

**ENVIRONMENTAL IMPACT OF CONSTRUCTION AND REPAIR
MATERIALS ON SURFACE AND GROUND WATERS**

**FINAL REPORT
VOLUME III: PHASE III METHODOLOGY, LABORATORY RESULTS,
AND MODEL DEVELOPMENT**

Prepared for
National Cooperative Highway Research Program
Transportation Research Board
National Research Council

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October 12, 2000**

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ACKNOWLEDGMENT

This work was sponsored by the American Association of State Highway and Transportation Officials (AASHTO), in cooperation with the Federal Highway Administration, and was conducted in the National Cooperative Highway Research Program (NCHRP), which is administered by the Transportation Research Board (TRB) of the National Research Council.

DISCLAIMER

The opinion and conclusions expressed or implied in the report are those of the research agency. They are not necessarily those of the TRB, the National Research Council, AASHTO, or the U.S. Government.

This report has not been edited by TRB.

ABSTRACT

The National Academy of Sciences, National Cooperative Highway Research Program, initiated and funded this study to identify the possible impacts of highway construction and repair (C&R) materials on the quality of surface and ground waters near the highway environment. The scope of the study involved the development of a validated methodology to assess such impacts, in three phases. Phases I and II involved 1) a survey of C&R materials, 2) laboratory testing of the chemical and toxicological characteristics of a selected number of these materials, and 3) development of a mathematical model to simulate the fate and transport of water quality constituents, including toxicity, along surface and subsurface pathways in the highway environment. These efforts are reported in companion Volumes I and II. Phase III, reported in this volume, focused on ten tasks aimed at confirming the project methodology, testing various hypotheses of the model development, developing additional leaching and sorption data, comparing ecotoxicological testing procedures developed during this project with standard EPA procedures, refinement of laboratory protocols, enhancing the model, and investigating the availability of field data for model testing. This Volume III is one of five volumes in the final report series.

In general, the assumptions of the methodology were confirmed by additional laboratory tests. Ecotoxicological tests developed during this study behave similarly to the EPA Synthetic Precipitation Leaching Procedure (SPLP). The refined model is available in the form of an Excel spreadsheet with macros written in Visual Basic for Application.

CHAPTER 1

INTRODUCTION AND RESEARCH APPROACH

1.1 INTRODUCTION

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

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

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

Phase I focused on a broad screening of common C&R material to identify the extent of the problem and to guide the succeeding phases. The deliverables of Phase I were a comprehensive list of the most commonly used C&R materials with their environmental impact assessment, a protocol for aquatic toxicity measurement and assessment, a preliminary description of a conceptual analytical model to predict the fate and transport of soluble toxicants in the soil-water matrix, and the description of an overall evaluation methodology to be used for additional/future C&R materials. This methodology is illustrated in Figure 1.1.1 and consists of a screening procedure, followed by laboratory testing and modeling, if necessary.

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

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

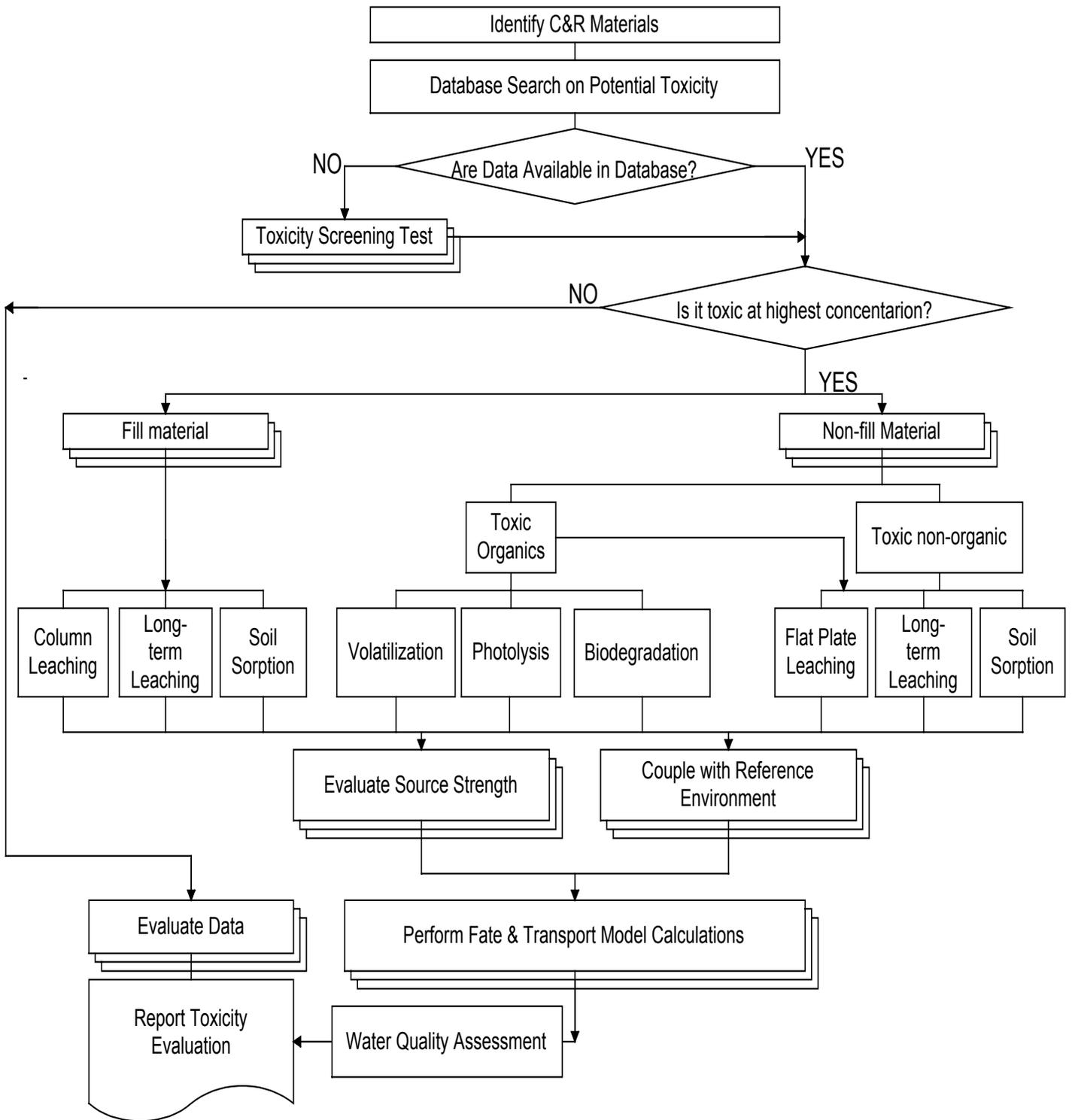


Figure 1.1.1 Evaluation Methodology

1.2 OBJECTIVES OF PHASE III

The objectives of Phase III included the following:

- Examination of the relationship between Phase I and Phase II laboratory results and scaled-up laboratory tests, e.g., large flat plates (Tasks 1,3,4,5,6).
- Validation of various modeling assumptions such as leaching from surfaces bounded by porous media and the extent of transport in highway shoulder areas (Tasks 2,5).
- Comparison of laboratory procedures used in this project with similar procedures used by the U.S. Environmental Protection Agency (Tasks 7,8).
- Enhancement and documentation of the computer model, including the ability to simulate long-term leaching processes (Tasks 6,9,10).

1.3 RESEARCH APPROACH

In Phase III, research results from Phase II have been extended to confirm selected aspects of the Phase II methodology and to examine the validity of scaled-up predictions from laboratory tests. Results of confirmation of the Phase II methodology have been compared to simulations from an enhanced version of the computer model

In Phase II, important processes that affect the chemical composition, aquatic toxicity, and fate of leachates from highway C&R materials were evaluated in laboratory tests. The tests provided information on the leachability of constituents in C&R materials under a range of conditions thought to provide reasonable estimates of expected leachate chemical concentrations. The tests provided information on the removal, reduction, and retardation of leachate constituents by natural processes. Algal and daphnia toxicity tests assessed the toxicity of the samples at the leachate source or after modification by removal, reduction, and retardation (RRR) processes, and chemical analyses enabled quantification of leachate chemical components at all stages of the laboratory tests. Each laboratory test resulted in the measurement of mass transfer rates of leachate chemical components under controlled conditions, the results of which were applied to specific mathematical models of the process.

Six reference environments were chosen to cover a wide range of highway construction material use. Specifically, these environments included permeable highway surface, impermeable highway surface, piling, fill, bore hole, and culvert (Table 1.3.1). The mathematical equations of leaching and RRR processes were included in the overall mathematical model for each reference environment. The linkage of each mathematical model to its reference environment is made through the fitting coefficients for the processes derived from the results of the battery of laboratory tests for each environment (Table 1.3.1).

Table 1.3.1. Linkage of laboratory tests to reference environments.

Test	Permeable highway	Impermeable highway	Piling	Fill	Bore Hole	Culvert
24-hr Batch Leaching	x	x	x	x	x	x
Dynamic Batch Leaching (controlled pH)	x	x	x	x	x	x
24-hr Batch Leaching after Heating	x	x	x	x	x	x
Column Leaching				x		
Flat Plate Leaching	x	x	x		x	x
Soil Sorption	x	x	x	x	x	x
Degradation by Photolysis	x	x				x
Biodegradation	x		x	x	x	x
Loss by Volatilization	x	x				x

Phase III work was broken down into ten separate tasks. Tasks 1 – 8 dealt with verification and refinement of the laboratory testing methodology, while Tasks 9 and 10 involved enhancements to the computer fate and transport model and evaluation of data set requirements to run the model. Research approaches for Tasks 1 – 10 are briefly described below.

1.3.1 Task 1. Confirmation of Phase II Methodology

In this task, confirmation of the Phase II methodology was examined at laboratory scale by linkage of leachate generation to soil columns to represent the impermeable highway, piling, and fill reference environments (Table 1.3.1, above). Full confirmation of the Phase II methodology was not possible at the laboratory scale due to constraints on the size of flat-plates that can be tested resulting in limitations on the volume of leachate that can be generated for RRR testing. Because of these constraints, the methodology was tested in relation to RRR processes in soil columns using leachate generated by the short-term batch leaching procedure.

1.3.2 Task 2: Leaching From Flat Surfaces With and Without Soil Confinement

Under field conditions, environments exist in which a flat, impermeable surface is buried in soil, and thus leaching occurs under confined conditions (soil is packed against flat surface). The Phase II methodology does not directly address leaching under these conditions, but implicitly assumes that leaching flux is not affected by confined conditions. The purpose of Task 2 was to confirm whether leachate flux from flat, impermeable surfaces is affected under confined conditions. These conditions are relevant to the reference environments of piling, fill, and culverts.

1.3.3 Task 3: Effect of Scale On Flat-Plate Leachate Composition

An assumption of the flat-plate leaching test is that the contaminant flux from the C&R material surface is directly proportional to surface area and thus scaleable to field conditions. However, because of various scale effects, testing at the laboratory scale can poorly represent field results. Determining scale effects is difficult because of the problems associated with preparation and handling of large test specimens. The research approach involved conducting flat plate experiments with samples of varying size. All other variables including leaching solution, testing time, and C&R material were held constant. The objective of Task 3 was to determine whether scale effects exist for chemical leaching with water in the flat-plate leaching test of highway C&R materials.

1.3.4 Task 4: Tests of Portland Cement and Portland Cement Concrete (PCC) With and Without Plasticizer

The leaching of chemical constituents from PCC and the effect of RRR processes on these constituents were assessed using the complete Phase II methodology (Figure 1.1.1). Preliminary screening for aquatic toxicity of various types of Portland cement such as Tilbury, Kaiser, Calaveras, Holman, Lehigh and Blue Circle indicated that their leachates were toxic to *S. capricornutum* in Phase I tests. In Phase I, Portland cement concrete leachate prepared from Tilbury cement (ground to pass a 1/4-inch sieve) with admixtures (air-entrainment or plasticizer) was observed to highly inhibit algal growth. However, after soil sorption (1:4 soil to leachate mass ratio) a complete removal of algal growth inhibitory effect was observed.

In this task, PCC (with and without plasticizer admixture) was subjected to the full testing methodology to determine leachate characteristics and parameters for the removal/reduction/retardation (RRR) factors in the fate and transport model. Laboratory tests included batch and long-term leaching, flat plate leaching, and sorption to Sagehill, and Woodburn soils. Photolysis, volatilization, and biodegradation tests were performed on the leachate and on separately prepared solutions of the plasticizer.

1.3.5 Task 5: Determine a Range of Typical Adsorption and Desorption Parameters for the C&R Materials on Sand and Gravel Utilized in Unbound Pavement Layers and Shoulders

A number of factors control sorption of leachate contaminants by permeable solid phases, including the chemical and physical characteristics of the contaminant and the composition of the surface of the solid. By gaining an understanding of these factors, conclusions can often be drawn about the impact of sorption on the movement and distribution of contaminants in the subsurface. Failure to account for sorption can result in significant underestimation of the mass of a contaminant at a site and of the time required for it to move from one point to another.

A range of typical adsorption and desorption parameters for C&R materials was determined for soils of varying physical and chemical characteristics. By a similar approach, the adsorption and desorption characteristics of C&R materials for a range of

sand and gravel were determined in this task. As for soils, results of laboratory adsorption experimental data were expressed in isotherms as mass adsorbed per unit mass dry solids (C_s) versus the concentration of the constituent (C) in solution. Equilibrium isotherm models were used to determine the maximum adsorption and desorption capacities and distribution coefficients from the experimental data.

1.3.6 Task 6: Aging Effects In C&R Materials

All testing and protocols used in Phase II involved the use of “new” materials, which for asphalt means recently placed, and for concrete, after 28 days of curing. Such new materials are assumed to represent a worst case related to the rates of chemical leaching by water. Such new materials would have maximum concentrations of materials at or near the leaching surface and would exhibit less diffusional limitation to leaching from precipitation. The effect of exposure time to the environment for highway materials has been termed aging. The various important environmental factors that could affect materials include time for solid or crystalline formation, exposure to air/oxygen, exposure to heat, and wet/dry cycles. In this task, the effect of aging was measured with flat plate experiments using open graded asphalt concrete (AC) amended with selected C&R materials. The various forms of aging were tested using Strategic Highway Research Project (SHRP) protocols and compared to the results for “new” amended AC. The forms of aging evaluated were the effect of heat, the effect of oxygen, the effect of exposure time, and the effect of wet and dry cycles of exposure.

1.3.7 Task 7: Comparison of Laboratory Test Protocols With EPA Protocols, Determinations of Test Statistical Variability, and Preparation of User's Manuals

Laboratory QA/QC applies to chemical analyses, biological tests, and leaching and RRR process tests. Both chemical analyses and biological tests follow standard methods and QA/QC protocols that have been reviewed and accepted by EPA and other agencies. The Project Team confirmed that the project’s standard testing methods and QA/QC protocols are consistent with published EPA methods and protocols by undertaking a thorough review and comparison between project methods/protocols and those of EPA. For leaching and environmental effects (RRR) processes, new test methods were developed as a part of this research, and thus no standard accepted procedures exist from EPA or other agencies. Standard QA/QC protocols specific to these tests have not been developed. In this task, the laboratory testing methods and QA/QC protocols for the leaching and RRR process tests were developed, refined, and validated. As a part of this process, replicate testing was performed on all methods to define the variability and degree of confidence of the results using statistically determined parameters (coefficient of variation, precision). To do this, a standard asphalt, called “standard asphalt cement concrete” (SACC), was developed that contains two model toxicants, one metal and one organic.

A user’s manual describing the overall screening methodology and laboratory test protocols has been developed as an additional part of this task. This includes the overall screening methodology and contains detailed leaching and RRR process test methods and associated QA/QC protocols, and in addition includes the aquatic toxicity tests and the

chemistry test methods and associated QA/QC protocols. The manual has been prepared and bound as a stand-alone document to facilitate distribution to government agencies and other future users.

1.3.8 Task 8: Leaching Methods Comparison Study

Comparison is inevitable between the distilled water leaching procedure of this study (short-term [24-hr] batch leaching procedure) and EPA's standard TCLP test (toxic characteristic leaching procedure; EPA Method 1311) and SPLP test (synthetic precipitation leaching procedure; EPA Method 1312). In this task, a carefully controlled laboratory comparison study was conducted of leaching results from the distilled water and EPA procedures applied to C&R materials assemblages. Leaching results included, as applicable, inorganic compounds (primarily metals), organic compounds, leachate TOC, and solution pH. Comparison was made by statistical techniques.

1.3.9 Task 9: Model Enhancement

The computer fate and transport simulation model developed in Phase II operated on a simple storm-event basis: a constant-intensity rainfall was input for a specified duration. The surface and subsurface runoff hydrograph and the corresponding concentration and/or organism sensitivity were computed for the duration of the runoff. Leaching thus corresponded to a "first flush" and did not account for presumed decrease in release of constituents with flushing time. Nor did it account for the possibility of desorption along the subsurface pathway. One of the principal changes to the model was to include a continuous simulation option. The simulation follows the pathway of the water to the site boundary, including the possibility of lateral groundwater flow. Sensitivity analyses were made and documented for user guidance, and the knowledge base for model parameters was expanded. Additional minor improvements and changes have been made. The database portion of the model has been updated to encompass all results of Phases I and II as well as any new information from Phase III. The model has been tested on a limited basis against the column studies of Task 1, in order to document model capabilities and prepare examples for documentation for the end user. More extensive applications could follow as a future additional work item from the data set evaluation of Task 10. A formal User's Manual was prepared for model dissemination.

1.3.10 Task 10: Data Set Assessment

To the best of the Project Team's abilities, model application has been explained and demonstrated as part of the documentation prepared under Task 9. However, assembly of actual test-site data for "real world" applications is time consuming and costly. Data typically must be reviewed and evaluated prior to model application. Missing data and parameters must be supplied, through estimates, or better, through additional information from the model site -- and there is almost always something missing. For Task 10, the NCHRP Review Panel members proposed data sets for which they had detailed information. This information (and as much of the data as feasible) was transmitted to the project team for evaluation. The team then determined whether individual data sets so offered were suitable for model testing. Model testing as such was not performed under this task. But the results will be valuable for future efforts at verification of model

performance and documented applicability to the “real world” and the engineering workplace.

CHAPTER 2

TASK 1: CONFIRMATION OF PHASE II METHODOLOGY

2.1 INTRODUCTION

In this task, confirmation of the Phase II methodology was examined at laboratory scale by linkage of leachate generation to soil columns to represent the impermeable highway, piling, and fill reference environments. Full confirmation of the Phase II methodology is not possible at the laboratory scale due to constraints on the size of flat-plates that can be tested resulting in limitations on the volume of leachate that can be generated for RRR testing. Because of these constraints, the methodology will be tested in relation to RRR processes in soil columns using leachate generated by the short-term batch leaching procedure. These experiments are, therefore, limited to confirming the extent of removal of leached chemicals from impermeable highway surfaces, pilings, or fill, by sorption on roadside soils and concomitant biodegradation. Photolysis and volatilization were not examined in the soil column experiments because these processes are not relevant for the piling and fill reference environments. These processes are considered insignificant for the impermeable highway reference environment because of short times of exposure for significant removal or reduction (see Phase II results in Volume II). In summary, leachate generated by the short-term batch procedure will be introduced into soil columns of varying length. Data collected will be the chemical composition and toxicity of the column influent and effluent. Column effluent data are represented in the form of a breakthrough curve of concentration vs. time or volume. A tracer run through the column is used to determine dispersion. Physical parameters of the column flow characteristics and dispersion, and RRR process parameters are then used in the mathematical model to generate a predicted breakthrough curve. Comparison of the experimental and model-generated breakthrough curves enables confirmation of the Phase II methodology.

Two C&R materials were selected for testing in Task 1. The leachate generated for testing must contain easily measurable concentrations of leachate chemical constituents at concentrations high enough so that soil column breakthrough can be achieved in a realistic time-frame for laboratory experimentation (days to few weeks). Wood pilings preserved with ACZA were proposed as one C&R test material. ACZA-treated wood has the advantage that its leachate contains high concentrations of metals and organics, thus enabling both sorption and biodegradation to be assessed in the soil columns, although biodegradation will likely be inhibited by metals toxicity. The second proposed test material was crumb rubber asphalt cement (CR-AC), which is more representative of typical highway C&R materials. CR-AC has been shown to leach both organic compounds (e.g., benzothiazole) and metals (Al, Hg) that are known toxic substances (see Phase II results in Volume II). Benzothiazole was shown to be removed by biodegradation, and benzothiazole plus the metals (Al, Hg) were removed by adsorption on the standard test soils. A modification of the test materials in Task 1 was made, since new CR-AC materials tested in Phase III do not have sufficient concentrations of organic compounds (specifically benzothiazole) in their leachates to warrant testing to confirm Phase II methodology. 2,4,6-trichlorophenol (TCP, used in Phase II for QA/QC testing; see Volume IV, Nelson et al., 2000b) was substituted as a surrogate leachate, in order to

produce measurable results that can be used to generate modeling parameters and allow comparison of laboratory and predicted model results.

2.2 LITERATURE REVIEW

2.2.1 Soil Sorption Concept

Soil in this study refers to the loose material composed of weathered rock and other minerals, and also partly decayed organic matter, that covers large parts of the land surface of the earth. Soil is the essential component of the terrestrial ecosystems of the earth. It supports plant growth and provides a habitat for large numbers of animals and microorganisms that decompose leaf litter and plant residues, thereby helping to cycle the nutrients on which plant growth depends (Wild, 1993). Soil consists of a large variety of materials composing the uppermost layer of the earth's crust upon which plants grow. In addition to solids, soil contains air and water. Typically, soil solids consist of about 95 % mineral matter and 5% organic material, although the proportions vary widely. The weathering (physical and chemical disintegration) of parent rocks form soils as the result of interactive geological, hydrological, and biological processes (Manahan, 1994).

The effect of mineral contents in soil can vary the soil properties as well. The main effects of the sand and silt fractions are on the physical properties of soils such as the drainage, water transmission and water content. The minerals in the sand and silt fractions have little effect on the chemical properties of soils. The clay fraction is different. The minerals in the sand and silt fractions are the residues from the disintegration of the parent material and hence are often known as primary minerals. The products of chemical weathering in the clay fraction are known as the secondary minerals. The minerals in the clay fraction impart chemical and physical properties to soil, which strongly influence its behavior, for instance in adsorbing cations, anions and pesticides and acting as a source of plant nutrients.

There are many fractions involved in soil sorption. One is the soil surface. In various applications it is often assumed that the equilibrium state is sufficient to account for the degree of change of a solute, spatially and/or temporally, because the reactions or processes occurring at the surface are fast relative to the other changes in the system. The validity of this local equilibrium approach rests at least in part with the rate of sorption of solute at the surface. Several retention mechanisms can be operative within a soil system. Cation exchange and specific adsorption are two mechanisms controlling metal adsorption. Heavy metals can also be retained by mechanisms other than sorption such as solid-state diffusion and precipitation reactions. Heavy-metal retention has been found to generally increase with increases in soil pH, cation exchange capacity, organic content, clay content, and the metal oxide content of a soil. In addition, the strength of metal retention generally increases as the initial concentration of the contaminant decreases. Soil organic matter has been of particular interest in studies of trace metal sorption by soils, because of its significant impact on cation exchange capacity, and more importantly,

the tendency of transition metal cations to form stable complexes with organic ligands (Elliott et al., 1986).

There are some important factors involved in soil surface adsorption. It can be divided into two terms related to intermolecular interactions. The first term is composed of van der Waals forces, hydrophobic bonding and water structure, hydrogen bonding, charge transfer, ligand exchange, ion exchange, direct and induced ion-dipole and dipole-dipole interactions, magnetic interactions, and chemisorption. The second term consists of the influence of organic matter, pH and temperature, which can have dramatic effects on soil surface adsorption. A study of DDT adsorption on soil suggests that this variability from soil to soil may be due, in part, to variations in the composition of the organic matter complex. The extraction of mineral soil with ether or alcohol produced a dramatic increase in the sorption efficiency. The amount of organic matter can limit the adsorbing surface per unit weight of organic matter. Sorption capacity tends to be increased with higher organic content.

The effect of temperature on soil surface adsorption shows the relationship of bonding and strength of adsorption. Adsorption is an exothermic process (the enthalpy is negative) so the higher the temperature, the less the adsorption. Change of temperature will have greater effect for reactions involved with stronger bonds. Much higher values for heats of adsorption would be observed for stronger bonding such as chemisorption. The acceleration of rate processes by elevated temperatures could increase the contribution from long-term adsorption at higher temperatures.

The pH value has a great effect on soil adsorption for weak acids and weak bases. Weak acids are in the free acid form at low pH value and are much more highly adsorbed in this form than as the anion. Weak bases are converted to cationic forms in the low pH range, and these also are more weakly adsorbed than the free base. The decreasing or increasing hydrogen ion concentration introduces a competitive effect and decreases adsorption as a hydrogen ion replaces the organic cation. Solubility and plant availability of most heavy metals in any given soil are known to be inversely related to pH (Sinha et al., 1978; Halstead et al., 1969; McBride and Blasiak, 1979)

Soil is a “messy” mixture and has many substances that provide adsorption sites. This case has to be carefully considered, because the sum of the adsorption from solutions of mixtures of complex molecules is equal to the sum of their individual adsorption at the same solution concentration in simple solutions. The basic theory of competitive adsorption in chromatography columns has been developed as the concept of coherency. A composition profile is coherent if, at a given time, all concentrations coexisting at any location in the column have the same velocity (Helfferich, 1968). For the condition that any location in the profile has the same velocity, it may be termed as having no dispersion effect.

2.2.2 Soil Properties Affecting Metal Sorption

The contamination of soils by heavy metals has resulted from a number of activities, including vehicle emissions; mining; smelting, and metal plating and finishing operations. The removal techniques of metals from soils basically involve contacting the soil surface with an extracted aqueous solution. The ways to mobilize the metals in soils have been identified by Pickering (1986) as changing the acidity, changing the system ionic strength, changing the oxidation/reduction (redox) potential, and forming complexes. The addition of complexing ligands can convert solid-bound heavy metal ions into soluble metal complexes.

For the last technique, the effectiveness of complexing ligands in promoting the release of metals depends on the strength of bonding to the solid surface, the stability and adsorbability of the complexes formed, and the pH value of the suspension (Robert et al., 1992). Studies on heavy-metal mobility in soil columns have shown that metals in solution are sorbed on soil surfaces (Korte et al., 1976). Batch experiments have been used to investigate competitive adsorption of heavy metals by soils (Elliot et al, 1986). Results from batch and column studies have mostly been used to elucidate the behavior of metal adsorption and to provide insight about the type and nature of adsorption sites.

2.2.3 Determination of Sorption Equilibrium Parameters in Column Experiments

There are two main experimental protocols for performing sorption equilibria. Basically, batch experiments are used to determine equilibrium sorption isotherms for soils or geomeia. These approaches are routinely performed in many environmental science laboratories, and they can easily simulate sorption processes with time constants of days to weeks. There are some disadvantages of this protocol, such as the poor separation of the medium-to-high molecular weight fraction of organic matter from the sorbed phase, which cannot often be achieved by ordinary centrifugation. Those problems are one of the reasons for observation of the particle concentration effect in which the distribution coefficient depends on the solid-to-solution ratio (Manahan,1994). An alternative protocol has been created using flow-through reactors for the determination of sorption parameters. This protocol allows simple and rapid measurement of nonlinear adsorption isotherms using column experiments and the assumption of local equilibrium of chromatography (Cleve et al., 1972). The batch experimental approach was used for determining leachate adsorption parameters in this study.

2.2.4 Bromide Tracer Study

Field monitoring of the subsurface of a saturated catchment or watershed needs to be performed for site treatment or understanding of the site characteristics. Sometimes the pattern of the sub-surface flow may be difficult to discover or to interpret by conventional hydrological experiments. There are two main kinds of tracers that are widely used in hydrology. The first is trace elements that already exist under the subsurface, such as chloride dissolved in rainwater. Chloride is carried into the soil by soil-water infiltration and remains there or in groundwater in concentrations that are greatly increased at

locations where most of the water is abstracted from the soil by the process of evapotranspiration. The second is an artificial tracer injected into the aquifer or soil water for determining hydrological parameters, such as flow rate and retardation effect. This kind of tracer must be carried by water and must be able to be recovered after a period of time. Any effects or reactions between the tracer and the geomeedia are prohibited.

Ideal tracers should be stable isotopes. For example, chloride is presented in the soil water as one of the balancing anions to commonly occurring Na, K, Ca and Mg. Unlike another anions, chloride is not a significant participant in geochemical reactions, but the amount of chloride can be varied by evaporation, root extraction and rainfall dilution. At this point, bromide is more stable for oxidizing reagents and also the bromide ion is unique and rare to find in nature. The unpopularity of using chloride as the conservative tracer comes from the wide existence of chloride ions in the subsurface and possible complex formation of chloride and metals (Marshall et al., 1996). KBr has been a popular conservative tracer for simulating hydrogeological parameters, because of its low cost and lower complexing capability with metals. To determine accurate values of hydrogeological parameters, tracers are required to have no reaction with or removal by geomeedia during transport.

2.2.5 Degradation Pathways of 2,4,6 Trichlorophenol

Chlorinated phenols have been widely used as herbicides, insecticides, fungicides, and wood preservatives. They are also found in Kraft pulp mill effluents in large quantities (Lindstorm and Nordin, 1976). The inadequate handling of chlorophenol-treated materials, accidental spills, and leaching from dumping sites have resulted in the serious contamination of soil and groundwater (Kitunen et al., 1987). Chlorophenol released into the natural environment is known to be significantly toxic and carcinogenic.

One of the chlorophenols widely used, as a wood preservative is 2,4,6-trichlorophenol (TCP). 2,4,6-trichlorophenol is an environmental contaminant originating from the manufacture of insecticides and herbicides or formed from these as a metabolite in soil. The biological degradation of chlorophenols has been regarded as an attractive means of treating contaminated regions because many soil microorganisms can convert chlorophenols into cell mass and harmless products such as CO₂ and chloride. Many different types of microorganisms are known to use trichlorophenol as their sole carbon and energy source, which include *Pseudomonas*, *Arthrobacter*, *Rhodococcus*, *Flavobacterium*, and *Azotobacter*.

The products of chlorophenol degradation are highly variable. They depend widely on additional compounds in the system, the microorganism species, and upon the surrounding system. Commonly, 2,4,6-trichlorophenol can be partially dechlorinated to 4-chlorophenol (4-CP) by anaerobic microorganisms (Armenante et al., 1993) that are normally present in nature. With unknown mixed cultures, the products of 2,4,6-TCP degradation will be a wide range of compounds with some significant amount of CO₂ and chloride ions in an aerobic environment.

2.3 EXPERIMENTAL METHODS

2.3.1 Experimental Approach

Column experiments: The experimental approach is focused on evaluating the retardation and breakthrough curve characteristics of the packed soil columns under continuous flow conditions through reaction with ACZA leachate and 2,4,6 trichlorophenol. Air-dried soils packed in two columns with varying lengths were selected to investigate whether the toxic constituents extracted from ACZA and TCP could be ameliorated by contact with the soils. Duplicate experiments (column runs) were made to ensure the repeatability of tests. Column experiments were conducted under uniform conditions with different lengths of column and soil weights eluted with ACZA and TCP leachate. Columns were initially flushed with deionized water to elute TOC and attain hydraulic stability. The initial parameters, TOC, pH and concentration, were measured to understand the background information both in leachates and column effluents.

As the drainage of rainfall or surface water penetrates throughout the depth of a soil aquifer, the contaminant ions adsorb onto the soil adsorbent and the contaminant concentration in the aquifer decreases. Finally, the adsorbent particles become saturated with the contaminants. The “breakthrough” curve of outflow contaminant concentration versus time is used to characterize the adsorption behavior of the soil as a function of process variables.

The simulation of a groundwater flow through soil aquifer material will be conducted by one-dimensional adsorption experiments in packed columns. The contaminant concentration in the column effluent is measured as a function of time in order to determine breakthrough curves. A tracer run through the column is used to determine dispersion and some physical parameters of the column flow characteristics. In order to understand the characteristic of the soil aquifer, the breakthrough is monitored by process variables such as flow rate, pH, and concentration of compound of interest. The investigation plan is performed through experiments for:

- Development of experimental column of breakthrough curves, and desorption with distilled water as a function of time or effluent pore volumes.
- Investigation of influent factors effect such as retardation factor and dispersion coefficient on adsorption kinetics, which were predicted as the great effect to the groundwater transport.
- Determination of adsorption capacity and removal by the adsorbent (soil) for the compounds of interest.
- Determination of removal of compound of interest by biodegradation.

Based on the objectives of this study, four sizes of glass soil columns (50,100,200, and 600-mm lengths, 25-mm inside diameter) and two hazardous materials leachates (ACZA-wood preservative and 2,4,6-TCP) were selected to perform the column experiments (Table 2.3.1.1). Hydrological characteristics of each soil column were initially determined by running bromide as a conservative tracer for calculating the retardation factor, dispersion coefficient and Peclet number (see Section 2.4.1). The Peclet number represents the ratio of advective to dispersive transport in solute transport. As the Peclet number increased, dispersion becomes less important relative to advection for contaminant transport.

Table 2.3.1.1. Summary of soil column operating conditions.

Column Designation	Soil type	Leachate	Length mm	Run No.	column volume mL	Pore Volume mL	Mass of Soil g	Packed density g/cm ³	% porosity
W-A-50-1	Woodburn	ACZA	50	1	24.6	9.8	39.0	1.6	49.3
W-A-50-2	Woodburn	ACZA	50	2	24.6	10.1	38.2	1.6	41.3
W-A-100-1	Woodburn	ACZA	110	1	54.0	27.9	69.2	1.4	46.8
W-A-100-2	Woodburn	ACZA	110	2	54.0	28.7	67.1	1.4	52.5
W-A-200-1	Woodburn	ACZA	200	1	98.2	42.7	147.0	1.5	43.5
W-A-200-2	Woodburn	ACZA	250	2	122.8	66.1	150.1	1.2	53.9
W-A-600-1	Woodburn	ACZA	600	1	294.6	118.3	467.2	1.6	40.2
S-A-50-1	Sagehill	ACZA	50	1	24.6	9.1	41.0	1.7	37.0
S-A-50-1	Sagehill	ACZA	50	2	24.6	8.0	43.8	1.8	32.7
S-A-100-1	Sagehill	ACZA	110	1	54.0	20.1	89.8	1.7	37.3
S-A-100-2	Sagehill	ACZA	110	2	54.0	23.8	80.2	1.5	44.0
S-A-200-1	Sagehill	ACZA	250	1	122.8	53.5	183.5	1.5	43.6
S-A-200-2	Sagehill	ACZA	250	2	122.8	55.1	179.4	1.5	44.9
W-T-50-1	Woodburn	TCP	50	1	24.6	9.8	38.97	1.6	40.1
W-T-50-2	Woodburn	TCP	50	2	24.6	13.6	28.9	1.2	55.6
S-T-100-1	Sagehill	TCP	110	1	54.0	27.0	71.6	1.3	50.0
S-T-100-2	Sagehill	TCP	110	2	54.0	25.8	74.9	1.4	47.7

Microorganism supply (“mother”) reactor: A 500-mL reactor, named the “mother reactor”, was seeded initially from 300-mL of mixed culture from the Corvallis Wastewater Reclamation Plant and fed by fill-and –draw with a nutrient solution containing phenol as substrate. The mother reactor was maintained to keep a constant number of cells (phenol-degrading microorganisms) in order to biodegrade 2,4,6-TCP in subsequent experiments. A 100-mL volume of mixed liquor was harvested from the mother reactor daily and replaced with 100-mL of the feed nutrient solution, which made the mean cell residence time equal to 5 days. The feed nutrient solution consisted of combination of 2.60 mL of 7.7 g/L of phenol solution plus nutrient solution to 100 mL, calculated to keep the same daily initial concentration of 40 mg/L of phenol as the sole carbon source for the microorganisms. The nutrient solution was prepared to fulfill the growth needs of the microorganisms. As shown in Lee et al. (1991), the solution consisted of 7 g of Na₂HPO₄, 3 g of K₂HPO₄ and, 1 g of NH₄NO₃, then added tap water until the total volume reaches 1 L before autoclaving. An additional 0.3 g of MgSO₄ and 0.015 g of FeSO₄·7H₂O were added to the previous autoclaved solution before autoclaving again. The nutrient solution is prepared fresh every week. Mixing is needed for nutrient media before addition to the mother reactor due to some precipitate that is formed.

The mother reactor was assumed to behave like a steady-state activated sludge reactor that basically maintains the cell number constant and achieves a high rate of removal by recycling the cells. In this reactor, the number of cells was maintained by limiting the substrate feed over time (40 mg/L of phenol feed daily) and cell concentration was monitored by determining turbidity (Hach-Model 2100P turbidimeter) as a surrogate parameter. The turbidity is reasonably proportional to the concentration of microorganisms (without the presence of solid phase precipitation in the mother reactor). This partially supported the assumption that all suspended solids in the reactor are microorganisms. The turbidity was found constant after 40 days of running the mother reactor. Total suspended solids were measured at approximately 1500 mg/L in the mother reactor.

2.3.2 Materials

2.3.2.1 C&R materials and soils

Two highway construction and repair (C&R) materials, ACZA and 2,4,6 trichlorophenol, were selected for testing. The leachate generated by these two materials must contain compounds of interest at sufficient concentrations to be measurable and to be toxic, so that the soil column breakthrough would be well defined. Wood pilings preserved with ACZA are proposed as one C&R test material. ACZA-treated wood has the advantage that its leachate contains high concentrations of metals and organics, thus enabling both sorption and biodegradation to be assessed in the soil columns, although biodegradation will likely be inhibited by metals toxicity. The second proposed test material is 2,4,6 trichlorophenol. TCP serves as a surrogate leachate (not directly leached from a highway C&R material) that contains a biodegradable toxic organic compound.

The methodology verification experiments were run using the Aridisol (Sagehill) soil and the Mollisol (Woodburn) soil. The Mollisol and Aridisol bracket the organic extremes for the three soils used in the project (Olyic Ultisol soil not used). Soil properties are listed in Table 2.3.2.1.1. The average diameter was found from a weighted average of diameters found in a sieve analysis by county soil surveys (Soil Survey of Benton County Area, Oregon, 1975; Soil Survey of Gilliam County, Oregon, 1984).

Table 2.3.2.1.1. Properties of standard test soils.

Soil Type	% Organic Matter	CEC meq/100g	Average diameter, mm
Sagehill (Aridisol)	1.91	11.7	0.30
Woodburn (Mollisol)	6.44	18.8	0.016

2.3.2.2 Preparation of ACZA leachate

Wood pilings preserved with ACZA contain high concentrations of toxic metals. Leachate preparation consisted of shaving commercially available wood-posts, treated with ACZA, to 3/8-inch depth. The wood shavings are collected, mixed together to obtain

uniformity, and then stored in polyethylene bags to prevent adsorption of atmospheric moisture. Requisite samples for leachate generations are taken from this bulk quantity.

ACZA leachate was prepared by adding distilled water to the wood shavings at a weight ratio of 1 part dry weight material to 20 parts by weight distilled water (1:20 ACZA shavings: distilled water). The materials were placed into nalgene bottles, which were sealed with lids that have been taped or covered with parafilm to prevent leakage. The elution jars were placed into a rotary extractor, padded with foam pads to prevent breakage, and mixed end-over-end for 24 hours. After 24 hours of mixing, the jars were removed from the extractors and the leachate was filtered through a prefilter (Whatman Qualitative paper) initially to remove larger particles and then through Whatman 0.45µm membrane filter paper.

The final leachate was measured for pH, TOC and the concentrations of arsenic, copper and zinc. Leachate was stored in the dark at 4°C before the analyses were performed. Leachate should not be stored for more than two weeks before analysis or use in experiments, as chemical changes may occur during storage, particularly with the TOC content. This requirement resulted in the preparation of several small quantities of leachate rather than one large volume with a range of leachate constituent concentrations (Table 2.3.2.2.1). In column studies, for the maximum length of column, a minimum of 14 liters of ACZA leachate was needed. Each column experiment was performed with a single leachate preparation. The initial concentration of metal and TOC were variable for each preparation of ACZA leachate.

Table 2.3.2.2.1. Initial ACZA leachate parameters after 24-hour batch leaching (typical: values vary somewhat for each batch).

	Al	As	Cu	Zn	pH	TOC
	mg/L	mg/L	mg/L	mg/L		mg/L
ACZA leachate	0.000	26-37	23-30	7-9	6.5-7.2	450-600

2.3.2.3 TCP solution preparation

800 mg/L TCP was prepared from 98% 2,4,6 TCP from Aldrich Chemical Company solution and kept in a dark amber glass container at 4 °C temperature. TCP feed solution (2 mg/l) was prepared from 2.5 mL of 800 mg/L TCP in 1000 mL of distilled water. To prevent the growth of unknown microorganisms in the system, the feed solution was autoclaved at 125°C for 60 minutes before use. Autoclaved feed solution was prepared weekly.

2.3.3 Experimental Methods

2.3.3.1 Batch experiments

Batch reactor experiments were conducted to determine the maximum removal or degradation capacity of soil only, bacterial cells only, and soil with cells. A 100-mL volume of cells from the mother reactor was harvested daily. To each of ten reactors was

added 20-mL of cells harvested from the mother reactor in glass sample bottles with variation of TCP concentration of 2, 5, and 20 mg/L, and 2 and 5 mg/L with nutrients. Nutrients are added to the reactors because of possible limitation of TCP degradation from lack of nutrients. No addition of soil was involved with these five reactors. Duplication of each reactor was performed to help ensure the experimental repeatability.

Four reactors were prepared by adding Sagehill soil and Woodburn soil with varying TCP concentrations of 2 and 5 mg/L. These four reactors were used as the control for comparison of physical adsorption and biodegradation of TCP with soil. Eight reactors (four reactors for each type of soil) were prepared by adding 20 mL of cells and 1 g of soil with varying TCP concentrations of 2, 5, and 20 mg/L. Autoclaved soils were employed in this experiment to ensure no indigenous bacteria were contributing to degradation processes.

2.3.3.2 Soil Column experiments

The three glass column lengths, 50, 100, and 200 mm, were wet packed with the selected soil to approximately constant porosity of 0.35 to 0.5. The columns were made from glass, with Teflon screw fittings. Hydraulic flow through the columns was set to approximate typical field conditions by using a constant head pump at a constant rate of 10 mL/hour. Initially, hydraulic tracer experiments using bromide were conducted to determine the retardation factor and dispersion coefficient. In normal column experiments, metals and organic compounds will be first adsorbed on the adsorbent material in the background electrolyte solution until equilibrium is achieved (column effluent equals column influent concentration). Then, the compound of interest will be extracted (desorbed) from the adsorbent bed (soil) by distilled water (rainfall simulation). Metals concentrations, pH and total organic carbon were monitored throughout the experiments.

2.3.3.3 Soil Column Preparation

The following procedure was used to prepare soil columns for each column experiment. The bottom outlet of an empty glass column was closed with a Teflon screw cap to prevent leaking. Deionized water was run up flow through the bottom of the column to ensure the void space between cap and column was not filled with air. Deionized water was allowed to flow continuously until approximately 1 cm of water depth is presented at the bottom of the glass column (Figure 2.3.3.3.1).

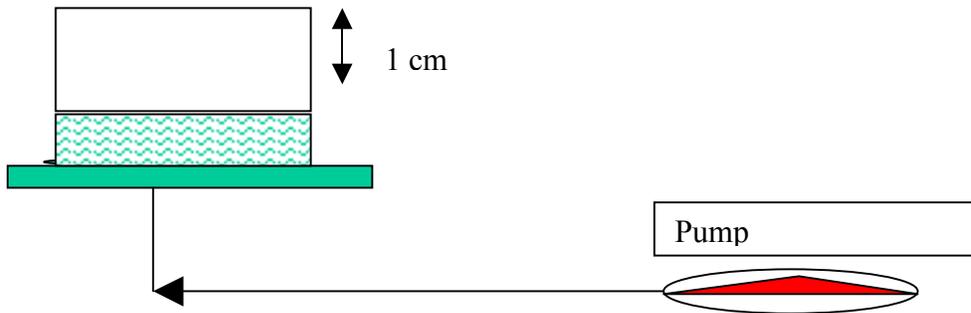


Figure 2.3.3.3.1. Bottom inlet view of soil column.

While the flow of deionized water is continuing, add soil particles to settle down under the water (Figure 2.3.3.3.2). At least 0.5 cm of water layer was left above the soil layer to ensure that the air bubbles do not penetrate into the soil.

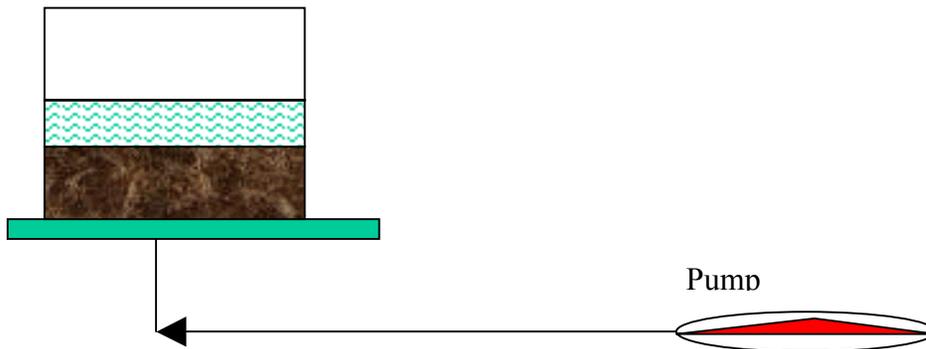


Figure 2.3.3.3.2. Soil column showing bottom inlet view and soil settle down under the water.

Continue adding more soil into the column while the water level is rising until the water level almost reaches the top of the column (Figure 2.3.3.3.3). At this final step, dry soil will be added quickly to fill out the column. The reason of doing that is the top of the column cannot be filled with wetted soil, otherwise, the top Teflon screw cannot be tightly capped. After capping is completely, flow is continued to stabilize soil and water system and eliminate existing air bubbles in the system for at least 24 hours before running experiments.

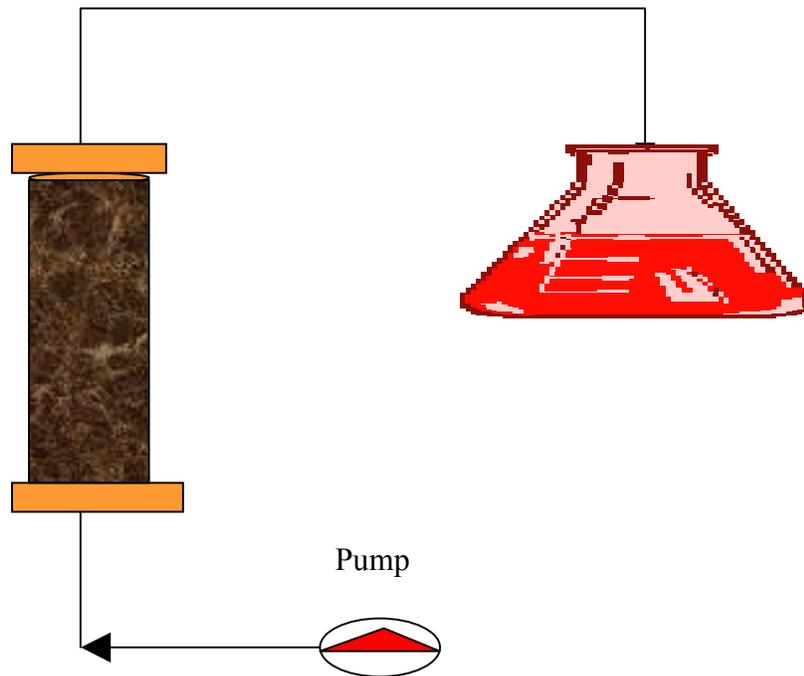


Figure 2.3.3.3.3. Complete soil column view showing packed soil and both top and bottom inlets.

2.3.4 Analytical Methods

2.3.4.1 Metal measurement

Inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian Liberty 160) was used for the determination of multiple metal concentrations. A detailed explanation of the ICP methods is given in Volume IV (Nelson et al., 2000b).

2.3.4.2 TOC measurement

The TOC in the leachate samples was measured by Total Organic Carbon (TOC) analyzer. A detailed explanation of the TOC methods is given in Volume IV (Nelson et al., 2000b).

2.3.4.3 TCP measurement

A ^{63}Ni electron captures detector or ECD was used for targeting analyzes qualification and quantification. The 30-meter length and 0.25 mm I.D. capillary column with a film thickness of 0.25 μM of Rezttec fused silica was used in the GC (Hewlett-Packard: HP6890 plus gas chromatographic). An initial oven temperature of 45 ° C was held for 3

minutes then increased at a rate of 35 ° C per minute to achieve a final temperature of 225 ° C. The final temperature was held for 4 minutes while injection and detector temperature were kept at final temperature. Helium gas was used as the carrier gas with the mixture of Argon and methane as the ratio of 95:5, respectively for detector auxiliary gas at 60 mL per minute as the constant rate.

The analysis of trichlorophenol was conducted by using a modified method described by Voss et al., (1980) and Smith (1993). The samples were first acetylated and then extracted into hexane. 100 µL samples were mixed in a screw-top culture tube with exact 1-mL of a reaction medium containing 43 g/L K₂CO₃ and 1 mg/L 2,4,6-tribromophenol as an internal standard. One hundred µL of acetic anhydride was added, the tube was capped, then shaken on a wrist-action shaker for 20 minutes. 2 mL of hexane were then added, and the tube shaken for an additional 20 minutes. The extracted hexane fraction was transferred to an auto-sampler vial and capped with a Viton septum and crimp-seal cap (Wang, 1995).

2.3.4.5 Phenol measurement

Analysis of phenol was carried out by using a Dionex Series 2000i High Pressure Liquid Chromatograph (HPLC) equipped with an ultraviolet lamp detector set at 253 nm wavelength and fitted with Phenomenex Ultracarb 5 ODS (30) 150 mm length and 4.6 mm I.D. column (Serial Number 16167) with pore size 5 micron. The eluent was composed of 60% of acetonitrile and 40% of deionized water. The flow rate was set at 0.8 mL/min.

2.4 RESULTS AND DISCUSSION

2.4.1 Bromide Tracer Soil Column Test

The retardation factor and dispersion coefficient were determined by bromide, a conservative tracer, to ensure the uniformity and homogeneity of packed columns. For a conservative tracer, the retardation factor should be 1.0. The CFITIM model (van Genuchten, 1981) was used to fit the Br⁻ tracer data and calculate Peclet numbers and retardation factors for the Br⁻ tracer test. This model computes a best-fit solution of the advective-dispersion equation with equilibrium sorption (see Appendix A, Equation A.5.1.2) using a least-squares criterion. The fitting parameters are the Peclet number and retardation factor for the dimensionless form of the equation. Calculated Peclet numbers and retardation factors are shown in Table 2.4.1.2 from the 20-mg/L KBr tracer breakthrough data. (All Task 1 data are summarized in Table 2.4.1.1 at the end of this chapter.) For Sagehill soil tests in the 100-mm and 200-mm columns, breakthrough curves and CFITIM fits to the Br⁻ data are shown in Figures 2.4.1.1 and 2.4.1.2. As indicated in these two figures, the model fits to Br⁻ data were good. These results are discussed below.

The main transport and fate processes of concern for the groundwater pathways studied in this project are advection, dispersion, diffusion, adsorption and biodegradation. The following definitions apply.

Flux: Transport of mass per unit area per unit time, i.e., with units of mass/area-time. Total mass transport in a given direction is the product of the flux and the flow area.

Advection: Advection is the transport of contaminants with flowing ground water at the seepage velocity in porous media.

$$\text{Mass transport by advection} = \eta A v_p C \quad (2.4.1.1)$$

where:

η = porosity,

v_p = seepage or pore velocity (Darcy velocity divided by the porosity, always less than the microscopic velocities of water molecules moving along individual flow paths, due to tortuosity),

C = concentration at any point, and

A = total cross-sectional area of solids and voids.

The flux is multiplied by the product of porosity and area in Equation 2.4.1.1 to reflect the fact that transport occurs only through the voids, not through the total cross sectional area.

Diffusion: Diffusion is a mass-transport process in which solute move from areas of higher concentration to areas of lower concentration. It occurs in laminar and turbulent flow, but in laminar groundwater flow it is expected to be just due to molecular diffusion, not turbulent eddies.

Hydrodynamic dispersion: Hydrodynamic dispersion is a diffusive-type flux in the direction of the flow caused by computing a spatial average concentration across void spaces within which there are velocity variations in the porous media.

Dispersion/diffusion causes sharp fronts to spread out and results in the dilution of the solute at the advancing edge of the contaminant front.

$$\text{Mass transport by dispersion} = - \eta A D_1 (dC/dz) \quad (2.4.1.2)$$

where:

D_1 = coefficient of hydrodynamic dispersion, and

dC/dz = the gradient of concentration.

The negative sign accounts for positive flux in the direction of decreasing concentration (in the direction of a negative gradient). Again, transport occurs only through the void spaces.

Hydrodynamic dispersion is the sum of molecular diffusion and mechanical dispersion,

$$D_l = D^* + D_h \quad (2.4.1.3)$$

where:

D^* = molecular diffusion in the porous medium, and

D_h = mechanical dispersion.

Mechanical dispersion is usually taken as a linear function of the seepage velocity,

$$D_h = \alpha_l v_p \quad (2.4.1.4)$$

where:

α_l = dispersivity (units of length).

Laboratory dispersivities are typically in the range of 0.1 – 10 mm (Fetter, 1999; Charbeneau, 2000). In the field, dispersivities are several orders of magnitude larger, up to 100 m or more (Gelhar et al., 1992; Charbeneau, 2000). The relative importance of molecular and hydrodynamic dispersion is discussed below, in conjunction with the Peclet number.

Sorption: The process of sorption can be divided into adsorption and absorption. Adsorption is an excess concentration at the surface of a solid, while absorption implies a more or less uniform penetration of the solid by a contaminant.

Biodegradation: Biodegradation represents the transformation of certain organics to simple CO_2 and water in the presence of microbes in the subsurface.

Peclet Number (Pe): The Peclet Number (Pe) is defined as the ratio of advective to dispersive transport of contaminants for one-dimensional, isotropic, saturated, steady flow in a homogeneous porous medium.

$$Pe = [v_p \eta C A] / [\eta D A (dC/dz)] \approx v_p L / D \quad (2.4.1.4)$$

where:

L = characteristic length,

D = a diffusion coefficient, and

$dC/dz \approx C/L$.

The characteristic length, L , is often taken as the column length for column studies but may also be taken as a characteristic of the grain size, such as average diameter, median diameter, or square root of the intrinsic permeability (Fetter, 1999; Charbeneau, 2000). The CFITIM program computes Pe based on the column length, and the diffusion coefficient is the hydrodynamic dispersion coefficient, D_l . Hence, for CFITIM analysis of column experiment data, the dispersion coefficient is given by

$$D_l = v_p L / Pe \quad (2.4.1.5)$$

with L = column length. Equation 2.4.1.5 is used to compute D_1 from the tracer experiments.

In natural soils, the Peclet number is usually based on the average grain diameter, d , and the diffusion coefficient is usually taken as D^* , the molecular diffusivity of the constituent in open water. Thus, the Peclet number is typically evaluated as

$$Pe = v_p d/D^* \quad (2.4.1.6)$$

In natural soils, for a Peclet number based on average grain diameter, when Pe is less than about 0.02, molecular diffusion governs, and is greater than the advective flux and the near-zero hydrodynamic dispersion flux (Fetter, 1999). In this case, the molecular diffusivity of the constituent in the porous medium is approximately 0.7 of the value of the molecular diffusivity of the constituent in open water (Bear, 1972; Fetter, 1999).

That is,

$$D_m \approx 0.7 D^* \quad (2.4.1.7)$$

For Pe greater than about 100, dispersion and advection are dominant, with the latter increasingly important as Pe continues to increase (Fetter, 1999). For a high advective flux relative to dispersion/diffusion, advection will be the dominant transport mechanism, and conservative solutes will move according to plug flow concepts.

Retardation Factor (R_d): Sorption causes contaminants to move more slowly than the flowing ground water because they are sorbed onto solid particles as they move with the ground water. This effect is called retardation. The retardation factor (R_d) is equivalent to the reciprocal of the ratio of velocity of the sorbing contaminant to that of the ground water, and ranges from 1 to several thousand in magnitude.

$$R_d = [1+(\rho_b/\eta)K_d] \quad (2.4.1.7)$$

where:

ρ_b = bulk density (mass/volume),

η = porosity, and

K_d = sorption distribution coefficient (volume/mass).

For 50 mm and 200 mm Sagehill soil columns, the breakthrough and desorption curve for 20 mg/L Br^- in distilled water are shown in Figures 2.4.1.1 and 2.4.1.2, respectively. Breakthrough occurred between 1 to 2 pore volumes of total flow through the column, followed by a rapid increase in the effluent Br^- concentration (C_e) until maximum adsorption capacity of the soil for removing Br^- was achieved (Figures 2.4.1.1 and 2.4.1.2). Breakthrough at a pore volume of 1.0 is the same as pure advection (plug flow) since that represents a travel distance at the pore velocity of the length of the column. Hence, the tracer results illustrate minimal dispersion and retardation.

Retardation factors from the CFITIM model were used to calculate K_d values (distribution coefficients). Theoretically, the retardation factor would not be less than 1.0 for any reason, because the bulk of the contaminant cannot travel faster than the water (advection). The low K_d values (Table 2.4.1.2) are indicative of the low retardation effect for bromide tracer in the soil columns. This is to be expected for the non-sorbing tracer.

Calculated dispersion coefficients are similar in magnitude and range from 600 to 1000 times the value of molecular diffusivity. Mechanical dispersion governs transport in the columns.

The column data may also be used to investigate the validity of Darcy's law, used in the model development. Darcy's law is

$$v_d = - K_s dh/ds \quad (2.4.1.8)$$

where:

v_d = Darcy velocity or specific discharge, mm/hr,
 K_s = saturated hydraulic conductivity, mm/hr, and
 dh/ds = gradient of hydraulic head in direction s .

Hydraulic head, h , is

$$h = p/(\rho g) + z \quad (2.4.1.9)$$

where:

p = pressure,
 ρ = water density,
 g = gravitational acceleration, and
 z = elevation.

The seepage or pore velocity, v_p , is related to the Darcy velocity by

$$v_p = v_d / \eta \quad (2.4.1.10)$$

Solutes are advected through the porous media with the pore velocity, v_p , which is faster than the spatial average Darcy velocity.

Darcy's law is valid as long as the Reynolds number, based on average grain diameter, does not exceed some value between 1 and 10 (Bear, 1972). Thus, for the soils used in this study, a Reynolds number is defined as

$$Re = v_d d / \nu \quad (2.4.1.11)$$

where ν is the kinematic viscosity of water, approximately 0.01 cm²/s or 3600 mm²/hr.

For the Woodburn and Sagehill column experiments, data from Tables 2.3.2.1.1 and 2.4.1.2 may be used to compute the Reynolds number, in Table 2.4.1.3. The very small magnitudes of the computed Reynolds numbers ensure laminar flow and the validity of Darcy's law.

Table 2.4.1.2. Summary of tracer (bromide) model transport parameters.

Values of R_d and Pe are from CFITIM model. Dispersion coefficient is found from the Peclet number (Equation 2.4.1.5) based on column length. The molecular diffusivity (D^*) is assumed to be $10^{-5} \text{ cm}^2/\text{s} = 3.6 \text{ mm}^2/\text{hr}$. The flow rate is 10 mL/hr and the diameter is 25 mm, for all columns.

Column Designation	R_d	Pe	Packed length mm	Porosity %	Bulk density g/cm ³	K_d cm ³ /g	v_p mm/hr	D_l mm ² /hr	D_l/D^*
W-A-50-1	1.2	0.9	50	49.3	1.6	0.062	41.3	2296	638
W-A-50-2	1.8	1.0	50	41.3	1.6	0.207	49.3	2466	685
W-A-100-1	1.7	1.9	110	46.8	1.4	0.234	43.5	2520	700
W-A-100-2	1.3	2.1	110	52.5	1.4	0.113	38.8	2033	565
W-A-200-1	1.2	3.1	200	43.5	1.5	0.058	46.8	3021	839
W-A-200-2	1.1	4.2	250	53.9	1.2	0.045	37.8	2250	625
W-A-600-1	1.2	12.0	600	40.2	1.6	0.050	50.7	2534	704
S-A-50-1	1	1.3	50	37.0	1.7	0.000	55.1	2118	588
S-A-50-2	1.2	1.1	50	32.7	1.8	0.036	62.3	2832	787
S-A-100-1	1.7	1.6	110	37.3	1.7	0.154	54.6	3755	1043
S-A-100-2	1.7	1.2	110	44.0	1.5	0.205	46.3	4244	1179
S-A-200-1	1.2	3.1	250	43.6	1.5	0.058	46.7	3768	1047
S-A-200-2	1.4	3.6	250	44.9	1.6	0.112	45.4	3151	875

Table 2.4.1.3 Reynolds number computation for Woodburn and Sagehill columns.

The Darcy velocity is obtained by multiplying the average seepage velocity by the average porosity for the Woodburn and Sagehill soils, in Table 2.4.1.2. The two values are about the same because the product of Darcy velocity and column cross-sectional area must equal approximately 10 mL/hr for both.

Soil column	Typical Darcy velocity, v_d mm/hr	Average grain diameter, d mm	Reynolds number
Woodburn	21	0.016	1×10^{-4}
Sagehill	21	0.30	1.8×10^{-3}

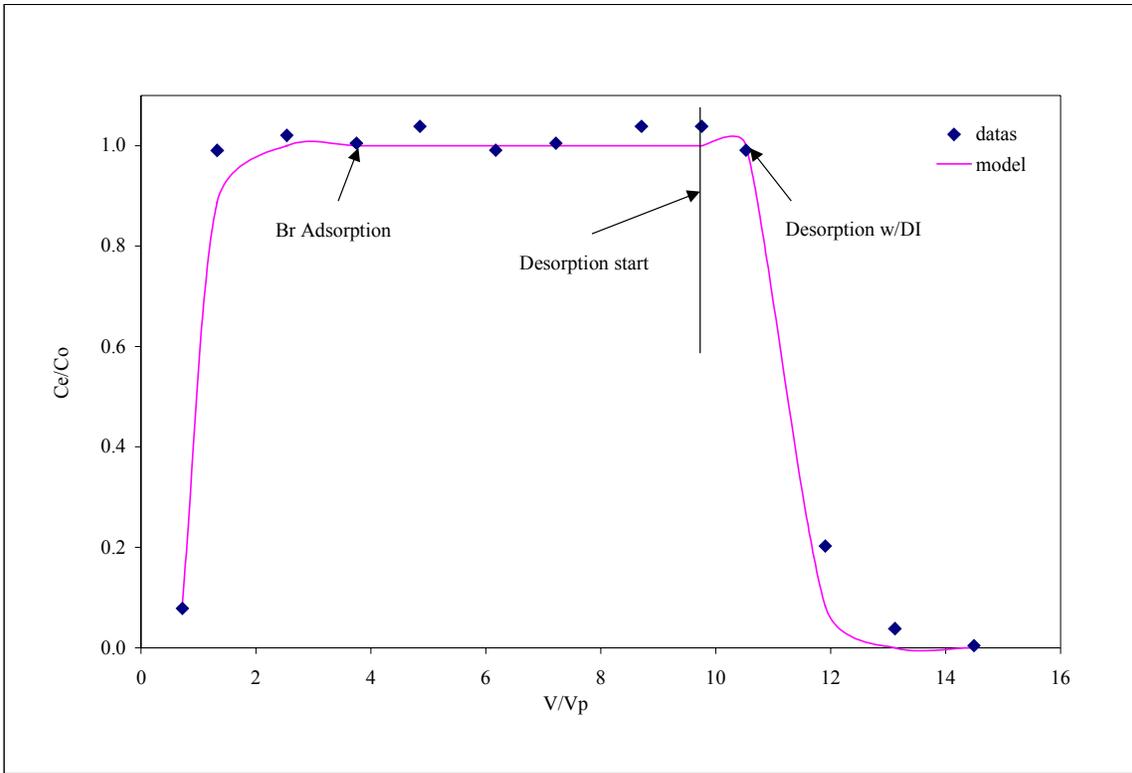


Figure 2.4.1.1. 50-mm Sagehill soil column breakthrough curve for 20 mg/L Br- in distilled water. Desorption conducted using distilled water.

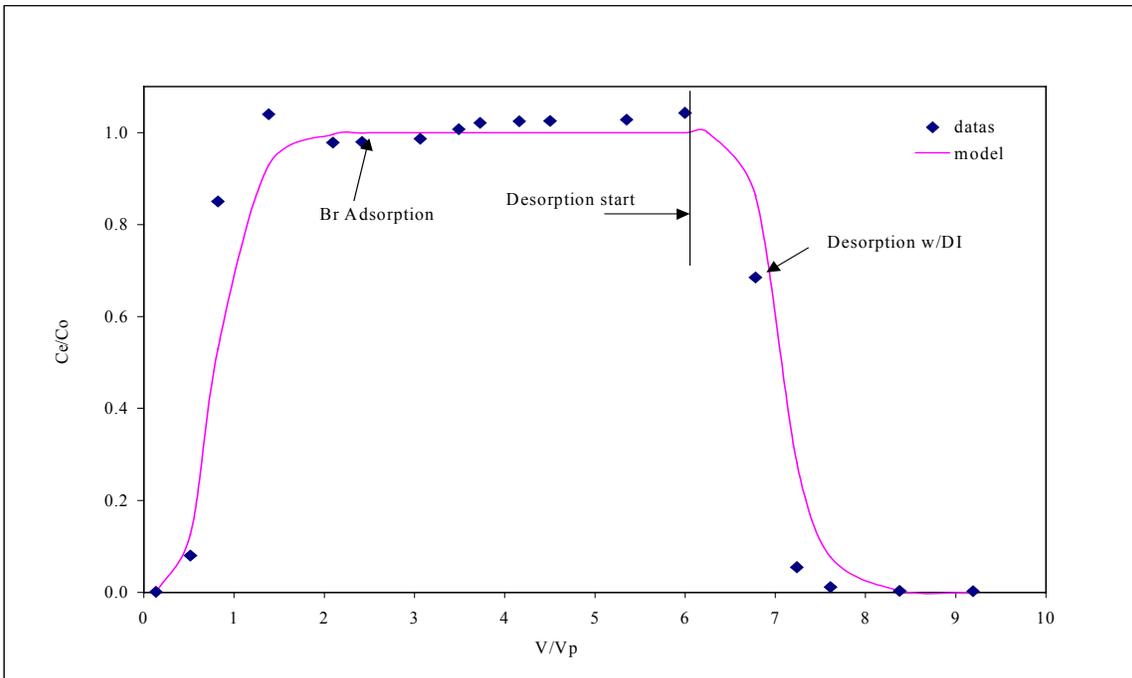


Figure 2.4.1.2. 200-mm Sagehill soil column breakthrough curve for 20 mg/L Br- in distilled water. Desorption conducted using distilled water.

2.4.2 ACZA Leachate Soil Column Sorption

Soil column experiments were conducted to more closely simulate field conditions of continuous hydraulic flow through a stationary porous medium. Columns of 50 mm, 100 mm, and 600 mm length with 25 mm inside diameters were packed with Woodburn and Sagehill soils to a porosity of about 36 to 50%. The columns were packed by adding 2-cm layers of soil and saturating with distilled water from the bottom up to ensure that no air pockets formed within the soil column. FMI (Fluid Metering, Inc.) pumps were used to control hydraulic flow (10 ml/hr) through the soil columns to approximate field conditions. ACZA leachate was prepared by the protocol described in Section 3.2.1 and kept at 4°C before experiments were performed. The concentrations of arsenic, copper and zinc were monitored throughout the run of the column experiments to depict breakthrough curves.

For the 200 mm soil column, the breakthrough curves for ACZA leachate for As, Cu and Zn adsorption and desorption on Sagehill soil are shown in Figures 2.4.2.1. For As breakthrough occurred between 20 to 30 pore volumes of total flow through the column, followed by a rapid increase in the effluent As concentration (C_e) until maximum adsorption capacity of the soil for removing As was achieved (Figure 2.4.2.1). For Cu and As equilibrium (at $C_e/C_o = 1$) was not achieved even after 80 pore volumes. As is adsorbed less than Cu and Zn. Existing as an oxyanion, As does not complex readily to soil organic matter, and its sorption may be further decreased by competition from negatively charged soluble organic compounds in the ACZA leachate. Cu forms relatively strong complexes with organic matter, and its sorption behavior appears to be more influenced by soluble organic ligands in the ACZA leachate than by soil organic matter. For Sagehill soil Cu and Zn are less affected by soluble complexation and is therefore more strongly adsorbed by the soils. During adsorption 52.1, 138.6, and 48.0 mg As, Cu, and Zn were removed from ACZA leachate, respectively. Desorption (beginning at $V_e/V_p = 85$) with distilled water removed 11.06, 0.60, and 0.08 mg As, Cu, and Zn from the column, respectively. That is about 21, 0.04, and 0.17 percent of the total adsorbed As, Cu, and Zn, respectively. The chemical analysis data are illustrated in the summary Table 2.4.1.1.

For the 100-mm soil column (replicate), the breakthrough curves for ACZA leachate for As, Cu and Zn adsorption and desorption on Sagehill soil are shown in Figures 2.4.2.2. For As breakthrough occurred between 20 to 30 pore volumes of total flow through the column, followed by a rapid increase in the effluent As concentration (C_e) until maximum adsorption capacity of the soil for removing As was achieved (Figure 2.4.2.2). However, equilibrium (at $C_e/C_o = 1$) was not achieved even after 200 pore volumes. For Cu and As, equilibrium (at $C_e/C_o = 1$) was not achieved even after 200 pore volumes. Arsenic is adsorbed less than Cu and Zn. Existing as an oxyanion, As does not complex readily to soil organic matter, and its sorption may be further decreased by competition from negatively charged soluble organic compounds in the ACZA leachate. Cu forms relatively strong complexes with organic matter, and its sorption behavior appears to be more influenced by soluble organic ligands in the ACZA leachate than by soil organic matter. For Sagehill soil Cu and Zn are less affected by soluble complexation and is

therefore more strongly adsorbed by the soils. During adsorption 22.59, 58.42, and 23.28 mg As, Cu, and Zn were removed from ACZA leachate. Desorption (beginning at $V_e/V_p = 210$) with distilled water removed 11.9, 0.1, and approximately 0.0 mg As, Cu, and Zn from the column, respectively. That is about 52.7, 0.17, and 0 percent of the total adsorbed As, Cu, and Zn were removed, respectively.

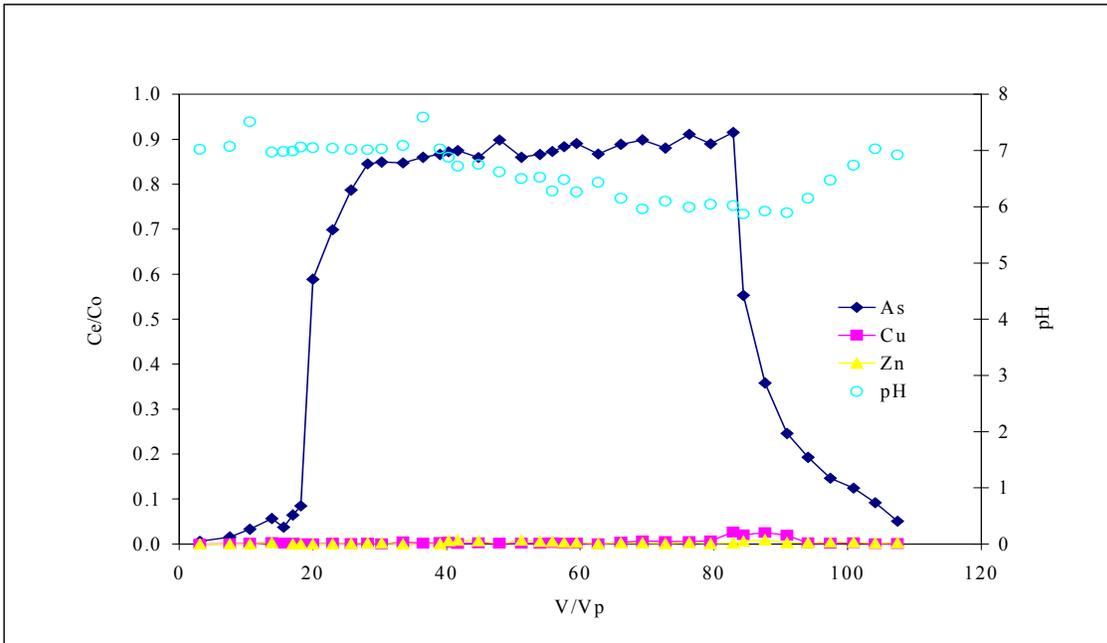


Figure 2.4.2.1. ACZA breakthrough curve for As, Cu, and Zn adsorption on Sagehill soil in 200-mm column. Desorption was conducted using distilled water.

For the 50-mm soil column (Woodburn soil), the breakthrough curves for ACZA leachate for As, Cu and Zn are shown in Figure 2.4.2.3. For As, breakthrough occurred between 5 to 10 pore volumes of total flow through the column, followed by a rapid increase in the effluent As concentration (C_e) until maximum adsorption capacity of the soil for removing As was achieved (Figure 2.4.2.3). Both Cu and Zn breakthrough occurred between 10 to 20 pore volumes of total flow through the column, followed by a rapid increase in the effluent Cu and Zn concentrations (C_e) until maximum adsorption capacity of the soil for removing Cu and Zn was achieved (Figure 2.4.2.3). However, equilibrium (at $C_e/C_0 = 1$) for both Cu and Zn was not achieved even after 150 pore volumes. Desorption (beginning at $V_e/V_p = 200$) conducted using distilled water to remove adsorbed As, Cu, and Zn from the soil column, is shown in Figure 2.4.2.3. During adsorption 12.41, 25.39, and 14.79 mg As, Cu, and Zn, respectively, were removed from ACZA leachate. Desorption (beginning at $V_e/V_p = 200$) with distilled water removed 7.7, 1.6, and 0.3 mg As, Cu, and Zn from the column, respectively. That is about 63, 6, and 2 percent of the total adsorbed As, Cu, and Zn, respectively.

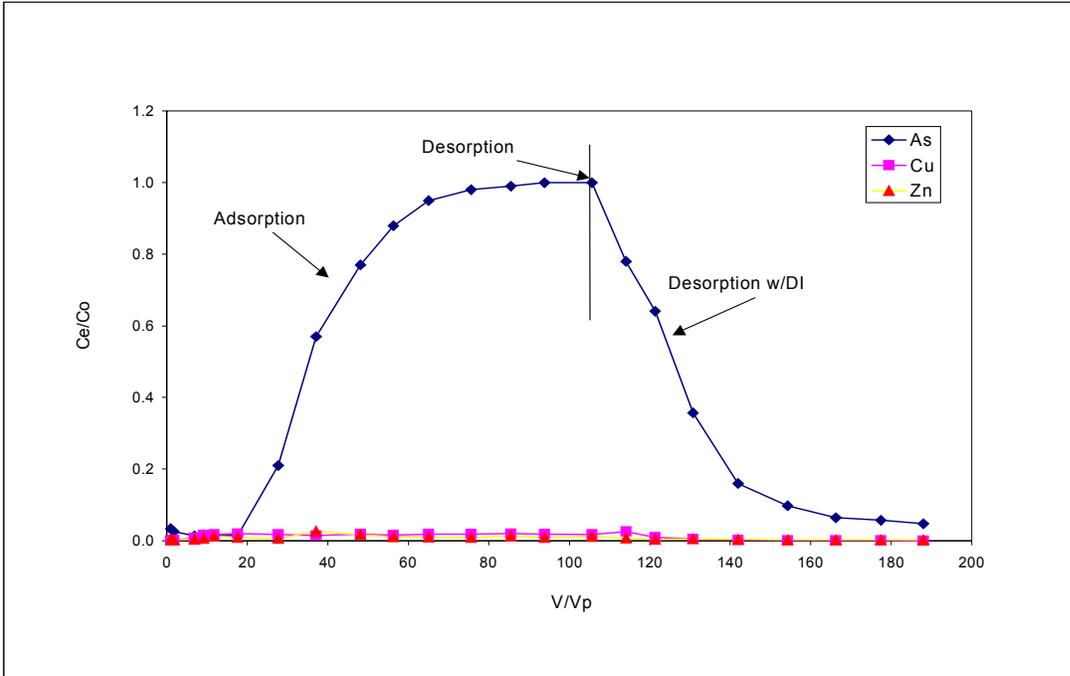


Figure 2.4.2.2. ACZA breakthrough curve for As, Cu, and Zn adsorption on Sagehill soil in 100-mm column (replicate). Desorption was conducted using distilled water.

