

**Research Report**

**Research Project T9902, Task 3  
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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Prepared for

**Washington State Transportation Commission**  
Department of Transportation  
and in cooperation with  
**U.S. Department of Transportation**  
Federal Highway Administration

January 1996

## TECHNICAL REPORT STANDARD TITLE PAGE

1. REPORT NO. <b>WA-RD 389.1</b>	2. GOVERNMENT ACCESSION NO.	3. RECIPIENT'S CATALOG NO.	
4. TITLE AND SUBTITLE <b>The Assessment of Groundwater Pollution Potential Resulting from Stormwater Infiltration BMP's</b>		5. REPORT DATE <b>January 1996</b>	
		6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) <b>Wade E. Hathhorn and David R. Yonge</b>		8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS <b>Washington State Transportation Center (TRAC) Civil and Environmental Engineering; Sloan Hall, Room 101 Washington State University Pullman, Washington 99164-2910</b>		10. WORK UNIT NO.	
		11. CONTRACT OR GRANT NO. <b>T9902-03</b>	
12. SPONSORING AGENCY NAME AND ADDRESS <b>Washington State Department of Transportation Transportation Building, MS 7370 Olympia, Washington 98504-7370</b>		13. TYPE OF REPORT AND PERIOD COVERED <b>Research Report</b>	
		14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES <b>This study was conducted in cooperation with the U.S. Department of Transportation, Federal Highway Administration.</b>			
16. ABSTRACT  <p>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.</p>			
17. KEY WORDS <b>Key words: Infiltration BMP's, highway runoff, heavy metals, facilitated transport, humic substances.</b>		18. DISTRIBUTION STATEMENT <b>No restrictions. This document is available to the public through the National Technical Information Service, Springfield, VA 22616</b>	
19. SECURITY CLASSIF. (of this report)  <b>None</b>	20. SECURITY CLASSIF. (of this page)  <b>None</b>	21. NO. OF PAGES  <b>57</b>	22. PRICE

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## 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

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, while the NOM-complexed had a retardation factor about 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. 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 shortcomings 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

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. To its credit, the infiltration option effectively addresses the hydraulic demands posed by the large, temporal volumes of waters generated during rainfall-runoff events. Yet, there are a number of associated environmental issues which have not been fully addressed. Some of the more relevant unanswered questions are those pertaining to the technology's ability to prevent long-term contamination of underlying groundwaters from pollutants derived during the runoff along roadways and other urban /rural land coverage.

Accordingly, 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. Nevertheless, there remain several points of scientific and operational concern. For example, problems due to clogging (and siltation) are common. Moreover, the effects produced under unsteady hydraulics due to the repetitive infiltration and drainage cycles of infiltration is not well understood. 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. 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 below.

Although present design criteria attempt to address the traditional issues pertaining to hydraulic control and pollutant retention, there are a number of fundamental and potentially influential fate and transport processes that are not directly (nor indirectly) considered. Moreover, the impact of these excluded processes on the overall transport behavior of these pollutants has not been adequately quantified. As an 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. 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.

Driving the need for further study is the ever growing realm of environmental regulation. In the State of Washington, for example, there are a number of important laws in place to protect the quantity and quality of existing groundwater resources. None more encompassing than that of the State's "Anti-degradation Policy" (WAC-173-200-030), which states that no mass is to be added to groundwaters which results in concentrations of any pollutant exceeding those that currently exist. Under this regulation, no activity is permitted, including the installation and operation of infiltration basins, which will alter the existing quality of underlying groundwater resources in any manner. Moreover, there is recent published concern over the potential for many of the collected sediments to become contaminated to such levels as they become defined as a hazardous waste (Jones, 1995). As such, there is a need to more fully understand the environmental performance of the stormwater disposal option via infiltration type technologies.

Recognizing these facts, investigations are established here to evaluate the importance and impacts imposed on trace metal transport in the presence (or absence) of natural organic matter (NOM) 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.

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 were 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.

## REVIEW OF PREVIOUS WORK

**Design of Infiltration Basins.** The current standards for the State of Washington with respect to infiltration basin design are those defined in the Stormwater Management Manual for the Puget Sound Basin (Ecology, 1992), hereto referred as the Manual. The Manual is a cooperative product put forth by the State's Departments of Ecology (WSDOE) and Transportation (WSDOT).

