Parameters. Values in boldface indicate the best fit model for each solute based upon the lowest mean weighted square error (MWSE).

	Pb	PHA	PFA
Langmuir			
Q, μmol kg^{-1}	3.65E-03	2.66E-05	**1.59E-04**
b, L μmol^{-1}	2.5	2.33	**0.208**
MWSE	0.0474	0.0440	**0.0145**
2-Site Langmuir			
Q_1, μmol kg^{-1}	**2.88E-04**	—	—
b_1, L μmol^{-1}	**2.97E+07**	—	—
Q_2, μmol kg^{-1}	**3.91E-03**	—	—
b_2, L μmol^{-1}	**1.26**	—	—
MWSE	**0.0267**	—	—
Freundlich			
K_f, (μmol kg^{-1})/(μmol L^{-1})$^{1/n}$	2.06E-03	**1.77E-05**	3.02E-05
$1/n$	0.425	**0.474**	0.518
MWSE	0.0457	**0.0267**	0.0178
Linear			
K_d, L kg^{-1}	1.01E-03	1.59E-05	1.11E-05
MWSE	0.506	0.1542	0.344
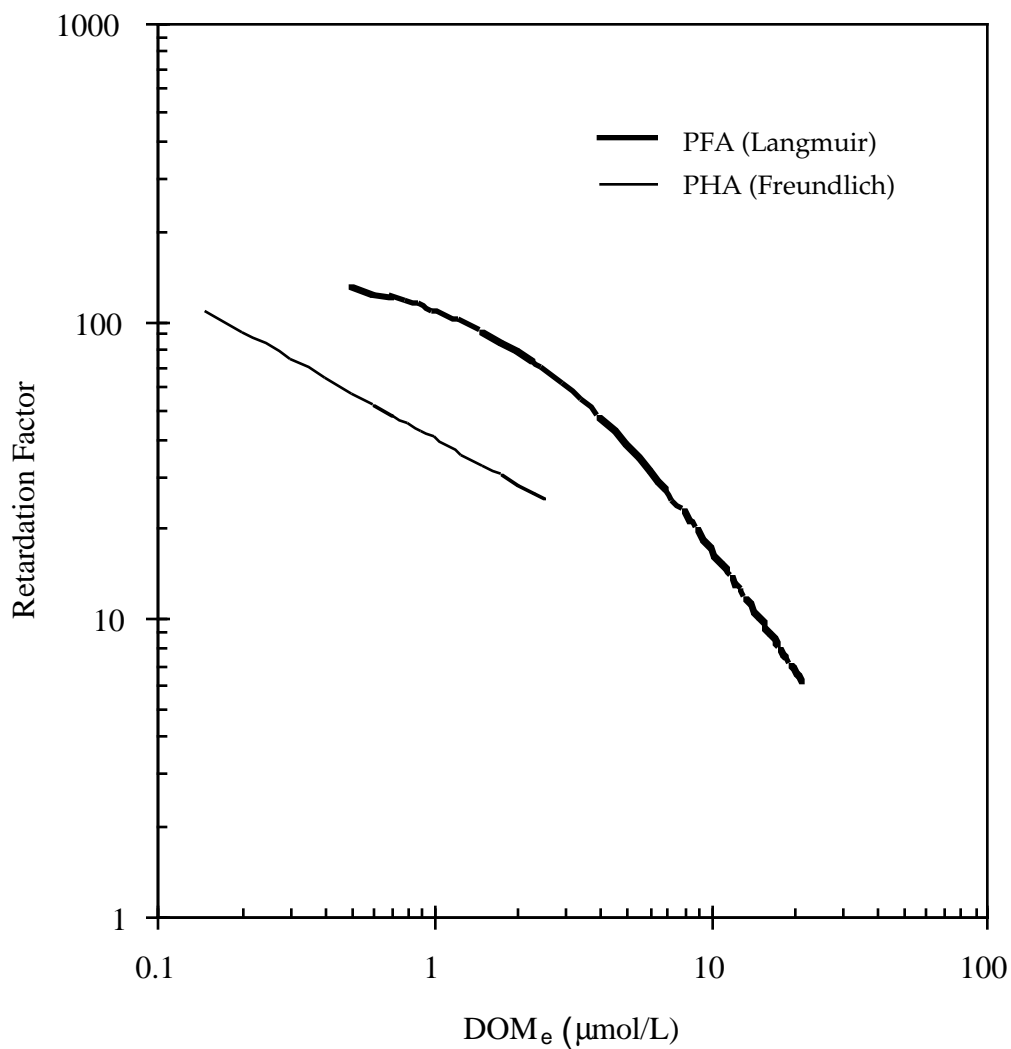
FIGURE C.5 Comparison of DOM Retardation Factors. This figure compares the retardation factors of DOM fractions as a function of soluble DOM concentration (DOM$_e$). Isotherm best fit model parameters are indicated in Table 4.2. The ranges shown indicate the ranges of observed DOM$_e$ concentrations in the sorption isotherm experiments. Retardation factors are calculated using Equation 4.1a-b in the text, with ρ_b = 1.68 g/ml and η = 0.36.

Lead-NOM Sorption. Equilibrium sorption of lead in the presence of DOM was observed. Solutions of 19.3 and 57.9 µmol Pb L^{-1} in the presence of 9.5 and 1.75 µmol L^{-1} ("Low" concentration levels of PHA and PFA, respectively) and 47.5 and 8.75 µmol L^{-1} ("High" concentration levels of PHA and PFA, respectively) were equilibrated. These "pre–equilibrated" Pb-DOM solutions were then added to 10 g L^{-1} soil and brought to equilibrium. Results are shown in Figure C.6.

Two general trends are apparent. First, Pb is more soluble in the presence of DOM than in the absence of DOM, evidenced by the shift downward and right of the Pb–DOM isotherm lines from the Pb–only line. This general behavior is violated by Pb sorption (at 57.9 µmol Pb L^{-1}) in the presence of low PHA concentrations (note the crossing of the "No DOM" and "PHA Low" lines at the point *A'* in Figure C.6).

The second trend is that PFA appears to enhance Pb solubility better than PHA, evidenced by the lower slopes of the PHA lines relative to the PFA lines. However, this trend reverses at low Pb concentrations (at the points *B'$_{low}$* and *B'$_{high}$* in Figure C.6), where Pb solubility is actually higher in the presence of PHA relative to PFA.

Lead-DOM Aqueous Binding. Figure C.7 presents the data from the Pb-DOM binding studies analogous to an isotherm plot (where DOM ≡ sorbent). It is shown that PHA has a much higher Pb binding capacity than PFA at the concentrations observed. Comparison of the results for PHA and PFA should be approached with caution, however, since the soluble Pb fraction in the PFA experiment contained approximately 30% of UV$_{254}$-absorbing material that was not retained on a 1,000 MWCO ultrafiltration membrane. However, the 1-2 order of magnitude difference in the results suggest that PHA has a greater affinity for Pb than PFA. Therefore, it is suspected that PFA does not play as significant of a role in Pb binding as PHA.

These results are not surprising, since humic acids are more hydrophobic and can have higher binding site densities (consequently, they should have a higher affinity for heavy metals than fulvic acids) than fulvic acids. These results show that, relative to PFA,

PHA could enhance the apparent solubility of Pb by complexation, if the DOM complex remained in solution. However, PHA could also inhibit the apparent solubility of Pb if sorption of Pb-PHA complexes or the sorption of Pb to sorbed PHA were significant. Of course, the latter assumes that the binding of Pb to PHA was functionally similar and independent of the speciation of PHA between soluble and sorbed phases.
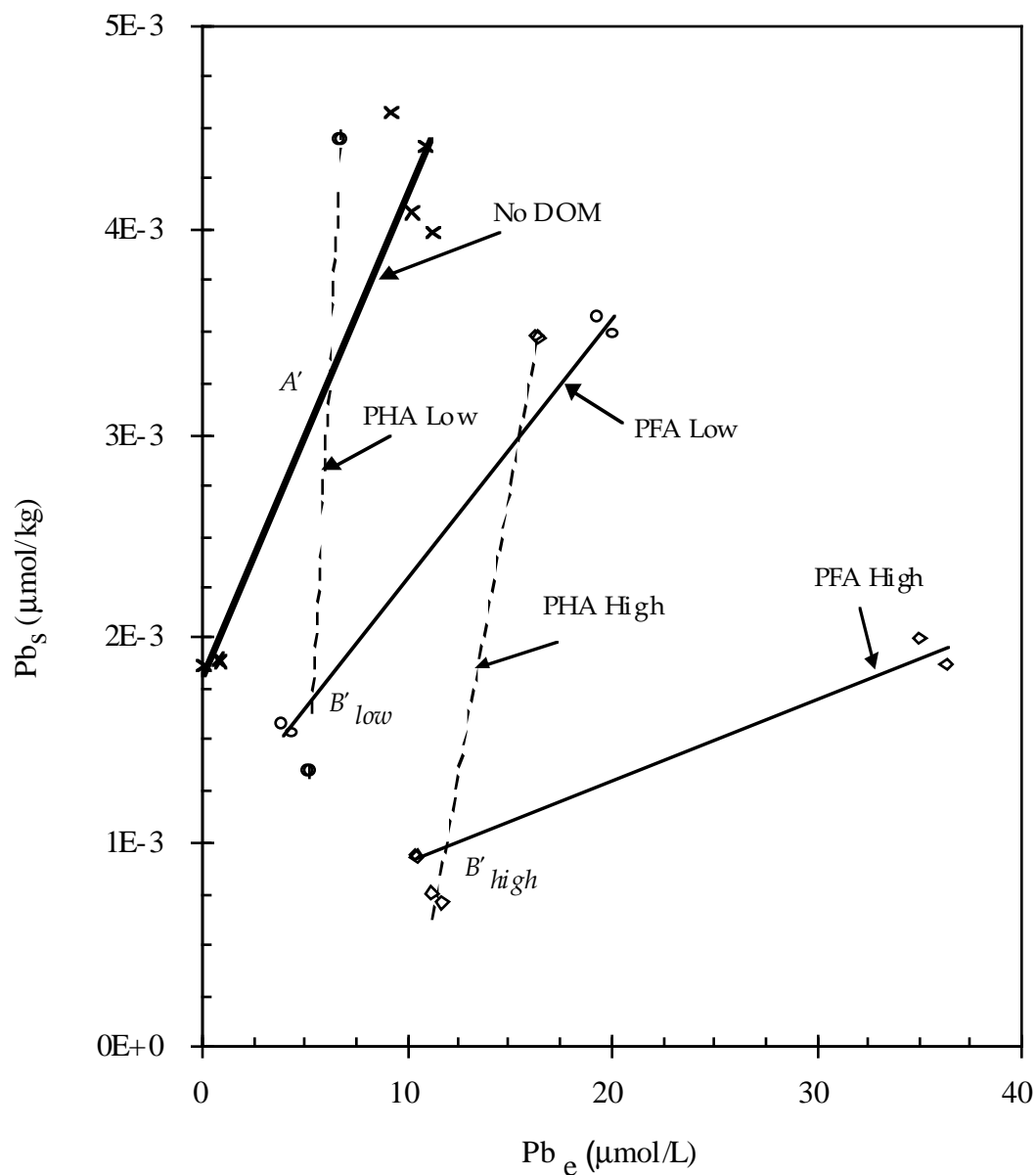
FIGURE C.6 Pb-DOM Sorption. Pb sorption onto Everett sand in the presence of DOM. Approximately 5-10% of UV_{254}-absorbing DOM was sorbed to the soil in all samples containing DOM. Pb_e represents the total Pb in solution (free + complexed) at equilibrium. Pb_s represents sorbed Pb. Points toward the upper right of each isotherm line are those where an initial Pb concentration of 57.9 μmol/L was added, while those toward the lower left of each isotherm line are those where an initial Pb concentration of 19.3 μmol/L was added. PHA and PFA represent experiments where Pb sorption in the presence of humic and fulvic acids, respectively, was evaluated. "No DOM" represents the control experiment where Pb sorption in the absence of DOM was evaluated. Low initial PHA and PFA concentrations ("Low") were 9.5 and 1.75 μmol/L, respectively. High initial PHA and PFA ("High") concentrations were 47.5 and 8.75 μmol/L, respectively.

119
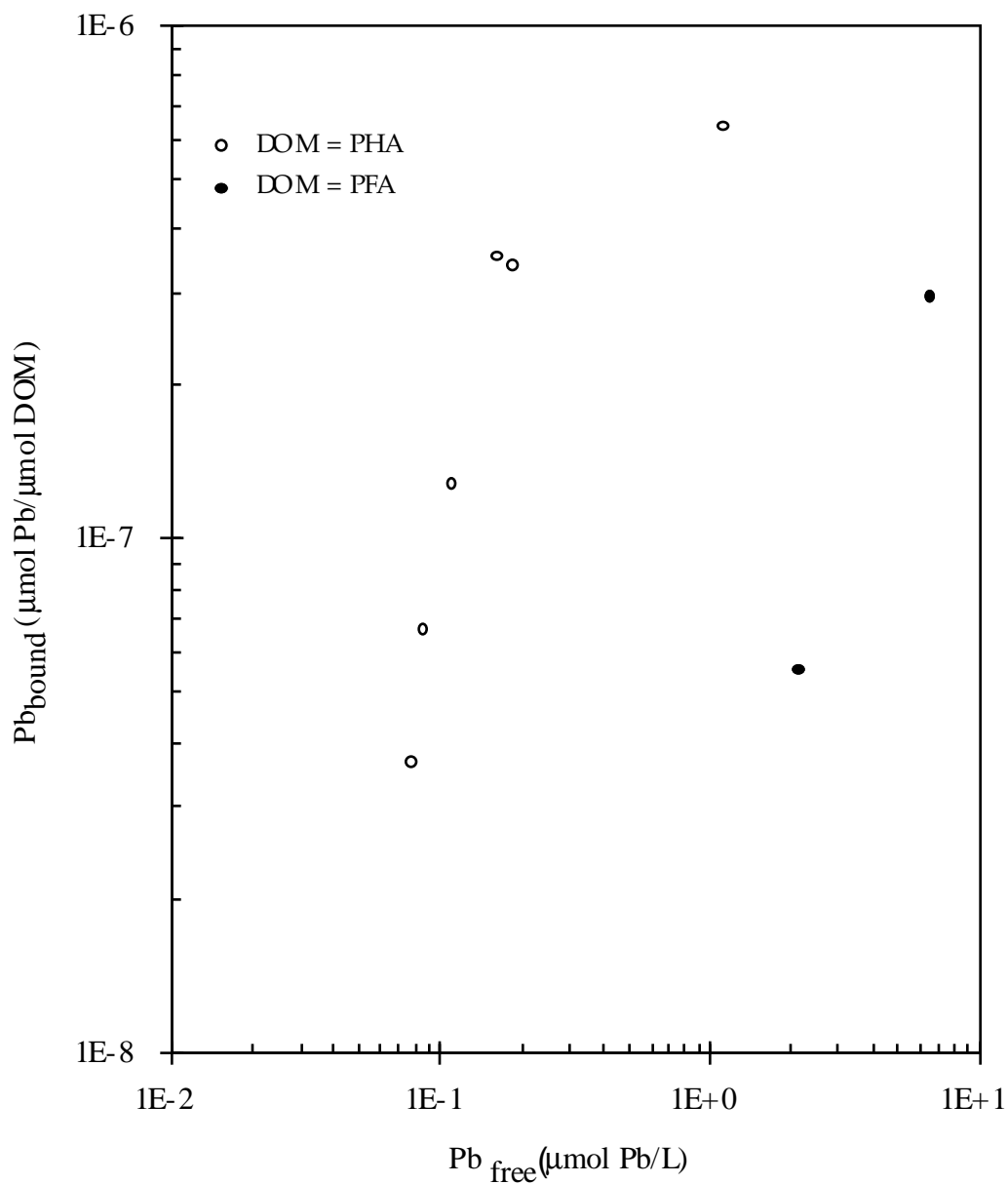
FIGURE C.7 Pb-DOM Binding. The data here are plotted in a manner analogous to a sorption isotherm (C_e vs. C_s). Points represent equilibrated samples containing varying Pb:DOM concentrations. Pb_{free} indicates uncomplexed Pb, measured as the concentration in a filtrate passing a 1,000 MWCO ultrafiltration membrane. Pb_{bound} indicates Pb complexed with DOM, determined by calculating the difference between a known total initial concentration and Pb_{free}, divided by the total DOM concentration.

Column Experiments. A nonlinear regression analysis using the program CXTFIT (Parker and van Genuchten, 1984) was used to determine the pore water velocity and dispersion coefficient from the breakthrough data. Since the volume of the end caps constituted a significant fraction of the total apparatus volume (22%) and could not be neglected, a reasonable approach to correct for it was applied in the regression analysis. This approach is described as follows.

The column apparatus consisted of a 28.0-mL cylindrical housing (2.5 cm diameter), in which 47.0 ± 0.2 g soil was packed, and capped at the ends by hemispherical end caps. This resulted in a bulk density of 1.68 g cm^{-3} and an estimated theoretical porosity ($\eta_{est} = 1 + r_b / r_s$) of 0.33 (0.31 – 0.34 represents the 95% confidence interval for this measurement). The volume of each of the caps (with associated tubing) was 4.0 mL. The volumes of the soil housing and end caps were determined gravimetrically by measuring the weight of the water required to fill each part. Tritiated water ($^{3}H_2O$) was applied as a continuous source to the column apparatus at a flow rate of 0.8 mL min^{-1}. Effluent samples were collected at 2-minute time intervals and analyzed for tritium (^{3}H) by scintillation counting to generate data for a breakthrough curve.

CXTFIT requires that the location (along a one-dimensional column) at which the data was collected (i.e., the column length) be specified. Thus, the geometry of the column was represented as three continuous cylinders of equal diameter denoting the influent end cap, the soil housing, and the effluent end cap, respectively. The length of the soil housing was determined by exact measurement to be 5.7 cm. The length of a cylinder representing each end cap was determined by finding the length of a cylinder having the same diameter as the soil housing (2.5 cm) and a volume equal to the actual volume measured in an end cap (4.0 mL). This procedure resulted in a total column apparatus length of 7.3 cm, the distance used as the column length in the regression analysis. It should be emphasized that the total porosity of this conceptual column includes the volume of each of the end caps plus the pore volume in the soil housing.

The regression analysis yielded a *fitted* pore water velocity of 0.33 cm min^{-1} (0.33 – 0.34 = 95% confidence interval). Knowing the estimated soil porosity from above (η_{est} = 0.33), the *predicted* pore water velocity (assuming the end caps do not appreciably influence the validity of the prediction based upon soil pore volume alone) can be determined by $v_{est} = Q / \eta_{est}A$ to be 0.49 cm min^{-1} (for a flow rate of 0.8 mL min^{-1}, the flow in the tracer experiment), a value higher than that obtained in the regression analysis of the breakthrough data. Thus, the influence of the end cap volume significantly impacts the measurement of pore water velocity and must be accounted for.