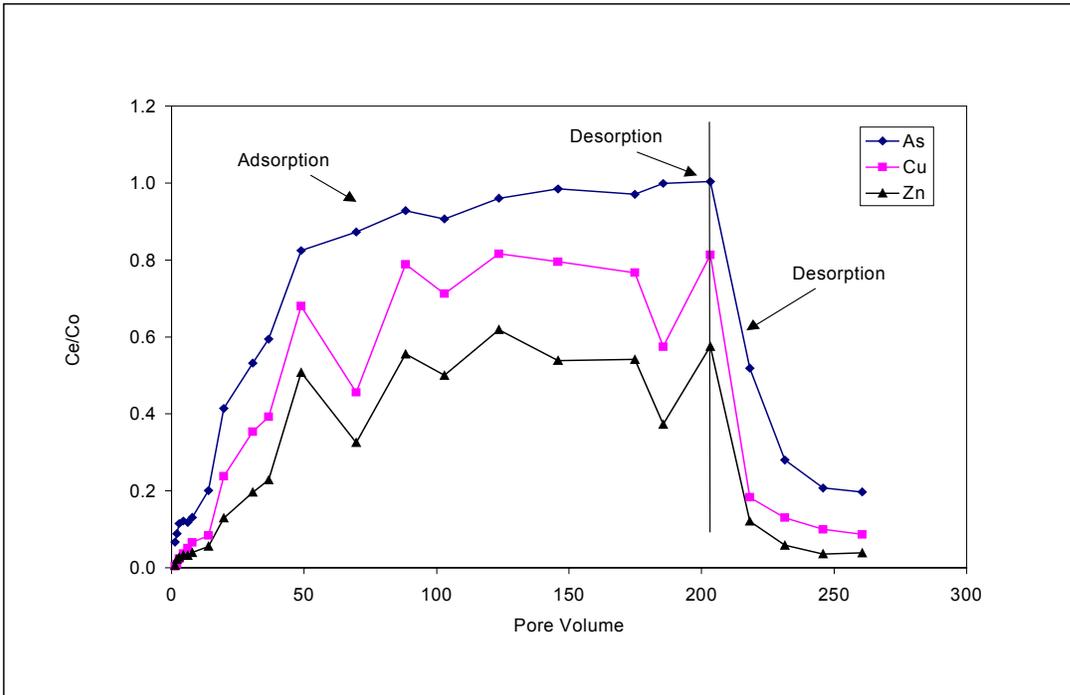


Figure 2.4.2.3. ACZA breakthrough curve for As, Cu, and Zn adsorption on Woodburn soil in 50-mm column (replicate). Desorption was conducted using distilled water.

For the 50-mm soil column, the breakthrough curves for ACZA leachate for As, Cu and Zn adsorption and desorption on Sagehill soil are shown in Figure 2.4.2.4. For As, breakthrough occurred between 20 to 30 pore volumes of total flow through the column, followed by a rapid increase in the effluent As concentration (C_e) until maximum adsorption capacity of the soil for removing As was achieved (Figure 2.4.2.4). For Cu and As equilibrium (at $C_e/C_o = 1$) was not achieved even after 300 pore volumes. Arsenic is adsorbed less than Cu and Zn. Existing as an oxyanion, As does not complex readily to soil organic matter, and its sorption may be further decreased by competition from negatively charged soluble organic compounds in the ACZA leachate. Cu forms relatively strong complexes with organic matter, and its sorption behavior appears to be more influenced by soluble organic ligands in the ACZA leachate than by soil organic matter. For Sagehill soil Cu and Zn are less affected by soluble complexation and is therefore more strongly adsorbed by the soils. During adsorption 16.8, 48.6, and 27.06 mg As, Cu, and Zn was removed from ACZA leachate. Desorption (beginning at $V_e/V_p = 400$) with distilled water removed 6.27, 3.92, and 0.88 mg As, Cu, and Zn from the column, respectively. That is about 37, 8, and 3 percent of the total adsorbed As, Cu, and Zn, respectively.

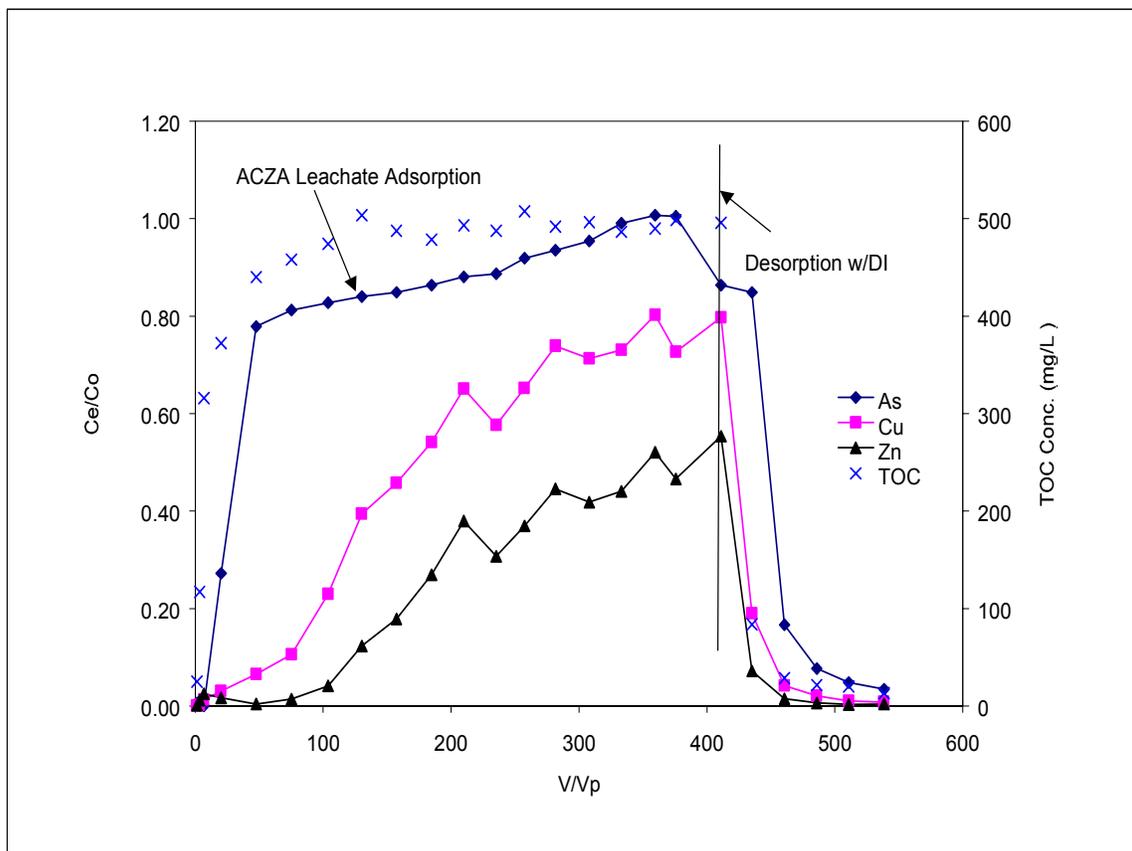


Figure 2.4.2.4. ACZA breakthrough curve for As, Cu, and Zn adsorption on Sagehill soil in 50-mm column. Desorption was conducted using distilled water.

For the 50-mm soil column (replicate), the breakthrough curves for ACZA leachate for As, Cu and Zn adsorption and desorption on Sagehill soil are shown in Figures 2.4.2.5. For As, breakthrough occurred between 20 to 30 pore volumes of total flow through the column, followed by a rapid increase in the effluent As concentration (C_e) until maximum adsorption capacity of the soil for removing As was achieved (Figure 2.4.2.5). However, equilibrium (at $C_e/C_o = 1$) was not achieved even after 400 pore volumes. For Cu and Zn equilibrium (at $C_e/C_o = 1$) was not achieved even after 400 pore volumes. Arsenic is adsorbed less than Cu and Zn. Existing as an oxyanion, As does not complex readily to soil organic matter, and its sorption may be further decreased by competition from negatively charged soluble organic compounds in the ACZA leachate. Cu forms relatively strong complexes with organic matter, and its sorption behavior appears to be more influenced by soluble organic ligands in the ACZA leachate than by soil organic matter. For Sagehill soil Cu and Zn are less affected by soluble complexation and is therefore more strongly adsorbed by the soils. During adsorption 14.14, 57.21, and 31.75 mg As, Cu, and Zn, respectively, were removed from ACZA leachate. Desorption (beginning at $V_e/V_p = 480$) with distilled water removed 12.88, 1.24, and 0.11 mg As, Cu, and Zn from the column, respectively. That is about 91, 2.2, and 0.35 percent of the total adsorbed As, Cu, and Zn, respectively.

For the 50-mm soil column (Woodburn soil), the breakthrough curves for ACZA leachate for As, Cu and Zn are shown in Figure 2.4.2.6. For As, breakthrough occurred between 30 to 40 pore volumes of total flow through the column, followed by a rapid increase in the effluent As concentration (C_e) until maximum adsorption capacity of the soil for removing As was achieved (Figure 2.4.2.6). Both Cu and Zn breakthrough occurred between 100 to 150 pore volumes of total flow through the column, followed by a rapid increase in the effluent Cu and Zn concentrations (C_e) until maximum adsorption capacity of the soil for removing Cu and Zn was achieved (Figure 2.1.2.8). However, equilibrium (at $C_e/C_o = 1$) for both Cu and Zn was not achieved even after 150 pore volumes. Desorption (beginning at $V_e/V_p = 280$) conducted using distilled water to remove adsorbed As, Cu, and Zn from the soil column, is shown in Figure 2.4.2.6. During adsorption 23.62, 49.70, and 26.93 mg As, Cu, and Zn, respectively, were removed from ACZA leachate. Desorption (beginning at $V_e/V_p = 280$) with distilled water removed 14.59, 0.0, and 0.0 mg As, Cu, and Zn from the column, respectively. That is about 62, 0, and 0 percent of the total adsorbed As, Cu, and Zn, respectively. The chemical analyses data are illustrated in the summary Table 2.4.1.1.

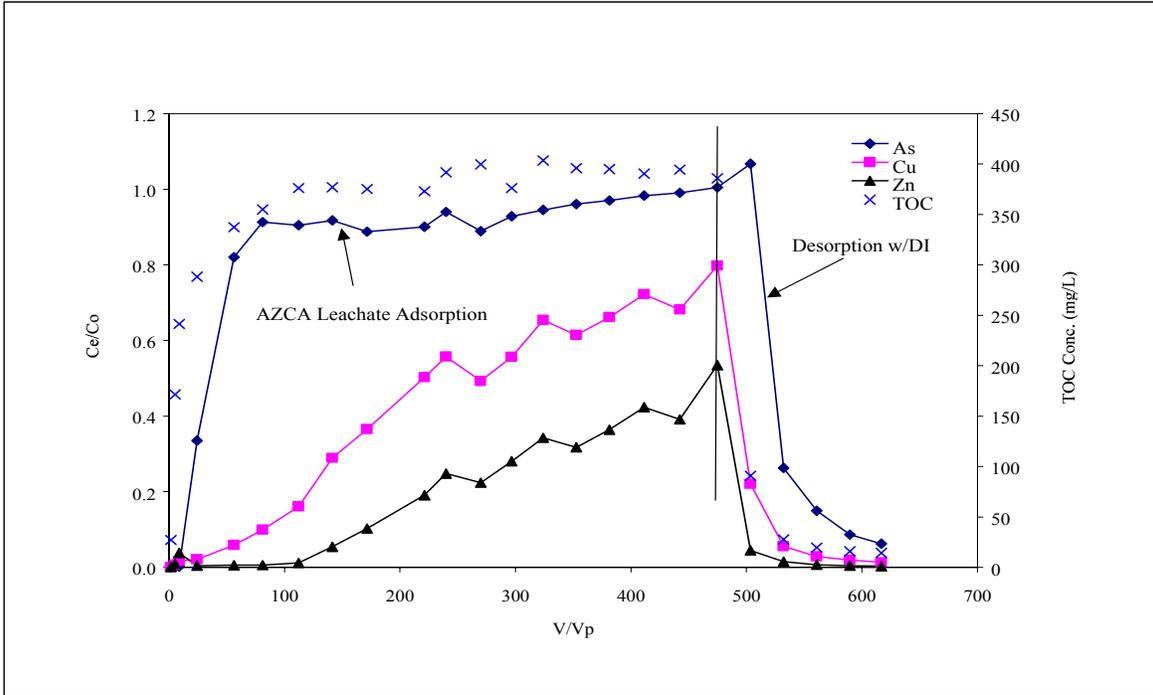


Figure 2.4.2.5. ACZA breakthrough curve for As, Cu, and Zn adsorption on Sagehill soil in 50-mm column (replicate). Desorption was conducted using distilled water.

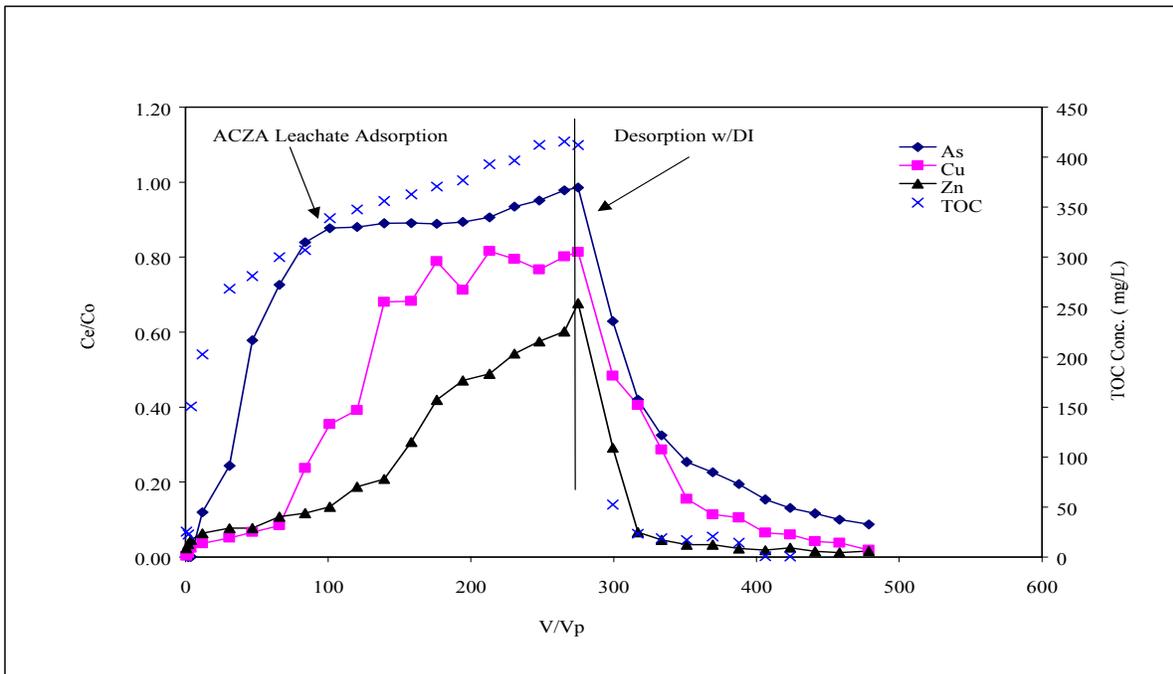


Figure 2.4.2.6. ACZA breakthrough curve for As, Cu, and Zn adsorption on Woodburn soil in 50-mm column (replicate). Desorption was conducted using distilled water.

Mass balance was performed to determine the amount of total metals adsorbed and desorbed during ACZA column experiments. Adsorbed arsenic was determined from the beginning of the presence of the ACZA until C/C_0 reached approximately 1. Desorbed arsenic mass was determined after deionized water was fed through the columns until the effluent concentration was about 10% of the feed solution ($C/C_0 \approx 0.1$). The summaries of sorbed and desorbed arsenic, copper, and zinc data are shown in Table 2.4.2.2. Average arsenic masses adsorbed in the soil columns are 0.411 and 0.326 mg/g for Woodburn and Sagehill soil columns, respectively. The fraction of sorbed arsenic metal that is recoverable in the desorption process with deionized water is greater for Sagehill soil than for Woodburn soil columns. This shows that Woodburn soil has slower elution for arsenic mass than Sagehill soil. The mass of arsenic, which has been eluted from each type of soil, seems to be consistent. For example, 7.7 and 17.5 mg of arsenic in W-A-50-1 and W-A-200-1 can be eluted after 12.41 and 56.35 mg of arsenic were sorbed in adsorption process, which is 62 and 31.1 % of the sorbed arsenic mass, respectively. This shows the slower process of desorption in the longer column to elute the contaminants. This might support the concept of local equilibrium such that the compound desorbed in the early column section would be adsorbed again in the later column section.

The arsenic isotherms from batch studies were selected to do the comparison in terms of the equilibrium adsorption capacity (C_s) for each soil. From the R^2 value, the Freundlich isotherm seems to give the best fit for both soils. In order to calculate equilibrium adsorption capacity of both soils at initial concentration of arsenic in ACZA leachate (approximately 25 mg/L), 25 mg/L was placed into the Freundlich equation.

There were averages of 0.45 and 0.1 mg of arsenic per gram of soil (C_s) in the batch studies (Table 2.4.2.2) for Woodburn and Sagehill, respectively, indicating greater adsorption capacity of the Woodburn soil vs. Sagehill soil. Similarly, the column studies showed an average C_s of 0.411 and 0.326 mg of arsenic per gram of soil for Woodburn and Sagehill, respectively. Thus, both the batch and column studies for ACZA indicate stronger sorption for the Woodburn than for the Sagehill soil. This is entirely to be expected for the higher-organic-content Woodburn soil and consistent with many other sorption experiments during this study.

The rates of copper and zinc adsorption in both soil columns were rapid, based on no appearance of Cu and Zn concentration profile at the beginning of column runs. The presence of copper and zinc in the effluent can be found for the 50 and 100-mm column lengths. In the longest column lengths, 200 and 250 mm, almost no concentration of copper and zinc can be detected in the effluent. This fact shows that soil has greater capacity to sorb copper and zinc than arsenic. At the saturation of soil with arsenic, the adsorption of copper and zinc was still progressing. Gao et al (1997) estimated that with 62 mg/L of dissolved organic carbon in solution, around 69% of copper and 15% of zinc exist as organo-metal complexes and suggested that formation of organo-metal complexes might be the dominant mechanism for adsorption and solution complexation for copper at low metal concentrations. This implies that copper is a stronger adsorbate than zinc. However, for the breakthrough curves of this study, the effluent concentration

of copper was greater than for zinc at most pore volume. This might result from the competition for ion exchange in the soil columns.

Table 2.4.2.2. Comparison of arsenic mass adsorbed in column and batch studies (Freundlich Isotherm).

Column Designation	C _o mg/l	Soil g	Mass As Adsorbed mg	C _s Column mg/g-soil	C _s Batch mg/g-soil	Mass As Desorbed mg
W-A-50-1	27.6	39	12.41	0.32	0.48	7.7
W-A-50-2	27.6	38.2	23.56	0.62	0.48	14.6
W-A-100-1	29.4	69.18	18.44	0.27	0.50	8.4
W-A-100-2	32.6	67.13	33.93	0.51	0.53	17.4
W-A-200-1	29.7	147	56.35	0.38	0.50	17.5
W-A-200-2	28.8	150.1	56.35	0.38	0.49	11.5
S-A-50-1	27.6	41	16.83	0.41	0.11	15.9
S-A-50-1	27.6	43.8	14.14	0.32	0.11	12.9
S-A-100-1	28.8	89.8	26.08	0.29	0.11	16.5
S-A-100-2	29.4	80.2	22.59	0.28	0.12	14.2

2.4.3 Algal bioassay analyses of ACZA/soil column leachates

A set of column leaching experiments was performed to investigate the removal of ACZA leachate toxicity at various soil depths. Soil columns of various lengths (50 mm, 100 mm, 200 mm) packed with either Woodburn or Sagehill soil were used. For biological analyses, only ACZA leachates were used as the representative C&R material leachates. During sorption, ACZA leachate was applied as the influent. Column effluents were collected at various time intervals and analyzed for toxicity and chemistry. For desorption, distilled water was used as the influent solution. In the following sections, algal toxicity results from Woodburn and Sagehill soil column studies are presented. To get sufficient sample volumes for toxicity analysis, about 4 to 5 effluent pore volumes were composited.

2.4.3.1 Woodburn Soil Columns

ACZA leachate applied initially to the soil column indicated a 1/EC50 value (or toxic unit, TU) of 769 for *S. capricornutum*. Metals such as arsenic, copper and zinc were observed to be above their toxic levels to the tested algae. Overall results indicated a good correspondence between metal levels in column effluents and algal toxicity. For instance, in a 50-mm column study, the first composited sample (15 pore volumes) exhibited a 1/EC50 value of 4.8 for *S. capricornutum*. The observed 160-fold reduction in the toxicity was obviously due to the sorption of known toxic metals such as arsenic, copper and zinc as shown by the chemical analysis. Figure 2.4.3.1.1 illustrates breakthrough curves for sum of metals and the associated toxicity in a 50-mm Woodburn column study. At the end of sorption phase (226 pore volumes), the effluent sample indicated a 1/EC50 value of 313.

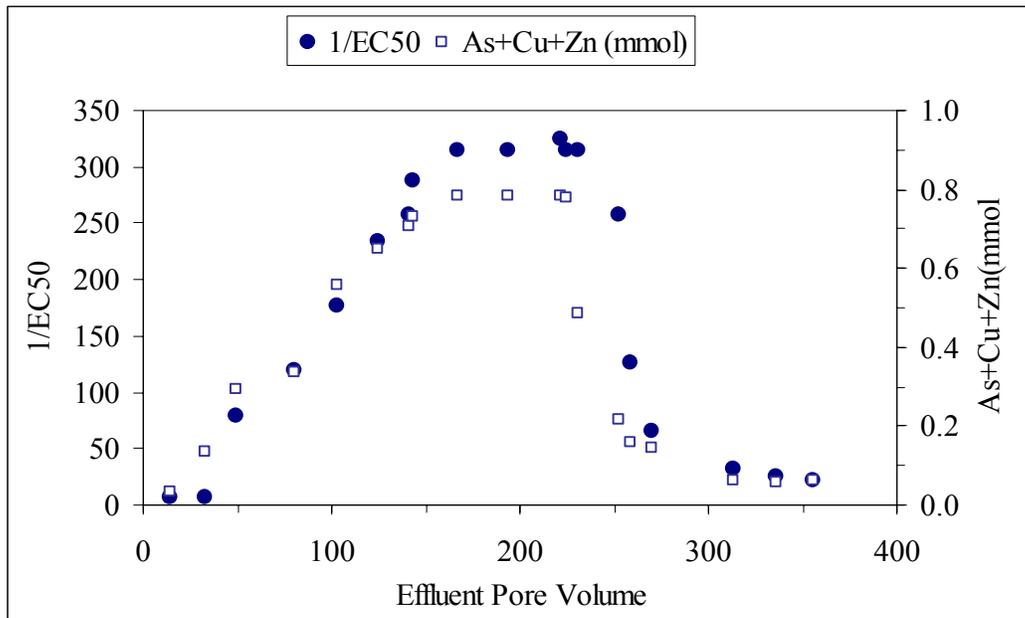


Figure 2.4.3.1.1 Algal toxicity and corresponding metals concentration as a function of effluent pore volumes in the 50-mm Woodburn soil column (I) study

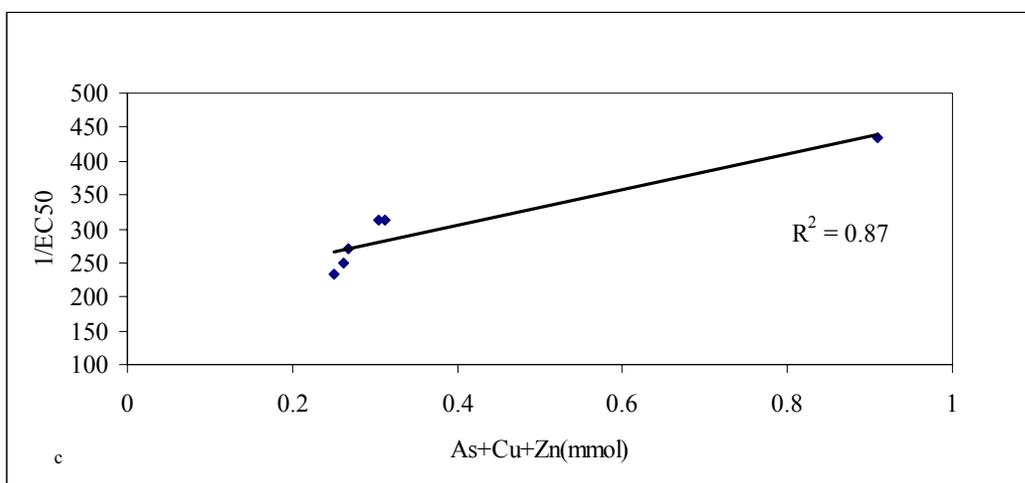
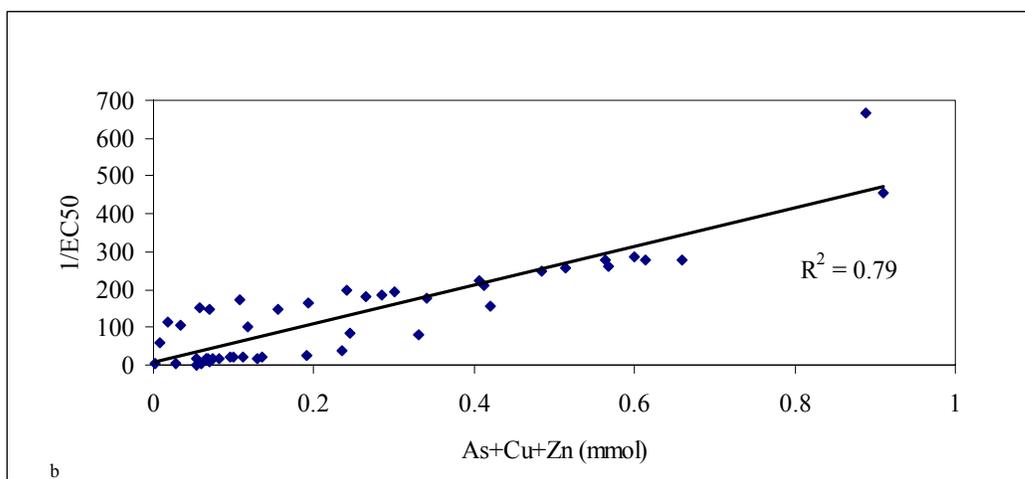
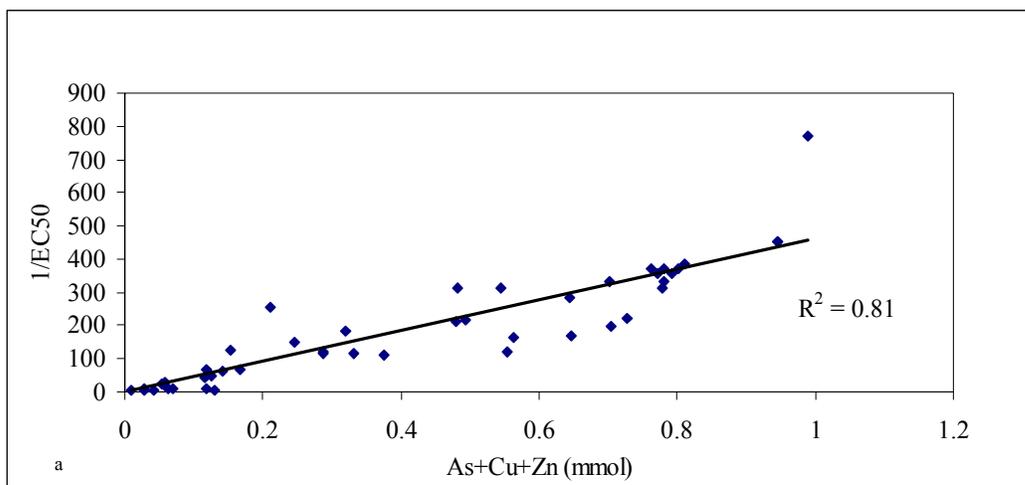


Figure 2.4.3.1.2 a, b, and c. Algal 1/EC50 values as function of sum of metals in 50 mm (a), 100 mm (b) and 200 mm (c) Woodburn column effluents. The regression for Woodburn (figure c) is probably not valid due to clustering of the data points.

During the desorption phase, a gradual decrease in the toxicity of the effluent was observed. Chemical analyses indicated a corresponding decrease in the metal concentrations, especially in arsenic. The first desorption sample collected at 232 pore volume indicated a 1/EC50 value of 313. This extremely high toxicity was caused by desorption of arsenic, copper and zinc from soil to the effluent. A 1/EC50 value of 21 was observed in the final effluent sample for desorption phase, indicating a significant decrease in the amount of metals leached from the soil.

A consistent pattern of change in toxicity with change in metals concentration was observed in all of 50-mm, 100-mm, and 200-mm Woodburn soil column studies. Figures 2.4.3.1.2 a, b, and c illustrates algal 1/EC50 values as a function of sum of metals concentration in column effluents. Correlation coefficients (R values) of 0.90, 0.89, and 0.93 ($p < 0.01$) were observed for the three soil columns (Table 2.4.3.1), respectively, indicating a good relationship between toxicity and chemistry data, except that the good regression for the Woodburn soil probably is just a result of the clustering of the data points.

Table 2.4.3.1 Coefficient of correlation (R) and coefficient of fit (R^2) values describing the relationship between chemistry and toxicity data from soil column tests.

Soil Column	Column Length (mm)	R	R^2
Woodburn	50	0.90	0.81
	100	0.89	0.79
	200	0.93	0.87
Sagehill	50	0.97	0.94
	100	0.98	0.95
	200	0.96	0.91

2.4.3.2 Sagehill Soil Columns

Algal toxicity results indicated a similar behavior between the toxicity and chemistry data for the Sagehill soil column effluents (Figure 2.4.3.2.1). For instance, in 50-mm column (I), during the sorption phase algal toxicity decreased (about 68-fold) in the initial column effluent ($1/EC_{50} = 454$) compared with influent toxicity ($1/EC_{50} = 6.7$). Obviously, this reduction in toxicity was due to the corresponding decrease in the toxic metal levels in the effluent as shown by the chemical analyses. At the end of the sorption phase (375 pore volumes) a $1/EC_{50}$ value of 417, a value close to the influent toxicity ($1/EC_{50} = 454$), was observed. During the desorption phase, a general decrease in the toxicity was observed with associated decrease in the toxic metal levels in the effluents. The first desorption sample indicated a $1/EC_{50}$ of 417 and a $1/EC_{50}$ value of 6 was observed in the final desorption sample.

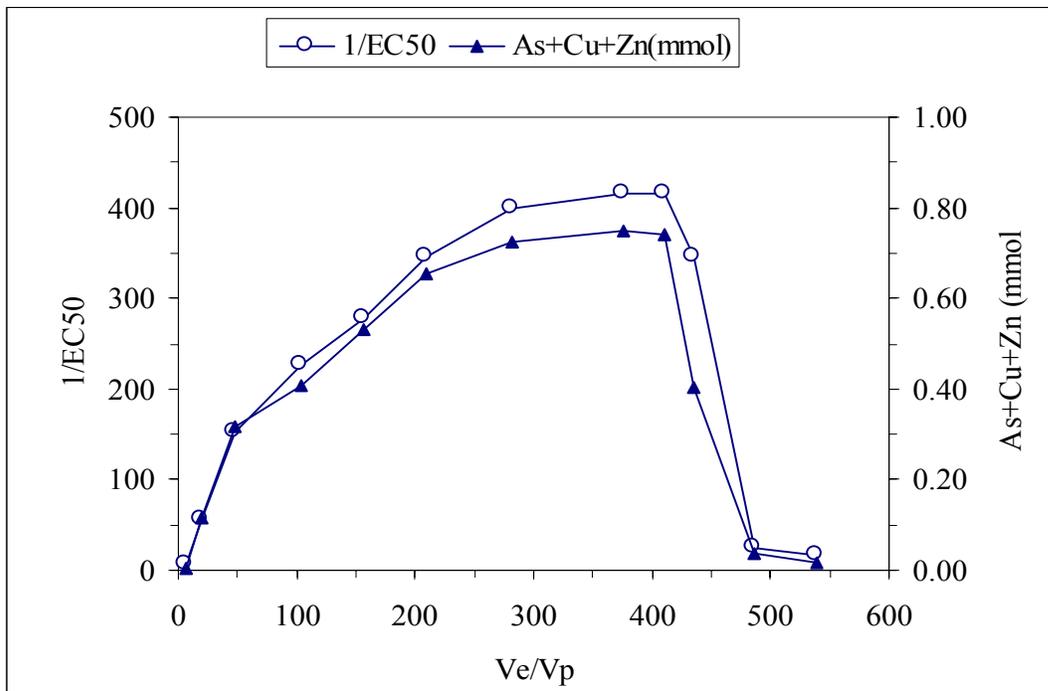


Figure 2.4.3.2.1 Algal toxicity and corresponding metals concentration as a function of effluent pore volumes in the 50 mm Sagehill soil column (I) study.

Based on R-values (Table 2.4.3.1) of 0.97, 0.98 and 0.96 for 50, 100, and 200 mm columns respectively, it can be concluded that a significant correlation ($p < 0.01$) existed between toxicity and the sum of metals present in the effluents. In addition, Figures 2.4.3.2.2 a, b, and c illustrate the strong linear relationship ($R^2 = 0.94, 0.95, \text{ and } 0.91$ for 50, 100, and 200-mm Sagehill columns respectively) between chemistry and algal toxicity.

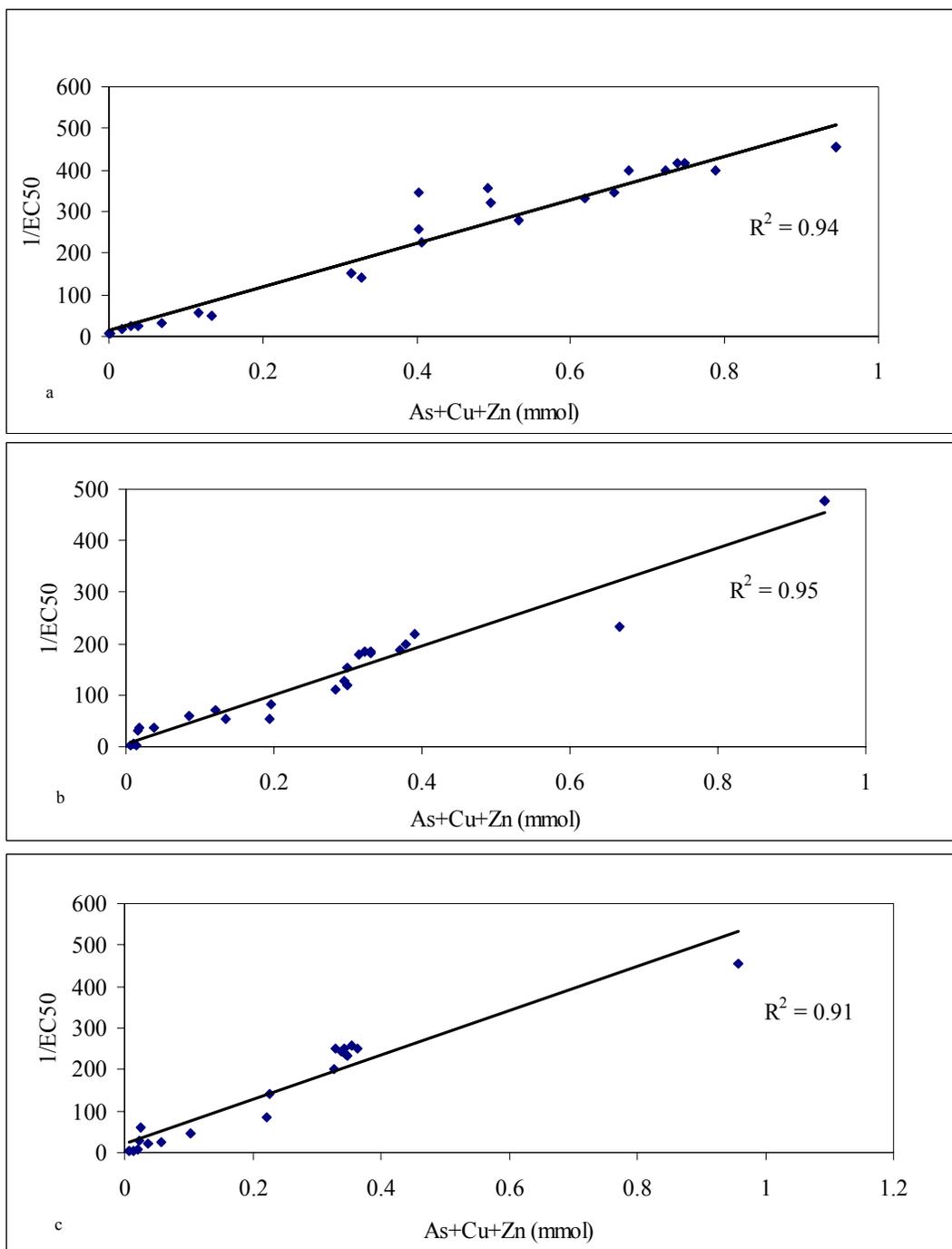


Figure 2.4.3.2.2 a, b, and c Algal 1/EC50 values as function of sum of metals in 50 mm (a), 100 mm (b) and 200 mm (c) Sagehill column effluents.

2.4.4 TCP Soil Sorption and Biodegradation

2.4.4.1 TCP batch reactor experiments

Batch reactor experiments were performed to determine TCP biodegradation removal rates and soil sorption capacities. Biodegradation rates were determined in reactors with microorganisms (bacterial cells) alone and in reactors with cells plus nutrients and cells plus soil to assess possible nutrient limitation and soil synergistic effects on the biodegradation rate constant. Additional batch experiments were run with bacterial cells plus autoclaved soil (to kill indigenous soil microorganisms) to determine by comparison the possible contribution to TCP biodegradation by indigenous soil microorganisms. Soil sorption capacities were determined by developing soil sorption isotherms from batch reactor data of reactors with soil alone. For these batch experiments, 20-mL reactors were used, into which were added TCP solutions (2, 5, or 15 mg/L initial concentrations), and as appropriate, microorganisms harvested from the “mother” (supply) reactor culture, nutrients, and test soils (Woodburn or Sagehill).

TCP removal rates were calculated separately for reactors with microorganisms only (biodegradation rate constant), with soil only (sorption rate constant), and with microorganisms plus soil (combined removal rate). Additional rate constants were determined for microorganisms with nutrients (media) added (to examine possible nutrient limitation in the leachate) and for autoclaved soil plus microorganisms (to determine possible removal effects by indigenous soil microorganisms). Both zero-order and first-order removal rate expressions were fit to the batch data. The batch reactor data for 1 g Sagehill soil with microorganisms at an initial TCP concentration of 2 mg/L shows an example of the fit for zero- and first-order rate expressions (Figure 2.4.4.1.1). Zero- and first-order removal rate constants for all batch reactor experiments are summarized in Table 2.4.4.1.1. For most batch experiments, a lag period existed for up to about two days before significant substrate removal occurred, after which removal progressed steadily. The lag period was ignored in determining the rate constants reported in Table 2.4.4.1.1.

The biodegradation rate constants generally increase at higher initial TCP concentrations for every condition (Table 2.4.4.1.1). This indicates that the substrate (TCP) is not toxic to the microorganisms (bacteria). The rate constants are composite values in that they implicitly include the concentration of active bacteria. The increasing rate constant value with higher initial substrate concentration indicates that microorganism concentration is not constant, but in fact increases over the several day time period of these biodegradation batch tests. The rate constants are thus conditional constants, specific to the conditions of these batch tests. In practice, values of biodegradation rate constants should be site-specific, determined for the soil-microorganism-substrate combination present at the highway location of interest.

The coefficient of fit (R^2 value) shows that the zero-order biodegradation rate expression seems to give the best data fit for most batch reactor experiments, although first-order in most cases also fits well. A zero-order rate expression implies that substrate concentration is in excess relative to needs of the bacteria, while a first-order expression

implies that substrate concentration is limiting bacterial metabolism rate. It is unclear which condition pertains to these experiments, but either model (zero or first order) predicts TCP biodegradation quite well.

Reactors with cells only and those with cells plus nutrients were run in duplicate to provide some idea of the variability of rate constant results. Generally, rate constants agree quite well in duplicate runs and clear trends are discernible between rate constants for the varying effects investigated.

Addition of nutrients (media) with bacterial cells caused greater rate of TCP removal with a corresponding increase in rate constants (Table 2.4.4.1.1). This clearly indicates a nutrient limitation in the cells-only reactors, as what little nutrients are available are supplied with the cells inoculum from the mother reactor. Sagehill soil by itself showed a very low TCP removal rate, but combined with cells showed a comparable removal rate to cells with nutrients. Soil apparently contributes sufficient trace nutrients to the bacterial cell culture to sustain active metabolism.

Reactors with soil added but no bacterial cells illustrate removal primarily by adsorption (Table 2.4.4.1.1). Woodburn soil shows a greater rate of removal by adsorption than Sagehill soil, consistent with adsorption capacity data. Rates of removal were generally higher when cells were added to soils, especially for Sagehill soil. Autoclaved soils with cells added had similar removal rates to cells-only reactors, showing that there is minimal TCP biodegradation by indigenous microorganisms present in the soils.

Table 2.4.4.1.1. Summary removal rates of 2,4,6 TCP with soil sorption and biodegradation. TCP concentrations are in mg/L.

Condition	TCP Conc	Reactor	Rate Constant		R ²	
			0 order	1 st oder	0 order	1 st oder
Cells Only	2	1	0.011	0.023	0.691	0.853
		2	0.018	0.024	0.934	0.891
	5	1	0.031	0.034	0.838	0.915
		2	0.069	0.044	0.993	0.874
	15	1	0.089	0.007	0.920	0.863
		2	0.095	0.008	0.948	0.912
Cells + Media	2	1	0.026	0.035	0.792	0.836
		2	0.016	0.020	0.825	0.933
	15	1	0.242	0.066	0.921	0.744
		2	0.250	0.048	0.792	0.761
Sagehill Soil	2		0.001	0.019	0.857	0.863
	15		0.005	0.039	0.861	0.751
Sagehill Soil + Cell	2		0.008	0.006	0.905	0.867
	5		0.054	0.021	0.994	0.996
	15		0.299	0.082	0.903	0.795
Autoclaved Sagehill Soil + Cell	2		0.014	0.009	0.961	0.941
Woodburn Soil	2		0.007	0.014	0.863	0.762
	5		0.028	0.031	0.808	0.863
Woodburn Soil + Cell	2		0.008	0.011	0.791	0.690
	5		0.011	0.015	0.439	0.667
	15		0.099	0.012	0.993	1.000
Autoclaved Woodburn Soil + Cell	2		0.009	0.005	0.980	0.970

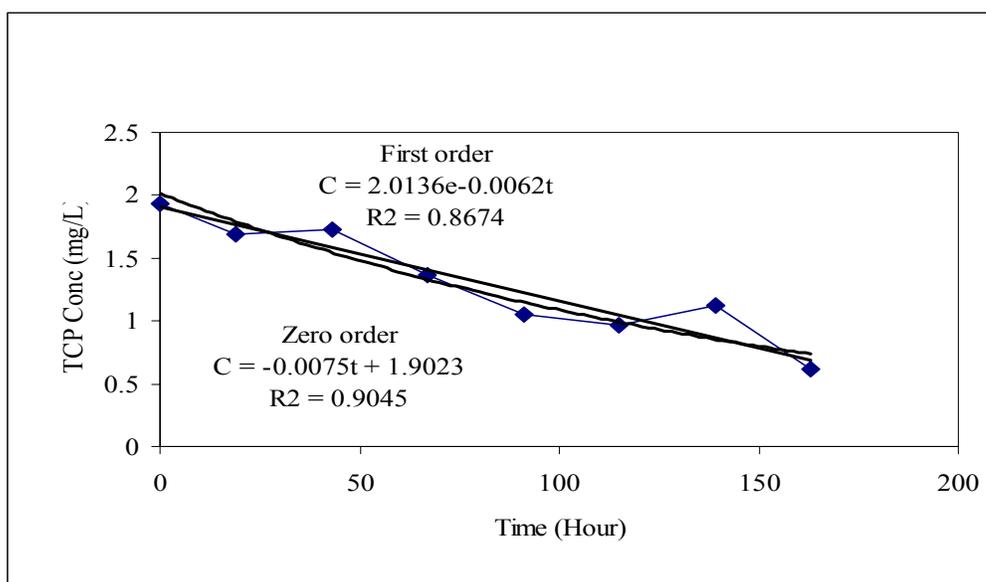


Figure 2.4.4.1.1 Batch reactor (20 mL) TCP removal curve (2 mg/L initial TCP concentration) with Sagehill soil (1 g) and microorganisms added.

Batch soil sorption experiments also were used to determine the sorption capacity of Sagehill and Woodburn soils. Sorption characteristics of the different soils (Sagehill and Woodburn) for 2,4,6-TCP were analyzed and evaluated using three soil isotherm models: linear, Langmuir and Freundlich. Calculated values of the Freundlich isotherm parameters, K_f and N , for Sagehill and Woodburn soils are presented in Table 2.4.4.1.2. The high R^2 coefficient value of 0.94 for the Woodburn soil demonstrates the excellent fit of these sorption data by the Freundlich isotherm model. For the Sagehill soil, sorption data were measured only near the maximum water concentration tested (about 1.9 mg/L), and there are no measurements for low concentrations as there are for the Woodburn soil. Hence, the data were clustered near one sorption capacity, and none of the three isotherm equations gave a statistically significant result (at the 95% level). The Sagehill soil sorption capacity (on the order of 0.001 mg/g) at the maximum water concentration tested is an order of magnitude less than for the Woodburn soil. It can be concluded that the sorptive capability of the Sagehill soil is much less than Woodburn soil for TCP, and that insufficient data were collected at low TCP concentrations to confirm a mathematical fit of any of the three sorption equations. Additional guidance on interpretation of data of the sort for the Sagehill soil is given in the discussion of the TCP sorption results in Volume II (Eldin et al., 2000).

Table 2.4.4.1.2. Freundlich sorption capacity (K_f) and intensity parameters (N) for sorption of 2,4,6-TCP by Sagehill and Woodburn soils

Soil Type	Model Isotherm	K_f	N	R^2
Sagehill	Freundlich	7.07×10^{-4}	0.79	0.09
Woodburn	Freundlich	2.26×10^{-2}	0.58	0.94

For 2 mg/L of TCP in solution, the maximum soil sorption capacities for TCP calculated by the Freundlich Isotherm (using the isotherm parameters in Table 2.4.4.1.2) were 1.23×10^{-3} mg/g and 3.399×10^{-2} mg/g for Sagehill and Woodburn soils, respectively. Batch results compared well with column studies that showed equilibrium adsorption capacities of 1.6×10^{-3} mg/g and 4.24×10^{-2} mg/g for Sagehill and Woodburn soils, respectively.

2.4.4.2 TCP soil column sorption background

Soil column experiments were conducted to more closely simulate field conditions of continuous hydraulic flow through a stationary porous medium, that is, highway runoff through roadside soils. As described extensively in Volumes II and IV, 2,4,6-TCP (TCP) was selected to serve as a surrogate highway material leachate for column studies because of its biodegradability and potential toxicity, and because of its known chemical properties. The soil column experimental methods for TCP have been discussed earlier in this chapter.

2.4.4.3 2,4,6-TCP soil column sorption results

TCP soil columns of 50 mm and 100 mm length with 25 mm inside diameters were packed with Woodburn and Sagehill soils to a porosity of about 40 to 55% (Table 2.4.4.3.1). The columns were packed by adding 2-cm layers of soil and saturating with distilled water from the bottom up to ensure that no air pockets formed within the soil column. TCP Sagehill and Woodburn soil column operating conditions are summarized in Table 2.4.4.3.1. FMI (Fluid Metering, Inc.) pumps were used to control hydraulic flow (10 mL/hr) through the soil columns to approximate field conditions. The CFITIM program (Van Genuchten, 1981) was run to calculate the retardation factor and Peclet number for TCP soil columns, results of which are presented in Table 2.4.4.3.2.

Table 2.4.4.3.1. Summary of soil column operating conditions for TCP leachate.

Column Designation	Soil type	Leachate	Length mm	Run No.	Column Volume ml	Pore Volume ml	Mass of Soil grams	Packed density g/cm ³	% Porosity
W-T-50-1	Woodburn	TCP	50	1	24.6	9.8	38.97	1.6	40.1
W-T-50-2	Woodburn	TCP	50	2	24.6	13.6	28.9	1.2	55.6
S-T-100-1	Sagehill	TCP	110	1	54.0	27.0	71.6	1.3	50.0
S-T-100-2	Sagehill	TCP	110	2	54.0	25.8	74.9	1.4	47.7

Table 2.4.4.3.2. Soil column modeling parameters determined by CFITIM for 2 mg/L TCP solution.

Values of R_d and Pe are from CFITIM model. Dispersion coefficient is found from the Peclet number (Equation 2.4.1.5) based on column length. The molecular diffusivity (D^*) is assumed to be $10^{-5} \text{ cm}^2/\text{s} = 3.6 \text{ mm}^2/\text{hr}$. The flow rate is 10 mL/hr and the diameter is 25 mm, for all columns.

Column Designation	R_d	Pe	Packed length mm	Porosity %	Bulk density g/cm ³	K_d cm ³ /g	v_p mm/hr	D_1 mm ² /hr	D_1/D^*
W-T-50-1	138	0.16	50	40.1	1.6	34.35	50.8	15876	4410
W-T-50-2	158	0.15	50	55.6	1.2	73.00	36.6	12213	3393
S-T-50-1	1.91	5.03	50	50.0	1.3	0.35	40.7	405	113
S-T-50-2	2.33	2.29	50	47.7	1.4	0.45	42.7	9322	259

The breakthrough curves of each soil column experiment were plotted, from which at least two important points can be noted. These are the first pore volume at which there is measurable breakthrough of the feed compound (TCP), and the cumulative pore volumes at which $C/C_0 = 1$ is reached. At initial breakthrough, the number of pore volumes shows the retardation effect between the geomeia and compound of interest. The pore volumes at which $C/C_0 = 1$ shows the time at which the geomeia has reached sorption saturation with the compound of interest. The sorption capacity at saturation is not directly proportional to the number of effluent pore volumes at $C/C_0 = 1$. However, the capacity of sorption can be determined by mass balance analysis.

For 100-mm Sagehill soil columns *without* microorganisms, the breakthrough curves for TCP sorption and desorption are shown in Figure 2.4.4.3.1. For both columns, breakthrough occurred between 2 to 3 pore volumes of total flow through the column, followed by a rapid increase in the effluent TCP concentration (C_e) until maximum adsorption capacity of the soil for removing TCP was achieved ($C/C_0 = 1$) (Figure 2.4.4.3.1). During adsorption 0.09, and 0.14 mg TCP was removed from the influent solution from column numbers 1 and 2, respectively (Table 2.4.4.3.3). Desorption (beginning at $V_e/V_p = 10$ and 25 for column numbers 1 and 2, respectively) with distilled water removed 0.071 and 0.091 mg TCP from the columns, respectively (Figure 2.4.4.3.1). That is, about 79 and 65 percent of the total adsorbed TCP is desorbed, respectively.

For 100 mm Sagehill soil columns *with* microorganisms, the breakthrough curves for TCP sorption and desorption are shown in Figures 2.4.4.3.2. For both columns, breakthrough occurred between 2 to 3 pore volumes of total flow through the column, followed by a rapid increase in the effluent TCP concentration (C_e) until maximum

adsorption capacity of the soil for removing TCP was achieved (Figure 2.4.4.3.2). During adsorption 0.15, and 0.13 mg TCP was removed from the influent solution from column number 1 and 2, respectively (Table 2.4.4.3.4). Desorption with distilled water (beginning at $V_e/V_p = 23$ and 33 for column numbers 1 and 2, respectively) removed 0.119 and 0.115 mg TCP from the columns, respectively. That is, about 76 and 88 percent of the total adsorbed TCP is desorbed, respectively (Figure 2.4.4.3.2).

For 50-mm Woodburn soil columns *without* microorganisms, the breakthrough curves for TCP sorption and desorption are shown in Figures 2.4.4.3.2. For both columns, breakthrough occurred between 5 to 6 pore volumes of total flow through the column, followed by a rapid increase in the effluent TCP concentration (C_e) until maximum adsorption capacity of the soil for removing TCP was achieved ($C/C_0 = 1$) (Figure 2.4.4.3.2). During adsorption, 1.28 and 1.50 mg TCP was removed from the influent solution for column numbers 1 and 2, respectively (Table 2.4.4.3.1). Desorption (beginning at $V_e/V_p = 80$ and 100 for column number 1 and 2, respectively) with distilled water removed 0.30 and 0.49 mg of TCP from the columns, respectively (Table 2.4.4.3.1). That is about 23 and 33 percent of the total adsorbed TCP is desorbed, respectively (Figure 2.4.4.3.2).

For 50-mm Woodburn soil columns *with* microorganisms, the breakthrough curves for TCP sorption and desorption are shown in Figure 2.4.4.3.2. For both duplicate columns breakthrough occurred between 5 to 6 pore volumes of total flow through the column, followed by a rapid increase in the effluent TCP concentration (C_e) until maximum adsorption capacity of the soil for removing TCP was achieved ($C/C_0 = 1$) (Figure 2.4.4.3.2). Due to complete removal of TCP in this experiment, no desorption experiments were conducted (Figure 2.4.4.3.2).

Table 2.4.4.3.3. Mass balance on 2-mg/L TCP adsorption *without* microorganisms on Woodburn and Sagehill soils.

Sample ID	Length	Soil	Ads. TCP	Des. TCP	Ads. TCP
	mm	g	mg	mg	mg/g soil
S-T-100-1	110	71.6	0.09	0.071	0.001
S-T-100-2	110	74.9	0.14	0.091	0.002
W-T-50-1	50	38.97	1.28	0.303	0.033
W-T-50-2	50	28.9	1.5	0.497	0.052

Table 2.4.4.3.4. Mass balance on 2-mg/L TCP adsorption with microorganisms on Sagehill and Woodburn soils.

Sample ID	Length	Soil	Ads. TCP	Des. TCP	Ads. TCP
	mm	g	mg	mg	mg/g soil
S-T-100-1	110	68.2	0.15	0.119	0.002
S-T-100-2	110	68.3	0.13	0.115	0.002
W-T-50-1	50	24.7	0.40	--	--
W-T-50-2	50	29.6	0.60	--	--

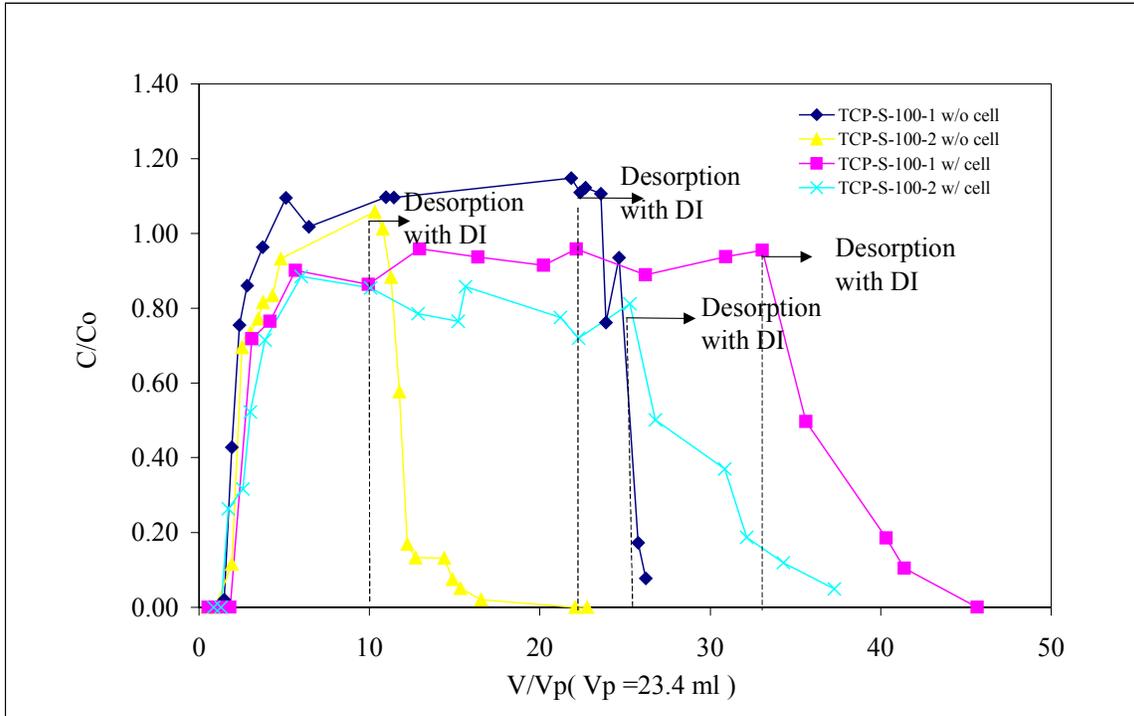


Figure 2.4.4.3.1. 2,4,6-TCP Sagehill 100-mm soil column breakthrough curves and desorption with and without microorganisms.

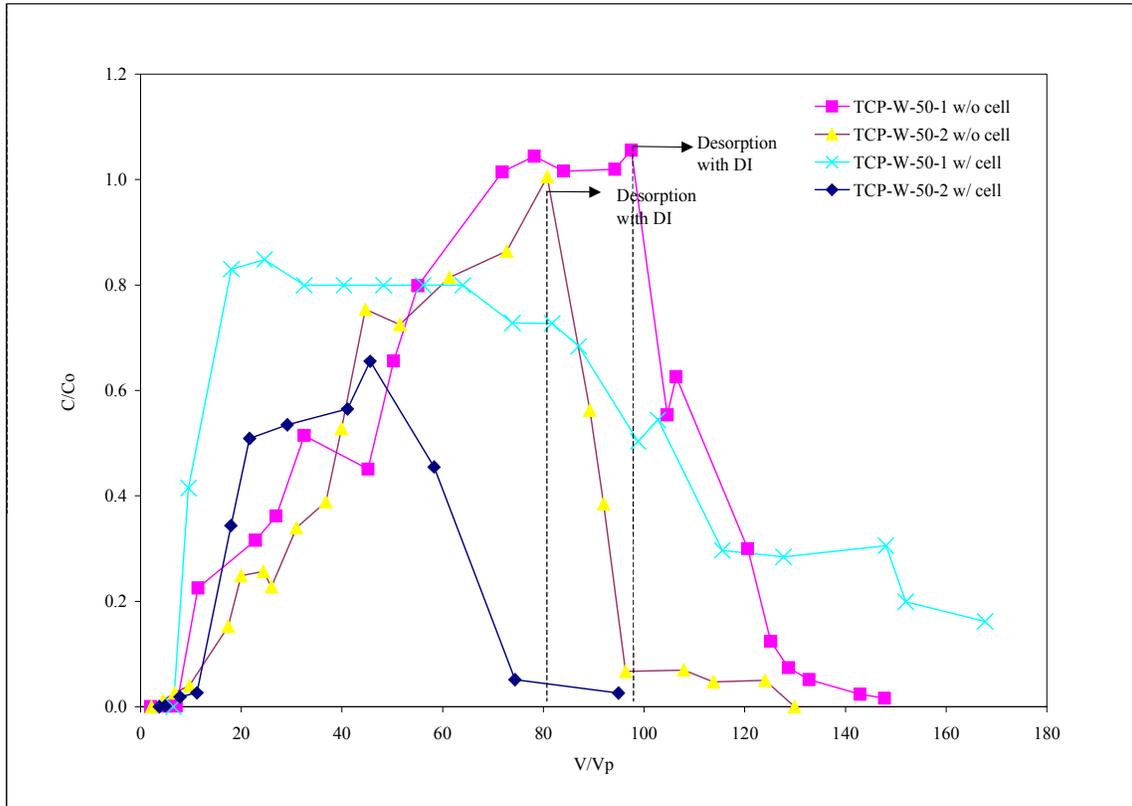


Figure 2.4.4.3.2. 2,4,6-TCP Woodburn 50-mm soil column breakthrough curves and desorption with and without microorganisms.

2.5 SUMMARY AND CONCLUSIONS

Based on the results of this study, the following conclusions are drawn in relation to removal of metals and organic in C&R (Construction and Repair highway materials) leachates by adsorption and biodegradation processes:

Soil columns are able to effectively represent retardation and removal of leachate constituents by adsorption and biodegradation processes.

For ACZA leachate, the mixture of metals (As, Cu, Zn) was differentially retarded by soil. Arsenic, present as the oxyanion arsenate (AsO_4^{3-}), was the least retarded, followed by copper (Cu^{2+}) and zinc (Zn^{2+}). It is hypothesized that copper was retarded less than zinc due to possible soluble complexation with organic compounds, either from ACZA leachate (50-150 mg/L TOC) or from the soil organic matter (approximately 400-650 mg/L TOC after column break-in period).

TCP leachate in soil columns exhibited retardation by sorption and removal by biodegradation processes. Sorption of TCP was reversible, and TCP was desorbed from the soil columns when flushed with deionized water.

Soil column mass balances showed that sorbed concentrations of ACZA metals and TCP at saturation (C_s values) were equivalent to those predicted for isotherms derived from batch reactor data for the Woodburn soil, but 2-4 times greater for Sagehill soil.

For the ACZA leachate, arsenic, being more weakly sorbed, was more rapidly desorbed, followed by Cu and Zn, when soil columns were flushed with deionized water.

Woodburn soil, a Mollisol with 6.44% of organic matter in the fine silty, mixed, mesic family of soils, exhibited higher sorption capacity and retardation of both ACZA metals and of TCP, than did Sagehill soil, an Aridisol with 1.91% of organic matter in the coarse-loamy mixed mesic family of soils.

Flow in all columns is laminar with Reynolds numbers in the range of 10^{-5} . Darcy's law is valid. From curve-fits to theoretical breakthrough curves, dispersion in the columns is on the order of molecular diffusivity.

Table 2.4.1.1. Task 1: Summary data for chemical and toxicity analyses.

Task 1: Confirmation of Phase II Methodology													
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results			Chemistry Test Results							
			Algal Toxicity			Sample Volume (ml)	Cumm. Vol. (ml)	Pore Volume	As (mg/L)	Cu (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Elutriate										
			% EC ₅₀	Lower 95% C.L.	Upper 95% C.L.								
	ACZA 100mm-Sagehill												
1	Ads 100mm-Sagehill		0.21	0.19	0.24				27.643	26.414	10.468		
2	Ads 100mm-Sagehill		28	21	36	30	30	1.70	0.257	0.093	0.012	119	6.63
3	Ads 100mm-Sagehill	NA	NA	NA	NA	70	100	5.66	2.640	0.070	0.011	227	6.89
4	Ads 100mm-Sagehill		1.4	1.1	1.9	106	206	11.65	8.900	0.150	0.010	242	7.51
5	Ads 100mm-Sagehill	NA	NA	NA	NA	250	456	25.80	13.196	0.202	0.011	272	7.41
6	Ads 100mm-Sagehill		0.91	0.71	1.2	210	666	37.68	20.671	0.448	0.024	268	7.40
7	Ads 100mm-Sagehill	NA	NA	NA	NA	252	918	51.94	21.113	0.645	0.014	349	7.38
8	Ads 100mm-Sagehill		0.65	0.52	0.83	200	1118	63.25	21.384	0.820	0.018	398	7.07
9	Ads 100mm-Sagehill	NA	NA	NA	NA	225	1343	75.98	21.300	0.261	0.000	448	6.86
10	Ads 100mm-Sagehill	NA	NA	NA	NA	215	1558	88.14	21.830	0.277	0.004	440	7.11
11	Ads 100mm-Sagehill		0.56	0.45	0.7	220	1778	100.59	23.284	0.274	0.013	445	7.14
12	Ads 100mm-Sagehill	NA	NA	NA	NA	200	1978	111.90	23.525	0.270	0.000	456	7.18
13	Ads 100mm-Sagehill	NA	NA	NA	NA	210	2188	123.79	23.873	0.262	0.000	409	7.27
14	Ads 100mm-Sagehill	NA	NA	NA	NA	190	2378	134.53	23.479	0.279	0.002	421	7.12
15	Ads 100mm-Sagehill		0.55	0.45	0.68	180	2558	144.72	24.417	0.274	0.002	418	7.43
16	Ads 100mm-Sagehill	NA	NA	NA	NA	170	2728	154.34	24.255	0.263	0.011	424	7.08
17	Ads 100mm-Sagehill	NA	NA	NA	NA	210	2938	166.22	24.341	0.245	0.038	427	7.24
18	Ads 100mm-Sagehill	NA	NA	NA	NA	140	3078	174.14	24.453	0.269	0.074	427	7.28
19	Ads 100mm-Sagehill		0.54	0.44	0.66	185	3263	184.60	23.818	0.242	0.062	445	7.39
20	Ads 100mm-Sagehill	NA	NA	NA	NA	177	3440	194.62	22.929	0.218	0.092	426	7.39
21	Ads 100mm-Sagehill	NA	NA	NA	NA	150	3590	203.10	24.209	0.216	0.113	415	7.42
22	Ads 100mm-Sagehill	NA	NA	NA	NA	140	3730	211.02	24.057	0.219	0.158	440	7.40
23	Ads 100mm-Sagehill		0.54	0.44	0.66	165	3895	220.36	24.405	0.212	0.160	436	7.41
24	Des 100mm-Sagehill		0.3	0.26	0.36	130	4025	227.71	49.162	0.486	0.166	235	7.31
25	Des 100mm-Sagehill		0.46	0.37	0.58	125	4150	234.79	28.718	0.280	0.141	87	6.82
26	Des 100mm-Sagehill		1.21	0.93	1.6	215	4365	246.95	14.514	0.115	0.086	70	6.55
27	Des 100mm-Sagehill		1.84	1.4	2.4	203	4568	258.43	6.783	0.540	6.243	38	6.77

Table 2.4.1.1. Task 1: Summary data for chemical and toxicity analyses (cont...).

Task 1: Confirmation of Phase II Methodology													
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results			Chemistry Test Results							
			Algal Toxicity			Sample Volume (ml)	Cumm. Vol. (ml)	Pore Volume	As (mg/L)	Cu (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Elutriate										
			% EC ₅₀	Lower 95% C.L.	Upper 95% C.L.								
	ACZA 100mm-Sagehill (second column)												
1	Ads 100mm-Sagehill		0.21	0.19	0.24				27.643	26.414	10.468		
2	Ads 100mm-Sagehill		24	21	29	20	20	0.94	0.914	0.018	0.034	25.84	7.1
3	Ads 100mm-Sagehill	NA	NA	NA	NA	17	37	1.74	0.710	0.055	0.021	29.04	6.98
4	Ads 100mm-Sagehill		18	15	23	108	145	6.81	0.388	0.210	0.040	220.5	6.75
5	Ads 100mm-Sagehill	NA	NA	NA	NA	50	195	9.16	0.470	0.411	0.064	250	7.02
6	Ads 100mm-Sagehill		3.2	2.7	3.7	55	250	11.74	0.410	0.474	0.135	265.9	7.12
7	Ads 100mm-Sagehill	NA	NA	NA	NA	125	375	17.61	0.408	0.514	0.096	288	7.13
8	Ads 100mm-Sagehill		1.7	1.3	2.1	215	590	27.70	5.803	0.473	0.064	310.2	6.89
9	Ads 100mm-Sagehill	NA	NA	NA	NA	200	790	37.09	15.748	0.382	0.280	373.3	6.92
10	Ads 100mm-Sagehill		0.78	0.61	1	235	1025	48.13	21.285	0.489	0.178	367.8	7.04
11	Ads 100mm-Sagehill	NA	NA	NA	NA	175	1200	56.34	24.326	0.422	0.109	394.4	6.94
12	Ads 100mm-Sagehill	NA	NA	NA	NA	185	1385	65.03	26.261	0.502	0.104	270.4	6.84
13	Ads 100mm-Sagehill		0.6	0.48	0.74	225	1610	75.59	27.090	0.505	0.096	272.2	6.99
14	Ads 100mm-Sagehill	NA	NA	NA	NA	210	1820	85.45	27.367	0.530	0.137	371.2	6.96
15	Ads 100mm-Sagehill	NA	NA	NA	NA	180	2000	93.90	27.643	0.507	0.089	287.9	6.57
16	Ads 100mm-Sagehill		0.5	0.39	0.65	250	2250	105.64	27.643	0.478	0.119	324.6	6.55
17	Des 100mm-Sagehill		0.84	0.64	1.1	180	2430	114.09	21.562	0.683	0.077	154.9	6.45
18	Des 100mm-Sagehill	NA	NA	NA	NA	155	2585	121.37	17.709	0.248	0.044	113.5	6.46
19	Des 100mm-Sagehill		1.9	1.5	2.1	200	2785	130.76	9.862	0.132	0.052	215.6	6.62
20	Des 100mm-Sagehill	NA	NA	NA	NA	240	3025	142.03	4.407	0.059	0.041	58.03	6.52
21	Des 100mm-Sagehill		2.7	2.1	3.4	260	3285	154.24	2.703	0.023	0.022	29.4	6.55
22	Des 100mm-Sagehill	NA	NA	NA	NA	255	3540	166.21	1.771	0.020	0.023	28.36	6.64
23	Des 100mm-Sagehill	NA	NA	NA	NA	240	3780	177.48	1.579	0.028	0.023	19.27	6.74
24	Des 100mm-Sagehill		2.8	2.2	3.6	225	4005	188.04	1.311	0.010	0.025	18.69	6.7

Table 2.4.1.1. Task 1: Summary data for chemical and toxicity analyses (cont...).

Task 1: Confirmation of Phase II Methodology													
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results			Chemistry Test Results							
			Algal Toxicity			Sample Volume (ml)	Cumm. Vol. (ml)	Pore Volume	As (mg/L)	Cu (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Elutriate										
			% EC ₅₀	Lower 95% C.L.	Upper 95% C.L.								
1	A ds 50mm -W oodburn (second column)		0.13	0.12	0.14								
2	Initial ACZA Leachate	NA	0.22	0.19	0.24				27.643	26.414	10.468		
3	A ds 50mm -W oodburn	NA	11	9	14	15	15	1.24	1.842	0.091	0.070	118.8	7.43
4	A ds 50mm -W oodburn	NA	NA	NA	NA	10	25	2.07	2.460	0.243	0.230	226.6	7.35
5	A ds 50mm -W oodburn	NA	NA	NA	NA	10	35	2.89	3.170	0.630	0.290	242	7.52
6	A ds 50mm -W oodburn	NA	NA	NA	NA	20	55	4.55	3.370	0.960	0.350	272.3	7.42
7	A ds 50mm -W oodburn	NA	NA	NA	NA	20	75	6.20	3.270	1.350	0.340	268.4	7.48
8	A ds 50mm -W oodburn	NA	NA	NA	NA	20	95	7.85	3.630	1.750	0.410	349.4	7.36
9	A ds 50mm -W oodburn	NA	1.5	1.2	1.9	75	170	14.05	5.555	2.225	0.585	397.4	7.3
10	A ds 50mm -W oodburn	NA	NA	NA	NA	70	240	19.83	11.454	6.270	1.350	415.2	6.91
11	A ds 50mm -W oodburn	NA	0.92	0.71	1.2	130	370	30.58	14.719	9.356	2.057	440.2	7.41
12	A ds 50mm -W oodburn	NA	NA	NA	NA	73	443	36.61	16.423	10.359	2.390	438	7.46
13	A ds 50mm -W oodburn	NA	NA	NA	NA	150	593	49.01	22.798	17.972	5.315	463.5	7.27
14	A ds 50mm -W oodburn	NA	0.61	0.49	0.76	250	843	69.67	24.130	12.027	3.407	445	7.41
15	A ds 50mm -W oodburn	NA	NA	NA	NA	227	1070	88.42	25.670	20.829	5.812	468.2	7.44
16	A ds 50mm -W oodburn	NA	NA	NA	NA	175	1245	102.89	25.060	18.816	5.230	474.7	7.36
17	A ds 50mm -W oodburn	NA	0.28	0.21	0.35	250	1495	123.55	26.550	21.545	6.476	481.7	7.1
18	A ds 50mm -W oodburn	NA	NA	NA	NA	270	1765	145.86	27.230	21.005	5.635	462.6	7.16
19	A ds 50mm -W oodburn	NA	NA	NA	NA	350	2115	174.78	26.830	20.249	5.664	469	7.25
20	A ds 50mm -W oodburn	NA	NA	NA	NA	130	2245	185.53	27.620	15.167	3.904	485.3	7.45
21	Des 50mm -W oodburn	NA	0.27	0.21	0.34	215	2460	203.29	27.750	21.488	6.028	493.2	7.32
22	Des 50mm -W oodburn	NA	0.83	0.66	1.1	180	2640	218.17	14.336	4.846	1.264	121.1	7.23
23	Des 50mm -W oodburn	NA	1.5	1.2	1.9	160	2800	231.39	7.735	3.435	0.609	68.37	6.75
24	Des 50mm -W oodburn	NA	2.1	1.7	2.5	175	2975	245.85	5.742	2.641	0.375	51.41	6.73
25	Des 50mm -W oodburn	NA	2.2	1.7	2.7	178	3153	260.56	5.441	2.283	0.403	62.43	6.85

Table 2.4.1.1. Task 1: Summary data for chemical and toxicity analyses (cont...).

Task 1: Confirmation of Phase II Methodology													
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results			Chemistry Test Results							
			Algal Toxicity			Sample Volume (ml)	Cumm. Vol. (ml)	Pore Volume	As (mg/L)	Cu (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Elutriate										
			% EC ₅₀	Lower 95% C.L.	Upper 95% C.L.								
1	Ads 50mm - Woodburn (third column)	NA	0.22	0.19	0.24				27.64	26.41	10.47		
2	Initial ACZA Leachate	4202405				1.0	1.0	0.76	0.05	0.09	0.25	2.551	6.82
3	Ads 50mm - Woodburn	4202406	18	16	20	1.7	2.7	2.05	0.00	0.24	0.36	2.255	7.02
4	Ads 50mm - Woodburn	NA	NA	NA	NA	2.5	5.2	3.95	0.03	0.63	0.48	150.70	6.27
5	Ads 50mm - Woodburn	4202409	13	11	15	10.5	15.7	11.93	3.30	0.96	0.66	202.70	7.04
6	Ads 50mm - Woodburn	NA	NA	NA	NA	2.50	4.07	30.93	6.72	1.35	0.80	268.40	6.95
7	Ads 50mm - Woodburn	NA	NA	NA	NA	2.10	6.17	46.89	15.99	1.75	0.81	281.00	6.93
8	Ads 50mm - Woodburn	4202412	0.55	0.65	0.45	2.50	8.67	65.89	20.07	2.23	1.13	300.00	6.95
9	Ads 50mm - Woodburn	NA	NA	NA	NA	2.35	11.02	83.76	23.21	6.27	1.22	307.10	6.77
10	Ads 50mm - Woodburn	4203403	0.46	0.39	0.53	2.30	133.2	101.24	24.25	9.36	1.40	339.00	6.87
11	Ads 50mm - Woodburn	NA	NA	NA	NA	2.50	158.2	120.24	24.34	10.36	1.96	347.80	6.74
12	Ads 50mm - Woodburn	4203406	0.35	0.3	0.42	2.50	183.2	139.24	24.61	17.97	2.18	356.20	6.85
13	Ads 50mm - Woodburn	NA	NA	NA	NA	2.50	208.2	158.24	24.62	18.03	3.21	362.80	7.36
14	Ads 50mm - Woodburn	NA	NA	NA	NA	2.35	231.7	176.10	24.57	20.83	4.39	370.70	6.79
15	Ads 50mm - Woodburn	4204403	0.3	0.24	0.36	2.40	255.7	194.34	24.71	18.82	4.93	376.90	6.77
16	Ads 50mm - Woodburn	NA	NA	NA	NA	2.45	280.2	212.96	25.05	21.55	5.12	392.90	6.71
17	Ads 50mm - Woodburn	NA	NA	NA	NA	2.30	303.2	230.44	25.84	21.00	5.68	396.60	7.32
18	Ads 50mm - Woodburn	4204426	0.27	0.22	0.34	2.30	326.2	247.92	26.29	20.25	6.02	412.20	6.70
19	Ads 50mm - Woodburn	NA	NA	NA	NA	2.30	349.2	265.40	27.04	21.17	6.30	415.70	6.66
20	Ads 50mm - Woodburn	4205406	0.26	0.21	0.33	1.27	361.9	275.06	27.25	21.49	7.09	412.10	6.63
21	Des 50mm - Woodburn	4205424	0.47	0.39	0.58	3.20	393.9	299.38	17.39	12.78	3.05	52.48	6.55
22	Des 50mm - Woodburn	NA	NA	NA	NA	2.30	416.9	316.86	11.61	10.71	0.69	23.36	6.43
23	Des 50mm - Woodburn	4205427	0.66	0.54	0.8	2.20	438.9	333.58	8.97	7.58	0.48	18.71	6.25
24	Des 50mm - Woodburn	NA	NA	NA	NA	2.32	462.1	351.21	7.00	4.10	0.34	17.09	6.23
25	Des 50mm - Woodburn	NA	NA	NA	NA	2.40	486.1	369.45	6.25	3.00	0.34	20.46	6.74
26	Des 50mm - Woodburn	4206406	10	9	11	2.40	510.1	387.69	5.38	2.78	0.23	14.23	6.44
27	Des 50mm - Woodburn	NA	NA	NA	NA	2.45	534.6	406.31	4.25	1.71	0.19	0.70	6.34
28	Des 50mm - Woodburn	NA	NA	NA	NA	2.27	557.3	423.57	3.62	1.58	0.26	0.55	6.48
29	Des 50mm - Woodburn	4206422	12	11	13	2.30	580.3	441.05	3.21	1.10	0.16		6.36
30	Des 50mm - Woodburn	NA	NA	NA	NA	2.25	602.8	458.15	2.76	1.00	0.13		6.24
31	Des 50mm - Woodburn	4206423	14	13	15	2.70	629.8	478.67	2.40	0.49	0.17		6.14

Table 2.4.1.1. Task 1 summary data for chemical and toxicity analyses (cont...).