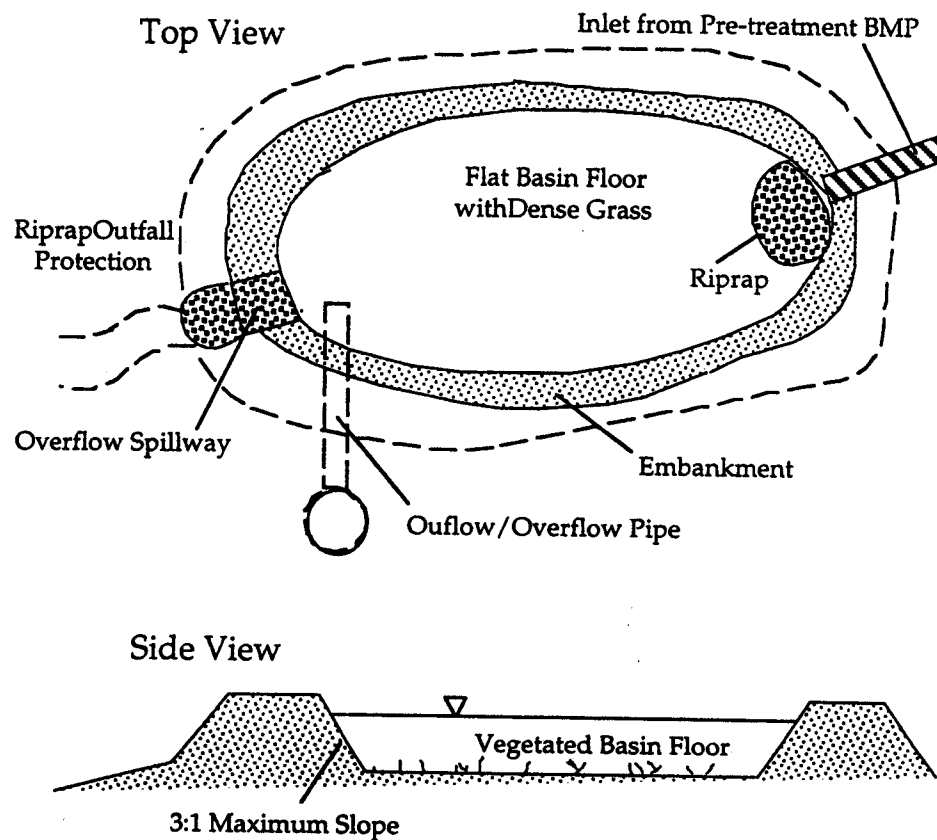
In many instances, infiltration is the preferred BMP due to "...its ability to both effectively treat runoff and control streambank erosion" (Ecology, 1992). Some advantages of infiltration basins include: (1) the ability to preserve the natural water balance of the site while serving larger developments; (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.



**Figure 1. Layout of Typical a Infiltration Basin**

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.

**The Potential Environmental Problem.** All roadways and other land based surfaces contain some form of pollutant(s). The constituents of primary concern include oxygen consuming organic materials, nutrients, toxic organics, oils and greases, and toxic metals. The latter being of greatest interest here, 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 found in at least 50% of the samples. Leading the list were lead, zinc, and copper, each detected in over 90% of the samples collected.

A study sponsored by the Federal Highway Administration provides extensive monitoring of roadway runoff quality (Driscoll, et.al., 1990). 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 (Table 1). From the Driscoll study, the average concentrations for copper, 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 .

Mobility and adsorption characteristics vary depending on whether the metal is dissolved or suspended via attachment to particulates (speciation). 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.

Given the presence of these pollutants in stormwater runoff, the relevant point of concern is one of the fate and transport of these constituents once disposed into an infiltration setting. Moreover, questions concerning the long-term accumulation and/or entry of contaminants into underlying groundwaters are of vital interest in determining the viability and sensibility of preferred infiltration technologies.

**Table 1. 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
<b>Average</b>	<b>11.9</b>	<b>0.035</b>	<b>0.276</b>	<b>0.524</b>

**Traditional Transport Theories.** Under classical theories, a two-phase system is often used in treating subsurface solute transport phenomena in both saturated and unsaturated flow. The solute can either exist in the mobile aqueous phase or be attached to the immobile solid matrix. The traditional approach assumes the total one-dimensional flux is due to advection (bulk motion due to the movement of the carrier fluid) and hydrodynamic dispersion (motion due to the variability in the advection and pore molecular diffusion). By combining the flux equation with mass conservation, several authors have derived the fundamental mass transport equation known as the advection-dispersion equation (ADE) (Fetter, 1993), (Bear and Verruijt, 1987).

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. As the contaminants migrate, their effective velocity is reduced compared with the surrounding groundwater, resulting in the retardation of the contaminant. This effect is normally thought to be due to kinetic mass transfer between the two traditional phases. The retardation factor, used to quantify this effect, represents the advective velocity of a contaminant relative to average pore water velocity. Traditionally, metals are thought to have very high retardation factors. This retardation of the pollutant created the idea of the soil treatment zone, i.e. the removal of pollutants during infiltration. However, the more correct interpretation is that the migration of the pollutants are "slowed or interrupted" and not necessarily ceased.

**Facilitated Transport Fundamentals and NOM Chemistry.** The concept of facilitated (or enhanced) transport has become an important issue as sources for errors in the predictions given by the ADE are considered. McCarthy and Zachara (1989) point out that mobile colloids present in the soil water, which are often times chemically similar to the immobile soil matrix, can sorb contaminants and stabilize them in the mobile phase. They argue groundwater systems should be considered a three-phase system consisting of the mobile aqueous phase, immobile solid matrix, and a mobile colloid phase. Often colloids

move faster than the bulk pore water because of ion repulsion (negatively charged colloids) and/or pore size exclusion (Mills, 1991), (Puls and Powell, 1992). If the contaminant is stabilized in the mobile phase by colloids moving faster than the pore water, then the contaminant will, in effect, have a retardation factor greater than one.