The fitted pore water velocity (v_{fit}) can be used to estimate the total porosity of the apparatus (effective soil porosity, η_{est}, + end cap volumes) by $\eta_{apparatus} = Q / v_{fit}A$, yielding a porosity of 0.49 and a corresponding apparatus pore volume of 18.0 mL. Since the exact volume of the end caps is known to be 8.0 mL, the effective pore volume of the soil can be determined by subtracting the end cap volume from the apparatus pore volume (18.0 mL – 8.0 mL) to get an effective pore volume of the soil of 10.0 mL. Knowing the volume of the soil housing (28.0 mL), the estimated effective soil porosity (η_{eff}) is found to be 0.36. This value is outside the 95% confidence interval for the n_{est}, predicted above, indicating a statistically significant difference. This discrepancy could have resulted from unquantified variability in the flow rate during this experiment. However, if the technique used in packing the soil and assembling the apparatus may have resulted in the failure to fill the housing with soil, leaving a slight gap near the end. This could have resulted in a porosity which was higher than the actual soil porosity, explaining the discrepancy.

A corrected velocity which describes the rate of tracer movement through the soil pores for a flow rate of 1.0 mL min^{-1} (the targeted flow rate in the other transport experiments) can be found by $v_{corrected} = Q / \eta_{eff}A = 0.57$ cm min^{-1}, which closely corresponds to the estimated pore water velocity found by $v_{est} = Q / \eta_{est}A = 0.62$ cm min^{-1}.

The dispersion coefficient (D) obtained in the same regression analysis was 0.050 $cm^2 min^{-1}$ (0.040 – 0.061 = 95% confidence interval). This value is probably higher than the true dispersion coefficient for the soil column alone, since it is expected that the end caps contribute a significant degree of dispersion. The true soil dispersion could not be estimated without knowing the individual contribution to the total apparatus dispersion by mixing in the end caps. However, the fitted value can be used as a conservative number for determining the column Peclet number (vL/D), which indicates the relative influence of advection vs. dispersion. The Peclet number (using the fitted v and D values from the regression analysis, both conservative estimates of actual values in the soil column) was calculated to be 48, well above the minimum value (8-10) at which advection begins to dominate transport (Fetter, 1993). This procedure was repeated three times, resulting in a column porosity of 0.36 ± 0.02 (standard deviation) and a dispersion coefficient of 0.052 ± 0.004. A representative normalized breakthrough curve for the transport of ^3H_2O through the column apparatus is shown in Figure 4.8. All solute breakthrough profiles were normalized for the *apparatus* pore volume determined from the *average* of those values determined from the three replicate ^3H_2O tracer experiments.

Figure C.9 shows the results of experiments 1H and 1F , where columns were fed with DOM-only solutions. As qualitatively predicted by the sorption isotherms, PHA breakthrough occurred sooner than that for PFA. It should be noted that the relative mobility of PHA is emphasized by realizing that its molar feed concentration was nearly five times less than that for PFA (see caption, Figure C.9). Both curves exhibit a rapid initial rise in breakthrough concentration (characteristic of nonlinear isotherm behavior) followed by extensive tailing (cf. inset, Figure C.9), characteristic of solute breakthrough governed by isotherm nonlinearity or rate-limited sorption (Brusseau, 1995). This is to be expected, since travel times in the column were much lower than those required for equilibrium to be established, and isotherms for both PHA and PFA exhibited nonlinearity. Furthermore, a flow interruption technique (Brusseau *et al.* 1989) was used to identify rate-

controlled sorption during the breakthrough of PHA. During the breakthrough of PHA, the flow was stopped for 30 minutes. Upon continuing flow, a sharp decrease in breakthrough concentration resulted as the pore water eluted, followed by breakthrough behavior similar to that obtained prior to stopping flow. This reduction in the pore water concentration confirms that while the pore water in the column was immobile, DOM sorption was still occurring onto the sediments, indicating that sorption had not attained equilibrium during continuous flow.

Replicates of experiments 1H and 1F carried out for 3.3 days resulted in a final breakthrough relative concentration of 0.92 and 0.97 for PFA and PHA, respectively.

Figure 4.10 shows the results of the Pb column experiments 2, 3H, and 3F. Column experiments were not carried out to complete breakthrough because of the difficulty in maintaining a stable flow with fatigued pump tubing and tubing rupture after operation for several days. These curves show that the presence of DOM in the feed resulted in significantly enhanced mobility of Pb, decreasing Pb retardation by factors of about 4-8. PHA enhanced Pb mobility relative to PFA. This phenomenon is consistent with the Pb-DOM aqueous binding experiments, which suggest that the extent of Pb complexation will be greater for PHA as the complexing ligand than for PFA. Furthermore, if one assumes that the mobility of DOM controls the mobility of Pb, then this behavior is expected. This is shown in the DOM-only breakthrough curves (Figure C.9), which show that PHA is more mobile than PFA.
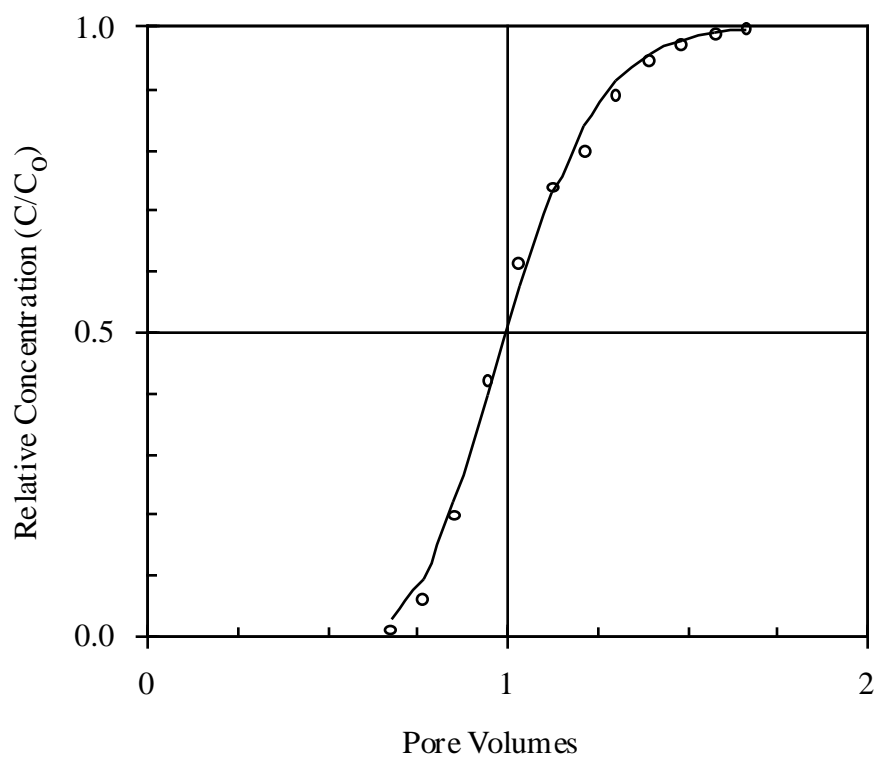
FIGURE C.8 Nonreactive Solute Breakthrough Profile. Solute = ^3H_2O (tritiated water). Relative concentration represents the ratio of the effluent ^3H concentration (cpm) to the feed ^3H concentration (cpm). Circles indicate observed breakthrough data from the column apparatus. Solid line indicates best fit to the convection dispersion equation using uncorrected parameters vs and D characteristic of the whole column apparatus (see text).
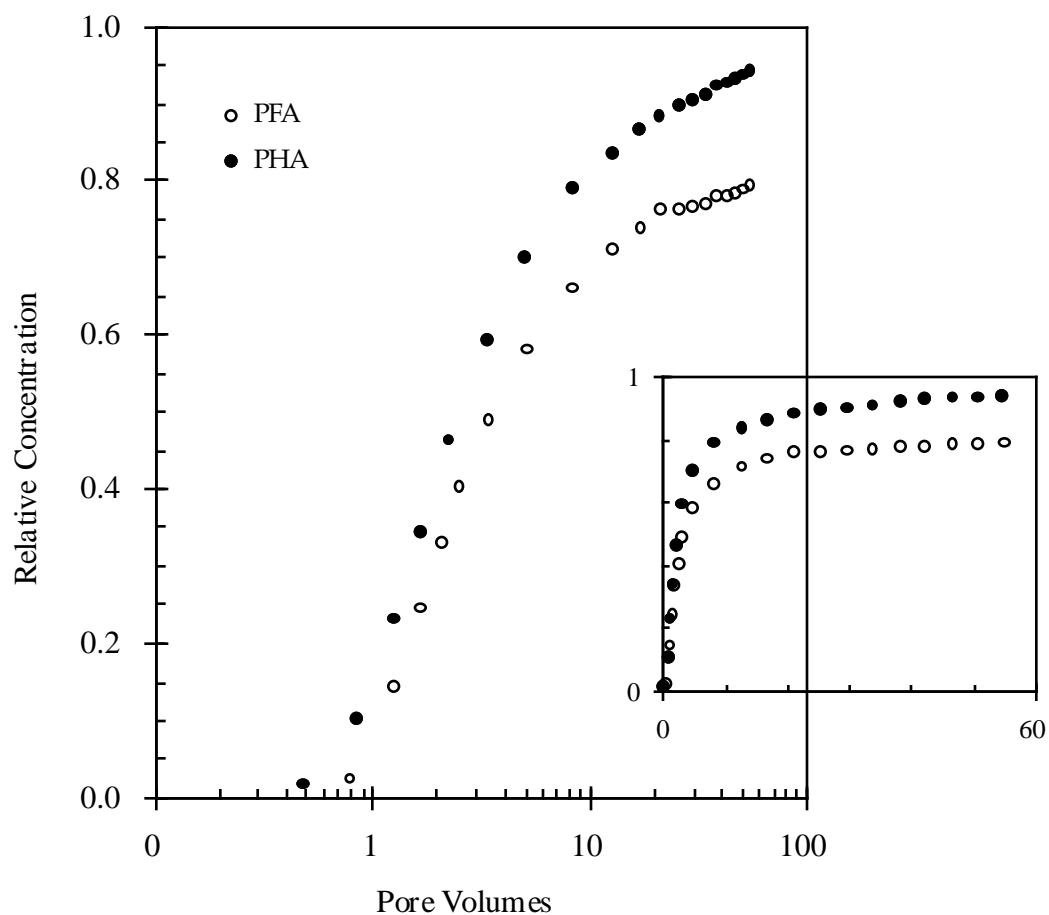
FIGURE C.9 DOM Breakthrough Profiles. Relative concentration represents the ratio of the effluent UV_{254} absorbance to the UV_{254} absorbance of the feed. The inset shows the same data plotted on an arithmetic pore volume scale to emphasize the extensive tailing characteristic of DOM breakthrough curves. Feed concentrations of PHA and PFA were 1.75 μmol/L and 9.50 μmol /L, respectively.
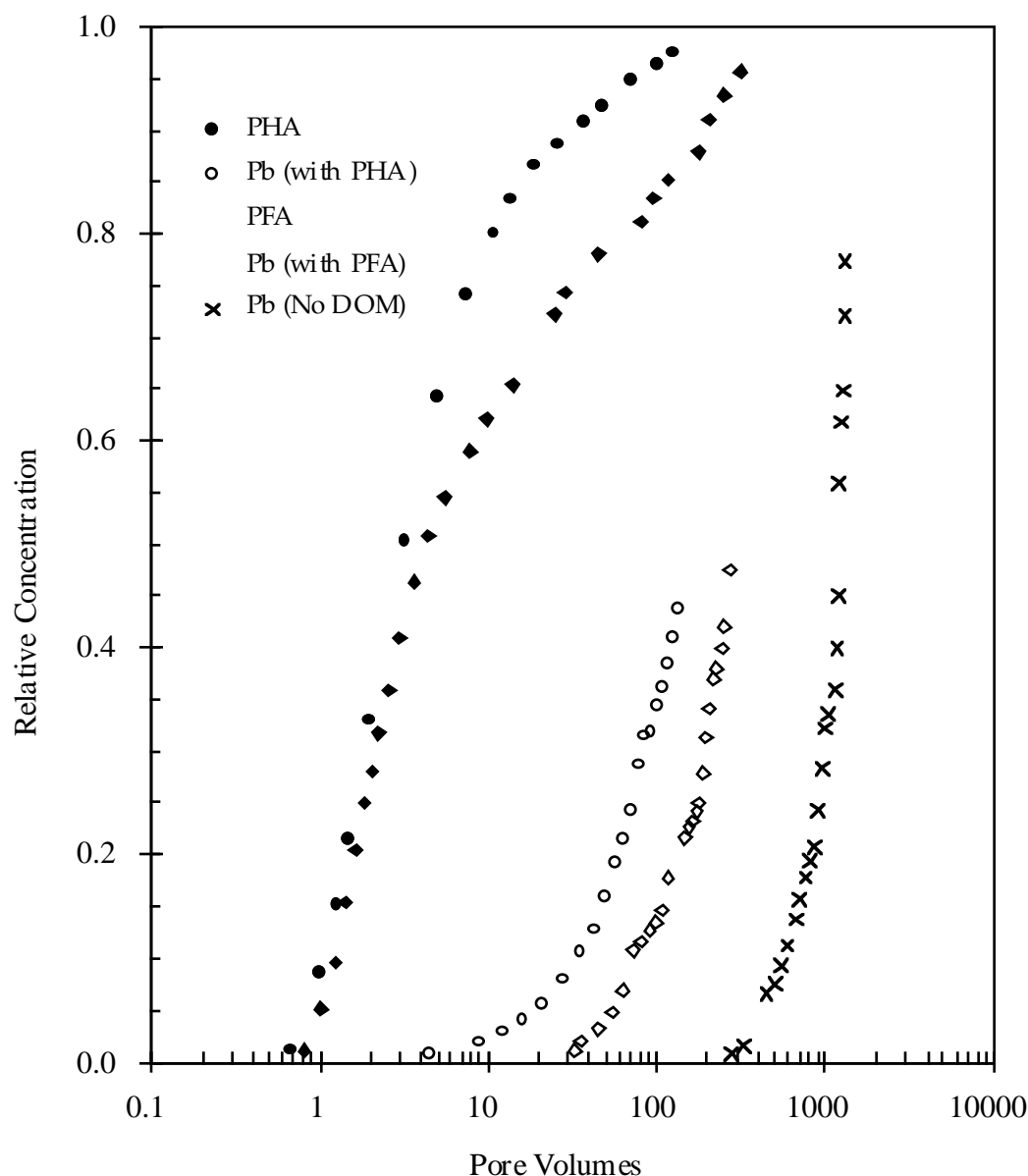
FIGURE C.10   Pb Breakthrough Profiles. Open symbols (and X's) represent measured Pb breakthrough profiles, while filled symbols represent measured DOM breakthrough profiles. Like symbols (open and filled) represent breakthrough profiles measured simultaneously in a single experiment. "Pb (No DOM)" indicates the breakthrough profile of Pb in the absence of simultaneously eluting DOM. "Pb (with PHA)" and "Pb (with PFA)" indicate breakthrough profiles of Pb simultaneously with either humic or fulvic acid, respectively. "PHA" and "PFA" indicate the DOM breakthrough profiles of humic and fulvic acids, respectively, when simultaneously eluted with Pb. Relative concentration represents the ratio of the effluent (Pb or DOM) concentration to the feed (Pb or DOM) concentration. Pb feed concentrations for Pb, Pb (with PHA), and Pb (with PFA) were 7.18, 6.13, and 5.74 µmol/L, respectively. DOM feed concentrations for Pb (with PHA) and Pb (with PFA) were 1.75 and 9.50 µmol/L, respectively.

127

Examination of the Pb breakthrough curves in Figure C.10 alone provides insufficient evidence for the possible mechanisms of cotransport in the column experiments. Also shown in Figure 4.10 are the DOM breakthrough curves from the same experiments. It can be seen that significant breakthrough of PHA occurs prior to breakthrough of Pb during the Pb-PHA experiment. If one assumes that the distribution of Pb between free and complexed states in solution remains unchanged throughout the course of the experiment, then observable Pb breakthrough should occur simultaneously with DOM. Moreover, the ratio of Pb:DOM should be definable if its binding constant (log K) is known. However, these results show the preliminary breakthrough of uncomplexed DOM for a significant amount of time prior to Pb, indicating that Pb speciation may be changing upon contact with the soil. The soil appears to be competing for complexed Pb, resulting in the preliminary breakthrough of previously-complexed DOM in a "Pb-cleansed" state. This is followed by release of Pb and subsequent complexation as the soil becomes saturated with DOM. This behavior was also observed in pilot scale lysimeters packed with the same soil (Igloria and Hathhorn, 1994).

Effluent pH measurements in each column experiment ranged from pH 6.7 to pH 7.1. The lower values were typically measured at the beginning of the experiment, increasingly slowly as solute breakthrough was completed. There was no correlation between effluent pH and either DOM or Pb breakthrough.

Appendix D

PHASE 2 DETAILED DISCUSSION OF RESULTS

HYDRAULICS OF THE SOIL COLUMNS

Each of the three soils studied were packed into columns, once for the metals-only tests, and again for the metals-NOM experiments. In order to test the in-place hydraulic integrity of the columns, a conservative (bromide) tracer test was conducted as described in Section 3.6. The focus of the test was to determine that no short-circuiting occurred in the soil columns due to uneven or improper packing. In general, these tests were conducted both prior to and following the loading sequences. The only exception being for Garrison where no final test was conducted due to time limitations. What follows discusses each soil's potential effectiveness, hydraulically, as an infiltration soil based on the results of the tracer tests and their behavior during the loading sequences.

For Springdale sand, the initial and final bromide breakthrough curves (BTCs) were well-behaved due to the uniform gradation and non-cohesive structure of the sand. Using the mid-point $(C/C_O = 0.5)$ of the BTC as an estimator of the advection, the pore volume (pv) of the column was estimated at 24 L for both the metals-only and metals-NOM experiments. With this in mind, the five applications of approximately 67 liters each, resulted in about 14 pv of water flushed through the Springdale soil column. During the metals-only runs, no evidence that side-wall flow (short-circuiting) or any other type of preferential flow was observed (see Figures D.1a and D.1b). However for the metals-NOM experiment, the final bromide tracer test showed that the soil column configuration changed. The apparent pore volume was reduced by half (see Figures D.2a and D.2b), and the streamtube velocities were also more uniform as the steeper S-shaped curve showed. Springdale was generally the easiest soil to work with in terms of packing the column and producing relatively consistent infiltration rates. It is, hydraulically, the best soil studied for infiltration. However, the sand has a much lower exchange capacity than the other soils tested, which may limit its use in a practical sense as an actual infiltration soil.

For the Everett soil, the initial and final tracer test results showed some differences (see Figures D.3a and D.3b). In the initial tracer test, some resident bromide from a prior

test was observed, evidently a result of insufficient flushing prior to subsequent testing. When the first Everett BTC was determined inadequate, the column was unpacked and the same soil was repacked after drying. If this early region of the BTC is discarded, the results reveal a well-behaved BTC. By contrast, the post-loading BTC revealed an increase in overall average streamtube velocity, with the $C/C_O = 0.5$ occurring some 2 hours earlier in the final test than the initial. The breakthrough *time* was the only data available for this test, so no pv estimate could be made. This relatively early breakthrough along with the level portion of the curve between 5 and 6 hours suggests that some pore structure reconfiguration may have developed during the five test applications (excluding, of course, the possibility of significant measurement error). Figure D.4 shows that the metals-NOM column pore volume was approximately 17.5 L (less than either of the Springdale columns). Because bromide is an unreactive tracer, the slight tailing which occurred in Everett is likely due to pore size effects on the breakthrough of bromide. This is reasonable since Everett has a wider grain size distribution than Springdale. Everett was relatively easy to pack into the columns and performed well hydraulically, i.e. the infiltration rates were consistently within the acceptable range. In a practical sense this loamy sand would most likely be used as an infiltration soil in the field, because it best satisfies the hydraulic and exchange capacity requirements.