Task 1: Confirmation of Phase II Methodology													
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results			Chemistry Test Results							
			Algal Toxicity			Sample Volume (ml)	Cumm. Vol. (ml)	Pore Volume	As (mg/L)	Cu (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as %										
			Elutriate										
% EC ₅₀	Lower 95% C.L.	Upper 95% C.L.											
	Ads 50mm -Sagehill (first column)												
1	Initial ACZA Leachate	NA	0.22	0.19	0.24				27.64	26.41	10.47	565.30	
2	Ads 50mm -Sagehill	4202401	15	13	17	12	12	1.32	0.18	0.01	0.01	25.06	6.31
3	Ads 50mm -Sagehill	NA	NA	NA	NA	20	32	3.52	0.02	0.05	0.13	117.00	6.97
4	Ads 50mm -Sagehill	NA	NA	NA	NA	29	61	6.72	0.01	0.35	0.26	316.00	6.68
5	Ads 50mm -Sagehill	4202402	1.8	1.3	2.4	122	183	20.15	7.53	0.80	0.17	372.20	6.65
6	Ads 50mm -Sagehill	4202407	0.66	0.55	0.81	250	433	47.68	21.53	1.73	0.04	440.10	6.69
7	Ads 50mm -Sagehill	NA	NA	NA	NA	250	683	75.20	22.45	2.79	0.15	458.00	6.66
8	Ads 50mm -Sagehill	4202410	0.44	0.36	0.56	260	943	103.83	22.86	6.07	0.43	474.10	7.20
9	Ads 50mm -Sagehill	NA	NA	NA	NA	240	1183	130.26	23.22	10.41	1.29	503.30	7.66
10	Ads 50mm -Sagehill	4203401	0.36	0.28	0.45	245	1428	157.24	23.46	12.09	1.87	487.40	7.28
11	Ads 50mm -Sagehill	NA	NA	NA	NA	250	1678	184.76	23.87	14.30	2.82	478.50	7.07
12	Ads 50mm -Sagehill	4203404	0.29	0.28	0.41	230	1908	210.09	24.34	17.19	3.97	493.10	7.16
13	Ads 50mm -Sagehill	NA	NA	NA	NA	230	2138	235.41	24.52	15.22	3.22	487.60	7.11
14	Ads 50mm -Sagehill	NA	NA	NA	NA	200	2338	257.44	25.39	17.23	3.87	507.50	7.16
15	Ads 50mm -Sagehill	4204401	0.25	0.24	0.26	220	2558	281.66	25.85	19.51	4.66	491.90	7.17
16	Ads 50mm -Sagehill	NA	NA	NA	NA	240	2798	308.09	26.37	18.83	4.38	496.30	7.20
17	Ads 50mm -Sagehill	NA	NA	NA	NA	228	3026	333.19	27.38	19.30	4.61	486.40	7.26
18	Ads 50mm -Sagehill	NA	NA	NA	NA	240	3266	359.62	27.83	21.19	5.45	489.80	7.25
19	Ads 50mm -Sagehill	4205401	0.24	0.23	0.26	147	3413	375.80	27.78	19.19	4.88	498.30	7.43
20	Des 50mm -Sagehill	4205404	0.24	0.22	0.25	320	3733	411.04	23.87	21.06	5.80	495.60	7.48
21	Des 50mm -Sagehill	4205422	0.29	0.26	0.4	220	3953	435.26	23.45	5.02	0.75	83.71	6.90
22	Des 50mm -Sagehill	NA	NA	NA	NA	230	4183	460.59	4.62	1.11	0.16	28.54	6.68
23	Des 50mm -Sagehill	4205425	4	3	5	230	4413	485.91	2.12	0.55	0.06	21.56	6.84
24	Des 50mm -Sagehill	NA	NA	NA	NA	227	4640	510.91	1.33	0.28	0.03	20.33	6.77
25	Des 50mm -Sagehill	4206404	6	5	7	250	4890	538.44	0.96	0.21	0.04	13.18	6.67

Table 2.4.1.1. Task 1 summary data for chemical and toxicity analyses (cont...).

Task 1: Confirmation of Phase II Methodology													
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results			Chemistry Test Results							
			Algal Toxicity			Sample Volume (ml)	Cumm. Vol. (ml)	Pore Volume	As (mg/L)	Cu (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as %										
			Elutriate										
% EC ₅₀	Lower 95% C.L.	Upper 95% C.L.											
	Ads 50 mm -Sagehill (second column)												
1	Initial IACZA Leachate	NA	0.22	0.19	0.24				27.64	26.41	10.47	465.30	
2	Ads 50 mm -Sagehill	4202403	14	13	16	12.5	12.5	1.56	0.00	0.02	0.01	27.25	6.92
3	Ads 50 mm -Sagehill	NA	NA	NA	NA	30	42.5	5.30	0.03	0.18	0.10	171.50	6.46
4	Ads 50 mm -Sagehill	NA	NA	NA	NA	28	70.5	8.78	0.06	0.45	0.40	241.50	6.51
5	Ads 50 mm -Sagehill	4202404	2	1.7	2.3	125	195.5	24.36	9.28	0.56	0.05	288.30	7.34
6	Ads 50 mm -Sagehill	4202408	0.7	0.52	0.81	255	450.5	56.14	22.67	1.56	0.06	337.30	6.96
7	Ads 50 mm -Sagehill	NA	NA	NA	NA	200	650.5	81.06	25.24	2.62	0.07	354.80	7.58
8	Ads 50 mm -Sagehill	4202411	0.39	0.34	0.48	250	900.5	112.21	25.01	4.26	0.13	376.10	7.82
9	Ads 50 mm -Sagehill	NA	NA	NA	NA	235	1136	141.49	25.37	7.65	0.57	377.00	7.87
10	Ads 50 mm -Sagehill	4203402	0.31	0.27	0.38	240	1376	171.40	24.54	9.66	1.08	375.10	7.20
11	Ads 50 mm -Sagehill	NA	NA	NA	NA	400	1776	221.24	24.89	13.27	2.00	373.00	7.10
12	Ads 50 mm -Sagehill	4203405	0.3	0.25	0.37	150	1926	239.93	25.99	14.71	2.60	391.70	7.06
13	Ads 50 mm -Sagehill	NA	NA	NA	NA	240	2166	269.84	24.58	13.02	2.34	399.70	7.00
14	Ads 50 mm -Sagehill	NA	NA	NA	NA	215	2381	296.63	25.66	14.69	2.94	376.00	7.04
15	Ads 50 mm -Sagehill	4204402	0.25	0.22	0.32	220	2601	324.04	26.13	17.27	3.59	403.40	7.55
16	Ads 50 mm -Sagehill	NA	NA	NA	NA	230	2831	352.70	26.56	16.22	3.33	395.80	7.67
17	Ads 50 mm -Sagehill	NA	NA	NA	NA	230	3061	381.36	26.82	17.48	3.81	395.00	7.69
18	Ads 50 mm -Sagehill	NA	NA	NA	NA	240	3301	411.26	27.18	19.08	4.43	390.50	7.68
19	Ads 50 mm -Sagehill	NA	NA	NA	NA	250	3551	442.42	27.38	18.01	4.10	394.40	7.27
20	Ads 50 mm -Sagehill	4205405	0.25	0.21	0.32	260	3811	474.81	27.78	21.07	5.60	385.80	7.63
21	Des 50 mm -Sagehill	4205423	0.22	0.19	0.23	230	4041	503.47	29.50	5.83	0.47	90.88	7.45
22	Des 50 mm -Sagehill	NA	NA	NA	NA	230	4271	532.13	7.27	1.47	0.16	27.64	7.32
23	Des 50 mm -Sagehill	4205426	3	2	4	230	4501	560.79	4.14	0.77	0.08	19.64	7.15
24	Des 50 mm -Sagehill	NA	NA	NA	NA	230	4731	589.45	2.40	0.52	0.05	15.97	7.15
25	Des 50 mm -Sagehill	4206405	4	3	5	220	4951	616.86	1.73	0.36	0.03	14.46	7.29

Table 2.4.1.1. Task 1 summary data for chemical analyses (cont..).

Task 1: Confirmation of Phase II Methodology						
Sample ID	Test Conditions	Time (hours)	Cumm. Vol. (ml)	Cumm. Pore Volume	TCP (mg/L)	C/Co
Sagehill TCP 100 mm Soil Column						
1	TCP Adsorption	3.25	32.50	1.47	0.04	0.02
2	TCP Adsorption	1.00	42.50	1.92	0.86	0.43
3	TCP Adsorption	1.00	52.50	2.38	1.51	0.75
4	TCP Adsorption	1.00	62.50	2.83	1.72	0.86
5	TCP Adsorption	2.00	82.50	3.74	1.93	0.96
6	TCP Adsorption	3.00	112.50	5.09	2.19	1.09
7	TCP Adsorption	3.00	142.50	6.45	2.04	1.02
8	TCP Adsorption	10.00	242.50	10.98	2.19	1.10
9	TCP Adsorption	1.00	252.50	11.43	2.19	1.10
10	TCP Adsorption	23.00	482.50	21.84	2.30	1.15
11	TCP Adsorption	1.17	494.17	22.37	2.22	1.11
12	TCP Adsorption	0.67	500.83	22.67	2.25	1.12
13	TCP Adsorption	2.00	520.83	23.58	2.21	1.11
14	TCP Desorption	0.67	527.50	23.88	1.52	0.76
15	TCP Desorption	1.67	544.17	24.64	1.87	0.94
16	TCP Desorption	2.50	569.17	25.77	0.35	0.17
17	TCP Desorption	1.00	579.17	26.22	0.15	0.08
Sagehill TCP 100 mm Soil Column (duplicate)						
1	TCP Adsorption	1.00	10.0	0.5	0.000	0.000
2	TCP Adsorption	1.00	20.0	1.0	0.000	0.000
3	TCP Adsorption	2.00	40.0	1.9	0.230	0.115
4	TCP Adsorption	1.25	52.5	2.5	1.391	0.696
5	TCP Adsorption	1.00	62.5	3.0	1.469	0.734
6	TCP Adsorption	1.00	72.5	3.5	1.543	0.771
7	TCP Adsorption	0.58	78.3	3.8	1.632	0.816
8	TCP Adsorption	1.17	90.0	4.3	1.667	0.834
9	TCP Adsorption	1.00	100.0	4.8	1.865	0.932
10	TCP Adsorption	11.50	215.0	10.3	2.115	1.058
11	TCP Adsorption	1.00	225.0	10.8	2.026	1.013
12	TCP Desorption	1.00	235.0	11.3	1.766	0.883
13	TCP Desorption	1.00	245.0	11.8	1.153	0.576
14	TCP Desorption	1.00	255.0	12.2	0.337	0.168
15	TCP Desorption	1.00	265.0	12.7	0.265	0.133
16	TCP Desorption	3.50	300.0	14.4	0.263	0.132
17	TCP Desorption	1.00	310.0	14.9	0.150	0.075
18	TCP Desorption	1.00	320.0	15.4	0.100	0.050
19	TCP Desorption	2.50	345.0	16.6	0.040	0.020
20	TCP Desorption	11.50	460.0	22.1	0.000	0.000
21	TCP Desorption	1.50	475.0	22.8	0.000	0.000

Table 2.4.1.1. Task 1 summary data for chemical analyses (cont..).

Task 1: Confirmation of Phase II Methodology						
Sample ID	Test Conditions	Time (hours)				
			Cumm. Vol. (ml)	Cumm. Pore Volume	TCP (mg/L)	C/Co
Woodburn TCP 50 mm Soil Column						
1	TCP Adsorption	2.00	20	2.0	0.000	0.000
2	TCP Adsorption	3.00	50	5.1	0.002	0.001
3	TCP Adsorption	2.00	70	7.1	0.002	0.001
4	TCP Adsorption	4.25	112.5	11.4	0.450	0.225
5	TCP Adsorption	11.25	225	22.8	0.632	0.316
6	TCP Adsorption	4.00	265	26.9	0.724	0.362
7	TCP Adsorption	5.50	320	32.5	1.029	0.514
8	TCP Adsorption	12.50	445	45.2	0.902	0.451
9	TCP Adsorption	5.00	495	50.3	1.312	0.656
10	TCP Adsorption	4.75	542.5	55.1	1.597	0.798
11	TCP Adsorption	16.50	707.5	71.8	2.029	1.014
12	TCP Adsorption	6.25	770	78.2	2.089	1.044
13	TCP Adsorption	5.75	827.5	84.0	2.032	1.016
14	TCP Adsorption	10.00	927.5	94.2	2.039	1.020
15	TCP Adsorption	3.25	960	97.5	2.112	1.056
16	TCP Desorption	7.00	1030	104.6	1.107	0.553
17	TCP Desorption	1.75	1047.5	106.4	1.252	0.626
18	TCP Desorption	14.00	1187.5	120.6	0.599	0.300
19	TCP Desorption	4.50	1232.5	125.2	0.248	0.124
20	TCP Desorption	3.50	1267.5	128.7	0.148	0.074
21	TCP Desorption	4.00	1307.5	132.8	0.103	0.051
22	TCP Desorption	10.00	1407.5	142.9	0.047	0.024
23	TCP Desorption	4.75	1455	147.7	0.032	0.016

Table 2.4.1.1. Task 1: Summary data for chemical analyses (cont..).

Task 1: Confirmation of Phase II Methodology						
Sample ID	Test Conditions	Time (hours)	Cum. Vol. (ml)	Cum. Pore Volume	TCP (mg/L)	C/Co
1	TCP Adsorption	3.00	30	2.2	0.000	0.000
2	TCP Adsorption	3.00	60	4.4	0.023	0.011
3	TCP Adsorption	3.25	92.5	6.8	0.053	0.026
4	TCP Adsorption	4.00	132.5	9.7	0.079	0.039
5	TCP Adsorption	10.50	237.5	17.4	0.305	0.152
6	TCP Adsorption	3.50	272.5	20.0	0.497	0.249
7	TCP Adsorption	6.00	332.5	24.4	0.513	0.257
8	TCP Adsorption	2.25	355	26.0	0.455	0.227
9	TCP Adsorption	6.75	422.5	31.0	0.679	0.340
10	TCP Adsorption	8.00	502.5	36.8	0.777	0.389
11	TCP Adsorption	4.25	545	39.9	1.055	0.528
12	TCP Adsorption	6.50	610	44.7	1.507	0.754
13	TCP Adsorption	9.25	702.5	51.5	1.450	0.725
14	TCP Adsorption	13.50	837.5	61.4	1.629	0.815
15	TCP Adsorption	15.50	992.5	72.7	1.728	0.864
16	TCP Desorption	11.00	1102.5	80.8	2.011	1.005
17	TCP Desorption	11.50	1217.5	89.2	1.125	0.562
18	TCP Desorption	3.75	1255	92.0	0.770	0.385
19	TCP Desorption	6.00	1315	96.4	0.134	0.067
20	TCP Desorption	15.75	1472.5	107.9	0.139	0.070
21	TCP Desorption	8.00	1552.5	113.8	0.095	0.047
22	TCP Desorption	14.00	1692.5	124.0	0.100	0.050
23	TCP Desorption	8.00	1772.5	129.9	0.000	0.000
Sagehill TCP 100 mm Soil Column With Cells						
1	TCP Adsorption	1.25	0.535	12.500	0.000	0.000
2	TCP Adsorption	1.00	0.963	22.500	0.000	0.000
3	TCP Adsorption	1.00	1.391	32.500	0.000	0.000
4	TCP Adsorption	1.00	1.818	42.500	0.000	0.000
5	TCP Adsorption	3.00	3.102	72.500	1.436	0.718
6	TCP Adsorption	2.50	4.172	97.500	1.530	0.765
7	TCP Adsorption	3.50	5.669	132.500	1.803	0.901
8	TCP Adsorption	10.00	9.948	232.500	1.727	0.863
9	TCP Adsorption	7.00	12.943	302.500	1.918	0.959
10	TCP Adsorption	8.00	16.366	382.500	1.874	0.937
11	TCP Adsorption	9.00	20.217	472.500	1.830	0.915
12	TCP Adsorption	4.50	22.143	517.500	1.916	0.958
13	TCP Adsorption	9.50	26.207	612.500	1.779	0.890
14	TCP Adsorption	11.00	30.914	722.500	1.876	0.938
15	TCP Adsorption	5.00	33.053	772.500	1.911	0.955
16	TCP Desorption	6.00	35.621	832.500	0.993	0.497
17	TCP Desorption	11.00	40.327	942.500	0.370	0.185
18	TCP Desorption	2.50	41.397	967.500	0.209	0.105
19	TCP Desorption	10.00	45.676	1067.500	0.000	0.000

Table 2.4.1.1. Task 1: Summary data for chemical analyses (cont..).

Task 1: Confirmation of Phase II Methodology						
Sample ID	Test Conditions	Time (hours)				
			Cumm. Vol. (ml)	Cumm. Pore Volume	TCP (mg/L)	C/Co
Sagehill TCP 100 mm Soil Column With Cells (duplicate)						
1	TCP Adsorption	2.000	0.857	20.000	0.000	0.000
2	TCP Adsorption	1.000	1.286	30.000	0.000	0.000
3	TCP Adsorption	1.000	1.714	40.000	0.527	0.264
4	TCP Adsorption	2.000	2.571	60.000	0.633	0.317
5	TCP Adsorption	1.000	3.000	70.000	1.045	0.522
6	TCP Adsorption	2.000	3.857	90.000	1.430	0.715
7	TCP Adsorption	5.000	6.000	140.000	1.771	0.885
8	TCP Adsorption	9.500	10.071	235.000	1.709	0.855
9	TCP Adsorption	6.500	12.857	300.000	1.570	0.785
10	TCP Adsorption	5.500	15.214	355.000	1.531	0.765
11	TCP Adsorption	1.000	15.643	365.000	1.715	0.857
12	TCP Adsorption	13.000	21.214	495.000	1.551	0.775
13	TCP Desorption	2.500	22.285	520.000	1.441	0.721
14	TCP Desorption	7.000	25.285	590.000	1.623	0.812
15	TCP Desorption	3.500	26.785	625.000	1.002	0.501
16	TCP Desorption	9.500	30.857	720.000	0.740	0.370
17	TCP Desorption	3.000	32.143	750.000	0.373	0.186
18	TCP Desorption	5.000	34.285	800.000	0.239	0.119
19	TCP Desorption	7.000	37.285	870.000	0.098	0.049

Table 2.4.1.1. Task 1: Summary data for chemical analyses (cont..).

Task 1: Confirmation of Phase II Methodology						
Sample ID	Test Conditions	Time (hours)				
			Cumm. Vol. (ml)	Cumm. Pore Volume	TCP (mg/L)	C/Co
	Sagehill TCP 100 mm	Soil Column With Cells (duplicate)				
1	TCP Adsorption	0.500	0.189	4.269	0.000	0.000
2	TCP Adsorption	4.000	1.769	40.000	0.485	0.242
3	TCP Adsorption	2.000	2.653	60.000	1.111	0.556
4	TCP Adsorption	3.500	4.200	95.000	1.716	0.858
5	TCP Adsorption	2.000	5.085	115.000	1.822	0.911
6	TCP Adsorption	3.000	6.411	145.000	1.545	0.772
7	TCP Adsorption	9.500	10.612	240.000	1.849	0.924
8	TCP Adsorption	4.000	12.380	280.000	1.745	0.873
9	TCP Adsorption	4.000	14.149	320.000	1.716	0.858
10	TCP Adsorption	5.000	16.360	370.000	1.759	0.879
11	TCP Adsorption	23.500	26.750	605.000	1.756	0.878
12	TCP Adsorption	24.500	37.583	850.000	1.853	0.927
13	TCP Adsorption	66.500	66.986	1515.000	1.771	0.885
14	TCP Desorption	54.000	90.863	2055.000	1.732	0.866
15	TCP Desorption	23.500	101.253	2290.000	0.800	0.400
16	TCP Desorption	24.000	111.865	2530.000	0.660	0.330
17	TCP Desorption	23.500	122.255	2765.000	0.580	0.290
18	TCP Desorption	23.500	132.646	3000.000	0.550	0.275
19	TCP Desorption	23.000	142.816	3230.000	0.500	0.250
20	TCP Desorption	16.000	149.890	3390.000	0.320	0.160
21	TCP Desorption	24.000	160.502	3630.000	0.180	0.090
22	TCP Desorption	23.500	170.892	3865.000	0.130	0.065
23	TCP Desorption	25.000	181.946	4115.000	0.110	0.055
24	TCP Desorption	24.000	192.558	4355.000	0.080	0.040
25	TCP Desorption	24.000	203.170	4595.000	0.100	0.050
26	TCP Desorption	23.500	213.560	4830.000	0.060	0.030
27	TCP Desorption	24.000	224.172	5070.000	0.080	0.040

Table 2.4.1.1. Task 1: Summary data for chemical analyses (cont..).

Task 1: Confirmation of Phase II Methodology						
Sample ID	Test Conditions	Time (hours)				
			Cumm. Vol. (ml)	Cumm. Pore Volume	TCP (mg/L)	C/Co
	Sagehill TCP 100 mm	50 mm Soil Column With Cells				
1	TCP Adsorption	11.00	7.221	110.000	0.000	0.000
2	TCP Adsorption	1	7.878	120.000	0.000	0.000
3	TCP Adsorption	7	12.473	190.000	0.000	0.000
4	TCP Adsorption	9	18.381	280.000	1.331	0.666
5	TCP Adsorption	4.5	21.336	325.000	1.478	0.739
6	TCP Adsorption	9.5	27.572	420.000	1.189	0.594
7	TCP Adsorption	11	34.793	530.000	0.832	0.416
8	TCP Adsorption	5	38.076	580.000	1.355	0.677
9	TCP Adsorption	17	49.236	750.000	0.714	0.357
10	TCP Adsorption	12.5	57.442	875.000	0.915	0.458
11	TCP Adsorption	13.5	66.304	1010.000	1.122	0.561
12	TCP Adsorption	10	72.869	1110.000	0.895	0.448
13	TCP Adsorption	14	82.060	1250.000	0.844	0.422
14	TCP Adsorption	11.5	89.609	1365.000	1.021	0.510
15	TCP Adsorption	14	98.800	1505.000	1.143	0.571
	Woodburn TCP 50 mm Soil Column With Cells (duplicate)					
1	TCP Adsorption	10	6.565	100.000	0.000	0.000
2	TCP Adsorption	4.5	9.519	145.000	0.830	0.415
3	TCP Adsorption	13	18.053	275.000	1.661	0.830
4	TCP Adsorption	10	24.618	375.000	1.697	0.849
5	TCP Adsorption	12	32.496	495.000	1.599	0.799
6	TCP Adsorption	12	40.373	615.000	1.599	0.799
7	TCP Adsorption	12	48.251	735.000	1.599	0.799
8	TCP Adsorption	12	56.129	855.000	1.599	0.799
9	TCP Adsorption	12	64.007	975.000	1.599	0.799
10	TCP Adsorption	15	73.854	1125.000	1.456	0.728
11	TCP Adsorption	12	81.731	1245.000	1.454	0.727
12	TCP Adsorption	8	86.983	1325.000	1.367	0.684
13	TCP Adsorption	18	98.800	1505.000	1.007	0.503
14	TCP Adsorption	6	102.739	1565.000	1.088	0.544
15	TCP Adsorption	19.5	115.540	1760.000	0.443	0.297
16	TCP Adsorption	18.5	127.685	1945.000	0.424	0.284
17	TCP Adsorption	31	148.036	2255.000	0.456	0.305
18	TCP Adsorption	6	151.975	2315.000	0.297	0.199
19	TCP Adsorption	24	167.730	2555.000	0.241	0.162

Table 2.1.2.1. Task 1: Summary data for chemical analyses (concluded).

Task 1: Confirmation of Phase II Methodology						
Sample ID	Test Conditions	Time (hours)				
			Cumm. Vol. (ml)	Cumm. Pore Volume	TCP (mg/L)	C/Co
	Sagehill TCP 100 mm in Soil Column With Cells (duplicate)					
1	TCP Adsorption	5	3.736	50.000	0.000	0.000
2	TCP Adsorption	1.5	4.857	65.000	0.003	0.001
3	TCP Adsorption	4	7.845	105.000	0.037	0.018
4	TCP Adsorption	4.5	11.208	150.000	0.052	0.026
5	TCP Adsorption	9	17.932	240.000	0.688	0.344
6	TCP Adsorption	5	21.668	290.000	1.017	0.509
7	TCP Adsorption	10	29.140	390.000	1.070	0.535
8	TCP Adsorption	16	41.095	550.000	1.129	0.565
9	TCP Adsorption	6	45.578	610.000	1.310	0.655
10	TCP Adsorption	17	58.280	780.000	0.910	0.455
11	TCP Adsorption	21.5	74.344	995.000	0.102	0.051
12	TCP Adsorption	27.5	94.891	1270.000	0.052	0.026

CHAPTER 3

TASK 2: LEACHING FROM FLAT SURFACES WITH AND WITHOUT SOIL CONFINEMENT

3.1 INTRODUCTION

Under field conditions, environments exist in which a flat, impermeable surface is buried in soil, and thus leaching occurs under confined conditions (soil is packed against a flat surface). The Phase II methodology does not directly address leaching under these conditions, but implicitly assumes that leaching flux is not affected by confined conditions. The purpose of Task 2 was to confirm whether leachate flux from flat, impermeable surfaces is altered under confined conditions. These conditions are relevant to the reference environments of piling, fill, and culverts.

The reference environment selected to test the effect of confinement on leaching is that of an embedded pile, as this is the most amenable to confinement and flow control in a laboratory experiment. Soil columns were used to test the embedded pile under confined and unconfined conditions. Because natural soils sorb leached contaminants, which are then retained in the column and not eluted, a non-sorbing “soil” is required. Thus, clean sand packed around the test pile was used to test the effect of soil confinement on leaching rate, while large glass beads (for mixing control) around the test pile served as the no-confinement control. Distilled water was pumped through the column, and contaminants were leached from the outer surface of the embedded piles into the flowing water and through the packing materials (sand or beads). Distilled water was pumped up-flow through the column to simulate leaching into flowing groundwater. Sand serves as the confining soil but is a weak adsorbent, thus allowing leached constituents to elute from the column for measurement. For the unconfined surface, the column is packed with large glass beads (marbles) for flow and mixing control (to avoid turbulent eddies and axial mixing not present in the sand-packed column). Adsorption to the glass beads is negligible due to the small total surface area and weak adsorption affinity.

3.2 MATERIALS AND METHODS

3.2.1 Test Materials

The tests were conducted with two C&R materials, PCC with plasticizer and wood posts preserved with ACZA. To fabricate the PCC pile, Portland cement concrete with plasticizer was formed into a pile (10-cm diameter, 40-cm long). The flat ends were sealed with wax (as in flat-plate leaching experiments), and placed in soil columns to mimic buried piles. An apparatus was fabricated for the embedded pile experiments, as shown in Figure 3.2.1.1.



Figure 3.2.1.1. PCC pile in leaching column with clean sand as a confining medium and glass beads as non-embedding (non-confining control) medium.

The embedding sand was silica, an Ottawa sand (99.5% SiO₂), with spherical grains of 70-mesh and particle size between 0.05-0.30 mm (ASTM C11), produced by Unimin Corp. The sand was acid washed and rinsed with distilled water until the pH of rinsing water was about 7.

The large, non-spherical glass beads of size 5/8 x 1/4 inch were purchased locally. The glass beads were acid washed and rinsed with distilled water until the pH of rinsing water was about 7.

3.2.2 Embedded Pile Leaching Experimental Method

Leaching from embedded piles was conducted by modifying the standard soil column procedure described in Volume IV (Nelson et al., 2000b) to include a pile confined by soil in a recirculating-flow glass column. The soil columns have dimensions of 15-cm inside diameter by 50-cm length. The pile was either a wood post treated with ACZA (10-cm diameter, 40-cm long) or PCC pile (10-cm diameter, 40-cm long). Distilled water was pumped up-flow in the packed annulus surrounding the pile in the column. A total volume of 17.8 L extraction water was recirculated at a flow rate of 8 L/d from a reservoir through the columns to maintain mixing (equal to approximate volume to surface area ratio of flat-plate leaching experiments). Experimental duration was 15-30 days. A schematic diagram of the experimental setup is shown in Figure 3.2.2.1.

a. Pile test with soil confinement

b. Pile test with no-confinement

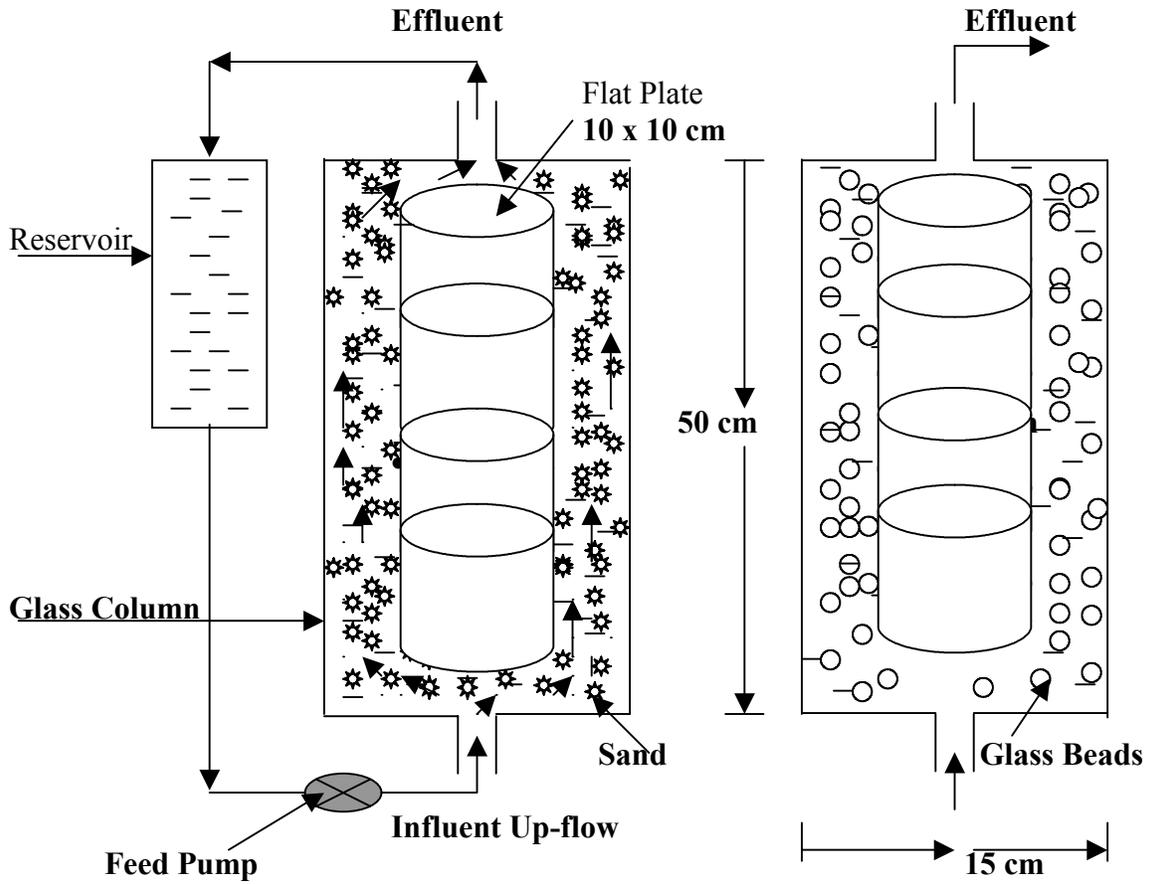


Figure 3.2.2.1. Schematic representation of the two soil columns with and without confinement around the PCC piles.

3.3 RESULTS AND DISCUSSION

3.3.1 ACZA Pile Leachate

The rate of leaching of contaminants from a confined flat surface such as an embedded pile is determined by recirculating-flow glass column experiments. Figures 3.3.1.1 and 3.3.1.2 show distilled water leaching of metals from ACZA piles for both confined (sand) and unconfined systems, respectively. As, Cu, and Zn concentrations increased initially at a greater rate for the unconfined pile compared to the confined pile, but reached the same concentrations after about 400 hours or 67 pore volumes (2000 mL) of flow, after which rate of leaching was low but equal for both piles until the test was terminated at about 650 hours (108 pore volumes of flow). Both columns, the original and duplicate, show almost the same as shown in Figures 3.3.1.1 and 3.3.1.2. Figures 3.3.1.3 and 3.3.1.4 (duplicate columns) show As, Cu, and Zn total mass leached for both confined (sand) and unconfined systems, respectively. Total metals mass released for both columns was almost the same for confined and unconfined systems, which shows that sand confinement has no effect on leached mass released from the ACZA pile. The chemical and toxicity analysis data are summarized in Table 3.3.1.1.

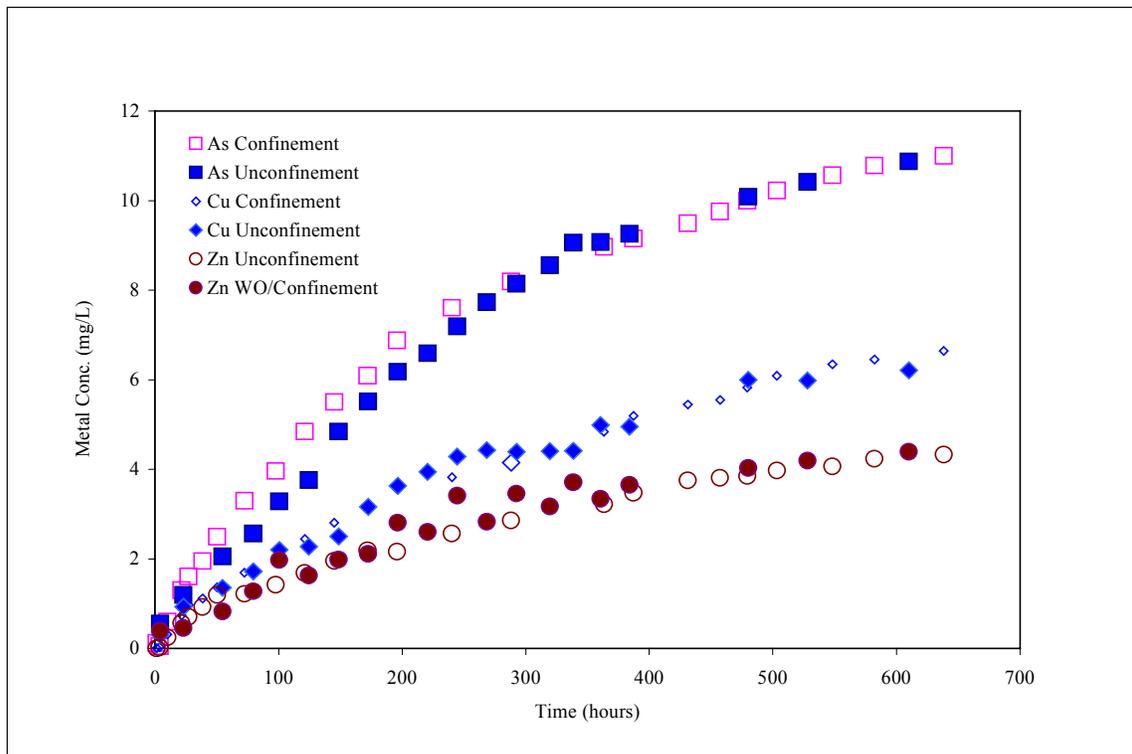


Figure 3.3.1.1. Arsenic, copper, and zinc leaching from ACZA pile with and without confinement, metal concentration vs. time.

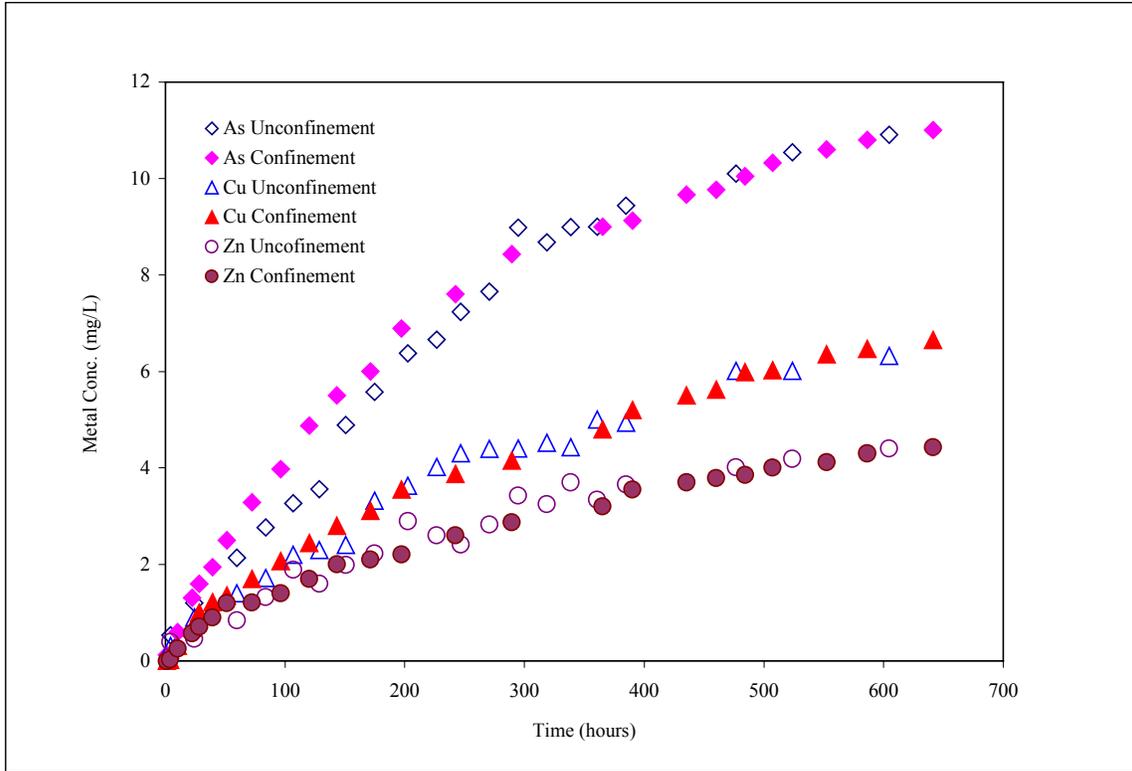


Figure 3.3.1.2. Arsenic, copper, and zinc leaching from ACZA pile with and without confinement, metal concentration vs. time (duplicate column).

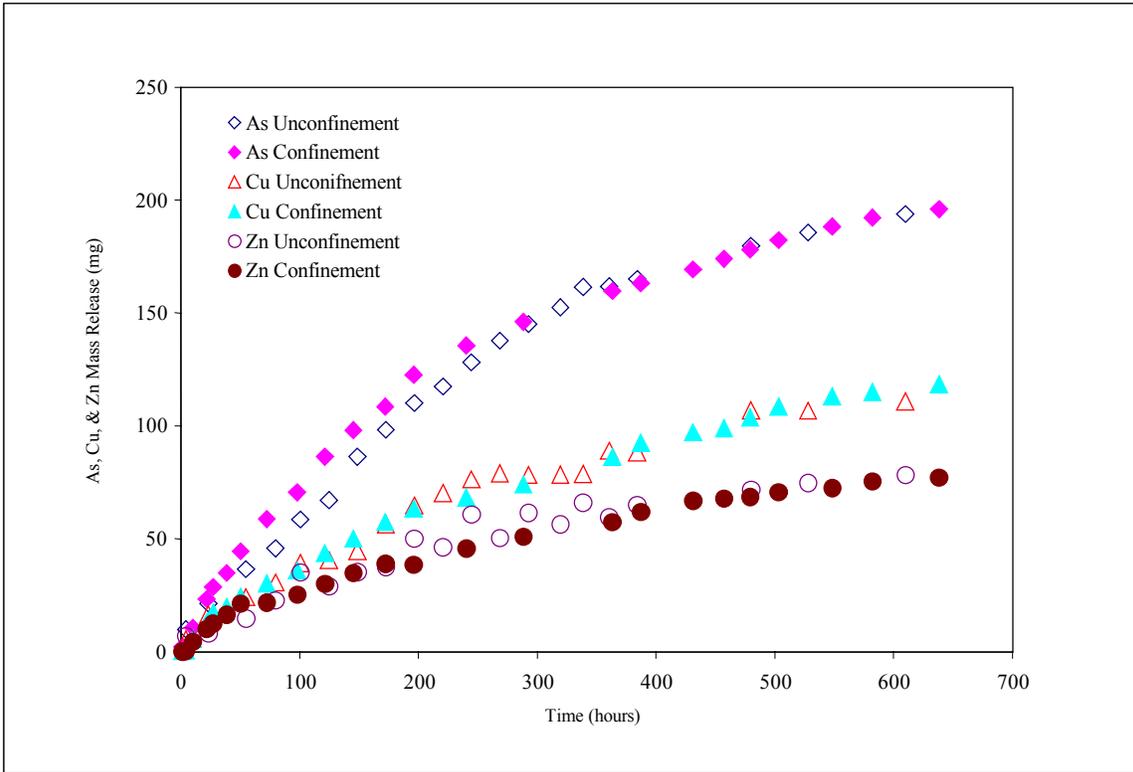


Figure 3.3.1.3. Arsenic, copper, and zinc leaching from ACZA pile with and without confinement, cumulative mass release vs. time.

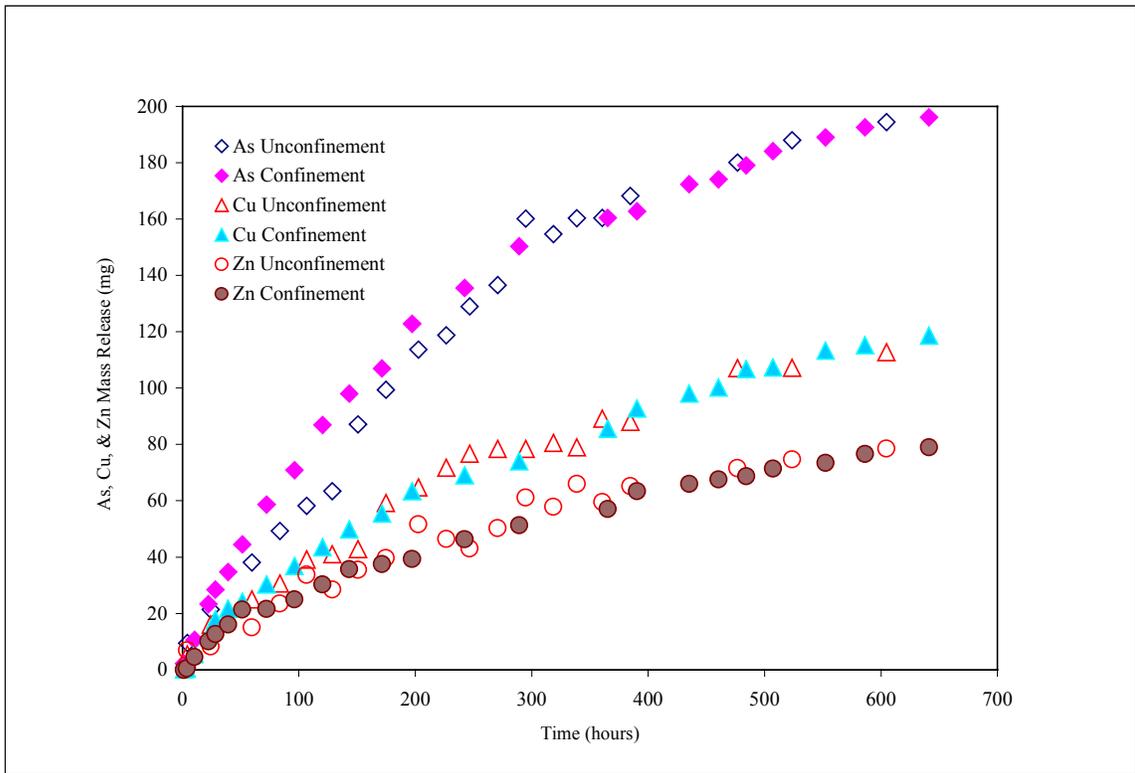
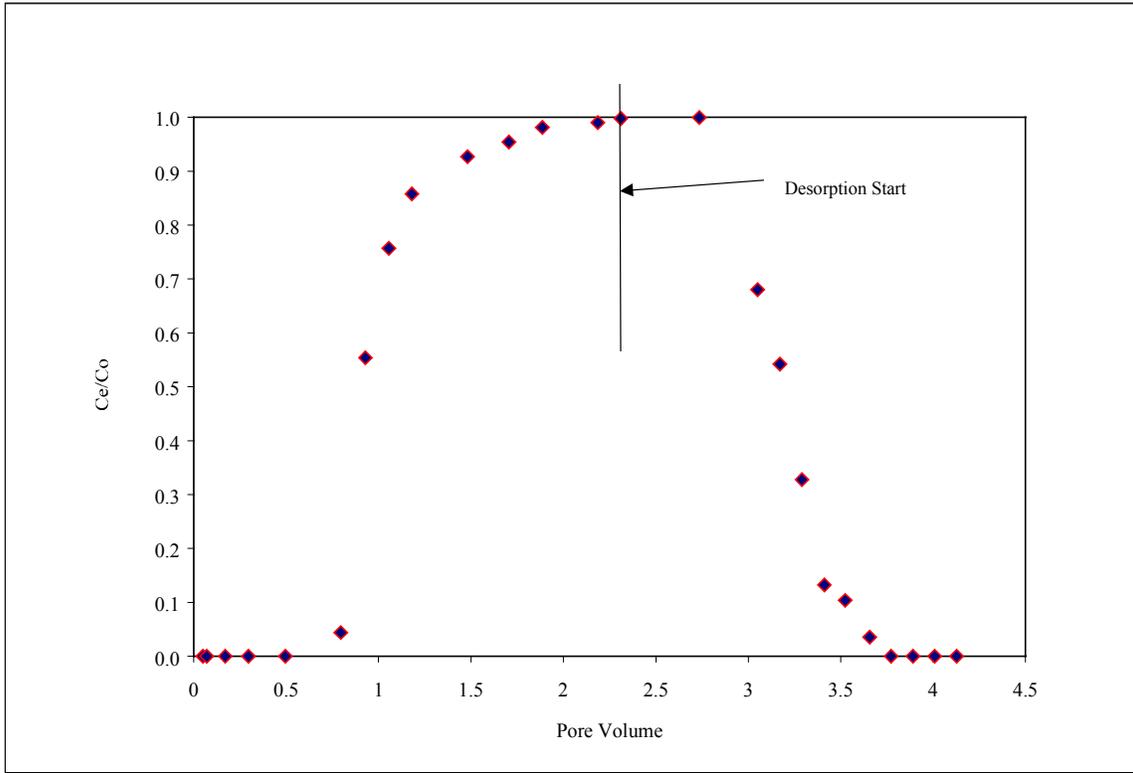


Figure 3.3.1.4. Arsenic, copper, and zinc leaching from ACZA pile with and without confinement, cumulative mass release vs. time (duplicate column).

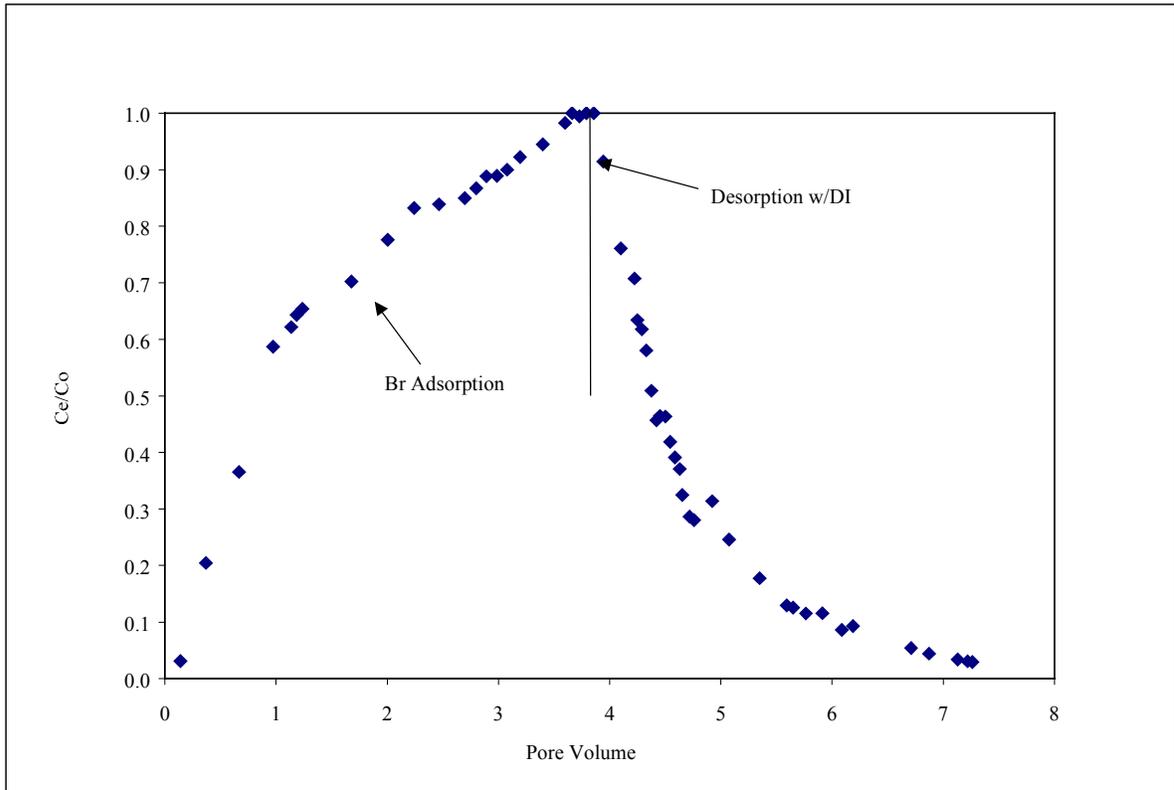
3.4.2 PCC Pile Leachate

3.4.2.1 PCC-with-plasticizer bromide tracer test

Figures 3.4.2.1.1 and 3.4.2.1.2 show 20 mg/L Br⁻ tracer breakthrough tests for PCC-with-plasticizer for the confined (sand) column and unconfined (glass marbles) columns, respectively. For the confined column, breakthrough occurred after about 0.8 pore volumes of total flow through the column, followed by a rapid increase in the effluent Br⁻ concentration (C_e) until maximum Br⁻ concentration ($C_e/C_o = 1.0$) was achieved at approximately 2.0 pore volumes (Figure 3.4.2.1.1). For the unconfined column, breakthrough occurred rapidly at about 0.1 pore volumes of total flow through the column, followed by a more gradual increase in the effluent Br⁻ concentration (C_e) until maximum Br⁻ concentration ($C_e/C_o = 1.0$) was achieved after about 4.0 pore volumes (Figure 3.4.2.1.2). Flushing of Br⁻ was conducted using distilled water for both columns (Figures 3.4.2.1.1 and 3.4.2.1.2). While the columns were filled with the bromide solution, 31.34 and 27.06 mg bromide was stored in the columns, respectively. Flushing with distilled water removed 30.23 and 25.68 mg bromide from confined and unconfined columns, respectively. That is about 96.5 and 95 percent of the total stored bromide was removed from the confined and unconfined columns, respectively. It is possible that there was some minor sorption onto the sand and glass bead media, but it is more likely that the flushing was simply incomplete since the bromide has been shown to adsorb very little (see Chapter 2). The bromide tracer results show that the confined (sand) column behaves similar to an ideal plug-flow reactor with little longitudinal dispersion and little retardation, compared to the unconfined (glass marbles) column that behaves more like a completely-mixed flow reactor, indicating that either back-mixing or short-circuiting is occurring, but with little retardation.



Figures 3.4.2.1.1. PCC confined (sand) column breakthrough curve for 20 mg/L Br- in distilled water. Flushing was conducted using distilled water.



Figures 3.4.2.1.2. PCC unconfined (glass marbles) column breakthrough curve for 20 mg/L Br- in distilled water. Flushing was conducted using distilled water.

3.4.2.2 PCC-with-plasticizer leaching test

Figure 3.4.2.2.1 shows distilled water leaching of metals from PCC-with-plasticizer for both confined (sand) and unconfined (marbles) systems. Ca concentrations for both confined and unconfined columns increased and reached their maximum values after about 300 hours of leaching time or 63.9 and 46.6 pore volumes, respectively. Aluminum concentration in the leachate was about 0.2 mg/L and slightly decreased with time as shown in Figure 3.4.2.2.1. Although leaching rates vary somewhat between confined (sand) and unconfined (glass marble) columns, ultimate concentrations for Ca (Figure 3.4.2.2.1) are the same for both column conditions. Al concentration was slightly greater for the unconfined columns than for confined columns. This might be explained by sorption or precipitation of Al on the sand. No PCC leachate sorption on the sand and marbles was determined in a batch leaching experiments. Therefore, Al precipitation is more likely to occur. Figure 3.4.2.2.2 shows duplicate results from both confined and unconfined columns. Both Figures show almost identical results for confined and unconfined columns. Maximum Ca and Al concentrations for confined and unconfined columns were 33 and 30 mg/L, respectively. Total mass release for both columns is almost the same for confined and unconfined systems (Figures 3.4.2.2.3 and 3.4.2.2.4), showing that sand confinement has no effect on leachate release from the PCC pile. The chemical and toxicity analysis data are summarized in Table 3.4.2.1.1.

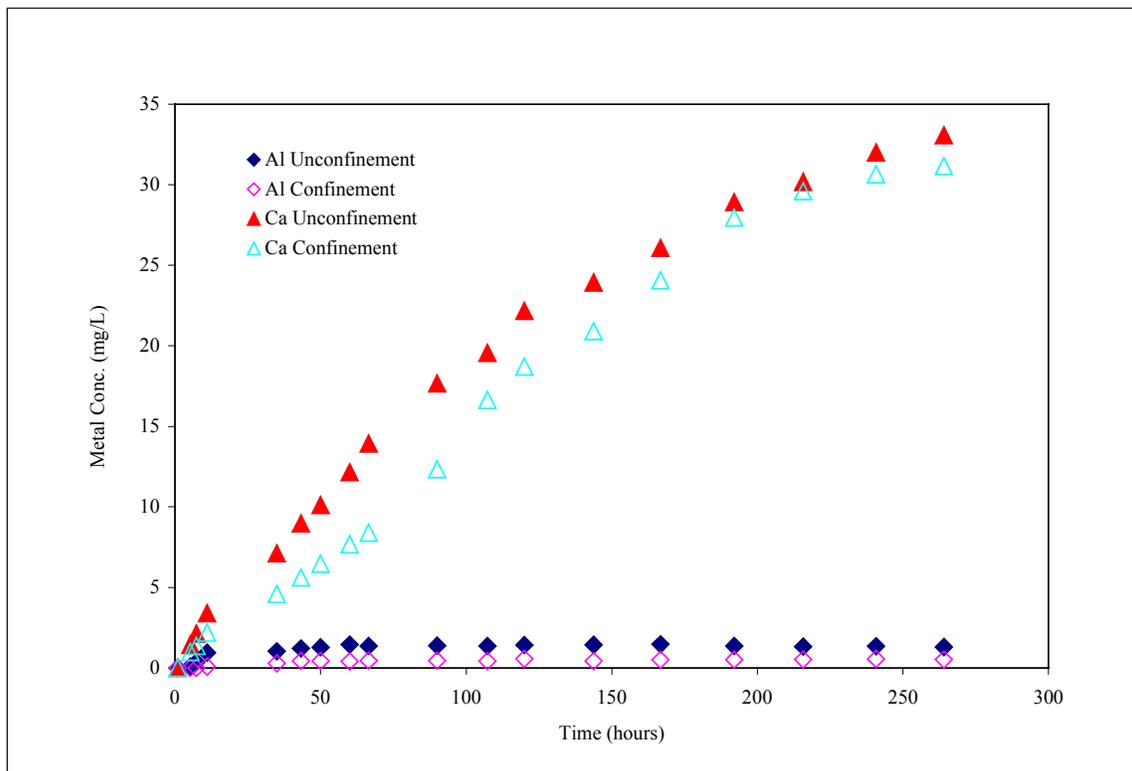


Figure 3.4.2.2.1. Aluminum and calcium leaching from PCC-with-plasticizer flat surface with and without confinement, concentration vs. time.

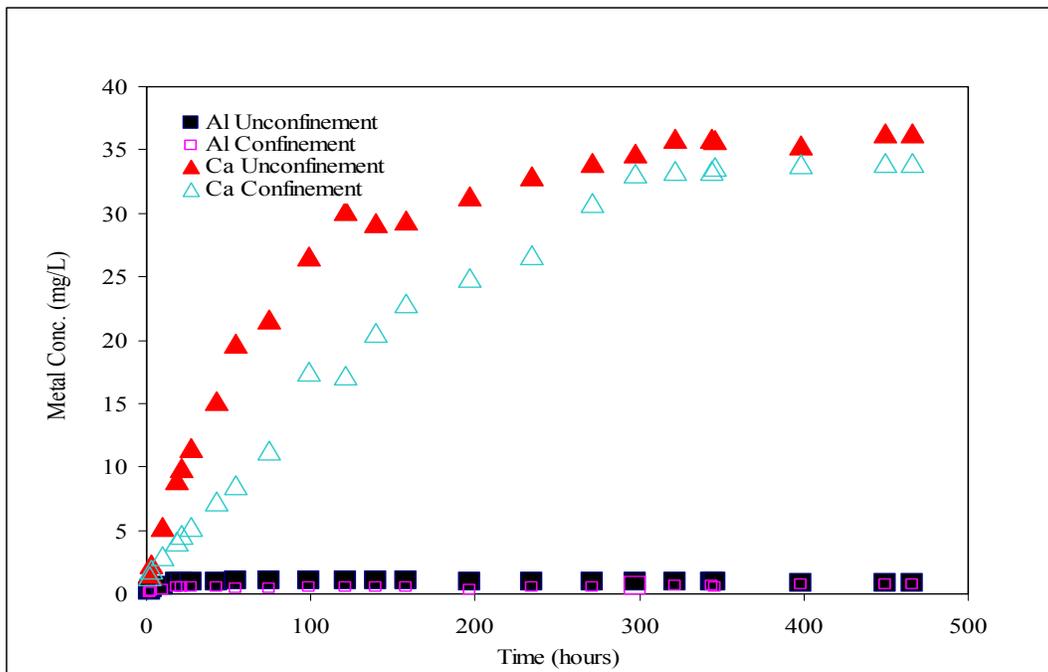


Figure 3.4.2.2.2. Aluminum and calcium leaching from PCC-with-plasticizer flat surface with and without confinement, concentration vs. time (duplicate).

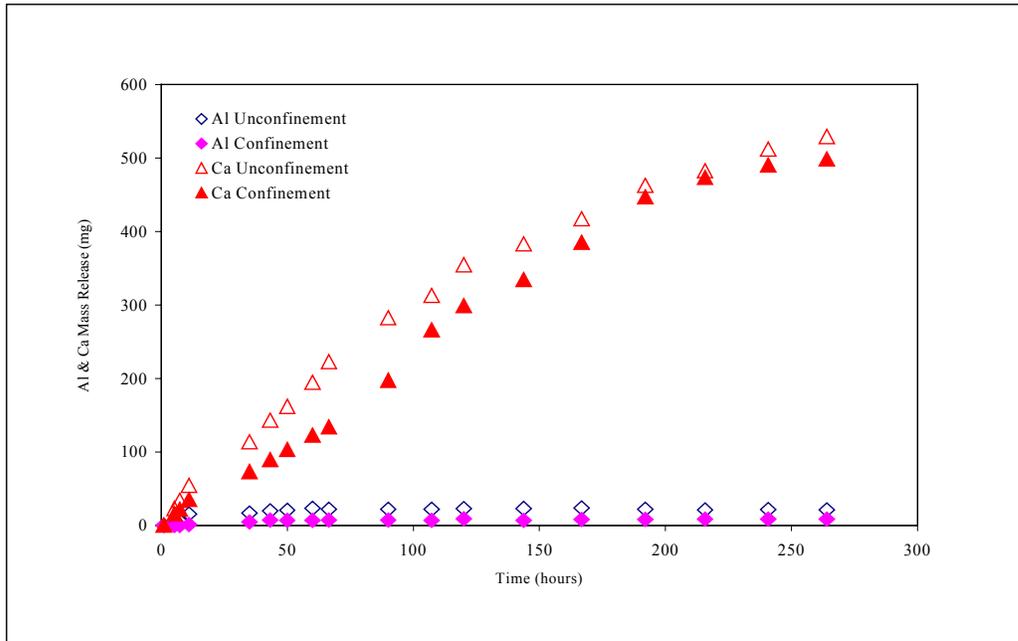


Figure 3.4.2.2.3. Aluminum and calcium leaching from PCC-with-plasticizer flat surface with and without confinement, mass released vs. time.

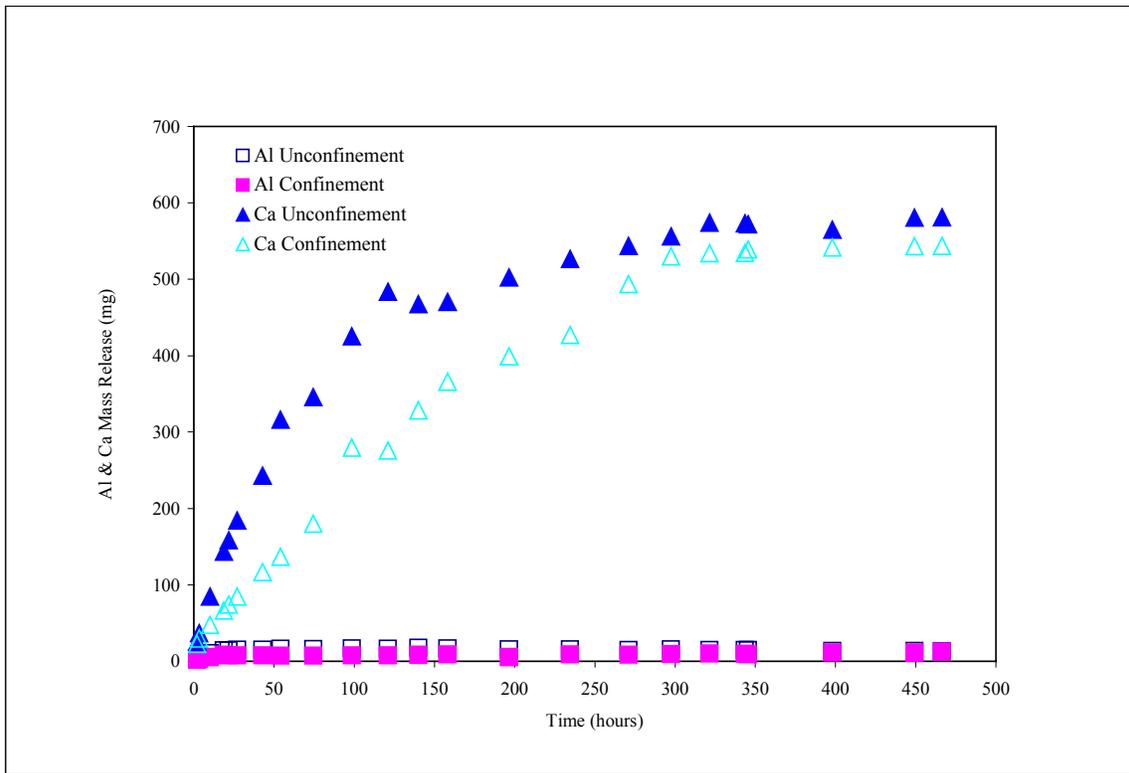


Figure 3.4.2.2.4. Aluminum and calcium leaching from PCC-with-plasticizer flat surface with and without confinement, mass released vs. time (duplicate).

3.4 SUMMARY AND CONCLUSIONS

The purpose of Task 2 was to confirm whether leachate flux from flat, impermeable surfaces is altered under confined conditions. These conditions are relevant to the reference environments of piling, fill, and culverts. Tests were conducted in glass columns containing PCC piles or ACZA-treated wood posts packed with Ottawa sand as the confining medium or glass beads for flow control in the unconfined column. Distilled water served as the leaching medium and was pumped continuously upflow through the columns and recirculated for up to 30 days. Leachates were collected over time and metals concentrations determined.

Results for metals in the leachates from the ACZA and PCC piles show a steady but decreasing rate of release over time, approaching a maximum concentration that may represent an equilibrium between the column and solution. The rate of metals released into the leachates from impermeable surfaces such as piling, fill, and culverts are affected only slightly, being lower under confined conditions. However, the total mass of metals released is the same, such that final concentrations approached the same maximum over time. Thus, the effect of confinement is neglected in modeling of leachates released from embedded surfaces.

Table 3.3.1.1. Task 2: Summary data for chemical analyses.

Task 2: Leaching From Flat Surface With and Without Soil Confinement						
		Time (hours)	Chemistry Results			
Sample ID	Test Conditions		As (mg/L)	Cu (mg/L)	Zn (mg/L)	Final pH
ACZA Unconfinement						
1	ACZAM-1	4	0.555	0.305	0.389	7.32
2	ACZAM-2	23	1.192	0.928	0.456	7.34
3	ACZAM-3	54.5	2.048	1.353	0.823	7.55
4	ACZAM-4	79.5	2.566	1.719	1.273	7.34
5	ACZAM-5	100.5	3.283	2.198	1.973	7.55
6	ACZAM-6	124.5	3.761	2.274	1.626	7.54
7	ACZAM-7	148.5	4.840	2.500	1.979	7.55
8	ACZAM-8	172.5	5.510	3.163	2.107	7.53
9	ACZAM-9	196.5	6.177	3.631	2.808	7.54
10	ACZAM-10	220.5	6.591	3.942	2.598	7.54
11	ACZAM-11	244.5	7.189	4.285	3.414	7.6
12	ACZAM-12	268.5	7.727	4.427	2.824	7.55
13	ACZAM-13	292.5	8.142	4.390	3.455	7.45
14	ACZAM-14	319.5	8.557	4.401	3.166	7.55
15	ACZAM-15	338.5	9.062	4.412	3.705	7.34
16	ACZAM-16	360.5	9.072	4.991	3.337	7.56
17	ACZAM-17	384	9.259	4.949	3.648	7.45
18	ACZAM-18	480	10.085	5.998	4.026	7.56
19	ACZAM-19	528	10.413	5.985	4.192	7.44
20	ACZAM-20	610	10.874	6.210	4.390	7.53

Table 3.3.1.1. Task 2: Summary data for chemical analyses (cont.).

Task 2: Leaching From Flat Surface With and Without Soil Confinement						
		Time (hours)	Chemistry Results			
Sample ID	Test Conditions		As (mg/L)	Cu (mg/L)	Zn (mg/L)	Final pH
ACZA Unconfinement (duplicate)						
1	ACZAM-1	4.2	0.533	0.308	0.390	7.42
2	ACZAM-2	24.2	1.199	0.900	0.464	7.44
3	ACZAM-3	59.7	2.138	1.401	0.844	7.54
4	ACZAM-4	83.7	2.766	1.720	1.322	7.55
5	ACZAM-5	106.7	3.267	2.200	1.893	7.45
6	ACZAM-6	128.7	3.561	2.301	1.600	7.54
7	ACZAM-7	150.7	4.889	2.407	1.989	7.55
8	ACZAM-8	174.7	5.576	3.322	2.227	7.45
9	ACZAM-9	202.7	6.377	3.630	2.899	7.56
10	ACZAM-10	226.7	6.661	4.022	2.605	7.56
11	ACZAM-11	246.7	7.235	4.305	2.414	7.51
12	ACZAM-12	270.7	7.657	4.399	2.824	7.55
13	ACZAM-13	294.7	8.982	4.399	3.432	7.52
14	ACZAM-14	318.7	8.677	4.521	3.246	7.55
15	ACZAM-15	338.7	8.992	4.432	3.699	7.54
16	ACZAM-16	360.7	8.997	5.001	3.342	7.56
17	ACZAM-17	384.7	9.437	4.934	3.656	7.53
18	ACZAM-18	476.7	10.099	6.008	4.016	7.56
19	ACZAM-19	523.7	10.543	6.012	4.189	7.54

Table 3.3.1.1. Task 2 Summary data for chemical analyses (cont.).

Task 2: Leaching From Flat Surface With and Without Soil Confinement						
		Time (hours)	Chemistry Results			
Sample ID	Test Conditions		As (mg/L)	Cu (mg/L)	Zn (mg/L)	Final pH
ACZA Confinement						
1	ACZAS-1	1.25	0.116	0.010	0.000	7.77
2	ACZAS-2	3.75	0.047	0.025	0.022	7.81
3	ACZAS-3	10	0.597	0.316	0.247	7.74
4	ACZAS-4	21.5	1.303	0.737	0.567	7.76
5	ACZAS-5	27	1.606	0.973	0.702	7.75
6	ACZAS-6	38.5	1.952	1.111	0.926	7.71
7	ACZAS-7	50.25	2.495	1.368	1.197	7.73
8	ACZAS-8	72.25	3.295	1.692	1.217	7.78
9	ACZAS-9	97.75	3.959	2.017	1.420	7.8
10	ACZAS-10	121.25	4.842	2.447	1.682	7.81
11	ACZAS-11	145	5.503	2.810	1.952	7.84
12	ACZAS-12	172	6.090	3.222	2.187	7.84
13	ACZAS-13	196	6.880	3.547	2.162	7.87
14	ACZAS-14	240.25	7.605	3.826	2.562	7.8
15	ACZAS-15	288.25	8.193	4.151	2.855	7.83
16	ACZAS-16	363.25	8.966	4.836	3.218	7.87
17	ACZAS-17	387.25	9.153	5.194	3.475	7.8
18	ACZAS-18	431.25	9.495	5.445	3.752	7.84
19	ACZAS-19	457.25	9.758	5.551	3.807	7.84
20	ACZAS-20	479.25	9.996	5.825	3.848	7.88
21	ACZAS-21	503.25	10.225	6.090	3.968	7.85
22	ACZAS-22	548.25	10.565	6.344	4.068	7.86
23	ACZAS-23	582.25	10.783	6.455	4.232	7.86
24	ACZAS-24	638.25	10.995	6.644	4.325	7.88

Table 3.3.1.1. Task 2: Summary data for chemical analyses (cont.).

Task 2: Leaching From Flat Surface With and Without Soil Confinement						
		Time (hours)	Chemistry Results			
Sample ID	Test Conditions		As (mg/L)	Cu (mg/L)	Zn (mg/L)	Final pH
ACZA Confinement (duplicate)						
1	ACZAS-1	1.25	0.124	0.010	0.000	7.76
2	ACZAS-2	3.8	0.047	0.025	0.029	7.77
3	ACZAS-3	10.3	0.596	0.312	0.255	7.76
4	ACZAS-4	22.3	1.309	0.688	0.570	7.79
5	ACZAS-5	28.3	1.599	1.001	0.712	7.8
6	ACZAS-6	39.3	1.949	1.222	0.900	7.81
7	ACZAS-7	51.3	2.499	1.356	1.200	7.84
8	ACZAS-8	72.3	3.289	1.703	1.213	7.83
9	ACZAS-9	96.3	3.977	2.067	1.400	7.88
10	ACZAS-10	120.3	4.876	2.444	1.702	7.86
11	ACZAS-11	143.3	5.501	2.799	2.003	7.85
12	ACZAS-12	171.3	6.003	3.113	2.104	7.84
13	ACZAS-13	197.3	6.891	3.554	2.210	7.8
14	ACZAS-14	242.3	7.604	3.877	2.600	7.84
15	ACZAS-15	289.3	8.432	4.150	2.877	7.85
16	ACZAS-16	365.3	8.999	4.799	3.200	7.86
17	ACZAS-17	390.3	9.127	5.201	3.555	7.8
18	ACZAS-18	435.3	9.666	5.502	3.700	7.86
19	ACZAS-19	460.3	9.765	5.621	3.789	7.88
20	ACZAS-20	484.3	10.043	5.987	3.854	7.86
21	ACZAS-21	507.3	10.325	6.022	4.008	7.84
22	ACZAS-22	552.3	10.600	6.356	4.119	7.83
23	ACZAS-23	586.3	10.799	6.467	4.301	7.85
24	ACZAS-24	641.3	11.002	6.653	4.432	7.84

Table 3.4.2.1.1. Task 2 : Summary data for chemical analyses (cont.).

Task 2: Leaching From Flat Surface With and Without Soil Confinement															
Sample ID	Test Conditions	Time (hours)	Toxicity Results			Chemistry Results									
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	Final pH
			Concentration as % Leachate												
			%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.										
PCC with Plasticizer Unconfinement															
1	PCC WPM-1	2	NA	NA	NA	0.206	BD	1.610	BD	BD	0.035	0.234	0.005	BD	6.85
2	PCC WPM-2	3	NA	NA	NA	0.384	BD	2.300	BD	0.026	0.036	0.267	0.000	BD	6.99
3	PCC WPM-3	10	NA	NA	NA	0.683	BD	5.300	BD	0.167	0.041	0.587	0.000	BD	10.11
4	PCC WPM-4	19	NA	NA	NA	0.912	BD	8.981	BD	0.235	0.059	0.866	0.005	BD	10.18
5	PCC WPM-5	22	NA	NA	NA	0.905	BD	9.907	BD	0.302	0.059	0.965	0.006	BD	10.13
6	PCC WPM-6	27	NA	NA	NA	0.952	BD	11.522	BD	0.376	0.062	1.051	0.007	BD	10.12
7	PCC WPM-7	43	NA	NA	NA	0.947	BD	15.204	BD	0.537	0.069	1.278	0.011	BD	10.17
8	PCC WPM-8	54	NA	NA	NA	1.029	BD	19.757	BD	0.684	0.057	1.617	0.027	BD	10.00
9	PCC WPM-9	75	NA	NA	NA	1.012	BD	21.613	BD	0.765	0.077	1.680	0.017	BD	10.06
10	PCC WPM-10	99	NA	NA	NA	1.053	BD	26.588	BD	1.004	0.061	2.077	0.022	BD	10.02
11	PCC WPM-11	121	NA	NA	NA	1.038	BD	30.226	BD	1.033	0.065	2.051	0.022	BD	10.37
12	PCC WPM-12	140	NA	NA	NA	0.960	BD	1.792	BD	0.884	1.003	1.017	0.975	BD	10.26
13	PCC WPM-13	158	NA	NA	NA	1.098	BD	29.207	BD	1.259	0.064	2.289	0.031	BD	10.61
14	PCC-W PM14	197	NA	NA	NA	1.070	BD	29.399	BD	1.341	0.046	2.355	0.028	BD	10.07
15	PCC-W PM15	235	NA	NA	NA	0.965	BD	31.398	BD	1.494	0.076	2.661	0.038	BD	10.07
16	PCC-W PM16	271	NA	NA	NA	0.970	BD	32.902	BD	1.576	0.081	2.762	0.039	BD	10.02
17	PCC-W PM17	298	NA	NA	NA	0.945	BD	33.964	BD	1.766	0.038	2.869	0.033	BD	10.07
18	PCC-W PM18	322	NA	NA	NA	0.969	BD	34.761	BD	2.107	0.036	3.154	0.040	BD	10.08
19	PCC-W PM19	344	NA	NA	NA	0.946	BD	35.855	BD	2.177	0.034	3.469	0.044	BD	10.04
20	PCC-W PM20	346	NA	NA	NA	0.933	BD	35.836	BD	2.350	0.033	3.569	0.045	BD	10.08
21	PCC-W PM21	398	NA	NA	NA	0.918	BD	35.750	BD	2.573	0.037	3.616	0.051	BD	10.15
22	PCC-W PM22	449	NA	NA	NA	0.855	BD	35.308	BD	2.675	0.030	3.802	0.049	BD	10.33
23	PCC-W PM23	466	NTE			0.847	BD	36.291	BD	2.995	0.057	4.122	0.053	BD	10.44

Table 3.4.2.1.1. Task 2 : Summary data for chemical analyses (cont.).