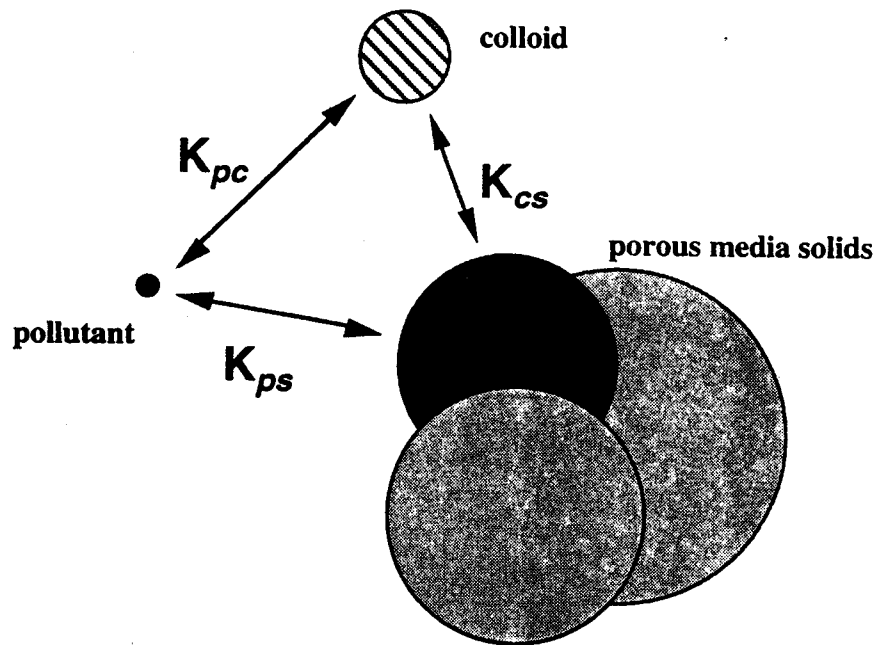
Although several types of colloids — defined as any particles with diameters less than 10  $\mu\text{m}$  — may be responsible for enhancing solute transport, this study focuses on macromolecular organic materials such as humic substances derived from vegetative decay and directly from the roadway runoff. Stabilization of the colloids in the aqueous phase is an important factor in providing for the mobile third phase. For example, humic substances must first be flushed from the organic-rich O and A horizon in the upper soil regimes or made available from infiltrating water. Then, factors including particle size, soil/water chemistry, and water flow rates must allow for the stabilization of these colloids in the aqueous phase.

Natural organic matter (NOM) refers to all living and senescent organisms 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.

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. DOM has molecular weights ranging from approximately 500 to 30,000 (Amy *et al.*, 1992). 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.

An extensive amount of research has examined the binding of DOM with heavy metals in aqueous systems ( Langford *et al.*, 1983; Perdue, 1989; Pettersson *et al.*, 1993; Stevenson, 1976). 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 intricate processes that govern the reactions of contaminants, colloids, and contaminant–colloid “complexes” with subsurface media. Briefly, a complex is a combination of cations with molecules (or anions) containing free pairs of electrons which improves electron stability in the outer shell of the cation. The molecule or anion is called the ligand. 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.



**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.

### **Experimental Considerations and Related Studies on Metals Mobility.**

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 examine the current understanding of the effects of organics on metals transport, several related studies are reviewed. A study in Stumm and Morgan (1981) found that in sea water, Cu(II) coordinated with organic ligands successfully, while cadmium was not affected by the organic functional groups. The study suggested many soluble trace metals exist as inorganic species, but at higher concentrations of organics, metal ions will develop organic complexes. 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. Finally, Holm and Zhu (1994) presented the results of metal sorption experiments involving landfill leachate-contaminated groundwater. They found that 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. Davis (1984) showed DOM increased  $\text{Cu}^{2+}$  sorption at  $\text{pH} < 6$ , while at high pH the metal-organic complexes remained dissolved.

## RESEARCH APPROACH

For logistical reasons, the work plan was broken into two main components: Phase 1 attempts to characterize partitioning among the metals-NOM-soil matrix; and Phase 2 pursues experimental investigations of the macro-scale transport behavior of the metals. Phase 1 experiments were designed to assess the pore-scale transport properties of a single metal solute (lead) in the presence of humic and fulvic acids. Here, strict controls on the geochemistry of the system, e.g. pH, ionic strength, were adhered to in an attempt to quantify the intricate details of the sorption process. By contrast, Phase 2 dealt with multiple metal solute 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 (the terms high/low refer to relative properties amongst those soils likely as candidates for infiltration basin siting). 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.

**TABLE 2. Soil Properties**

Parameter	Everett	Springdale	Garrison
% Sand	83.2	93.8	53.6
% Silt	12.0	4.0	40.0
% Clay	4.8	2.2	6.4
Organic Content, %	0.35	0.13	3.22
CEC, cmol(+)/kg	17.4	3.2	20.6
CO <sub>3</sub> <sup>2-</sup> , mmol(-)/L	< 0.2	< 0.2	< 0.2
HCO <sub>3</sub> <sup>-</sup> , mmol(-)/L	0.5	0.8	1.7
Cl <sup>-</sup> , mmol(-)/L	0.8	0.8	1.1
Ca, mmol(+)/L	0.32	1.46	3.10
Mg, mmol(+)/L	0.10	0.14	1.37
Na, mmol(+)/L	1.35	0.26	0.78
K, mmol(+)/L	0.05	0.09	0.20
Cd <sup>a</sup> , µg/g	< 0.1	< 0.1	0.13
Cu <sup>a</sup> , µg/g	149	107	39
Pb <sup>a</sup> , µg/g	2.53	14.2	233
Zn <sup>a</sup> , µg/g	19	12	39

<sup>a</sup>Background metals measured on soils less than #40 U.S. Sieve

**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 nonindigenous 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<sup>-1</sup>, corresponding to 8.75 and 47.5 μmol L<sup>-1</sup> 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.