For the Garrison metals-only tests, only a single initial run was made. The mid-point of the BTC yielded pv = 12 L, much less than either Everett or Springdale. Although bromide was detected rather early in the test (which may suggest that minor side-wall flow or preferential paths may have been present), there was a wide range of pore velocities and no indication of anomalous steep or flat portions to the "front." There were some fluctuations in the readings between 25 L and 30 L, but the general shape of the BTC was deemed acceptable in terms of yielding a "smooth" curve (see Figure D.5). Difficulties encountered were primarily due to the poorly-graded nature of the soil yielding generally low permeabilities. Figure D.6 shows the steep breakthrough of bromide through the

131

Garrison metals-NOM column. The Garrison tests for the metals-NOM experiments were stopped after the fourth run, because a very low permeability (fine silt) layer had formed near the base of the column. The decision was ultimately made to discontinue the test and to deem the results unreliable. The problems encountered in testing Garrison showed its likelihood of posing hydraulic problems in the field, and would not be effective as an infiltration soil (at least those near surface soils which may contain significant quantities of the observed silt).

Additionally, the columns were tested for hydraulic conductivity during each loading period. The bar graphs (Figure D.7) illustrate the variability in hydraulic conductivity that resulted for each of the soils tested during the metals-only runs. The five runs for Everett produced a range of values from approximately 3×10^{-4} cm/s to 6×10^{-4} cm/s; Springdale remained fairly constant, ranging from 3.4×10^{-4} cm/s to 4×10^{-4} cm/s; and Garrison consistently decreased with each run, yielding values ranging from 0.5×10^{-5} cm/s to 1.8×10^{-5} cm/s. The range as well as the actual values were slightly greater for the metals-NOM runs, as shown in Figure D.8. The values for Everett ranged from 8×10^{-4} cm/s to 18×10^{-4} cm/s, which are higher than the values from the metals-only runs. Generally, the conductivity decreased for Springdale, and ranged from 4×10^{-4} cm/s to 11×10^{-4} cm/s.

There are several possible explanations for the fluctuating hydraulic conductivities. The periods between loadings allowed pore water to redistribute and evaporate to different extents, leading to varying initial water contents in the soil for each subsequent run. Different time intervals allowed between successive runs, ranged from 2 days to one week. Since hydraulic conductivity is dependent on both the antecedent water content and the potential, the resulting hydraulic conductivity during each infiltration period would have varied accordingly. Entrapped air due to the lateral confinement of the column is also a likely cause. In field situations, lateral drainage allows air to be displaced by incoming water. Here, the water column above and the PVC walls on the sides could have prevented

the air from being displaced and was trapped in pockets. The extent to which this occurs could have contributed to the observed variations in conductivity. Moreover, the fine silts and sands, particularly for Garrison soil, may have "washed" their way into larger pore spaces, wherein reducing the effective area for flow. Finally, there may have been consolidation of the media with each subsequent run. Most reasonable for the Garrison soil, because of the steady decline in hydraulic conductivity. Although the time involved would most likely make this effect small.

It is unlikely that the noted changes in hydraulic performance could be avoided during the five loadings. For example, approximately 67 kg (150 lbs) is loaded on top of the columns with each run; the wetting and drying cycle may also cause reconfiguration of the soil column structure altering the porosities; and the column conditions between runs may also yield different water contents, and hence hydraulic conductivity. All of these can produce much different breakthrough curves after five loadings. Though the mechanisms which caused changes to occur may be inherent to the experimental design, some of the effects mentioned can occur in the field, as well. Even though air-entrapment may not be as substantial in field situations, it can still have an effect in producing varying infiltration rates. Moreover, the hydraulic conductivity dependence on the moisture distribution of the soil profile is likely more severe in the field as the soils may be exposed to more extreme drying (desiccation) periods.

As important as the infiltration rate may be in the hydraulic performance of a basin, it seemed to play a secondary role in the attenuation of metals. The experiments did not show increased metals removal with decreased infiltration rate, as might have been expected. In the end, the higher average hydraulic conductivity (unsaturated) columns yielded greater mass removal. One would expect the removal to decrease as infiltration rates increase since elluent residence times are shorter for the columns with higher conductivities, and effective rates of sorption are frequently controlled by rates of solute transport rather than by sorption reactions per se (Weber, 1990). Since exchange kinetics

for the metals involved generally occur on the order of seconds (Bodek, 1988), and an average of 24 hours was required to finish one run, the varying infiltration rates played minor roles in affecting the metals removal ability of each soil. Details of the metals attenuation patterns will be detailed in the following sections.
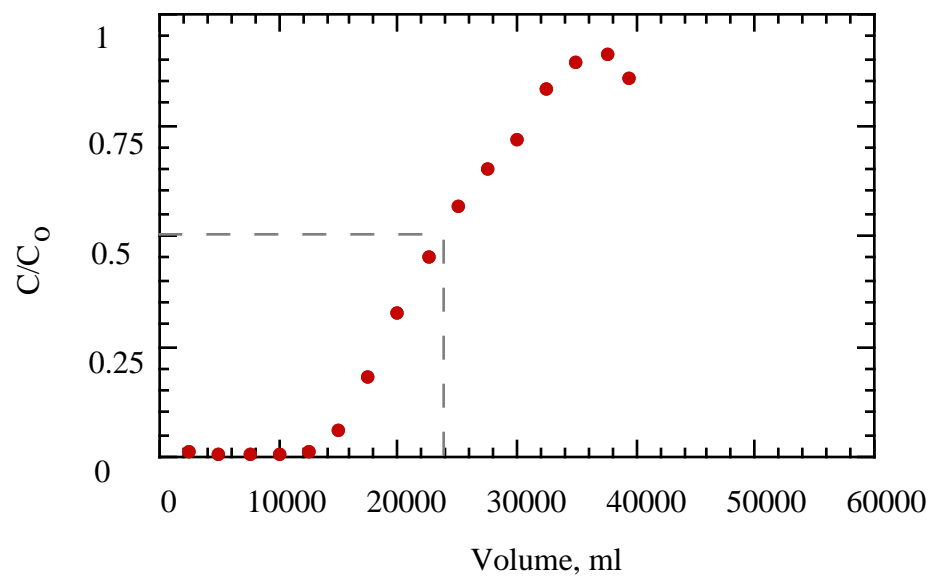
Figure D.1a   Springdale Metals-only Initial Bromide Tracer Test
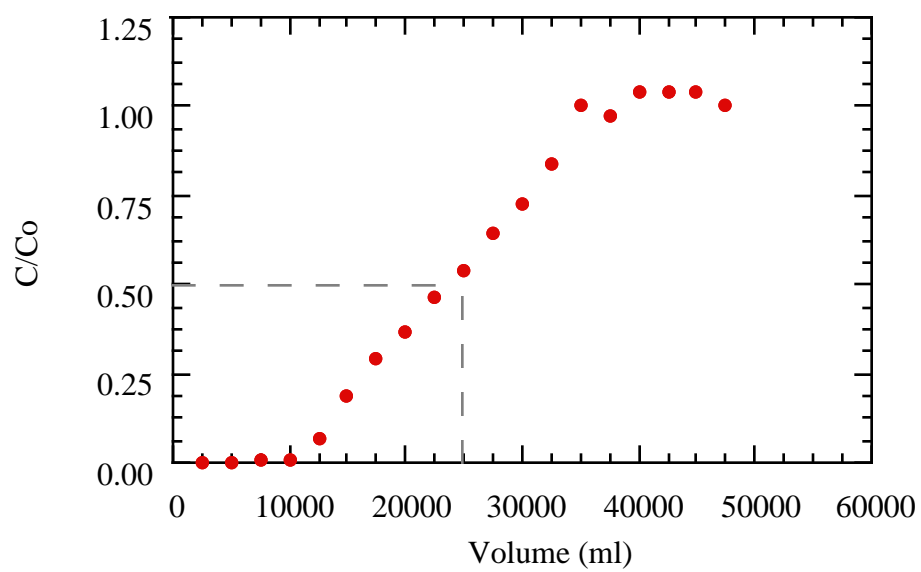
Figure D.1b   Springdale Metals-only Final Bromide Tracer Test
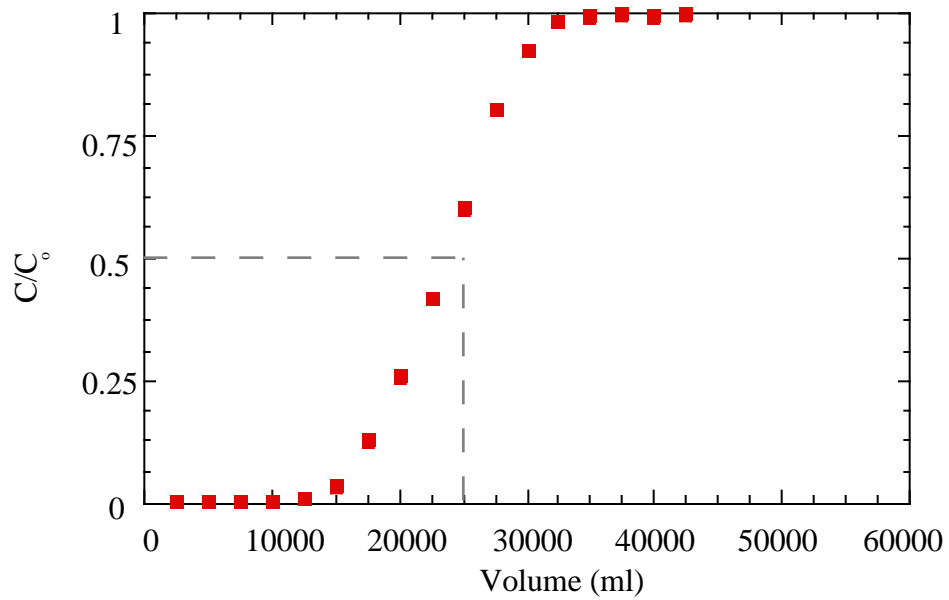
Figure D.2a   Springdale Metals-NOM Initial Bromide Tracer Test
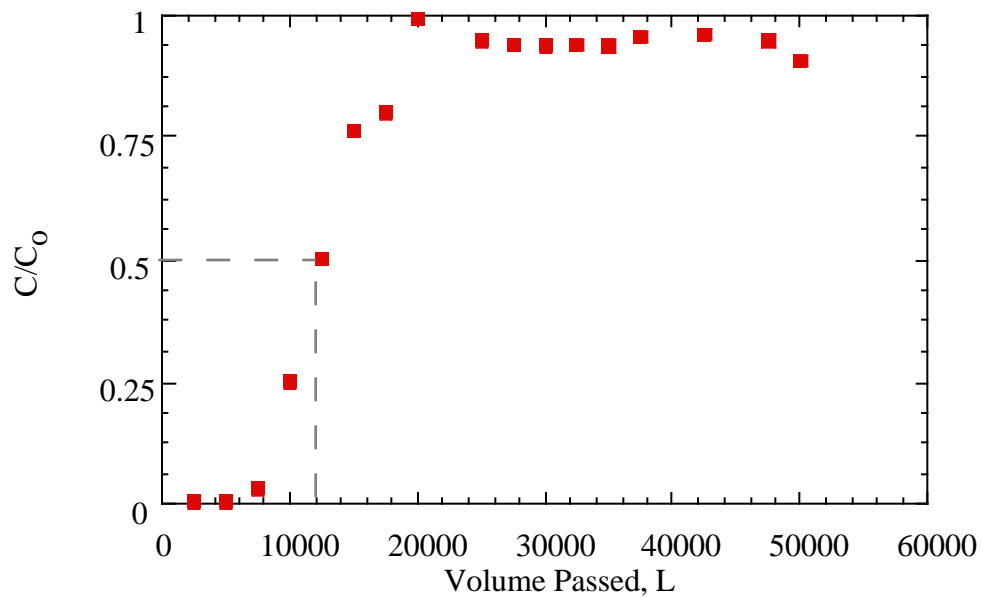
Figure D.2b   Springdale Metals-NOM Final Bromide Tracer Test
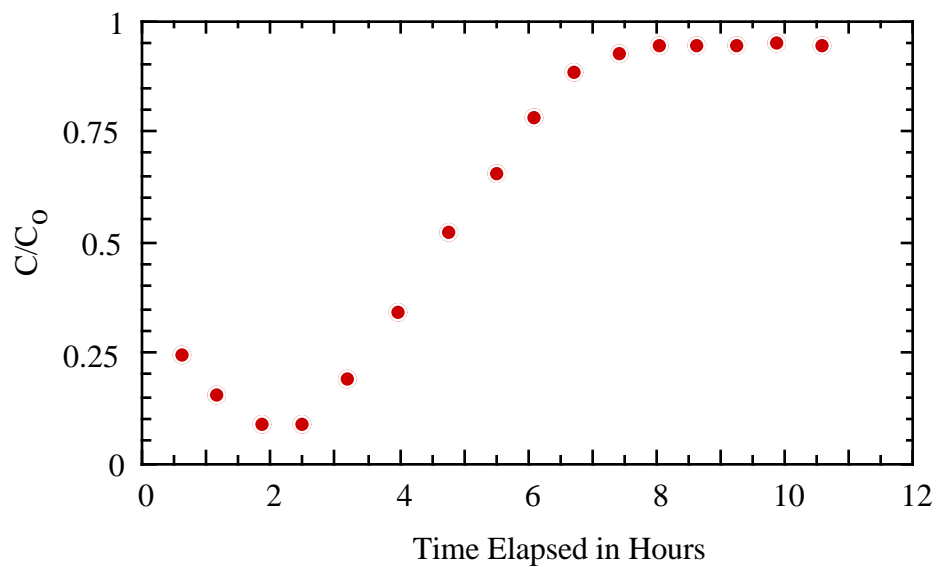
Figure D.3a   Everett Metals-only Initial Bromide Tracer Test
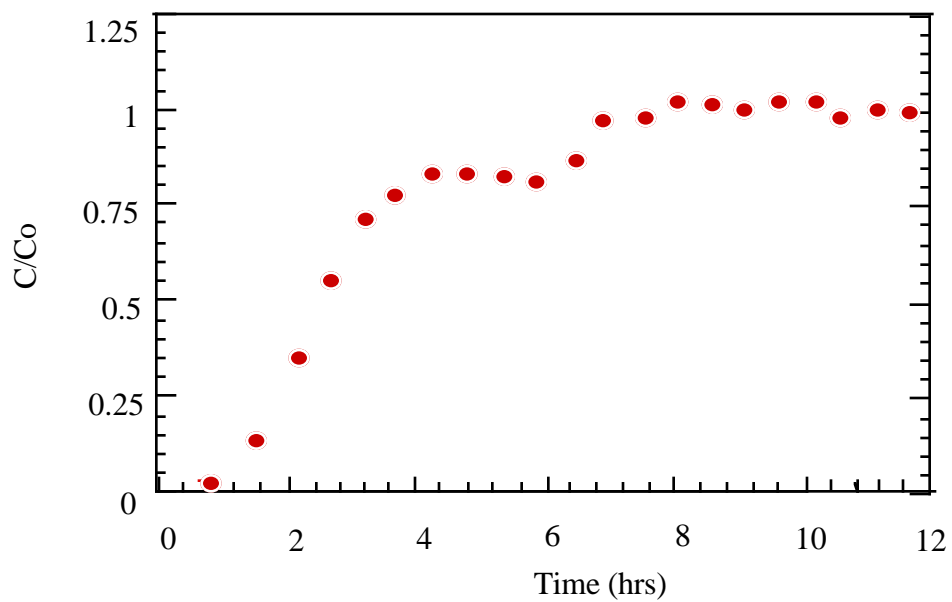
Figure D.3b   Everett Metals-only Final Bromide Tracer Test
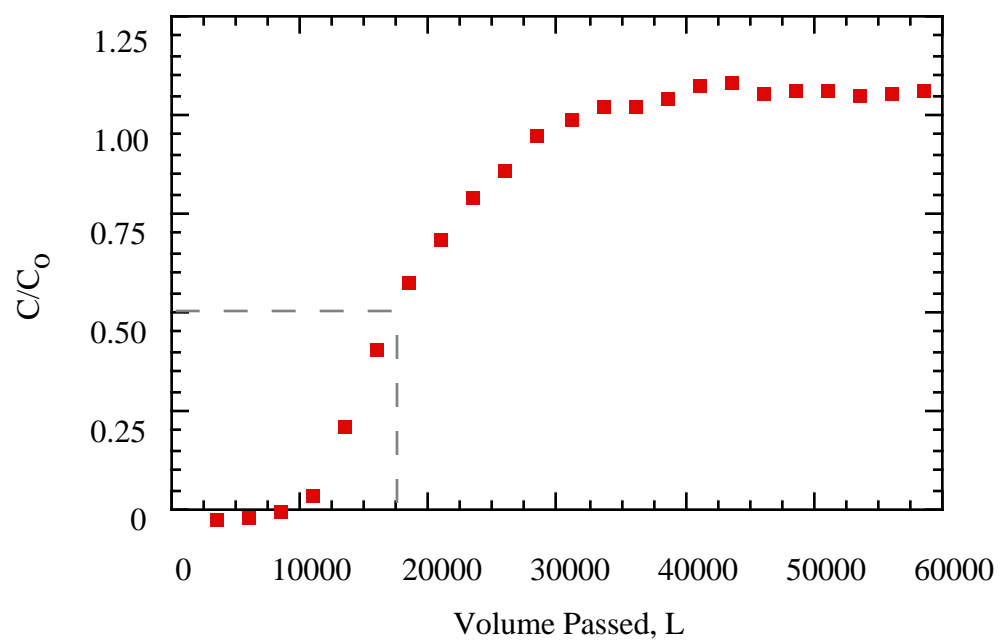
Figure D.4   Everett Metals-NOM Initial Bromide Tracer Test
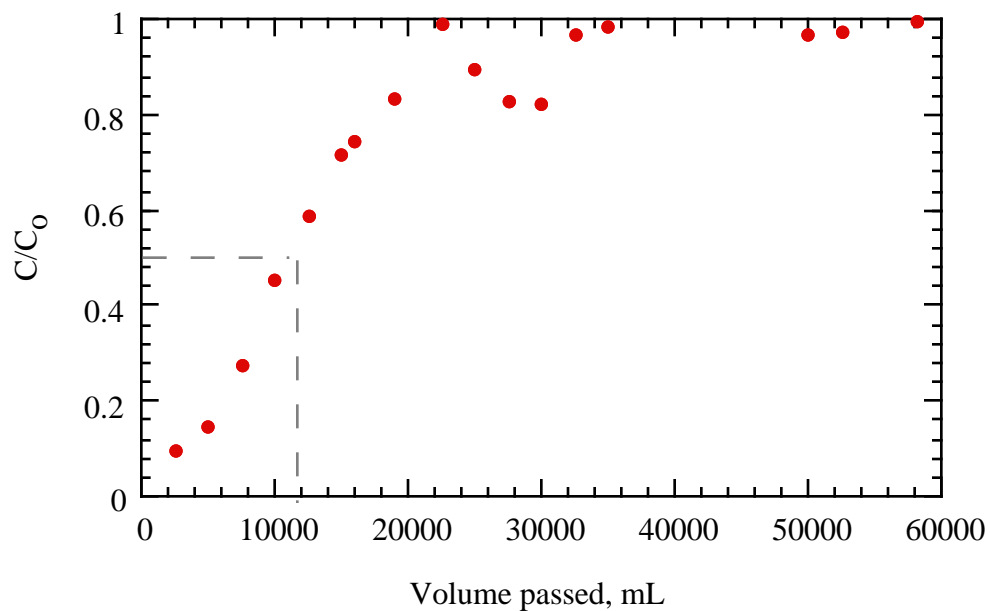
Figure D.5 Garrison Metals-only Initial Bromide Tracer Test
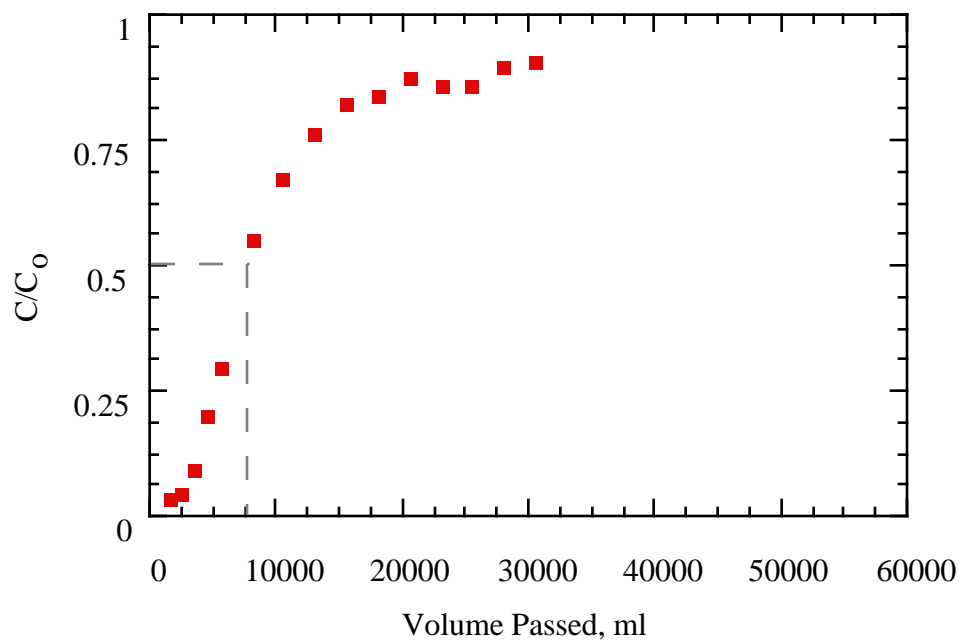
Figure D.6   Garrison Metals-NOM Initial Bromide Tracer Test
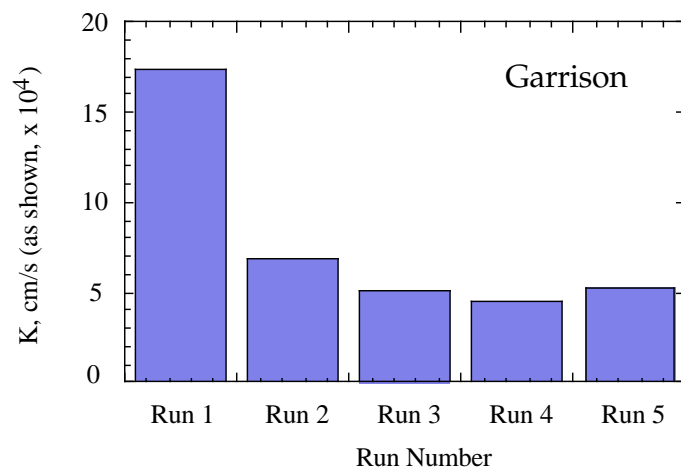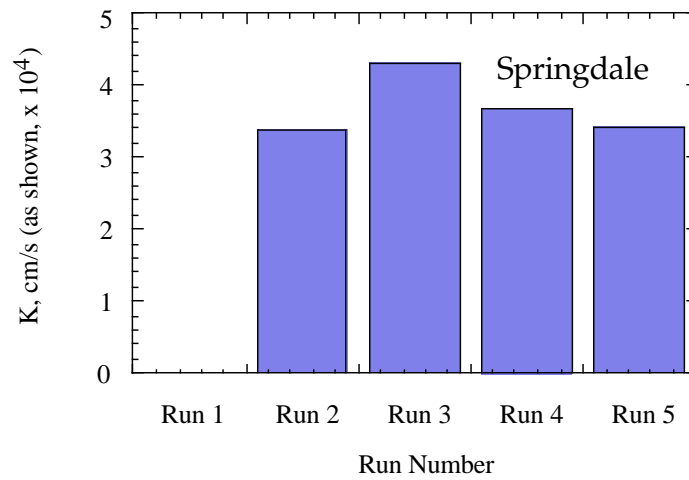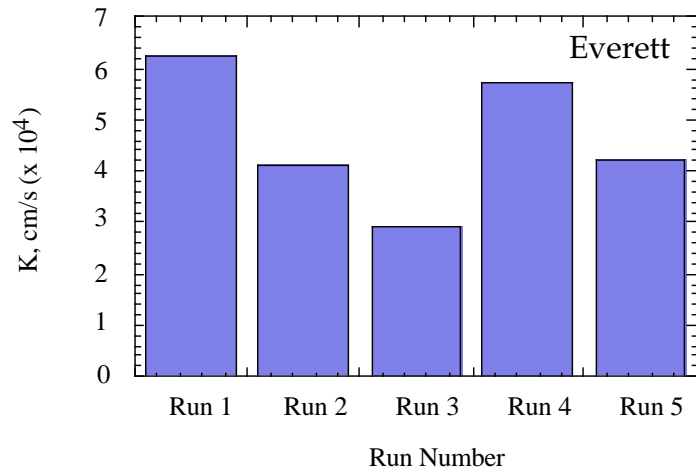
Figure D.7 Average Hydraulic Conductivities for Metals-only Runs
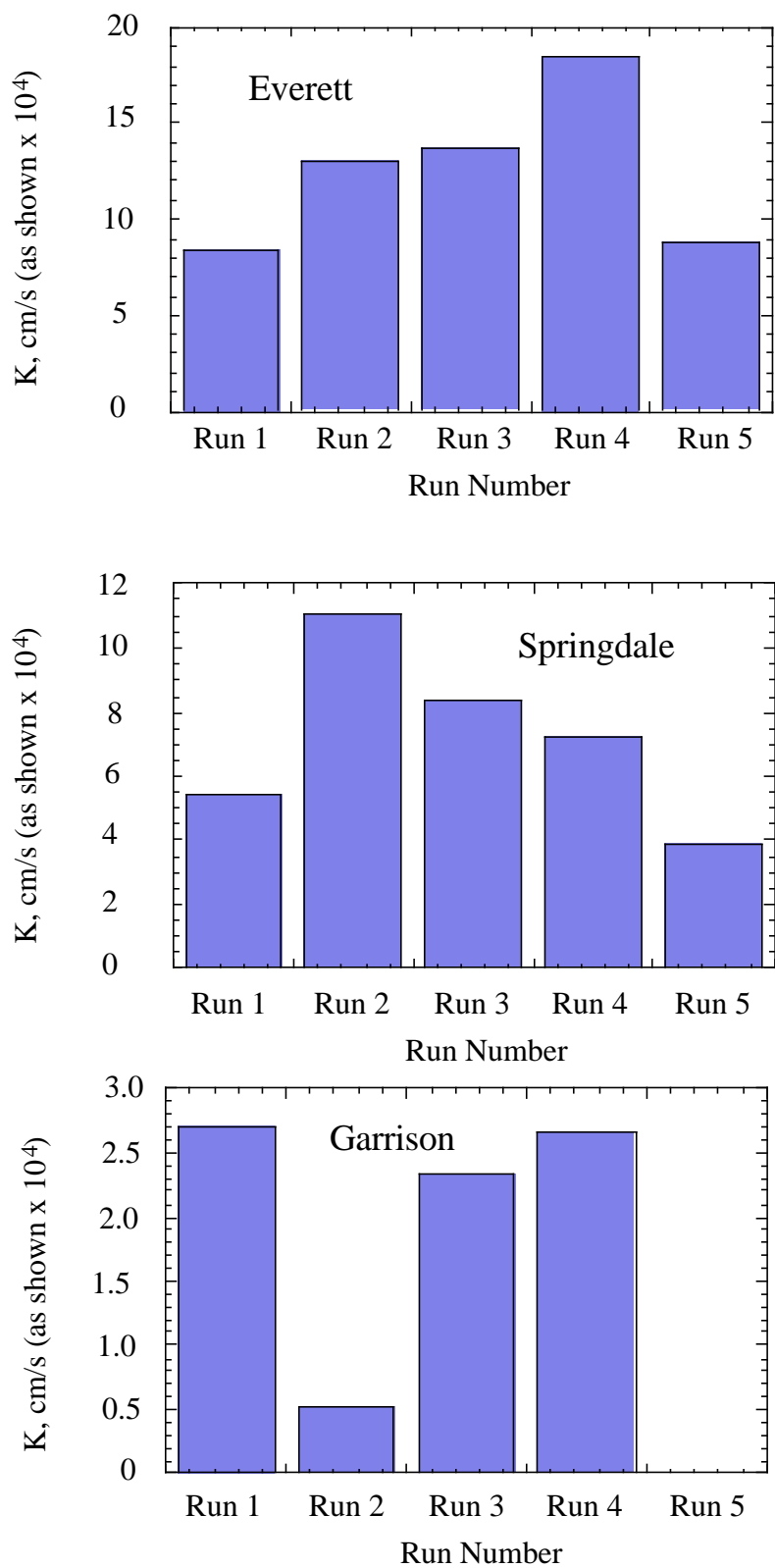
Figure D.8   Average Hydraulic Conductivities for Metals-NOM Runs