Task 2: Leaching From Flat Surface With and Without Soil Confinement																
Sample ID	Test Conditions	Time (hours)	Toxicity Results					Chemistry Results								
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	Final pH	
			Concentration as % Leachate													
			%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.											
	PCC with Plasticizer Confinement															
1	PCC WPS-1	2	NA	NA	NA	0.118	BD	1.415	BD	0.121	0.033	0.178	0.019	BD	7.77	
2	PCC WPS-2	3	NA	NA	NA	0.218	BD	1.885	BD	0.031	0.038	0.181	0.013	BD	6.43	
3	PCC WPS-3	10	NA	NA	NA	0.350	BD	2.974	BD	0.059	0.048	0.408	0.020	BD	9.60	
4	PCC WPS-3	19	NA	NA	NA	0.532	BD	4.162	BD	0.187	0.059	0.520	0.029	BD	9.85	
5	PCC WPS-4	22	NA	NA	NA	0.488	BD	4.639	BD	0.320	0.062	0.556	0.031	BD	9.86	
6	PCC WPS-5	27	NA	NA	NA	0.489	BD	5.295	BD	-0.418	0.059	0.588	0.031	BD	9.45	
7	PCC WPS-6	43	NA	NA	NA	0.491	BD	7.304	BD	0.536	0.049	0.764	0.034	BD	9.34	
8	PCC WPS-7	54	NA	NA	NA	0.454	BD	8.564	BD	0.663	0.043	0.933	0.031	BD	9.65	
9	PCC WPS-9	75	NA	NA	NA	0.468	BD	11.267	BD	0.708	0.054	1.174	0.034	BD	9.71	
10	PCC WPS-10	99	NA	NA	NA	0.495	BD	17.486	BD	0.979	0.033	1.510	0.039	BD	10.77	
11	PCC WPS-11	121	NA	NA	NA	0.488	BD	17.242	BD	0.899	0.033	1.481	0.038	BD	9.54	
12	PCC WPS-12	140	NA	NA	NA	0.529	BD	20.530	BD	1.081	0.025	1.696	0.041	BD	9.27	
13	PCC WPS-13	158	NA	NA	NA	0.562	BD	22.857	BD	1.304	0.024	1.826	0.044	BD	9.36	
14	PCC-WPS 14	197	NA	NA	NA	0.347	BD	24.941	BD	1.632	0.019	2.196	0.046	BD	9.23	
15	PCC-WPS 15	235	NA	NA	NA	0.552	BD	26.697	BD	1.723	0.013	2.296	0.048	BD	10.06	
16	PCC-WPS 16	271	NA	NA	NA	0.547	BD	30.835	BD	1.902	0.019	2.562	0.051	BD	10.09	
17	PCC-WPS 17	298	NA	NA	NA	0.593	BD	33.115	BD	2.181	0.013	2.839	0.056	BD	10.12	
18	PCC-WPS 18	322	NA	NA	NA	0.640	BD	33.380	BD	2.239	0.010	2.912	0.057	BD	10.16	
19	PCC-WPS 19	344	NA	NA	NA	0.622	BD	33.400	BD	2.309	0.009	2.890	0.057	BD	10.18	
20	PCC-WPS 20	346	NA	NA	NA	0.557	BD	33.682	BD	2.451	0.011	2.916	0.058	BD	10.21	
21	PCC-WPS 21	398	NA	NA	NA	0.725	BD	33.836	BD	2.648	0.008	3.114	0.060	BD	10.23	
22	PCC-WPS 22	449	NA	NA	NA	0.708	BD	33.958	BD	2.777	0.006	3.276	0.064	BD	11.11	
23	PCC-WPS 23	466	NTE			0.783	BD	33.971	BD	2.962	0.030	3.534	0.065	BD	10.19	

Table 3.2.1.1. Task 2: Summary data for chemical analyses (cont..).

Task 2: Leaching From Flat Surface With and Without Soil Confinement															
Sample ID	Test Conditions	Time (hours)	Toxicity Results			Chemistry Results									
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	Final pH
			Concentration as % Leachate												
			%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.										
PCC with Plasticizer Unconfinement															
1	PCC WPM-1	1	NA	NA	NA	BD	BD	0.015	-0.006	0.113	0.003	0.007	0.002	BD	6.75
2	PCC WPM-2	6	NA	NA	NA	BD	BD	1.116	-0.005	0.233	0.033	0.326	0.013	BD	6.90
3	PCC WPM-3	8	NA	NA	NA	BD	BD	1.407	-0.005	0.096	0.033	0.294	0.017	BD	10.01
4	PCC WPM-4	12	NA	NA	NA	0.070	BD	2.204	-0.006	0.095	0.037	0.418	0.022	BD	10.03
5	PCC WPM-5	30	NA	NA	NA	0.298	BD	4.780	-0.005	0.172	0.019	0.343	0.000	BD	10.03
6	PCC WPM-6	45	NA	NA	NA	0.440	BD	5.697	-0.005	0.454	0.068	0.882	0.030	BD	10.07
7	PCC WPM-7	49	NA	NA	NA	0.441	BD	6.455	-0.003	0.483	0.062	0.884	0.034	BD	10.06
8	PCC WPM-8	61	NA	NA	NA	0.418	BD	7.708	-0.004	0.590	0.070	1.113	0.036	BD	10.12
9	PCC WPM-9	66	NA	NA	NA	0.450	BD	8.516	-0.004	0.556	0.054	1.166	0.038	BD	10.02
10	PCC WPM-10	87	NA	NA	NA	0.461	BD	12.446	-0.002	0.714	0.047	1.460	0.041	BD	10.04
11	PCC WPM-11	110	NA	NA	NA	0.478	BD	16.779	-0.002	0.774	0.024	1.217	0.013	BD	10.17
12	PCC WPM-12	125	NA	NA	NA	0.557	BD	18.736	-0.002	1.674	0.037	2.309	0.050	BD	10.18
13	PCC WPM-13	145	NA	NA	NA	0.550	BD	21.118	-0.003	1.451	0.031	2.696	0.051	BD	10.24
14	PCC-W PM14	160	NA	NA	NA	0.500	BD	24.012	-0.001	1.674	0.037	2.698	0.054	BD	10.22
15	PCC-W PM15	196	NA	NA	NA	0.510	BD	28.112	0.000	1.961	0.036	2.471	0.053	BD	10.28
16	PCC-W PM16	215	NA	NA	NA	0.532	BD	29.119	-0.002	2.310	0.033	2.638	0.053	BD	10.26
17	PCC-W PM17	240	NA	NA	NA	0.544	BD	30.701	-0.003	2.227	0.032	2.818	0.055	BD	10.30
18	PCC-W PM18	270	NA	NA	NA	0.540	BD	31.222	0.000	2.587	0.034	3.009	0.055	BD	10.31

Table 3.4.2.1.1. Task 2: Summary data for chemical analyses (cont..).

Task 2: Leaching From Flat Surface With and Without Soil Confinement															
Sample ID	Test Conditions	Time (hours)	Toxicity Results			Chemistry Results									
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	Final pH
			Concentration as % Leachate												
			%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.										
PCC with Plasticizer Confinement (duplicate)															
1	PCC WPM-1	1	NA	NA	NA	BD	BD	0.014	BD	0.113	0.003	0.007	0.002	BD	6.95
2	PCC WPM-2	5	NA	NA	NA	BD	BD	0.986	BD	0.233	0.033	0.326	0.013	BD	6.92
3	PCC WPM-3	7	NA	NA	NA	BD	BD	1.367	BD	0.096	0.033	0.294	0.017	BD	10.07
4	PCC WPM-4	11	NA	NA	NA	0.074	BD	2.199	BD	0.095	0.037	0.418	0.022	BD	10.03
5	PCC WPM-5	35	NA	NA	NA	0.287	BD	4.580	BD	0.172	0.019	0.343	0.000	BD	10.07
6	PCC WPM-6	43	NA	NA	NA	0.441	BD	5.610	BD	0.454	0.068	0.882	0.030	BD	10.11
7	PCC WPM-7	50	NA	NA	NA	0.432	BD	6.452	BD	0.483	0.062	0.884	0.034	BD	10.16
8	PCC WPM-8	60	NA	NA	NA	0.405	BD	7.678	BD	0.590	0.070	1.113	0.036	BD	10.11
9	PCC WPM-9	67	NA	NA	NA	0.449	BD	8.396	BD	0.556	0.054	1.166	0.038	BD	10.03
10	PCC WPM-10	90	NA	NA	NA	0.455	BD	12.338	BD	0.714	0.047	1.460	0.041	BD	10.04
11	PCC WPM-11	107	NA	NA	NA	0.420	BD	16.631	BD	0.774	0.024	1.217	0.013	BD	10.27
12	PCC WPM-12	120	NA	NA	NA	0.556	BD	18.707	BD	1.674	0.037	2.309	0.050	BD	10.16
13	PCC WPM-13	144	NA	NA	NA	0.430	BD	20.907	BD	1.451	0.031	2.696	0.051	BD	10.34
14	PCC-WPM14	167	NA	NA	NA	0.502	BD	24.072	BD	1.674	0.037	2.698	0.054	BD	10.34
15	PCC-WPM15	192	NA	NA	NA	0.508	BD	27.955	BD	1.961	0.036	2.471	0.053	BD	10.23
16	PCC-WPM16	216	NA	NA	NA	0.526	BD	29.588	BD	2.310	0.033	2.638	0.053	BD	10.36
17	PCC-WPM17	241	NA	NA	NA	0.545	BD	30.656	BD	2.227	0.032	2.818	0.055	BD	10.35
18	PCC-WPM18	264	NA	NA	NA	0.530	BD	31.155	BD	2.587	0.034	3.009	0.055	BD	10.33

Table 3.4.2.1.1. Task 2: Summary data for chemical analyses (cont..).

Task 2: Leaching From Flat Surface With and Without Soil Confinement									
Sample ID	Time	Cumm. Time	Volume	Cumm. Vol.	Pore Volume	Flow rate	Calculated	C/Co	Mass Balance
	hrs	hrs	ml	ml		ml/hr			mg Br ADS
PCC with Plasticizer Bromide Tracer									
PCC W PM-Br-1	0.17	0.17	157.0	157.0	0.07	923.53	0.53	0.03	2.79
PCC W PM-Br-2	0.20	0.37	109.0	266.0	0.12	545.00	0.99	0.05	4.68
PCC W PM-Br-3	0.25	0.62	150.0	416.0	0.18	600.00	1.91	0.10	7.15
PCC W PM-Br-4	1.67	2.29	150.0	566.0	0.25	89.82	2.63	0.14	9.50
PCC W PM-Br-5	1.00	3.29	300.0	866.0	0.38	300.00	5.87	0.32	13.24
PCC W PM-Br-6	1.58	4.87	350.0	1216.0	0.53	221.52	7.28	0.40	17.12
PCC W PM-Br-7	1.25	6.12	265.0	1481.0	0.64	212.00	8.66	0.47	19.68
PCC W PM-Br-8	1.17	7.29	255.0	1736.0	0.75	217.95	9.80	0.53	21.86
PCC W PM-Br-9	1.17	8.46	250.0	1986.0	0.86	213.68	10.33	0.56	23.86
PCC W PM-Br-10	2.86	11.32	600.0	2586.0	1.12	209.79	12.81	0.70	27.17
PCC W PM-Br-11	2.17	13.49	450.0	3036.0	1.32	207.37	13.96	0.76	29.14
PCC W PM-Br-12	1.60	15.09	360.0	3396.0	1.48	225.00	15.19	0.83	30.27
PCC W PM-Br-13	2.85	17.94	600.0	3996.0	1.74	210.53	16.93	0.92	31.12
PCC W PM-Br-14	1.16	19.10	250.0	4246.0	1.85	215.52	17.74	0.97	31.27
PCC W PM-Br-15	1.15	20.25	250.0	4496.0	1.95	217.39	18.19	0.99	31.30
PCC W PM-Br-16	1.05	21.30	230.0	4726.0	2.05	129.00	18.16	0.99	31.34
PCC W PM-Br-17, Des	1.07	22.37	640.0	5366.0	2.33	200.00	14.80	0.81	9.47
PCC W PM-Br-18, Des	1.20	23.57	241.0	5607.0	2.44	200.67	9.58	0.52	11.78
PCC W PM-Br-19	1.14	24.71	242.0	5849.0	2.54	211.72	7.79	0.42	13.66
PCC W PM-Br-20	1.03	25.74	223.0	6072.0	2.64	216.50	5.09	0.28	14.80
PCC W PM-Br-21	1.20	26.95	267.0	6339.0	2.76	222.31	33.01	1.80	23.61
PCC W PM-Br-22	1.02	27.97	232.0	6571.0	2.86	227.45	1.88	0.10	24.05
PCC W PM-Br-23	1.10	29.06	235.0	6806.0	2.96	214.03	0.64	0.03	24.20
PCC W PM-Br-24	1.01	30.08	236.0	7042.0	3.06	233.20	0.45	0.02	24.30
PCC W PM-Br-25	1.13	31.21	250.0	7292.0	3.17	221.24	0.32	0.02	24.38
PCC W PM-Br-26	1.00	32.21	220.0	7512.0	3.27	220.00	0.21	0.01	24.43

Table 3.4.2.1.1. Task 2: Summary data for chemical analyses (concluded).

Task 2: Leaching From Flat Surface With and Without Soil Confinement									
Sample ID	Time	Cumm. Time	Volume	Cumm. Vol.	Pore Volume	Flow rate	Calculated	C/Co	Mass Balance
	hrs	hrs	ml	ml		ml/hr			mg Br ADS
PCC with Plasticizer Bromide Tracer (duplicate)									
PCC W PS Init.	0.00						15.06		
PCC W PS-1	0.17	0.17	37.0	100.0	0.05	217.65	0.00	0.00	0.56
PCC W PS-2	0.20	0.37	42.0	142.0	0.07	210.00	0.00	0.00	1.19
PCC W PS-3	0.25	0.62	200.0	342.0	0.17	800.00	0.00	0.00	4.20
PCC W PS-3	1.67	2.29	250.0	592.0	0.30	149.70	0.00	0.00	7.97
PCC W PS-4	1.00	3.29	400.0	992.0	0.50	400.00	0.00	0.00	13.99
PCC W PS-5	1.58	4.87	600.0	1592.0	0.80	379.75	0.66	0.04	22.64
PCC W PS-6	1.25	6.12	265.0	1857.0	0.93	212.00	8.34	0.55	24.42
PCC W PS-7	1.17	7.29	255.0	2112.0	1.06	217.95	11.40	0.76	25.35
PCC W PS-9	1.17	8.46	250.0	2362.0	1.18	213.68	12.92	0.86	25.89
QC Standard	2.86	11.32	600.0	2962.0	1.48	209.79	13.96	0.93	26.55
PCC W PS-10	2.17	13.49	450.0	3412.0	1.71	207.37	14.37	0.95	26.86
PCC W PS-11	1.60	15.09	360.0	3772.0	1.89	225.00	14.78	0.98	26.96
PCC W PS-12	2.85	17.94	600.0	4372.0	2.19	210.53	14.92	0.99	27.05
PCC W PS-13	1.16	19.10	250.0	4622.0	2.31	215.52	15.03	1.00	27.06
PCC-W PS14, Des	1.15	20.25	850.0	5472.0	2.74	739.13	15.06	1.00	12.80
PCC-W PS15, Des	1.05	21.30	630.0	6102.0	3.05	600.00	12.47	0.68	20.66
PCC-W PS16	1.07	22.37	240.0	6342.0	3.17	224.30	9.94	0.54	23.05
PCC-W PS17	1.20	23.57	241.0	6583.0	3.29	200.67	6.01	0.33	24.49
PCC-W PS 18	1.14	24.71	242.0	6825.0	3.41	211.72	2.43	0.13	25.08
PCC-W PS 19	1.03	25.74	223.0	7048.0	3.52	216.50	1.90	0.10	25.50
PCC-W PS20	1.20	26.95	267.0	7315.0	3.66	222.31	0.65	0.04	25.68
PCC-W PS21	1.02	27.97	232.0	7547.0	3.77	227.45	0.00	0.00	25.68
PCC-W PS22	1.10	29.06	235.0	7782.0	3.89	214.03	0.00	0.00	25.68
PCC-W PS23	1.01	30.08	236.0	8018.0	4.01	233.20	0.00	0.00	25.68
PCC-W PS24	1.23	31.31	237.0	8255.0	4.13	192.68	0.00	0.00	25.68

CHAPTER 4

TASK 3: EFFECT OF SCALE ON FLAT-PLATE LEACHATE COMPOSITION

4.1 INTRODUCTION

An assumption of the flat-plate leaching test is that the contaminant flux from the C&R material surface is directly proportional to surface area and thus scaleable to field conditions. However, testing at the laboratory scale because of various scale effects can poorly represent field results. Determining scale effects is difficult because of the problems associated with preparation and handling of large test specimens. The research approach involved conducting flat plate experiments with samples of varying size. All other variables including leaching solution, volume/area ratio, testing time, and C&R material were held constant. The objective of Task 3 was to determine whether mass was leached from the flat plates at the same rate for plates of different surface areas. An additional scale issue is whether or not leached concentrations are proportional to the volume to area ratio, since this is how the results are scaled up to field conditions. Hence, an additional segment of this task was to investigate this effect.

4.2 MATERIALS AND METHODS

4.2.1 Materials

The flat plates were made of a municipal solid waste incinerator bottom ash (MSWIBA, from Massachusetts) asphalt cement mix (MSWIBA-AC). MSWIBA-AC leachates have demonstrated toxicity in Phase I-II testing and contain a mixture of both metals and organic compounds. Flat plate samples were generated in three sizes: 4-inch thick by 4-inch diameter cylinders (standard flat plates), 4-inch thick by 6-inch diameter cylinders, and 4.5-inch thick by 6 x 9.25 inch rectangular prisms. Only one end of the cylinders was exposed for leaching, as in the standard flat-plate leaching test, the other surfaces being sealed with wax, and all surfaces of the rectangular prism were exposed. These specimens gave exposure area ratios to the 4-inch diameter circle of 1 to 2.25 to 19.76, respectively for the 4-inch diameter circle, 6-inch diameter circle, and 4.5 x 6 x 9.25 inch prism.

Only a limited number of flat plate specimens remained available at the stage of the project at which the effect of variable volume to area was investigated. Hence, only six, 4-inch diameter flat plates were used for this purpose, three for leaching into a 0.5 L volume and three for leaching into a 2.0 L volume, to compare with the standard leaching into 1.0 L volume.

4.2.2 Methods

The flat plate tests were run as developed in Section 3.5 of Volume IV (Nelson et al., 2000b). The cylindrical specimens were placed in a container and coated in wax such that only the top surface is exposed to the overlying distilled water when immersed. Water was added proportional to the exposure surface areas (1 L, 2.25 L, and 19.76 L) for

4-inch cylinder, 6-inch cylinder, and 4.5 x 6 x 9.25 inch prism, respectively, such that the water volume to surface areas ratio is constant at 1 L per 12.6 cm² or 79.6 cm³/cm² for all three tests. The overlying water was mixed with a 3-inch long stirring paddle at 60 rpm; a single paddle was used for the single-cylinder reactors and two paddles were used for the rectangular prism reactor.

Eighteen replicate disk specimens were used for each size of the 4-inch and 6-inch flat plate cylinders to enable duplicate sampling. Three replicate groups were maintained. Disks from each group were sacrificed (overlying water was removed and the disks no longer used) according to Table 4.2.2.1. That is, five of the six disks from each replicate group were sacrificed by 190 hrs, for both the 4-inch and 6-inch cylinder tests. At intermediate times, and after hour 190, the remaining disks were sampled by extracting approximately 10 mL for analysis, *followed by replacement with distilled water*. Thus, there is a small dilution effect not accounted for in the following analysis.

Only four prism samples were prepared. Hence, all sampling was done with replacement for tests on three of these assemblages. However, the volume of water (19.76 L) was so large as to minimize any dilution effect.

This was not true for the final tests on six remaining 4-inch cylinders. For purposes of varying the ratio of volume to surface area, three replicates were leached into a volume of 0.5 L and three leached into a volume of 2.0 L. In both cases, sampling was done by extracting 10 mL and replacing with distilled water. Hence, the dilution effect is considerable for the 500-mL test and has not been accounted for in the analysis that follows. The effect is to measure lower (more dilute) concentrations than would otherwise occur. For the 2-L sample the effect will not be as great, but is still there.

Table 4.2.2.1. Hours at which cylindrical disks were sacrificed (no longer used), because of collection of entire water sample.

Sacrificed Disk	4-inch, hour	6-inch, hour
1	30.5	24
2	72	77
3	96	101.3
4	120	126.3
5	190	190

The water samples were analyzed specifically for TOC and metals, i.e., Al and Ca, and scanned for other metal and toxic organic compounds. The water samples also were analyzed for algal EC50 and *D. magna* LC50 toxicity values.

The concentration and toxicity of the leachate was plotted vs. time for each flat-plate specimen size. For the tests in which only the surface area was varied, the same volume to surface area ratio was maintained for all three plate sizes, and the concentration vs.

time relationship for all three plate sizes should be the same – if there is no scale effect. For instance, if the flux is the same from the 6-inch plate as the 4-inch plate, the leachate concentration (mass/volume) should be the same for both, since the volume of leachate is increased in proportion to the increase in plate area. Hence, for the same leaching time, the leached concentrations should be the same for all plate sizes.

4.3 RESULTS AND DISCUSSION

4.3.1 Chemical Analyses

Results for Al, Ca, K, Mg, and Na concentrations in leachate from the MSWIBA-AC specimens in the flat plate experiments are tabulated in Table 4.3.1.1. Of interest is an overlay of data for the three plate sizes. This is shown for calcium and TOC in Figures 4.3.1.1 and 4.3.1.2. Clearly, the flux is the same for the three plate sizes, although leaching of TOC from the 4-inch disk is somewhat slower than for the other two plates. But the same asymptotic concentration is reached.

This can also be demonstrated by comparing the asymptotic concentrations at a common sampling time near the end of the experiment, 270 hrs in this case. These asymptotic concentrations are compared in Table 4.3.1.2. Although a formal statistical comparison was not done, the values are clearly the same.

Table 4.3.1.2 Comparison of asymptotic concentrations for MSWIBA-AC leachate for three different flat plate sizes. Concentrations are average values at 270 hrs for triplicate experiments.

Test	TOC mg/L	Al mg/L	Ca mg/L	K mg/l	Mg mg/L	Na mg/L
4-inch disk	2.13	0.66	5.24	3.53	0.37	10.48
6-inch disk	2.17	0.67	5.16	3.79	0.38	10.77
4x6x9.25 inch prism	2.17	0.67	5.32	3.42	0.38	10.06

In order to evaluate the effect of the volume to surface area ratio, average concentrations from the three replicates are compared at approximately 250 hours in Table 4.3.1.3. Unfortunately, dilution effects definitely influence these values. If concentrations were inversely proportional to the volume:area ratio, then concentrations leached into the 0.5-L volume would be twice as high as the 1-L samples, and 2-L samples would be half as much as the 1-L samples. This is roughly true for the 2-L sample, with concentration ratios of 0.51-0.66 for all constituents except aluminum. But dilution of the leachate collected in the 0.5-L sample reduces the concentration for all constituents, but apparently by varying amounts. For instance, at the final sampling time (250 hrs) for the 0.5-L leachate volume, 60 mL of distilled water have replaced the six 10-mL samples removed for earlier analysis. Hence, concentrations for the 0.5-L leachate volume are expected to be too low, by an undetermined amount.

Aluminum data for the final 0.5-L and 2-L samples are very irregular relative to the other sampling within this task. Aluminum is often solubility-limited, and this could explain the irregular behavior, but the reason for the very low values compared to the other flat plate samples is unknown. Hence, no conclusions can be drawn from the Al data taken from the 0.5-L and 2-L leachate volumes.

One additional look at these data is provided in Figures 4.3.1.3 and 4.3.1.4, which show leaching of TOC and calcium as a function of time for the three different leaching volumes. In each case, concentrations are higher for the lower volume, but not in the ratio expected for the 0.5-L volume leachate.

Fortunately, an additional investigation of the effect of volume to area ratio was conducted as part of Task 7, in conjunction with the testing of the standard asphalt cement concrete (SACC). The reader is referred to Section 8.5.2.3 and Figure 8.5.2.3.1 for a conclusive demonstration that the leached concentration is directly, inversely proportional to the leachate volume and that the modeling assumptions are thus valid.

Table 4.3.1.3. Comparison of metals concentrations for MSWIBA-AC leachate for three different volume-to-surface-area ratios. Concentrations are average values for triplicate experiments.

Test	Sampling Time	TOC	Al	Ca	K	Mg	Na
	hrs	mg/L	mg/L	mg/L	mg/l	mg/L	mg/L
0.5-L volume:	250						
Concentration, mg/L		2.17	0.15	6.42	3.20	0.67	10.41
Ratio to 1-L volume		1.01	0.23	1.24	0.82	1.88	1.23
1-L volume:	245						
Concentration, mg/L		2.14	0.64	5.17	3.88	0.35	8.43
Ratio to 1-L volume		1.00	1.00	1.00	1.00	1.00	1.00
2-L volume:	250						
Concentration, mg/L		1.37	0.08	2.62	2.18	0.18	5.54
Ratio to 1-L volume		0.64	0.13	0.51	0.56	0.51	0.66

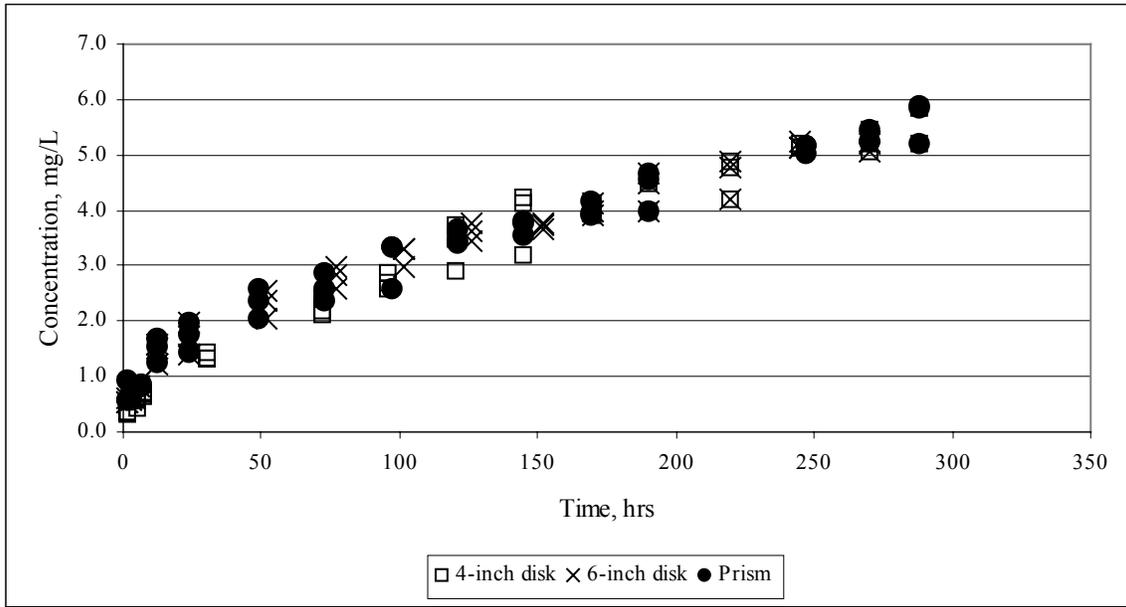


Figure 4.3.1.1. Flat plate leaching results (triplicate experiments) for calcium leaching from MSWIBA-AC asphalt mix, for three plate sizes, concentration as a function of time.

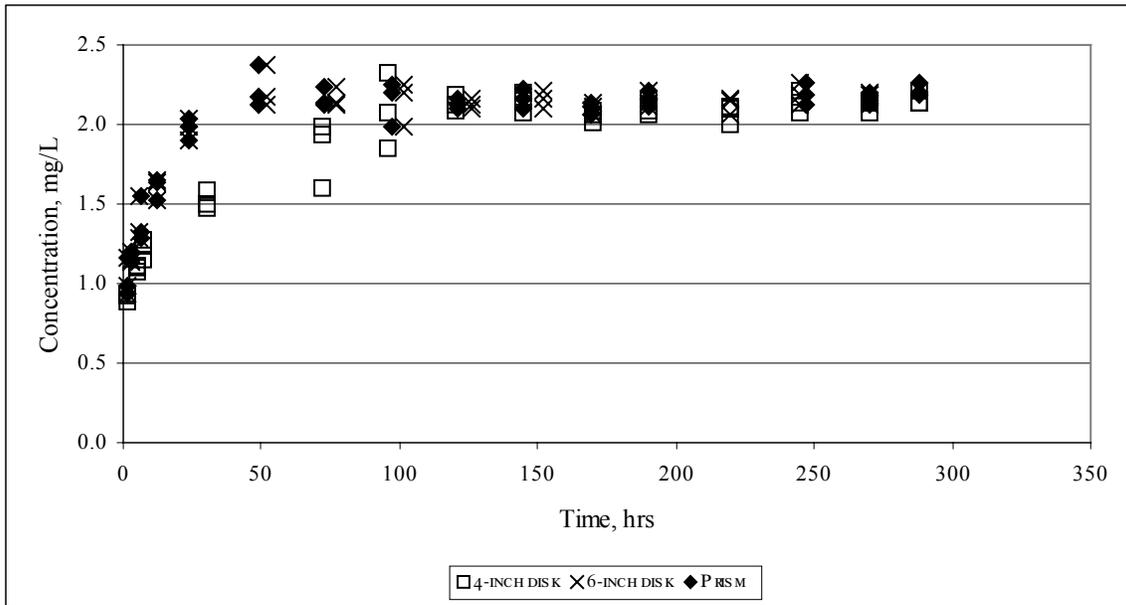


Figure 4.3.1.2. Flat plate leaching results (triplicate experiments) for TOC leaching from MSWIBA-AC asphalt mix, for three plate sizes, concentration as a function of time.

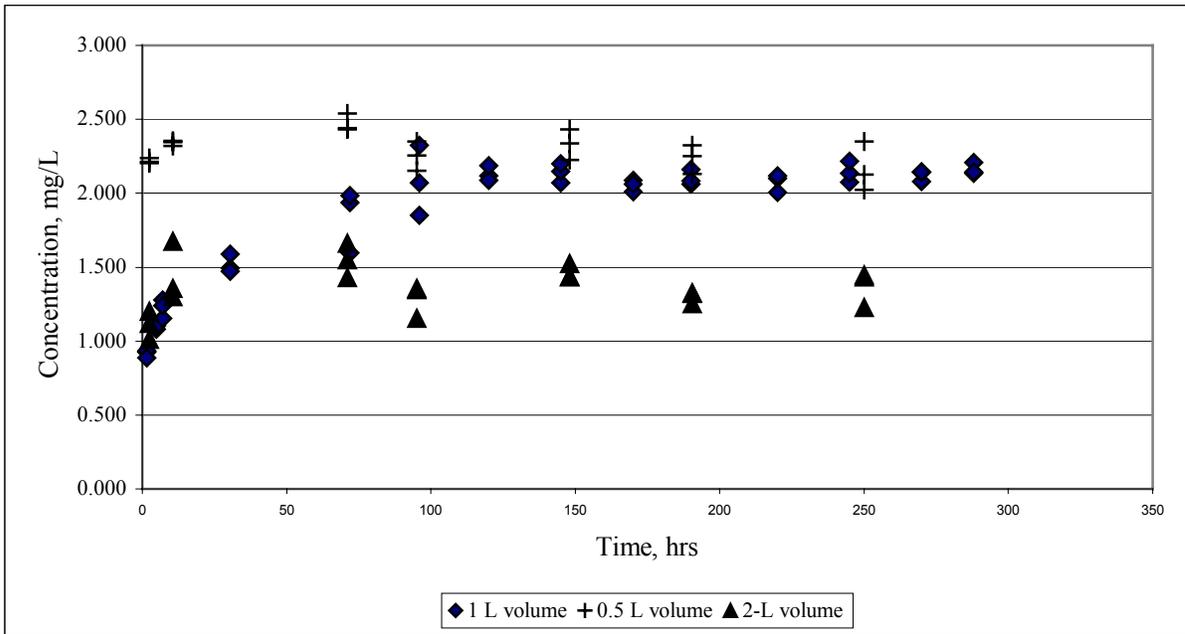


Figure 4.3.1.3. TOC leaching (triplicate experiments) as a function of time from 4-inch disks into varying leachate volumes.

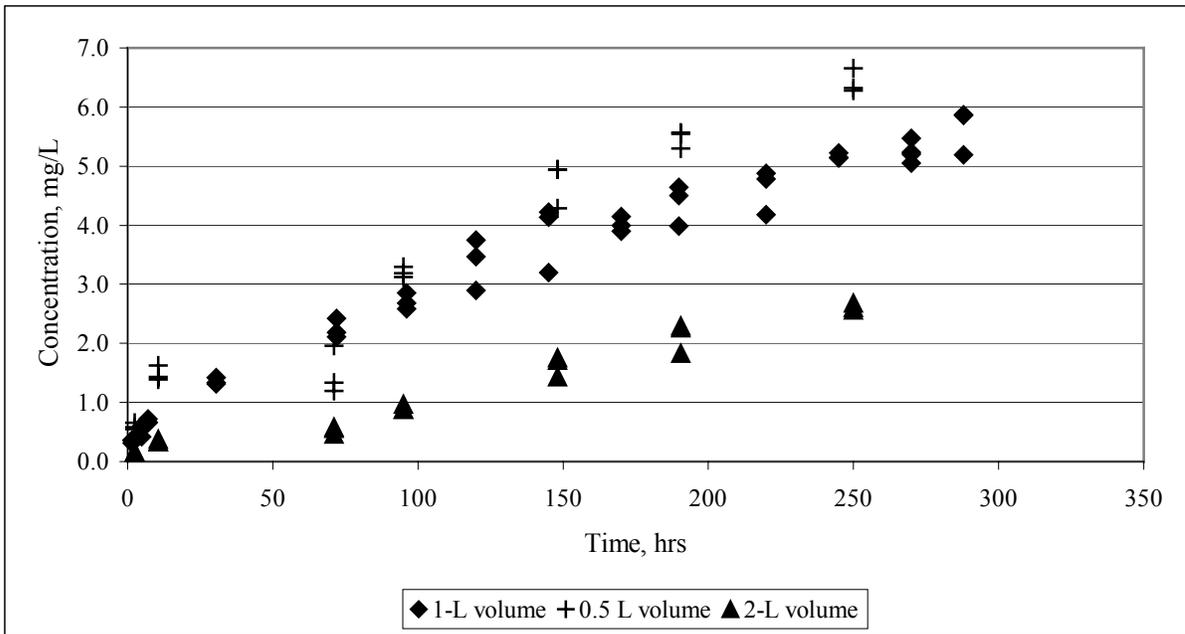


Figure 4.3.1.3. Calcium leaching (triplicate experiments) as a function of time from 4-inch disks into varying leachate volumes.

4.3.2 Analysis of Turbulence

For mixing with impeller blades, a form of Reynolds number has been defined for use in design of large mixers (Tchobanoglous and Schroeder, 1985), e.g., mixing of coagulating chemicals in water treatment plants, as follows:

$$Re = n d^2/\nu \quad (4.3.2.1)$$

where:

n = impeller angular velocity, revolution/s,

d = impeller diameter, cm

ν = kinematic viscosity, approximately 0.010 cm²/s for water at 20°C.

In this special computation, there is no conversion of angular velocity to radian/s or direct computation of the tangential velocity of the impeller.

Assuming the analysis may be applied to bench-scale mixers, for the flat-plate mixers used in this study, n = 60 rpm = 1 rev/s and d = 3 inches = 7.5 cm. Hence,

$$Re = 1 \times 7.5^2 / 0.01 = 5625 \quad (4.3.2.2)$$

The transition from laminar flow begins at about Re = 10 and fully turbulent flow exists for Re greater than about 5000. Hence, leaching in the flat-plate beakers may be considered fully turbulent and not diffusion-limited.

4.3.3 Biological Analyses

To investigate the scale-up effects, samples were leached from flat plates of three different sizes as explained in section 4.2.2. Samples were collected at 170 hrs from the leaching tests for toxicity analyses. Algal test results indicated mild growth inhibitory effects only in the range of 28% to 46% growth inhibition at 80% concentration of flat plate leachate samples. Statistically no significant difference in toxicity of leachates generated from different size flat plates was observed. EC50 values for these samples could not be calculated as the maximum observed effects were less than 50% at the highest concentration tested (no toxic effect, or NTE). No toxic effect was observed in *D. magna* mortality tests for all the flat plate samples generated in this test. As evidenced from Summary Table 4.3.1.1, except aluminum, no other toxic metals were present at significant quantity in the flat plate leachates. The low-level growth inhibitory effect observed for algae was possibly due to the low concentrations of aluminum present in the leachates.

4.4 CONCLUSIONS

Two issues were examined during this task.

1. Is the leaching rate the same for surface areas of different sizes? Flat plates with three different surface areas were leached into distilled water, such that the volume to surface area ratio was the same for each. In this case, concentrations collected as a function of time are expected to be the same for each plate area, and the results show unequivocally that this is true. That is, there is no scale effect just on the basis of size of the leaching areas, for the sizes studied. Fluxes are similar at all sampled times. However, the larger the flat plate size, the less likely it is that results will be anomalous due only to a minor sample irregularity but in a small area.

2. Does the leaching rate vary linearly with the ratio of leachate volume to surface area? This is important because model results are scaled to the highway environment on the basis of this volume to area ratio. The results generally support this hypothesis, but overall, they are inconclusive. This is primarily because of dilution effects introduced into the sampling procedure due to a very limited number of 4-inch disks remaining for this experiment.

Table 4.3.1.1. Task 3: Summary data for chemical analyses.

Task 3: Effect of Scale on Flat-Plate Leachate Composition																
Sample ID	Test Conditions	Time (hr)	Tox Lab ID	Toxicity Results			Chemistry Test Results									
				Algal Toxicity			TOC (mg/L)	Al (mg/L)	Ba (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sb (mg/L)	Sr (mg/L)	Zn (mg/L)
				Concentration as %												
				Elutriate												
%EC ₅₀ or %LC ₅₀	Lower 95% C.L.	Upper 95% C.L.														
MSWIBA ASPHALT 4-inch Flat-Plate																
1	SS-ASPH-1 1.5 HR	1.5	NA	NA	NA	NA	0.927	BD	BD	0.366	0.279	0.014	0.612	BD	BD	BD
2	SS-ASPH-2 1.5 HR	1.5	NA	NA	NA	NA	0.935	BD	BD	0.354	0.355	0.013	0.430	BD	BD	BD
3	SS-ASPH-1 1.5 HR	1.5	NA	NA	NA	NA	0.887	BD	BD	0.312	0.211	0.008	0.401	BD	BD	BD
4	SS-ASPH-1 4.75 HR	4.75	NA	NA	NA	NA	1.107	BD	BD	0.418	0.738	0.037	1.254	BD	BD	BD
5	SS-ASPH-2 4.75 HR	4.75	NA	NA	NA	NA	1.081	BD	BD	0.571	0.646	0.032	1.287	BD	BD	BD
6	SS-ASPH-3 4.75 HR	4.75	NA	NA	NA	NA	1.104	BD	BD	0.603	0.662	0.028	1.270	BD	BD	BD
7	SS-ASPH-1 7 HR	7	NA	NA	NA	NA	1.153	BD	BD	0.666	0.976	0.049	1.552	BD	BD	BD
8	SS-ASPH-2 7 HR	7	NA	NA	NA	NA	1.278	BD	BD	0.661	0.873	0.049	1.418	BD	BD	BD
9	SS-ASPH-3 7 HR	7	NA	NA	NA	NA	1.239	BD	BD	0.727	0.878	0.054	1.798	BD	BD	BD
10	SS-ASPH-1 30.5HR	30.5	NA	NA	NA	NA	1.495	BD	BD	1.313	1.550	0.072	2.504	BD	BD	BD
11	SS-ASPH-2 30.5HR	30.5	NA	NA	NA	NA	1.472	BD	BD	1.420	1.532	0.072	2.787	BD	BD	BD
12	SS-ASPH-3 30.5HR	30.5	NA	NA	NA	NA	1.589	0.004	BD	1.338	1.340	0.074	2.353	BD	BD	BD
13	SS-ASPH-1 72HR	72	NA	NA	NA	NA	1.598	0.039	BD	2.106	2.698	0.126	3.415	BD	BD	BD
14	SS-ASPH-2 72HR	72	NA	NA	NA	NA	1.938	0.043	BD	2.187	2.261	0.110	4.295	BD	BD	BD
15	SS-ASPH-3 72HR	72	NA	NA	NA	NA	1.986	0.042	BD	2.420	2.266	0.117	3.923	BD	BD	BD
16	SS-ASPH-1 96HR	96	NA	NA	NA	NA	1.851	0.064	BD	2.579	3.041	0.152	5.256	BD	BD	BD
17	SS-ASPH-2 96HR	96	NA	NA	NA	NA	2.324	0.060	BD	2.678	2.783	0.153	5.138	BD	BD	BD
18	SS-ASPH-3 96HR	96	NA	NA	NA	NA	2.069	0.067	BD	2.854	3.049	0.164	5.826	BD	BD	BD
19	SS-ASPH-1 120HR	120	NA	NA	NA	NA	2.120	0.111	BD	3.466	3.374	0.196	7.107	BD	BD	BD
20	SS-ASPH-2 120HR	120	NA	NA	NA	NA	2.089	0.106	BD	3.746	3.261	0.190	6.309	BD	BD	BD
21	SS-ASPH-3 120HR	120	NA	NA	NA	NA	2.186	0.093	BD	2.898	2.615	0.189	6.541	BD	BD	BD
22	SS-ASPH-1 145HR	145	NA	NA	NA	NA	2.071	0.130	BD	4.134	3.683	0.225	7.591	BD	BD	BD
23	SS-ASPH-2 145HR	145	NA	NA	NA	NA	2.146	0.128	BD	4.224	3.548	0.213	7.178	BD	BD	BD
24	SS-ASPH-3 145HR	145	NA	NA	NA	NA	2.199	0.145	BD	3.204	3.104	0.215	7.233	BD	BD	BD
25	SS-FP-1 170 HR	170.0	4222401	NTE			2.011	0.517	BD	3.902	3.692	0.292	8.582	BD	BD	BD
26	SS-FP-1 170 HR	170.0	4222402	NTE			2.086	0.588	BD	3.991	2.918	0.264	7.911	BD	BD	BD
27	SS-FP-1 170 HR	170.0	4222403	NTE			2.061	0.581	BD	4.143	3.417	0.238	7.353	BD	BD	BD
28	SS-FP-1 190 HR	190.0	NA	NA	NA	NA	2.061	0.539	BD	3.987	3.923	0.319	8.412	BD	BD	BD
29	SS-FP-1 190 HR	190.0	NA	NA	NA	NA	2.161	0.582	BD	4.647	3.056	0.290	8.004	BD	BD	BD
30	SS-FP-1 190 HR	190.0	NA	NA	NA	NA	2.083	0.598	BD	4.498	2.767	0.261	8.912	BD	BD	BD
31	SS-FP-1 220 HR	220.0	NA	NA	NA	NA	2.005	0.551	BD	4.183	4.160	0.255	9.129	BD	BD	BD
32	SS-FP-1 220 HR	220.0	NA	NA	NA	NA	2.099	0.524	BD	4.883	3.292	0.252	9.110	BD	BD	BD
33	SS-FP-1 220 HR	220.0	NA	NA	NA	NA	2.117	0.512	BD	4.784	3.004	0.249	8.148	BD	BD	BD
34	SS-FP-1 245 HR	245.0	NA	NA	NA	NA	2.074	0.646	BD	5.146	4.367	0.390	8.707	BD	BD	BD
35	SS-FP-1 245 HR	245.0	NA	NA	NA	NA	2.136	0.624	BD	5.139	3.470	0.355	8.459	BD	BD	BD
36	SS-FP-1 245 HR	245.0	NA	NA	NA	NA	2.217	0.640	BD	5.221	3.816	0.315	8.125	BD	BD	BD
37	SS-FP-1 270 HR	270.0	NA	NA	NA	NA	2.141	0.656	BD	5.204	3.291	0.412	11.062	BD	BD	BD
38	SS-FP-1 270 HR	270.0	NA	NA	NA	NA	2.079	0.701	BD	5.229	3.476	0.381	10.817	BD	BD	BD
39	SS-FP-1 270 HR	270.0	NA	NA	NA	NA	2.144	0.650	BD	5.048	3.752	0.334	10.104	BD	BD	BD
40	SS-FP-1 270 HR	270	NA	NA	NA	NA	2.144	0.650	BD	5.471	3.582	0.333	9.930	BD	BD	BD
41	SS-FP-1 288 HR	288	NA	NA	NA	NA	2.137	0.701	BD	5.189	4.025	0.434	11.392	BD	BD	BD
42	SS-FP-1 288 HR	288	NA	NA	NA	NA	2.209	0.741	BD	5.869	4.257	0.400	9.927	BD	BD	BD
43	SS-FP-1 288 HR	288	NA	NA	NA	NA	2.144	0.651	BD	5.863	4.679	0.349	9.988	BD	BD	BD

Table 4.3.1.1. Task 3: Summary data for chemical analyses (cont.).

Task 3: Effect of Scale on Flat-Plate Leachate Composition																
Sample ID	Test Conditions	Time (hr)	Tox Lab ID	Toxicity Results			Chemistry Test Results									
				Algal Toxicity			TOC (mg/L)	Al (mg/L)	Ba (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sb (mg/L)	Sr (mg/L)	Zn (mg/L)
				Concentration as % Elutriate												
				%EC ₅₀ or %LC ₅₀	Lower 95% C.L.	Upper 95% C.L.										
MSWIBA ASPHALT 6-inch Flat-Plate																
1	SS-FP-1 1.25 HR	1.3	NA	NA	NA	0.986	BD	BD	0.548	1.174	0.006	0.155	BD	BD	BD	
2	SS-FP-2 1.25 HR	1.3	NA	NA	NA	0.938	BD	BD	0.546	1.120	0.002	0.179	BD	BD	BD	
3	SS-FP-3 1.25 HR	1.3	NA	NA	NA	1.158	BD	BD	0.625	1.211	0.003	0.329	BD	BD	BD	
4	SS-FP-1 2.75 HR	2.8	NA	NA	NA	1.132	0.051	BD	0.607	1.234	0.005	0.404	BD	BD	BD	
5	SS-FP-2 2.75 HR	2.8	NA	NA	NA	1.155	0.059	BD	0.576	1.189	0.005	0.410	BD	BD	BD	
6	SS-FP-3 2.75 HR	2.8	NA	NA	NA	1.204	0.065	BD	0.637	1.270	0.007	0.622	BD	BD	BD	
7	SS-FP-1 5.5 HR	5.5	NA	NA	NA	1.329	0.060	BD	0.828	1.514	0.012	0.732	BD	BD	BD	
8	SS-FP-2 5.5 HR	5.5	NA	NA	NA	1.290	0.058	BD	0.813	1.420	0.012	0.794	BD	BD	BD	
9	SS-FP-3 5.5 HR	5.5	NA	NA	NA	1.546	0.040	BD	0.888	1.459	0.014	1.293	BD	BD	BD	
10	SS-FP-1 12 HR	12.0	NA	NA	NA	1.523	0.065	BD	1.506	1.664	0.022	1.157	BD	BD	BD	
11	SS-FP-2 12 HR	12.0	NA	NA	NA	1.640	0.066	BD	1.221	1.478	0.021	1.307	BD	BD	BD	
12	SS-FP-3 12 HR	12.0	NA	NA	NA	1.649	0.063	BD	1.570	1.557	0.024	1.992	BD	BD	BD	
13	SS-FP-1 24 HR	24.0	NA	NA	NA	1.989	0.161	BD	1.720	1.998	0.043	2.002	BD	BD	BD	
14	SS-FP-2 24 HR	24.0	NA	NA	NA	2.037	0.182	BD	1.411	2.803	0.043	2.457	BD	BD	BD	
15	SS-FP-3 24 HR	24.0	NA	NA	NA	1.902	0.232	BD	1.988	2.928	0.045	2.298	BD	BD	BD	
16	SS-FP-1 52 HR	52.0	NA	NA	NA	2.375	0.295	BD	2.361	1.995	0.529	3.406	BD	BD	BD	
17	SS-FP-2 52 HR	52.0	NA	NA	NA	2.120	0.174	BD	2.038	2.202	0.295	4.172	BD	BD	BD	
18	SS-FP-3 52 HR	52.0	NA	NA	NA	2.171	0.256	BD	2.559	2.234	0.301	3.978	BD	BD	BD	
19	SS-FP-1 77 HR	77.0	NA	NA	NA	2.140	0.546	BD	2.853	2.847	0.702	4.579	BD	BD	BD	
20	SS-FP-2 77 HR	77.0	NA	NA	NA	2.237	0.504	BD	2.995	2.441	0.794	5.671	BD	BD	BD	
21	SS-FP-3 77 HR	77.0	NA	NA	NA	2.122	0.556	BD	2.577	3.217	0.882	5.759	BD	BD	BD	
22	SS-FP-1 101.3 HRS	101.3	NA	NA	NA	2.197	0.680	BD	3.305	3.121	0.731	5.608	BD	BD	BD	
23	SS-FP-2 101.3 HRS	101.3	NA	NA	NA	2.250	0.582	BD	2.996	2.714	0.360	6.237	BD	BD	BD	
24	SS-FP-3 101.3 HRS	101.3	NA	NA	NA	1.992	0.671	BD	3.314	3.001	0.634	6.511	BD	BD	BD	
25	SS-FP-1 126.3 HR	126.3	NA	NA	NA	2.101	0.506	BD	3.633	3.331	0.844	6.721	BD	BD	BD	
26	SS-FP-2 126.3 HR	126.3	NA	NA	NA	2.131	0.575	BD	3.773	2.818	0.602	6.479	BD	BD	BD	
27	SS-FP-3 126.3 HR	126.3	NA	NA	NA	2.160	0.594	BD	3.440	3.356	0.186	7.062	BD	BD	BD	
28	SS-FP-1 152.3 HR	152.3	NA	NA	NA	2.219	0.542	BD	3.733	3.607	0.255	7.405	BD	BD	BD	
29	SS-FP-2 152.3 HR	152.3	NA	NA	NA	2.099	0.595	BD	3.662	3.347	0.231	7.102	BD	BD	BD	
30	SS-FP-3 152.3 HR	152.3	NA	NA	NA	2.158	0.513	BD	3.776	3.268	0.214	7.942	BD	BD	BD	
31	SS-FP-1 170 HR	170.0	4225401	NTE		2.062	0.516	BD	3.904	3.641	0.294	8.686	BD	BD	BD	
32	SS-FP-2 170 HR	170.0	4225402	NTE		2.137	0.587	BD	3.993	2.867	0.267	8.015	BD	BD	BD	
33	SS-FP-3 170 HR	170.0	4225403	NTE		2.112	0.579	BD	3.116	2.965	0.290	7.459	BD	BD	BD	
34	SS-FP-1 190 HR	190.0	NA	NA	NA	2.112	0.537	BD	3.989	3.872	0.321	9.597	BD	BD	BD	
35	SS-FP-2 190 HR	190.0	NA	NA	NA	2.212	0.580	BD	4.649	3.005	0.292	8.609	BD	BD	BD	
36	SS-FP-3 190 HR	190.0	NA	NA	NA	2.134	0.597	BD	4.501	2.716	0.264	8.716	BD	BD	BD	
37	SS-FP-1 220 HR	220.0	NA	NA	NA	2.056	0.550	BD	4.185	4.108	0.257	8.833	BD	BD	BD	
38	SS-FP-2 220 HR	220.0	NA	NA	NA	2.150	0.523	BD	4.885	3.241	0.254	9.775	BD	BD	BD	
39	SS-FP-3 220 HR	220.0	NA	NA	NA	2.168	0.511	BD	4.786	2.952	0.251	8.953	BD	BD	BD	
40	SS-FP-1 245 HR	245.0	NA	NA	NA	2.125	0.644	BD	5.148	4.315	0.393	9.811	BD	BD	BD	
41	SS-FP-2 245 HR	245.0	NA	NA	NA	2.187	0.623	BD	5.141	3.419	0.358	9.564	BD	BD	BD	
42	SS-FP-3 245 HR	245.0	NA	NA	NA	2.268	0.638	BD	5.224	3.764	0.317	9.029	BD	BD	BD	
43	SS-FP-1 270 HR	270.0	NA	NA	NA	2.193	0.654	BD	5.206	4.240	0.414	11.167	BD	BD	BD	
44	SS-FP-2 270 HR	270.0	NA	NA	NA	2.131	0.699	BD	5.231	3.425	0.384	10.922	BD	BD	BD	
45	SS-FP-3 270 HR	270.0	NA	NA	NA	2.195	0.649	BD	5.050	3.700	0.337	10.209	BD	BD	BD	

Table 4.3.1.1. Task 3: Summary data for chemical analyses (cont..).

Task 3: Effect of Scale on Flat-Plate Leachate Composition																
Sample ID	Test Conditions	Time (hr)	Tox Lab ID	Toxicity Results			Chemistry Test Results									
				Algal Toxicity			TOC (mg/L)	Al (mg/L)	Ba (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sb (mg/L)	Sr (mg/L)	Zn (mg/L)
				Concentration as % Elutriate												
				%EC ₅₀ or %LC ₅₀	Lower 95% C.L.	Upper 95% C.L.										
MSWIBA ASPHALT 4.5 x 6.0 x 9.25 inch Flat-Plate																
1	SS-FP-1 1.25 HR	1.25	NA	NA	NA	0.986	BD	BD	0.571	0.804	0.004	0.208	BD	BD	BD	
2	SS-FP-2 1.25 HR	1.25	NA	NA	NA	0.938	BD	BD	0.569	0.750	0.001	0.232	BD	BD	BD	
3	SS-FP-3 1.25 HR	1.25	NA	NA	NA	1.152	BD	BD	0.948	0.837	0.002	0.492	BD	BD	BD	
4	SS-FP-1 2.75 HR	2.75	NA	NA	NA	1.132	0.051	BD	0.630	0.864	0.003	0.426	BD	BD	BD	
5	SS-FP-2 2.75 HR	2.75	NA	NA	NA	1.155	0.059	BD	0.599	0.819	0.004	0.463	BD	BD	BD	
6	SS-FP-3 2.75 HR	2.75	NA	NA	NA	1.204	0.065	BD	0.561	0.900	0.005	0.787	BD	BD	BD	
7	SS-FP-1 6.25 HR	6.25	NA	NA	NA	1.329	0.060	BD	0.852	1.144	0.010	0.801	BD	BD	BD	
8	SS-FP-2 6.25 HR	6.25	NA	NA	NA	1.290	0.058	BD	0.836	1.050	0.010	0.863	BD	BD	BD	
9	SS-FP-3 6.25 HR	6.25	NA	NA	NA	1.546	0.040	BD	0.842	1.089	0.012	1.362	BD	BD	BD	
10	SS-FP-1 12 HR	12	NA	NA	NA	1.523	0.065	BD	1.530	1.294	0.021	1.225	BD	BD	BD	
11	SS-FP-2 12 HR	12	NA	NA	NA	1.640	0.066	BD	1.244	1.108	0.020	1.376	BD	BD	BD	
12	SS-FP-3 12 HR	12	NA	NA	NA	1.649	0.063	BD	1.694	1.187	0.023	2.061	BD	BD	BD	
13	SS-FP-1 24 HR	24	NA	NA	NA	1.989	0.161	BD	1.743	1.628	0.041	2.071	BD	BD	BD	
14	SS-FP-2 24 HR	24	NA	NA	NA	2.037	0.182	BD	1.434	2.433	0.041	2.526	BD	BD	BD	
15	SS-FP-3 24 HR	24	NA	NA	NA	1.902	0.232	BD	1.960	2.558	0.044	2.367	BD	BD	BD	
16	SS-FP-1 49 HR	49	NA	NA	NA	2.375	0.295	BD	2.385	1.625	0.089	3.429	BD	BD	BD	
17	SS-FP-2 49 HR	49	NA	NA	NA	2.120	0.174	BD	2.062	1.832	0.082	4.195	BD	BD	BD	
18	SS-FP-3 49 HR	49	NA	NA	NA	2.171	0.256	BD	2.582	1.864	0.084	4.201	BD	BD	BD	
19	SS-FP-1 73 HR	73	NA	NA	NA	2.140	0.546	BD	2.877	2.477	0.133	4.602	BD	BD	BD	
20	SS-FP-2 73 HR	73	NA	NA	NA	2.237	0.504	BD	2.374	2.071	0.120	5.694	BD	BD	BD	
21	SS-FP-3 73 HR	73	NA	NA	NA	2.122	0.556	BD	2.601	2.847	0.120	5.782	BD	BD	BD	
22	SS-FP-1 97 HRS	97	NA	NA	NA	2.197	0.680	BD	3.329	2.751	0.175	5.631	BD	BD	BD	
23	SS-FP-2 97 HRS	97	NA	NA	NA	2.250	0.582	BD	2.569	2.344	0.159	6.260	BD	BD	BD	
24	SS-FP-3 97 HRS	97	NA	NA	NA	1.992	0.671	BD	3.337	2.631	0.154	6.534	BD	BD	BD	
25	SS-FP-1 121 HR	121	NA	NA	NA	2.101	0.506	BD	3.656	2.960	0.218	6.744	BD	BD	BD	
26	SS-FP-2 121 HR	121	NA	NA	NA	2.131	0.575	BD	3.417	2.448	0.197	6.502	BD	BD	BD	
27	SS-FP-3 121 HR	121	NA	NA	NA	2.160	0.594	BD	3.463	2.986	0.184	7.085	BD	BD	BD	
28	SS-FP-1 145 HR	145	NA	NA	NA	2.219	0.542	BD	3.756	3.237	0.254	7.440	BD	BD	BD	
29	SS-FP-2 145 HR	145	NA	NA	NA	2.099	0.595	BD	3.555	2.977	0.230	7.638	BD	BD	BD	
30	SS-FP-3 145 HR	145	NA	NA	NA	2.158	0.513	BD	3.799	2.898	0.213	7.978	BD	BD	BD	
31	SS-FP-1 169 HR	169	4224401	NTE		2.063	0.516	BD	3.927	3.271	0.292	8.722	BD	BD	BD	
32	SS-FP-2 169 HR	169	4224402	NTE		2.138	0.587	BD	3.947	2.497	0.265	8.751	BD	BD	BD	
33	SS-FP-3 169 HR	169	4224403	NTE		2.113	0.579	BD	4.169	2.995	0.239	7.493	BD	BD	BD	
34	SS-FP-1 190 HR	190	NA	NA	NA	2.113	0.537	BD	3.972	3.502	0.320	9.633	BD	BD	BD	
35	SS-FP-2 190 HR	190	NA	NA	NA	2.213	0.580	BD	4.672	2.635	0.291	8.644	BD	BD	BD	
36	SS-FP-3 190 HR	190	NA	NA	NA	2.150	0.597	BD	4.573	2.346	0.262	8.752	BD	BD	BD	
37	SS-FP-1 247 HR	247	NA	NA	NA	2.125	0.644	BD	5.171	3.945	0.391	10.847	BD	BD	BD	
38	SS-FP-2 247 HR	247	NA	NA	NA	2.188	0.623	BD	5.164	3.049	0.356	9.600	BD	BD	BD	
39	SS-FP-3 247 HR	247	NA	NA	NA	2.268	0.638	BD	5.037	3.394	0.316	9.765	BD	BD	BD	
40	SS-FP-1 270 HR	270	NA	NA	NA	2.193	0.654	BD	5.229	3.870	0.413	10.203	BD	BD	BD	
41	SS-FP-2 270 HR	270	NA	NA	NA	2.131	0.699	BD	5.254	3.055	0.382	9.958	BD	BD	BD	
42	SS-FP-3 270 HR	270	NA	NA	NA	2.195	0.649	BD	5.474	3.330	0.335	10.035	BD	BD	BD	
43	SS-FP-1 288 HR	288	NA	NA	NA	2.188	0.700	BD	5.192	3.974	0.436	11.497	BD	BD	BD	
44	SS-FP-2 288 HR	288	NA	NA	NA	2.260	0.739	BD	5.871	3.205	0.403	10.032	BD	BD	BD	
45	SS-FP-3 288 HR	288	NA	NA	NA	2.195	0.650	BD	5.865	3.627	0.351	10.092	BD	BD	BD	

Table 4.3.1.1. Task 3: Summary data for chemical analyses (concluded).

Task 3: Effect of Scale on Flat-Plate Leachate Composition															
Test Conditions	Time (hr)	Tox Lab ID	Toxicity Results			Chemistry Test Results									
			Algal Toxicity			TOC (mg/L)	Al (mg/L)	Ba (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sb (mg/L)	Sr (mg/L)	Zn (mg/L)
			Concentration as %												
			Elutriate												
%EC ₅₀ or %LC ₅₀	Lower 95% C.L.	Upper 95% C.L.													
MSWIBA ASPHALT 4-inch Flat-Plate with 1:0.5 ratio															
FP500-1	2.5	NA	NA	NA	NA	2.212	BD	BD	0.584	0.291	0.023	1.642	BD	BD	0.019
FP500-2	2.5	NA	NA	NA	NA	2.205	BD	BD	0.549	0.329	0.005	1.873	BD	BD	-0.004
FP500-3	2.5	NA	NA	NA	NA	2.237	BD	BD	0.652	0.232	0.013	1.486	BD	BD	-0.003
FP500-1	10.5	NA	NA	NA	NA	2.354	BD	BD	1.384	0.508	0.048	2.273	BD	BD	0.012
FP500-2	10.5	NA	NA	NA	NA	2.320	BD	BD	1.433	0.609	0.034	1.971	BD	BD	0.000
FP500-3	10.5	NA	NA	NA	NA	2.345	BD	BD	1.628	0.485	0.051	2.128	BD	BD	0.001
FP500-1	71	NA	NA	NA	NA	2.442	BD	BD	1.960	0.638	0.079	3.734	BD	BD	0.011
FP500-2	71	NA	NA	NA	NA	2.431	BD	BD	1.191	0.755	0.060	3.269	BD	BD	-0.003
FP500-3	71	NA	NA	NA	NA	2.541	0.034	BD	1.331	0.688	0.089	2.926	BD	BD	-0.002
FP500-1	95	NA	NA	NA	NA	2.154	0.043	BD	3.118	1.968	0.144	4.657	BD	BD	0.006
FP500-2	95	NA	NA	NA	NA	2.255	0.038	BD	3.186	1.029	0.115	4.504	BD	BD	-0.001
FP500-3	95	NA	NA	NA	NA	2.349	0.035	BD	3.291	1.023	0.157	4.790	BD	BD	-0.001
FP500-1	148	NA	NA	NA	NA	2.338	0.086	BD	4.930	1.626	0.281	6.543	BD	BD	0.010
FP500-2	148	NA	NA	NA	NA	2.433	0.116	BD	4.284	1.544	0.247	6.476	BD	BD	-0.001
FP500-3	148	NA	NA	NA	NA	2.225	0.178	BD	4.943	1.708	0.304	6.408	BD	BD	0.005
FP500-1	190.5	NA	NA	NA	NA	2.323	0.133	BD	5.567	2.140	0.367	6.825	BD	BD	0.012
FP500-2	190.5	NA	NA	NA	NA	2.133	0.193	BD	5.547	2.057	0.349	7.770	BD	BD	-0.004
FP500-3	190.5	NA	NA	NA	NA	2.253	0.203	BD	5.298	2.137	0.392	7.499	BD	BD	0.011
FP500-1	250	NA	NTE			2.350	0.142	BD	6.326	2.619	0.526	10.523	BD	BD	0.023
FP500-2	250	NA	NTE			2.025	0.122	BD	6.638	3.336	0.699	10.237	BD	BD	0.031
FP500-3	250	NA	NTE			2.125	0.184	BD	6.279	3.641	0.772	10.465	BD	BD	0.034
MSWIBA ASPHALT 4-inch Flat-Plate with 1:2 ratio															
FP2000-1	2.5	NA	NA	NA	NA	1.012	BD	BD	0.160	0.245	0.005	1.115	BD	BD	-0.002
FP2000-2	2.5	NA	NA	NA	NA	1.201	BD	BD	0.167	0.256	0.000	1.323	BD	BD	-0.002
FP2000-3	2.5	NA	NA	NA	NA	1.120	BD	BD	0.166	0.189	-0.002	1.394	BD	BD	-0.003
FP2000-1	10.5	NA	NA	NA	NA	1.354	BD	BD	0.375	0.439	0.010	1.866	BD	BD	0.005
FP2000-2	10.5	NA	NA	NA	NA	1.301	BD	BD	0.334	0.547	0.010	1.811	BD	BD	-0.003
FP2000-3	10.5	NA	NA	NA	NA	1.675	BD	BD	0.337	0.429	0.006	1.705	BD	BD	-0.001
FP2000-1	71	NA	NA	NA	NA	1.662	BD	BD	0.564	0.620	0.022	2.728	BD	BD	0.005
FP2000-2	71	NA	NA	NA	NA	1.431	BD	BD	0.577	0.616	0.023	2.974	BD	BD	0.000
FP2000-3	71	NA	NA	NA	NA	1.549	BD	BD	0.462	0.612	0.011	2.284	BD	BD	-0.003
FP2000-1	95	NA	NA	NA	NA	1.154	BD	BD	0.882	0.902	0.037	3.849	BD	BD	0.025
FP2000-2	95	NA	NA	NA	NA	1.355	0.068	BD	0.885	1.057	0.050	3.345	BD	BD	-0.001
FP2000-3	95	NA	NA	NA	NA	1.349	0.002	BD	0.970	0.973	0.029	3.031	BD	BD	0.003
FP2000-1	148	NA	NA	NA	NA	1.438	0.070	BD	1.433	1.534	0.072	4.433	BD	BD	0.050
FP2000-2	148	NA	NA	NA	NA	1.433	0.071	BD	1.710	1.629	0.110	4.380	BD	BD	-0.001
FP2000-3	148	NA	NA	NA	NA	1.525	0.077	BD	1.757	1.395	0.062	4.536	BD	BD	0.000
FP2000-1	190.5	NA	NA	NA	NA	1.323	0.076	BD	1.836	1.710	0.102	5.598	BD	BD	0.090
FP2000-2	190.5	NA	NA	NA	NA	1.325	0.076	BD	2.266	1.953	0.159	5.586	BD	BD	0.037
FP2000-3	190.5	NA	NA	NA	NA	1.253	0.051	BD	2.297	1.548	0.092	5.182	BD	BD	0.012
FP2000-1	250	NA	NTE			1.445	0.089	BD	2.563	2.092	0.138	5.635	BD	BD	0.013
FP2000-2	250	NA	NTE			1.225	0.022	BD	2.684	2.196	0.199	5.740	BD	BD	0.039
FP2000-3	250	NA	NTE			1.435	0.141	BD	2.610	2.247	0.206	5.230	BD	BD	0.030

CHAPTER 5

TASK 4: EVALUATION OF PORTLAND CEMENT CONCRETE (PCC) WITH- AND WITHOUT-PLASTICIZER FOR LEACHING AND RRR PROCESSES

5.1 INTRODUCTION

The leaching of chemical constituents from Portland cement concrete (PCC) and the effect of RRR processes on these constituents were assessed using the complete Phase II methodology. In this task, PCC leachate was subjected to chemical and toxicity testing to identify specific constituents that are responsible for the observed aquatic toxicity. PCC (with- and without-plasticizer admixture) was subjected to the full testing methodology to determine leachate characteristics and parameters for the removal/reduction/retardation (RRR) factors in the fate and transport model. Laboratory tests included batch and long-term leaching, flat plate leaching, and sorption to Sagehill and Woodburn soils. Photolysis, volatilization, and biodegradation tests were performed on the leachate and on separately prepared solutions of the plasticizer.

The specific objectives of Task 4 included:

- Perform aquatic toxicity screening tests for Portland cement concrete prepared with and without plasticizer.,
- Perform a complete sequence of leaching (including flat-plate) and RRR laboratory tests with supporting aquatic toxicity tests and chemical analyses to determine modeling parameters for PCC with-and without-plasticizer.

The algal chronic toxicity test was performed to assess the integrated effects of a variety of chemicals present in the PCC leachates. The standard 24-hr leachate was tested for toxicity at full leachate strength. Daphnia acute toxicity tests were also performed. However, precipitation problems caused by high calcium levels (about 700 mg/L) in the PCC leachates rendered the test results invalid. Chemical precipitation can cause immobilization of Daphnia ultimately resulting in their death (Lamb and Bailey, 1981). Thus, it will be misleading to conclude that Daphnia mortality was caused by PCC toxicity.

PCC leachate is a complex mixture containing both inorganics and organics at significant levels. Chemical characterization of 24-hour batch leachates from both PCC with and without plasticizer indicated about 2-5 mg/L of aluminum, 700 mg/L of calcium and above 5 mg/L of TOC. Algal EC50 values were observed to be ~14% and ~44% for PCC with and without plasticizer respectively. Conventional approaches to identify toxicants using analytical methods often limit their search to “priority pollutants” that are only a fraction of all the existing chemicals. Even if all the chemicals are identified, trying to pinpoint the cause for toxicity in such complex mixtures is likely to fail because this approach does not include matrix effects, and toxicant bioavailability. PCC leachates

with only aluminum and calcium at significant levels pose a similar question regarding the cause for observed growth inhibitory effects in algae. To find an answer to this question, it is important to understand the various mechanisms by which aluminum and calcium can cause growth inhibitory effects in algae.

Phosphorus is an important nutrient for the growth of unicellular algal species such as *S. capricornutum*. The bioavailability of phosphorus is dependent upon abiotic and biotic factors. Abiotic factors such as precipitation, pH and formation of complexes in the presence of elements such as calcium, aluminum and iron often control the bioavailable forms of phosphorus. According to Otsuki and Wetzel (1972), high pH values combined with high concentrations of calcium levels can coprecipitate phosphorus and CaCO₃. Precipitation of calcium as calcium phosphates is strongly influenced by kinetics of nucleation, crystal growth and chemical composition of the medium (Jenkins et al., 1971). According to Diaz et al. (1994), high pH values (> 9) and high calcium levels (> 100 mg/L) can bring about appreciable amounts of precipitation. There are numerous other studies that have shown phosphorus removal by adding aluminum, calcium and iron in water treatment processes.

In laboratory studies, Minzoni (1984) and Peterson et al. (1974) have observed the removal of phosphorus by aluminum in water. Cooke et al. (1993) have shown the use of aluminum (as alum) to precipitate phosphate and particles in treatment of lakes, further indicating the phosphorus removal capacity of aluminum in water. According to Kong and Chen (1995), aluminum can also affect the enzyme (acid phosphatase) production in algae *S. capricornutum*. Acid phosphatase is an important enzyme that significantly contributes to phosphate availability in algal cells. An EC₅₀ value of about 0.6 mg/L was observed from the algal chronic toxicity test conducted by the OSU Ecotoxicology Laboratory. Based on above studies, the primary mechanism that causes growth inhibition in algae seems to be limitation of phosphorus, an essential nutrient for the growth of algal cells.

5.2 EXPERIMENTAL APPROACH

Leachates were generated following the standard highway materials leaching procedures of this study documented in Volume IV (Nelson et al., 2000b). The PCC was crushed to ¼-inch minus size for short-term and long-term batch leachate generation. Flat-plate leachates were generated using the standard 100 mm x 100 mm cast discs. PCC leachate was generated for source strength evaluation by the short-term batch, long-term batch, and flat-plate procedures. Leachate from the short-term (24-hr) procedure was evaluated for removal of toxicity and chemical constituents by RRR process tests, including volatilization, photolysis, biodegradation, and soil sorption, where appropriate. Data collected included the chemical composition and toxicity of the leachates over time in all tests.

5.2.1 Test Materials

PCC was prepared from Tilbury cement with and without plasticizer admixture. A standard 28-day water cure was used prior to testing. The plasticizer compound was also tested in diluted aqueous solutions.

5.2.2 Test Soils

Two standard soils, Sagehill and Woodburn, were used in soil sorption batch tests, as described in Volume IV, Section 3.6.

5.2.3 Analysis of Experimental Data

Data collected for leaching and RRR process testing include detailed chemical constituent concentrations and toxicity results versus time. For specifically identified contaminants or surrogate chemicals, these data serve as primary data inputs for calibration of parameters in the leaching and RRR process models and ultimately for the comprehensive fate and transport model.

5.3 RESULTS AND DISCUSSION

5.3.1 PCC Batch Leaching Tests

5.3.1.1 Chemical analysis

Batch leaching tests were conducted using a known weight of PCC with and without plasticizer, at a ratio of 250 g solid material to 1000 mL of distilled water. Both short-term (24 hr) and long-term (7 days) dynamic batch-leaching experiments were conducted according to the protocols described in Volume IV. Results of the batch leaching and all data from this task are given in the summary Table 5.3.1.1.

Batch leaching tests using total calcium concentration indicated that the maximum leaching rate occurred within 24 hr as shown in Figures 5.3.1.1.1 to 5.3.1.1.4 for PCC with and without plasticizer. The leaching occurred rapidly as shown in Figures 5.3.1.1 to 5.3.1.2 in that maximum TOC concentration is reached within the 24 hours. The calcium concentration initially was about 600 mg/L and decreased with time to about 400 mg/L (Figure 5.3.1.1.3 and Figure 5.3.1.1.4), most likely due to precipitation. Aluminum concentration was about 2 mg/L after 7 days of leaching time (Figures 5.3.1.1.3 and 5.3.1.1.4). Leaching rates during the 24 hr short-term test probably represent well the case of first-flush chemical releases from new construction materials; typical leaching rates of weathered materials probably are best described by the slower loss rates observed after several days of leaching.

The TOC batch leaching experiments for PCC with and without plasticizer were modeled as:

$$\text{PCC-without-plasticizer} \quad C_{\text{TOC}} = 9.55 \times (1 - e^{-0.02t}) \quad R^2 = 0.96$$

PCC-with-plasticizer

$$C_{\text{TOC}} = 6.7 \times (1 - e^{-0.05t}) \quad R^2 = 0.96$$

with concentration in mg/L and t in hours. The use of these equations offers the advantage of the use of only two fitting coefficients, C_a and k. Spreadsheet programs can easily solve such regression equations. However, not all of the leaching curves have proven to be readily fit with this equation. More complex models, such as using two terms, one for the short-term release and one for the long-term release, would provide closer fits over the entire range of time. However, such models would require much more extensive methods of coefficient estimation.

Comparisons of PCC with and without plasticizer for metals leachate show that for metals (Ca and Al) the results are the same as shown in Figures 5.3.1.3 and 5.3.1.4, while TOC results show higher values for PCC-with-plasticizer than PCC-without-plasticizer as shown in Figure 5.3.1.1.1 and 5.3.1.1.2.

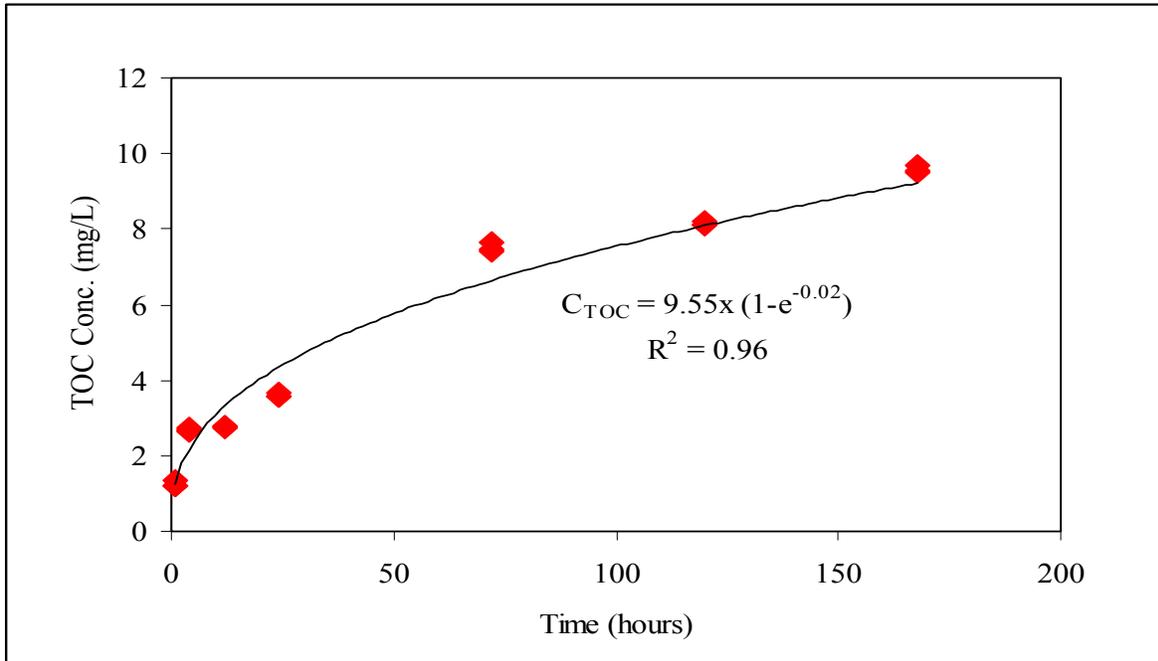


Figure 5.3.1.1.1 PCC-without-plasticizer batch leaching experiment, TOC concentration as a function of time (triplicate experiments).