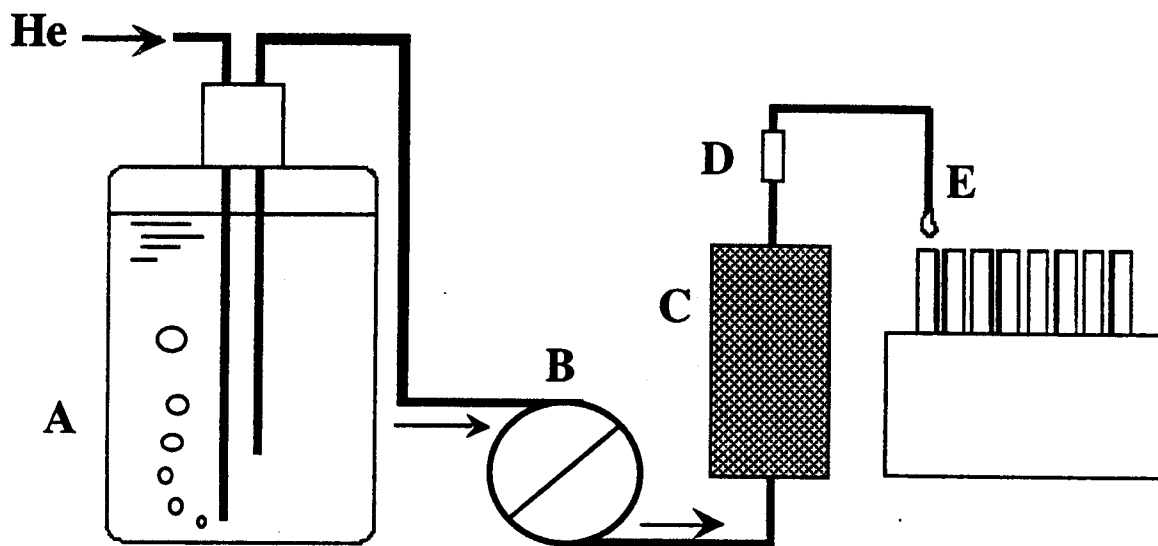
Kinetic sorption was studied in batch systems containing equal soil and solute concentrations. Each experiment consisted of several replicated batches, each analyzed for soluble (Pb or DOM) concentrations over a range of time intervals between 30 seconds and 204 hours. Rate of sorption was observed for 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 saturated soil-packed glass columns. 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. 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. Experiments involving Pb were ended prior to complete breakthrough because of the significant retardation of Pb in the column. Effluent pH also was monitored throughout each transport experiment.

Column homogeneity, dispersion, and channeling were evaluated simultaneously by analyzing the breakthrough curve (BTC) of a nonreactive tracer ( $^3\text{H}_2\text{O}$ ). 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 Experimental Approach.** 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. This information was then used to quantify the overall performance of the columns subject to different loadings (i.e. with and without the addition of NOM) and soil types.

The soil columns were designed and constructed with the intention of modeling one-dimensional infiltration of water through approximately 1 meter of soil. Since metals were to be measured, the use of any metal material in the apparatus was avoided as much as possible. The column was constructed of two sections of 0.33 m diameter PVC pipe with two intermediate sampling ports (ISP-1 and ISP-2) placed at 30 cm intervals along the length of the column with an exit sampling port (ESP) at the bottom of the column. The lower section allowed approximately 90 cm of soil to be packed. The upper section of the column stored the "storm runoff" equivalent to 90 cm of water to be infiltrated (Figure 4).

Each of three soils collected were tested in this phase. Each soil tested, after being packed into the columns, underwent the following general procedures: (i) initial and final bromide tracer tests were conducted for each repacked soil column to test for hydraulic integrity; (ii) after determining the soil column to be performing properly, the soil was allowed to drain before applying the stormwater, and so was run initially unsaturated before each application; and (iii) a sequence of five metals-only storm events were applied, wherein a minimum of two days and a maximum of one week was allowed between subsequent tests. In addition, two syringes installed at equal intervals along the column were used to obtain pore water samples for total metals, total organic carbon (TOC), and pH at designated intervals of depth infiltrated. At the conclusion of loading, the soil was

then unpacked and soil samples were taken for metals extraction to attempt to determine the mass distribution along the profile. This same procedure was then used on a newly packed soil column to which metals-NOM stormwater was applied.

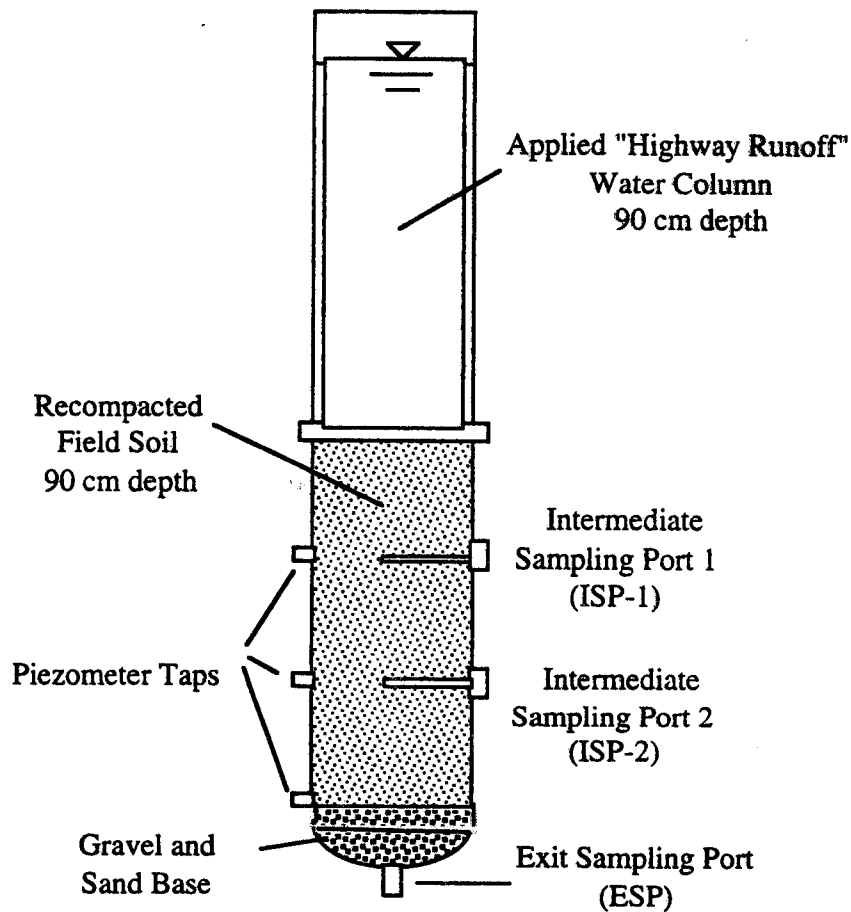
The metals stock solution was prepared by dissolving metal salts ( $\text{CdCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{PbNO}_3$ ,  $\text{ZnCl}_2$ ) in a 1 N  $\text{HNO}_3$  solution. A measured volume of the stock was mixed with deionized water to obtain a feed concentration of metals ( $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ) approximating the average stormwater concentrations. A measured volume of NOM stock was added to the mixing tank to produce about 50 mg/l TOC in the applied stormwater (the same order-of-magnitude as typical highway stormwater TOC concentrations). The NOM solution was derived by a NaOH extraction procedure using standard garden peat. The supernatant contains a mixture of humic acids, fulvic acids, and humin. The total organic carbon concentration was measured and used as a relative measure of the organic matter in the stock.