RESULTS OF METALS-ONLY EXPERIMENTS:
Metals and TOC Concentrations

Presented below are the results for the metals-only stormwater simulations. To provide structure and coherency, the information is presented in three main subsections describing the results from each soil. Throughout the column simulation experiments, pore water samples were collected at each of the two intermediate sampling ports (ISP-1 and ISP-2) and the exit port (ESP). The associated discussion will revolve around individual data taken from selected sample locations and the extent to which metals and TOC concentrations changed from port to port. Recall that total organic carbon (TOC) was chosen as the primary parameter quantifying the relative amounts of organics (NOM) in solution. Though no NOM was added to the "stormwater" in these experiments, measurements of TOC were made to determine if any organics were leached off the soils which may facilitate metals transport. The remainder of the results included herein were selected as being representative of the overall column performance.

To condense the data presentation, the five runs were combined to develop plots of concentration versus cumulative volume eluted. Since no water was applied between runs, the volumes indicated are those of the true volume eluted at that sampling time (not including the tracer test). Each run was approximately 67 liters. Therefore, the end of the first, second, third, fourth, and fifth runs corresponded (approximately) to 67, 135, 200, 270, and 335 liters, respectively. The corresponding results for each of the soils have been separated into their own respective subsections shown below.

Everett Soil Column Results. In the Everett soil column experiments, the average aqueous cadmium concentrations sampled from the uppermost port (ISP-1) were less than 5 µg/l. These levels were indicative of concentrations at or below those found in the background of the feed water. Moreover, the cadmium concentrations remained fairly constant throughout the depth of the column. This implies that most of the cadmium was attenuated within the top 30 cm to levels which would normally be present if non-highway runoff was infiltrating. Average cadmium concentrations from each port continued to

142

decrease with each successive run indicating Everett still potentially had the ability to attenuate cadmium (refer to Figure D.9).

For lead, attenuation patterns similar to those of cadmium were observed. Subject to initial loadings of around 250 μg/l, average concentrations for both ports ISP-1 and ISP-2 ranged between 50 μg/l and 100 μg/l. Moreover, at the ESP, concentrations were consistently below 25 μg/l. After the five loadings, Everett showed continued potential to attenuate additional lead as final concentrations at the ESP had a decreasing trend through the five loadings (refer to Figure D.10).

Copper, on the other hand, was not effectively removed. In fact, as Figure D.11a and D.11b show, there was a significant increase in solution phase copper as concentrations exceeded that of the feed concentrations (~30 μg/l) in both ISP-1 and ISP-2 samples. This observation was likely due to desorption and/or dissolution in the upper 30 cm. However, by the time ESP samples were taken, most concentrations remained below the initial feed level indicating that complete front breakthrough had yet to occur. Although unusual in pattern, this observation led to the belief that copper was desorbed at the top of the column and adsorbed in the lower portion of the column. This may be due to the competition from other metals (e.g. lead and cadmium) for exchange sites in the near surface soils, and possible elution of copper ions due to the tendency to attain equilibrium with respect to solubility limits producing a "roll-over" effect for the displaced copper.

For zinc, displacement patterns similar to copper were observed wherein concentrations passing ISP-1 often exceeded those added, indicating again that desorption or solubilization from the soil had occurred through the upper 30 cm of the Everett column. Though eventually sample concentrations for zinc went below the initial feed level of 750 μg/l at the ESP, they remained at a level approximately 50% of that value (refer to Figure D.12). Though there was a steady decrease in zinc concentrations with each lower port, zinc continued to be observed at the ESP throughout the runs, indicating a small to

143

moderate affinity for the soil. There was also evidence of this fact in the batch experiments where an average of 18% removal was achieved in Everett.

The attenuation patterns of Everett for each metal were distinguishable. Cadmium and lead were attenuated primarily within the top third of the soil column with resulting final concentrations at the ESP reduced to background levels. Copper and zinc showed desorption or dissolution in the top two-thirds of the column and concentrations were eventually reduced to no less than 50% of their initial values. Observation of resulting trends and behavior of each metal showed Everett still possessed the ability to attenuate the metals, i.e. the sorption sites were not fully occupied. Note however, that there was mass reaching the ESP or the lower boundary.

By inspection of Figure D.13, an organics "washing" effect may have occurred in Everett. With background concentrations in the feed water averaging 5 µg/l, the observed increase in TOC from the samples were due to some dissolution and/or leaching. Note, that without the addition of supplemental NOM, a progression of the peak TOC concentrations can be observed moving down the column in the each of the sequential loadings, ultimately yielding fairly constant values during runs 4 and 5. Seemingly, by this time, all of the organic carbon that could be "washed off" the soil did so by the third run. This observation shows much different organic characteristics can develop within the soil over time in as little as five events.
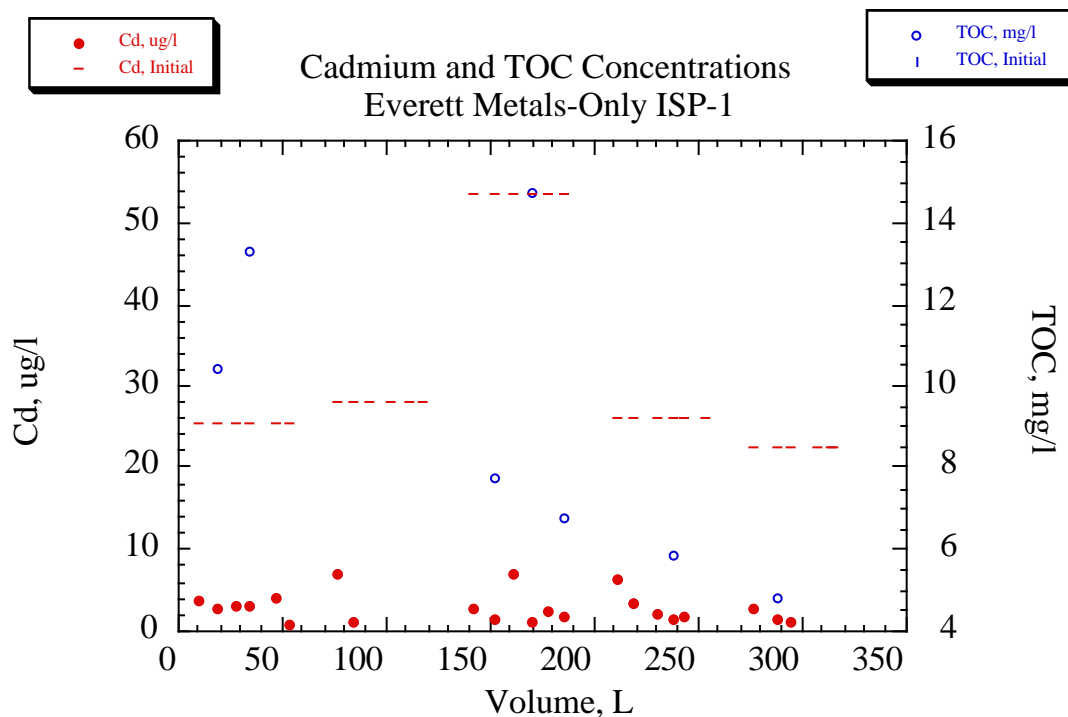
Figure D.9   Cadmium Concentrations from Everett Metals-only (ISP-1)
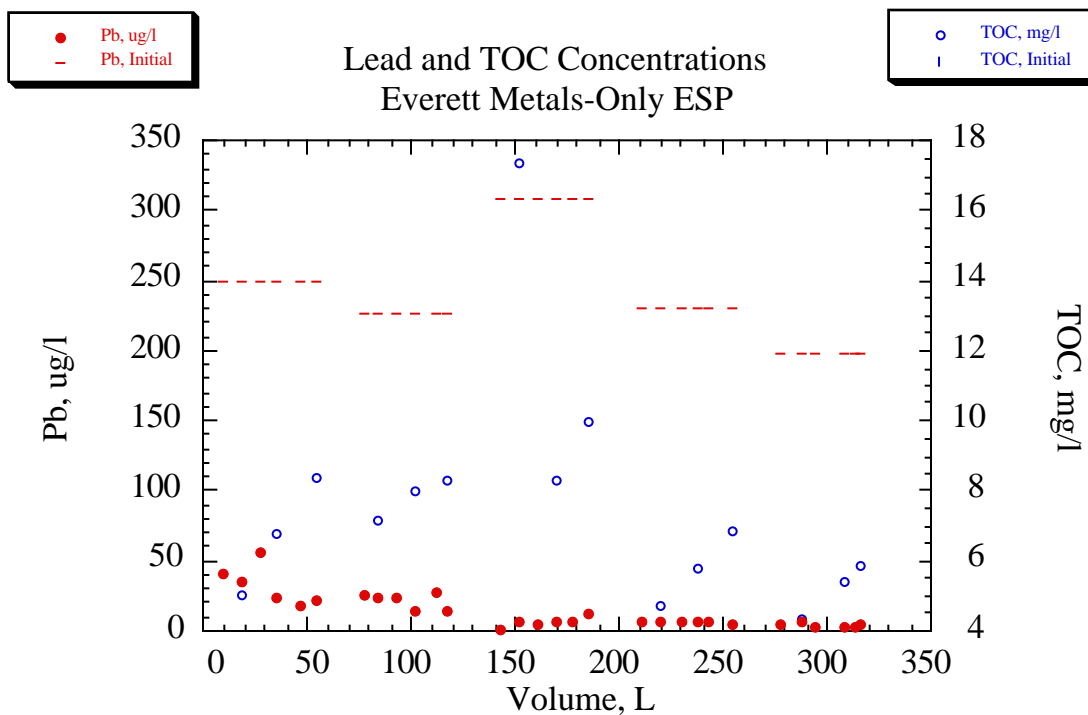(sample concentrations below 5 µg/l)