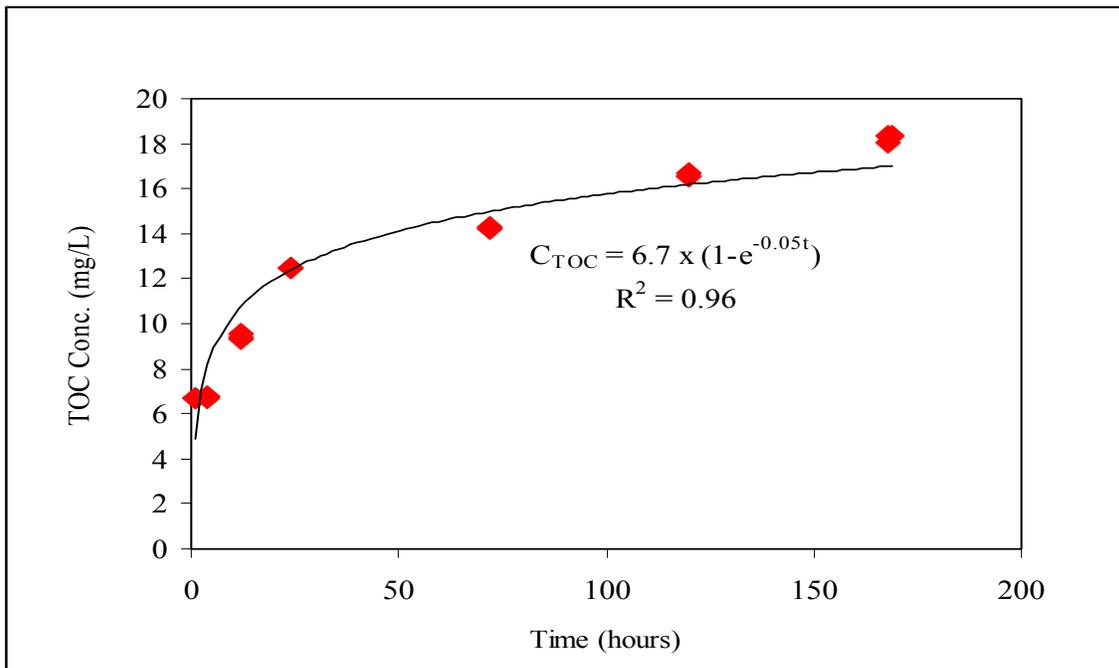


Figure 5.3.1.1.2. PCC-with-plasticizer batch leaching experiment, TOC concentration as a function of time (triplicate experiments).

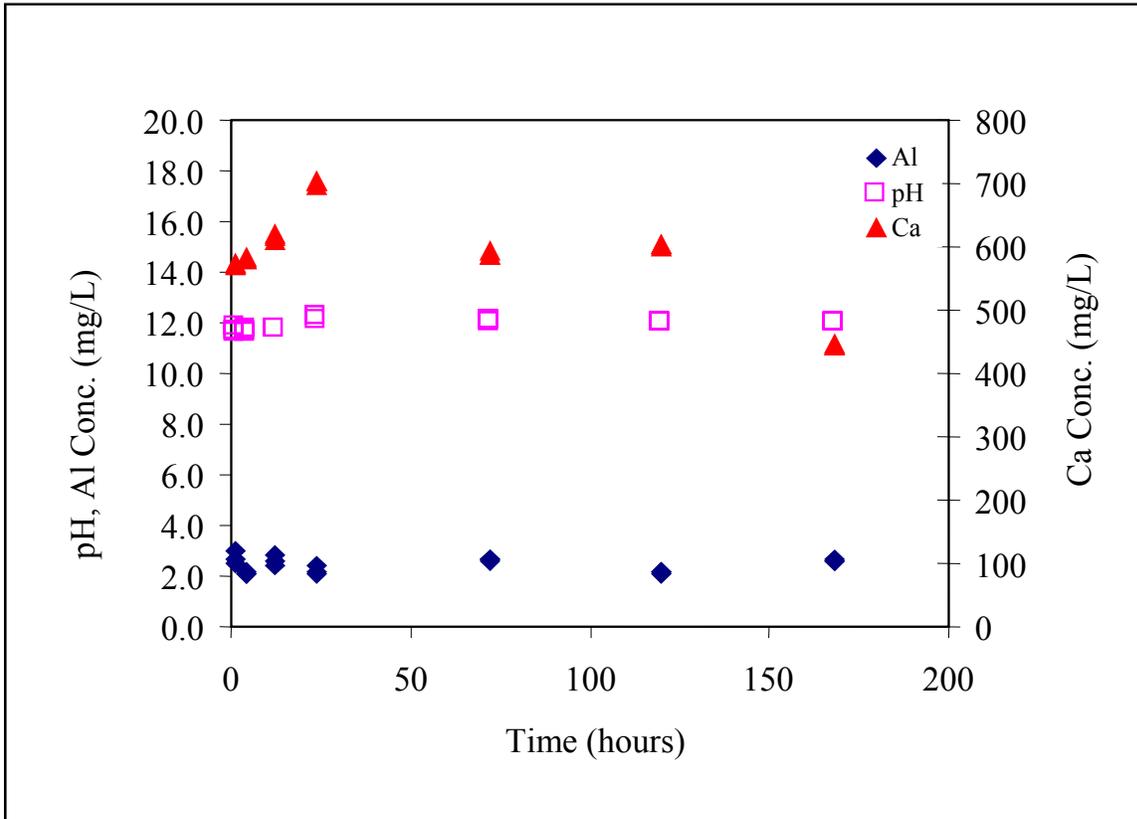


Figure 5.3.1.1.3. PCC-without-plasticizer long-term batch leaching experiment, calcium and aluminum concentrations as a function of time (triplicate experiments).

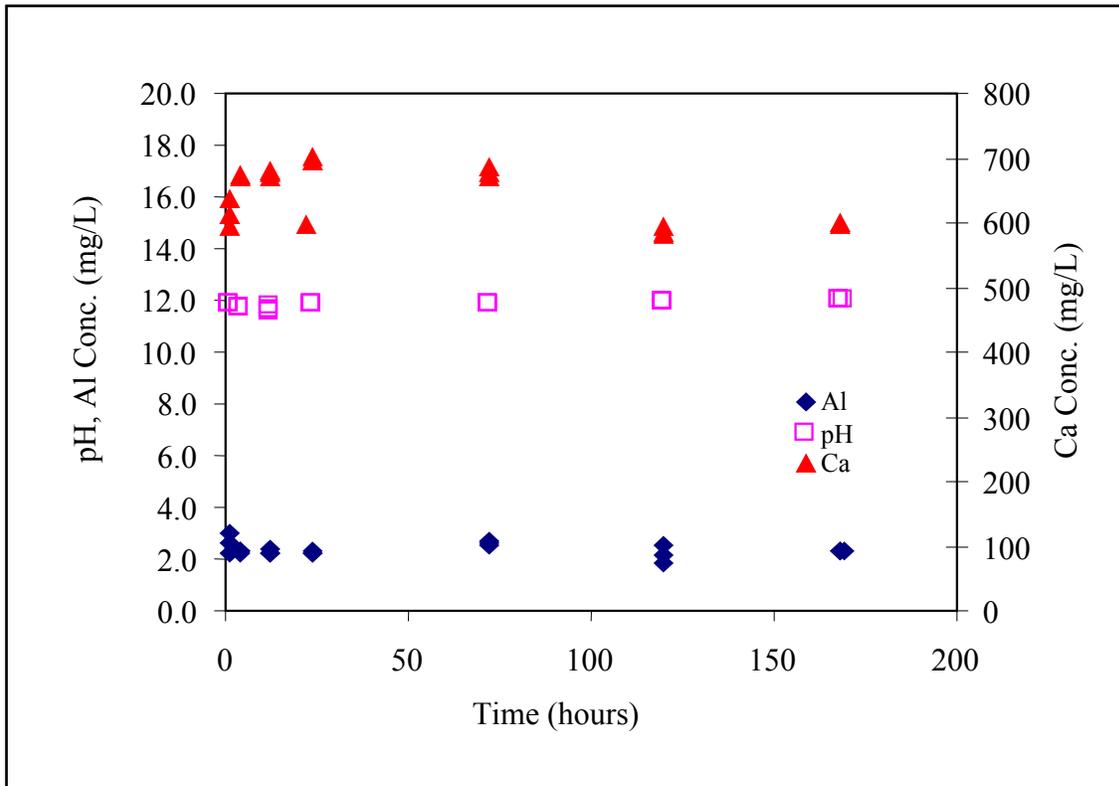


Figure 5.3.1.1.4. PCC-with-plasticizer long-term batch leaching experiment, calcium and aluminum concentrations as a function of time (triplicate experiments).

5.3.1.2 Toxicity analysis

Biological analyses of leachates generated from short- and long-term batch leaching were performed using *S. capricornutum* and *D. magna* bioassays. Results of *S. capricornutum* bioassays are illustrated in Figure 5.3.1.2.1. As indicated earlier, Daphnia results were invalidated because of the immobilization caused by the precipitation of high levels of calcium (~700 mg/L) in the test solutions.

PCC-with-plasticizer: One-hour leachate indicated a 1/EC50 value of 2.0 (average of three values) for *S. capricornutum*. A steep increase in algal 1/EC50 value was observed in leachates generated between 1 hr and 24 hrs (1/EC50 = 5.6). However, no significant change in algal 1/EC50 value ($p > 0.05$) was observed between 24-hr leachate and 168-hr leachates, indicating that constituents responsible for the observed algal growth inhibition were released within 24 hours.

PCC-without-plasticizer: One-hour leachate indicated a 1/EC50 value of 2.5 (average of three values) for *S. capricornutum*. Algal 1/EC50 values indicated no significant change ($p > 0.05$) between 1-hr leachate and 168-hr leachate (1/EC50 = 2.5). These results indicated that chemical components responsible for growth inhibition of algae were released within an hour.

In conclusion, algal growth inhibitory effect of PCC-with-plasticizer increased between 1-hr and 24-hr leachates, but there was no further increase between 24-hr and 168-hr leachates. In contrast, no significant change in algal 1/EC50 values was observed between 1-hr and 168-hr leachates of PCC-without-plasticizer. Results also indicated that PCC-with-plasticizer exhibited a higher 1/EC50 of 5.6 compared with PCC-without-plasticizer (1/EC50 = 2.5 in 168-hr leachate).

Over all, a good correspondence was observed between algal toxicity and chemistry data. In PCC-without-plasticizer samples, aluminum was present at levels between 3-5 mg/L and calcium as high as 700 mg/L. In samples collected between 1 and 168 hrs of leaching no significant change in concentrations of both these elements was observed. A similar effect was observed in the algal test results (Figure 5.3.1.2.1). In PCC-with-plasticizer samples, aluminum and calcium were present at concentrations about the same as in PCC-without-plasticizer samples. However, there were significant differences between PCC with- and PCC-without-plasticizer in the leaching of TOC. First, between 1-hr and 24-hrs leachates, the amount of TOC leached from PCC-with-plasticizer samples was at least 3-4 fold higher than the amount leached from PCC-without-plasticizer. Obviously, increases in the amount of TOC can be attributed to the plasticizer known to contain >50% naphthalene sulfonate. Toxicity analysis of diluted plasticizer tested individually has indicated a moderate toxicity to algae (%EC50 = 54). Correspondingly, the higher toxicity observed in the PCC-with-plasticizer can be attributed to the additive effects of aluminum, calcium and plasticizer in the leachate. Secondly, there was a sharp increase in the TOC leaching between 1 hr and 24 hr and, as discussed in the Section 5.3.1.1, TOC concentrations reached their maximum within 24

hr of leaching. From Figure 5.3.1.2.1 it is evident that a similar response was shown by algal test results.

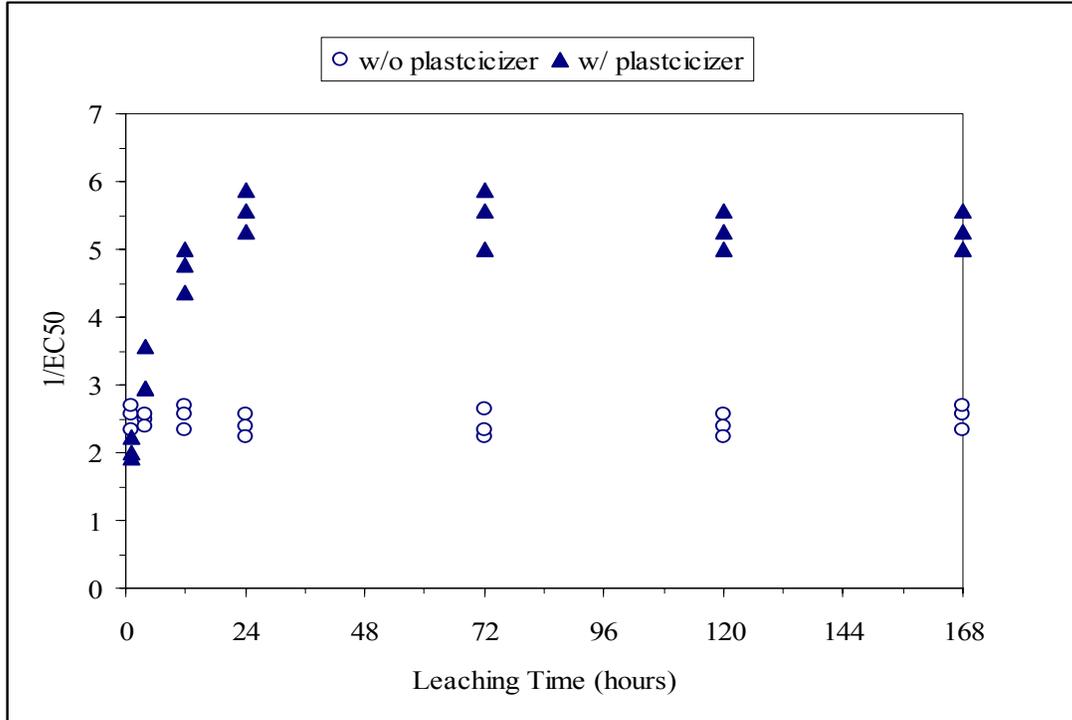


Figure 5.3.1.2.1 Algal %EC50 values for PCC leachates with and without plasticizer as a function of leaching time (triplicate experiments).

5.3.1.3 Effect of pH on Aluminum Toxicity to Algae

A variety of chemical factors are known to influence aluminum toxicity in algae, such as pH, calcium, dissolved organic matter (DOM), and phosphorus complex formation. The most important factor controlling the toxicity of aluminum is pH. The solubility and speciation of aluminum are directly controlled by pH, so total exposures of dissolved aluminum may change as a function of pH. It should be noted that pH values, total soluble aluminum levels, and the corresponding algal toxicity values in the PCC samples generated during the short- and long-term leaching tests did not change significantly between 1 to 168 hours (Figure 5.3.1.1.3, Figure 5.3.1.1.4 and Figure 5.3.1.2.1). Therefore, no significant change in algal toxicity was also observed.

A separate study conducted by Oregon State University (Lee, 2000) examined algal toxicity effects of aluminum at various pH values (pH 6 through pH 9). In this study, PCC leachate and soluble aluminum (as aluminum chloride) were tested for algal

toxicity. The primary focus was to study the effect of pH in controlling the toxicity of aluminum to algae.

For PCC leachate, the algal growth inhibitory effects were studied at concentrations of 5%, 10%, 20%, 40% and 80% and at nominal pH values of 6, 7, 8 and 9. Algal growth inhibition is based on chlorophyll a concentration using fluorometric measurement. Results indicated that the highest growth inhibitory effect was observed for all test concentrations at pH 6 (Figure 5.3.1.3.1). Algal growth inhibitory effect decreased at pH 7 for concentrations 5%, 10% and 20%. At pH 8, growth inhibitory effect was found to be the lowest for all test concentrations except at 5%, which decreased to no effect at pH 8.5. However, for the higher PCC concentrations tested, a significant increase in algal growth inhibitory effect was observed at pH 8.5 (initial test pH 9). Overall, lowest algal toxicity was observed around pH 8 in for PCC leachate.

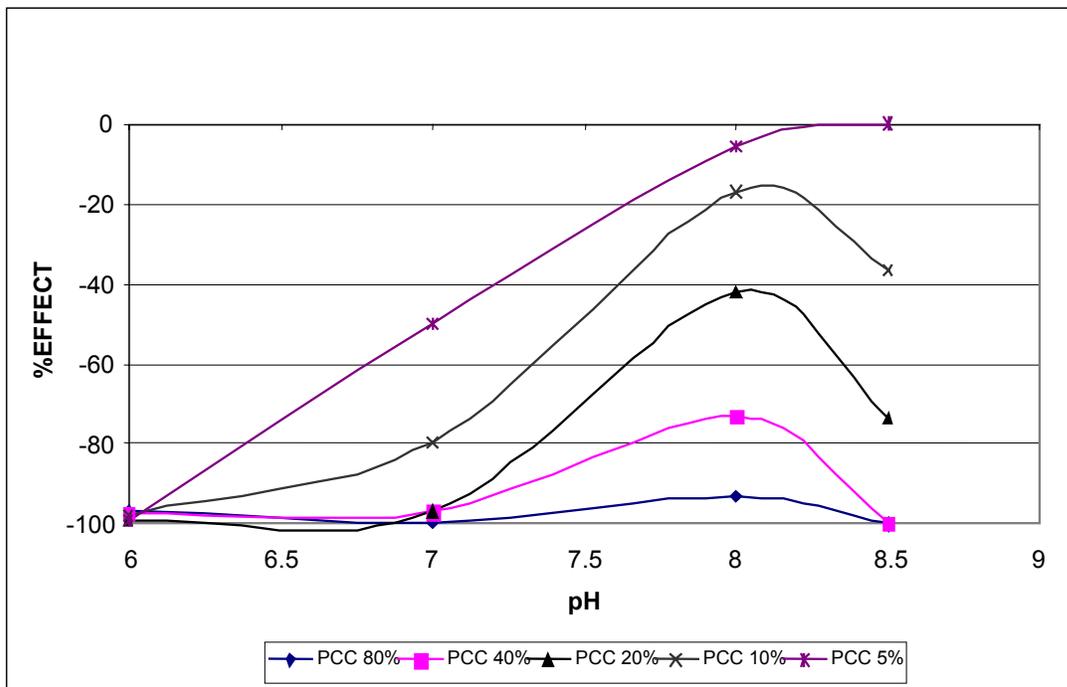


Figure 5.3.1.3.1. Algal growth inhibition as a function of pH for varying PCC leachate concentrations. %Effect indicates % algal growth inhibition in PCC leachates compared to control solutions.

The algal growth inhibitory effects of Al (at concentrations ranging from 500 µg/L to 2000 µg/L total aluminum added as soluble aluminum chloride) were studied at pH levels of 6, 7, 8 and 9. Results from these tests showed that pH is an important factor controlling aluminum toxicity to algae. Algal growth inhibition was observed to be a maximum at pH 6 and minimum at pH 7 relative to other pH levels (Figure 5.3.1.3.2). However, aluminum toxicity tended to increase again at alkaline pH levels (pH 8 and pH 9). At pH 6, the growth inhibitory effect of aluminum was nearly 100% at all concentrations. In contrast, at pH 7, the inhibitory effect was observed to be greatly

decreased at all concentrations, and far less than 50% in samples with 100, 250 and 500 $\mu\text{g/L}$ of aluminum. Precipitates were sometimes observed at the end of the algal tests at pH 6 and pH 7. Apparently, *S. capricornutum* exhibits an amphoteric-like response to aluminum, showing a minimum inhibitory response in the pH range of 7-8, with increasing inhibition at pH values below 7 and above 8. This is consistent with aluminum speciation and solubility predictions, which show minimum aluminum solubility near pH 7 and changing speciation from the Al^{3+} ion to aluminum hydroxide complexes as pH is increased from acidic to basic values (Snoeyink and Jenkins, 1980).

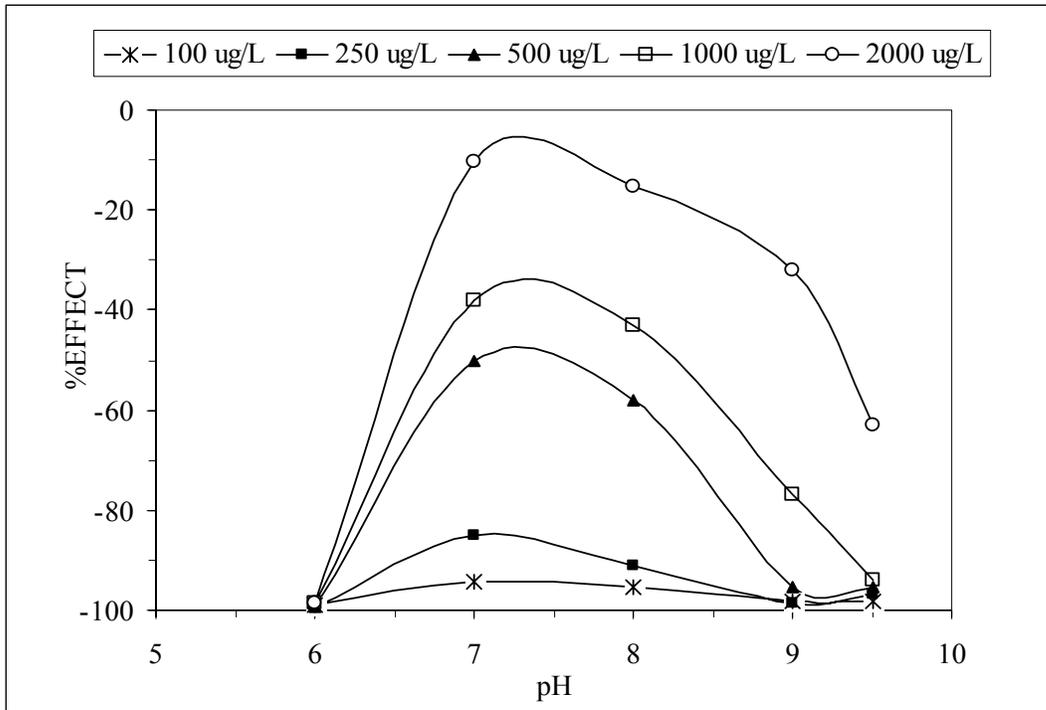


Figure 5.3.1.3.2. Algal growth inhibition as a function of pH for varying aluminum concentrations (added as AlCl_3). %Effect indicates % algal growth inhibition in AlCl_3 solution compared to control solutions.

Aluminum speciation was simulated using the computer program MINEQL+ based on the measured monomeric inorganic Al for each pH level (Lee, 2000). Monomeric, inorganic Al was used for simulation because it is this component that is most likely to be in equilibrium. Results indicated that $\text{Al}(\text{OH})^{2+}$ was the predominant soluble aluminum species at pH 6, with Al^{3+} also being important. The simulation showed that polymeric Al might also have been formed in relative abundance at pH 6. Thus, the maximum toxicity observed at pH 6 could be due to the additive effect of both highly toxic monomeric and polymeric soluble ions in the solution. At pH 7, the significant reduction ($p < 0.05$) observed in Al toxicity to *S. capricornutum* could be due to the formation of precipitated forms of Al. Al may also have precipitated with phosphorus, thus inhibiting algal growth.

In general, algal growth inhibitory effects decreased between pH 7 and pH 8 in PCC leachates. Correspondingly, in AlCl₃ solution lowest effect was observed at pH 7. It should be noted here that the chemistry of PCC leachate is much more complex than the chemistry of aluminum chloride solution alone. Chemical analysis of PCC leachate has indicated significant levels of calcium (~700 mg/L) apart from aluminum (~2.5 mg/L). The presence of high levels of calcium at high pH values could significantly affect the algal toxicity (Diaz et al. 1994). Based on the results from algal toxicity tests, chemical analysis and aluminum speciation modeling using MINEQL+, it can be concluded that aluminum toxicity to algae has been significantly affected by pH variation.

5.3.2 Flat Plate Test

5.3.2.1 Chemical analysis

Flat plate leaching tests were used to determine the rate of leaching of contaminants from a material surface. In these tests, the material (78.5 cm² of flat surface, 6.25 cm deep) was placed in the bottom of a beaker and the beaker was then filled with 1 liter of distilled water and stirred. The flux of contaminants (mg/cm²-hr) then was determined by the increase of concentration in the overlying water as a function of time. Results for calcium and TOC in leachate from the PCC without and with plasticizer in the flat plate experiments are shown in Figure 5.3.2.1 and Figure 5.3.2.2, respectively. The chemical analysis data are summarized in Table 5.3.2.1. The equations for power function increase of calcium and aluminum concentrations (determined by linear regression) are given as:

PCC-without-plasticizer	$C_{Ca} = 4.2 t^{0.32}$	$(R^2 = 0.94)$
PCC-without-plasticizer	$C_{Al} = 4.27 t^{-0.55}$	$(R^2 = 0.41)$
PCC-with-plasticizer	$C_{Ca} = 5.83 t^{0.26}$	$(R^2 = 0.93)$
PCC-with-plasticizer	$C_{Al} = 10.95 t^{-0.19}$	$(R^2 = 0.19)$

For example, at a time of 1 hr, for a volume of 1 L and surface area of 78.5 cm², the release rate, dC/dt, is 1.34 mg/L-hr, and the resulting flux is $F = 1.91 \times 10^{-1}$ mg/cm²-hr for calcium. Aluminum concentration in the flat plate leachate was about 2 mg/L and slightly decreased with time due to decreasing pH as shown in Figure 5.3.2.2.

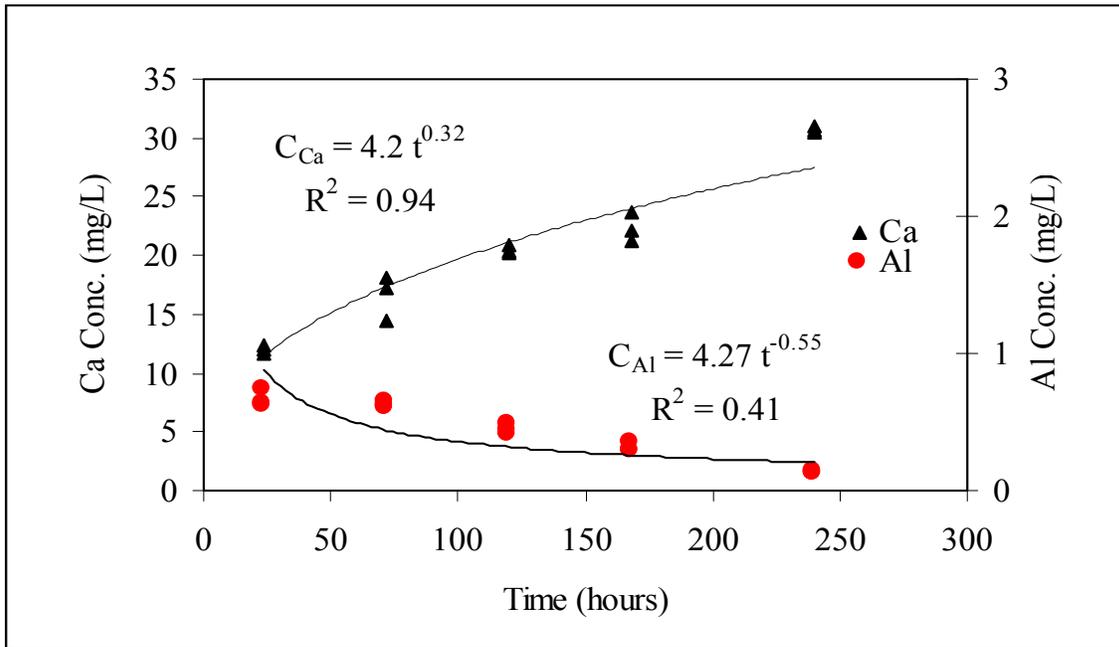


Figure 5.3.2.1. Flat plate leaching results for PCC-without-plasticizer, calcium and aluminum concentrations as a function of time (triplicate experiments).

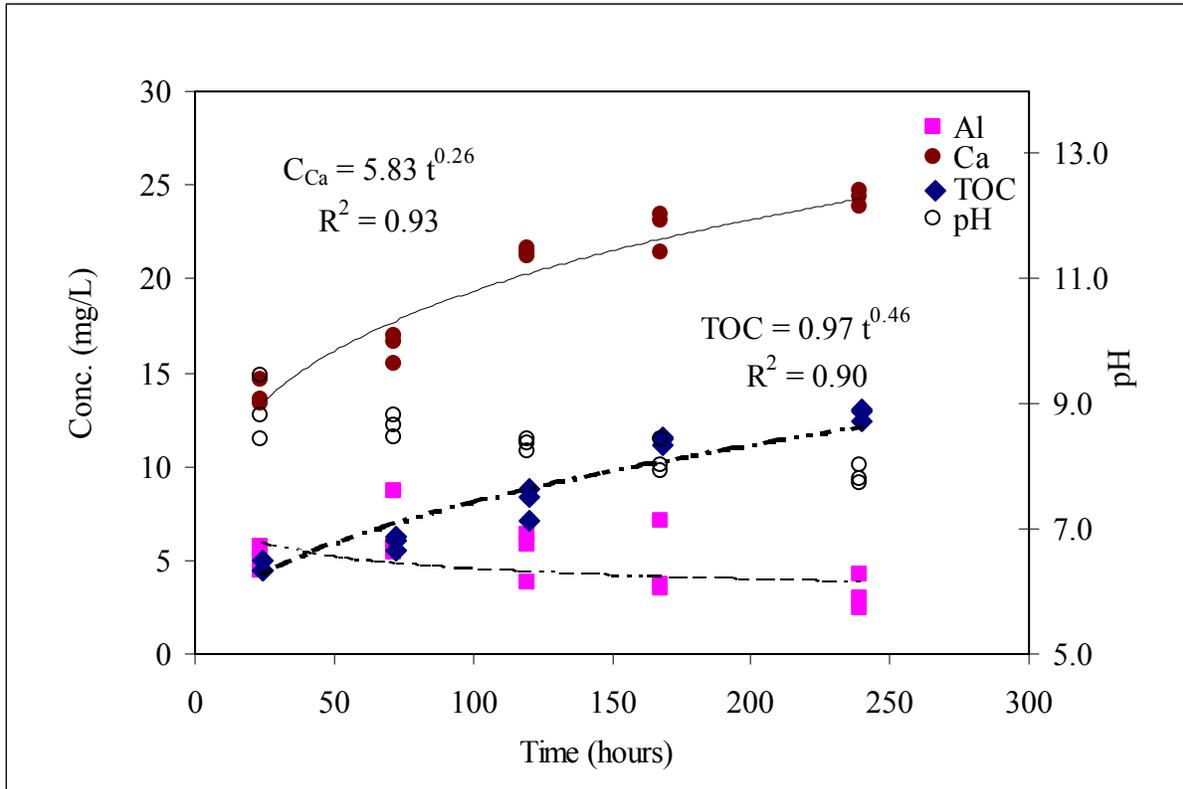


Figure 5.3.2.2. Flat plate leaching results for PCC-with-plasticizer: calcium, aluminum, and TOC concentrations as a function of time (triplicate experiments).

5.3.2.2 Toxicity analysis

PCC-with-plasticizer: Flat plate leachates collected on day 1 indicated an EC50 value of 31% (average of three replicates). Day 10 leachates indicated an EC50 value of 27%. As evident from Figure 5.3.2.2.1, only a small increase in algal toxicity was observed in leachates collected between day 1 and day 10. Results also indicated a good correspondence between toxicity and chemistry of the collected leachates.

PCC-without-plasticizer: Results indicated no detectable toxicity for *S. capricornutum* in all the flat plate leachates collected between day 1 and day 10.

In conclusion, only the flat plate leachates from PCC-with-plasticizer material indicated moderate algal toxicity and the toxicity level increased only a little between day 1 and day 10.

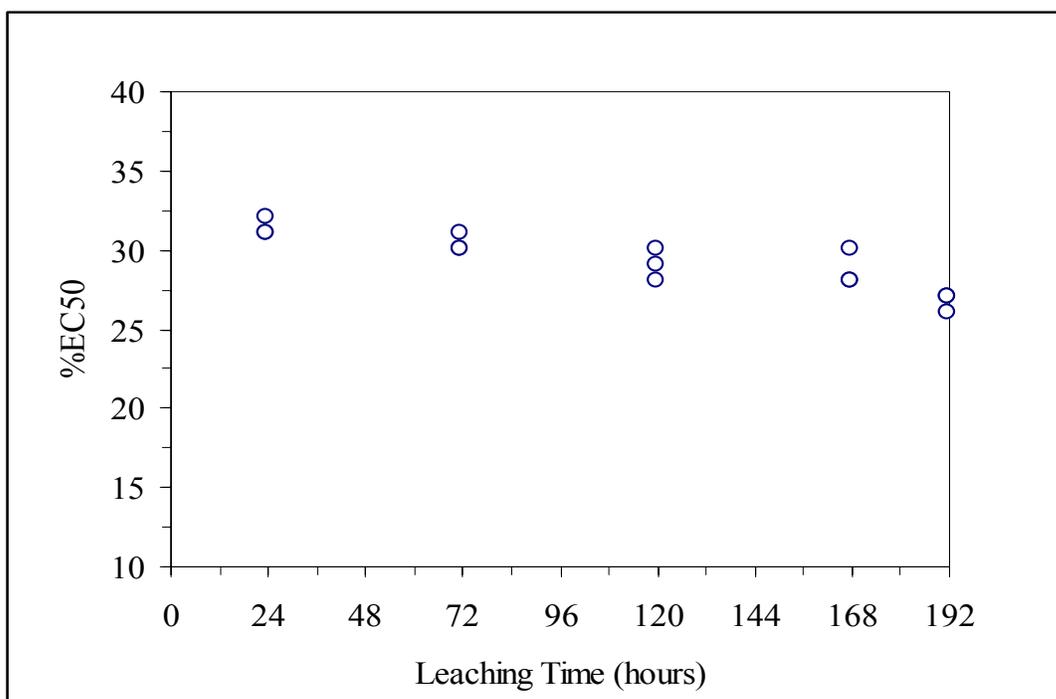


Figure 5.3.2.2.1 Algal toxicity of PCC-with-plasticizer leachates as a function of leaching time (triplicate experiments).

5.3.3 PCC Photolysis With and Without Plasticizer

5.3.3.1 Chemical analysis

The results of the photolysis degradation of TOC in PCC-with-plasticizer leachate are shown in Figure 5.3.3.1.1 and Figure 5.3.3.2.2. Over 7 days, no changes in TOC concentrations were observed. The lack of change in TOC indicates only nonvolatile organics are present. No changes in metals concentration were observed. As metals are nonvolatile, results confirm their conservation in the solution. The chemical analyses data are summarized in Table 5.3.3.1 at the end of this chapter.

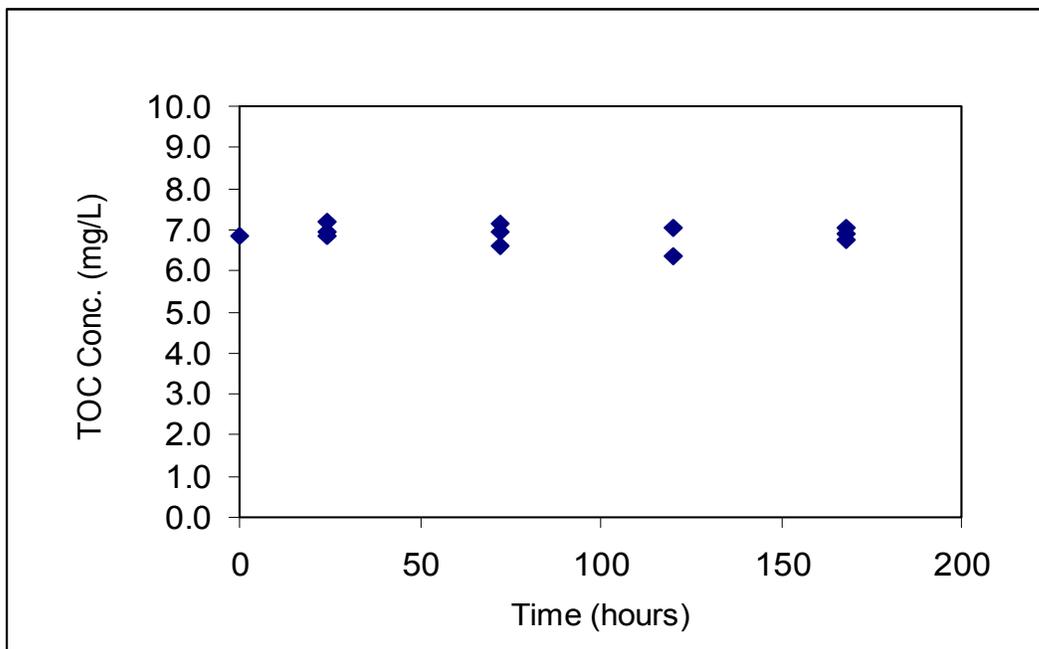


Figure 5.3.3.1.1. TOC concentration as a function of time in PCC-with-plasticizer leachate photolysis experiment (triplicate experiments).

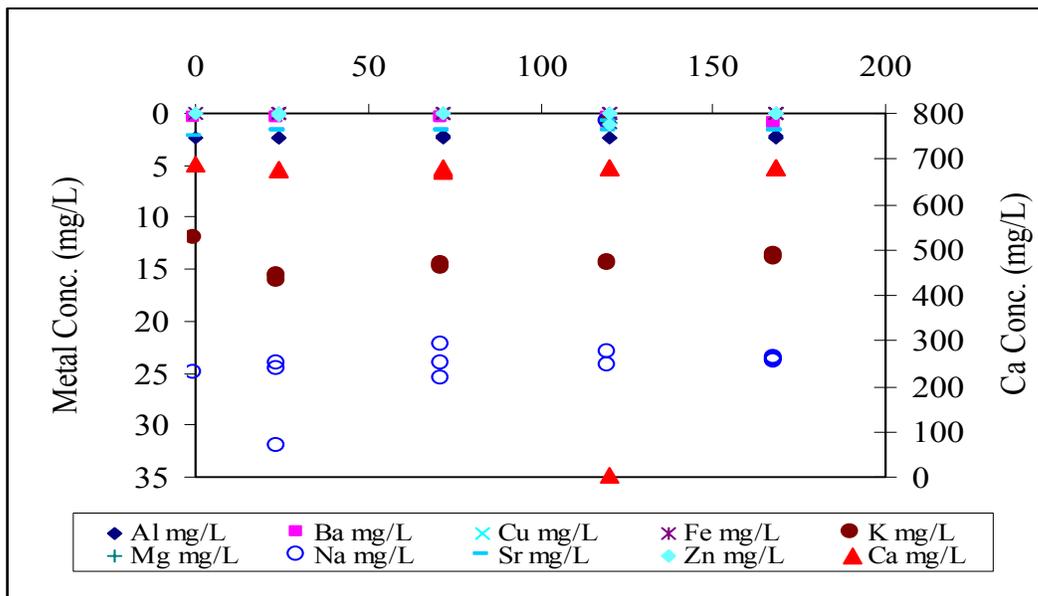


Figure 5.3.3.1.2. Metals concentration as a function of time in PCC-without-plasticizer leachate photolysis experiment (triplicate experiments).

5.3.3.2 Toxicity analysis

PCC-with-plasticizer and PCC-without-plasticizer leachates indicated EC50 values of 21% and 43% (initial algal toxicity at 0-hour) respectively. After photolysis, day 1 and day 10 PCC-with-plasticizer leachates exhibited EC50 values of 20% and 21% respectively. Similarly, day 1 and day 10 PCC-without-plasticizer leachates indicated EC50 values of 46% and 50% after photolysis. From Figure 5.3.3.2.1 it is evident that there was no significant change in the algal EC50 values by photolysis for both PCC with- and without plasticizer leachates. Correspondingly, chemical analyses also indicated no detectable change in the metal and TOC concentrations of the leachates during the photolysis of both the leachates.

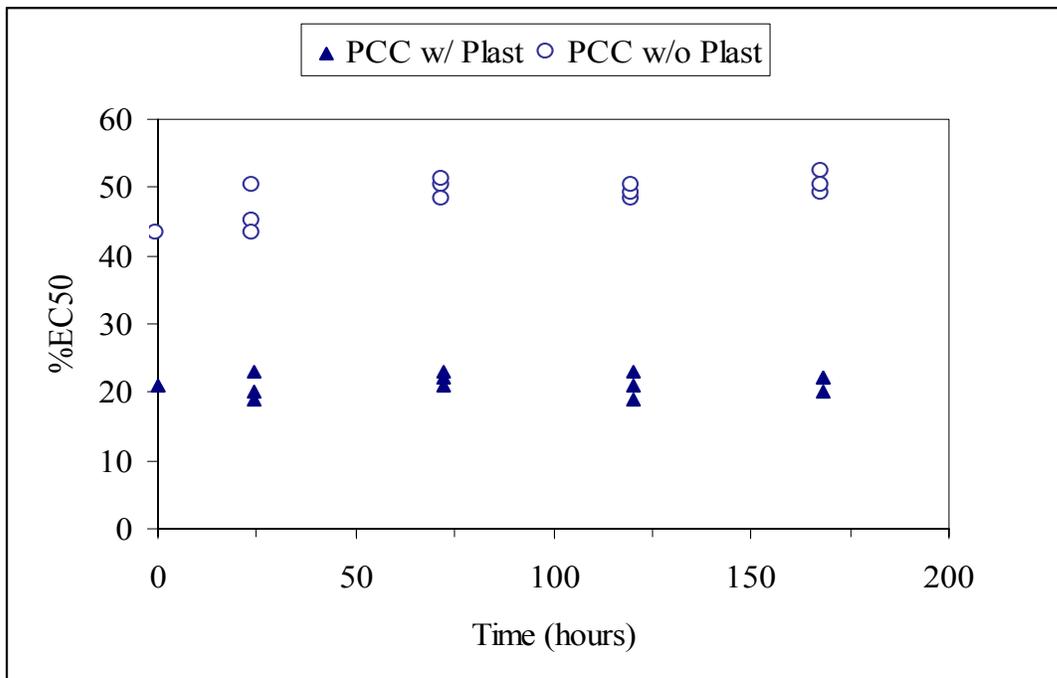


Figure 5.3.3.2.1. Relationship between the algal %EC50 values and exposure time of PCC with and without plasticizer leachates during the photolysis experiment (triplicate experiments).

5.3.4 Soil Sorption Tests

5.3.4.1 Chemical analysis

Soil sorption of leachate from PCC with and without plasticizer was studied by preparing 6 soil:leachate mixtures. The PCC samples with and without plasticizer were leached for 24-hours, filtered through a 0.45 micrometer filter, and added to Woodburn and Sagehill soils. Both soil types demonstrated the ability to adsorb metal ions and reduce toxicity in algal tests. The six solid:liquid (grams:mL) ratios were the standard 1g: 4 mL as well as 1:10, 1:20, 1:40, 1:100, and 1:200. PCC with and without plasticizer leachate soil sorption data are given in the summary Table 5.3.1.1.

The sorption characteristics of both test soils (Woodburn and Sagehill) for 24-hr PCC with and without plasticizer batch leachate were analyzed and evaluated using the three soil isotherm models employed in this study: linear, Langmuir and Freundlich. Only equilibrium models were used to determine the maximum sorption and desorption capacities and distribution coefficients from the experimental data. The partitioning of solutes between liquid and solid phases in a porous medium as determined by laboratory experiments is commonly expressed in two-ordinate graphical form, where mass adsorbed per unit mass dry solids (C_s) is plotted against the concentration of the constituent C in solution.

Isotherm plots of calcium data and isotherm equations for Woodburn and Sagehill soils are shown in Figures 5.3.4.1.1 and 5.3.4.1.2, and Figures 5.3.4.1.3 and 5.3.4.1.4, respectively. The fitted parameters are shown in Tables 5.3.4.1.1 and 5.3.4.1.2.

The chemical analysis data are summarized in Table 5.3.1.1. For the relevant metals sorption, Sagehill is as effective as the Woodburn soil, as evidenced by maximum sorbed concentrations in a similar range. With the exception of the Langmuir isotherm for the Sagehill data, all fits are statistically significant at the 95% level, with the Freundlich isotherm model tending to have the highest R^2 values. However, it is unclear that an asymptotic value of the saturation concentration has been reached for any of the four sorption experiments, and the regressions should be used with care.

Table 5.3.4.1.1.. Summary of isotherm parameters for calcium adsorption on Woodburn and Sagehill soils for PCC-without-plasticizer leachate.

Soil type	Langmuir			Freundlich			Linear	
	Q	b	R^2	K_f	N	R^2	K_d	R^2
Woodburn	33.44	4.5×10^{-3}	0.84	9.5×10^{-1}	0.54	0.97	5×10^{-2}	0.98
Sagehill	NA	NA	NA	1.5×10^{-2}	1.12	0.89	4.0×10^{-2}	0.86

Table 5.3.4.1.3. Summary of isotherm parameters for calcium adsorption on Woodburn and Sagehill soils for PCC-with-plasticizer leachate.

Soil type	Langmuir			Freundlich			Linear	
	Q	b	R ²	K _f	N	R ²	K _d	R ²
Woodburn	28.37	6.6x10 ⁻³	0.96	1.6	0.42	0.96	3.15x10 ⁻²	0.92
Sagehill	NA	NA	NA	1.0x10 ⁻²	1.09	0.74	2.0x10 ⁻²	0.55

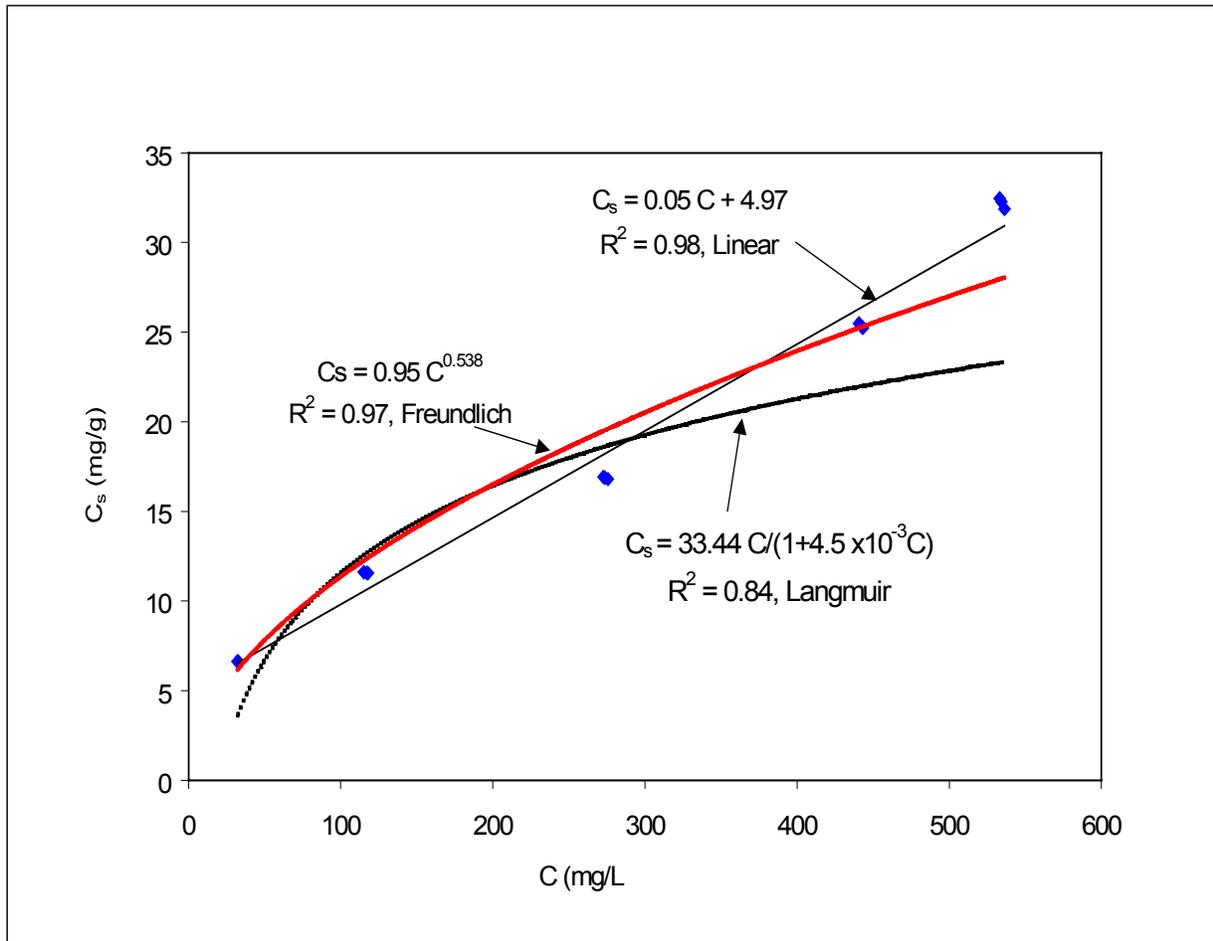


Figure 5.3.4.1.1. Isotherm sorption models (Freundlich, Langmuir, and linear) for calcium of PCC-without-plasticizer leachate sorption by Woodburn soil. Data points are shown for triplicate experiments.

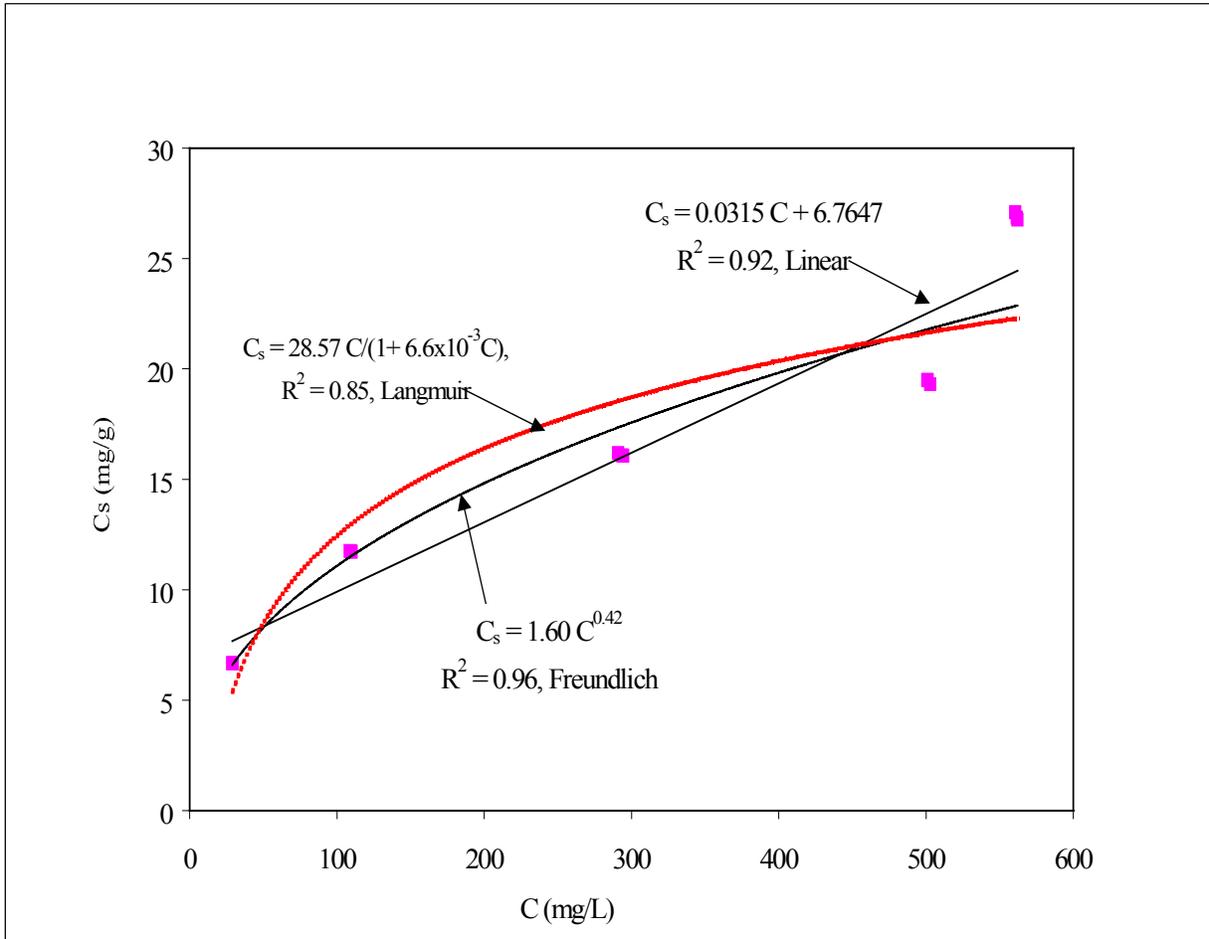


Figure 5.3.4.1.2. Isotherm sorption models (Freundlich, Langmuir, and linear) for calcium of PCC-with-plasticizer leachate sorption by Woodburn soil. Data points are shown for triplicate experiments.

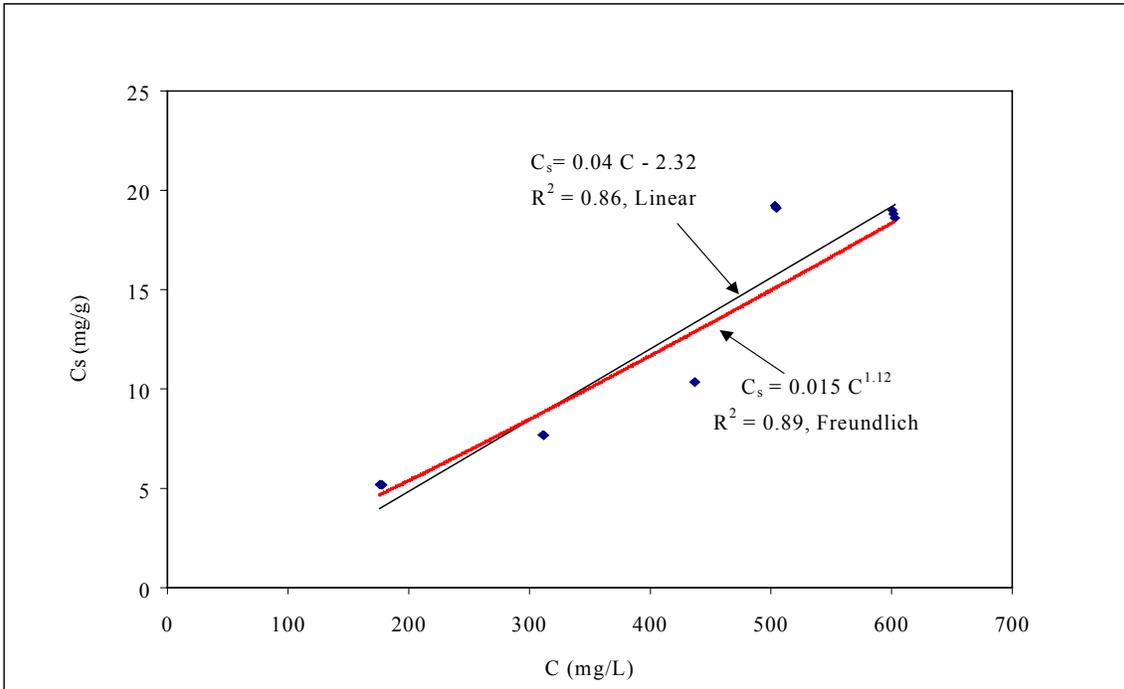


Figure 5.3.4.1.3. Isotherm sorption models (Freundlich and linear) for calcium of PCC without plasticizer leachate sorption by Sagehill soil. Data points are shown for triplicate experiments.

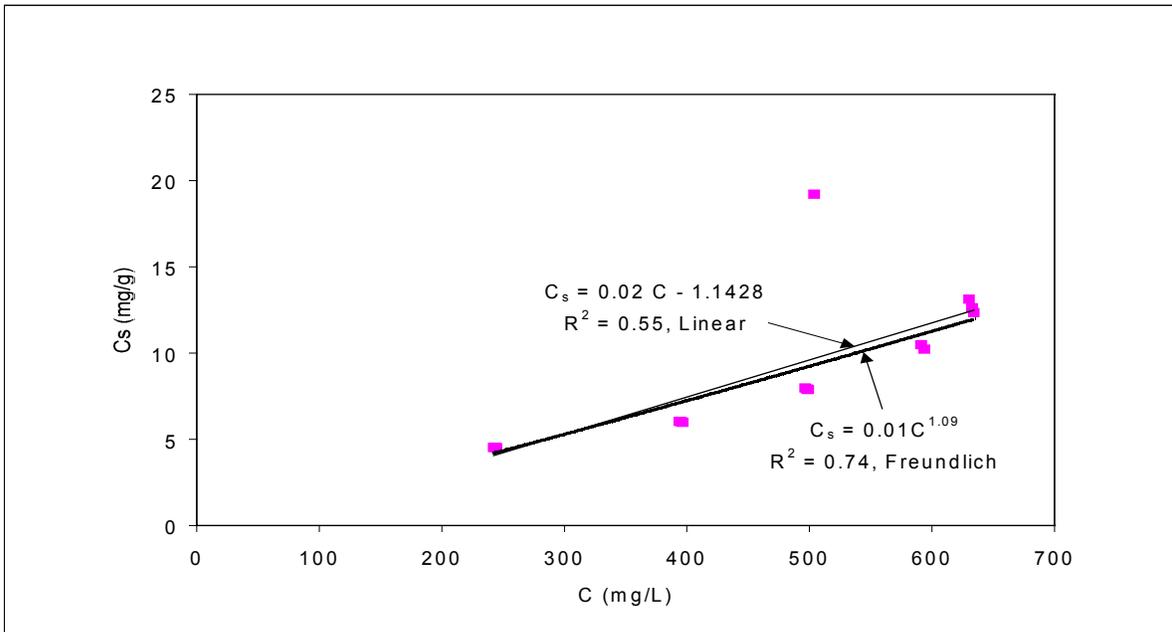


Figure 5.3.4.1.4. Isotherm sorption models (Freundlich and Linear) for calcium of PCC with plasticizer leachate sorption by Sagehill soil. Data points are shown for triplicate experiments.

5.3.4.2 Toxicity analysis

Batch sorption studies were performed to investigate the toxicity reduction of PCC leachates due to sorption by Woodburn and Sagehill soils. PCC leachate was added at soil-to-liquid ratios of 1:200, 1:100, 1:40, 1:20, and 1:10 and tumbled in a head-over-end rotator. Biological and chemical analyses were performed on leachates generated at the end of 24-hours.

PCC-with-plasticizer sorption on Woodburn soil: The initial PCC-with-plasticizer leachate indicated a 1/EC50 value of 5.6 for *S. capricornutum*. At 5 g/L and 10 g/L, no significant change in toxicity for *S. capricornutum* was observed (Figure 5.3.4.2.1). However, a 43%, 51%, and 65% reduction in toxicity (in toxic units) compared with the initial toxicity of the leachate was observed at 25 g/L, 50 g/L, and 100 g/L. These results along with chemical analyses indicate that constituents responsible for algal growth inhibition were reduced significantly by Woodburn soil from PCC-with-plasticizer leachates.

PCC-without-plasticizer sorption on Woodburn soil: The initial PCC-without-plasticizer leachate indicated a 1/EC50 value of 2.6 for *S. capricornutum*. Similarly to PCC-with-plasticizer, no significant reduction in the toxicity of PCC-without-plasticizer leachate was observed at 5 g/L and 10 g/L. From Figure 5.3.4.2.1, it is evident that at 25 g/L, 50 g/L and 100 g/L toxicity of the leachate was significantly reduced (by 30%, 40%, and 50% respectively) by the Woodburn soil. Chemical analyses also indicated good correspondence with toxicity results.

PCC-with-plasticizer sorption on Sagehill soil: The initial PCC-with-plasticizer leachate indicated a 1/EC50 value of 5.6 for *S. capricornutum*. Results indicated no significant reduction in algal toxicity at 5 g/L, 10 g/L, and 25 g/L (Figure 5.3.4.2.2). At 50 g/L and 100 g/L only a mild reduction in algal toxicity (by 15% and 16% respectively) was observed compared with the initial toxicity.

PCC-without-plasticizer sorption on Sagehill soil: The initial PCC-without-plasticizer leachate indicated a 1/EC50 value of 2.6 for *S. capricornutum*. At 5 g/L and 10 g/L no significant reduction in toxicity compared with the initial toxicity of the leachate was observed. However, a measurable reduction in toxicity was observed at 25 g/L, 50 g/L and 100 g/L (13%, 19%, and 30%) soil to liquid ratio in the Sagehill soil sorption test.

In comparing the algal toxicity reduction at 100 g/L (maximum soil mass tested), it was observed that Woodburn soil significantly reduced PCC-with-plasticizer and PCC-without-plasticizer leachate toxicity by 65% and 50%, respectively. In contrast, Sagehill soil exhibited only a mild reduction of algal toxicity by about 16% (for PCC-with-plasticizer) and 30% (PCC-without-plasticizer). The higher organic content Woodburn soil reduced the algal toxicity of both PCC leachates significantly more than the sandier Sagehill soil. From chemical data, calcium appears to be the dominant element inhibiting the growth of algal cells. In fact, there was a strong correspondence between reduction in calcium levels and reduction in algal 1/EC50 values. However, no similar reduction in

the levels of aluminum and TOC (a surrogate measure for plasticizer) associated with reduction in toxicity levels was observed. This discrepancy opens up a set of possible explanations. One possible explanation is that aluminum found in these samples is not entirely from PCC but also from the soils. For instance, aluminum levels increased from 2.3 mg/L to 12 mg/L in the PCC-with- plasticizer sorption test in 10 g/L and 100 g/L of Woodburn soil. This clearly indicates that there is additional leaching of aluminum from soils also. However, results from toxicity tests indicated significant decrease in algal toxicity inspite of this higher aluminum levels in soil sorption samples. It is important to note here that aluminum toxicity to aquatic life is strongly dependent upon the type of species and forms, such as inorganic and organic (EPA, 1988). Aluminum forms complexes with many types of both synthetic and natural organic material including humic and fulvic acids. In general, organic-bound aluminum is not available for algal uptake and the presence of organic C should, in most cases, ameliorate algal toxicity (Gensemer and Playle, 1999). Using synthetic organic chelator EDTA, Riseng et al. (1991) found that increasing EDTA concentrations indeed diminished toxicity consistent with decreases in Al^{3+} activity. Thus, it is likely that the significant decrease in algal toxicity can mostly be attributed to aluminum complexation with organics leached from soils.

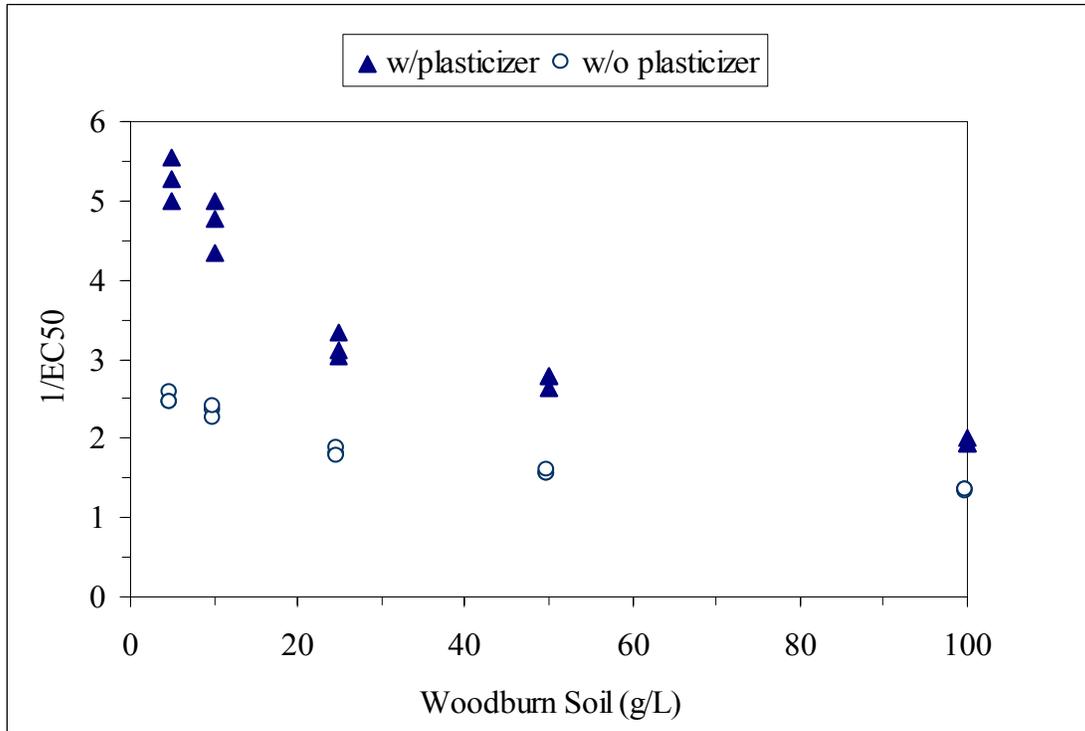


Figure 5.3.4.2.1. Relationship between algal toxicity and Woodburn soil mass in g/L PCC leachates in the sorption test (triplicate experiments).

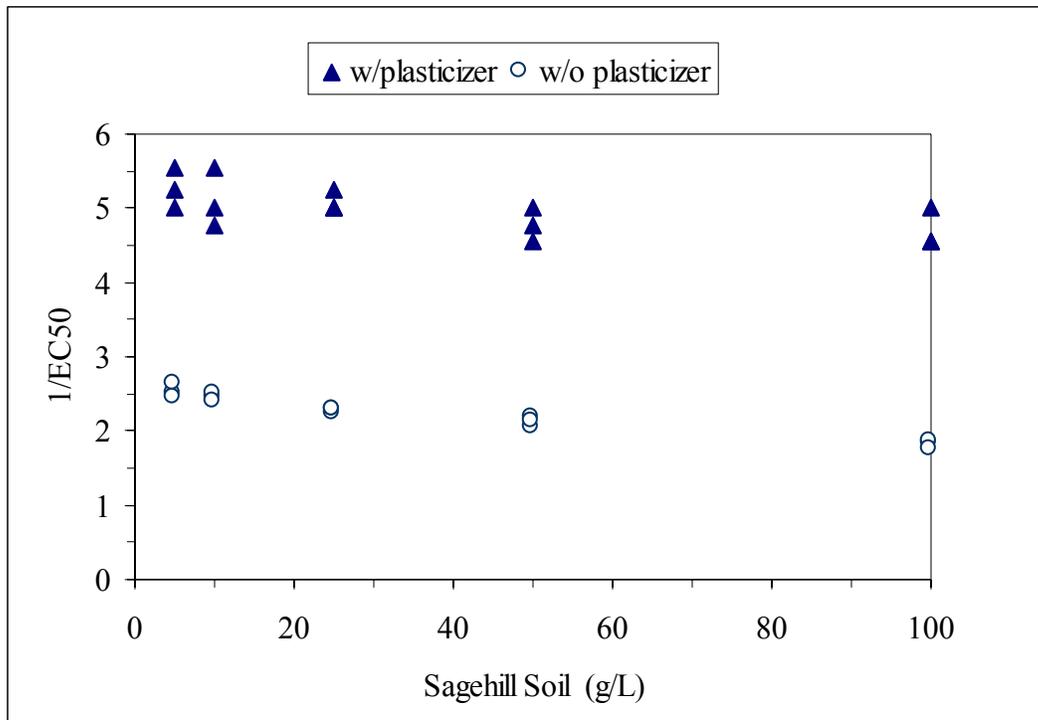


Figure 5.3.4.2.2. Relationship between algal toxicity and Sagehill soil mass in g/L PCC leachates in the sorption test (triplicate experiments).

5.3.5 GC/MS Analysis of PCC With and Without Plasticizer

Summary of Method: Calibration and QA/QC procedures follow original EPA methods 1624 and 1625 (Gas Chromatography-Mass Spectrometry Methods for Analysis of the Semivolatile Organic Priority Pollutants, USEPA, 1989c). Extraction of polycyclic aromatic hydrocarbons (PAHs) from the samples is according to the method of Shackelford and McGuire, Environmental Research laboratory, EPA (1986). This method consists of extraction of the organics into methylene chloride (CH_2Cl_2), drying of the extract by passing it through a sodium sulfate column, concentration of the extract by Kuderna-Danish evaporation, and analysis of the concentrate by GC/MS.

Instrument: The instrument used to separate and quantify each component was a Hewlett-Packard Model 6890 gas chromatograph with a Hewlett-Packard Model 5793 mass-spectrometer detector. The column used in the GC was a HP DB5 fused silica capillary column (30 m length, 0.25 mm I.D., 0.25 μm film thickness). The GC/MS operating conditions (Method File) are specified below:

An initial oven temperature of 50°C is held for 1.5 minutes and then increased at a rate of 10°C per min to achieve a temperature of 200°C. The temperature is further increased from 200°C to 300°C at a rate of 20°C per min and held for 5 minutes while injection and source temperatures are kept at a constant 250°C and 280°C, respectively. Helium was the carrier gas for this method.

The original GC/MS spectrum for PCC-without-plasticizer shows that more than 30 peaks were detected (Figure 5.3.5.1). Table 5.3.5.1 shows organic compounds were determined from the GC/MS library matches for the detectable peaks. Figure 5.3.5.2 also shows 2-Chlorocyclohexen-1-one ($\text{C}_6\text{H}_8\text{O}$) and the GC/MS library match.

Table 5.3.5.1. Organic compounds determined from the GC/MS library match for PCC-without-plasticizer.

Compound (ID)	Scan Time (min)	Quality of match (%)
2-Chlorocyclohexen-1-one ($\text{C}_6\text{H}_8\text{O}$)	5.639	83
1-Hexanol, 2-ethyl ($\text{C}_8\text{H}_{18}\text{O}$)	7.082	83
Octadecane, 3-ethyl-5-(2-ethylbutyl) ($\text{C}_{26}\text{H}_{54}$)	10.735	83
Nonanoic acid ($\text{C}_9\text{H}_{18}\text{O}_2$)	11.052	87
Docosane ($\text{C}_{22}\text{H}_{46}$)	11.374	86
Eicosane ($\text{C}_{20}\text{H}_{42}$)	11.518	91
Hexadecane ($\text{C}_{16}\text{H}_{34}$)	11.506	89
Decanoic acid ($\text{C}_{10}\text{H}_{20}\text{O}_2$)	12.300	94
Heneicosane ($\text{C}_{21}\text{H}_{44}$)	18.369	91
Decahydro-9-ethyl-4,4,8,10-tetramethylnaphthalene ($\text{C}_{16}\text{H}_{30}$)	20.636	89

File : D:\HPCHEM\1\DATA\PCC_WOPL.D
Operator : Mohammad Azizian
Acquired : 13 Jan 1999 10:09 am using AcqMethod MFA_HW
Instrument : OSU GC/MS
Sample Name : PCC WO Plasticizer
Misc Info : EPA Method CH2Cl2 2 uL Inj.
Vial Number: 1

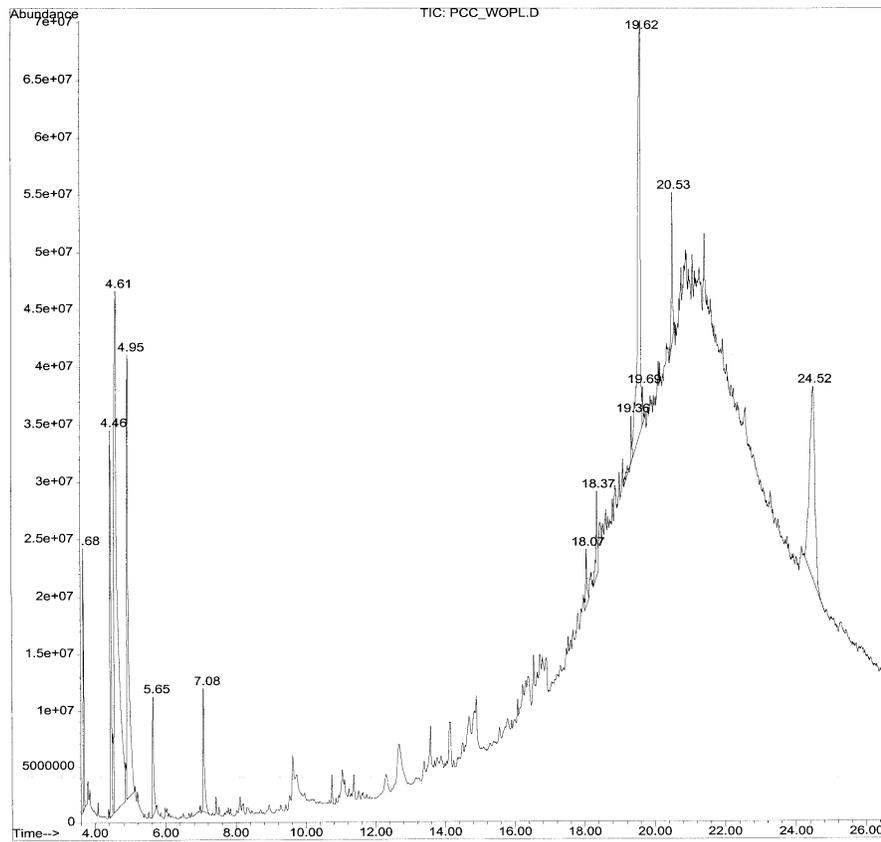


Figure 5.3.5.1. GC/MS spectrum of the PCC-without-plasticizer leachate, abundance vs. time.

Library Searched : D:\DATABASE\NBS75K.L
Quality : 83
ID : 2-Cyclohexen-1-one

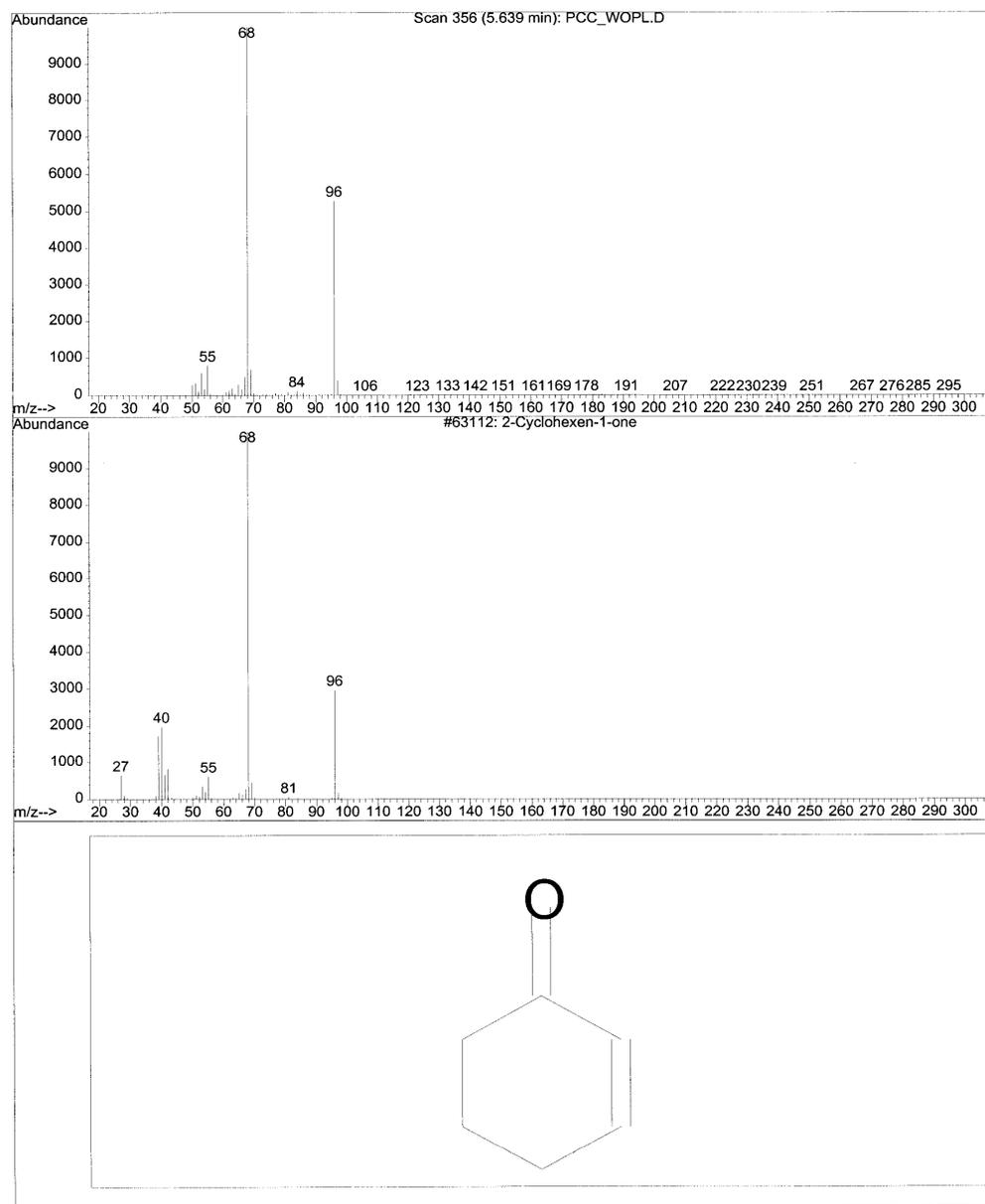


Figure 5.3.5.2. GC/MS spectrum of 2-chlorocyclohexene-1-one (C_6H_8O) and the GC/MS library match, abundance vs. time.

The original GC/MS spectrum for PCC-with-plasticizer shows that more than 50 peaks were detected (Figure 5.3.5.3). Table 5.3.5.2 shows organic compounds that were determined from the GC/MS library matches for the detectable peaks

Table 5.3.5.2. Organic compounds determined from the GC/MS library match for PCC-with-plasticizer.

Compound (ID)	Scan Time (min)	Quality of match (%)
Isoquinoline (C ₉ H ₇ N)	10.383	91
Dodecane, 2,6,11-trimethyl (C ₁₅ H ₃₂)	11.378	89
Octadecane (C ₁₈ H ₃₈)	16.084	87
1-Pentadecene (C ₁₅ H ₃₀)	15.894	87
Phenol, nonyl (C ₁₅ H ₂₄ O)	16.262	94
Pentadecane (C ₁₅ H ₃₂)	16.544	86
1,2-Benzenedicarboxylic acid, diisooctyl ester	16.837	84
Bis (2-ethylexyl) phthalate (C ₂₄ H ₃₈ O ₄)	21.428	91
Eicosane, 2-methyl (C ₂₁ H ₄₄)	21.618	80

No PAH compounds were detected in both PCC with and without plasticizer, and all other organic compounds identified by GC/MS were present in trace quantities expected to be nontoxic; as such, these compounds probably do not contribute to the observed toxicity of the sample.