The analytical equipment used included the Varian Atomic Absorption Spectrometer, Shimadzu Total Organic Carbon Analyzer, and Orion Ionalyzer with a Bromide Ion Selective Electrode. *Standard Methods* (Greenberg, 1992) 3111-B was used for flame analysis and *Analytical Methods for Graphite Tube Atomizers* published by Varian was used for furnace analysis. *Standard Methods* 5310-B was used as a reference for the TOC analysis. 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 3. Summary of Procedures**

Procedure Number	Description	Analysis	Sampling Port
P1	Bromide Tracer Test	Bromide Concentration	ESP*
P2	Metals-only solution	metals concentration	ESP/ISP**
	Cd, Cu, Pb, Zn	TOC	ESP/ISP
	5 simulated events	pH	ESP/ISP
P4	Metals-NOM solution on new soil	metals concentration	ESP/ISP
		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 section is divided into subsections discussing and summarizing the main findings of the two phases of the study. 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 field 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.

### PHASE 1 DISCUSSION

**DOM Kinetics.** The addition of PHA to the soil-water mixture resulted in significant liberation of free hydrogen ions, possibly from hydrolysis of the PHA. This resulted in a sharp drop in pH and corresponding "uptake" (precipitation) of PHA. After approximately 0.1 days, the electrostatic reactions tended to stabilize, after which uptake kinetics could be observed. 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 caused the earlier breakthrough of PHA relative to PFA and allowed 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 (Oden *et al.*, 1993; Murphy *et al.*, 1990). Murphy *et al.* (1990) 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.

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 5) 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 6). 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 7) 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, Pb solubility at high equilibrium Pb concentrations was inhibited in the presence of low concentrations of PHA 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 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.

To predict column behavior then, Pb speciation over expected pore water concentration ranges must be considered. The feed solution to the column was about  $6 \mu\text{mol Pb L}^{-1}$ . Careful examination of Figure 7 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 6.

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.

**Lead Detachment from DOM Complexes.** Although it cannot be confirmed with the data collected 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).

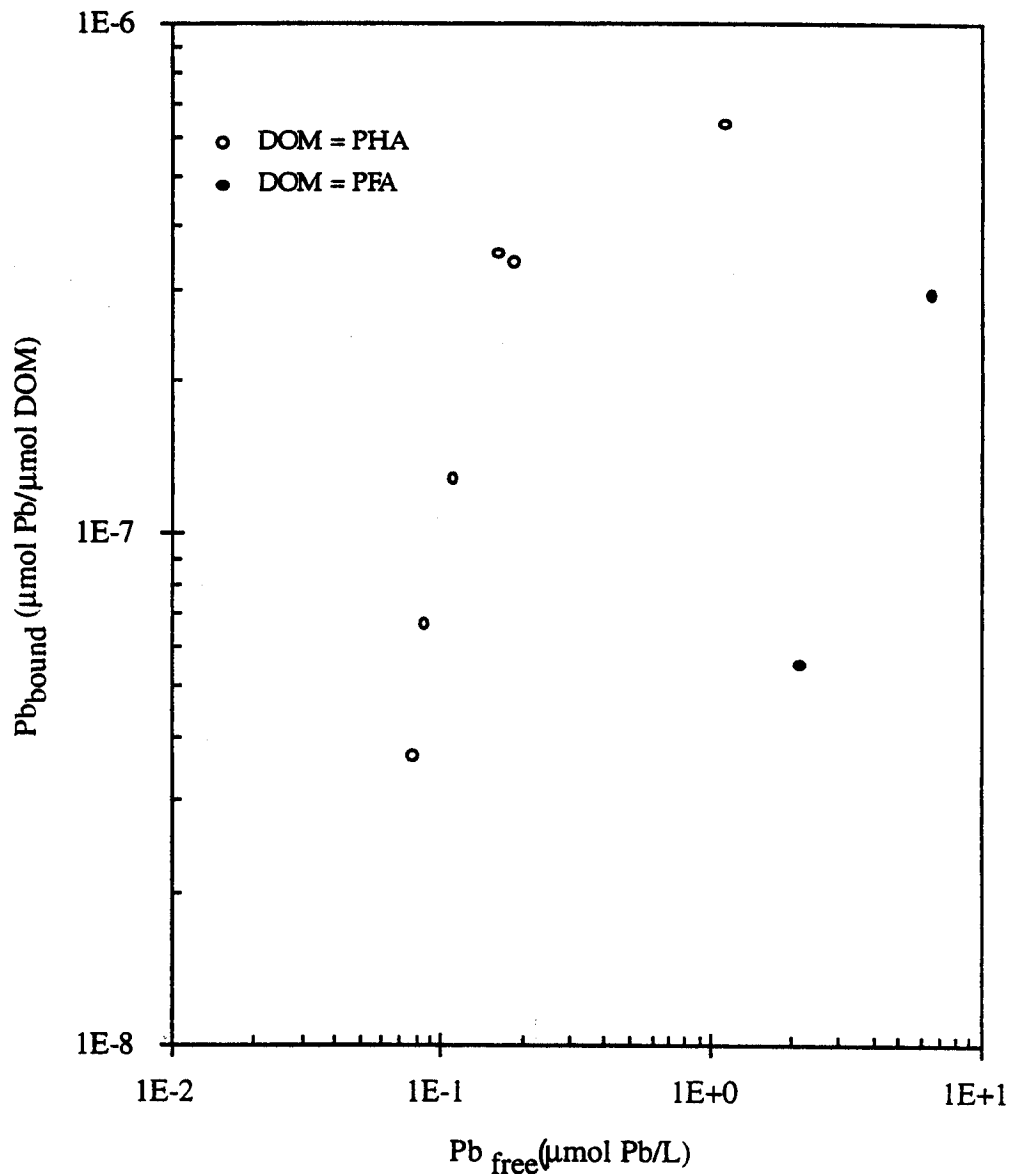
An alternative to the cleansing theory for explaining the breakthrough of DOM prior to Pb is the possibility of decreased mobility of the Pb-DOM complex relative to DOM alone. The results from the Pb-DOM aqueous binding study suggest that the amount of Pb in the complexed state in the PHA-Pb feed solution 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.