Figure D.10   Lead Concentrations from Everett Metals-only (ESP)
(sample concentrations fell below 25 µg/l)
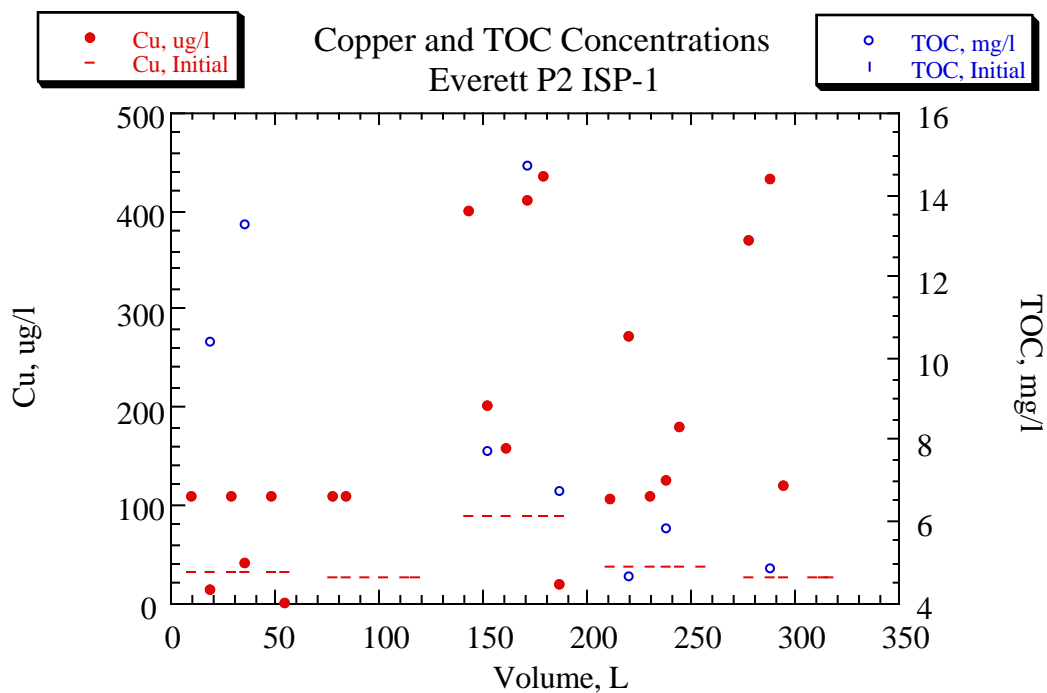
Figure D.11a   Copper Concentrations from Everett Metals-only (ISP-1)
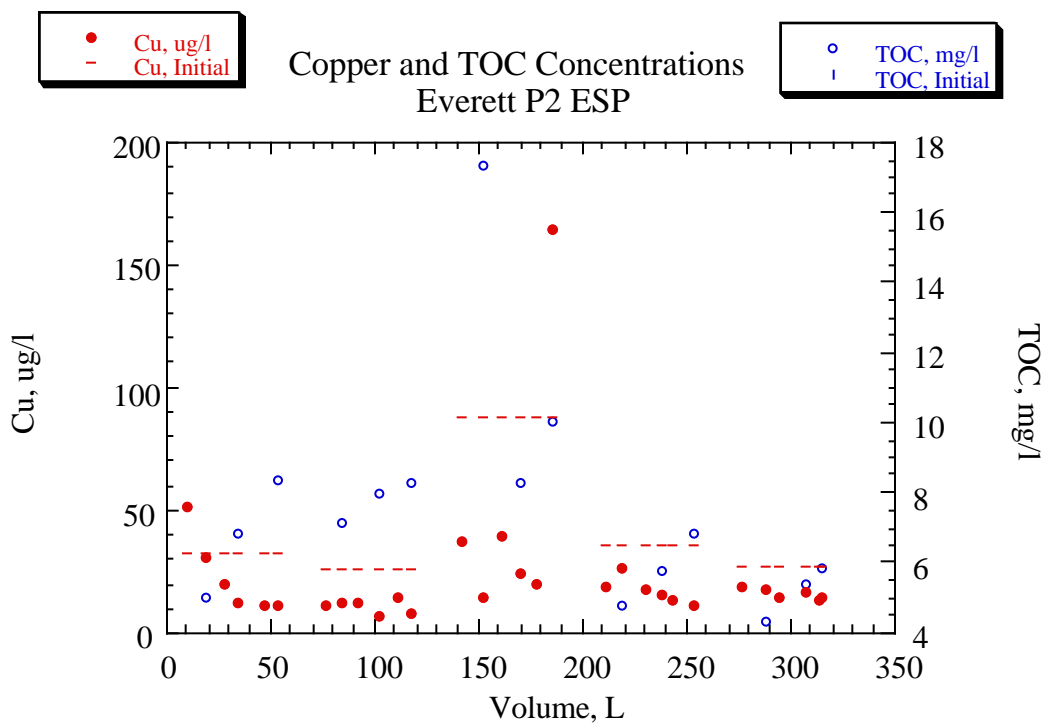(sample concentrations exceed initial concentrations)

Figure D.11b   Copper Concentrations from Everett Metals-only (ESP)
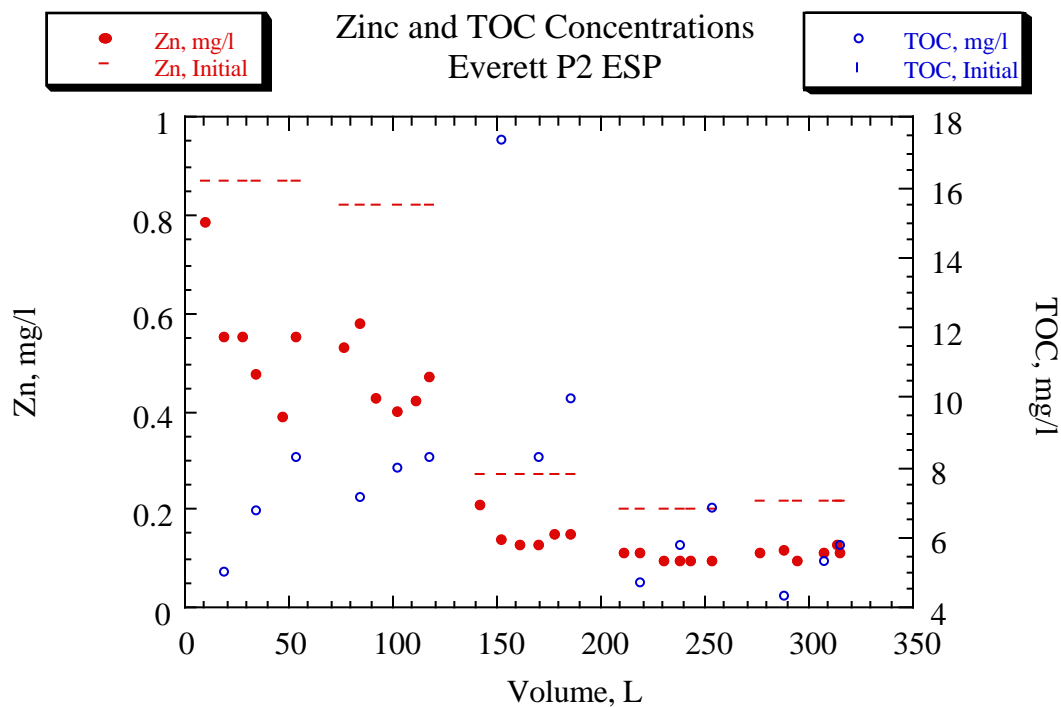(concentrations reduced to below initial concentrations)

146

Figure D.12   Zinc Concentrations from Everett Metals-only (ESP)
(sample concentrations decrease after second run, i.e. 120 L)
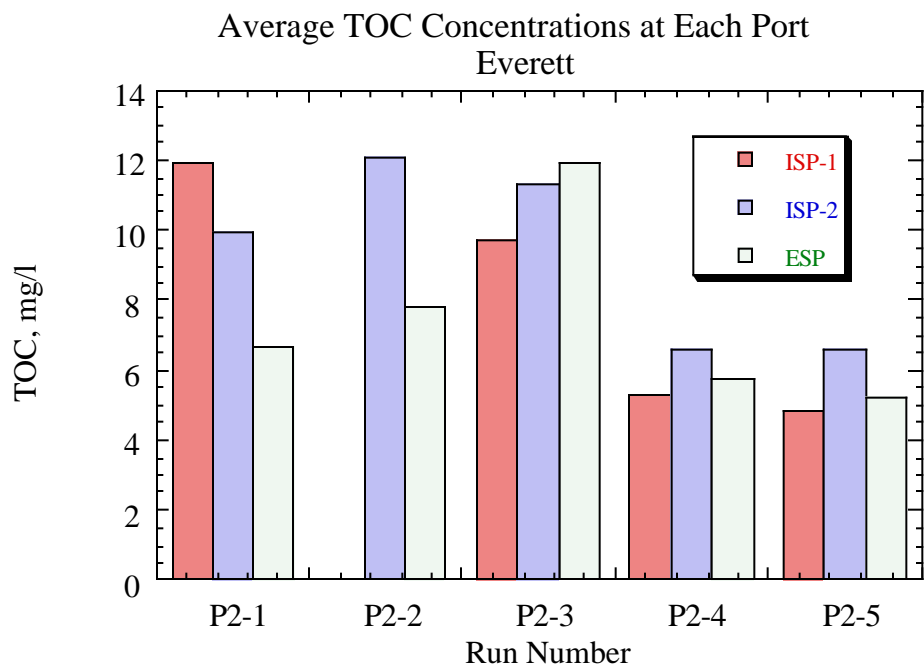
Figure D.13   Average TOC Concentrations from Everett Metals-only

Springdale Soil Column Results. The next metals-only stormwater loadings were applied to Springdale soil. Figure D.14 shows that lead concentrations measured from the first three runs were near detection levels with an increasing trend after the third loading. Cadmium concentrations measured from each of the ports remained below 10 µg/l. Similar to the Everett results, cadmium and lead were effectively attenuated by Springdale, though not to the extent that Everett achieved, likely due to the lower CEC and organic content.

The upper-layer desorptive effects associated with copper were further exacerbated relative to the Everett soil behavior, resulting in extremely poor removals. Although the increase in copper concentrations were not as large as in Everett, Figure D.15 shows that the effluent (ESP) concentrations exceeded the initial values for many of the samples throughout the five runs. Moreover, the concentrations from each of the ports were about the same, suggesting minimal attenuation of copper throughout the length of the column. This result indicates a possibility that solubility controls with respect to carbonates and other inorganic ligands may have been present. In addition, sorption of the solubilized species of copper was even less attenuated, because of the generally lower CEC and organic content of Springdale. In this case sorption/exchange may have been non-existent because of the speciation of the copper after dissolution from the soil as inorganic complexes.

Zinc removal was poor and several samples taken from each of the ports had measured concentrations above the feed solution. Concentrations were at or around the initial concentrations of 750 µg/l, even at the exit port. Additionally, because there was minimal reduction of concentration with depth, there appeared to be an equilibrium wherein zinc would remain at approximately the same concentration either due to solubility equilibrium or attainment of the soil sorption capacity.

To define the attenuation patterns on a sequential pore volume basis is nearly impossible. Nevertheless, the general conclusion is that cadmium and lead are attenuated to

a greater extent than copper or zinc. Furthermore, as with Everett, the existing copper and zinc were apparently desorbed, formed complexes with inorganic ligands, or were simply from the Springdale soil which had much lower affinity for the soil than the free ion.

Figure D.16 shows samples from the Springdale soils had very low TOC concentrations, averaging less than 4 μg/l. There are some questions as to the validity of the measured values for this set of runs because of possible equipment maintenance problems. Standards were intermittently sampled during analysis, most falling within acceptable error. However, after the samples from the third run were tested, it was discovered that debris formed a plug in the tube measuring total carbon. After the equipment was cleaned, the readings for TOC increased slightly for the samples taken from the final run. If reliable, the data might be explained under two rationales: either no organic carbon leached from the Springdale soil, and/or those present in solution tended to sorb to Springdale. In any case, the average concentrations from the last trial are not much different than the final run for Everett. In other words, even though Everett had a higher initial soil organic content than Springdale, the TOC concentrations leached from both soils were very similar after only five events. With this in mind, it might be concluded that initial soil analysis for candidate soils may not be accurate predictors of long-term soil characteristics when infiltrating water changes the in-situ soil properties as the soil is loaded, e.g. leaching of the organics. This is an important consideration when designing an infiltration facility's projected design life based on an assumed constant parameter such as organic content.
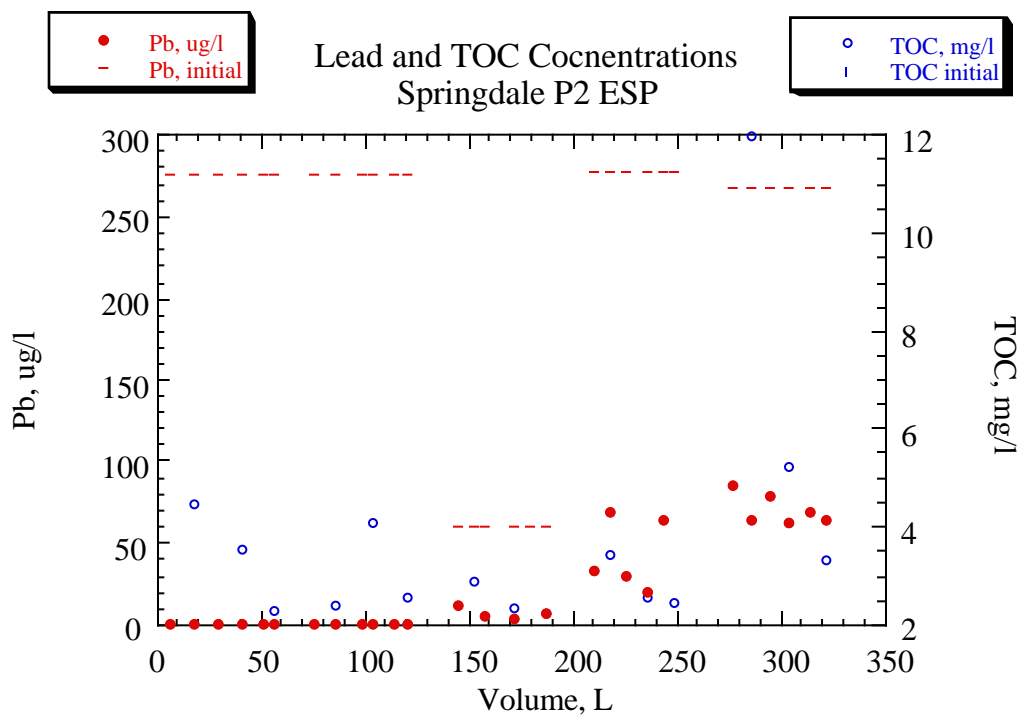
Figure D.14 Lead Concentrations from Springdale Metals-only (ESP)
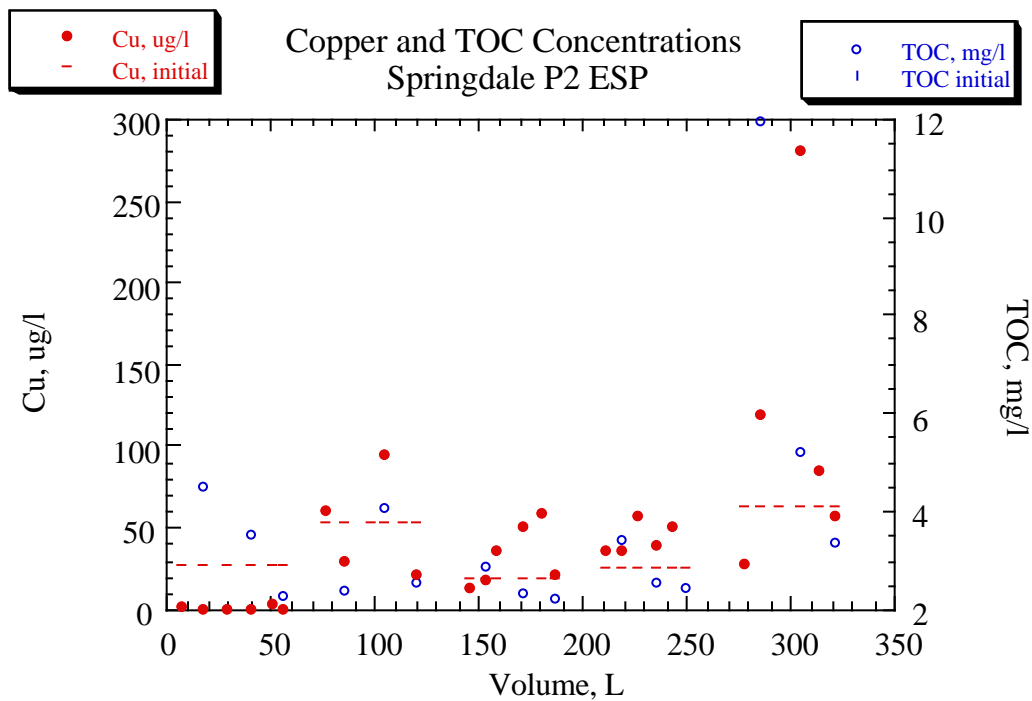(increase in sample concentrations during last two runs)

Figure D.15 Copper Concentrations from Springdale Metals-only (ESP)
(sample concentrations continue to exceed initial concentrations at exit)
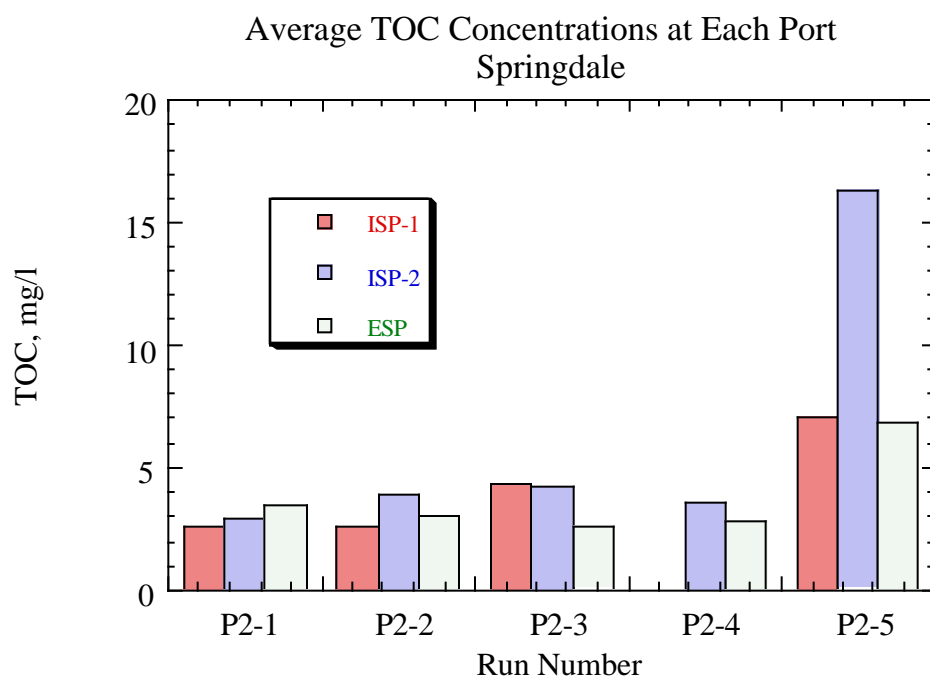
150

Figure D.16   Average TOC Concentrations from Springdale Metals-only

Garrison Soil Column Results. The final soil tested for metals-only loadings was Garrison. There was noticeable improvement in the attenuation of all four metals, with cadmium and lead being nearly completely attenuated in the upper-third of the column. Throughout these experiments, cadmium remained near detection levels (less than 2 µg/l) at ISP-1, while lead concentrations were generally less than 10 µg/l. Lead and zinc were both removed effectively, with concentrations reaching the ESP at or near background levels (see Figure 4.17a. and 4.17b.). Again, as lead and cadmium were effectively removed through the upper third of the column, some zinc and copper concentrations exceeded initial feed values at ISP-1. This result is confirmation of the competitive sorption effects and possible dissolution and complex formation displayed by both of the previous soils.