File : D:\HPCHEM\1\DATA\PCC_WPL.D
Operator : Mohammad Azizian
Acquired : 13 Jan 1999 11:55 am using AcqMethod MFA_HW
Instrument : OSU GC/MS
Sample Name: PCC W /Plasticizer
Misc Info : EPA Method CH2Cl2 2 uL Inj.
Vial Number: 1

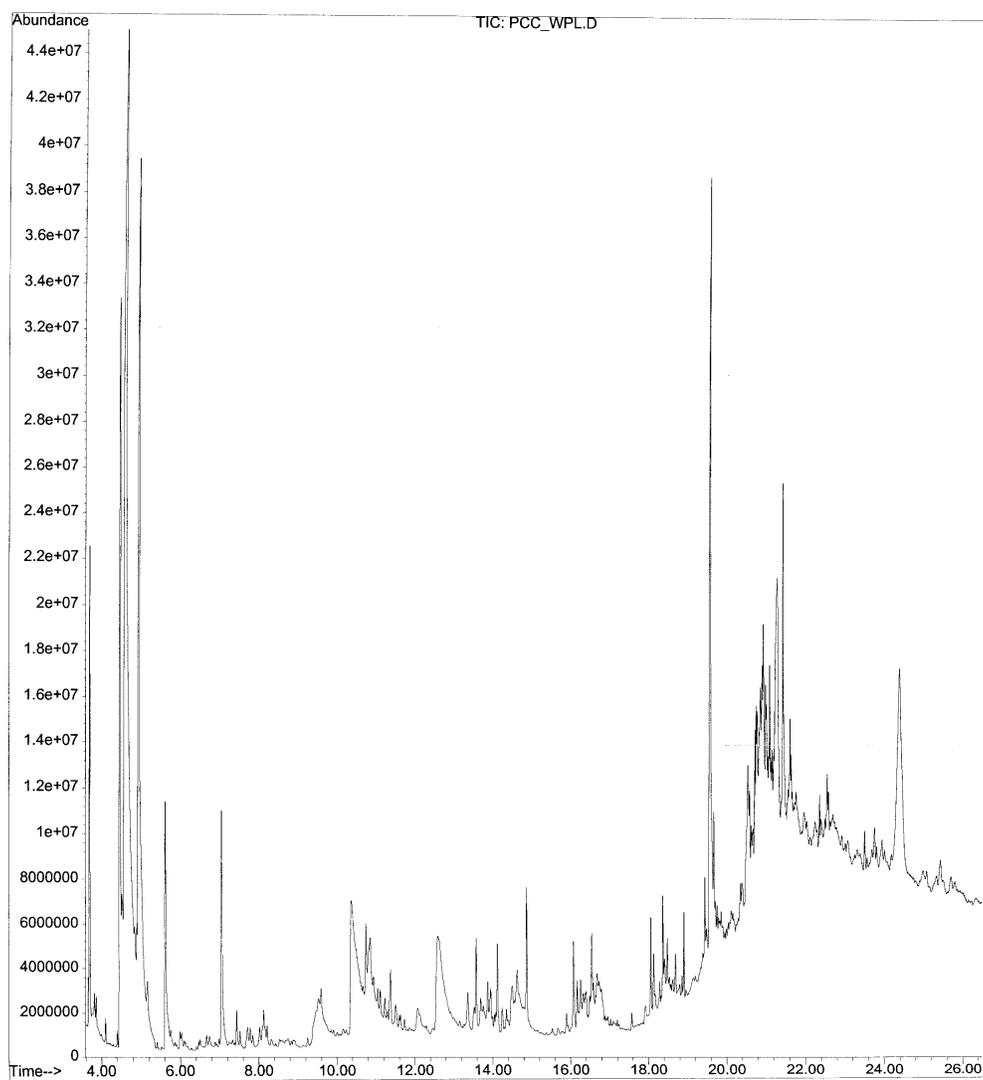


Figure 5.3.5.3. GC/MS spectrum of the PCC-with-plasticizer leachate, abundance vs. time.

5.4 SUMMARY AND CONCLUSIONS

PCC (with and without plasticizer admixture) was subjected to the complete Phase II testing methodology to determine leachate characteristics and parameters for the removal/reduction/retardation (RRR) factors in the fate and transport model. Laboratory tests included batch and long-term leaching, flat plate leaching, and sorption to Sagehill and Woodburn soils. Photolysis tests were performed on the leachate and on separately prepared solutions of the plasticizer. Additional algal toxicity tests were run on PCC leachates and soluble AlCl_3 solutions at varying pH values to further investigate the influence of pH on soluble aluminum toxicity.

Both PCC-with and without-plasticizer leachates showed high levels of calcium (~700 mg/L) and significant levels of aluminum (2-5 mg/L). PCC-with-plasticizer had slightly higher level of TOC compared with PCC-without-plasticizer. Algal growth inhibitory effects by PCC leachates were attributed to phosphorus limitation and co-precipitation due to high levels of calcium and aluminum at alkaline pH. The higher inhibitory effect exhibited by PCC-with-plasticizer leachate compared with PCC-without-plasticizer could be due to the additive effect of plasticizer along with calcium and aluminum. In batch sorption studies, Woodburn soil showed greater sorption capacity for calcium than Sagehill soil. Similarly, Woodburn soil showed greater removal of toxicity than Sagehill soil. In addition, aluminum and TOC were released from Woodburn and Sagehill soils to the PCC leachates, and thus a simple relationship for aluminum and TOC sorption could not be derived from sorption studies. No substantial change in organics was observed due to photolysis of PCC leachates. Toxicity results also indicated no significant change ($p > 0.05$) between controls and photolysis samples.

Additional algal toxicity tests run on PCC leachates and soluble AlCl_3 solutions at varying pH values demonstrated the important effect of pH on aluminum toxicity (measured as inhibition of algal growth). Results showed that algal growth inhibition is minimum in the pH range of 7-8 that is most typical of natural soils, and higher at pH values below or above this range. Changes in aluminum toxicity with pH value may be due to aluminum removal by precipitation or to changes in soluble aluminum speciation. For PCC leachates, algal growth inhibition may also be caused by phosphate nutrient precipitation with either aluminum or calcium.

In conclusion, although leachates from both PCC materials contain Al and Ca at levels likely to cause algal growth inhibition, once leached into the soil, factors such as pH, competing cations, and organic complexation significantly reduce the bioavailability and subsequent toxicity of these contaminants. Laboratory results from Phase I and Phase III showed significant reduction and complete removal of algal toxicity after soil sorption. These results indicate that the use of PCC and PCC with plasticizers should not be of concern regarding aquatic toxicity. Over all, there was a good correspondence between the toxicity and chemistry data of the PCC leachates generated during leaching and RRR process testing methodology. It should be noted that the reasons stated for toxicity and its subsequent removal by soil sorption are based mostly on cited literature; this study did not pinpoint the causes.

Table 5.3.1.1. Task 4 Summary data for chemical and toxicity analyses.

Task 4: Tests of Portland Cement and Portland Cement Concrete																
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results					Chemistry Results								
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Leachate													
%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.														
	PCC w/o Plasticizer Leaching Kinetics															
1	PCC_WOPK 1HR	4208410	39	35	44	2.484	0.267	573.242	BD	9.394	BD	14.084	1.001	BD	1.20	11.71
2	PCC_WOPK 1HR	4208411	43	39	45	3.040	0.264	573.976	BD	9.450	BD	14.317	1.003	BD	1.21	11.62
3	PCC_WOPK 1HR	4208412	37	35	41	2.662	0.275	571.621	BD	9.223	BD	14.109	1.000	BD	1.32	11.65
4	PCC_WOPK 4 HRS	4208413	40	37	43	2.133	0.268	579.364	BD	9.680	BD	15.839	1.012	BD	2.67	11.80
5	PCC-WOPK 4 HRS	4208414	42	39	45	2.116	0.270	582.499	BD	9.573	BD	15.811	1.018	BD	2.75	11.64
6	PCC-WOPK 4 HRS	4208415	39	35	41	2.109	0.271	580.002	BD	9.507	BD	15.425	1.022	BD	2.66	11.59
7	PCC _p WOPK 12 HRS	4208416	38	36	41	2.823	0.260	610.281	BD	11.757	BD	21.164	1.086	BD	2.74	11.71
8	PCC_WOPK 12 HRS	4208417	42	39	45	2.409	0.259	617.678	BD	11.616	BD	21.479	1.083	BD	2.77	11.76
9	PCC_WOPK 12 HRS	4208418	36	33	40	2.596	0.250	619.900	BD	11.678	BD	21.214	1.080	BD	2.79	11.76
10	PCC_WOPK 24 HRS	4208419	38	35	42	2.447	0.660	695.647	BD	15.110	BD	24.271	2.109	BD	3.56	12.28
11	PCC_WOPK 24HRS	4208420	40	36	43	2.058	0.664	704.648	BD	15.860	BD	25.678	2.151	BD	3.66	12.20
12	PCC_WOPK 24HRS	4208421	39	36	45	2.153	0.657	702.132	BD	15.405	BD	24.874	2.128	BD	3.57	12.25
13	PCC_WOPK DAY 3	4209410	38	33	43	2.640	0.603	585.613	BD	22.664	BD	47.352	2.121	BD	7.47	12.10
14	PCC_WOPK DAY 3	4209411	41	36	45	2.644	0.611	591.669	BD	23.591	BD	47.368	2.163	BD	7.39	12.14
15	PCC_WOPK DAY 3	4209412	40	36	45	2.592	0.607	586.645	BD	23.327	BD	47.320	2.123	BD	7.66	12.10
16	PCC_WOP-1 DAY5	4209413	42	37	47	2.090	0.833	599.269	BD	24.956	BD	51.436	2.691	BD	8.09	12.03
17	PCC_WOP-2 DAY5	4209414	39	35	41	2.152	0.843	604.618	BD	25.324	BD	52.374	2.734	BD	8.12	11.95
18	PCC_WOP-2 DAY6	4209415	40	36	43	2.133	0.845	602.763	BD	25.155	BD	51.867	2.718	BD	8.21	12.70
19	PCC_WOP-1 DAY 7	4209416	37	35	42	2.543	0.726	443.290	BD	34.279	BD	84.295	2.699	BD	9.48	12.00
20	PCC_WOP-2 DAY7	4209417	36	33	42	2.662	0.730	447.412	BD	34.197	BD	85.188	2.709	BD	9.68	12.05
21	PCC_WOP-2 DAY7	4209418	41	36	46	2.600	0.743	444.661	BD	34.244	BD	84.992	2.732	BD	9.55	11.99

Table 5.3.1.1. Task 4 Summary data for chemical and toxicity analyses (cont.).

Task 4: Tests of Portland Cement and Portland Cement Concrete																
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results			Chemistry Results										
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Leachate													
			%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.											
	PCC w/Plasticizer Leaching Kinetics															
1	PCC_WPK 1HR	4208401	55	51	60	2.974	0.282	593.635	BD	9.072	BD	14.887	1.035	BD	6.70	11.87
2	PCC_WPK 1 HR	4208402	50	46	54	2.219	0.238	636.273	BD	7.428	BD	12.312	0.893	BD	6.72	11.82
3	PCC_WPK 1 HR	4208403	52	47	56	2.616	0.259	612.654	BD	8.130	BD	13.609	0.964	BD	6.71	11.83
4	PCC_WPK 4 HRS	4208404	34	30	39	2.196	0.304	669.260	BD	9.643	BD	16.638	1.174	BD	6.79	11.70
5	PCC_WPK 4 HRS	4208405	34	30	39	2.275	0.302	675.158	BD	9.715	BD	17.275	1.179	BD	6.73	11.70
6	PCC_WPK 4 HRS	4208406	28	25	31	2.315	0.344	670.277	BD	9.709	BD	16.877	1.144	BD	6.70	11.70
7	PCC_WPK 12 HRS	4208407	23	20	26	2.203	0.445	671.900	BD	12.587	BD	21.028	1.636	BD	9.36	11.74
8	PCC_WPK 12 HRS	4208408	21	18	23	2.347	0.452	681.140	BD	12.259	BD	21.307	1.669	BD	9.54	11.55
9	PCC_WPK 12 HRS	4208409	20	18	22	2.266	0.445	677.576	BD	12.446	BD	21.218	1.553	BD	9.35	11.62
10	PCC_WPK 24 HRS	4208410	19	17	22	2.279	0.539	696.011	BD	14.640	BD	23.926	1.924	BD	12.50	11.83
11	PCC_WPK 24 HRS	4208411	18	15	20	2.194	0.549	700.972	BD	14.453	BD	24.521	1.936	BD	12.45	11.83
12	PCC_WPK 24 HRS	4208412	16	14	18	2.216	0.551	695.432	BD	14.544	BD	24.204	1.934	BD	12.50	11.81
13	PCC_WPK 3 DAYS	4209401	16	14	18	2.675	0.731	672.043	BD	21.143	BD	39.135	2.379	BD	14.29	11.85
14	PCC_WPK 3 DAYS	4209402	17	15	19	2.527	0.743	686.065	BD	20.471	BD	39.518	2.417	BD	14.24	11.86
15	PCC_WPK 3 DAYS	4209403	20	18	22	2.591	0.722	677.033	BD	20.778	BD	39.027	2.408	BD	14.26	11.92
16	PCC_WPK-1 DAY5	4209404	19	17	22	1.816	0.820	593.106	BD	24.870	BD	51.716	2.672	BD	16.52	11.92
17	PCC_WPK-2 DAY5	4209405	20	18	22	2.540	0.740	582.743	BD	27.344	BD	66.370	2.541	BD	16.55	11.86
18	PCC_WPK-2 DAY6	4209406	16	14	18	2.181	0.778	585.884	BD	26.333	BD	59.076	2.587	BD	16.66	11.89
19	PCC-WP-1 DAY7	4209407	16	14	18	2.291	0.962	598.377	BD	29.137	BD	61.734	3.057	BD	18.31	11.97
20	PCC_WP-2 DAY7	4209408	21	18	24	2.279	0.958	600.778	BD	28.914	BD	63.485	3.009	BD	18.02	11.91
21	PCC_WP-2 DAY8	4209409	19	17	21	2.305	0.945	597.666	BD	29.012	BD	62.116	3.011	BD	18.33	11.95

Table 5.3.1.1. Task 4 Summary data for chemical and toxicity analyses (cont.).

Task 4: Tests of Portland Cement and Portland Cement Concrete																
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results					Chemistry Results								
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Leachate													
%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.														
	PCC flat plate w/plasticizer															
1	Flat plate w/plasticizer DAY(1)	4242434	32.0	30.0	34.0	5.216	BD	13.231	BD	1.113	0.069	2.133	0.010	BD	4.56	9.41
2	Flat plate w/plasticizer DAY(1)	4242435	31.0	30.0	33.0	5.643	BD	13.459	BD	0.956	0.013	2.156	0.024	BD	4.48	8.80
3	Flat plate w/plasticizer DAY(1)	4242436	31.0	29.0	33.0	4.339	BD	14.568	BD	1.003	0.034	2.034	0.016	BD	5.08	8.40
4	Flat plate w/plasticizer DAY(3)	4243401	30.0	28.0	32.0	8.583	BD	16.544	BD	1.915	0.124	3.345	0.027	BD	5.61	8.80
5	Flat plate w/plasticizer DAY(3)	4243402	31.0	29.0	32.0	5.300	BD	15.327	BD	1.989	0.059	3.459	0.028	BD	6.15	8.62
6	Flat plate w/plasticizer DAY(3)	4243403	30.0	28.0	32.0	5.608	BD	16.816	BD	1.429	0.043	3.429	0.021	BD	6.33	8.42
7	Flat plate w/plasticizer DAY(5)	4244411	30.0	28.0	31.0	3.756	BD	21.509	BD	2.230	0.263	4.230	0.027	BD	9.11	8.34
8	Flat plate w/plasticizer DAY(5)	4244412	28.0	26.0	30.0	6.263	BD	21.126	BD	2.108	0.084	4.103	0.039	BD	7.23	8.41
9	Flat plate w/plasticizer DAY(5)	4244413	29.0	27.0	31.0	5.707	BD	21.310	BD	2.379	0.276	4.379	0.032	BD	8.45	8.22
10	Flat plate w/plasticizer DAY(7)	4244414	28.0	36.0	30.0	3.579	BD	22.952	BD	4.426	0.297	5.235	0.032	BD	11.63	8.00
11	Flat plate w/plasticizer DAY(7)	4244415	28.0	26.0	30.0	6.949	BD	23.285	BD	2.936	0.173	5.346	0.036	BD	11.26	8.39
12	Flat plate w/plasticizer DAY(7)	4244416	30.0	28.0	31.0	3.420	BD	21.268	BD	2.404	0.064	5.404	0.078	BD	11.63	7.90
13	Flat plate w/plasticizer DAY(10)	4244417	27.0	25.0	29.0	2.338	BD	24.234	BD	3.370	0.344	6.433	0.040	BD	13.32	7.70
14	Flat plate w/plasticizer DAY(10)	4244418	27.0	25.0	29.0	2.897	BD	24.588	BD	3.125	0.092	6.187	0.075	BD	13.14	7.78
15	Flat plate w/plasticizer DAY(10)	4244419	26.0	24.0	28.0	4.120	BD	23.711	BD	4.025	0.260	6.782	0.036	BD	12.52	7.98

Table 5.3.1.1. Task 4 Summary data for chemical and toxicity analyses (cont.).

Task 4: Tests of Portland Cement and Portland Cement Concrete																
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results			Chemistry Results										
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Leachate													
			%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.											
	PCC flat plate w/o plasticizer															
1	Flat plate w/o plasticizer DAY(1)	4245401	NTE			0.612	0.012	11.946	BD	2.962	0.103	2.845	0.065	BD	3.23	8.30
2	Flat plate w/o plasticizer DAY(1)	4245402	NTE			0.622	0.023	11.685	BD	1.054	0.013	0.794	0.072	BD	3.16	8.21
3	Flat plate w/o plasticizer DAY(1)	4245403	NTE			0.725	0.006	12.428	BD	1.111	0.051	0.640	0.053	BD	3.16	8.36
4	Flat plate w/o plasticizer DAY(3)	4245404	NTE			0.643	0.009	17.321	BD	2.012	0.033	1.406	0.093	BD	3.86	8.62
5	Flat plate w/o plasticizer DAY(3)	4245405	NTE			0.616	0.001	14.479	BD	2.122	0.049	1.618	0.092	BD	3.88	8.50
6	Flat plate w/o plasticizer DAY(3)	4245406	NTE			0.598	0.000	18.049	BD	2.269	0.046	1.457	0.070	BD	3.89	8.64
7	Flat plate w/o plasticizer DAY(5)	4245407	NTE			0.435	0.012	20.170	BD	4.058	0.063	3.216	0.118	BD	4.46	8.53
8	Flat plate w/o plasticizer DAY(5)	4245408	NTE			0.410	0.006	20.346	BD	2.212	0.125	3.219	0.071	BD	4.66	8.46
9	Flat plate w/o plasticizer DAY(5)	4245409	NTE			0.485	0.003	20.876	BD	4.498	0.028	4.216	0.122	BD	4.60	8.36
10	Flat plate w/o plasticizer DAY(7)	4245410	NTE			0.289	0.002	21.191	BD	2.432	0.118	2.197	0.081	BD	5.36	8.37
11	Flat plate w/o plasticizer DAY(7)	4245411	NTE			0.290	0.002	22.042	BD	3.627	0.129	3.068	0.074	BD	5.45	8.24
12	Flat plate w/o plasticizer DAY(7)	4245412	NTE			0.337	0.004	23.764	BD	3.039	0.111	2.245	0.092	BD	5.55	8.32
13	Flat plate w/o plasticizer DAY(10)	4245413	NTE			0.121	0.002	30.482	BD	3.181	0.062	2.461	0.088	BD	5.77	8.21
14	Flat plate w/o plasticizer DAY(10)	4245414	NTE			0.115	0.002	30.622	BD	3.300	0.049	2.380	0.089	BD	5.67	8.11
15	Flat plate w/o plasticizer DAY(10)	4245415	NTE			0.127	0.002	30.944	BD	3.169	0.052	2.979	0.088	BD	5.66	8.09

Table 5.3.1.1. Task 4 Summary data for chemical and toxicity analyses (cont.).

Task 4: Tests of Portland Cement and Portland Cement Concrete																
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results					Chemistry Results								
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Leachate													
%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.														
	PCC photolysis w/plasticizer															
1	PCC w/plasticizer init leachate	4204422	21	18	23	2.315	0.521	687.596	BD	12.055	BD	25.000	2.339	BD	6.865	8.96
2	PCC w/plasticizer Day (1)	4203407	19	16	21	2.301	0.504	677.822	BD	15.737	BD	24.162	1.828	BD	6.845	9.50
3	PCC w/plasticizer Day (1)	4203408	20	16	24	2.297	0.493	675.432	BD	16.294	BD	32.048	1.821	BD	7.180	9.47
4	PCC w/plasticizer Day (1)	4203409	20	18	23	2.344	0.504	674.313	BD	15.827	BD	24.753	1.834	BD	6.960	9.43
5	PCC w/plasticizer Day (3)	4204404	22	20	24	2.319	0.503	677.786	BD	14.918	BD	22.378	1.802	BD	7.125	9.24
6	PCC w/plasticizer Day (3)	4204405	21	19	24	2.228	0.581	674.062	BD	14.534	BD	24.093	1.777	BD	6.613	9.32
7	PCC w/plasticizer Day (3)	4204406	21	16	25	2.324	0.547	678.832	BD	14.798	BD	25.629	1.815	BD	6.959	8.20
8	PCC w/plasticizer Day (5)	4204410	19	18	21	2.331	1.143	680.413	BD	14.245	BD	24.165	1.876	BD	6.376	6.00
9	PCC w/plasticizer Day (5)	4204411	19	17	23	2.335	1.089	680.137	BD	14.475	BD	24.272	1.881	BD	7.060	9.32
10	PCC w/plasticizer Day (5)	4204412	21	16	24	2.298	0.493	679.301	BD	14.637	BD	23.164	1.866	BD	6.348	9.12
11	PCC w/plasticizer Day (7)	4204416	22	16	25	2.298	1.123	680.557	BD	13.746	BD	23.930	1.850	BD	6.915	9.37
12	PCC w/plasticizer Day (7)	4204417	20	18	24	2.252	1.113	681.346	BD	14.065	BD	23.737	1.853	BD	7.023	9.40
13	PCC w/plasticizer Day (7)	420418	22	17	25	2.324	1.120	680.552	BD	13.876	BD	23.716	1.849	BD	6.761	9.45

Table 5.3.1.1. Task 4 Summary data for chemical and toxicity analyses (cont.).

Task 4: Tests of Portland Cement and Portland Cement Concrete																
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results					Chemistry Results								
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Leachate													
%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.														
1	PCC photolysis w/o plasticizer															
1	PCC w/o plasticizer init leachate	4204423	43	39	50	2.463	0.455	662.034	BD	13.054	BD	24.675	2.040	BD	4.160	9.29
2	PCC w/o plasticizer Day (1)	4203410	45	41	52	2.314	0.631	683.474	BD	15.681	BD	22.503	2.166	BD	4.336	9.40
3	PCC w/o plasticizer Day (1)	4203411	50	35	44	2.276	0.728	669.585	BD	15.486	BD	22.796	2.171	BD	4.613	9.47
4	PCC w/o plasticizer Day (1)	4203412	43	35	49	2.300	0.770	680.442	BD	15.303	BD	22.505	2.179	BD	4.559	9.46
5	PCC w/o plasticizer Day (3)	4204407	50	46	54	2.328	0.645	687.333	BD	15.677	BD	22.669	2.216	BD	3.876	9.40
6	PCC w/o plasticizer Day (3)	4204408	48	43	55	2.330	1.095	676.316	BD	15.295	BD	24.058	2.235	BD	4.760	9.25
7	PCC w/o plasticizer Day (3)	4204409	51	48	53	2.230	1.593	676.179	BD	14.846	BD	24.660	2.230	BD	4.148	9.51
8	PCC w/o plasticizer Day (5)	4204413	48	42	55	2.284	0.640	687.860	BD	14.852	BD	22.077	2.236	BD	4.143	9.41
9	PCC w/o plasticizer Day (5)	4204414	49	45	56	2.354	0.645	688.827	BD	15.134	BD	20.846	2.252	BD	3.978	9.50
10	PCC w/o plasticizer Day (5)	4204415	50	43	55	2.284	0.643	687.572	BD	14.794	BD	21.223	2.228	BD	3.788	9.42
11	PCC w/o plasticizer Day (7)	4204419	52	43	57	2.351	1.582	677.466	BD	14.619	BD	23.671	2.234	BD	3.907	9.44
12	PCC w/o plasticizer Day (7)	420420	49	45	55	2.310	1.596	678.287	BD	14.298	BD	24.273	2.231	BD	3.763	9.42
13	PCC w/o plasticizer Day (7)	4204421	50	42	58	2.265	1.589	676.558	BD	14.621	BD	23.980	2.212	BD	3.931	9.45

Table 5.3.1.1. Task 4 Summary data for chemical and toxicity analyses (cont.).

Task 4: Tests of Portland Cement and Portland Cement Concrete																
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results					Chemistry Results								
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Leachate													
			%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.											
	PCC w/Plasticizer Woodburn Soil															
1	PCC WP 24 HRS Leach.	NA	18	17	21	2.279	0.539	696.011	-0.002	14.640	BD	23.926	1.924	BD	8.43	8.63
2	PCC-WP-WB-1 5 g/L	4205407	20	18	21	2.135	0.441	562.244	0.004	11.148	BD	20.679	1.440	BD	12.480	7.66
3	PCC-WP-WB-2 5 g/L	4205408	18	16	19	2.235	0.465	560.548	0.003	11.234	BD	20.007	1.397	BD	12.470	7.73
4	PCC-WP-WB-3 5 g/L	4205409	19	18	20	2.096	0.462	561.755	0.004	11.535	BD	20.096	1.403	BD	12.280	8.57
5	PCC-WP-WB-1 10 g/L	4205410	20	19	22	4.195	0.401	501.247	0.011	10.864	BD	23.442	1.432	BD	20.780	8.40
6	PCC-WP-WB-2 10 g/L	4205411	21	19	22	4.195	0.401	500.968	0.010	10.746	BD	22.998	1.346	BD	20.990	7.56
7	PCC-WP-WB-3 10 g/L	4205412	23	21	25	4.195	0.397	502.977	0.013	10.453	BD	23.034	1.396	BD	20.210	7.77
8	PCC-WP-WB-1 25 g/L	4205413	32	30	34	5.589	0.296	294.531	0.025	11.915	BD	18.422	1.249	BD	19.600	7.74
9	PCC-WP-WB-2 25 g/L	4205414	30	31	32	5.458	0.289	291.057	0.024	12.001	BD	18.577	1.250	BD	19.100	7.27
10	PCC-WP-WB-3 25 g/L	4205415	33	31	35	5.396	0.301	293.856	0.022	11.875	BD	18.000	1.265	BD	19.503	9.48
11	PCC-WP-WB-1 50 g/L	4205416	38	36	40	6.596	0.138	109.610	0.047	12.364	BD	16.047	0.667	BD	30.960	7.41
12	PCC-WP-WB-2 50 g/L	4205417	36	34	38	6.447	0.141	110.117	0.049	12.007	BD	16.022	0.645	BD	30.110	8.02
13	PCC-WP-WB-3 50 g/L	4205418	36	34	38	6.057	0.137	108.700	0.049	12.488	BD	15.897	0.601	BD	30.120	7.40
14	PCC-WP-WB-1 100 g/L	4205419	52	51	53	11.466	0.093	29.041	0.128	7.004	0.204	11.163	0.108	BD	40.210	7.90
15	PCC-WP-WB-2 100 g/L	4205420	52	50	54	11.747	0.089	29.000	0.131	7.112	0.200	11.000	0.112	BD	40.990	8.12
16	PCC-WP-WB-3 100 g/L	4205421	50	49	52	12.005	0.095	29.117	0.130	7.000	0.211	10.985	0.115	BD	40.290	8.07

Table 5.3.1.1. Task 4: Summary data for chemical and toxicity analyses (cont.).

Task 4: Tests of Portland Cement and Portland Cement Concrete																
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results					Chemistry Results								
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Leachate													
			%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.											
1	PCC w/o Plasticizer Woodburn Soil															
1	PCC_WOPK 24 hrs Leach.te	4206422	38	35	41	2.4468	0.6596	695.6465	BD	15.1101	BD	24.2707	2.1087	0.0040	5.19	9.06
3	PCC_WOP-WB-1 5 g/L	4206407	39	36	43	2.3050	0.4103	536.2693	0.0102	12.9105	BD	25.2949	1.4444	0.0045	18.710	8.91
4	PCC_WOP-WB-2 5 g/L	4206408	41	38	45	2.2890	0.4259	534.2789	0.0112	12.9979	BD	24.9946	1.4266	0.0057	18.560	9.11
5	PCC_WOP-WB-3 5 g/L	4206409	41	38	45	2.3165	0.4004	533.2699	0.0146	12.7847	BD	25.0046	1.4027	0.0037	18.340	8.79
6	PCC_WOP-WB-1 10 g/L	4206410	43	38	49	2.1298	0.2996	442.7653	0.0066	13.4400	BD	24.8373	1.4146	0.0043	16.710	8.56
7	PCC_WOP-WB-2 10 g/L	4206411	45	39	50	2.0008	0.3012	440.7465	0.0057	13.1168	BD	24.7744	1.4365	0.0035	16.550	8.42
8	PCC_WOP-WB-3 10 g/L	4206412	42	37	47	2.2569	0.3057	443.2567	0.0036	13.2675	BD	24.9946	1.4000	0.0039	16.900	8.44
9	PCC_WOP-WB-1 25 g/L	4206413	56	48	64	7.7187	0.1941	275.6974	0.0176	14.2985	BD	22.5815	1.1358	0.0117	20.510	8.24
10	PCC_WOP-WB-2 25 g/L	4206414	54	47	62	7.6996	0.1889	273.6975	0.0166	14.3068	BD	22.3479	1.1407	0.0134	20.220	8.16
11	PCC_WOP-WB-3 25 g/L	4206415	57	53	62	7.8547	0.1905	272.6576	0.0180	14.1177	BD	22.0057	1.1000	0.0128	20.080	8.21
12	PCC_WOP-WB-1 50 g/L	4206416	65	60	69	12.7901	0.1272	117.8399	0.0334	13.7863	0.0051	19.8060	0.6207	0.0182	33.180	8.62
13	PCC_WOP-WB-2 50 g/L	4206417	65	61	70	12.8046	0.1307	115.0763	0.0400	13.8035	0.0050	19.2659	0.6146	0.0180	33.010	8.54
14	PCC_WOP-WB-3 50 g/L	4206418	63	59	67	12.6635	0.1200	116.9955	0.0325	13.6946	0.0048	19.5535	0.6003	0.0178	33.110	8.52
15	PCC_WOP-WB-1 100 g/L	4206419	75	NCL	NCL	13.4552	0.0746	32.1291	0.0622	9.5144	0.1315	16.6733	0.1244	0.0141	62.930	8.46
16	PCC_WOP-WB-2 100 g/L	4206420	77	NCL	NCL	13.3997	0.0751	32.6635	0.0602	9.4846	0.1300	16.5576	0.1305	0.0133	62.000	8.49
17	PCC_WOP-WB-3 100 g/L	4206421	75	NCL	NCL	13.5579	0.0740	32.1291	0.0622	9.4665	0.1300	16.0035	0.1277	0.0139	62.120	8.52

Table 5.3.1.1. Task 4 Summary data for chemical and toxicity analyses (cont.).

Task 4: Tests of Portland Cement and Portland Cement Concrete																	
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results					Chemistry Results									
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH	
			Concentration as % Leachate														
			%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.												
	PCC w/ Plasticizer Sagehill Soil																
1	PCC WP-24 HRS Leach.	NA	18	16	21	2.2789	0.5385	696.0112	BD	14.6399	BD	23.9262	1.9243	0.0094	8.23	9.21	
2	PCC WP-SG-1 5 g/L	4207401	19	15	22	2.4530	0.4445	630.3962	0.0046	12.6851	BD	23.4980	1.8049	0.0219	9.237	9.45	
3	PCC WP-SG-2 5 g/L	4207402	18	16	23	2.3629	0.4449	632.9137	0.0036	12.7258	BD	23.2811	1.8116	0.0162	9.330	9.18	
4	PCC WP-SG-3 5 g/L	4207403	20	16	24	2.4727	0.4514	634.3107	0.0034	12.7300	BD	23.4711	1.8103	0.0326	9.450	9.42	
5	PCC WP-SG-1 10 g/L	4207404	21	17	23	2.2983	0.2787	503.9038	0.0056	13.8144	BD	25.7745	1.5145	0.0070	18.050	9.23	
6	PCC WP-SG-2 10 g/L	4207405	18	15	20	2.3866	0.2824	591.2568	0.0047	13.7065	BD	25.4667	1.5171	0.0131	18.230	9.45	
7	PCC WP-SG-3 10 g/L	4207406	20	16	24	2.4836	0.2824	593.8552	0.0057	13.9802	BD	24.8964	1.5158	0.0180	18.770	9.25	
8	PCC WP-SG-1 25 g/L	4207407	20	18	22	2.4576	0.1849	499.1241	0.0105	14.1596	BD	22.7704	1.3932	0.0093	9.783	9.31	
9	PCC WP-SG-2 25 g/L	4207408	19	16	23	2.4839	0.1802	496.5753	0.0085	13.3477	BD	22.5271	1.3980	0.0000	9.550	9.20	
10	PCC WP-SG-3 25 g/L	4207409	20	18	24	2.5205	0.1800	498.0777	0.0114	13.1117	BD	22.2218	1.3891	0.0007	9.709	9.38	
11	PCC WP-SG-1 25 g/L	4207410	20	17	23	2.6003	0.1988	396.6961	0.0158	13.9509	BD	22.2298	1.2368	0.0036	10.340	9.45	
12	PCC WP-SG-2 50 g/L	4207411	22	17	26	2.5258	0.1968	394.1875	0.0175	13.4832	BD	22.0375	1.2256	0.0107	10.870	9.24	
13	PCC WP-SG-3 50 g/L	4207412	21	18	24	2.5794	0.1995	395.4459	0.0156	13.6818	BD	21.9286	1.2272	0.0069	10.990	9.25	
14	PCC WP-SG-1 100 g/L	4207413	22	16	25	2.5794	0.1995	243.6457	0.0156	13.6818	BD	21.9286	1.2272	BD	11.830	9.24	
15	PCC WP-SG-2 100 g/L	4207414	22	17	24	2.4307	0.0962	242.5241	0.0381	13.0751	BD	17.8911	0.9127	BD	11.800	9.42	
16	PCC WP-SG-3 100 g/L	4207415	20	16	24	2.3418	0.1042	244.6862	0.0360	13.0162	BD	18.0441	0.9107	BD	11.120	9.46	

Table 5.3.1.1. Task 4 Summary data for chemical and toxicity analyses (cont.)

Task 4: Tests of Portland Cement and Portland Cement Concrete																
Sample ID	Test Conditions	Tox Lab ID	Toxicity Results					Chemistry Results								
			Algal Toxicity			Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sr (mg/L)	Zn (mg/L)	TOC (mg/L)	Final pH
			Concentration as % Leachate													
			%EC ₅₀	Lower 95% C.L.	Upper 95% C.L.											
	PCC w/o Plasticizer Sagehill Soil															
1	PCC_WOPK 24 hrs Leach.te	NA	NA	NA	NA	2.4468	0.6596	695.6465	BD	15.1101	BD	24.2707	2.1087	0.0140	5.280	9.34
2	PCC_WOP-SG-1 5 g/L	NA	NA	NA	NA	2.3757	0.3056	602.6568	0.0049	12.1880	BD	24.7402	1.3468	0.0081	8.490	9.42
3	PCC_WOP-SG-2 5 g/L	NA	NA	NA	NA	2.2986	0.3054	601.5454	0.0047	12.0867	BD	24.6724	1.4333	0.0073	8.660	9.33
4	PCC_WOP-SG-3 5 g/L	NA	NA	NA	NA	2.3677	0.3168	600.6558	0.0048	12.0007	BD	23.9854	1.3556	0.0078	8.760	9.42
5	PCC_WOP-SG-1 10 g/L	NA	NA	NA	NA	2.2676	0.2447	504.1281	0.0076	12.4452	BD	23.7478	1.3419	BD	8.174	9.22
6	PCC_WOP-SG-2 10 g/L	NA	NA	NA	NA	2.3126	0.2507	503.3459	0.0078	12.4359	BD	23.8023	1.2875	BD	8.108	9.21
7	PCC_WOP-SG-3 10 g/L	NA	NA	NA	NA	2.3076	0.2396	504.5678	0.0077	12.3242	BD	23.6924	1.3597	BD	8.554	9.32
8	PCC_WOP-SG-1 25 g/L	NA	NA	NA	NA	2.3278	0.2515	436.8543	0.0150	12.6168	BD	23.6072	1.2993	BD	12.560	9.30
9	PCC_WOP-SG-2 25 g/L	NA	NA	NA	NA	2.3025	0.2493	436.7957	0.0148	12.7032	BD	23.5726	1.1996	BD	12.440	9.41
10	PCC_WOP-SG-3 25 g/L	NA	NA	NA	NA	2.2948	0.2520	437.0003	0.0147	12.5823	BD	23.4790	1.3007	BD	12.770	9.40
11	PCC_WOP-SG-1 50 g/L	NA	NA	NA	NA	2.2371	0.1326	311.6923	0.0245	13.6746	BD	24.1022	1.2246	BD	8.245	8.96
12	PCC_WOP-SG-2 50 g/L	NA	NA	NA	NA	2.2223	0.1297	310.9566	0.0256	13.5968	BD	24.3790	1.3480	BD	8.200	8.69
13	PCC_WOP-SG-3 50 g/L	NA	NA	NA	NA	2.1957	0.1300	311.9679	0.0254	13.7035	BD	24.5898	1.2015	BD	8.299	8.72
14	PCC_WOP-SG-1 100 g/L	NA	NA	NA	NA	2.0153	0.0724	176.0046	0.0516	12.4276	BD	19.3103	0.7092	BD	9.084	8.59
15	PCC_WOP-SG-2 100 g/L	NA	NA	NA	NA	2.1155	0.0680	178.0115	0.0500	12.3966	BD	19.2277	0.6834	BD	9.221	8.63
16	PCC_WOP-SG-3 100 g/L	NA	NA	NA	NA	2.0047	0.0697	177.0046	0.0497	12.5055	BD	19.0121	0.7001	BD	9.000	8.52

CHAPTER 6

TASK 5: DETERMINE A RANGE OF TYPICAL ADSORPTION AND DESORPTION PARAMETERS FOR THE C&R MATERIALS ON SAND AND GRAVEL UTILIZED IN UNBOUND PAVEMENT LAYERS AND SHOULDERS

6.1 INTRODUCTION

A number of factors control sorption of leachate contaminants by permeable solid phases, including the chemical and physical characteristics of the contaminant and the composition of the surface of the solid. By gaining an understanding of these factors, conclusions can often be drawn about the impact of sorption on the movement and distribution of contaminants in the subsurface. Failure to account for sorption can result in significant underestimation of the mass of a contaminant at a site and of the time required for it to move from one point to another.

Of the various parameters that affect the fate and transport of contaminants in the environment, water solubility is one of the most important. Highly soluble chemicals are easily and quickly distributed by components of the hydrologic cycle and have relatively low adsorption coefficients for soils and sediments.

Some of the most important characteristics of solids affecting the sorption behavior of subsurface materials are mineralogy, texture, homogeneity, organic carbon content, surface charge, and surface area. The combination of these characteristics describes the surfaces offered as sorption sites to contaminants in water passing through the subsurface matrix. For example, silts and clays have much higher surface areas than sand. Sandy materials offer little in the way of sorptive surface area to passing contaminants. Even the most porous and highly productive aquifers, composed of sand and gravel, usually have some fine-grained material, and a few percent of silts and clays can result in a substantive increase in the sorptive behavior of the aquifer material. Sands and gravels contain very few clay minerals, with Ca-rich minerals and quartz the only other distinguishable minerals.

A range of typical adsorption and desorption parameters for C&R materials has been determined for three soils of varying physical and chemical characteristics. By a similar approach, the adsorption and desorption characteristics of C&R materials for a range of sand and gravel have been determined. As for soils, results of laboratory adsorption experimental data were expressed in the form of isotherms as mass adsorbed per unit mass dry solids (C_s) versus the concentration of the constituent (C) in solution. Equilibrium isotherm models were used to determine the maximum adsorption and desorption capacities and distribution coefficients from the experimental data.

The present study was conducted in order to determine the adsorption behavior of two soils and three sand/gravel mixtures on a C&R material with known toxicity: ACZA. The specific objectives of this task were to:

- Examine the adsorption potential of selected soils towards the constituents of ACZA.

- Model suitable isotherms for adsorption and determine their parameters, as this would help in developing a predictive model for the fate and transport of the constituent metals found in ACZA.

6.2 LITERATURE REVIEW

6.2.1 Soil Sorption

Soil is both a porous material through which solutions and suspensions can move and a highly absorbent material that preferentially adsorbs molecules and suspensions from solution/suspension. Soil systems have a variety of organic and inorganic components, each containing a continuum of complexing sites (Kinniburgh et al., 1975; Garcia-Miragaya and Page, 1976). Thus, sites present on both solid and soluble soil components are able to interact with metals to form complex linkages varying in selectivity (Hendrickson and Corey, 1981). The surfaces of fine-grained soil particles are chemically active, bearing positive, negative or electrically neutral charges. Oppositely charged metallic ions from leachate solutions in the soil are attracted towards these charged surfaces. The amount of ions attracted depends on the degree of acidity or alkalinity of the soil, its chemical composition and the amount of organic matter (Evans, 1989).

Soils typically contain a vast array of metals and complexing ligands. These impart electrical charges to the soils through different mechanisms of charge generation, either from isomorphous substitutions among ions of differing valence in soil minerals or from the reactions of surface functional groups with ions in the soil solution. Four different types of surface charge account for the net total particle charge in soils: permanent structural charge, net proton charge, inner-sphere complex charge and outer-sphere complex charge.

Permanent structural or constant charges are associated with the surfaces of the soil clay minerals, whereas pH-dependent or variable charges are due to reactions of protons at the edges and surfaces of oxide and (oxy)hydroxide minerals and with certain functional groups present in humic substances. The total intrinsic charge on soil particles is the sum of the permanent structural charge plus the net proton and variable charges. (Sposito, 1989).

The permanent structural charge is created by charge imbalances in the structure of soil particles due to isomorphous substitution or by non-ideal occupancy. For example, the substitution of Si^{4+} by Al^{3+} will generate a negative charge, as will also the substitution of Al^{3+} by Mg^{2+} . Positive charges also are generated by substituting Ti^{4+} for Al^{3+} or Al^{3+} for Mg^{2+} . However the overall charge on the unit structure of the clay minerals is always negative. Even though positive charges can be generated by structural imperfections, these are always neutralized by the negative charges (Evans, 1989).

The net proton charge is associated with the edges of clay minerals, the surfaces of secondary oxides, hydroxides and oxyhydroxides of metals like Al, Fe and Mn, with the surfaces of amorphous and poorly crystalline aluminosilicates and with carboxylic acid and phenolic groups in humics. These adsorb H^+ and OH^- ions and develop an electrical charge due to the proton association and dissociation reactions. The association of protons with the surface conveys to the

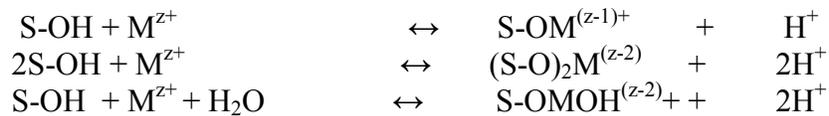
surface a positive charge whereas the dissociation of protons under less acidic conditions gives it a negative charge. These charges are different in that the magnitude and sign of the charge depend on the pH of the soil.

Even though soil particles may bear electrical charge, soils themselves are always electrically neutral. The balancing charge arises from the ions in the soil solution that are not bound into surface complexes but still are adsorbed by soil particles called the diffuse-ion swarm. These ions move about freely in the soil solution while remaining near enough to solid surfaces to create the effective surface charge (Sposito, 1989).

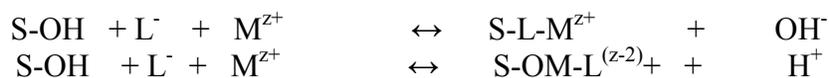
The solid phase of soils containing oxides or hydroxides is covered with surface hydroxyl groups in the presence of water. These groups are capable of donating protons. The deprotonated surface groups therefore behave as Lewis bases and can adsorb metal ions, which is typically a competitive complex formation. The following criteria are characteristic for all surface complexation models (Dzombak and Morel, 1990): sorption takes place at specific surface coordination sites; sorption reactions can be described by mass law equations; surface charge results from sorption reaction itself; and the effect of surface charge on sorption can be considered by applying a correction factor derived from electric double layer theory to the mass law constants for surface reactions.

Typical adsorption reactions are (Schindler and Stumm 1987):

Metal Binding:



Ternary Surface Complex Formation:



The adsorption reactions that occur between the metallic ions and the charged surfaces of soil particles may involve either the formation of: a) outer sphere complexes or ion pairs which are relatively weak associations between a hydrated cation and a complexing ligand in which one or both of the charged species retains a hydration shell, and b) inner sphere complexes that are strong bonds between metal and complexing ligands in which a covalent bond is formed between a metal ion and a ligand. The nature of association between the soil surface and the metal ion depends on the mechanism of retention of the latter with the surface. The degree of adsorption depends on either the respective charges on the adsorbing surface and the metallic cation or on the intrinsic formation constants for the complex forming reactions.

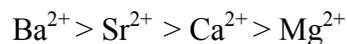
Additionally, outer and inner sphere complexes may have negative or positive charges or be electrically neutral (Stumm, 1992). Points of zero charge are pH values at which one or more of the surface charge components become zero. The three most important points of zero charge are:

point of zero charge (PZC), point of zero net proton charge (PZNPC), and point of zero net charge (PZNC). PZC is the pH value at which the net total charge on the particle vanishes. So at pH values below the PZC there is an increase in the number of positively charged sites and at pH values above the PZC there are more negatively charged sites. The charged sites on constant and variable charge surfaces are important for the retention of metals (Sposito, 1990).

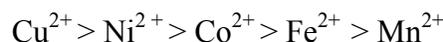
6.2.2 Metal Cation Sorption on Soils

6.2.2.1 Sorption at mineral surfaces

Metal cations adsorb onto soil particles via outer-sphere complexes, inner-sphere complexes and diffuse ion mechanisms. The relative affinity of a metal cation for soil adsorbent depends on the composition of the soil solution. However, the relative order of decreasing interaction strength among the three mechanism is: inner-sphere complex > outer-sphere complex > diffuse-ion. For inner sphere complex the structure of the metal cation and the surface functional group are important, for the diffuse-ion the metal cation valence and surface charge are critical whereas for the outer-sphere complex valence of the cation is most important. Thus, the relative affinity of a soil adsorbent for free metal cation will increase with the formative capacity of inner sphere complexes. For alkali and earth alkali cations the tendency to get sorbed increases with the ionic radius of the ion:



For transition elements, the electron configuration of the ions influences the adsorption affinity:



Also, in inner sphere complexes the surface hydroxyl groups act as σ -donor ligands, which increase the electron density of the coordinated metal ion. Thus, Cu (II) bound inner spherically is different than if it were bound outer spherically or as diffuse layer (Stumm, 1992). The reactivity of a surface is modified by formation of inner sphere complexes. The effect of pH on metal cation adsorption is due to the result of change in net proton charge on the soil. As pH increases, the soil particles become more negative due to proton dissociation and the metal cation adsorbing capacity is increased. An adsorption edge can be determined by reacting the metal cation with soil under increasing pH conditions. However, the presence of complex forming ligands complicates the prediction of metal cation adsorption affinity (Sposito, 1989).

6.2.2.2 Sorption by organic matter

Various studies of retention of metals by various organic fractions of the soils have given the following order or degree of adsorption :

At pH 4.7, Hg = Fe = Pb = Al = Cr > Cu > Cd > Ni = Zn > Co > Mn

At pH 5.8, Hg = Fe = Pb = Al = Cr = Cu > Cd > Zn > Ni > Co > Mn

Since the retention mechanisms involve not only the formation of inner sphere complexes but also ion exchange and precipitation reactions, it is therefore difficult to evaluate the extent of complexation reactions relative to other types. Inner sphere complexes are formed by the association between cations and coordinating functional groups found in humic substances, in which the functional groups act as complexing organic ligands. Generally, chelated complexes are also formed due to additional linkages. Humic substances contain a complex mixture of functional groups whose metal-complexing abilities vary considerably. Also the abundance and abilities of these functional groups are constrained and controlled by the composition and structure of the humic materials present in soil. It is therefore difficult to predict the adsorption behavior of these organics towards metals (Evans, 1989).

With increase in pH, stronger adsorption of metals occurs with the organics, due to dissociation of functional groups on the organic phase as there is less competition from H^+ . Thus, the sorption trend among metals is a result of a combination of metal complexes with both DOM in the solution phase and organic matter on the solid-phase, as well as competition among the metal ions.

6.2.3 Soil Properties Affecting Sorption

The exchange and specific adsorption capacities of a soil are determined by the number and kind of sites available. Adsorption of metal cations can be correlated to soil properties like pH, redox potential, clay, soil organic matter, Fe and Mn oxides, and calcium carbonate content (McLean and Bledsoe, 1992).

6.2.4 Factors Affecting Metal Sorption

6.2.4.1 Effect of competing cations

For specific adsorption sites, trace cationic metals are preferred over the major cations (Na, Ca and Mg). But as the specific adsorption sites get saturated, exchange reactions dominate and competition for these sites with soil major ions becomes important. Trace metals also compete with each other for adsorption sites. So the presence of other cations, whether major or trace metals can significantly effect the adsorption of the metal of interest (Sposito, 1989).

6.2.4.2 Effect of pH

The pH affects several mechanisms of metal retention by soils. The pH dependence of adsorption reactions of cationic metals is partly due to the preferential adsorption of the hydrolyzed metal species in comparison to the free metal. The ratio of hydrolyzed metal species increases with pH. The pH of the soil system is an important parameter that affects sorption/desorption, precipitation/dissolution, complex formation and oxidation/reduction reactions (Stumm, 1992).

6.2.5 Sorption Isotherms

Adsorption in soils is studied in the laboratory by reacting the soil with a solution of known composition at fixed temperature for a predetermined period of time and by chemical analysis of

the reacted soil, the soil leachate or both to determine their compositions. The reaction time should be enough to permit detectable accumulation of the adsorbate but short enough to avoid unwanted side reactions like redox, precipitation etc. The amount adsorbed represents the surface excess of that species, and this can be positive, zero or negative in value.

Adsorption is described in terms of isotherms, which show the relationship between the bulk activity of adsorbate and the amount adsorbed at constant pressure and temperature. Adsorption isotherms are plotted with the concentration adsorbed (C_s), against the equilibrium concentration of the solution (C), and are of four types: S-curve, L-curve, H-curve and C-curve. The L-curve is most common in soil chemistry and it is mathematically described by the Langmuir equation or Freundlich equation. A brief description of these different types is given below:

S-Curve isotherm: It is characterized by an initially small slope that increases with adsorptive concentration. This behavior suggests that the affinity of the soil particles for the adsorbate is less than that of the aqueous solution. After the solution is saturated, the surfaces start to adsorb, resulting in an increasing adsorption at higher concentrations of the adsorbate.

L-Curve isotherm: It is characterized by an initial slope that does not increase with the concentration of adsorbate in the soil solution. This type of isotherm is due to a high affinity of the soil particles for the adsorbate at low surface coverage together with a decreasing amount of adsorbing surface remaining as the surface excess of the adsorbate increases.

H-Curve isotherm: Its typical large initial slope suggests a very high relative affinity of the soil for an adsorbate. This is either due to inner-sphere complexation or significant Van der Waals interactions in the adsorption process.

C-Curve isotherm: It has an initial slope that remains independent of adsorptive concentration until the maximum possible adsorption is achieved. This is caused either by a constant partitioning of an adsorbate between the soil interface and the soil solution, or by a simultaneous increase in the amount of adsorbing surface as the surface excess of the adsorbate increases (Sposito,1989).

6.2.6 Sorption Isotherm Models

The Langmuir isotherm model is valid for single-layer adsorption. It describes the situation where the surface of the solid consists of an array of adsorption sites of equal energy with each site being capable of adsorbing one species (Alloway ,1990). The maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, the energy of adsorption is assumed to be constant and there is no transmigration of adsorbate in the plane of the surface (Weber and Borchardt,1972). Mathematically it is expressed as,

$$C_s = QbC / (1+bC) \quad (6.2.6.1)$$

where Langmuir sorption capacity (Q) and sorption constant (b) are coefficients. In particular, $C_s = Q$, the asymptotic value, for large values of C . (Elsewhere in this Volume III, coefficients b and Q may also be called α and β .)

The empirical Freundlich form is based on the fact that solids have heterogeneous surface energies, in which the energy term, b (in the Langmuir type), varies as a function of surface charge due to variations in the energy of adsorption (Weber, 1972). The general form of the Freundlich isotherm is

$$C_s = K_f C^N \quad (6.2.6.2)$$

where K_f and N are adjustable parameters. When $N \approx 1$, the Freundlich isotherm reduces to a linear form, in which the distribution coefficient, $K_d = K_f$. Similarly, for the Langmuir isotherm, when $bC \ll 1$, Equation 6.2.6.1 reduces to a linear form in which $K_d = Qb$.

In practice, the coefficients of both the Langmuir and Freundlich isotherms are usually determined by suitable linearization of the data, followed by a regression analysis. The Freundlich equation generally agrees well with the Langmuir equation and experimental data over moderate ranges of concentration, C . It does not reduce to a linear adsorption expression at very low concentrations nor does it agree well with the Langmuir equation at very high concentrations, since parameter N must reach some limit when the surface is fully covered (Weber, 1972). When there is clearly an asymptotic limit to the sorbed concentration, C_s , the Langmuir form is preferred.

6.2.7 Arsenic Chemistry and Sorption Behavior

The two predominant forms of arsenic in soils and natural waters are As(V), as an oxyanion arsenate species and As(III), as an arsenite species. Arsenic acid has pK_a of 2.2, 6.97 and 11.53 and so As(V) would be present as $HAsO_4^{2-}$ and $H_2AsO_4^-$ in natural pH ranges. Arsenious acid has a pK_a of 9.2 and As (III) would be present as $HAsO_2$ and AsO_2^- . Both As(V) and As (III) are subject to chemically and microbiologically mediated oxidation-reduction and methylation reactions in soils and natural waters (Masscheleyn et al., 1991). Arsenate is generally stable under positive redox potentials, while reduction to arsenite can occur under reducing conditions with negative redox potentials as in flooded soils and other environments with anaerobic biological activity (Oscarson et al., 1983; Masscheleyn et al., 1991; Pierce and Moore, 1982).

Arsenic, being an anion in the form of arsenate and arsenite, has a rate of adsorption independent of the other competing cations copper and zinc. Adsorption of arsenic is considered to be specific adsorption or ligand exchange with surface hydroxyls and/or surface aqueous groups (Goldberg, 1986; Pierce and Moore, 1982). The adsorption of both arsenate and arsenite is strongly pH dependent. Arsenate, like phosphate, forms insoluble precipitates with iron, aluminum and calcium (McLean and Bledsoe, 1992). Maximum adsorption of arsenate by aluminum and iron oxides occurs at pH 3-4 and steadily decreases as pH increases. The adsorption of both forms of arsenic is related to pH, chemical and physical properties, and cation exchange capacity (CEC) of soils (Nriagu, 1994). The clay fraction and iron oxides have also been frequently implicated in the sorption of As by soils (Jacobs et al., 1970; Wauchope et al., 1975; Elkhatib et al., 1984a,b).

A likely mechanism for sorbing on iron oxides was suggested to be the penetration of the coordination shell of the Fe atom, displacement of OH or OH_2 ligands from the surface, and the

formation of covalent bonds with structural cations (Elkhatib et al., 1984a,b). Livesey and Huang (1981) suggested that Al and Fe compounds in soils, particularly Al compounds, are closely associated with As adsorption by the soils.

6.2.8 Copper Chemistry and Sorption Behavior

Copper occurs mainly as divalent cation (Cu^{2+}), although copper complexes have been isolated in the I, II and III oxidation states (Leckie and Davis, 1979). Copper has a single 's' electron outside the completed 'd' shell due to its electronic configuration. This partial filling of the 'd' subshell causes copper to have a relatively large tendency to form complexes and to have variable oxidation states (Leckie and Davis, 1979). The fate and mobility of copper in solution is affected by its complexation. Hydroxyl ion is the common ligand and is the major complexing species for copper in aqueous systems, the others being nitrate, sulfate, organics and halides. Free copper, Cu^{2+} , concentration decreases as pH increases and $\text{Cu}(\text{OH})_2$ becomes the dominant copper species when the pH is above neutral.

Copper (Cu^{2+}) is strongly adsorbed on oxide surfaces in soils including iron and manganese oxides (Davis and Leckie, 1978; McKenzie, 1980). Cu is more strongly adsorbed than Zn, Ni and Co and is also less soluble (Rose and Bianchi-Mosquera, 1993). At neutral pH, almost 100% of copper will be bound to oxide surfaces (Kooner, 1992). Sorption studies of copper onto soil and its individual components have suggested that the specific sorption of Cu by soils is dominated by hydrous oxides of Fe and Mn and organic matter (Quirk and Posner, 1975; Farrah and Pickering, 1976a,b; Forbes et al., 1976; Davis and Leckie, 1978). Organic matter can increase the ability of hydrous oxides to sorb heavy metals even at low pH levels. High soil organic matter can lower the zero point of charge (ZPC) and is related to the ability of soils to adsorb copper (Petruzelli et al., 1978; Morais et al., 1976). The desorption of organic acids from soils may occur as the organic acids dissociate and the surface charges of the mineral become more negative at higher pH (Bingham et al., 1965).

6.2.9 Zinc Chemistry and Sorption Behavior

Zinc occurs mainly in its divalent cation form. Dissolved zinc can exist as a free metal ion, or as simple and strong metal complexes (organic and inorganic). In soils, Zn is usually distributed as free ions (Zn^{2+}) and organo-zinc complexes in soil solution, adsorbed and exchangeable Zn in the colloidal fraction of the soil and secondary minerals and insoluble complexes in the solid phase. Distribution of zinc is governed by the equilibrium constants of precipitation and dissolution, complexation and de-complexation, and adsorption and desorption. This depends on the concentration of Zn^{2+} and other ions in the soil, the adsorption sites in the soil, the ligands available for forming complexes, pH, and the redox potential of the soil. The solubility of Zn is directly proportional to the pH. Thus, the solubility of Zn will increase at decreasing pH values of the soil.

Zinc is readily adsorbed by clay minerals, carbonates and hydrous oxides (McClean and Bledsoe, 1992), on ferric hydroxide at pH values above 7, silica and alumina, manganese dioxide, and organically coated minerals (Nriagu, 1980). Sorption of zinc in soils can be influenced by soil pH, clay minerals, organic matter content, iron and aluminum oxides content, CEC, carbonates

content (McBride, 1989). Since heavy metals like Zn, Ni and Cu are strongly retained through specific adsorption sites on soil surfaces, the presence of these other cations can influence Zn sorption, specifically in the presence of higher concentrations of the competing metals with limited amounts of sorption surfaces (Elrashidi and Connor, 1982).

Zinc sorption was found to be reduced to a greater extent due to removal of the oxide fraction of soil clays compared to Cu sorption (Cavallaro and McBride, 1984) suggesting a relatively greater importance of oxides (and a lesser importance of organic matter) for Zn adsorption. The study concluded that zinc sorption is more strongly affected by the removal of iron and aluminum oxides than Cu, perhaps because Cu tends to preferentially bond at organic sites.

6.3 EXPERIMENTAL APPROACH

The testing approach consisted of evaluating the adsorption capacity of the soils and sand/gravel mixtures by batch reaction with ACZA leachate. Two soils and three types of sand and gravel mixtures with varying compositions were selected to investigate whether the toxic constituents eluted from ACZA-treated wood posts could be ameliorated by contact with the soils.

For meeting the objectives of this study, batch reactor experiments were conducted under uniform conditions with different amounts of soils added with ACZA leachate, for each experiment. Preliminary experiments were conducted with each type of soil, sand/gravel and ACZA leachate to understand the background concentrations, resulting pH and amount of adsorption of the contaminants. Once these were known, varying amounts of soils were calculated for each set of experiments, so that a complete isotherm could be developed. In the case of sand and gravel materials, the background pH from these materials was higher than that of the test soils. The pH of the ACZA leachate, used for sand/gravel mixtures, was adjusted in order to obtain approximately constant pH for the range of concentrations of the adsorption isotherm. This was not done in the case of soils as they maintained a uniform pH.

6.4 MATERIALS

6.4.1 Soil and Sand/Gravel Samples

All chemicals used in this study were ACS reagent grade and all glass and plasticware were washed with acetone, acid bath and with distilled water prior to use. Distilled deionized water (DDW; Barnstead Nano Pure II deionizer) was used in the preparation of all solutions. Sterile, Nalgene bottles made of HDPE were used as elution jars and as batch reactors.

The soils used in this study were of two types, Woodburn (Mollisol) and Sagehill (Aridisol), obtained from previously selected Oregon sites. The sand/gravel mixtures used were from three sources, identified as 33RO1, 63RO1 and Morse Brothers. The sand-and-gravel mixtures were prepared per ODOT specifications (see Chapter 8, Task 7, Section 8.4.1 of this report). The chemical and physical analyses of these soils and sand/gravel mixtures were completed and the summary is provided in Table 6.4.1.1. The analysis shows that Woodburn soil has much higher organic matter content than all the other materials tested and Morse Brothers sand/gravel has the highest organic matter among the sand/gravel materials.

For both the soil and sand/gravel mixtures, the leachate prepared with distilled water from each material was analyzed for the background concentrations of different elements. The analysis reveals the presence of higher amounts of aluminum, iron and manganese in Woodburn soil compared to Sagehill soil and also in Morse Brothers sand/gravel compared to the other sand/gravel mixtures (results not reported here).

Table 6.4.1.1. Bulk soil chemical properties.

Soils	% Organic matter (LOI)	CEC (meq/100g)
Sagehill	1.91	11.7
Woodburn	6.44	18.8
33RO1	-	NA
63RO1	0.15	NA
Morse Bros.	1.7	NA

LOI = Loss on Ignition, CEC = Cation Exchange Capacity
meq = milliequivalents, NA = not available

6.4.2 Preparation of ACZA leachate

The preparation consisted of shaving commercially available wood posts, treated with ACZA, to 3/8-inch thickness. The wood shavings are collected, mixed together to obtain uniformity and then stored in polyethylene bags to prevent absorption of atmospheric moisture. Requisite samples are taken from this bulk quantity. ACZA leachate was prepared by adding deionized water at a weight ratio of 1 part dry weight material to 40 parts by weight deionized water (1:40 ACZA shavings: deionized water). The materials were placed into elution jars (Nalgene bottles), which were sealed with lids that were taped or covered with parafilm to prevent leakage. The elution jars were placed into a rotary extractor, padded with foam pads to prevent breakage, and mixed end-over-end for 24 hours. After 24 hours of mixing the jars were removed from the extractors and the leachate was filtered through a pre-filter (Whatman Qualitative paper) initially to remove larger particles and then through Whatman 0.45- μ m filter paper.

The final leachate was measured for pH, TOC and the concentrations of arsenic, copper and zinc. Leachates were stored in the dark at 4°C, until analyses were completed. Leachate should not be stored for more than 48 hours before analysis or isotherm experiments, as chemical changes may occur during storage particularly with TOC content. This requirement resulted in the preparation of several small quantities of leachate rather than one large volume.

6.5 METHODS

6.5.1 Batch Experimental Setup

The calculated amount of soil, which varied from 10-500 g/L of ACZA leachate and 50-500 g/L of ACZA leachate in the case of a sand/gravel mixture, was added to the Nalgene bottles and the leachate was added to it. The bottles were closed tightly, sealed with parafilm to prevent any leakage, and placed in the rotary tumbler and mixed end-over-end for 24 hours. The mixture of

soil and ACZA leachate was transferred to polycarbonate bottles and centrifuged for ten minutes at 10,000 rpm. The mixture was then filtered through pre-filter (Whatman Qualitative paper) and then through Whatman 0.45- μm filter using a vacuum pump. The final leachate is measured for pH, TOC and concentrations of arsenic, copper and zinc for the entire batch.

pH maintenance: In the case of sand and gravel mixtures, the background pH of the materials was found to be higher than that of soils, in the range of 8-9. Since the ACZA leachate had a pH around 7, the leachate pH was adjusted to 8.8-8.9 with 0.1M NaOH. This was done to maintain uniform pH across the batch of differing amounts of gravel. In the case of soils this was not done, as the pH was in the range of 6-7 for the different soils and thus was not greatly affected by the ACZA leachate.

6.5.2 Analytical Methods

6.5.2.1 Measurement of Arsenic, Copper and Zinc by ICP-AES

Inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian Liberty 160) was used for the determination of multiple metals like As, Cu and Zn in solution. A detailed explanation of the analytical method for ICP analysis is given in Volume IV (Nelson et al., 2000b).

6.5.2.2 Measurement of TOC by TOC Analyzer

The TOC in the leachate samples was measured using a TOC analyzer (Rosemount Analytical, Inc., Dohrmann Division, model DC-190). Sample handling, machine maintenance, and overall operating procedures for the Total Organic Carbon (TOC) analyzer was carried out in accordance with the procedures specified by the manufacturer as well as in Standard Methods 505A: *Organic Carbon (Total): Combustion-Infrared Method*. A detailed explanation of the analytical method for TOC analysis is given in Volume IV.

6.6 RESULTS

6.6.1 Preliminary Experiments

From previous experiments with ACZA, it was known that a weight ratio of 1 part of ACZA-treated wood shavings: 4 parts of deionized water resulted in a leachate that had high concentrations of metals and had high levels of toxicity. In order to obtain a leachate with reasonable concentrations of metals, whereby its adsorption could be studied effectively, varying proportions of ACZA wood shavings to deionized water of 1:20, 1:30 and 1:40 were prepared and analyzed for chemistry and toxicity. From the results, it was concluded that the ratio of 1:40 of ACZA wood shavings: deionized water yielded a suitable leachate that can be studied for adsorption. This ratio was then used for further experiments.

To determine whether the batch adsorption time of 24 hrs was sufficient to obtain complete and equilibrium adsorption, a kinetic study was conducted with ACZA leachate and Woodburn and Sagehill soils. In this experiment, the batch adsorption experiment was carried out for a period of 5 days. Samples were collected at 1 hr, 2 hrs, 4 hrs, 10 hrs, 24 hrs, 48 hrs, 72 hrs, 96 hrs and 120 hrs. The leachate samples were then analyzed for metals and the adsorption curve was plotted with concentration of metal vs. time (Figures 6.6.1.1 to 6.6.1.6). From this experiment, it was found that the rate of adsorption was rapid initially, then decreased considerably after 24hrs. Since greater than 90% of the adsorption occurred within 24 hrs, it was decided to proceed with further experiments with the 24hr batch adsorption period as a sufficient amount of time for equilibration.

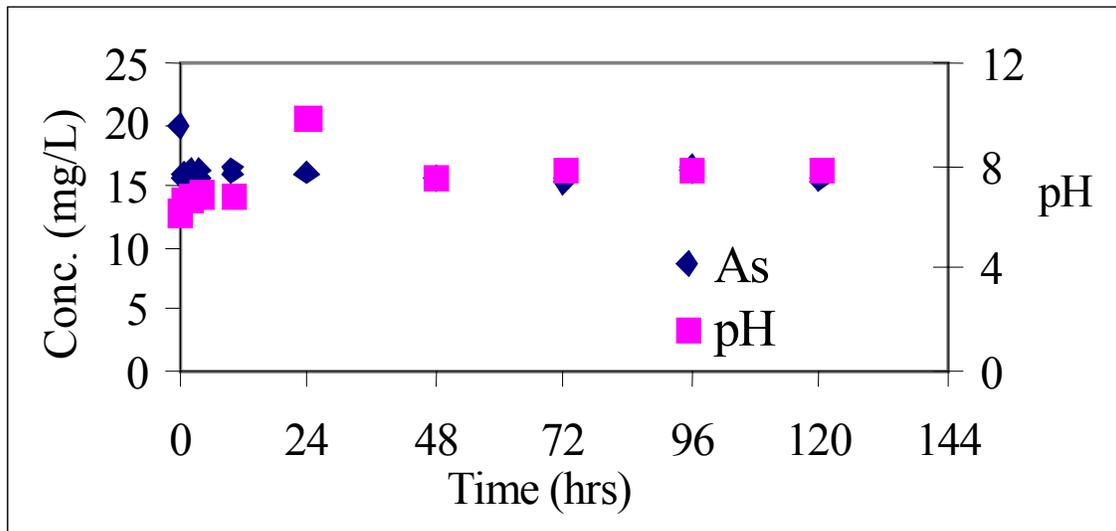


Figure 6.6.1.1. Kinetic study of As adsorption on Sagehill soil.

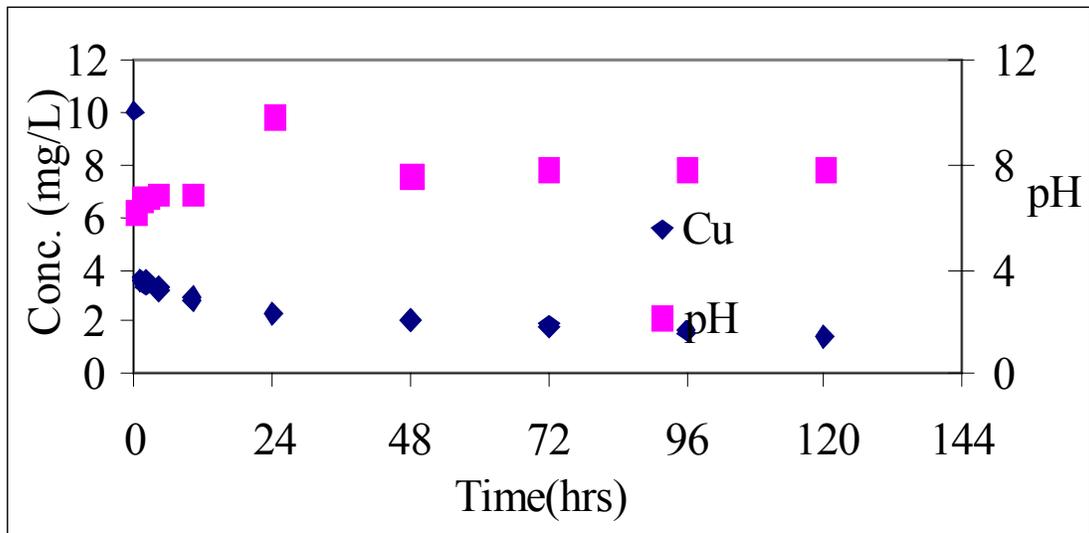


Figure 6.6.1.2. Kinetic study of Cu adsorption on Sagehill soil.

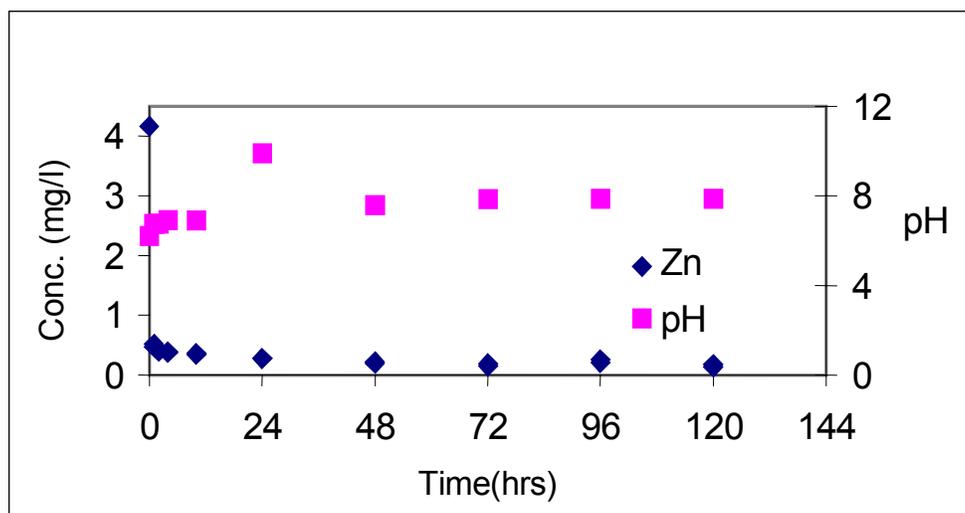


Figure 6.6.1.3. Kinetic study of Zn adsorption on Sagehill soil.

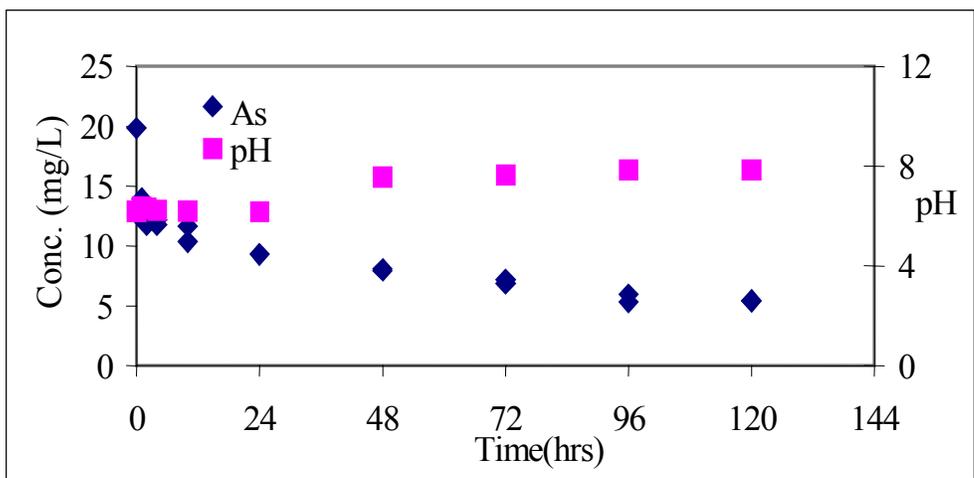


Figure 6.6.1.4. Kinetic study of As adsorption on Woodburn soil.

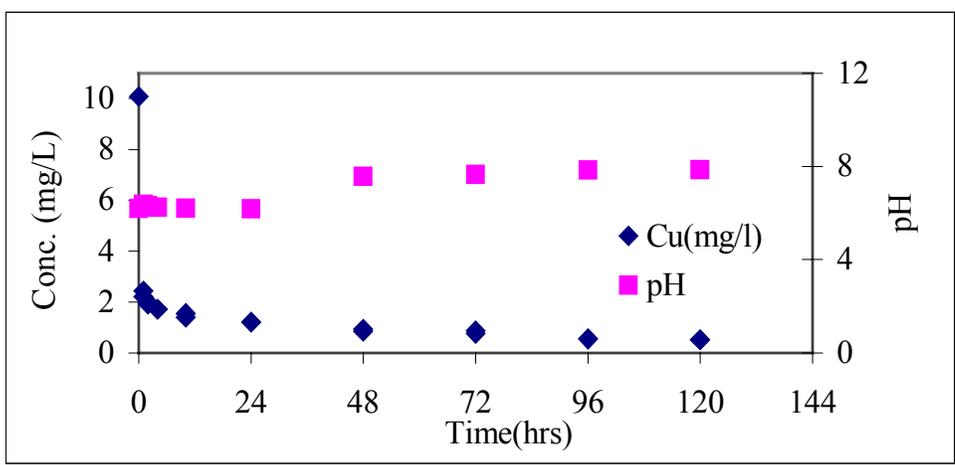


Figure 6.6.1.5. Kinetic study of Cu adsorption on Woodburn soil.

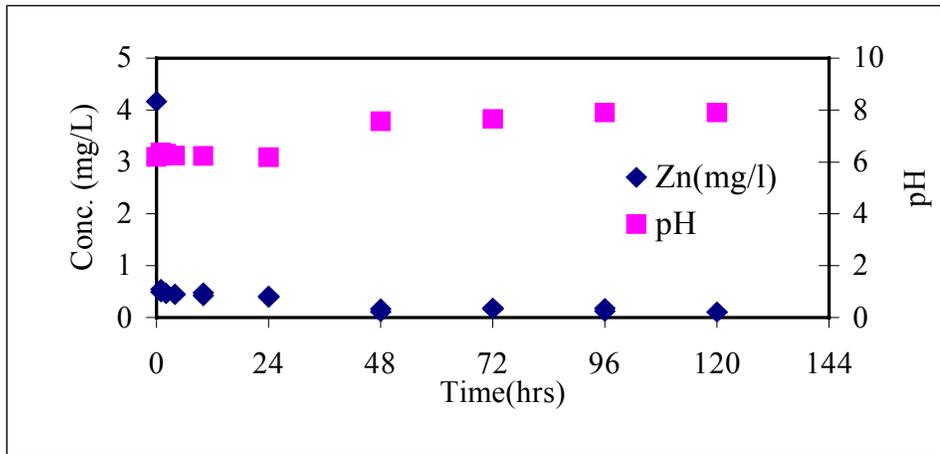


Figure 6.6.1.6. Kinetic study of Zn adsorption on Woodburn soil.