#### **Main Results of Phase 1.**

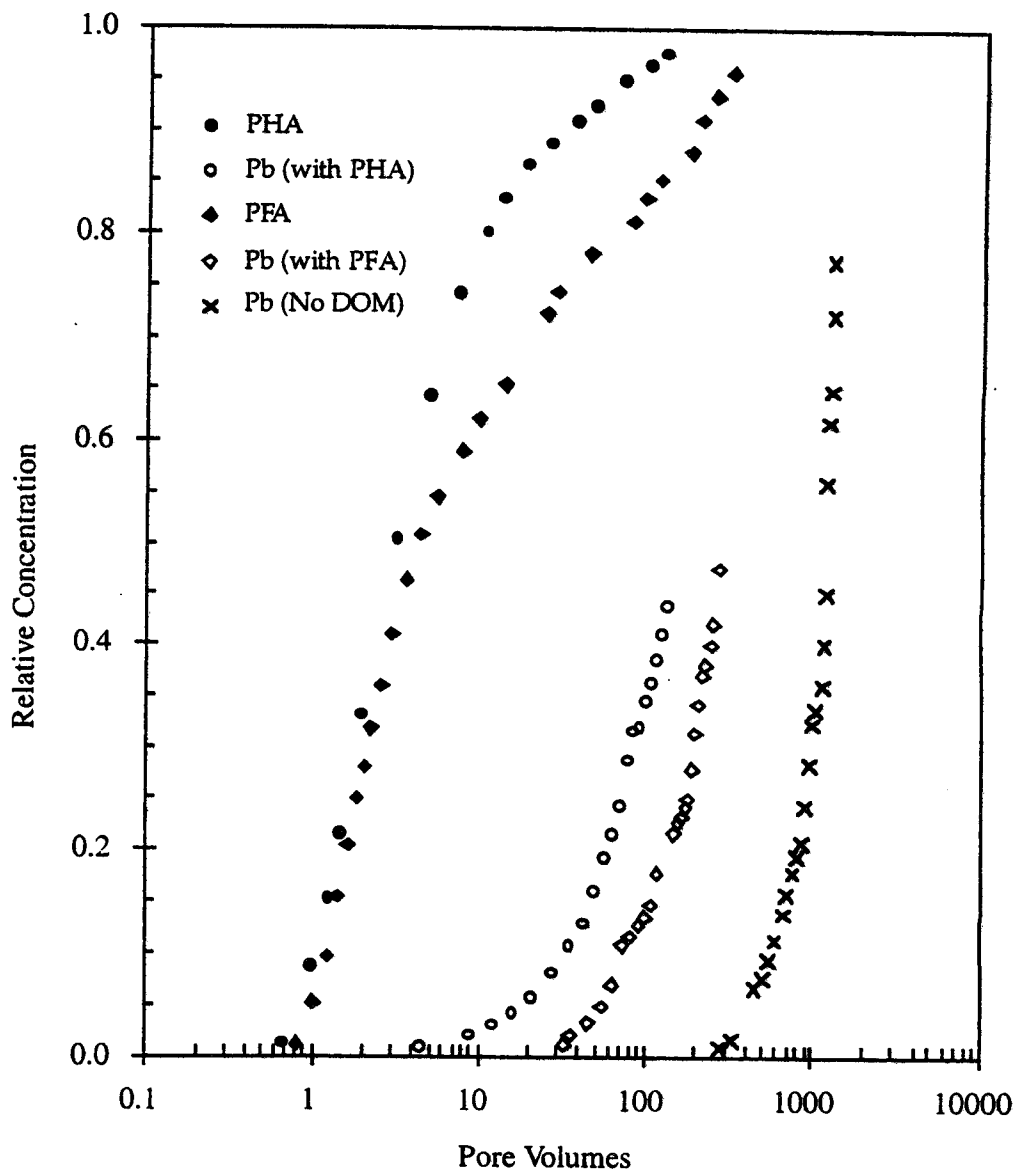
- The column experiments show that PHA breakthrough occurs prior to PFA breakthrough, consistent with the results from the sorption isotherms.
- Size exclusion of the larger PHA molecules from smaller intraparticle pores (and failure of the PHA to access intraparticle binding sites which are accessible 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 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.