As a note of problems of sort, samples from ISP-2 yielded much higher concentrations than ISP-1, but it is suspected that these five fold increases are due to sampling faults generated by large suctions applied via the sampling syringe which caused unnatural desorption from the soil (see Figure 4.18). As was mentioned in Chapter 3, a vacuum often formed at ISP-2 which necessitated increased suction to be applied in order to extract a large enough sample for testing. This may have forced excess copper to desorb.

Though no NOM was added to this set of Garrison metals-only tests, relatively high TOC concentrations were measured from each port (Figure D.20). It is believed that non-equilibrium dissolution of organics had taken place from the organics-rich Garrison. Demonstrating this fact are the data in Figures D.14 and D.15, which show the general pattern of decreasing TOC concentrations within each trial. Between loading events additional time was available for organic matter to go into solution as the pore water essentially "sat" in the column or redistributed at a very slow rate. As a result, the early samples taken from each port yielded higher concentrations. As water was flushed through the column, pore water NOM's were eluted and could not be replaced at a dissolution rate

(in comparison to the local residence time of the water) sufficient to produce equilibrium, and yielded decreasing TOC concentrations during the run.

Due to the much higher organic matter present within Garrison soil, the "washing" effect observed in Everett did not take place. The five loadings were insufficient to remove the leachable organics at its dissolution rate. One important point to make is that the TOC concentrations from Garrison were much higher than the feed solution implying organics were definitely leached from Garrison. But at the same time, metals concentrations, especially copper and zinc, were greatly reduced. This suggests metals did not coordinate with the organics that were leached, i.e. the organics which tended to be in solution did not coordinate with the metals to any great degree.
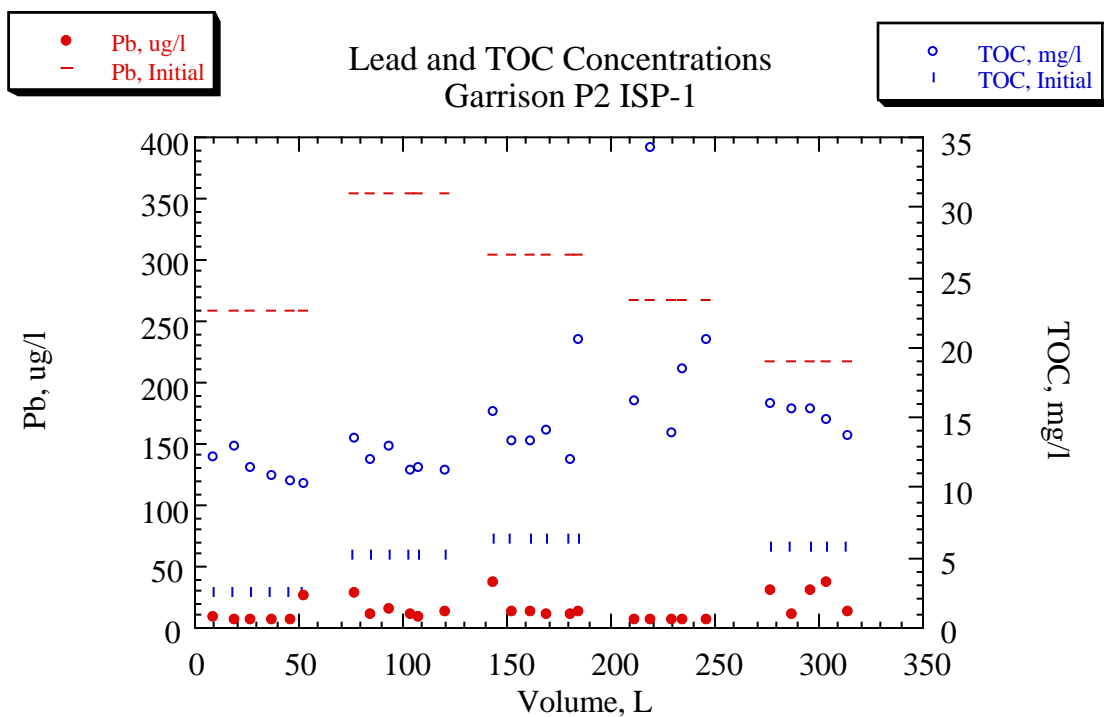
Figure D.17a   Lead Concentrations from Garrison Metals-only (ISP-1)
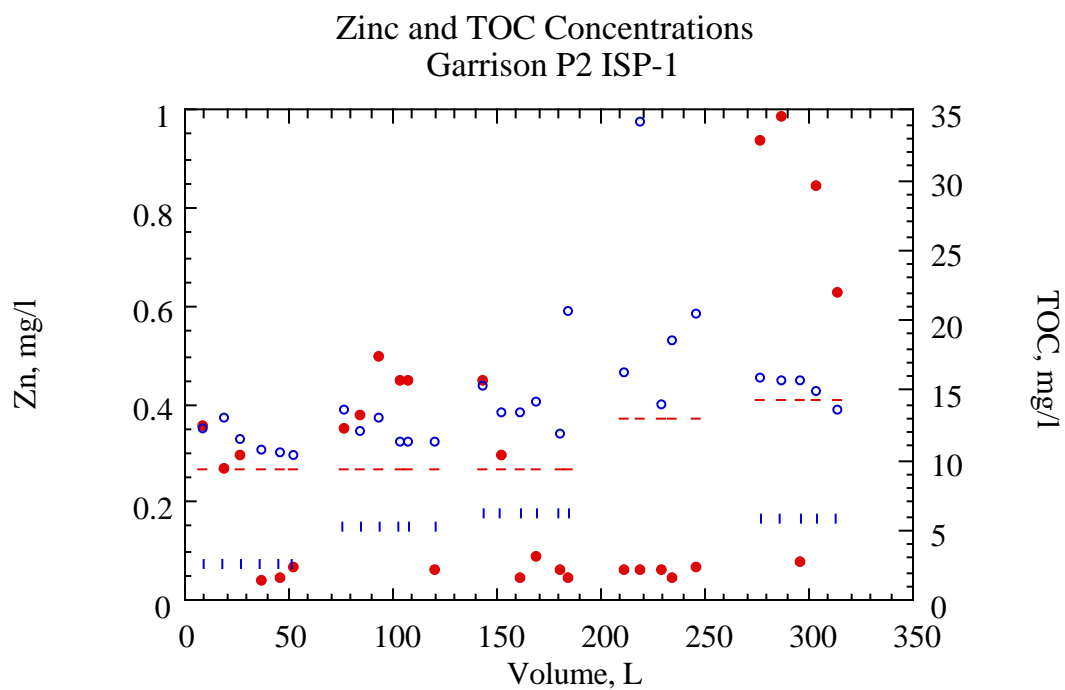

Figure D.17b   Zinc Concentrations from Garrison Metals-only (ISP-1)
(sample concentrations of lead are reduced significantly by first port, while
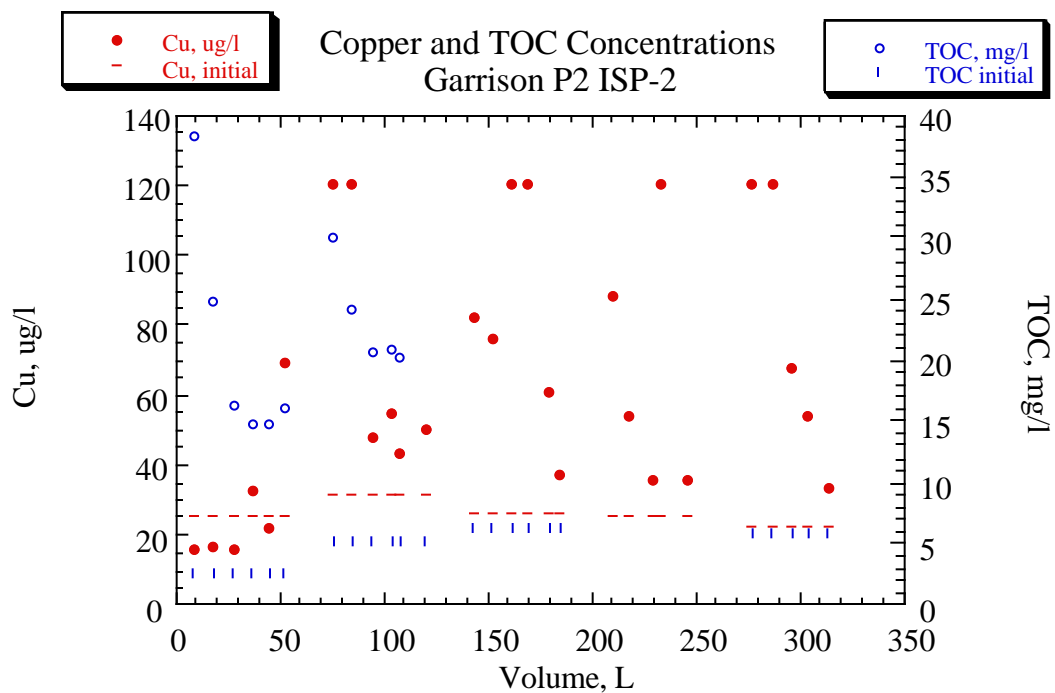zinc concentrations exceed initial concentrations for several samples)

154

Figure D.18   Copper Concentrations from Garrison Metals-only (ISP-2)
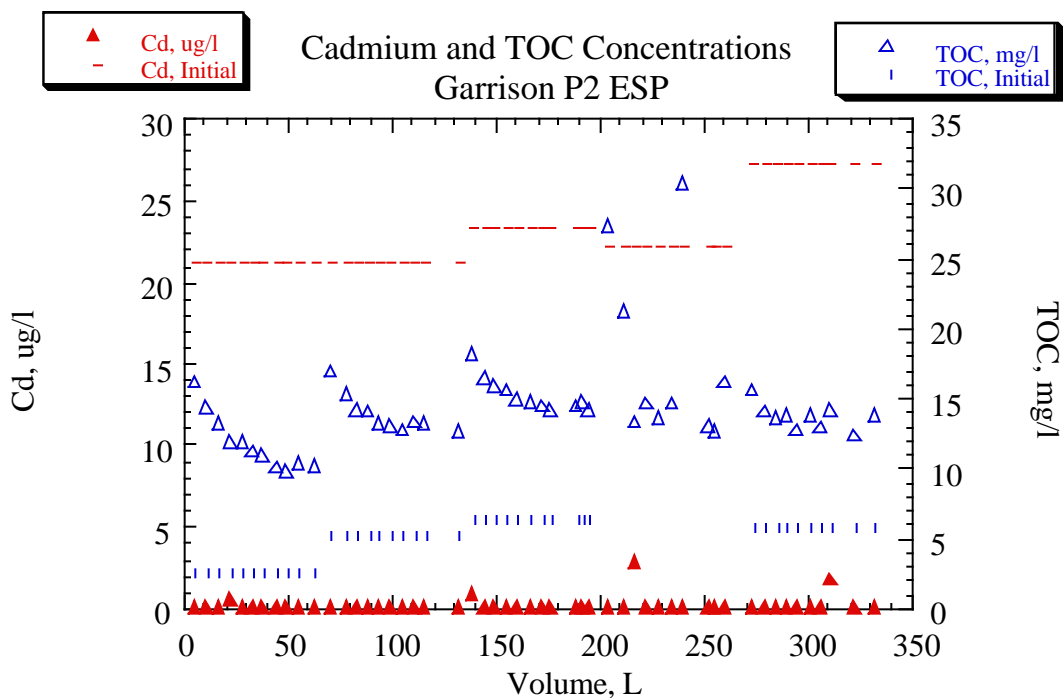(concentrations exceed initial concentrations five-fold)

Figure D.19   TOC Non-equilibrium Dissolution

Average TOC Concentrations from Each Port
Garrison

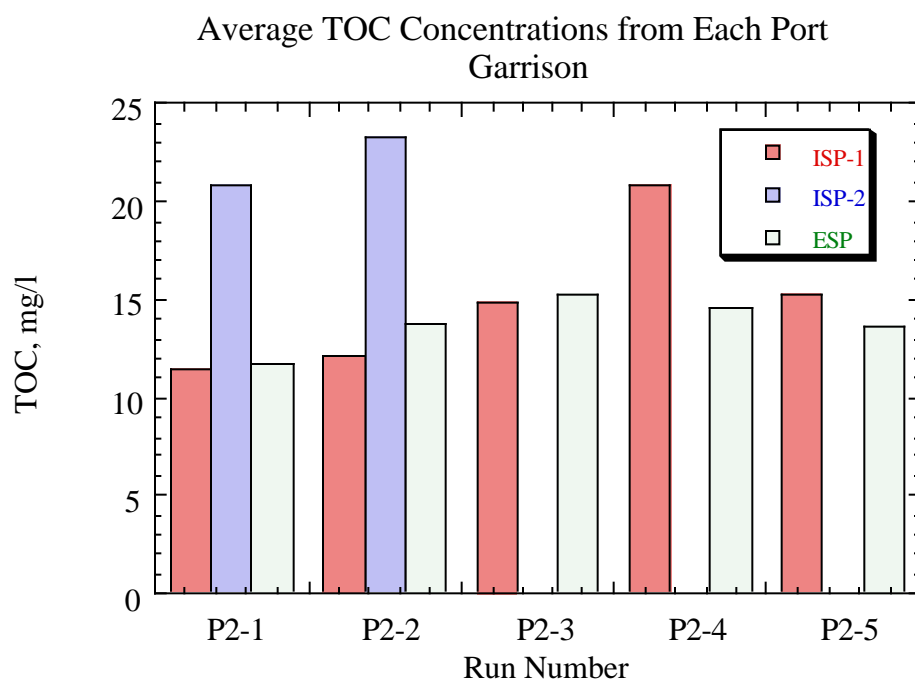**Figure D.20   Average TOC Concentrations from Garrison Metals-only**
(no available data from ISP-2; Garrison leaches high concentration of organics)

RESULTS OF METALS-NOM EXPERIMENTS:
Metals and TOC Concentrations

Presented below are the results for the metals-NOM stormwater loadings. For consistency, the following discussion is presented in a similar format to the metals-only results, and select plots are, again, included in this section which highlight points concerning the metals-NOM sample concentrations. TOC concentration data are also included in the following figures and will be referred to when discussing NOM effects. The remaining plots can be found in Appendix C.

Everett Soil Column Results. Similar to the results in the metals-only tests, the samples from Everett soil at ISP-1 showed little or no breakthrough for cadmium and lead and moderate or almost no net attenuation of copper and zinc (see Figures D.21a and D.22a). The reductions to approximately 8% of the initial concentrations for both cadmium and lead revealed greater removals (almost 10% more) within the upper soils as compared to those observed for the Everett metals-only experiment. Zinc, too, experienced greater early removal, being reduced by some 50% of its initial concentration prior to ISP-1. Furthermore, although not actually removed, copper tended to desorb to a lesser extent. These facts suggest the organics may be providing a greater sorption capacity in the upper soil for the sorption of the metals, most notably copper and zinc, and any inorganic complex species. As a result, the concentrations of each of the metals at the ESP (again compared to the metals-only results) were lower (see Figures D.21b and D.22b). In fact, the ESP concentrations for zinc, cadmium, and lead were all reduced to near detection levels, while copper was reduced to levels between 15% and 20% of the initial value.

For TOC, the concentrations throughout the column showed an increasing trend with each run. Although the ISP-1 TOC concentrations were reduced to approximately 10% of the initial concentrations (40 mg/l) during the first run, the concentrations steadily increased through the remainder of the loadings. This observation appears to be nothing more than the leading edge of a breakthrough curve produced under a sequence of "impulsed" TOC releases. If sustained, the resulting breakthrough curve at ISP-1 (as