It can be seen that the rate of adsorption for As, Cu and Zn is higher for the Woodburn soil than for the Sagehill soil. Within the metals, arsenic seems to be adsorbed relatively less than Cu and Zn. From the results it was concluded that the batch adsorption isotherms would be carried out with 10 g/L, 50 g/L, 100 g/L, 150 g/L, 200 g/L, 250 g/L, 400 g/L and 500 g/L of the soils in ACZA leachate solution. The ACZA leachate was prepared in bulk for the isotherm experiments, about 6 liters for each batch experiment. From this, different samples as indicated above were run and each reactor experiment was conducted in triplicate to obtain more reliable results. The soil sorption was conducted for 24 hrs, the leachate filtered and analyzed. For different concentrations of the soils, the amount adsorbed was calculated and isotherms plotted for each of the metals As, Cu and Zn, respectively. Three types of models were fit for the data, namely linear, Langmuir and Freundlich.

6.6.2 Linear Regression of Data for Langmuir Parameters

In order to obtain the Langmuir parameters, Q (maximum adsorption capacity) and b (adsorption energy), the data were linearized in the form $C/C_s = C/Q + 1/Qb$. From the linear form, the coefficients for each of the soils and for each of the metals were calculated. The Langmuir isotherm was then developed using these parameters. As an example, the linearized form for the different metals for the Woodburn soil is given in Figures 6.6.2.1 to 6.6.2.3.

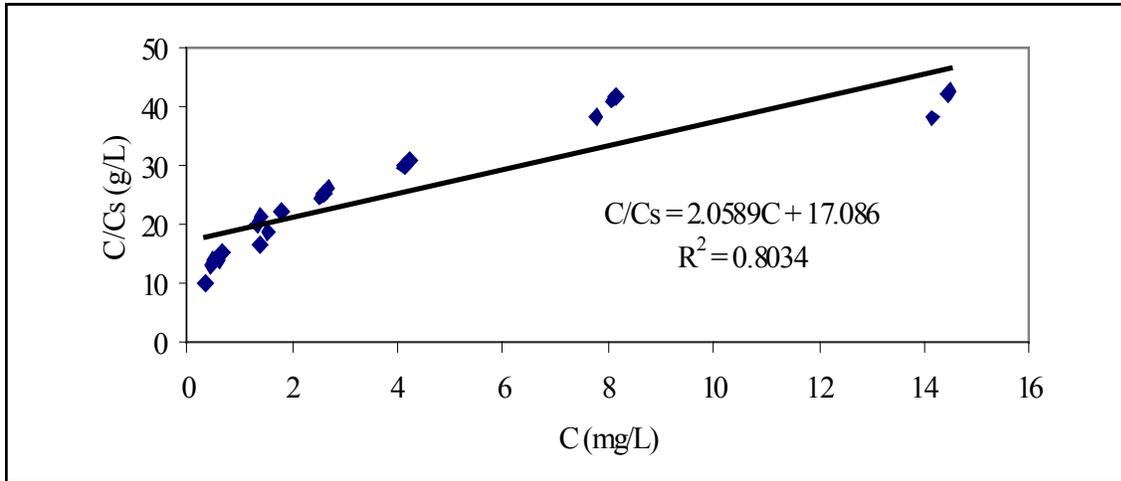


Figure 6.6.2.1. Linearized Langmuir plot of As adsorption on Woodburn soil.

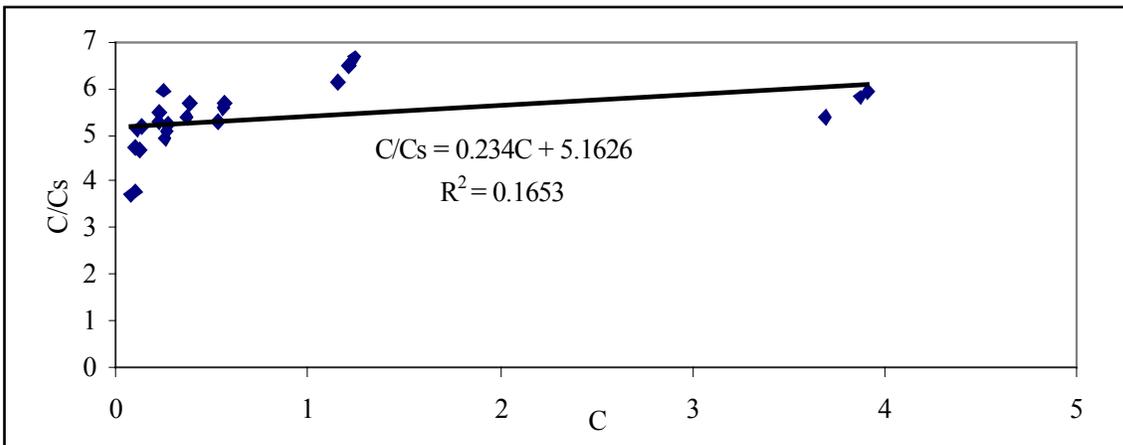


Figure 6.6.2.2. Linearized Langmuir plot of Cu adsorption on Woodburn soil.

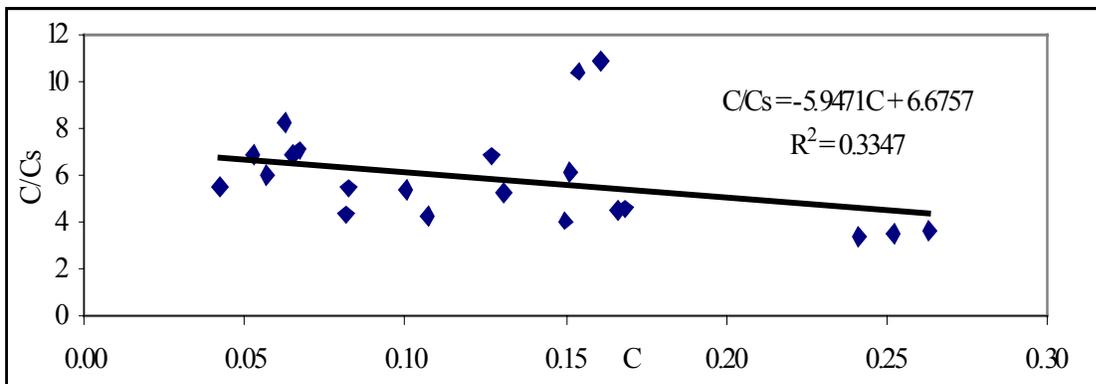
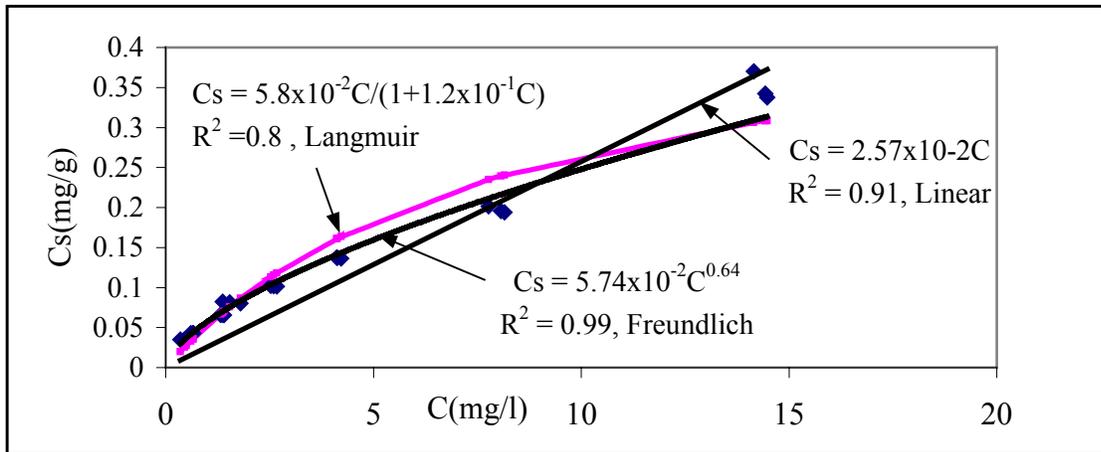


Figure 6.6.2.3. Linearized Langmuir plot of Zn adsorption on Woodburn soil.

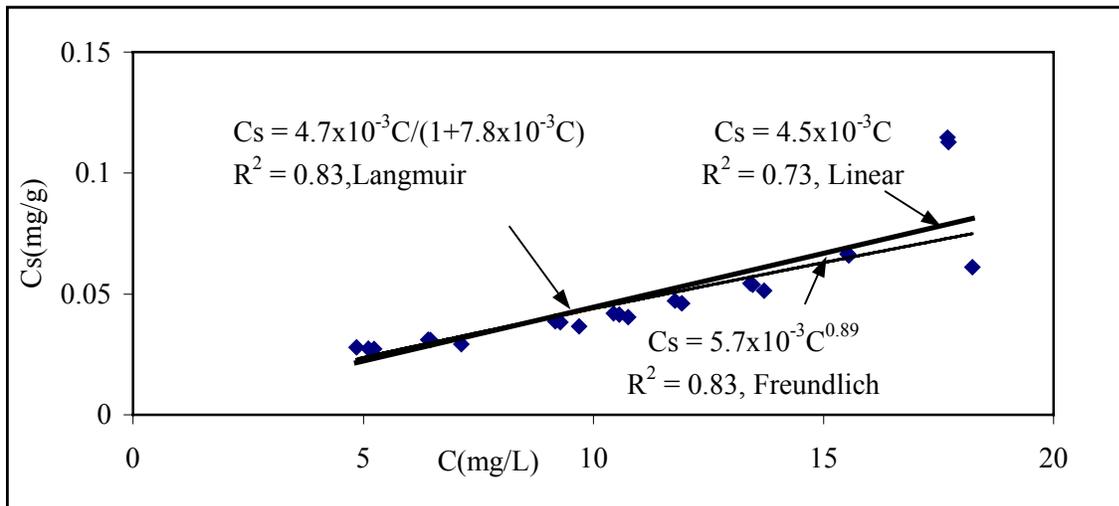
6.6.3 Discussion of Metal Behavior and Isotherms

6.6.3.1 Arsenic adsorption on soils and sand/gravels

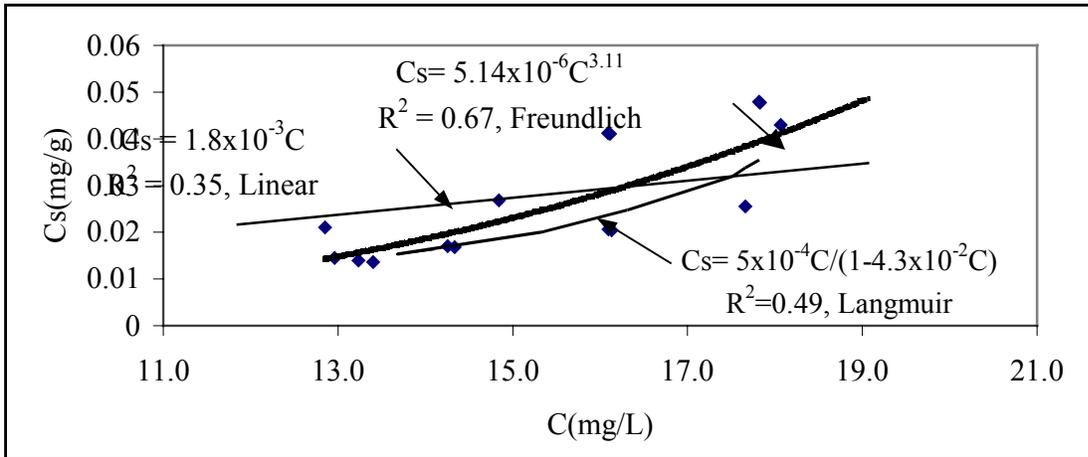
The adsorption isotherms of arsenic for the soils and sand/gravel mixture were computed, and these are shown in Figures 6.6.3.1.1 to 6.6.3.1.5. A summary of the parameters obtained from the isotherms is shown in Table 6.6.3.1.1.



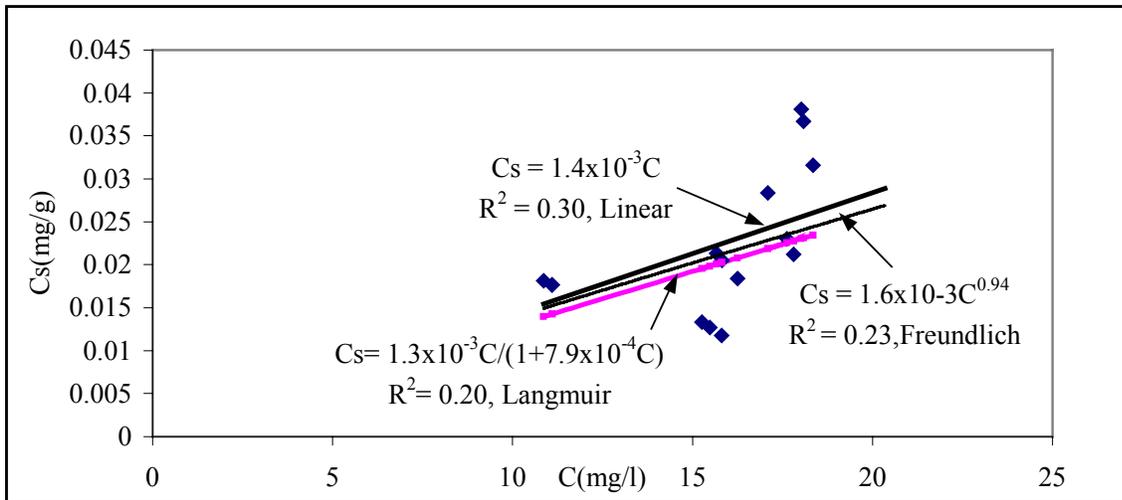
Figures 6.6.3.1.1. Arsenic adsorption isotherm for the Woodburn soil.



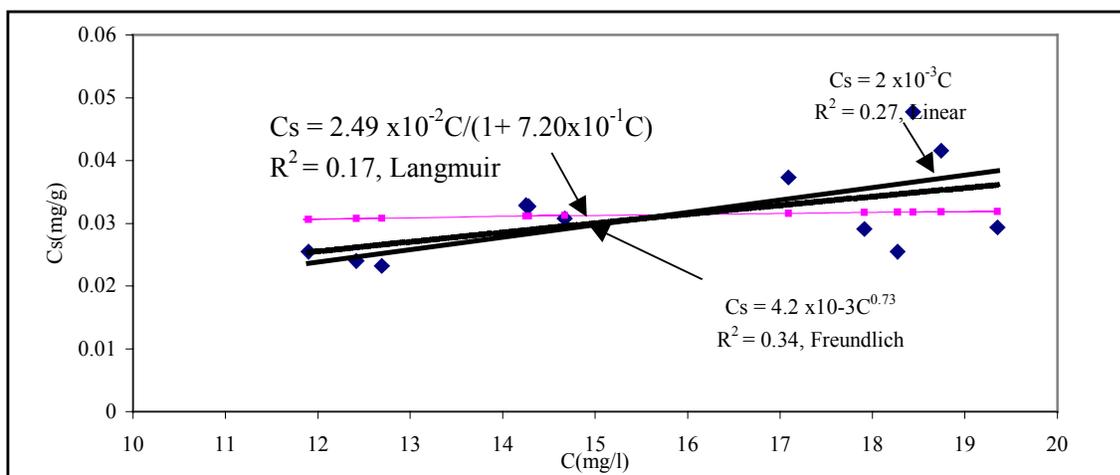
Figures 6.6.3.1.2. Arsenic adsorption isotherm for the Sagehill soil.



Figures 6.6.3.1.3. Arsenic adsorption isotherm for the 63RO1 sand/gravel mixture.



Figures 6.6.3.1.4. Arsenic adsorption isotherm for the 33RO1 sand/gravel mixture.



Figures 6.6.3.1.5. Arsenic adsorption isotherm for the Morse Brothers sand/gravel mixture.

The parameters obtained from the adsorption isotherms for the different soils and sand/gravels are summarized below (Table 6.6.3.1.1)

Table 6.6.3.1.1. Summary of isotherm parameters for arsenic adsorption from ACZA leachate on different soils and sand/gravel mixtures.

Soil type	Langmuir			Freundlich			Linear	
	Q (mg/g)	b (L/mg)	R ²	K _f	N	R ²	K _d (L/g)	R ²
Woodburn	4.8x10 ⁻¹	1.2x10 ⁻¹	0.94	5.7x10 ⁻²	0.64	0.99	2.57x10 ⁻²	0.91
Sagehill	5.9x10 ⁻¹	7.8x10 ⁻³	0.83	5.7x10 ⁻³	0.89	0.83	4.5x10 ⁻³	0.73
33RO1	1.633	7.9x10 ⁻⁴	0.31	1.6x10 ⁻³	0.94	0.23	1.4x10 ⁻³	0.3
63RO1	NA	NA	-	5.1x10 ⁻⁶	3.11	0.67	1.8x10 ⁻³	0.35
Morse Bros.	3.4x10 ⁻²	7.2x10 ⁻¹	0.33	4.2x10 ⁻³	0.73	0.34	2.1x10 ⁻³	0.27

NA = Not applicable

A comparison of the R² values for the different models of fit shows that the linear or Freundlich forms fit the data better than the Langmuir form. For the 63RO1 sand/gravel mixture the isotherm was concave in shape and the Langmuir equation could not be applied. This is similar to the results by Jiang (1994) in which he found that the Freundlich equation fits better for the experimental data than the Langmuir equation. However, clustering of data (i.e., a group of data points at high solute concentrations, with no data points at low concentrations) for all three sand/gravel mixtures casts doubt on the usefulness of the isotherms for those materials. The plotted values for C_s are more likely to reflect asymptotic (saturation) concentrations for the sorbed material than a functional relationship with C.

However, using computed K_d values for comparison, the adsorption capacities between the different soils showed that the arsenic adsorption potential was in the following order: Woodburn > Sagehill > Morse Bros. > 63RO1 > 33RO1. Woodburn soil has a higher cation

exchange capacity and organic matter than Sagehill soil and this could contribute to its higher adsorption capacity. Not surprisingly, the two soils exhibit a higher adsorptive capacity for arsenic than do the three sand/gravel mixtures.

The parameters for arsenic adsorption show that adsorption is less than that of copper or zinc. Since the pH of the leachate solution was around 6.5-7.0, this could be expected as arsenic adsorption decreases with increasing pH (Galba, 1994). Particularly with the sand and gravel materials, reduced arsenic sorption was exhibited. In addition to the obvious lower organic content of these three materials, this effect could also result because the pH of the ACZA leachate used for these experiments was adjusted to a higher range of 8.8-9.0.

Adsorption studies of arsenic with soils/amorphous iron oxides have used either the Langmuir or Freundlich isotherms to successfully model the data (Nriagu, 1994). Pierce and Moore (1980) found that As(III) sorption by amorphous iron hydroxides complied with the Langmuir isotherm formulation. Gupta and Chen (1978) also used the Langmuir form for As(III) sorption on alumina. Elkhatib et al. (1984) used the Freundlich isotherm to describe arsenite sorption by West Virginia soils.

A compilation of arsenic isotherm parameters obtained from literature is given in Table 6.6.3.1.2 and it can be seen that these values agree well with those determined in this study.

Table 6.6.3.1.2. Isotherm parameters for arsenic adsorption obtained from literature.

Study	Langmuir			Freundlich		
	Q(mg/g)	b (L/mg)	R ²	K _f	N	R ²
Elkhatib et al. (1984)				3.36x10 ⁻² , 7.74x10 ⁻²	2.28, 1.83	0.98, 0.99
Livesey and Huang (1981)	2.5x10 ⁻¹ , 2.7x10 ⁻¹	not calculated				

6.6.3.2 Copper adsorption on soils and sand/gravels

Copper was found to be rapidly adsorbed to the soils and sand/gravel materials. This agrees with literature indicating that copper is strongly adsorbed onto soils. The fitted adsorption isotherms for copper onto the different soils and sand/gravel mixtures were plotted (Figures 6.6.3.2.1 to 6.6.3.2.5). The summary table consisting of the parameters obtained from the isotherms is shown in Table 6.6.3.2.1.

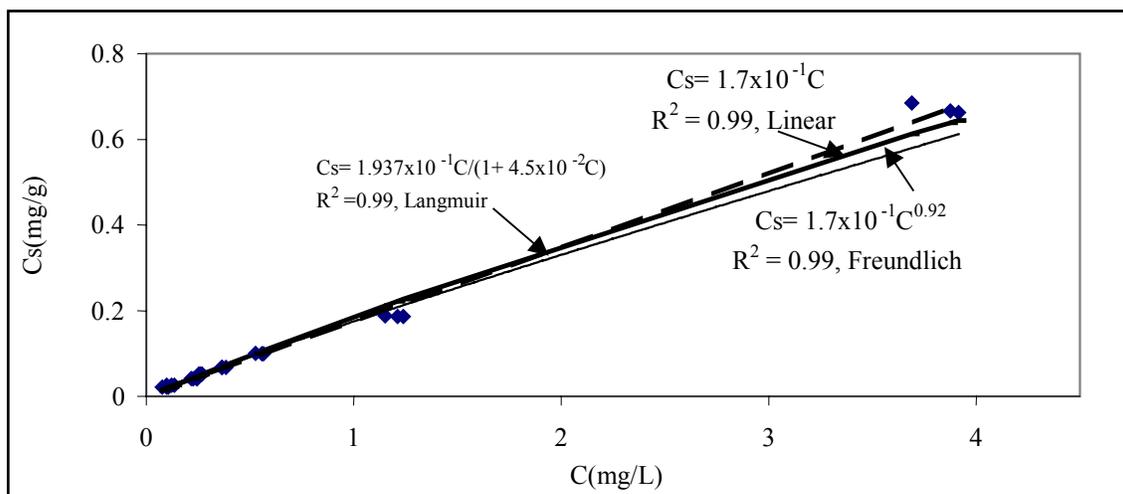


Figure 6.6.3.2.1. Copper adsorption isotherm for the Woodburn soil.

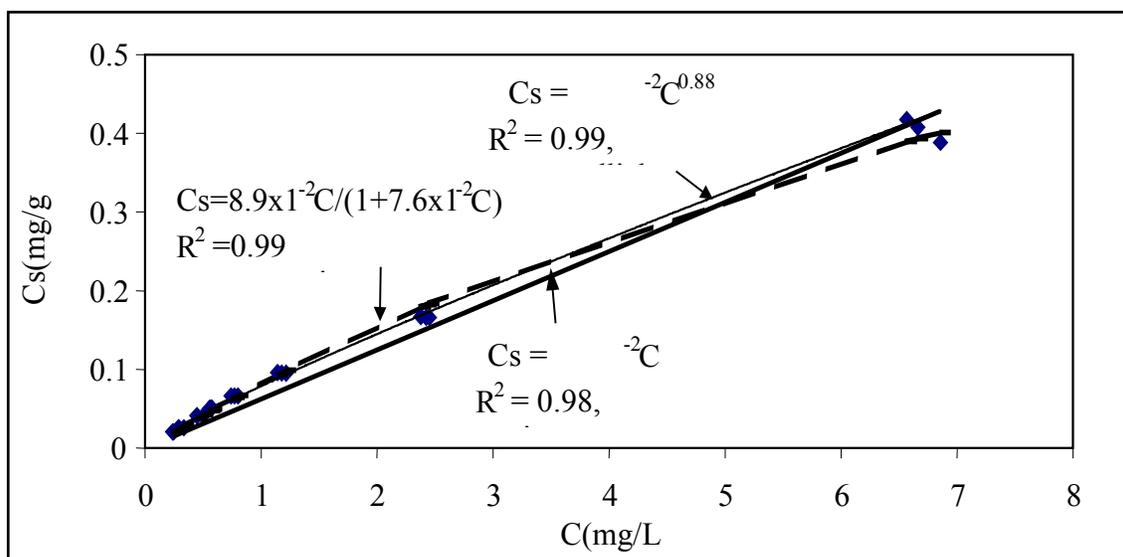


Figure 6.6.3.2.2. Copper adsorption isotherm for the Sagehill soil.

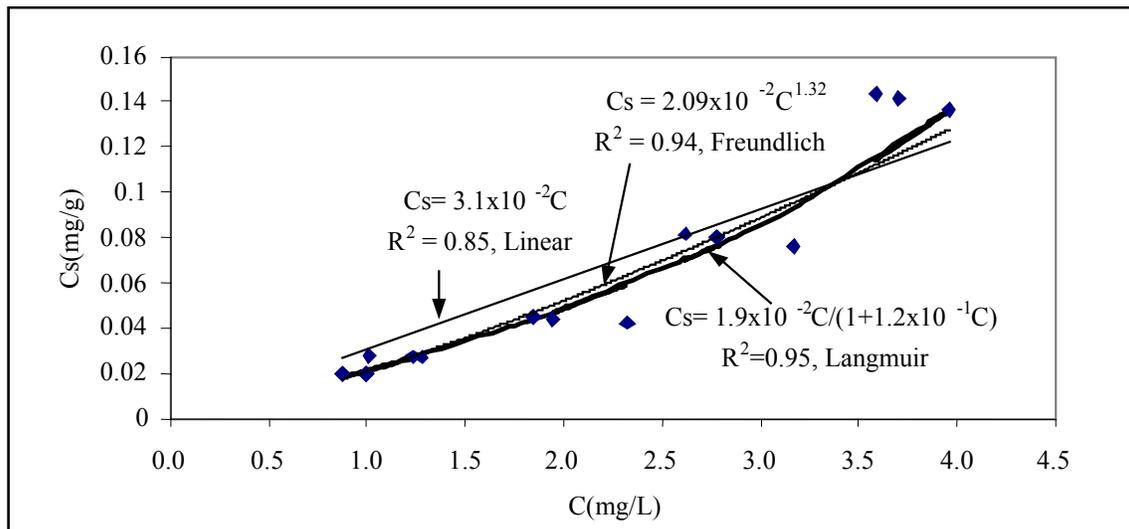


Figure 6.6.3.2.3. Copper adsorption isotherm for the 63RO1 sand/gravel mixture.

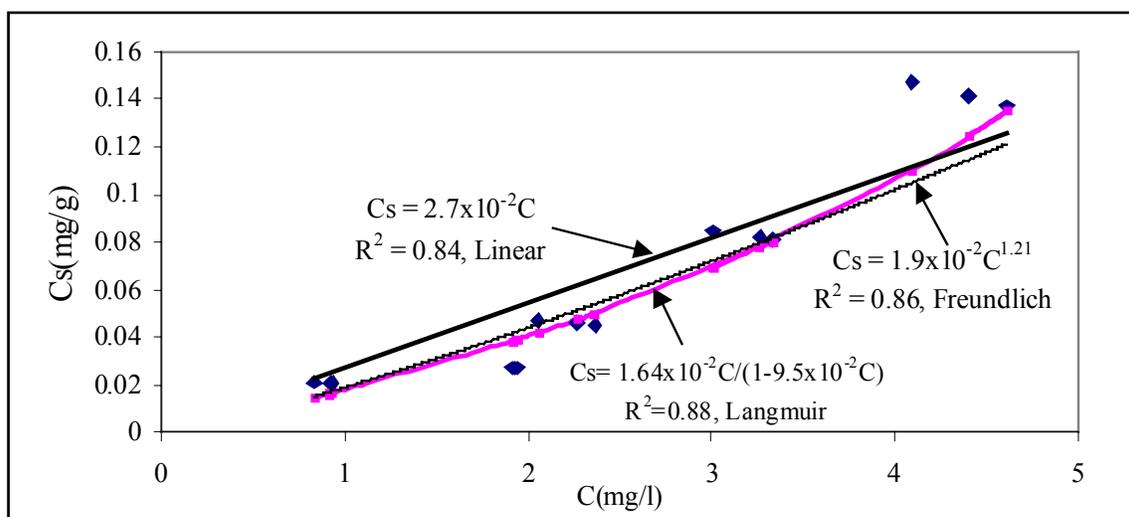


Figure 6.6.3.2.4. Copper adsorption isotherm for the 33RO1 sand/gravel mixture.

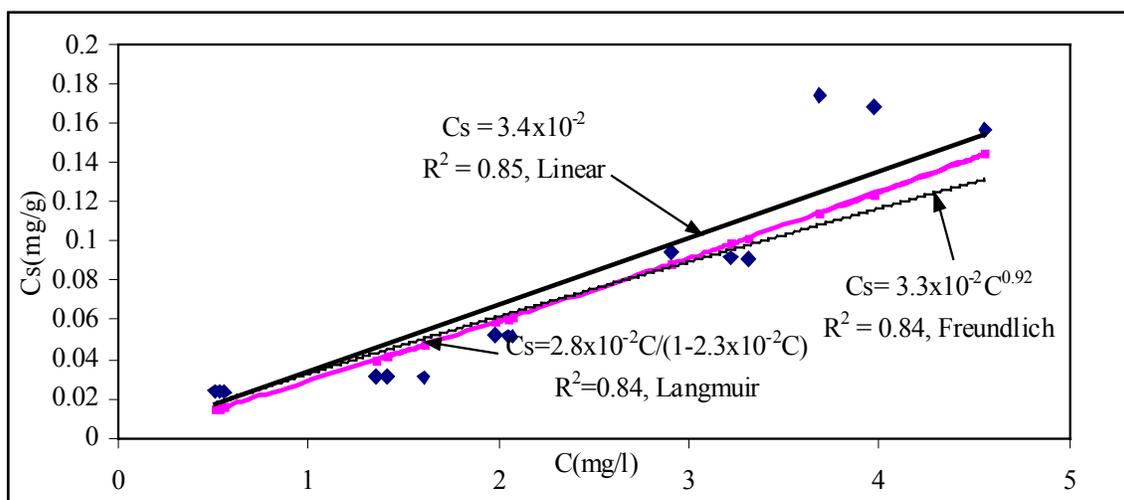


Figure 6.6.3.2.5. Copper adsorption for the Morse Brothers sand/gravel mixture.

Table 6.6.3.2.1. Summary of isotherm parameters for copper adsorption from ACZA leachate on different soils and sand/gravel mixture.

Soil type	Langmuir			Freundlich			Linear		
	Q (mg/g)	b (L/mg)	R ²	K _f	N	R ²	K _d (L/g)	R ²	p- value
Woodburn	4.27	4.5x10 ⁻²	0.99	1.7x10 ⁻¹	0.92	0.99	1.7x10 ⁻¹	0.99	0.644
Sagehill	1.166	7.6x10 ⁻²	0.99	7.9x10 ⁻²	0.88	0.99	6.3x10 ⁻²	0.98	2.8x10 ⁻⁶
33RO1	NA	NA	-	1.9x10 ⁻²	1.21	0.86	2.7x10 ⁻²	0.84	1.9x10 ⁻⁵
63RO1	NA	NA	-	2.09x10 ⁻²	1.32	0.94	3.1x10 ⁻²	0.85	1.5x10 ⁻²
Morris Bro	NA	NA	-	3.3x10 ⁻²	0.92	0.84	3.4x10 ⁻²	0.85	0.223

NA – Not applicable

Comparison of the R² values show that the Freundlich and linear isotherm models fit the data well. The Langmuir model did not fit the data for the three sand/gravel materials tested because the least-squares fitting procedure resulted in concave-upward shapes. If the maximum sorption capacity were assumed, e.g., from an average of C_s values for high solute concentrations, the Langmuir shape could be “forced” through the data, but this exercise was not performed as part of this study.

The isotherms for the different soils show an almost linear trend suggesting that the presence of zinc does not interfere with the adsorption of copper. Jarvis (1981), in his study on copper sorption by soils at low concentrations, found that at initial concentrations of 100 μM (6.5 mg/L) and less, sorption was linearly correlated to the concentration of Cu remaining in solution, whereas at higher concentrations in solution of Cu at 200 μM and more, the Freundlich isotherm gave a better fit. Sidle et al. (1990) obtained good Freundlich first for sorption of Cu²⁺, but both

the linear and Freundlich isotherms are statistically significant, and both could be used simply on the basis of convenience.

Comparison of the linear distribution coefficients (K_d) for copper for different soils show that the Woodburn soil has a higher affinity compared to Sagehill soil, whereas the sand and gravel materials show relatively lesser affinity than the soils. Again, this is not surprising. Woodburn soil has the highest organic matter, followed by the Sagehill soil, and then by sand and gravel materials. It is known that even at low initial concentrations of copper, high proportions of the metal are present as soluble organic complexes. Different soluble organic matter-metal complexes exist in the final solutions from different soils, and these modify the sorption behavior of Cu. It has been estimated that the ratio of complexed Cu to Cu^{2+} in the soil solution is in the range of 10^2 to $10^{2.5}$ and most of the complexed Cu is associated with soluble organic ligands (McBride and Blasiak, 1979; Jarvis, 1981).

In the present study, the organic matter was present at concentrations of around 300 mg/L in the ACZA leachate and 35 mg/L and 8 mg/L in the Woodburn and Sagehill soil leachates, respectively. Thus, copper would exist in a higher percentage as an organo-complex and so correspondingly less of it would be available for adsorption to soil surfaces. The adsorption distribution coefficient (K_d) for Cu is less than that of Zn for all of the soils and sand/gravel materials. Rose and Bianchi-Mosquera (1993) found that Cu adsorbs more strongly than Zn, Ni and Co onto soils and is also relatively less soluble. The present study indicates that the formation of organo-copper complexes is more favored than adsorption onto soil surfaces due to the presence of high amount of organic matter in solution. Cu^{2+} exists predominantly in organically complexed forms whereas Zn^{2+} , because of its lesser tendency to form soluble complexes with organic matter, is complexed to a smaller degree (McBride and Blasiak, 1979; McBride and Tyler, 1982). These results are also consistent with the study of Gao et al. (1997) who found significant correlation between Cu sorption and soil organic matter. In their study they estimated that even with 62 mg/L of dissolved organic carbon in solution, around 69% of copper and 15% of zinc exist as organo-metal complexes and suggested that formation of organo-metal complexes might be the dominant mechanism for adsorption and solution complexation for copper at low metal concentrations.

For the sand and gravel materials, the isotherm plots for copper adsorption show an S-type curve corresponding to competition for Cu^{2+} ions between organic matter and the soil particles. Once the concentration of copper exceeds the complexing capacity of the organics in solution (in the case of sand/gravels, this is lower as there are lesser amounts of organics present) the soil particle surface gains in competition and begins to adsorb copper ions significantly. In the case of soils this is not observed, as there is a greater amount of organics in solution to complex the copper present in the leachate. Thus the adsorption that takes place with soils is predominantly due to complexation with organic matter.

The presence of arsenic in the solution would not decrease (it may even increase) the adsorption of copper as they compete for different sites. The studies of Benjamin and Bloom (1981) have concluded that anions either increase or have no effect on trace metal adsorption, suggesting that the competition between the anions and cations for surface sites is low and the anion adsorption sites are physically and electrically different from the adsorption sites of cations.

A compilation of the parameters calculated for copper adsorption onto different soils obtained from literature is given in Table 6.6.3.2.2. Linear sorptive capacities are less in this study than from the two values cited by Gao et al. (1997). No Langmuir data were found in the literature.

Table 6.6.3.2.2. Isotherm parameters for copper adsorption obtained from literature.

Study	Freundlich		Linear
	K_f	N	K_d (L/g)
Yuan and Lavkulich (1997)	4.27, 9.3×10^{-2}	1.51, 0.59	
Gao et al. (1997)			2.676, 0.916
Bibak (1997)	20.99	0.363	

6.6.3.3 Zinc adsorption on soils and sand/gravels

Zinc was found to adsorb rapidly on both the soils and sand/gravel mixtures. The different adsorption isotherms for the soils and sand/gravel mixtures computed by regression analysis are shown in Figures 6.6.3.3.1 to 6.6.3.3.5. The parameters compiled from the isotherms for zinc adsorption are summarized in Table 6.6.3.3.1.

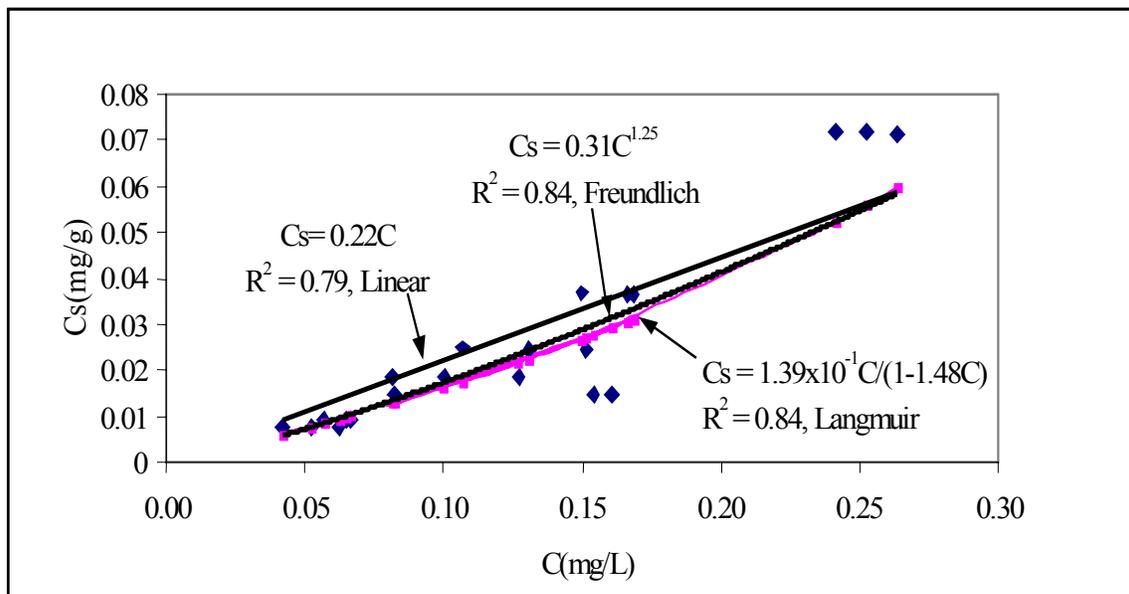


Figure 6.6.3.3.1. Zinc adsorption isotherm for the Woodburn soil.

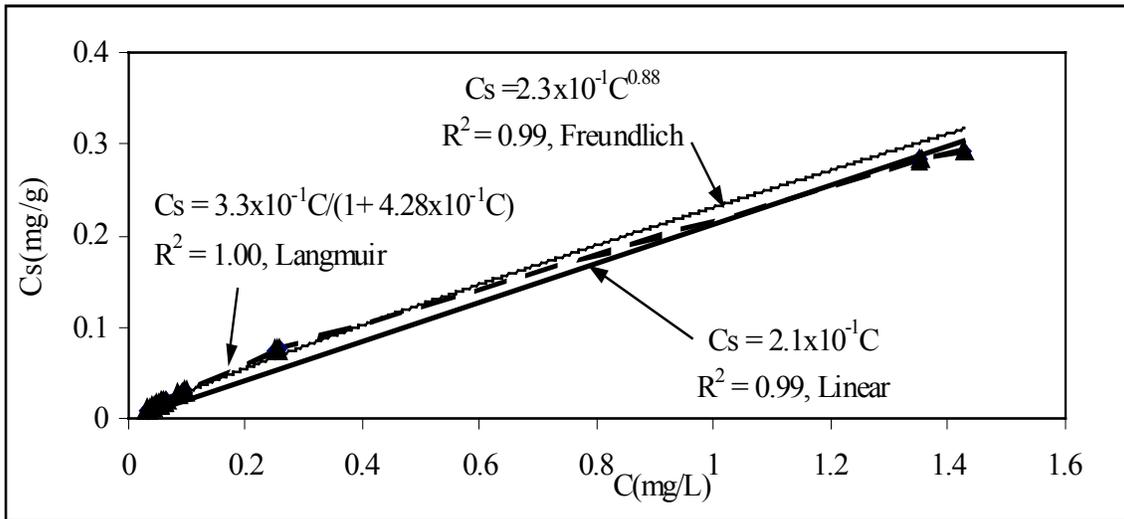


Figure 6.6.3.3.2. Zinc adsorption isotherm for the Sagehill soil.

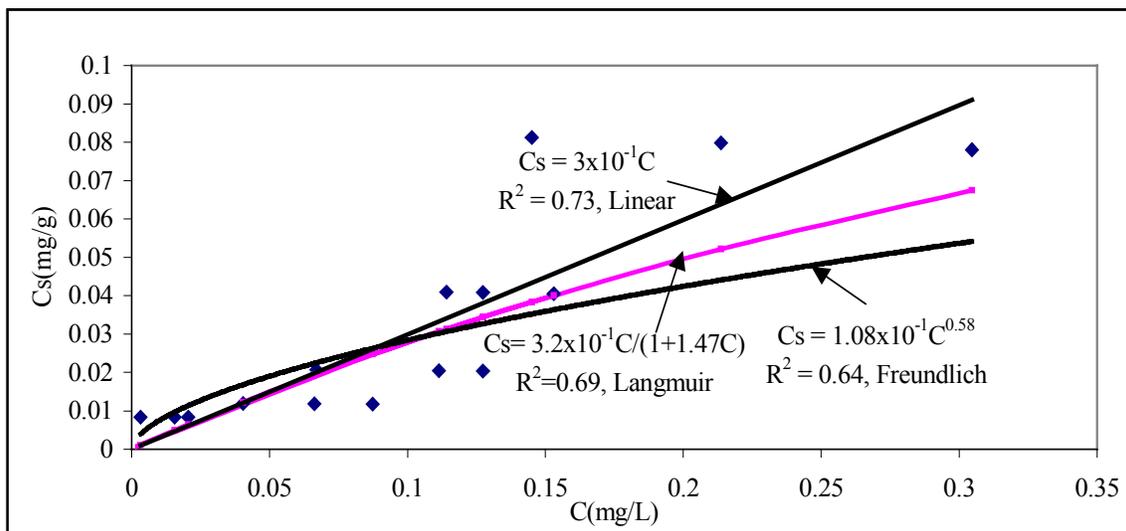


Figure 6.6.3.3.3. Zinc adsorption isotherm for the 33RO1 sand/gravel mixture.

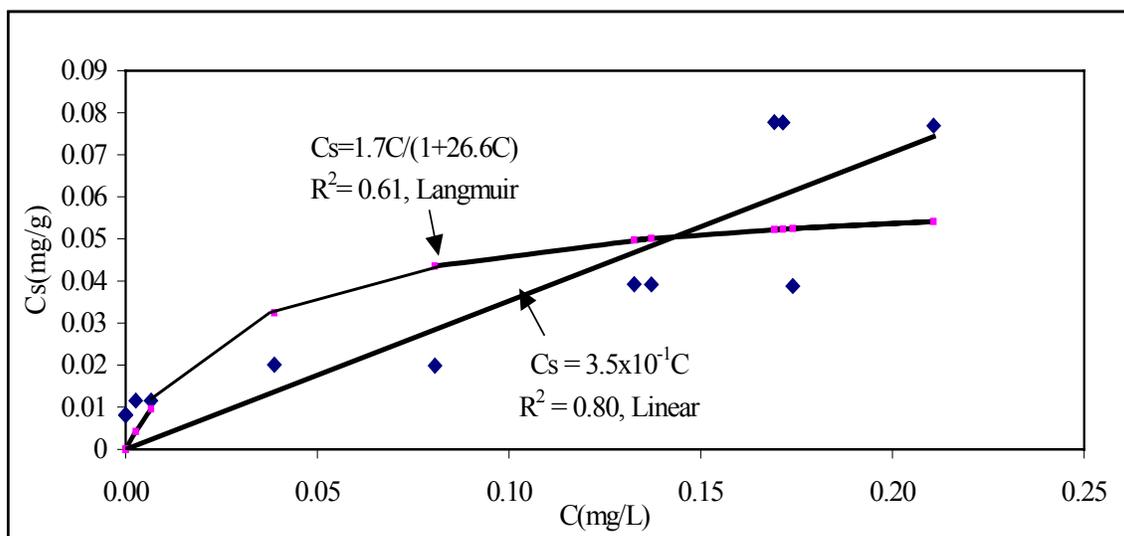


Figure 6.6.3.3.4. Zinc adsorption for the 63RO1 sand/gravel mixture.

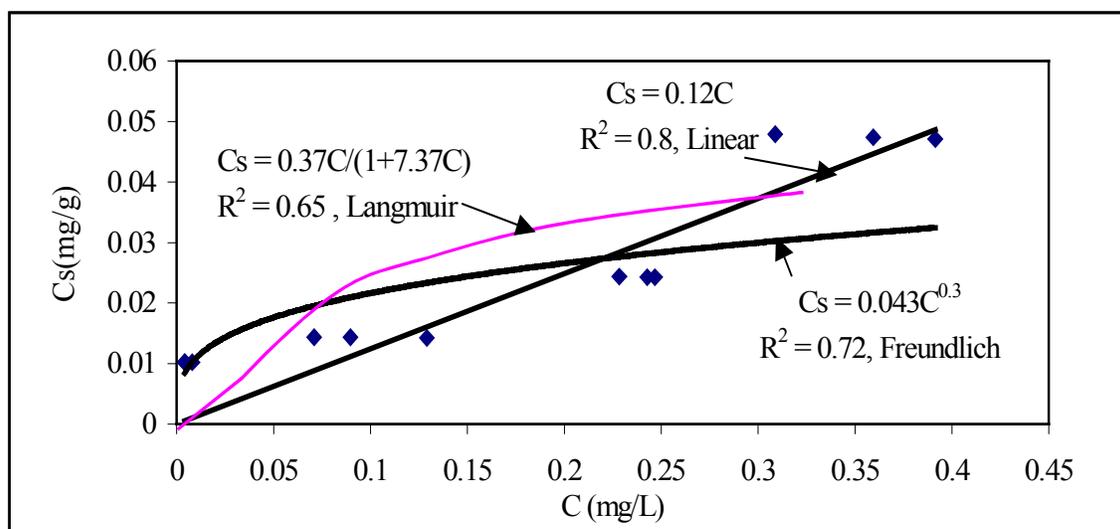


Figure 6.6.3.3.5. Zinc adsorption isotherm for the Morse Brothers sand/gravel mixture.

Table 6.6.3.3.1. Summary of isotherm parameters for zinc adsorption from ACZA leachate on different soils and sand/gravel mixtures.

Soil type	Langmuir			Freundlich			Linear		
	Q (mg/g)	b (L/mg)	R ²	K _f	N	R ²	K _d (L/g)	R ²	p-value
Woodburn	NA	NA	-	3.1x10 ⁻¹	1.25	0.84	2.2x10 ⁻¹	0.79	5.0x10 ⁻⁸
Sagehill	7.74x10 ⁻¹	4.3x10 ⁻¹	1.0	2.3x10 ⁻¹	0.88	0.99	2.1x10 ⁻¹	0.99	8.1x10 ⁻⁵
33RO1	2.2x10 ⁻¹	1.47	0.69	1.08x10 ⁻¹	0.58	0.64	3x10 ⁻¹	0.73	0.85
63RO1	NA	NA	-	NA	NA	-	3.5x10 ⁻¹	0.8	1.3x10 ⁻⁴
Morse Bros.	1.04x10 ⁻¹	2.61	0.7	6.7x10 ⁻²	0.4	0.66	1.7x10 ⁻¹	0.73	0.91

NA – Not applicable

Comparing the different fitted models shows a mixed bag of statistical fits. Linear models are acceptable for all five materials. In the case of two of the materials, the Langmuir form did not fit the data, whereas the Freundlich form did not fit the data for 63RO1 sand/gravel mix.

Zinc sorption at low concentrations has been described by a Langmuir equation (Shuman, 1975) and at extremely low Zn concentrations (0.23 µg/g for one soil and 0.1 µg/g for another soil), it was described by either Langmuir or Freundlich sorption isotherms (Kuo and Kikkelsen, 1979). With higher Zn concentrations, they found that the Freundlich equation was better in describing the sorption. Taylor et al. (1995), in their study on zinc sorption by Alabama soils, found that both the Langmuir and Freundlich isotherms had to be resolved into two linear portions to fit the data better and suggested that zinc sorption in soil solution was controlled by two different sites varying in their binding energies. They concluded that there was the presence of more than one type of site or sorption mechanism for Zn.

Comparing the adsorption (K_d) among the materials shows that zinc is adsorbed equally by all the soils and sand/gravel materials (except Morse Brothers, which is a little lower). Since organic matter does not play a major role in the adsorption of zinc, it is possible that the specific sites for zinc adsorption are present equally in all the materials tested. It should be noted that the pH values in the sand/gravel leachates were kept higher than those in soils, which might have contributed to a higher amount of adsorption.

The present study of ACZA metals sorption with the selected soils/ sand and gravels showed that Zn is adsorbed relatively higher than Cu based on the distribution coefficient (K_d) whereas previous studies (Gao et al., 1997; Sposito, 1990) have concluded that the following selectivity of metals applies (based on the distribution coefficients):

$$\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd} > \text{Ni}$$

This could be explained by the fact that copper forms relatively stable and stronger complexes with organic matter compared to Zn as soluble organic concentrations (TOC) were high, and relatively low amounts of zinc (compared to copper) are present in the leachate, resulting in insufficient saturation of the adsorption sites.

Due to the presence of high amounts of organic matter in ACZA leachate and also in soils, copper is complexed to a larger extent as organo-metal complexes and hence lesser amounts are available for sorption by soil, since both are competitive complex formation reactions. This results in the availability of more sites that could effectively adsorb zinc and hence give a higher distribution coefficient for zinc sorption. Kuo and Baker (1980) found that competition of Zn with Cu for surface adsorption sites could increase the concentration of Cu in solution, thereby lowering the sorption of Cu at higher pH levels. Elrashidi and Connor (1982) found that the competition between Cu and Zn is influenced by both the sorbing capacity of the soil and the metal concentration in the soil solution. Since zinc was present at a much lower concentration compared to copper in the present study, it may not have saturated the adsorption sites on the soils giving a greater adsorption capacity for it.

A compilation of parameters that were available from the literature for the adsorption of zinc onto soils is given in Table 6.6.3.3.2. The parameters generally are in good agreement with the values obtained in the present study.

Table 6.6.3.3.2. Isotherm parameters for zinc adsorption obtained from literature.

Study	Langmuir		Freundlich		Linear
	Q (mg/g)	b	K_f	N	K_d (L/g)
Gao et al. (1997)					1.981, 1.114
Yuan and Lavkulich (1997)	5.4×10^{-1} , 7.6×10^{-3}	8.6×10^{-1} , 9.1×10^{-1}			
Taylor et al. (1995)	2.5×10^{-1}				
Elrashidi and Connor (1982)			8.08×10^{-1}	1.03	
Kiekens (1990)	2	1.3×10^{-2}			
Bibak (1997)			5.607	0.566	

6.7 SUMMARY AND CONCLUSIONS

Different soils and sand/gravels were used to adsorb the constituents of ACZA leachate, namely arsenic, copper and zinc. Using the adsorption data, isotherms were constructed for the different materials. From a comparison of the distribution coefficients, it was found that zinc was the most strongly adsorbed followed by copper and then by arsenic.

Arsenic adsorption is relatively lower because the pH of the leachate was around 6.5-7.0 in the case of soils, and 8.8-9.0 in the case of sand/gravels. Arsenic adsorption is higher at lower pH and decreases as pH is increased (being an oxyanion). At higher pH values, the surface hydroxyl groups are deprotonated, resulting in an increased negative charge on the soil, and this reduces the adsorption potential of arsenic on the soils.

Copper adsorption was found to be lesser when compared to that of zinc. Although the literature suggests that copper is more strongly bound than zinc, the presence of high amounts of soluble organic matter in both the leachate and the soils (particularly Woodburn) are possible reasons for the reversed trend. Copper forms strong soluble organo-metal complexes that compete with soil surface complexation (adsorption), resulting in lower copper adsorption onto soil sites. Evidence for this hypothesis was seen in the decreased partition coefficients for the sand/gravel materials (which contain much smaller quantities of organic matter) compared to soils.

Zinc was adsorbed the greatest by all materials tested. Since zinc forms weaker soluble organic complexes than copper, its adsorption was less affected by the high amount of soluble organic matter present.

Amongst the soils, Woodburn adsorbed all metals highest, followed by Sagehill soil. The sand/gravel mixtures adsorbed the metals the least. This is reasonable based on the composition of the individual materials (lower organic matter content). However, there was some sorption on the sand/gravel mixtures, indicating that this mitigating effect should be included in the analysis of contaminant transport from highway C&R materials.

Table 6.6.3.1.1. Task 5: Summary data for chemical analyses.

Task 5: Determination of Adsorption and Desorption Parameters for C&R materials on Sand and Gravel																				
Sample ID	Test Conditions	Time (hr)	Tox Lab ID	Toxicity Results			Chemistry Test Results													
				Algal Toxicity			TOC (mg/L)	Al (mg/L)	As (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	Fe (mg/L)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)	P (mg/L)	Sb (mg/L)	Sr (mg/L)
				Concentration as %																
				Elutriate																
%EC ₅₀ or %LC ₅₀	Lower 95% CL	Upper 95% CL																		
1	ACZA Sagehill Soil Sorption	24	4230401	NIE			NIE	4.865	BD	0.170	7.538	0.021	4.948	6.158	1.955	0.055	2.805	0.586	0.025	BD
1	ACZA Elutriate	24	4232426	NA			180.9	0.008	18.847	0.087	0.399	10.741	0.001	2.524	0.052	0.001	1.676	0.018	0.125	0.001
2	Sagehill 10 g/L	24	4232427	NA			180.9	0.263	18.235	0.117	8.648	6.858	0.336	5.789	1.505	0.181	2.509	0.076	0.121	0.028
3	Sagehill 10 g/L	24	4232428	NA			208.3	0.405	17.699	0.105	8.605	6.665	0.397	5.449	1.534	0.180	2.340	0.199	0.116	0.028
4	Sagehill 10 g/L	24	4232429	NA			189.8	0.393	17.719	0.108	8.878	6.567	0.381	5.596	1.579	0.179	2.455	0.108	0.114	0.029
5	Sagehill 50 g/L	24	4232430	NA			184.6	1.910	15.559	0.173	18.364	2.452	2.102	12.826	3.968	0.205	3.084	0.403	0.101	0.063
6	Sagehill 50 g/L	24	4232431	NA			179.0	1.494	15.517	0.163	18.342	2.378	1.719	12.527	3.838	0.192	2.813	0.433	0.101	0.062
7	Sagehill 50 g/L	24	4232432	NA			182.0	1.719	15.533	0.169	17.310	2.426	1.899	12.121	3.895	0.195	2.670	0.453	0.112	0.071
8	Sagehill 100 g/L	24	4232433	NA			166.4	1.650	13.706	0.168	29.403	1.180	1.727	19.077	5.581	0.163	3.334	0.458	0.094	0.096
9	Sagehill 100 g/L	24	4232434	NA			161.1	1.886	13.459	0.171	28.732	1.143	1.958	18.420	5.432	0.159	3.398	0.395	0.094	0.093
10	Sagehill 100 g/L	24	4232435	NA			134.1	1.277	13.409	0.207	27.903	1.216	1.352	18.156	5.192	0.170	3.520	0.362	0.111	0.094
11	Sagehill 150 g/L	24	4232436	NA			155.3	0.596	11.774	0.179	35.252	0.740	0.456	21.185	6.343	0.207	3.264	0.401	0.088	0.114
12	Sagehill 150 g/L	24	4232437	NA			160.8	0.579	11.918	0.155	33.371	0.803	0.466	20.215	6.042	0.094	3.170	0.424	0.093	0.107
13	Sagehill 150 g/L	24	4232438	NA			151.4	0.891	11.922	0.172	35.320	0.772	0.800	21.985	6.396	0.145	3.368	0.451	0.090	0.112
14	Sagehill 200 g/L	24	4232439	NA			149.3	0.397	10.757	0.200	40.734	0.578	0.195	23.763	7.157	0.140	3.754	0.544	0.087	0.130
15	Sagehill 200 g/L	24	4232440	NA			149.2	0.349	10.564	0.197	40.517	0.568	0.160	24.367	7.108	0.124	4.319	0.450	0.087	0.129
16	Sagehill 200 g/L	24	4232441	NA			150.6	0.405	10.443	0.211	41.641	0.557	0.188	24.261	7.302	0.152	4.098	0.465	0.084	0.133
17	Sagehill 250 g/L	24	4232442	NA			147.6	0.377	9.175	0.204	46.441	0.447	0.159	26.164	8.088	0.177	3.710	0.439	0.078	0.145
18	Sagehill 250 g/L	24	4232443	NA			144.7	0.406	9.284	0.218	45.675	0.447	0.189	25.707	7.979	0.193	4.240	0.505	0.065	0.144
19	Sagehill 250 g/L	24	4232444	NA			148.5	0.400	9.691	0.174	42.785	0.500	0.204	23.796	7.411	0.086	3.353	0.504	0.078	0.139
20	Sagehill 400 g/L	24	4232445	NA			165.2	0.405	6.410	0.250	54.691	0.290	0.114	30.376	9.407	0.176	4.706	0.506	0.065	0.171
21	Sagehill 400 g/L	24	4232446	NA			142.0	0.432	6.458	0.245	57.886	0.288	0.160	30.875	9.778	0.175	4.495	0.408	0.059	0.179
22	Sagehill 400 g/L	24	4232447	NA			133.8	0.325	7.135	0.196	54.654	0.335	0.052	27.255	9.325	0.079	3.795	0.571	0.073	0.166
23	Sagehill 500 g/L	24	4232448	NA			133.4	0.416	4.852	0.253	64.564	0.238	0.074	30.073	10.970	0.155	5.409	0.463	0.069	0.197
24	Sagehill 500 g/L	24	4232449	NA			137.0	0.379	5.117	0.251	63.650	0.239	0.059	30.495	10.647	0.166	4.740	0.410	0.067	0.193

CHAPTER 7

TASK 6: AGING EFFECTS IN C&R MATERIALS

7.1 INTRODUCTION

All testing and protocols used in earlier Phase II testing involved the use of “new” materials, which for “asphalt” means recently placed, and “concrete” means after 28 days of curing. Such new materials are assumed to represent a worst case related to the rates of chemical leaching by water. Such new materials would have maximum concentrations of materials at or near the leaching surface and would exhibit less diffusion limitation to leaching from precipitation. In contrast, aged materials are believed to release relatively lower concentrations due to the effect of various environmental factors. The purpose of this task is to examine the effects of accelerated aging in MSWIBA asphalt.

7.2 EXPERIMENTAL APPROACH

The effect of exposure time to various environmental factors for highway materials (termed “aging”) was investigated using open graded asphalt concrete amended with MSWIBA (municipal solid waste incinerator bottom ash). Two major effects dominate aging of asphalt mixtures: 1) loss of volatile components and oxidation in the construction phase (short-term aging); and 2) progressive oxidation of the in-place mixture in the field (long-term aging) (Bell et al., 1994). A loose mixture of MSWIBA asphalt was used for all the tests in this task. In these experiments the process of aging was accelerated by exposing the loose MSWIBA asphalt mix to increased temperature and oxygen. Change in chemical and toxicological characteristics due to aging was examined as a function of time

7.2.1 Effect of Heat and Oxidation: Forced Draft Oven Method

For the preliminary investigation within this task, the forced-draft oven aging procedures as recommended in the SHRP (Strategic Highway Research Program) protocol (SHRP-A-383) were adapted to the needs for aging of asphalt. Aging test was performed initially in a forced draft oven for 4-hours at 135°C for short-term aging and for 5-days at 85°C for long-term aging. The effect of heating was tested by exposure at 135°C for 4 hours, and up to 5 days at 85°C. The higher temperature represents heating in the batching process, and the lower temperature, aging in the environment. Compressed air supply was maintained at 1 atm. pressure to provide fresh supply of oxygen required for oxidation. Samples were taken out of the oven at regular time intervals during the long-term aging and 24-hour batch leachates prepared. A battery of chemical and toxicological tests was performed to study the effect of short-term and long-term aging of highway material using these leachates. Various forms of aging were tested using SHRP protocols and compared to the results for “new” MSWIBA amended AC (asphalt concrete).

7.2.2 Effect of Heat and Oxidation: Pressure Aging Vessel Method

Forced-draft oven aging as indicated in Section 7.3.1.3 did not result in substantial changes in either the chemistry or toxicity of the MSWIBA-asphalt samples. So, the possibility of accelerating the process of oxidation by increasing the air pressure to about 5 to 10 atmospheres was attempted. Accordingly, the OSU team proposed a change in the testing protocol based on SHRP-A-383 Procedure (Bell et al., 1994). The short-term aging procedure was kept the same but the long-term aging test was modified to use a Pressure Aging Vessel (PAV) System, PRENTEX Model 9300. For long-term aging the temperature was maintained at the same 85°C but the supplied air pressure was increased to 10 atmospheres. This was expected to facilitate the exposure of samples to compressed air at a higher oxygen concentration and thereby accelerate the oxidation process. For chemical analyses, ICP and GC/MS analyses, and for biological analyses, algal chronic tests were performed on aged samples. Short-term aging was conducted for four hours and long-term aging for 30 days. Samples were taken at regular time intervals during long-term aging process and 24-hour batch leachates prepared for chemical and toxicological evaluations.

7.2.3 Effect of Wet and Dry Cycles

The effect of wet-dry cycles was tested by alternating leaching and dry exposure with one day of leaching followed by one day of dry exposure to air. For wet cycles, batch leaching with 1:4 solid-to-liquid mass ratio was performed. The leaching solution was removed at end of days 1, 3, 5, 7, and 9, and added at the beginning of days 0, 2, 4, 6, and 8. The cumulative concentration versus time curve for the sample was compared to the cumulative concentration versus time curve for new material using actual exposure time to water in both cases.

Aging effects were incorporated into the fate and transport model through changes in the coefficients used in the leaching equations (Section 10.3). Parameters may be varied according to material and age. Wet and dry cycle variation can be accomplished similarly, depending on the experimental results. For example, if leaching follows the typical exponential path, it is possible that a “reversal” along the path of concentration vs. time may occur, that is, a regeneration of leaching capacity might be observed during dry cycles. Such a mechanism can be incorporated into the model if it is observed, based on the laboratory results (however, it was not observed). The alternative is that leaching occurs simply as a function of wet-weather hours, regardless of interruptions by dry weather. The laboratory data adjudicate this question.

7.3 RESULTS AND DISCUSSION

7.3.1 Short- and Long-term Aging of MSWIBA-Asphalt

7.3.1.1 Chemical analyses

MSWIBA-asphalt long-term and short-term aging with oxidation at 85 °C and 10 atmospheric pressure: The results of TOC leachate for both short-term aging and long-term aging of MSWIBA-asphalt with oxidation at 85°C and 10 atmospheric pressure are shown in Figure 7.3.1.1.1. Over 5 days, no changes in TOC concentration were observed. The lack of change in TOC indicates that only high molecular weight or nonvolatile organics are present. Nor were changes in metals concentration observed (Figure 7.3.1.1. 2). As metals are nonvolatile, results confirm their conservation in the solution. No changes in the GC/MS spectra were observed for both short-term and long-term experiments, indicating that no oxidation of the hexane and dichloromethane extractable organic compounds occurred. GC/MS analyses were performed on MSWIBA-asphalt leachate on a measured volume of the MSWIBA leachate (1 L), which was serially extracted in a separatory funnel three times with methylene chloride. The extracts were concentrated to a volume of 1 mL by Kuderna-Danish evaporation. Chemical composition was determined by mass spectrometry (Hewlett-Packard Model 6890 gas chromatograph connected to a Hewlett-Packard Model 5970 mass-spectrometer, Reztec fused silica capillary column 30 meter in length, 0.32 mm ID). The original GC/MS spectrum for MSWIBA shows that more than 45 peaks were detected (Figure 7.3.1.1.3). Organic compounds and their chemical formulae were determined from the GC/MS analysis and library match, as shown in Table 7.3.1.1. 1.

Table 7.3.1.1. 1. GC/MS analysis and library match of MSWIBA-asphalt leachate.

Organic compound	Chemical formula
Cyclopentasiloxane, decamethyl	C ₁₀ H ₃₀ O ₅ Si ₅
Benzaldehyde, 2-hydroxy	C ₇ H ₆ O ₂
Cyclohexasiloxane, dodecamethyl	C ₁₂ H ₃₆ O ₆ Si ₆
Benzenamine, N,N, 3-Trimethyl	C ₉ H ₁₃ N
Ethanone, 1-(4-methylphenyl)	C ₉ H ₁₀ O
Benzaldehyde, 4-hydroxy-3-methoxy	C ₈ H ₈ O ₃
Dodecanoic Acid	C ₁₂ H ₂₄ O ₂
[1,1' - Biphenyl]-2-ol	C ₁₂ H ₁₀ O
Diethylphthalate	C ₁₂ H ₁₄ O ₄
Tetradecanoic acid	C ₁₄ H ₂₈ O ₂
Bis(2-ethylhexyl) phthalate	C ₂₄ H ₃₈ O ₄
Octadecanoic acid, 2-methylpropyl	C ₂₂ H ₄₄ O ₂
1,2 - Benzenedicarboxylic acid, 2-butoxyethyl butyl ester	C ₁₈ H ₂₆ O ₅

No PAH compounds were detected in MSWIBA-asphalt leachate, and all other organic compounds identified by GC/MS were present in trace quantities expected to be nontoxic; as such, these compounds probably do not contribute to the observed toxicity of the sample.

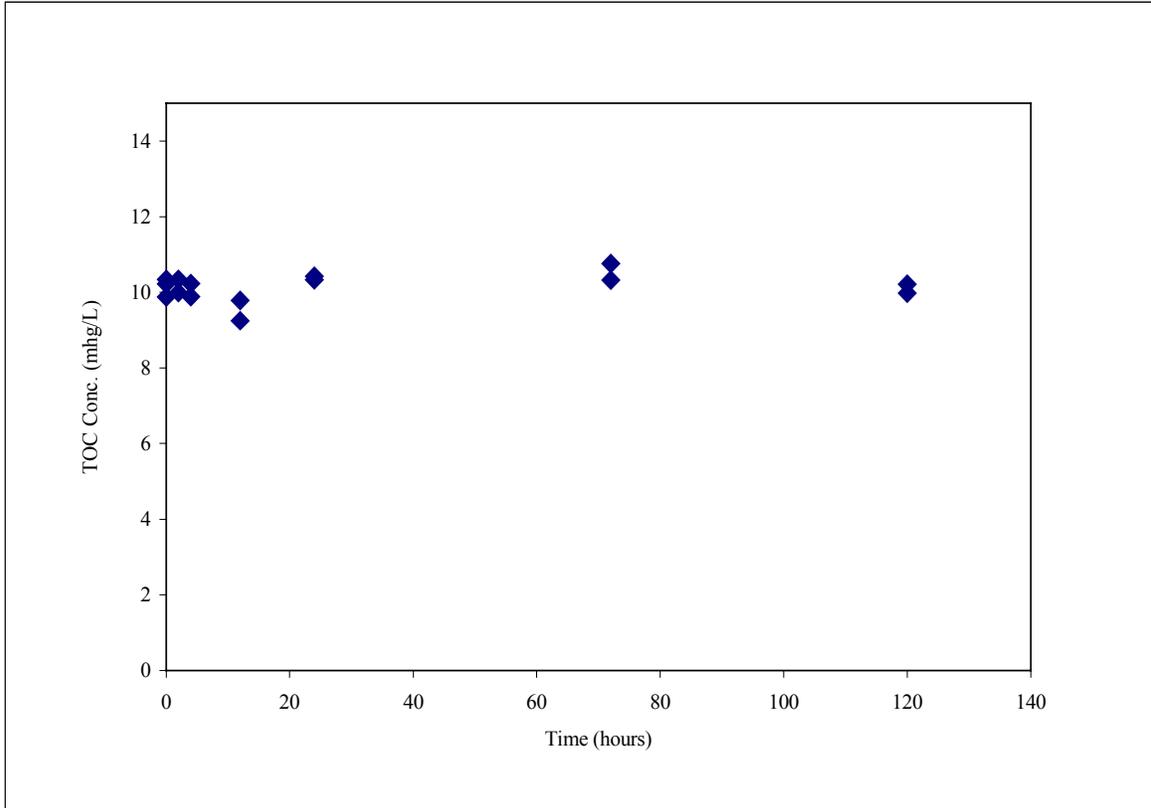


Figure 7.3.1.1.1. Simulation of aging of MSWIBA-asphalt mixture , TOC concentration in leachate as a function of aging time (duplicate tests).

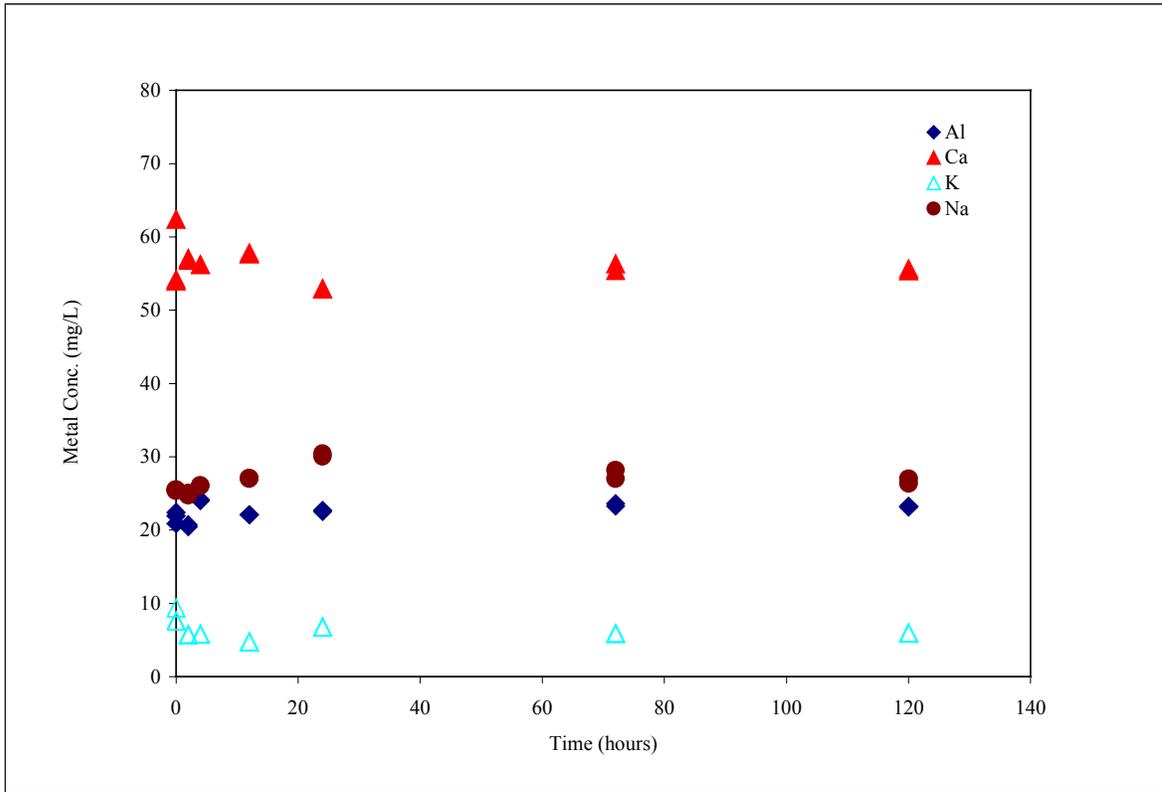
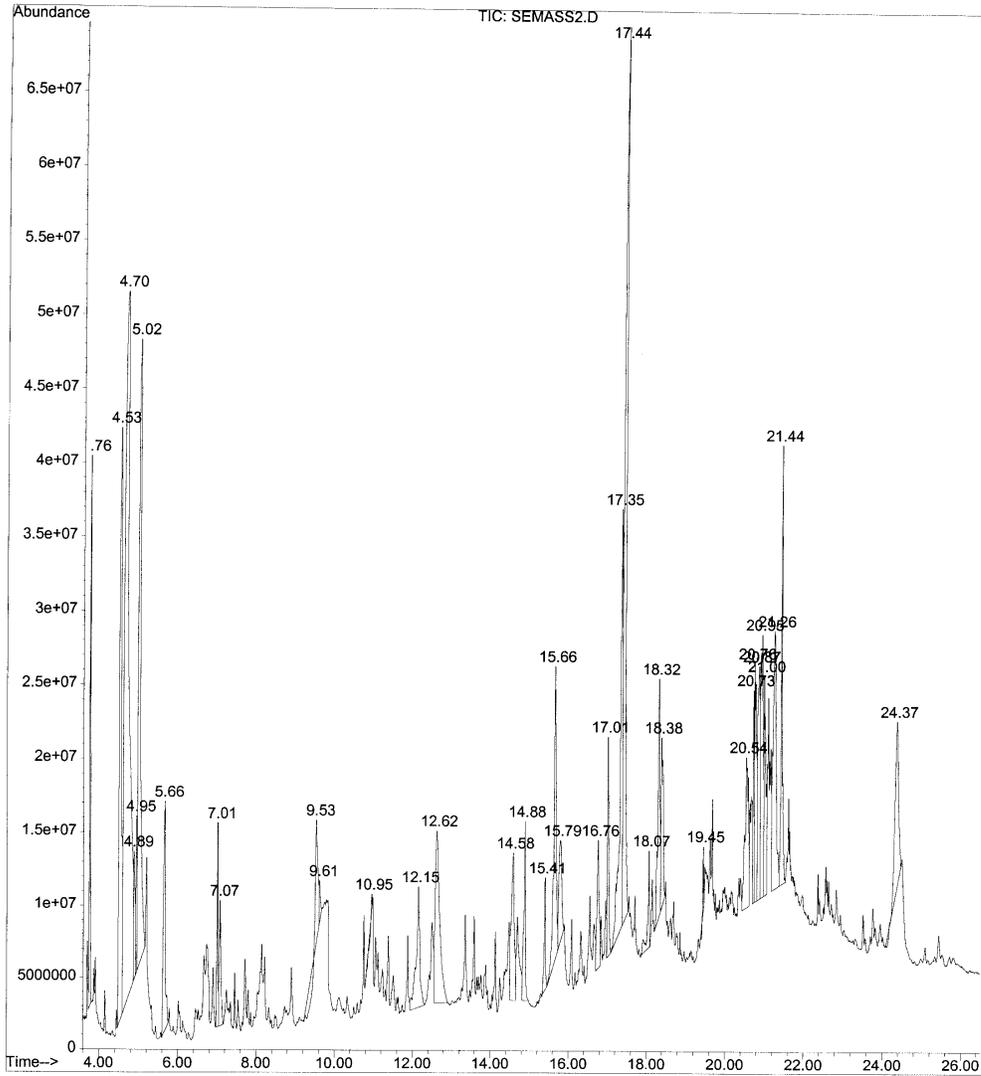


Figure 7.3.1.1.2. Simulation of aging of MSWIBA-asphalt mixture, metals concentrations in leachate as a function of aging time (duplicate tests).

File : D:\HPCHEM\1\DATA\SEMASE2.D
Operator : Mohammad Azizian
Acquired : 18 Feb 1999 1:55 pm using AcqMethod MFA_HW
Instrument : OSU GC/MS
Sample Name: Semass Leachate
Misc Info : EPA method Ext. w CH2Cl2 .
Vial Number: 1



7.3.1.2 Toxicity analyses

Results from algal toxicity analyses of leachates generated from MSWIBA-asphalt after short- and long-term aging indicated little or no effect due to aging. Earlier, leachates prepared from un-aged samples (control samples not exposed to heating and oxidation) were analyzed for algal toxicity. Statistically, there were no significant differences between aged (exposed to air at 1 atmosphere pressure for 5-days at oven temperature of 85 °C for long-term aging) and un-aged samples. Figure 7.3.1.2.1 indicates an EC50 value (average of duplicates) of 1.3% for control samples. Although a small decrease in algal toxicity was observed with increase in aging time there were overlap of confidence limits indicating statistically no change in toxicity. As evident from chemical analyses, no significant change in TOC was observed between aged and un-aged samples (Figure 7.3.1.1.1).