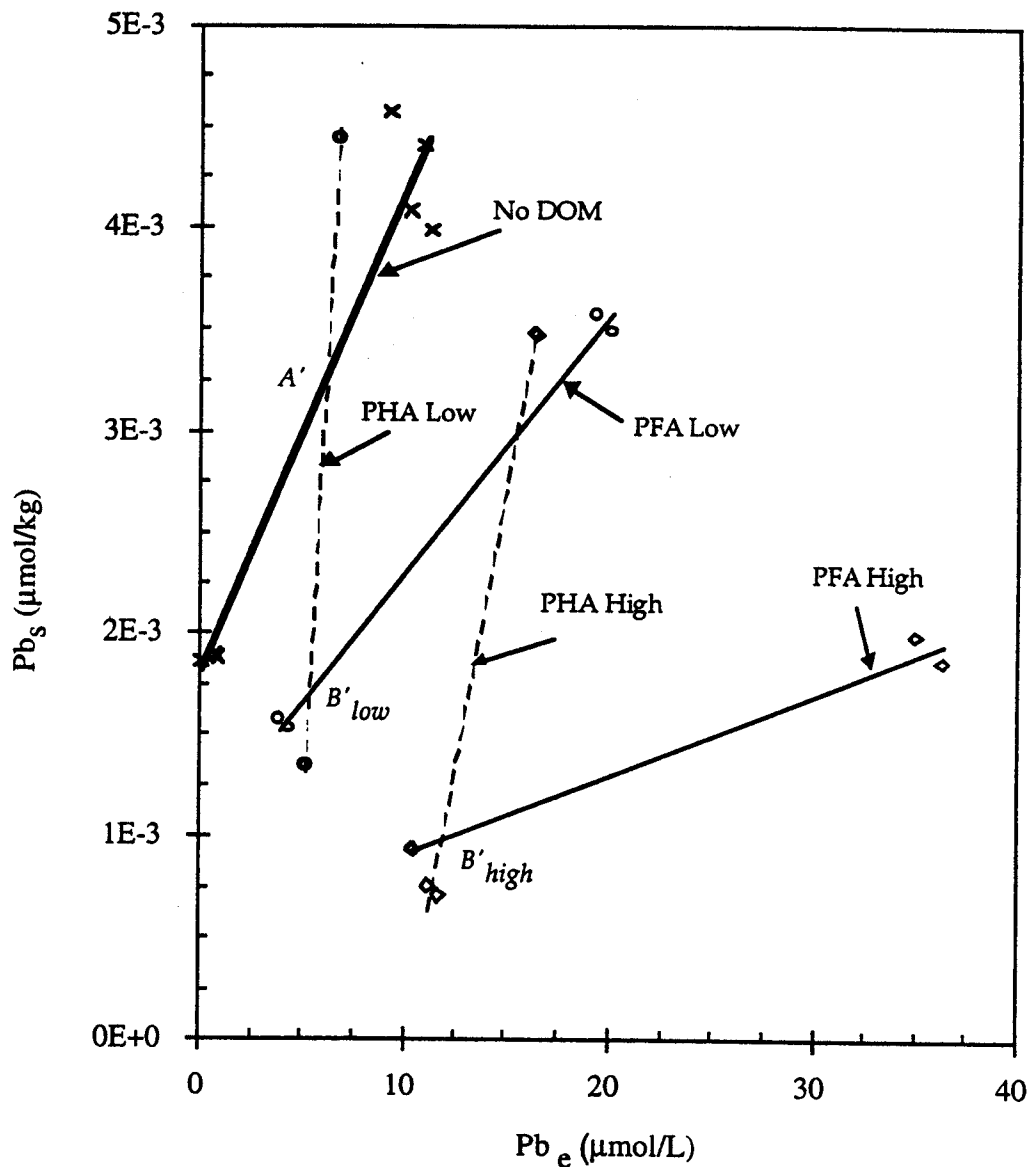
- PFA enhances Pb solubility better than PHA. At low concentrations, Pb solubility is greater in the presence of PHA than in the presence of PFA, suggesting that soluble DOM is controlling relative speciation.
- Although it cannot be confirmed with the data presented here, size exclusion may also be 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.



**FIGURE 5 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.



**FIGURE 6 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  $\mu\text{mol/L}$ , respectively. DOM feed concentrations for Pb (with PHA) and Pb (with PFA) were 1.75 and 9.50  $\mu\text{mol/L}$ , respectively.



**FIGURE 7 Pb-DOM Sorption.** Pb sorption onto Everett sand in the presence of DOM. Approximately 5-10% of UV<sub>254</sub>-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  $\mu\text{mol/L}$  was added, while those toward the lower left of each isotherm line are those where an initial Pb concentration of 19.3  $\mu\text{mol/L}$  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  $\mu\text{mol/L}$ , respectively. High initial PHA and PFA ("High") concentrations were 47.5 and 8.75  $\mu\text{mol/L}$ , respectively.

## **PHASE 2 DISCUSSION**

Phase 2 of the study involved performing the large scale column experiments on three near surface soils having a range of soil properties adequate for infiltration as required by the Manual. A summary of the findings from Phase 2 is 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.

**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.

**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 solubility limits. Because cadmium is generally thought to have a lower affinity for soils than copper, the latter explanation is more likely.