157

shown in Figure D.21a) would "plateau" at a concentration less than the feed due to the true temporal nature of the release. This fact may already be in evidence in runs 4 and 5. In other words, if the sequential pulse loadings of runoff were regarded as a continuous feed scenario, Figure D.21a shows the retarded, dispersed front of an "organics wave". In this state, the soil at depths less than or equal to ISP-1 (i.e. closer to the surface) are essentially saturated with added NOM's and, as such, present a potential condition of maximum attenuation capacity given that the organics and the existing soil are the predominant exchange/sorption sites. Moreover, the perturbations shown between loadings is concluded to be a reflection of the non-equilibrium dissolution kinetics occurring during the periods of essentially stagnant hydraulics in which the soil moisture is slowly redistributing. To strengthen this argument of breakthrough for the TOC, similar data can be seen in that observed for the ESP (Figure D.21b). Here, however, there is a lag-time followed by a more drawn-out "plume" possessing a lower peak.
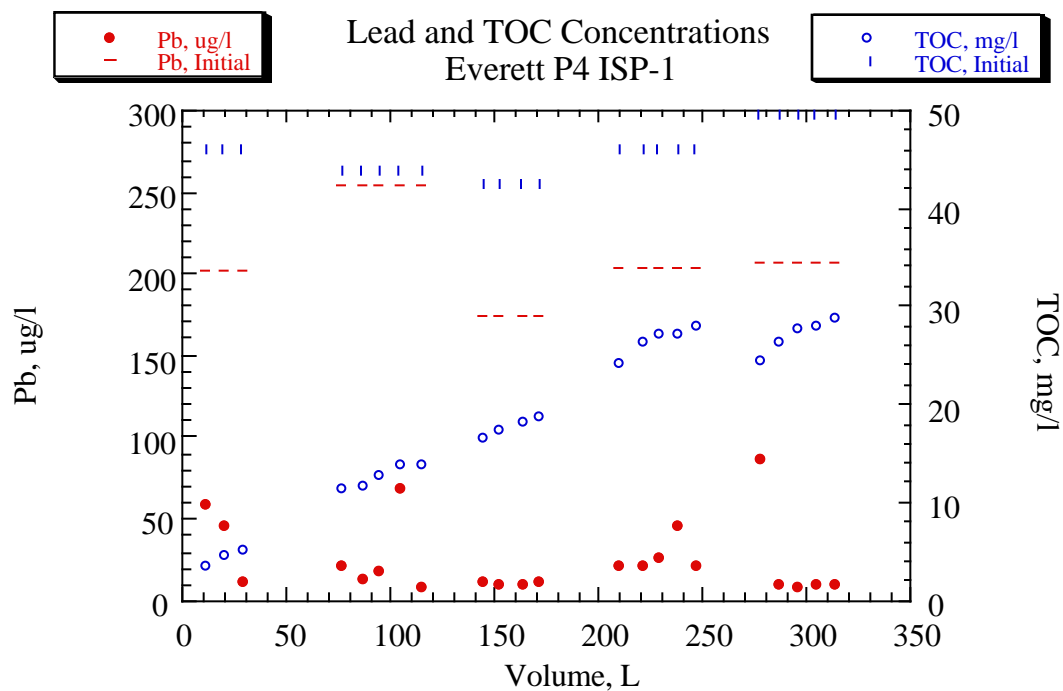
Figure D.21a   Lead Concentrations from Everett Metals-NOM (ISP-1)
(sample concentrations significantly reduced by port 1)
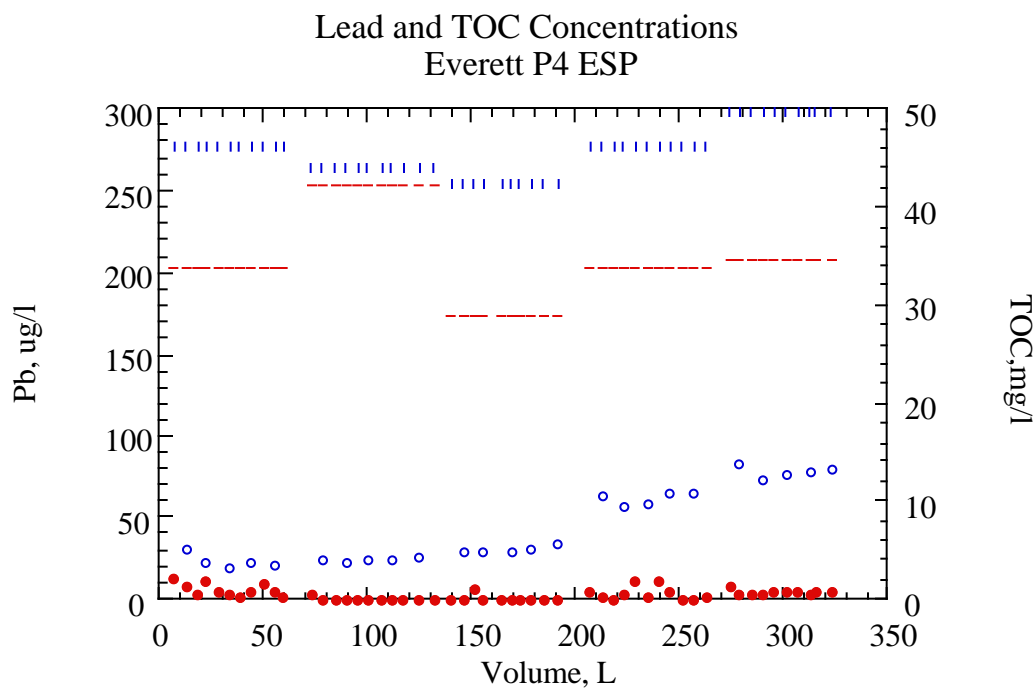

Figure D.21b.   Lead Concentrations from Everett Metals-NOM (ESP)
(sample concentrations near detection levels at exit port)
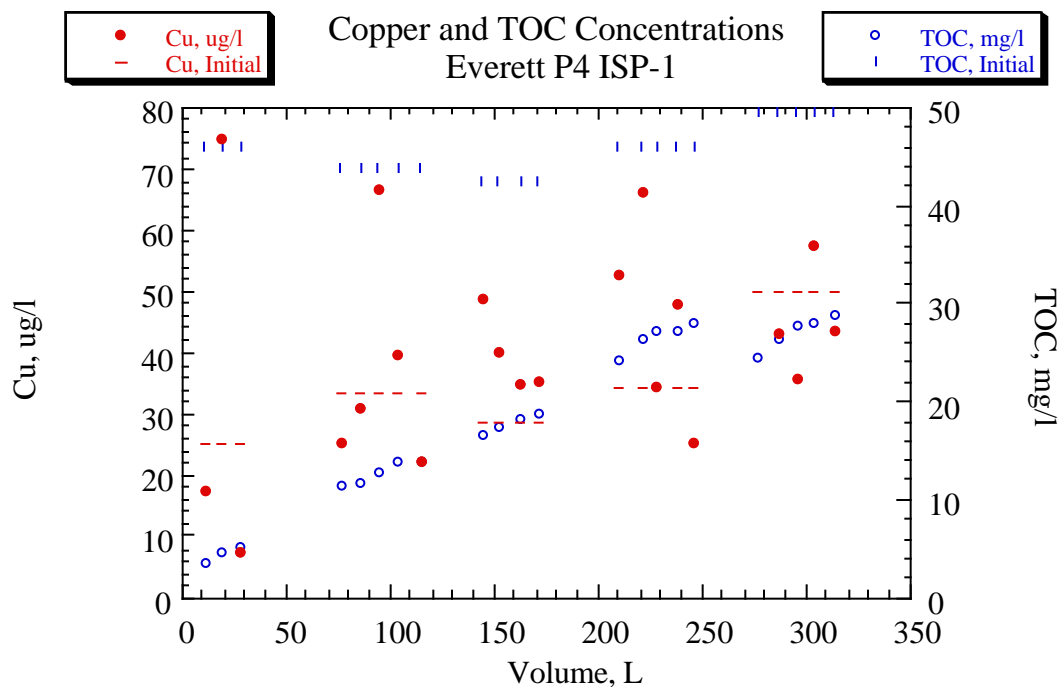
Figure D.22a   Copper Concentrations from Everett Metals-NOM (ISP-1)
(sample concentrations above initial concentrations)
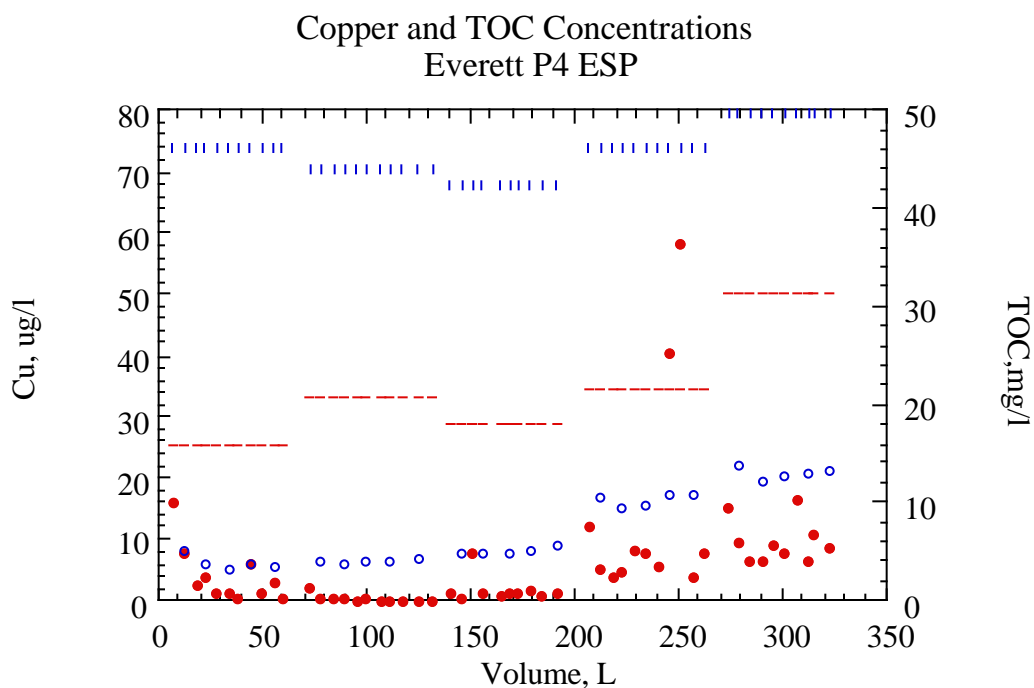

Figure D.22b   Copper Concentrations from Everett Metals-NOM (ESP)
(sample concentrations increasing trend after third run)

Springdale Soil Column Results. As in the metals-only tests with Springdale, cadmium and lead concentrations were again greatly reduced by the time samples were taken at ISP-1. Cadmium sample concentrations were below 2 µg/l throughout the column and near detection limits at the ESP. Although variable, lead concentrations were typically below 25 µg/l at ISP-1 and less than 10 µg/l at the ESP. In a now predictable fashion, a majority of the mass for these two metals was removed within the top third of the column.

Copper and zinc sorption increased as well. As Figures D.23a and D.23b show, zinc concentrations were reduced to less than 50% of the initial concentrations at ISP-1, but not reduced to any greater degree throughout the rest of the column. Note, however, that no desorption occurred from any of the three ports, unlike the case for the metals-only runs. Similarly, copper was not desorbed/solubilized to the extent it was during the metals-only experiments. Concentrations of copper from ISP-1 remained generally less than initial concentrations. The final concentrations sampled from the ESP were reduced to approximately 35% of the initial concentrations. Figures D.24a and D.24b show the comparison between the first and last sampling port for copper discussed above.

As in Everett metals-NOM tests, the concentrations of each of the metals at the ESP (again compared to the metals-only runs) were lower. The ESP concentrations for cadmium and lead were reduced to near detection levels, while copper and zinc remained well below their initial concentration. This result is unlike the metals-only runs when copper remained at approximately the initial values. These observations again suggest the added NOM produced increased attenuation of the metals, primarily for copper and zinc. Unfortunately, TOC samples from the first three runs could not be analyzed. TOC samples did not preserve long enough during the period when the TOC analyzer was under repair and maintenance.The results obtained from ISP-1 from the last two trials showed no distinguishable trends. However, the ESP results did seem to show a pattern of elution. The TOC concentration starts low then increases to a near steady state. The first sample

taken with low concentration is likely the residual water in the column which allowed the dissolved organics adequate time to equilibrate with the soil. As the "new" water travels through the column, less time is available for the same amount of sorption to occur. Like the Everett soil, organics were attenuated by Springdale as indicated by the reductions in TOC with depth.

Garrison Soil Column Results. Due to uncontrollable circumstances, the data for the Garrison metals-NOM run was deemed unusable. During the procedures, extremely low infiltration rates were observed which resulted from the formation of a low permeable layer at the bottom of the Garrison column (probably due to the washing of fines). Although measures were taken to attempt to "break-up" this layer, hydraulic failure persisted and the experiments were stopped. No useful data was obtained.

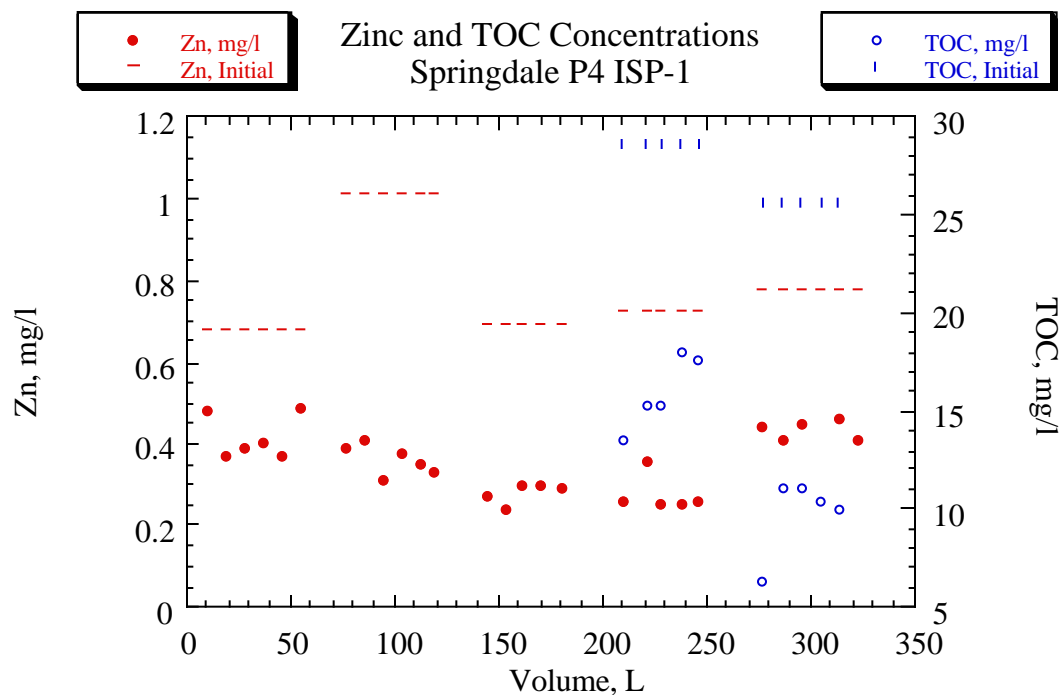**Figure D.23a   Zinc Concentrations from Springdale Metals-NOM (ISP-1)**
(sample concentrations reduced to approximately   half initial concentrations)

Figure D.23b   Zinc Concentrations from Springdale Metals-NOM (ESP)
(sample concentrations not significantly reduced from port 1 to exit port)

163

Figure D.24a Copper Concentrations from Springdale Metals-NOM (ISP-1)
(sample concentrations reduced slightly from initial concentrations at port 1)

Figure D.24b   Copper Concentrations from Springdale Metals-NOM (ESP)
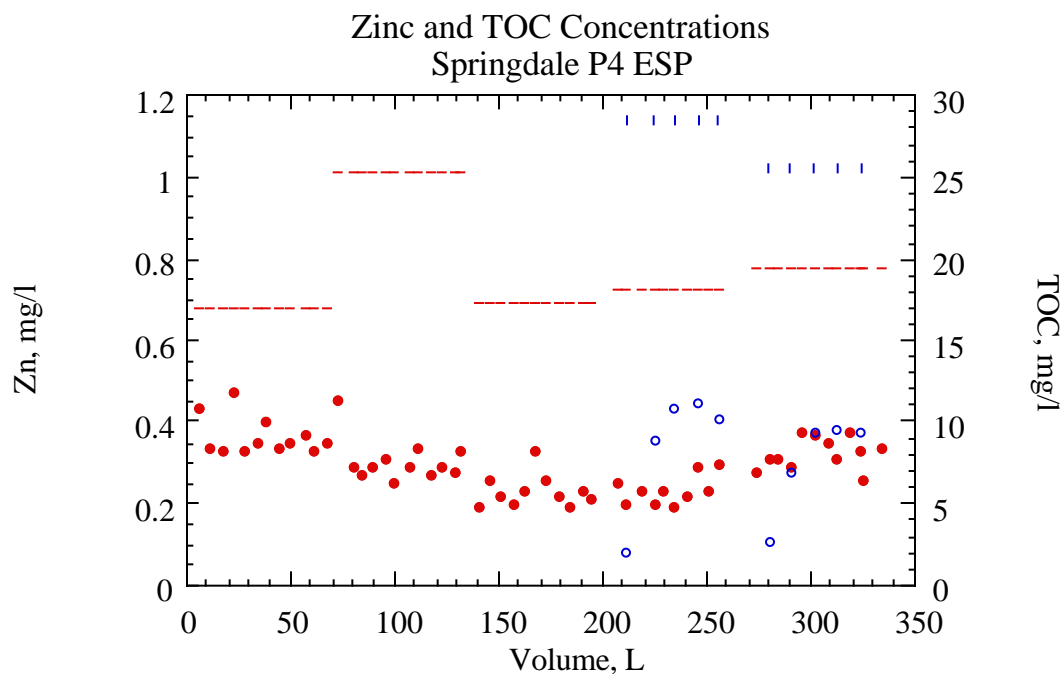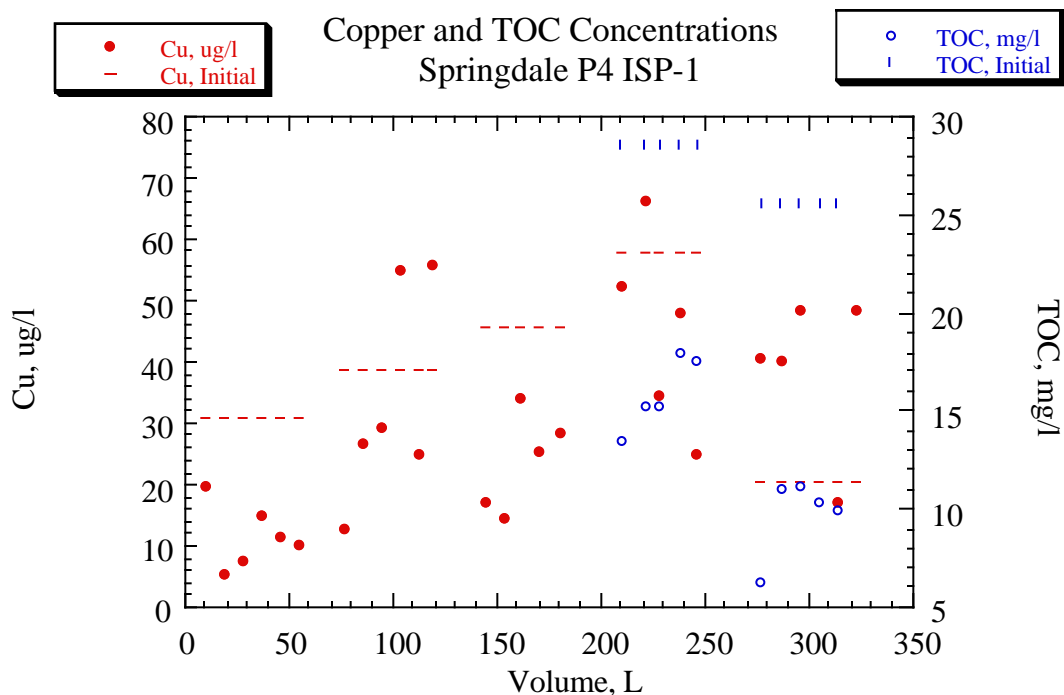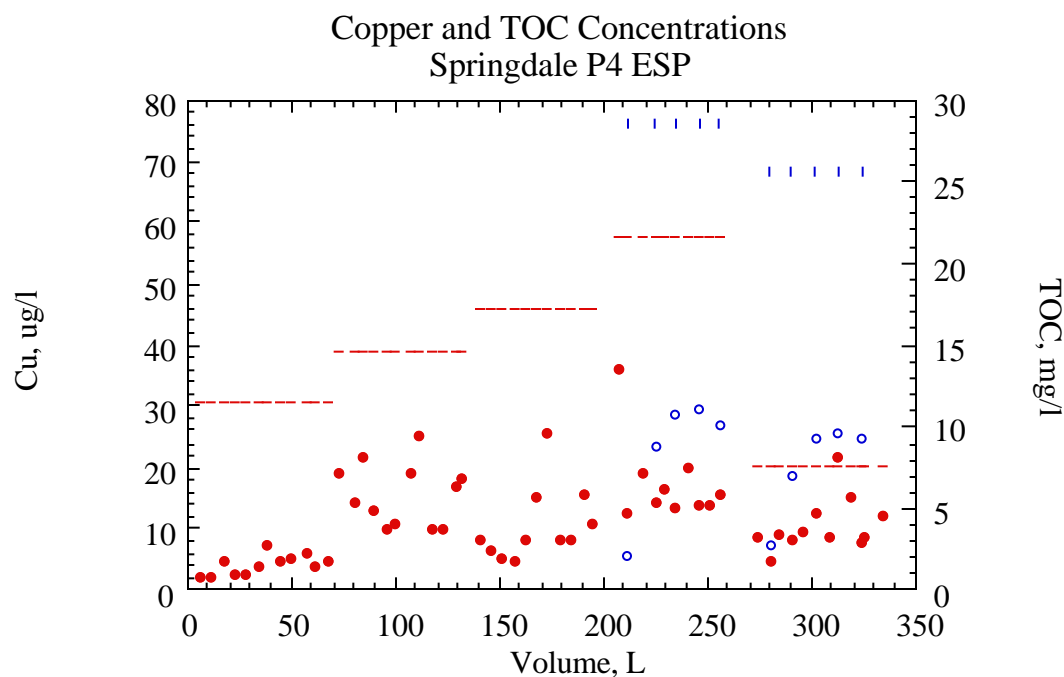(sample concentrations reduced to approximately half the initial concentrations)

Appendix E

SOIL DESSICATION-CRACKING AND PREFERENTIAL FLOW

One of the primary advantages of infiltration is the potential to handle the large volumes of stormwater runoff. The proper choice of soils to achieve both the hydraulic and pollutant removal demands is difficult to attain because these objectives are at odds with each other. Higher pollutant removal often requires higher silt and clay content and organic content soils. Correspondingly, soils with these characteristics often have much lower infiltration rates (hydraulic conductivity). Another associated problem of soils with high silt/clay/organic content is their potential to develop dessication cracks. These cracks, if connected such that essentially conduit flow to the water table results, nullifies the engineer's soil selection to achieve pollutant removal. Ironically, it is the soils with the greatest pollutant removal capabilities which also have the greatest potential to develop these rapid transport paths.