The order of potential mobility for the experiments performed here are listed in Table 4. 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  $Cu > Zn > Pb > Cd$ . This ordering is based on the calculated removal efficiencies by each soil. 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. However, studies evaluating metals mobility often do so under varying aqueous conditions (i.e. varying pH and ionic strength), and rarely over multi-component solutions.

**Table 4. Order of Relative " Mobility" for Soil Columns**

<b>Soil</b>	<b>Metals-only Runs</b>	<b>Metals-NOM Runs</b>
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, hindered it. The observations made during the present study suggest a possible explanation. The organic ligands may have decreased mobility of the metals by sorbing onto the soil matrix via physical straining of the NOMs due to their large macromolecular nature. This may have provided additional sorption sites for the metals. As a result of the loading conditions (the impulse release approaching a continuous release), an accumulation of NOM's in the near surface soils likely 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.  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ . 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, e.g. with either carbonate ( $\text{CO}_3^{2-}$ ) or sulfate ( $\text{SO}_4^{2-}$ ). 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. 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, copper concentrations in the upper third of the column 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 metal-organic coordination (complexation) occurs, any organics which attaches to the soil matrix would likely lead to increased metal sorption. On the other hand, if organics leaching increases, then more of the metals would be eluted. This would be the case if the metals had no preference in 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 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 removed from the elluent (infiltrating water).

The data collected did not allow determination of which of these processes was dominant. Both of these phenomena likely 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 other species of metals, e.g. the inorganic complex species, in the metals-only experiments. In other words, the organic ligands (from the added NOM) appear to have out-competed the inorganic ligands (e.g. carbonates, sulfates, chlorides) to form organic complexes with a greater affinity for the soil matrix, leading to the much lower aqueous concentrations. This was most apparent in the case of copper. However, with enough applications of NOM loaded runoff, the migration of this NOM-rich region

may eventually break through 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 phase 1, 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.

**Mass Removal Efficiency.** Table 5 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 5. Percent of Metals Mass Attenuated**

<b>Cadmium</b>	<b>Everett</b>	<b>Springdale</b>	<b>Garrison</b>
Metals-only	96	82	99
Metals-NOM	99	99	

<b>Copper</b>	<b>Everett</b>	<b>Springdale</b>	<b>Garrison</b>
Metals-only	41	2	72
Metals-NOM	82	69	

<b>Lead</b>	<b>Everett</b>	<b>Springdale</b>	<b>Garrison</b>
Metals-only	95	91	99
Metals-NOM	99	97	

<b>Zinc</b>	<b>Everett</b>	<b>Springdale</b>	<b>Garrison</b>
Metals-only	42	24	97
Metals-NOM	92	62	

**Table 6. Range of Soil Solution pH from Columns\***

<b>Experiment</b>	<b>Soil Solution pH</b>
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

**Dominant Transport Mechanisms.** 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. 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 6). 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. The log solubility product for common minerals with copper and zinc are much higher than those with cadmium or lead, 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. The observed reduction in copper and zinc concentrations with depth may also be explained in terms of complexation. The smaller log stability constants possessed by cadmium and lead than those for copper and zinc 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 addition of the organics is postulated to have had a three-fold effect causing increased copper and zinc attenuation: i) the organics competed with inorganic ligands in solution resulting in decreased inorganic complexes; ii) organic-complexes formed with a much higher affinity for the soil matrix than the inorganic complexes resulting in increased attenuation; and 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.

**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. Additionally, the NOM used, though arguably more "realistic" than using manufactured humic or fulvic acids, was still not what actually occurs in nature. 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. Organic properties of the soil seem to be better measures of a soil's direct ability to attenuate copper and zinc. 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.



- The hydraulics of the system can be highly variable due to the intermittence of loading associated with infiltration practices. However, the infiltration rate plays a secondary role when considering metals removal at these concentrations.
- Speciation and background metals present in the soil are important factors to consider, because they can affect expected metals removal rates of soils. The background copper and zinc which was leached from the soils can be an unaccounted source of heavy metals not considered in current guidelines.
- An increase in NOM in the feed solution resulted in increased attenuation of metals by the soils tested. 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 processes that contributed to non ideal behavior in breakthrough experiments. These processes may have included: i) nonlinear equilibrium sorption over the concentration range studied; ii) non equilibrium sorption kinetics during transport resulting from diffusion into intraparticle porosity; iii) size exclusion of organic macromolecules; and iv) complexation dynamics occurring during transport. 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.

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.

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, metals

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. 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.

## IMPLEMENTATION

### RECOMMENDATIONS

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  $\mu\text{g/g}$  for lead, 20  $\mu\text{g/g}$  for copper, 1  $\mu\text{g/g}$  cadmium, and 50  $\mu\text{g/g}$  zinc should be avoided (details are discussed in the Appendix).
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.

Finally, the approach used in this study can be extended and incorporated with future studies on other related BMP's, e.g. filter strips. Everett soil was found to be suitable for additional study, both for its prominence in the state and its potential as a suitable infiltration soil.

## **ACKNOWLEDGMENTS**

This research was funded by the Washington State Department of Transportation. We would like to acknowledge the staff at the Department of Civil and Environmental Engineering at Washington State University for their technical assistance and input provided by Dr. Richelle Allen-King and Dr. Kent Keller at Washington State University.

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## APPENDIX

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.

**Typical Background Metals Concentrations  $\mu\text{g/g}$  of Soil**

<u>Metal</u>	<u>Range</u>	<u>Median</u>
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  $\mu\text{g/g}$  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.

**Metals Background Concentrations  $\mu\text{g/g}$  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