The soils in this study were oven dried to investigate potential problems in the field due to the potential development of preferential flow paths formed from these cracks. The soils were packed into permeameter cells under packing procedures in ASTM D-5084. They were then dried in an oven for 24 hours at 100 ˚C. Four soils were tested including: Garrison sandy loam, Springdale sand and the two Loamy sands Alderwood and Everett. Alderwood had a slightly greater silt content than Everett.

As suspected, the results indicated that the soils with the higher silt and clay content showed formation of cracks in the surfaces, i.e. in Alderwood and Garrison. Garrison which had significant clay content and also high organic content showed some separation along the walls of the permeameter, indicating a tendency for shrinkage. There was no indication, however, that the cracks were connected to a significant degree through the entire depth of the permeameter. The sand showed no crack formation at all.

Figure E.1 Garrison/Springdale Dessication. Shown above are Garrison sandy loam (left) and Springdale sand (right) after drying in an oven for 24 hours to investigate dessication crack formations. Garrison showed some shrinkage and separation from the cell walls. Springdale sand showed no observable crack formations or shrinkage.

Figure E.2 Alderwood/Everett Dessication. Shown above are Alderwood loamy sand (left) and Everett loamy sand (right) after drying in an oven for 24 hours. Alderwood showed no separation from the cell walls, but dessication cracks were observable from the soil surface. Everett showed minimal to no crack formation.

167

Appendix F

REVIEW OF CONTAMINANT-COLLOID TRANSPORT MODELS

The models presented here are either one dimensional representations or have been simplified accordingly. Thus, the reader should be aware that higher dimensioned models are easily achievable at the expense only of computational complexity and possible numerical stability.

COMET (EPA). The EPA multimedia exposure assessment model CML contains a colloid–metal transport model (COMET (Mills *et al.*, 1991)) which casts transport of multiple species of bulk dissolved (truly dissolved and colloidal) contaminants in terms of the classic CDE. An equilibrium, linear model accounts for sorption of the contaminant to multiple colloid species, and, independently, to the solid matrix. Simplification of COMET to a single dimension along the direction of flow and for a single species each of metal and colloid yields

$$(R_d + K_{pc}S_c)\frac{dC_m}{dt} + (U + U_cK_{pc}S_c)\frac{dC_m}{dx} = \frac{d}{dx}D_e\frac{dC_m}{dx} \qquad (F.1)$$

where
C_m = total (dissolved + colloidal) mobile concentration of contaminant;
K_{pc} = partitioning coefficient of contaminant with colloid;
S_c = colloid concentration;
U = pore water velocity;
U_c = effective velocity of colloid;
D_e = effective dispersion coefficient, which accounts for the sum of hydrodynamic dispersion of the soluble contaminant (D) and the hydrodynamic dispersion of the colloid (D_c), defined by
$$D_e = D + D_c = D(1 + S_cK_{pc}) \ ;$$
R_d = retardation of the contaminant resulting from partitioning onto the immobile solid matrix, defined by
$$R_d = 1 + K_{ps}\frac{\rho_b}{\eta}$$

where
K_{ps} = partitioning coefficient of contaminant with immobile solid matrix;
ρ_b = bulk density of the porous medium; and
η = saturated porosity of the porous medium.

As can be seen for the one–dimension, single specie case above, parameterization of the model requires estimation of K_{ps} for each metal specie and K_{pc}, U_c, and D_c for each colloid specie. It was shown in Mills *et al.* (1991) that the model is particularly sensitive to partitioning coefficients; consequently, sufficient quantification of K_{ps} and K_{pc} would probably require laboratory–scale experiments. Thus, proper parameterization of the model for even relatively simple systems would require extensive and costly laboratory research when considering multiple species.

A major assumption of COMET is that the interaction of the colloid with the solid matrix is completely described in terms of an effective velocity, U_c. There is some utility in using the effective velocity approach and decoupling the reaction between the colloid and the solid matrix. It incorporates retardation of the colloid and its enhanced transport (relative to the pore water) resulting from size exclusion processes. However, the approach decouples the fundamental processes affecting the effective colloid velocity and reduces it to a fitting parameter that would not delineate these mechanisms in the study of a complex system.

Magee *et al.* (1991) and Corapcioglu and Jiang (1993). Magee *et al.*, (1991) present a modified retardation factor for the mobile contaminant that accounts for partitioning of the colloid onto the immobile solid matrix (K_{cs}):

$$R^* = \frac{(1 + K_{pc}S_c + K_{ps}\rho_b/\eta)}{1 + \dfrac{(U_c/U)K_{pc}S_c}{1 + (K_{cs}\rho_b/\eta)}} \qquad (F.2)$$

This relationship is approximately equivalent to the retardation factor used in COMET ($R_d + K_{pc}S_c$) when partitioning of the contaminant to the colloid is weak and for low colloid concentrations. Thus, it appears that (F.2) may be more applicable over a wider range of colloid–contaminant concentrations. Its applicability over (F.1) is further extended by incorporating a complete description of colloid transport in terms of retardation

(due to sorption of the colloid to the immobile solid matrix, K_{cs}) and enhanced transport (resulting from size exclusion, U_c/U), rather than combining size exclusion and sorption (retardation) of the colloid into a single advection term as in (F.1). Otherwise, the difference in formulating the influence of the effective colloid velocity is merely an operational one: the two approaches differ only in their theoretical development. In COMET, effective velocity influences the travel distance of the colloid, while in the approach of Magee *et al.* (1991), it influences the travel time of the colloid.

One shortcoming of (F.2) is that the partitioning between the colloid and contaminant is assumed to be constant during transport, and that dissolved contaminants in solution cannot sorb to immobile (sorbed) colloids. Corapcioglu and Jiang (1993) build upon the formulation of Magee *et al.* (1991) to develop a retardation factor which accounts for the equilibrium dynamics between sorbed and mobile colloids and contaminant partitioning (in the term $\rho_c K_{pc} K_{cs} S_c$). Thus (neglecting size exclusion),

$$R^{**} = 1 + \frac{\rho_b}{\eta} \frac{K_{ps} + \rho_c K_{pc} K_{cs} S_c}{1 + K_{pc} S_c} \qquad \text{(F.3)}$$

where ρ_c = mass density of colloid.

Corapcioglu and Jiang (1993) use this retardation factor in their equilibrium model for colloid–facilitated transport:

$$R^{**} = \frac{dC_d}{dt} = D_e \frac{d^2 C_d}{dx^2} - U \frac{dC_d}{dx} \qquad \text{(F.4)}$$

where D_e is equivalent to the effective dispersion described in COMET and C_d is the dissolved (not total mobile) contaminant concentration. (An analytical solution to equation (E.4) in terms of the total mobile contaminant concentration is also presented in that study.)

The equilibrium models presented by Magee *et al.* (1991) and Corapcioglu and Jiang (1993) illustrate an important step forward in cotransport modeling. Their conceptual framework can be tailored to a wide variety of colloid–contaminant–porous media systems; they recognize the primary sorption and complexation interactions between colloids, contaminants, and subsurface media; and an analytical solution to the problem is available. In addition, their equilibrium model has been verified by experimental data and was successful in predicting contaminant transport in the presence of mobile colloids. In addition, their modeling approach was formulated upon a local equilibrium assumption and a linear sorption isotherm between contaminant, colloid, and solid matrix. This assumption may not be applicable for systems in which DOM transport is dependent upon sorption kinetics or isotherm nonlinearity (such as that observed by Dunnivant *et al.* (1992)).

Corapcioglu and Jiang (1993) recognized this limitation and developed a transport model coupled with the classic two–way electrokinetic model based upon first–order sorption/desorption rate coefficients. The reader is referred to that study for details of the approach. Despite its ability to incorporate sorption kinetics in lieu of an equilibrium approach, it does not address isotherm nonlinearity and remains unverified with experimental data. Furthermore, the simplicity of a first–order rate model is not necessarily descriptive of sorption kinetics in systems that conform to a more realistic "dual process" sorption hypothesis, where sorption is described partially by an instantaneous reaction component and partially by a rate–limited component. This could be particularly applicable in systems where diffusion into an intraparticle structure is significant.

Jardine *et al.* (1992). A promising approach by Jardine *et al.* (1992) is the first major effort to attempt to incorporate isotherm nonlinearity and nonequilibrium reaction kinetics into modeling DOM sorption. They recognized the computational complexity required to assess transport behavior in systems involving DOM; consequently, they were able to simplify modeling approaches. Recognizing that DOM is a complex mixture of subcomponents having different sorption characteristics, they make no attempt to model the

172

transport of individual components. Rather, they determined that sorption of DOM onto soil may be successfully modeled as a dual process system (i.e., "fast" and "slow," or "strong" and "weak" sites). Thus, they cast subsurface DOM transport in terms of two–site sorption, each site considering time dependent sorption and isotherm nonlinearity (described by the Langmuir formulation). They calibrated and experimentally verified components found in each of three models: CXTFIT (Parker and van Genuchten, 1984), DISPER (Fluhler and Jury, 1983), and SOTS (Selim and Amacher, 1988). A summary of the models is shown in Table F.1.

Although cotransport of contaminants is not considered in Jardine *et al.* (1992), DOM transport was successfully modeled. At low DOM concentration, single site processes with linear or nonlinear sorption isotherms were sufficient to model transport. At higher concentrations, however (> 10 mg DOC L^{-1}), two–site modeling was required to describe transport. They concluded that sorption kinetics, as opposed to isotherm nonlinearity, controlled the breakthrough behavior of DOM, characterized by extensive tailing of the breakthrough curve at long times. Thus, sorption of DOM to the media was governed by an initial rapid sorption followed by slow sorptive equilibration.

CTC — Colloid Transport Code (Jain and Nuttall, 1993). The Poiseuille flow principle is extended in the Colloid Transport Code (CTC), a model describing the transport of colloids through fractures in tuff (Jain and Nuttall, 1993).

$$\frac{dS_{cd}}{dt} = -U_{max}\left(1 - \left(\frac{y}{\delta}\right)^2\right)\frac{\partial S_{cd}}{\partial x} + D_x\frac{\partial^2 S_{cd}}{\partial x^2} + D_y\frac{\partial^2 S_{cd}}{\partial y} \qquad (F.5)$$

where S_{cd} is concentration of mobile colloids; y is the distance of the colloid from the centerline of the tube; δ is the tube radius; U_{max} is the maximum velocity of flow in the tube (i.e., flow at the centerline); and D_x, D_y are the hydrodynamic dispersion of colloidal suspension (presented as an empirical function of particle radii).

This model was coupled with another transport equation for diffusion of the colloid into the tuff (i.e., the tube walls), not shown, and with the classic electrokinetic model for sorption:

TABLE F.1 Summary of Dual Process Reactive Transport Models.

CXTFIT	A two-site nonequilibrium model in which adsorption on type-1 sites is instantaneous and reversible, and on type-2 sites follows first-order kinetics with respect to the adsorbed solute mass. Equilibrium adsorption is described on both sites by linear isotherms. Assumes that adsorption and desorption rates are equal.
DISPER	A two-site nonequilibrium model where both sites are governed by reversible first-order kinetics with respect to the adsorbed solute. Equilibrium adsorption process is defined by the nonlinear Langmuir formulation. Assumes that adsorption and desorption rates are equal.
SOTS	A two-site nonequilibrium model which describes solute retention during transport in terms of a reversible second-order kinetic approach. Does not require knowledge of isotherm shape, only sorption capacity of medium. Considers different adsorption and desorption rate coefficients.

$$\frac{dS_{cd}}{dt} = k_f S_{cd} - k_r S_{cs} \qquad (F.6)$$

where

k_f, k_r = first–order sorption and desorption rate coefficients;

S_{cs} = concentration of immobile (sorbed) colloids.

This model approaches colloidal transport through fractures and streamtubes based upon characterization of the fracture size and distribution of fractures in the subsurface. Obviously, the model's predictive ability is sensitive to these parameters, and may not be adequate for describing transport in heterogeneous media unless characterization of the fractures could be accomplished. In addition, CTC is limited to describing the transport of toxic colloids and is not necessarily applicable to describing dynamics of a contaminant–colloid–solid matrix system. Conceptually, however, the model illustrates some useful concepts that could be incorporated into a more comprehensive description of particle transport in heterogeneous media.

Modeling Cotransport in Heterogeneous Media. Approaches based upon the convection dispersion equation are useful for describing transport in uniform, homogeneous porous media. Certainly, at the laboratory scale in column experiments, they produce solutions that are quite satisfactory. However, because they do not account for media heterogeneity, their applicability to field scale systems is limited. The failure to extend a CDE model to the field scale by laboratory scale parameterization (based upon a constant degree of hydrodynamic dispersion) results from the influence of scale dependent physical heterogeneity upon the dispersive transport of the solute and the failure of the Fickian diffusion model in the CDE to describe dispersion across a range of scales (Freeze,

1975). Further, it is widely recognized that physical heterogeneity governs advective transport by providing preferential flow paths (streamtubes characterized by a velocity significantly higher than the ensemble average velocity). Thus, dispersion of a solute plume may result not from the classical concept of dispersion (hydrodynamic dispersion resulting from pore scale velocity gradients, and diffusion) rooted in the CDE, but from the result of widely variable advection via preferential pathways.

Prevalent in some types of heterogeneous media are preferential pathways resulting from fractures, such as in volcanic tuff formations. Corapcioglu and Jiang (1993), invoking the principle of Poiseuille flow through a tube, recognize that the parabolic velocity distribution in the streamtube will result in colloids traveling along the tube's centerline being transported faster than the mean pore water velocity. Conversely, the velocity along the walls of the tube will be less than the tube's mean velocity, resulting in a retarded velocity of the colloidal particles relative to the mean pore water velocity. Consequently, the colloids will be more susceptible to interactions with the walls of the tube, further enhancing retardation.

Appendix G

DETERMINING LOADINGS AND PRE-SCREENING

SOILS FOR METALS

The values for soil background concentrations of metals listed on page 65 were not obtained through experimental measurements. These values were meant to be suggestions based on both literature review and indirectly through the results of the soil column experiments. The following was the basis for determining the recommended values.

1. Values of background concentration of contaminated soils (sewage sludge soils, fly ash soils, and soils near smelters) and typical "clean" soils were reviewed, as well as values for hazardous waste designated soils.

2. The background values of the three Washington State soils tested in this study were determined using a nitric acid digestion procedure described in the methods section). These were compared to the soils' effectiveness in removing the metals from the infiltrating runoff.

3. Values were chosen such that they were lower than the concentrations in the "ineffective" soils tested and greater than the "effective" soils, but not above typical background concentrations of natural soils.

Table G.1 Typical Background Metals Concentrations μg/g of Soil

Metal	Range	Median
Cd	0.01-1	0.1
Cu	1-100	20
Pb	1-100	20
Zn	1-1000	100

The main reasoning behind the suggested values was to consider the observed effectiveness of each of the soils in attenuating the metals in relation to typical or expected background concentrations of natural soils, and to choose values which could be implemented in a practical manner. Cadmium and lead were effectively attenuated by Everett and Garrison. With each of the soils showing very low cadmium background, the suggested value of 1 $\mu g/g$ should be easy to implement. Springdale was not able to effectively attenuate lead and zinc in a relative to the other soils, even with relatively low backgrounds of these metals. However, since a sand (springdale) will unlikely be used as an infiltration soil the median concentrations for copper, lead, and zinc were acceptable.

Table G.2 Metals Background Concentrations $\mu g/g$ of Soils Tested

Soil	Cd	Cu	Pb	Zn
Springdale	0.072	77	10.2	8.6
Everett	0.016	24	0.40	3.4
Garrison	0.03	9.0	54	9.0
Average	< 1	37	21	6.9
Suggested	1	20	20	50

Several EPA approved methods are listed for metals analysis of soils. The toxicity characteristic leaching procedure (TCLP) is used for hazardous waste designation of soils and sediments (EPA 1311/6010 TCLP-Metal Screen). Cadmium and copper are federally regulated based on these procedures. However, this study was aimed at NPDES related issues. Also, it is unlikely that sites chosen for BMP's are located in potential hazardous waste sites. Therefore the following EPA methods are referenced as applicable methods for pre-screening soils (modifications of the EPA procedures were used in the extraction process in this study):

EPA 200.2 Sample Preparation Procedure for Spectrochemical
Determination of Total Recoverable Metals.

EPA 200.9 Determination of Trace Elements by Stabilized Temperature
Graphite Furnace Atomic Absorption Spectrometry.

These and other analytical methods are included in the EPA document *Methods for the Determination of Metals in Environmental Samples* EPA-600/R-94/111 May 1994 (PB95-125472). These methods are intended for NPDES effluents and are useful for ambient waters, sediments and soils. For approval in compliance monitoring programs consult the Code of Federal Registers (40 CFR Part 136 for NPDES and Part 141 for Drinking Water).

The following metal extraction procedure is suggested:

EPA 3050 Acid Digestion of Sediments, Sludges and Soils. Trace Micro-element screen: Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Ti, Zn.

The EPA document *USEPA Method Study 37 SW-846, Method 3050, Acid Digestion of Sediments, Sludges and Soils* EPA/600/4-89/012 April 1989 (PB89-181952) includes instructions for quality control, sample preparation and analysis of samples by flame atomic absorption and graphite furnace atomic absorption spectrometry.

Finally, the EPA document *Summary of USEPA Approved Methods Standard Methods and Other Guidance for 301(h) Monitoring Variables* EPA/503/4-90/002 September 1985 (PB95-169835) lists the following as approved test procedures for priority pollutants:

Cadmium EPA 213.1, 213.2

Copper - EPA 220.1, 220.2

Lead - EPA 239.1, 239.2

Zinc - EPA 289.1, 289.2