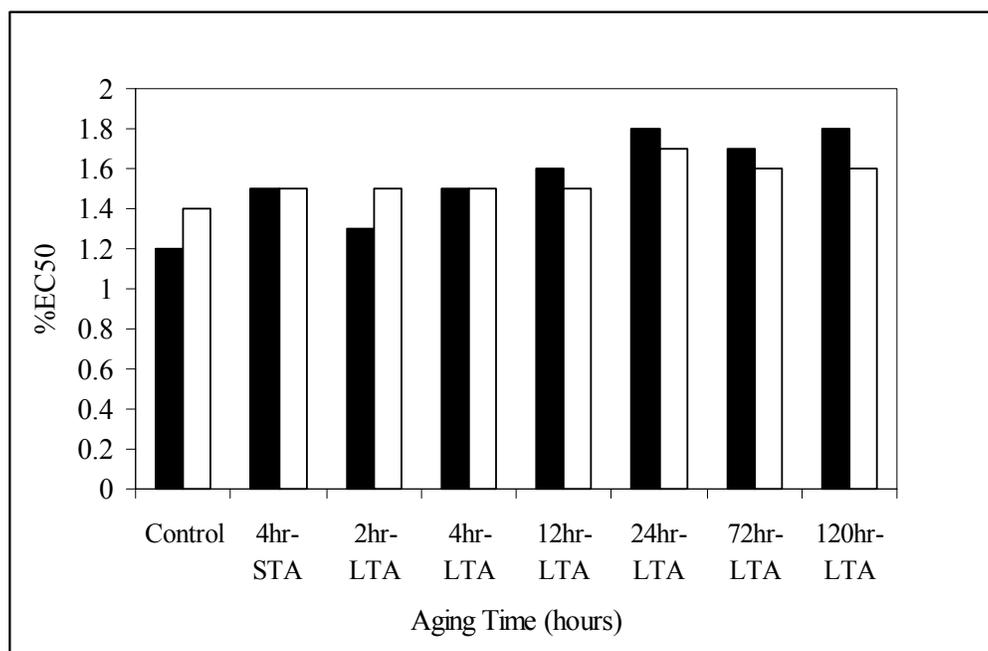


Figure 7.3.1.2.1 Algal toxicity of MSWIBA-asphalt leachates generated from short-term aging (STA) and long-term aging (LTA) by forced-draft oven method. The two bars represent the duplicate tests for each sample.

Over all, accelerated aging test by heating at 85°C and oxidation at 1 atmosphere pressure did not indicate significant change in either the chemistry or toxicity of the MSWIBA asphalt samples. No substantial decrease in TOC indicated that effectiveness of volatilization of possible toxic organics may be far less than required to decreasing the toxicity. Aluminum is observed to be another factor that is contributing to the non-reduction in toxicity of the aged samples. As exemplified by the chemical analyses (Summary Table 7.3.1.1.1), no substantial change in aluminum concentrations (~20 mg/L) was observed during the aging process. Organics also showed no significant change indicating oxidation of organics were not substantial.

The possibility of accelerating the oxidation process by increasing the air pressure to 10 atmospheres was tried. The testing protocol was modified based on SHRP-A-383 (Bell et al.,

1994). Using a Pressure Aging Vessel (PAV) System (PRENTEX, Model 9300) instead of the forced-draft-oven used earlier, the temperature was maintained at the same 85°C but the pressure was increased to 10 atmospheres. This modification facilitated the exposure of samples to a higher oxygen concentration and thus accelerated the oxidation process.

Toxicity analyses of pressure aging sample: Algal toxicity results (Figure 7.3.1.2.2) indicated no change in toxicity due to short-term aging (at 135°C for 4-hours). In contrast, a significant reduction in algal toxicity due to long-term aging at 85°C and 10 atm. pressure. During long-term aging, samples were taken at 2, 4, 12, 24, 72, 120, 360, 720 hours for toxicological and chemical analyses to assess the change in toxicity and chemistry of the samples by the effect of heating and oxidation. No significant decrease in toxicity was observed until 120 hours of aging. In particular, there was obvious overlapping of confidence limits of %EC50 values of control samples and samples aged up to 120-hours. However, there was a substantial increase in algal EC50 value from 1.7% to 3.8% (average of duplicate tests) between 120-hours and 360-hours, indicating a reduction in toxicity. A similar change (3.8% to 6.2%) in algal EC50 values was also observed between 360-hr and 720-hr sample aging, again indicating a statistically significant reduction in leachate toxicity due to aging of the MSWIBA-asphalt samples.

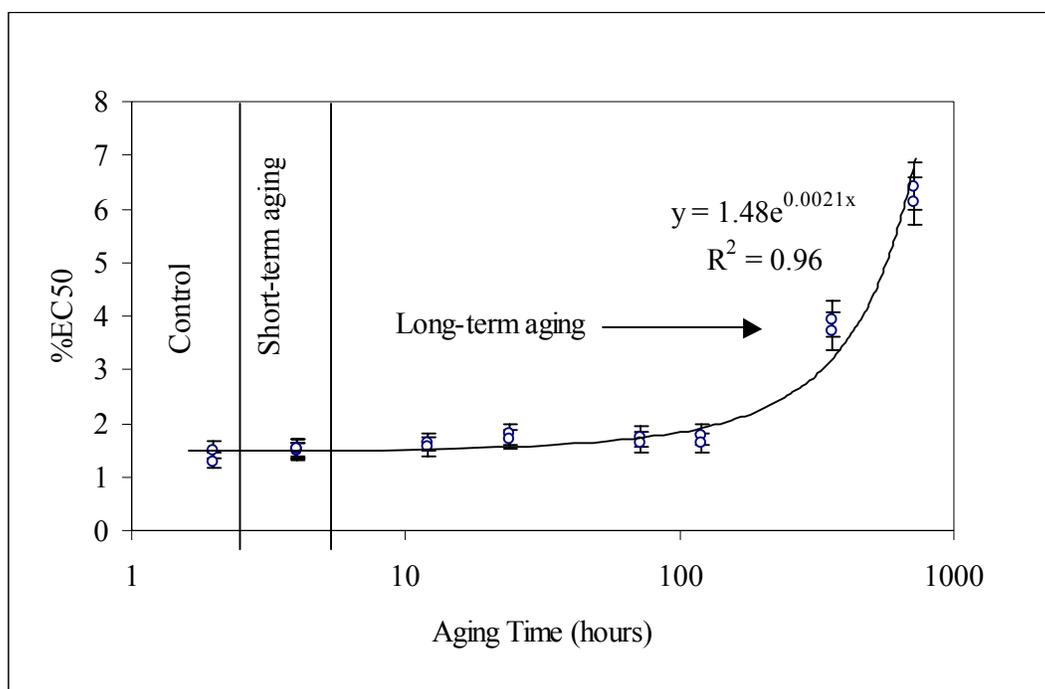


Figure 7.3.1.2.2 Algal EC50 values for short- and long-term aging samples (duplicates tests). Error bars indicate the upper and lower confidence limits for each EC50 value.

In contrast, chemical components remained largely unchanged as is evident from the chemical analysis of leachates from short- and long-term aging samples. Apparently, no simple relationship prevails between the toxicity reduction of aged samples and chemical components. In particular, concentrations of TOC (~10 mg/L) and total soluble aluminum (~20 mg/L) were largely unchanged following short- and long-term aging processes. Total soluble aluminum may

not be the best factor for determining toxicity, as a substantial decrease in toxicity was observed after 360- and 720-hours of aging. Evidently, during the aging process, either aluminum speciation changes (e.g., formation of inorganic or organic soluble complexes) or the effects of oxidation and volatilization reduced the toxicity of leachable soluble organic compounds without affecting the TOC substantially.

7.3.2 Effect of Wet/Dry Cycles on MSWIBA-asphalt Leachate

7.3.2.1 Chemical Analyses

The effect of intermittent wetting on leaching characteristics of MSWIBA-asphalt was investigated by alternating leaching and dry exposure, with one day of leaching followed by one day of dry exposure to air. The leaching solutions were removed for testing on days 1, 3, 5, 7, 9, 11 and 13 and exposed to dry air on days 2, 4, 6, 8, 10, and 12 to simulate alternate wetting and drying. Leachates thus generated were analyzed for both chemistry and toxicity. To compare and evaluate if leaching occurs as a function of wetting hours or regeneration of leaching occurs during the dry cycles, a control test was also set up. This test involves 7-days of wetting only without dry exposure time in between. After each 24-hours of leaching, leachate is removed and fresh leaching medium added to the material. Both chemical and biological analyses of these leachates were performed. The resulting metals concentrations in leachate for wet and dry cycle leaching of MSWIBA-asphalt with distilled water are shown in Figure 7.3.2.1.1. The equation for power function fit of aluminum and calcium concentration decrease with time are given as:

$$\begin{aligned} C_{Al} &= 18.05 (t)^{-0.87} & (R^2 &= 0.98) \\ C_{Ca} &= 37.00 (t)^{-1.03} & (R^2 &= 0.98) \end{aligned}$$

All chemical and toxicity analyses data are summarized in Table 7.3.1.1.1.

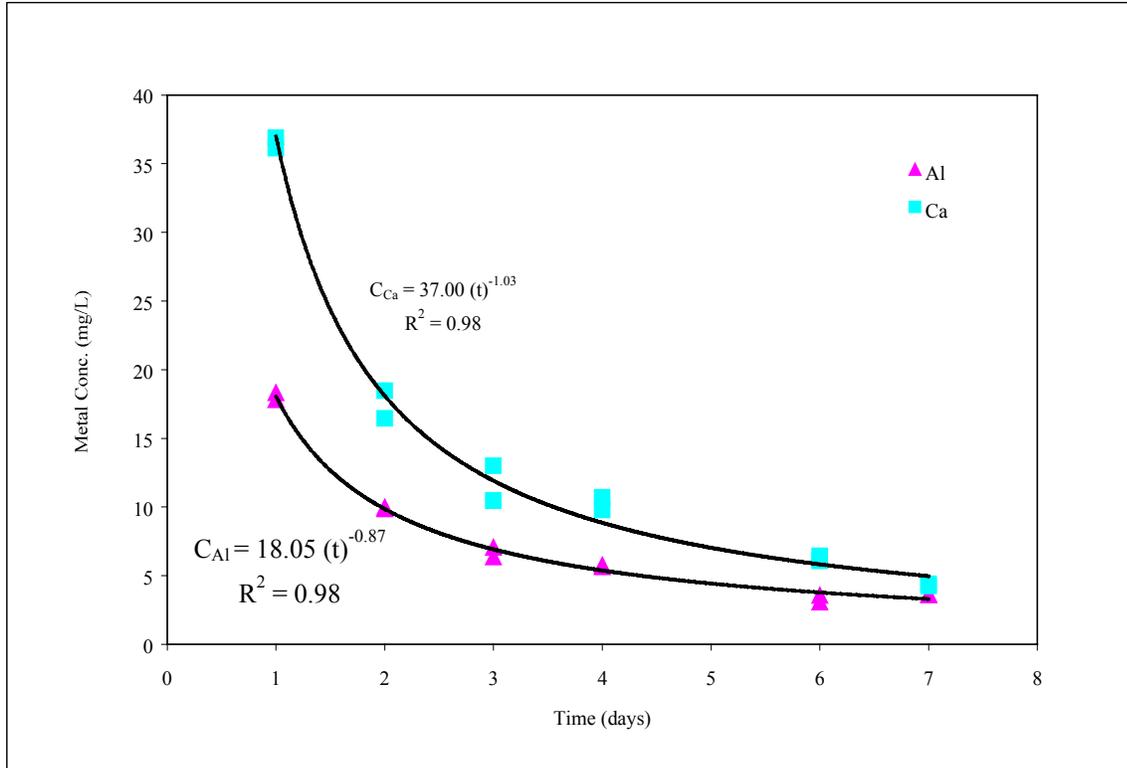


Figure 7.3.2.1.1 Al and Ca in wet and dry cycle leachate from MSWIBA-asphalt as a function of time (duplicate tests).

The results of TOC in leachate from wet and dry cycle leaching of MSWIBA-asphalt with distilled water are shown in Figure 7.3.2.1.2. The equation for power function decrease of TOC concentration with time is given as:

$$C_{\text{TOC}} = 8.10 (t)^{-0.77} \quad (R^2 = 0.89)$$

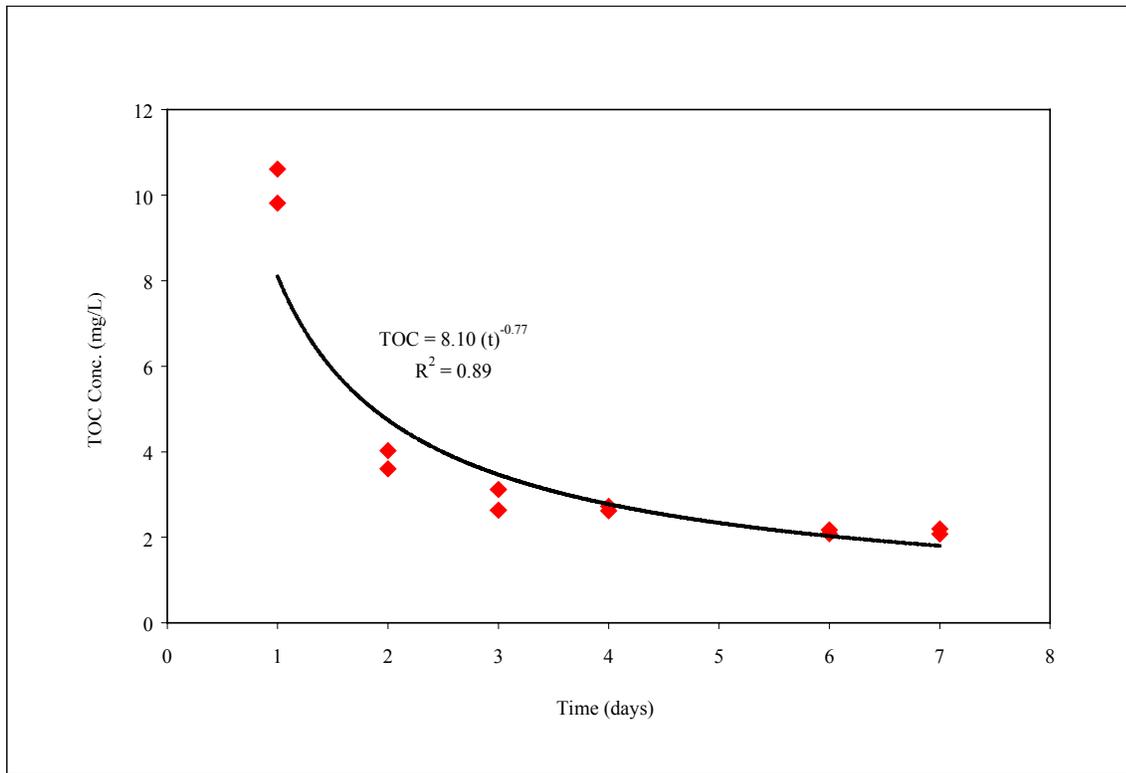


Figure 7.3.2.1.2 TOC in wet and dry cycle leachate from MSWIBA-asphalt as a function of time (duplicate tests).

The effect of wet cycle only leaching was tested by continuous wet leaching, without dry exposure to air, as a control for one week. The results of metal leachate for wet cycles leachate of MSWIBA-asphalt with distilled water are shown in Figure 7.3.1.2.3. The equations for power function decrease of aluminum and calcium concentration with time are given as:

$$C_{Al} = 27.82 (t)^{-0.59} \quad (R^2 = 0.99)$$

$$C_{Ca} = 50.31 (t)^{-0.88} \quad (R^2 = 0.98)$$

Although Al and Ca leaching rates vary somewhat between wet and dry cycle and the wet cycle only, ultimate concentrations for Al and Ca for both wet and dry cycle and the wet cycles only are the same (Figure 7.3.2.1.4).

These results confirm the assumptions of the fate and transport model, namely, that leaching rates decline with time, and that the leaching is a function only of wet-weather hours. Hence, no modifications were made to the model as a result of this task.

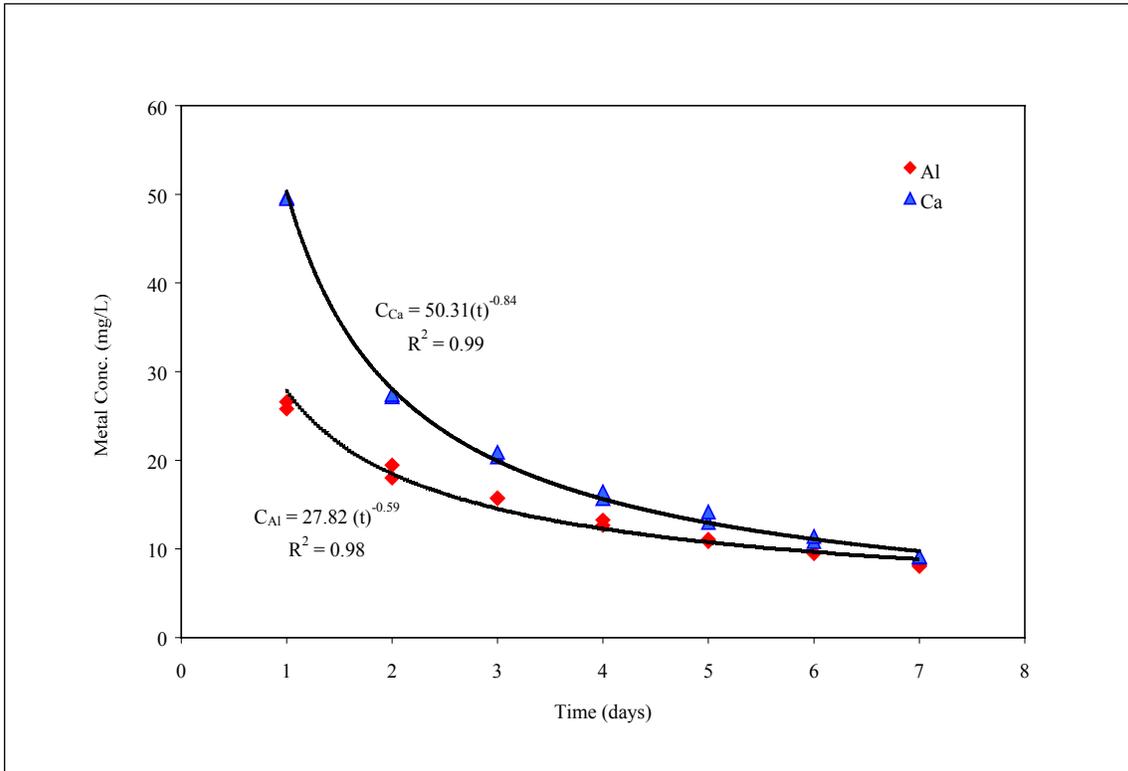


Figure 7.3.2.1.3. Al and Ca in wet cycles only leachate from MSWIBA-asphalt as a function of time (duplicate tests).

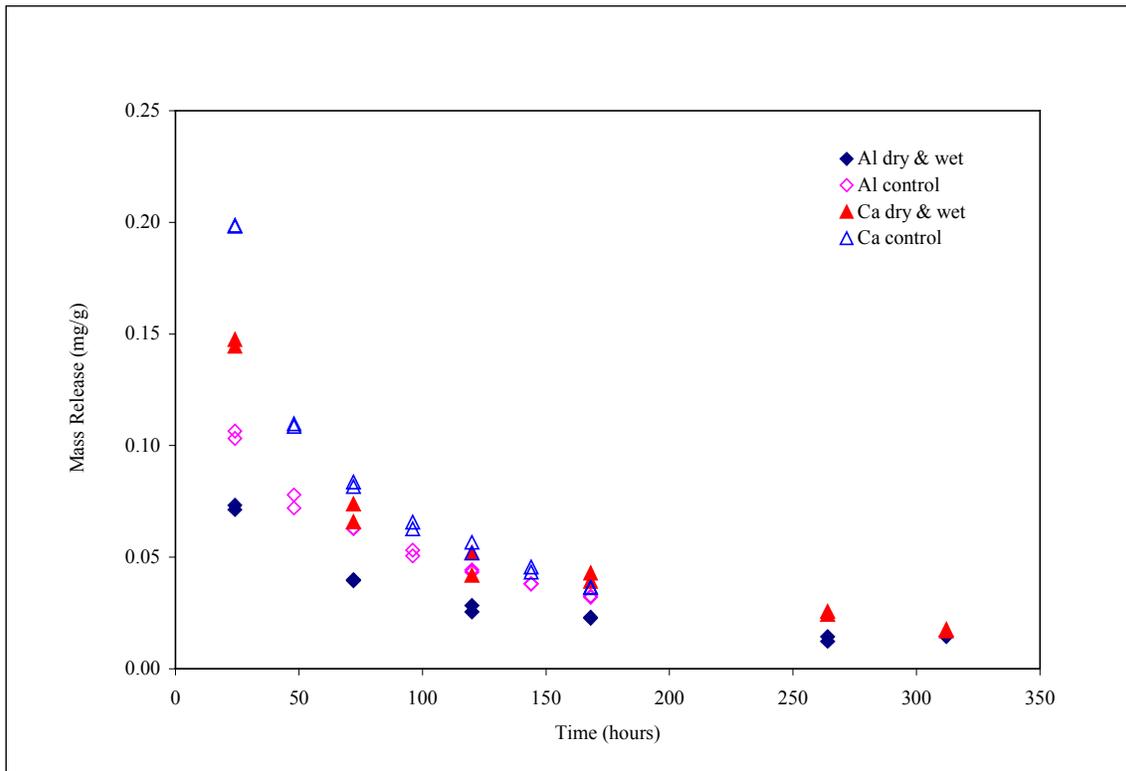


Figure 7.3.2.1.4. Al and Ca mass release in wet and dry cycles and wet cycles only MSWIBA-asphalt leachate as a function of time (duplicate tests).

MSWIBA-asphalt batch leaching tests: Batch leaching tests were conducted using the standard 250 gm of MSWIBA-asphalt per 1 L leaching solution (solid/solution mass ratio = 1:4) as a control test for wet and dry cycle test. Long-term (7 days) dynamic batch leaching experiments at ambient pH (~9) were conducted at the same solid/solution mass ratio. Batch leaching tests indicated that the maximum leaching rate occurred within 48 hr. as exemplified by the data for Ca, Al, Na, and K (Figure 7.3.2.1.5) and for TOC leachate (Figure 7.3.2.1.6). Metals in the leachate were measured for a suite of twenty-one metals of which only Al, Ca, K, and Na were determined to be above the ICP detection limits. The chemistry analyses and toxicity data are summarized in Table 7.3.1.1.1 at the end of this chapter for all Task 6 procedures.

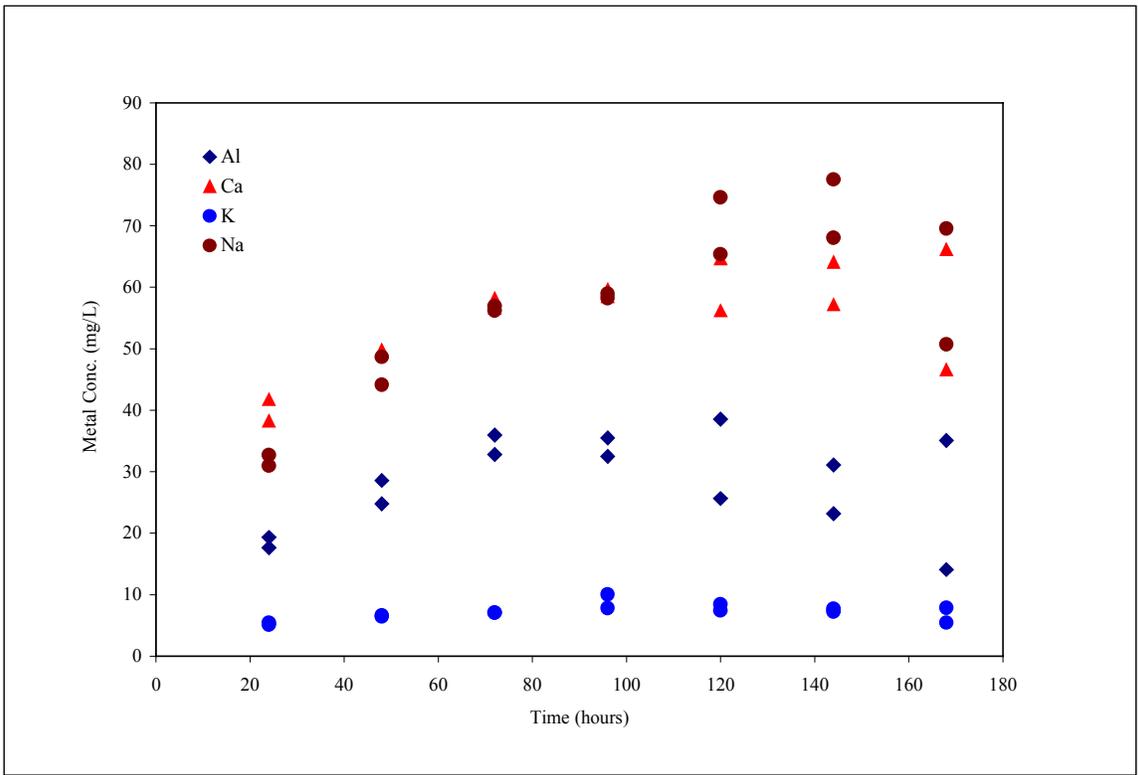


Figure 7.3.2.1.5. MSWIBA-asphalt batch leaching results for Ca, Al, Na, and K, concentration as a function of time (duplicate tests).

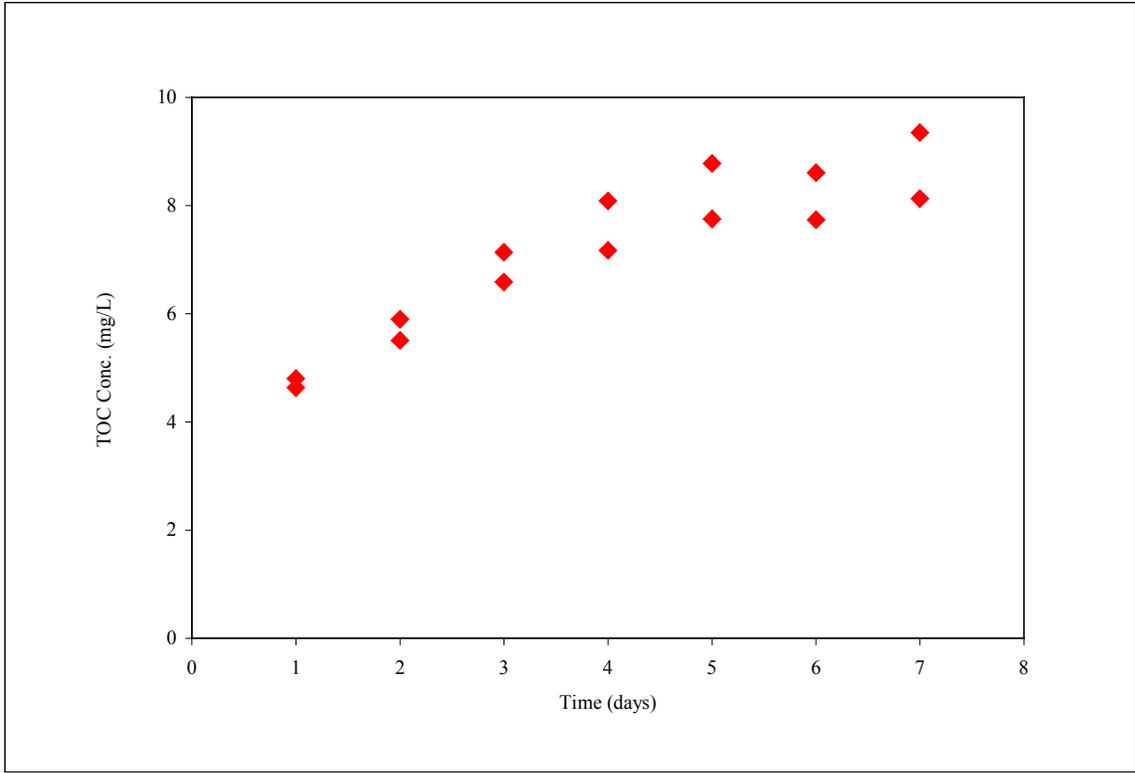


Figure 7.3.2.1.6. MSWIBA-asphalt batch leaching results for TOC, concentration as a function of time (duplicate tests).

7.3.2.2 Toxicological analyses

96-hour *Selenastrum capricornutum* toxicity tests were performed on samples leached during the wet and dry cycle test. First wet-cycle sample exhibited an EC50 value of about 2%. The second wet-cycle (day 3) sample exhibited an EC50 value increased to 3.3% indicating a 50% decrease in toxicity. A similar trend in decreasing toxicity with each additional wetting day was observed. The final wet-cycle sample (day 13) exhibited an EC50 value of 6.3%, indicating a 3-fold decrease in toxicity compared with the first wet-cycle sample. Observed EC50 values ranged from about 2% in day-1 leachates to 6% in day-13 leachates (Figure 7.3.2.2.1). This decline in algal toxicity indicated a good correlation with decrease in aluminum, calcium and TOC concentrations in the corresponding leachates shown in Figures 7.3.2.1.1 and 7.3.2.1.2.

In the control test, that involved wet-cycles only, a similar trend in the reduction of toxicity compared with reduction of toxicity in the wet and dry cycle test was observed (Figure 7.3.2.2.1). A consistent pattern was apparent in the reduction of algal toxicity with increasing wet hours in samples with as well as without intermittent exposure to dry air. Data from chemical analyses also indicated a similar pattern in the leaching of chemical components (Figures 7.3.2.1.1 and 7.3.2.1.2). The algal toxicity tests confirm that the leaching from MSWIBA-asphalt occurs simply as function of wet-weather hours regardless of interruptions by dry weather.

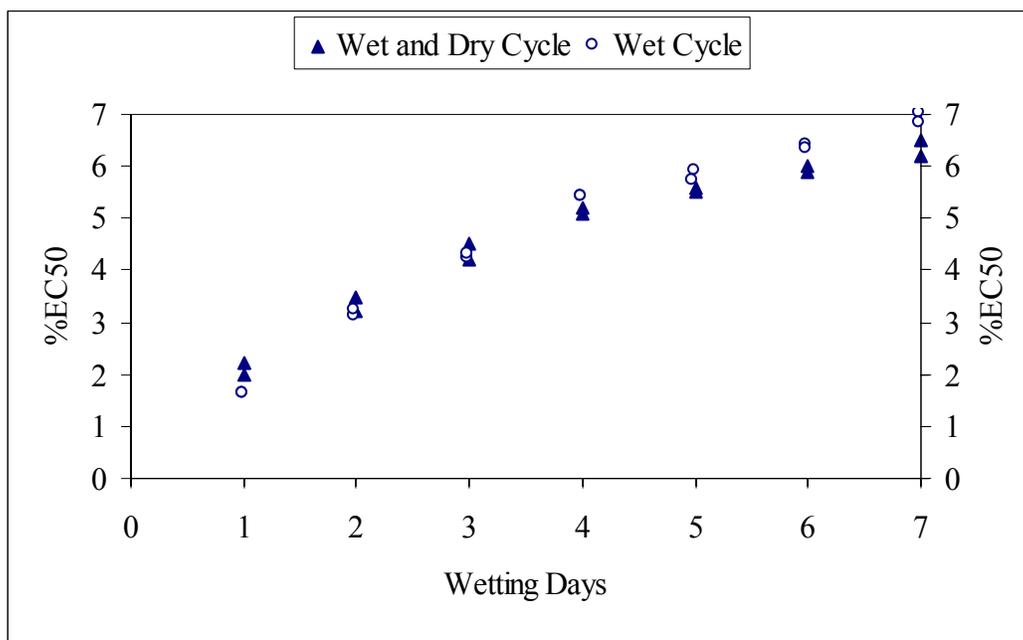


Figure 7.3.2.2.1 Algal %EC50 values for wet and dry cycle test and wet cycle test as control (duplicate tests).

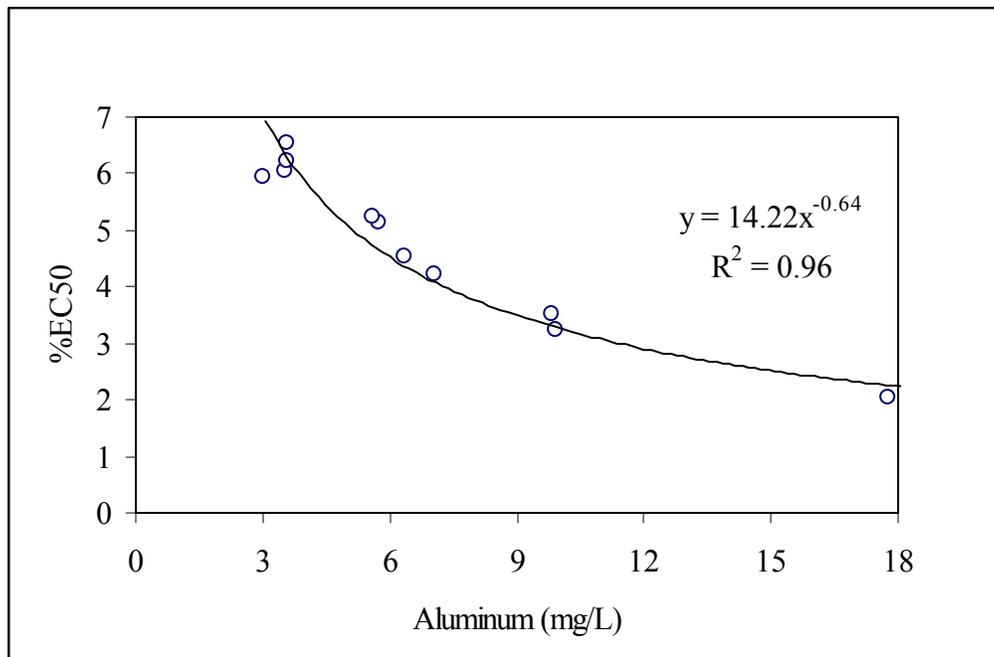


Figure 7.3.2.2.2 Relationship between algal %EC50 values and aluminum concentrations from wet and dry cycle test.

Aluminum is reported to be toxic to *S. capricornutum* at concentrations of about 0.4-0.9 mg/L (EPA, 1988). An EC50 value of about 0.6 mg/L was observed for aluminum tested individually by OSU Ecotoxicology Laboratory. MSWIBA-asphalt leachates generated from these wet and dry cycle tests had Al concentrations ranging from ~3 mg/L to 25 mg/L. Figure 7.3.2.2.2 illustrates the good inverse correlation ($R^2=0.96$) between %EC50 and aluminum concentrations for a power-function data fit.

7.4 SUMMARY AND CONCLUSIONS

Aging is defined as the effect of exposure time to the environment for highway C&R materials. Environmental factors that could affect C&R materials aging include time for solid or crystalline formation, exposure to air/oxygen, exposure to heat, and wet/dry cycles. The various forms of aging were tested using Strategic Highway Research Program (SHRP) protocols and compared to the results for “new” MSWIBA amended asphalt. The effect of heating and oxidation and the effect of wet and dry cycle in the aging process of asphalt were studied as a function of time.

Short-term aging (135°C for 4-hours) did not show any significant change in both toxicity and chemistry. Long-term aging (85°C for 30-days), however, exhibited significant reduction in algal toxicity after 360- and 720-hours of aging. No simple relationship was observed between the toxicity reduction in aged samples and chemical components. TOC levels in aged samples remained largely unchanged even after 30-days of oxidation under 10 atm. pressure. Apparently, during the aging process, either aluminum speciation changes (e.g., formation of inorganic or

organic soluble complexes) or the effects of oxidation and volatilization reduced the toxicity of leachable soluble organic compounds without affecting the TOC substantially.

MSWIBA-asphalt leachates generated from wet and dry cycle tests had aluminum levels ranging from ~3 mg/L to 25 mg/L. Results indicated a significant correlation ($p < 0.01$) between %EC50 values and aluminum levels in MSWIBA-asphalt leachates. A similar trend in the reduction of toxicity for both “wet” cycle (continuous leaching without dry exposure) and “wet and dry” cycle tests (with intermittent exposure to dry air) was observed. This consistent pattern in toxicity reduction with increasing wetting hours both in samples with and without intermittent exposure to dry air strongly agreed with leaching behavior of chemical components (aluminum and TOC in particular) as well.

Comparison of results between “wet and dry” cycle and “wet” cycle only tests indicated that the leaching of chemical components from MSWIBA-asphalt occurs simply as function of wet-weather hours regardless of interruptions by dry weather. Hence, this supports the assumption in the fate and transport model that leaching rates decline simply as a function of wet-weather hours.

Table 7.3.1.1.1. Task 6: Summary data for chemical and toxicity analyses.

Task 6: Aging Effects in C&R materials																		
Sample ID	Test Conditions	Time (hr)	Tox Lab ID	Toxicity Results			Chemistry Test Results											
				Algal Toxicity			TOC (mg/L)	Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sb (mg/L)	Sr (mg/L)	Zn (mg/L)	Final pH
				Concentration as % Elutriate														
				% EC ₅₀ or % LC ₅₀	Lower 95% C.L.	Upper 95% C.L.												
MSWIBA-Asphalt Aging Test Leachates																		
1	Semass-asphalt control	0	4228401	1.3	1.2	1.5	5.938	21.045	0.072	41.913	0.008	5.288	0.310	23.931	0.050	0.176	BD	8.4
2	Semass-asphalt control	0	4228402	1.4	1.3	1.6	6.143	22.948	0.071	45.377	0.004	5.133	0.313	23.030	0.038	0.181	BD	8.32
3	Short-term aging	4	4228403	1.5	1.3	1.6	6.712	23.127	0.084	45.309	0.002	5.954	0.309	22.814	0.038	0.169	BD	8.29
4	Short-term aging	4	4228404	1.5	1.3	1.6	6.867	21.824	0.087	45.832	0.001	5.325	0.313	23.136	0.048	0.235	BD	8.14
5	Long-term aging	2	4228405	1.3	1.2	1.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	BD	8.3
6	Long-term aging	2	4228406	1.5	1.3	1.7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	BD	8.27
7	Long-term aging	4	4228407	1.5	1.4	1.7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	BD	8.05
8	Long-term aging	4	4228408	1.5	1.4	1.7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	BD	8.09
9	Long-term aging	12	4228409	1.6	1.5	1.8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	BD	8.18
10	Long-term aging	12	4228410	1.5	1.4	1.7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	BD	8.10
11	Long-term aging	24	4228411	1.8	1.6	2.0	8.19	22.117	0.062	46.528	0.005	6.417	0.350	45.236	0.049	0.178	BD	8.26
12	Long-term aging	24	4228412	1.7	1.5	1.9	7.796	22.345	0.060	46.752	0.005	6.705	0.351	47.085	0.036	0.175	BD	8.24
13	Long-term aging	72	4228413	1.7	1.6	1.9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	BD	8.13
14	Long-term aging	72	4228414	1.6	1.5	1.8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	BD	8.24
15	Long-term aging	120	4228415	1.8	1.6	2.0	9.05	22.204	0.061	47.555	0.003	6.642	0.353	45.762	0.042	0.175	BD	8.30
16	Long-term aging	120	4228416	1.6	1.5	1.8	9.499	22.333	0.061	47.142	0.003	6.474	0.354	46.678	0.045	0.176	BD	8.16
17	Long-term aging	360	4230401	3.7	3.4	4.1	10.45	22.672	0.060	47.050	0.002	6.474	0.352	46.389	0.048	0.176	BD	8.22
18	Long-term aging	360	4230402	3.9	3.6	4.3	10.31	22.386	0.060	47.043	0.003	6.465	0.350	46.873	0.053	0.175	BD	8.30
19	Long-term aging	720	4232401	6.1	5.7	6.6	10.5	22.877	0.113	44.418	0.028	6.910	0.347	39.933	0.035	0.196	BD	8.17
20	Long-term aging	720	4232402	6.4	6.0	6.9	10.44	22.098	0.061	41.453	0.010	6.700	0.347	36.943	0.032	0.172	BD	8.09
MSWIBA-Asphalt Wet and Dry Cycles Leachate																		
1	Wet and Dry Cycles Day-1 Leachate	24	4229401	2.0	1.9	2.2	10.610	17.820	0.049	36.879	0.014	5.839	0.189	23.265	0.030	0.239	BD	8.2
2	Wet and Dry Cycles Day-1 Leachate	24	4229402	2.2	2.1	2.2	9.819	18.322	0.057	36.135	0.014	6.136	0.190	23.846	0.034	0.141	BD	8.22
3	Wet and Dry Cycles Day-3 Leachate	72	4229403	3.2	2.9	3.5	4.029	9.968	0.029	18.458	0.001	2.570	0.404	8.787	0.026	0.145	BD	8.25
4	Wet and Dry Cycles Day-3 Leachate	72	4229404	3.5	3.3	3.8	3.600	9.879	0.052	16.450	0.006	2.505	0.389	8.533	0.032	0.071	BD	8.3
5	Wet and Dry Cycles Day-5 Leachate	120	4229405	4.2	3.9	4.6	3.121	7.080	0.035	13.004	0.001	1.556	0.552	4.547	0.019	0.117	BD	7.95
6	Wet and Dry Cycles Day-5 Leachate	120	4229406	4.5	ncf	ncf	2.632	6.378	0.044	10.459	0.001	1.529	0.480	4.234	0.012	0.043	BD	8.01
7	Wet and Dry Cycles Day-7 Leachate	168	4230403	5.1	4.7	5.6	2.619	5.757	0.074	9.768	0.009	1.221	0.647	4.715	0.010	0.100	BD	8.2
8	Wet and Dry Cycles Day-7 Leachate	168	4230404	5.2	4.8	5.8	2.722	5.645	0.078	10.702	0.010	1.267	0.529	4.128	0.015	0.045	BD	8.04
9	Wet and Dry Cycles Day-9 Leachate	216	4230405	5.6	5.2	6.2	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	BD	8.16
10	Wet and Dry Cycles Day-9 Leachate	216	4230406	5.5	5.1	6.2	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	BD	8.23
11	Wet and Dry Cycles Day-11 Leachate	264	4230407	6.0	5.4	6.6	2.173	3.577	0.012	6.427	0.012	2.255	0.352	4.028	-0.002	0.066	BD	8.28
12	Wet and Dry Cycles Day-11 Leachate	264	4230407	5.9	5.5	6.4	2.080	3.071	0.021	6.064	0.013	2.168	0.310	4.832	-0.014	0.026	BD	8.1
13	Wet and Dry Cycles Day-13 Leachate	312	4231401	6.2	5.8	6.7	2.075	3.597	0.044	4.226	0.010	2.409	0.351	4.273	-0.007	0.027	BD	8.2
14	Wet and Dry Cycles Day-13 Leachate	312	4231402	6.5	6.1	6.9	2.192	3.630	0.077	4.397	0.008	1.370	0.789	4.429	0.023	0.101	BD	8.11

Table 7.3.1.1.1. Task 6: Summary data for chemical and toxicity analyses (concluded).

Task 6: Aging Effects in C&R materials																		
Sample ID	Test Conditions	Time (hr)	Tox Lab ID	Toxicity Results			Chemistry Test Results											
				Algal Toxicity			TOC (mg/L)	Al (mg/L)	Ba (mg/L)	Ca (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sb (mg/L)	Sr (mg/L)	Zn (mg/L)	Final pH
				Concentration as % Elutriate														
				% EC ₅₀ or % LC ₅₀	Lower 95% C.L.	Upper 95% C.L.												
MSWIBA-Asphalt Wet Cycles Leachate																		
1	Semass AC Control A 1	24	4232401	1.6	1.4	1.8	6.372	25.791	0.133	49.675	BD	5.839	0.250	37.708	0.065	0.196	BD	8.9
2	Semass AC Control B 1	24	4232402	1.6	1.4	1.9	3.074	26.603	0.153	49.549	BD	6.928	0.350	41.517	0.086	0.186	BD	8.68
3	Semass AC Control A 2	48	4232403	3.1	2.8	3.4	2.101	17.997	0.162	27.156	BD	2.659	0.312	14.590	0.051	0.110	BD	9.05
4	Semass AC Control B 2	48	4232404	3.2	2.9	3.5	1.967	19.456	0.131	27.421	BD	3.898	0.338	18.774	0.065	0.103	BD	8.94
5	Semass AC Control A 3	72	4232405	4.2	3.9	4.6	1.633	15.760	0.134	20.386	BD	1.886	0.366	9.913	0.117	0.083	BD	9.17
6	Semass AC Control B 3	72	4232406	4.3	4.0	4.7	1.731	15.679	0.102	20.910	BD	2.757	0.370	12.238	0.049	0.078	BD	9.21
7	Semass AC Control A 4	96	4232407	5.4	5.0	5.8	1.480	13.262	0.129	15.667	BD	1.409	0.413	7.849	0.089	0.063	BD	9.16
8	Semass AC Control B 4	96	4232408	5.4	5.1	5.7	6.844	12.645	0.100	16.421	BD	1.800	0.450	8.087	0.039	0.061	BD	9.2
9	Semass AC Control A 5	120	4232409	5.9	5.3	6.4	3.563	11.080	0.110	12.961	BD	1.257	0.429	6.408	0.073	0.051	BD	9.19
10	Semass AC Control B 5	120	4232410	5.7	5.2	6.3	2.587	10.835	0.097	14.153	BD	1.523	0.468	6.231	0.048	0.051	BD	8.96
11	Semass AC Control A 6	144	4232411	6.4	6.1	6.7	2.176	9.499	0.107	10.819	BD	1.056	0.457	5.569	0.041	0.042	BD	9.1
12	Semass AC Control B 6	144	4232412	6.3	5.9	6.8	1.832	9.490	0.093	11.384	BD	1.193	0.459	5.418	0.049	0.040	BD	8.8
13	Semass AC Control A 7	168	4233401	7.0	6.6	7.5	1.987	8.123	0.129	9.063	BD	0.831	0.462	4.871	0.037	0.035	BD	8.7
14	Semass AC Control B 7	168	4233402	6.8	6.3	7.4	1.901	8.005	0.142	9.132	BD	0.903	0.451	4.972	0.054	0.033	BD	9.1
MSWIBA-Asphalt Long-Term Batch Leachate																		
1	Semass AC Longterm Control A 1	24	4235401	2.5	2.2	2.8	4.634	17.674	0.092	38.265	BD	5.124	0.325	30.970	0.023	0.145	BD	8.26
2	Semass AC Longterm Control B 1	24	4235402	2.4	2.2	2.7	5.802	19.344	0.070	41.761	BD	5.417	0.149	32.697	0.037	0.137	BD	8.24
3	Semass AC Longterm Control A 2	48	4235403	1.9	1.7	2.2	6.898	28.574	0.098	49.813	BD	6.618	0.249	44.163	0.036	0.180	BD	8.38
4	Semass AC Longterm Control B 2	48	4235404	1.8	1.6	2.1	6.509	24.776	0.142	49.463	BD	6.455	0.113	48.661	0.066	0.173	BD	8.29
5	Semass AC Longterm Control A 3	72	4235405	1.6	1.5	1.7	5.589	32.815	0.125	56.594	BD	7.099	0.204	56.917	0.048	0.236	BD	8.53
6	Semass AC Longterm Control B 3	72	4235406	1.6	1.5	1.7	7.139	35.929	0.127	58.196	BD	7.058	0.170	56.199	0.065	0.211	BD	8.37
7	Semass AC Longterm Control A 4	96	4235407	1.0	0.8	1.2	7.175	35.478	0.102	58.470	BD	7.824	0.152	58.956	0.075	0.218	BD	8.39
8	Semass AC Longterm Control B 4	96	4235408	1.2	1.0	1.4	8.089	32.493	0.116	59.608	BD	10.051	0.179	58.202	0.043	0.234	BD	8.47
9	Semass AC Longterm Control A 5	120	4235409	1.1	1.0	1.2	6.753	25.644	0.092	56.179	BD	8.453	0.217	74.595	0.052	0.215	BD	8.61
10	Semass AC Longterm Control B 5	120	4235410	0.9	0.7	1.1	8.779	38.562	0.103	64.622	BD	7.417	0.144	65.366	0.093	0.244	BD	8.54
11	Semass AC Longterm Control A 6	144	4236401	1.2	1.0	1.4	7.738	31.092	0.141	57.173	BD	7.732	0.119	68.060	0.042	0.238	BD	8.66
12	Semass AC Longterm Control B 6	144	4236402	1.1	1.0	1.2	8.608	23.175	0.132	64.051	BD	7.257	0.204	77.533	0.062	0.295	BD	8.51
13	Semass AC Longterm Control A 7	168	4236403	0.9	0.7	1.1	8.131	14.101	0.091	46.588	BD	5.462	0.274	50.702	0.058	0.191	BD	8.69
14	Semass AC Longterm Control B 7	168	4236404	1.0	0.9	1.1	9.350	35.101	0.090	66.147	BD	7.877	0.155	69.528	0.085	0.264	BD	8.42

CHAPTER 8

TASK 7: COMPARISON OF LABORATORY TEST PROTOCOLS WITH EPA PROTOCOLS, DETERMINATION OF TEST STATISTICAL VARIABILITY, AND PREPARATION OF USER'S MANUAL

8.1 INTRODUCTION

Laboratory QA/QC applies to chemical analyses, biological tests, and leaching and RRR process tests. Both chemical analyses and biological tests follow standard methods and QA/QC protocols that have been reviewed and accepted by EPA and other agencies. During Phase II of this project, the project team confirmed that the project's standard testing methods and QA/QC protocols are consistent with published EPA methods and protocols by undertaking a thorough review and comparison between the project's methods/protocols and those of EPA (Nelson et al., 2000a,b). For leaching and environmental effects (RRR) processes, new test methods were developed as a part of this research, and thus no standard accepted procedures exist from EPA or other agencies. Standard QA/QC protocols specific to these tests had not been developed. In this task, the laboratory testing methods and QA/QC protocols for the leaching and RRR process tests have thus been developed, refined, and validated. As a part of this process, performed replicate testing was performed on all methods to define the variability and degree of confidence of the results using statistically determined parameters (coefficient of variation, precision). To do this, a "standard asphalt" (standard asphalt cement concrete, or SACC) was developed that contains two model toxicants, one metal and one organic. This facilitates validation of this project's new laboratory protocols when adopted by other labs.

A user's manual describing the overall screening methodology and laboratory test protocols has been developed as an additional part of this task (Volume IV). This includes the overall screening methodology and contains detailed instructions for leaching and RRR process test methods and associated QA/QC protocols, as well as for biotoxicity tests and chemistry test methods and their associated QA/QC protocols. The manual is a stand-alone document to facilitate distribution to government agencies and other future users (Nelson et al., 2000b).

Development of an overall evaluation methodology for assessing the environmental impact of construction and repair (C&R) materials was initiated during Phase I of this research. Laboratory testing protocols for toxicity evaluation from EPA and other sources were reviewed. Laboratory chemical analyses required in support of the assessment methodology were also implemented in Oregon State University's (OSU's) laboratories. In some cases, test methods evolved and changes were implemented following completion of Phases I and II. In order to assure that the methods and procedures for biotoxicity and chemical testing are current and consistent with accepted EPA methods, a thorough review and comparison of this project's methods and those of EPA were conducted.

Removal/reduction/retardation (RRR) processes in natural environments can be approximated by a series of laboratory tests or analyses. The basic approach is to measure the mass transfer of chemicals under controlled conditions to determine rates that can be applied to specific mathematical models. Both equilibrium (batch leaching under controlled pH) and non-equilibrium tests (column leaching under various flow rates, and flat plate surface leaching) have been

developed to describe the full range of leaching processes anticipated for C&R materials. The batch leaching tests simulate equilibrium leaching behavior (i.e., the concentration of a chemical that will leach under a defined pH), whereas column tests provide cumulative release data that describe leaching rates (concentration vs. time) under conditions of constant surface renewal (constant flow of clean water past the material). The flat plate tests determine the leaching rates from a defined surface where mass transfer across the solid/liquid boundary controls the leaching or flux rate (expressed in mg/cm²-hr).

Experimental methods were developed to determine the rates and magnitudes of RRR loss or degradation processes for toxic constituents leached from C&R materials. Processes include adsorption, volatilization, photolysis, and biodegradation.

Methods used in leaching and RRR process assessment are in Volume IV (Nelson et al., 2000b). No standard accepted procedures exist from EPA or other agencies with which to compare these new leaching and RRR process methods. In order to facilitate implementation of these methods by other laboratories, they must be standardized in terms of equipment, materials, and procedures. This has been done by a two-step process that included evaluation of current methods to determine whether changes are needed in equipment, materials, or procedures, and by replicate testing to develop statistical data on test repeatability and reproducibility.

Standard QA/QC protocols specific to the leaching and RRR process tests had not been developed. QA/QC protocols were thus developed and validated in this project for the leaching and RRR process tests. This led to the development of the "standard asphalt" (standard asphalt cement concrete, or SACC), which contains two model toxicants, one metal and one organic. The selected toxicants are easily determined by common analytical methods and of known toxicity in the standard toxicity tests using algae and daphnia. The toxicants are zinc as the metal, as it is already a reference toxicant, and 2,4,6-trichlorophenol (TCP) as the organic compound. Besides being readily determined by gas chromatography, TCP undergoes the degradation processes of volatilization, photolysis, and biodegradation. Test statistics on duplicate samples were also developed.

8.2 TEST MATERIALS

The "standard asphalt" used in testing for this task was developed in the OSU Environmental Engineering Laboratory. The asphalt was formulated as a typical ODOT assemblage with the inclusion of the two reference toxic materials, zinc and TCP. Preliminary testing was required to determine the method of incorporating the toxic substances into the standard asphalt and their leachable concentrations. The overall goal of the standard asphalt assemblage formulation is that repeatable leachate toxicant concentrations are produced at low levels typical of C&R materials assemblages but above the respective EC50 or LC50 values for algae and daphnia toxicity tests.

8.3 LEACHATE GENERATION

Leachates were generated following the standard highway materials leaching procedures of this study (Volume IV, Nelson et al., March 2000). The "standard asphalt" was crushed to ¼ - inch minus size for short-term and long-term batch leachate generation. Flat-plate leachates were

generated using the standard 4x4 inch compacted discs. Two standard test soils, Sagehill and Woodburn, were used in standard asphalt leachate soil sorption batch tests.

8.4 STANDARD ASPHALT ASSEMBLAGE FORMULATION

A method of incorporating the toxic substances into a standard asphalt has been developed that generates acceptable leachate concentrations. The asphalt is formulated as a typical ODOT assemblage with the inclusion of two reference toxic materials, zinc as a metal, and 2,4,6-trichlorophenol (TCP) as an organic compound. Both Zn and TCP are soluble compounds and they are likely to come into contact with water. The overall goal of the standard asphalt assemblage formulation is that repeatable leachate toxicant concentrations are produced at low levels typical of C&R materials assemblages but above the respective EC50 or LC50 values for algae and daphnia toxicity tests. Experimental methods were conducted to determine the rates and magnitudes of loss or degradation processes for toxic constituents leached from the standard asphalt. Processes included long-term and short-term leaching kinetics, flat plate leaching, soil sorption, volatilization, photolysis, and biodegradation

8.4.1 Preparation of Aggregates

The locally available aggregates were used in this task and aggregate gradations were determined using ASTM procedure C136 (ASTM, 1994). Oregon Department of Transportation (ODOT) specification (Oregon Department of Transportation, 1996) Section 02630, “Base Aggregate” was used to delineate the gradation limits. These limits are shown in Table 8.4.1.1.

Table 8.4.1.1. Base aggregate specification (ODOT, 1996).

Sieve Size, mm	Percent Passing	
	Upper Specification Limit	Lower Specification Limit
25.0	100	100
19.0	100	90
9.5	75	55
6.3	60	40
2.00	1	
¹ Of the fraction passing the 6.3 mm sieve, 40% to 60% shall pass the 2.00 mm sieve		

8.4.2 Inclusion of Zn and TCP in Aggregate Mix

To resemble waste-modified asphalt mixes, zinc as a soluble metal ion (Zn^{2+}) and 2,4,6-TCP as an organic compound (aqueous solution) were adsorbed onto aggregates using the following procedure. The aggregate mixture with Zn and TCP was prepared by adding 50 mL of 2% zinc sulfate solution to 1 kg aggregate, mixing thoroughly, and drying at 135°C for 3 hours. Then, 50 mL of 1000-mg/L TCP solution was added to the aggregate under vigorous mixing. The aggregate with Zn and TCP was then dried in an oven under a hood at 135°C for 3 hours.

8.4.3 Preparation of Standard Asphalt Cement Concrete (SACC) Mixture

To prepare the standard asphalt cement concrete (SACC) mixture, an ODOT mix design (ODOT, 1993) was used to determine the aggregate and optimum binder content (5.4% of total mix by mass). The same asphalt binder (SHRP PG 64-22) was used for all mixes.

The SACC mixture was prepared by placing a hot mixing bowl on a scale and adding 1 kg of the hot 135°C Zn and TCP aggregates mixture. Add 54 g (5.4% w/w) hot asphalt binder (135°C) into the mixture and remove the mixing bowl from the scale. Then, mix the asphalt binder and aggregates until the aggregates are thoroughly coated. The SACC mixture was then aged following the protocol developed by the Strategic Highway Research Program (AASHTO PP2, 1994), that is, spread the mix in a flat shallow aluminum pan and place the pan in an oven at 135°C for 4 hours. This aging simulates the binder viscosity changes that occur in conventional mixing and placement of asphalt mixes. All of these preparations were carried under the hood to prevent TCP vapor contamination in the lab. A control standard asphalt cement concrete mixture was prepared by using the same method without Zn and TCP inclusion in the aggregates.

8.5 RESULTS AND DISCUSSION

8.5.1 Standard Asphalt Long-Term and Short-Term Batch Leaching Test

8.5.1.1 Chemical analysis

Long-term and short-term batch leaching tests were conducted using the SACC (standard asphalt) developed in our laboratory. Batch leaching tests were conducted using a known weight of SACC (250 g) per 1 L leaching solution (solid/solution mass ratio = 1:4). Long-term (7 days) dynamic batch leaching experiments at ambient pH (~6.5) were conducted. Batch leaching tests indicated that the maximum leaching rate occurred within 48 hr as shown by the data for Zn and TCP (Figure 8.5.1.1.1). All chemical analysis data are summarized in Table 8.5.1.1.1.

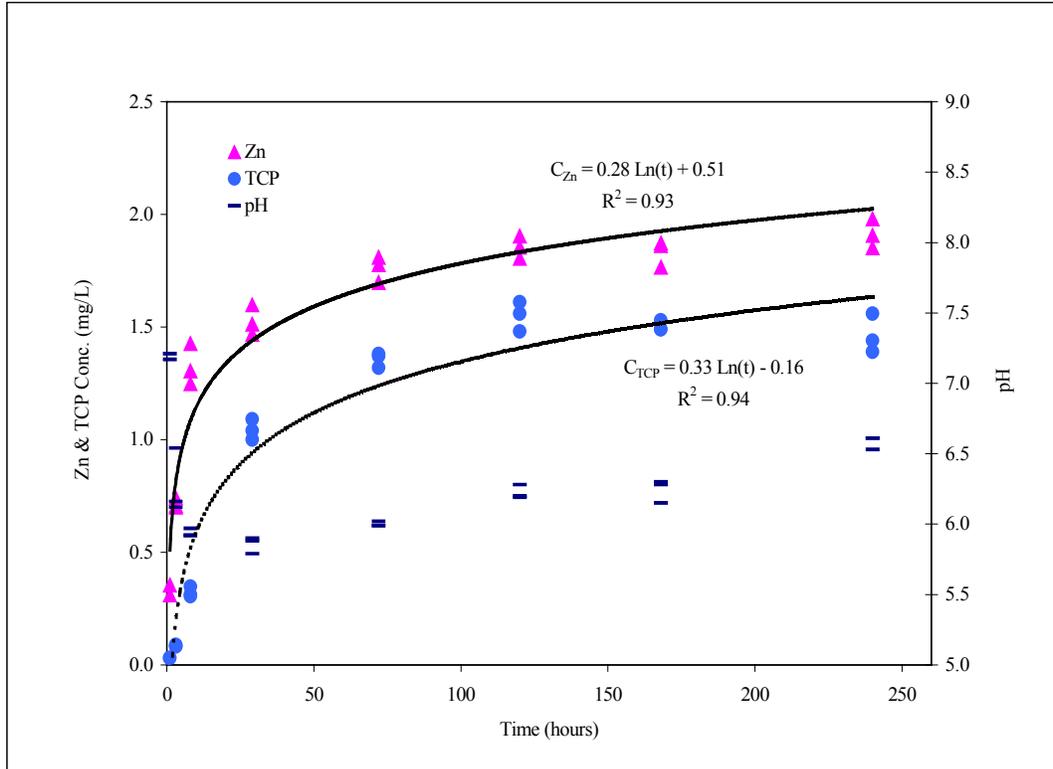


Figure 8.5.1.1.1. Short-term and long-term standard asphalt (SACC) batch leaching results for Zn and TCP concentration as a function of time.

8.5.1.2 Batch leaching test at different solid-to-liquid ratios

24-hr standard asphalt (SACC) batch leaching experiments were conducted to examine the effects of different of solid-to-liquid ratios. Solid-to-liquid ratios can affect concentration of leachate if adsorption or desorption processes are controlling the concentration. The concentration of very soluble compounds is directly dependent on the solid-to-liquid ratio. On the other hand, compounds for which concentrations are controlled by solubility will have the same concentrations at all solid-to-liquid ratios, provided enough solid is present to saturate the system.

The choice of solid-to-liquid ratio for use in the test is based on practical considerations. A very high solid-to-liquid ratio, such as is used in the saturation test, is most likely to result in many components being saturated. This makes it difficult to estimate the total release of component from the waste, since many elutions will be necessary to elute the leachable fraction of the component. A very high ratio can lead to difficulties in stirring or separation techniques and can take a long time to stabilize. The most commonly used solid-to-liquid ratios are around 1:10. In this experiment, solid-to-liquid ratios of 2:1, 1:1, 1:4, 1:8, and 1:20 were used to examine the effect of surface area on standard asphalt batch leaching. Results show that leachate concentrations of Ca, Mg, Na, and Zn are directly dependent on the solid-to-liquid ratio (Figure 8.5.1.2.1). TCP leachate concentrations from the standard asphalt test are also directly dependent on solid-to-solution ratio (Figure 8.5.1.2.2). The chemical analysis data are summarized in Table 8.5.1.1.1.

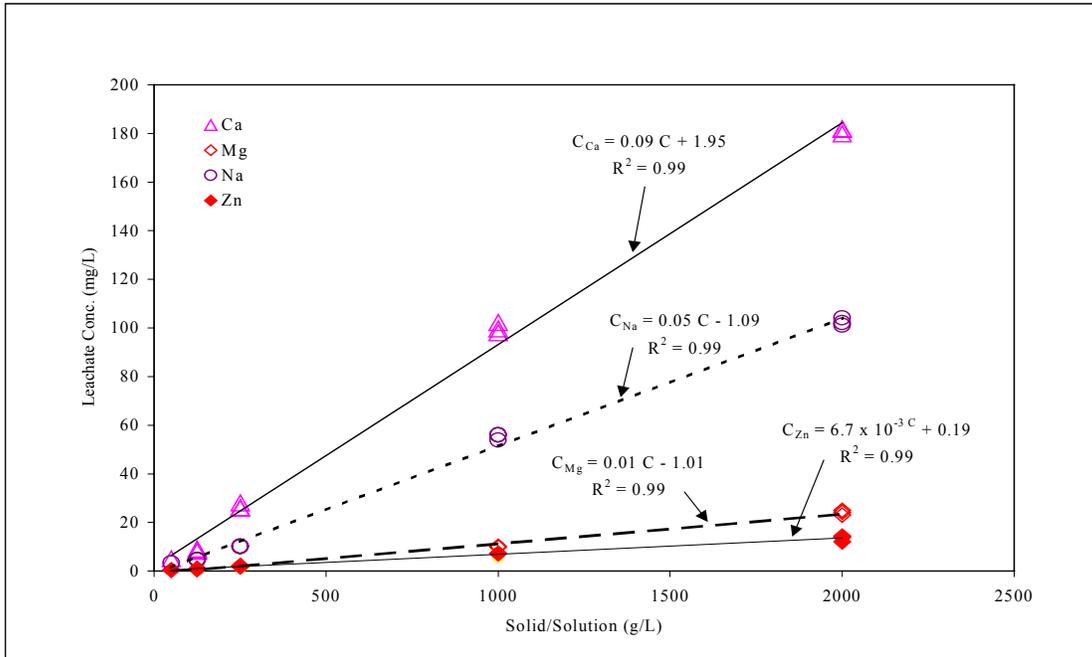


Figure 8.5.1.2.1. Effect of solid-to-solution ratio on metals concentrations in leachate from the standard asphalt (SACC) (triplicate experiments).

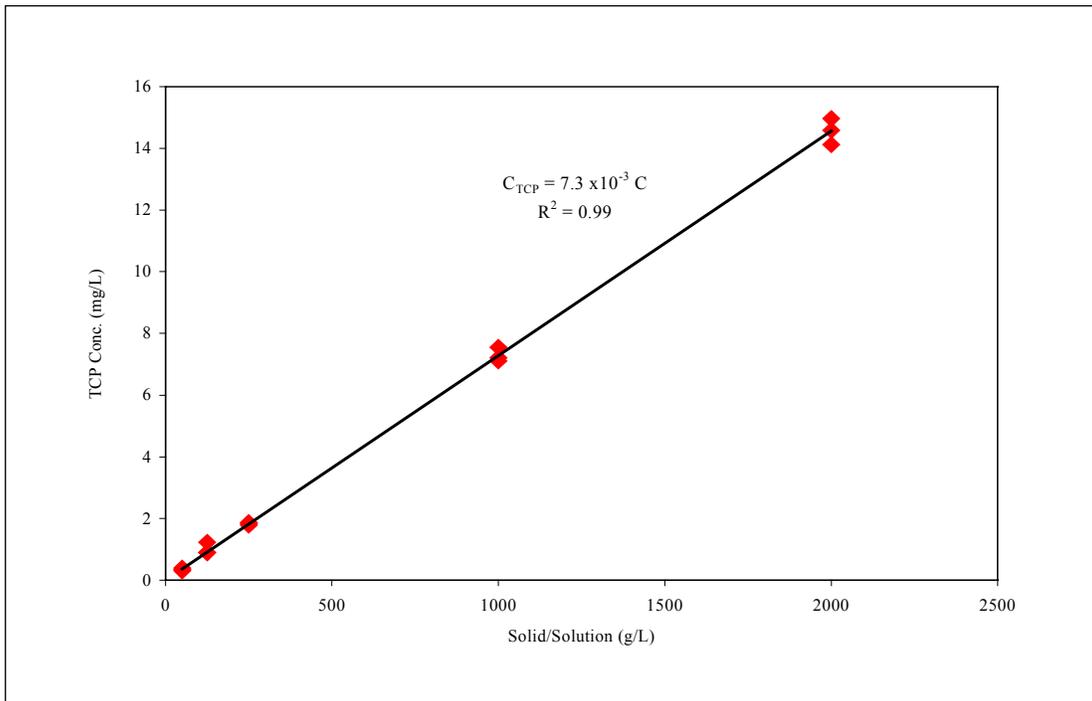


Figure 8.5.1.2.2. Effect of solid-to-solution ratio on TCP concentrations in leachate from the standard asphalt (SACC) (triplicate experiments).

8.5.1.3 Determinations of long-term and short-term batch leaching test statistical variability

Triplicate samples were run through a series of long-term and short-term batch leaching tests on the standard asphalt (SACC). The average value, variance, standard deviation (SD), relative standard deviation (RSD, SD/mean, same as coefficient of variation) which is the method precision, deviation of measurement value from the average value (bias), and relative bias or percent of error, for both zinc and 2,4,6-trichlorophenol are presented in Tables 8.5.1.3.1 and 8.5.1.3.2, respectively. These results indicate that, based on single operator characteristics, the long-term and short-term batch leaching tests for standard asphalt data are acceptable with less than 5 percent error.

Table 8.5.1.3.1. Standard asphalt (SACC) long-term and short-term batch leaching test statistical variability for zinc.

Sample ID	Zn mg/L	Data Analysis					
		Average	Variance	(+/-)S.D [*]	RSD ^{**}	Bias ^{***}	% Error ^{****}
TCP-ZN-1 3 HR	0.741	0.716	0.000	0.021	2.984	0.024	3.384
TCP-ZN-2 3 HR	0.700	0.716				-0.016	-2.256
TCP-ZN-3 3 HR	0.708	0.716				-0.008	-1.128
TCP-ZN-1 8 HR	1.427	1.327	0.008	0.091	6.868	0.100	7.538
TCP-ZN-2 8 HRS	1.249	1.327				-0.078	-5.902
TCP-ZN-3 8 HRS	1.305	1.327				-0.022	-1.635
TCP-ZN-1 29 HRS	1.598	1.526	0.004	0.066	4.333	0.072	4.707
TCP-ZN-2 29 HRS	1.513	1.526				-0.014	-0.885
TCP-ZN-3 29 HRS	1.468	1.526				-0.058	-3.823
TCP-ZN-1 72 HRS	1.776	1.761	0.003	0.057	3.234	0.015	0.876
TCP-ZN-2 72 HRS	1.809	1.761				0.048	2.706
TCP-ZN-3 72 HRS	1.698	1.761				-0.063	-3.582
TCP-ZN-1 5 DAYS	1.905	1.855	0.002	0.050	2.670	0.050	2.681
TCP-ZN-2 5 DAYS	1.854	1.855				0.000	-0.023
TCP-ZN-3 5 DAYS	1.806	1.855				-0.049	-2.658
TCP-ZN-1 7 DAYS	1.862	1.834	0.003	0.059	3.210	0.028	1.545
TCP-ZN-2 7 DAYS	1.873	1.834				0.039	2.145
TCP-ZN-3 7 DAYS	1.766	1.834				-0.068	-3.690
TCP-ZN-1 10 DAYS	1.907	1.913	0.004	0.065	3.379	-0.006	-0.327
TCP-ZN-2 10 DAYS	1.85197	1.913				-0.061	-3.203
TCP-ZN-3 10 DAYS	1.9808	1.913				0.068	3.530

SD^{}* : standard deviation

*RSD^{**}* : relative standard deviation (SD/average)x100

*Bias^{***}*: deviation of measurement value from the average value

*% Error^{****}* : relative Bias (Bias/average)x100

Table 8.5.1.3.2. Standard asphalt (SACC) long-term and short-term batch leaching test statistical variability for TCP.

Sample ID	TCP mg/L	Data Analysis					
		Average	Variance	(+/-)S.D *	RSD **	Bias ***	% Error ****
TCP-ZN-1 3 HR	0.084	0.084	0.000	0.004	4.164	0.000	-0.395
TCP-ZN-2 3 HR	0.081	0.084				-0.003	-3.953
TCP-ZN-3 3 HR	0.088	0.084				0.004	4.348
TCP-ZN-1 8 HR	0.305	0.322	0.001	0.023	7.173	-0.017	-5.181
TCP-ZN-2 8 HRS	0.312	0.322				-0.010	-3.005
TCP-ZN-3 8 HRS	0.348	0.322				0.026	8.187
TCP-ZN-1 29 HRS	1.000	1.043	0.002	0.045	4.322	-0.043	-4.153
TCP-ZN-2 29 HRS	1.040	1.043				-0.003	-0.319
TCP-ZN-3 29 HRS	1.090	1.043				0.047	4.473
TCP-ZN-1 72 HRS	1.370	1.357	0.001	0.032	2.369	0.013	0.983
TCP-ZN-2 72 HRS	1.380	1.357				0.023	1.720
TCP-ZN-3 72 HRS	1.320	1.357				-0.037	-2.703
TCP-ZN-1 5 DAYS	1.560	1.550	0.004	0.066	4.231	0.010	0.645
TCP-ZN-2 5 DAYS	1.480	1.550				-0.070	-4.516
TCP-ZN-3 5 DAYS	1.610	1.550				0.060	3.871
TCP-ZN-1 7 DAYS	1.490	1.503	0.001	0.023	1.536	-0.013	-0.887
TCP-ZN-2 7 DAYS	1.530	1.503				0.027	1.774
TCP-ZN-3 7 DAYS	1.490	1.503				-0.013	-0.887
TCP-ZN-1 10 DAYS	1.560	1.463	0.008	0.087	5.971	0.097	6.606
TCP-ZN-2 10 DAYS	1.440	1.463				-0.023	-1.595
TCP-ZN-3 10 DAYS	1.390	1.463				-0.073	-5.011

*SD ** : standard deviation

*RSD ** : relative standard deviation (SD/average)x100

*Bias***: deviation of measurement value from the average value

*% Error***** : relative Bias (Bias/average)x100

8.5.1.4 Toxicity Analysis

The 96-hour algal chronic toxicity test and 48-hour daphnia acute toxicity test were performed on samples collected from short- and long-term leaching experiments. Results indicated very high toxicity for *Selenastrum capricornutum* and moderate to low toxicity for *Daphnia magna*. Chemical analyses indicated that Zn was released within an hour of leaching at concentrations high enough ($Zn > 0.74$ mg/L) to cause toxic effects to both daphnia and algae.

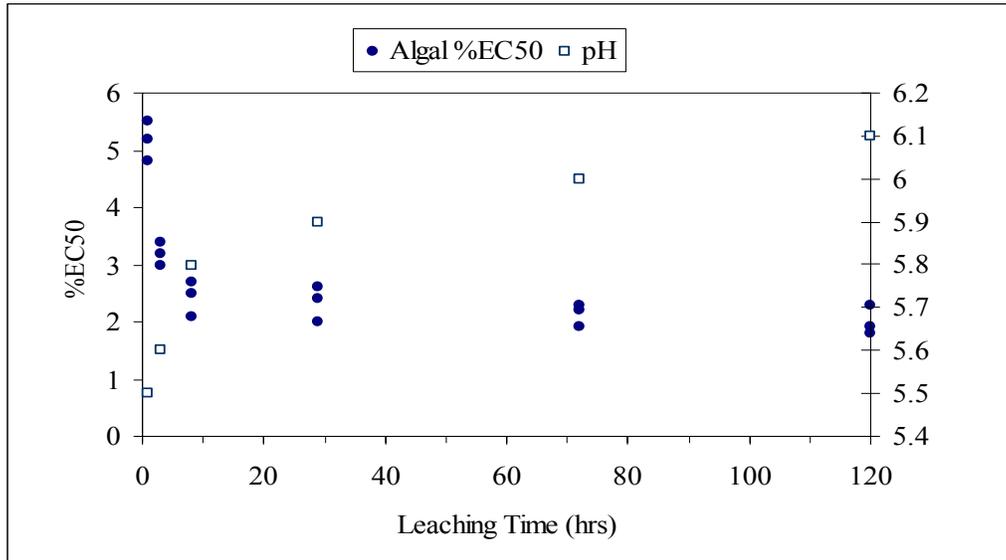


Figure 8.5.1.4.1. Algal %EC50 values as a function of leaching time for standard-asphalt (SACC) (triplicate experiments).

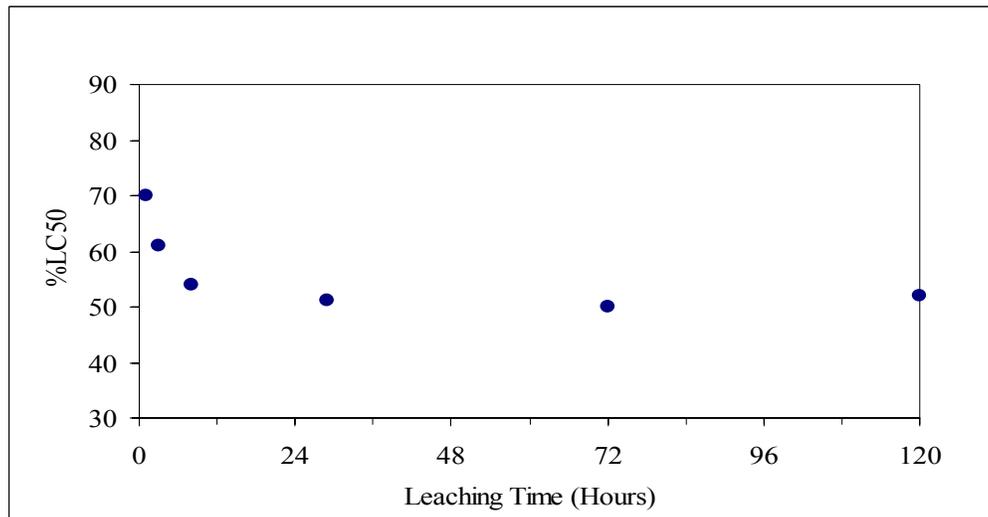


Figure 8.5.1.4.2. Daphnia %LC50 values as a function of leaching time for standard-asphalt (SACC) (triplicate experiments).

However TCP was released at relatively a slower rate initially (0.08 mg/L in 1-hr sample) and reached a maximum of about 1.5 mg/L in day-7 samples. Maximum %EC50 and %LC50 values

for algae and daphnia were reached within 24-hours of standard-asphalt leaching as shown by Figures 8.5.1.4.1 and 8.5.1.4.2.

8.5.2 Standard Asphalt Leachate Flat Plate Test

8.5.2.1 Chemical analysis

Flat plate leaching tests were conducted using the standard asphalt (SACC). Flat plate leaching tests were used to determine the rate of leaching of contaminants from a material surface. The tests were conducted as described in Volume IV. The flux of contaminants ($\text{mg}/\text{cm}^2\text{-hr}$) then was determined by the increase of concentration in the overlying water as a function of time. Results for zinc and TCP in leachate from the standard asphalt in the flat plate experiments are shown in Figure 8.5.2.1.1. A power function was used to represent the flat plate data. The equations for power function increase of zinc and TCP concentrations (determined by linear regression) are given as:

$$\begin{aligned}C_{\text{Zn}} &= 0.01 t^{0.72} \quad (R^2 = 0.99) \\C_{\text{TCP}} &= 2.3 \times 10^{-3} t^{0.79} \quad (R^2 = 0.99)\end{aligned}$$

For example, at a time of 1 hr, for a volume, V , of 1 L and surface area, A , of 78.5 cm^2 , the rate of change of concentration with time, dC/dt , is $7.2 \times 10^{-3} \text{ mg}/\text{L}\text{-hr}$, and the resulting flux is $F = (V/A) dC/dt = 9.1 \times 10^{-5} \text{ mg}/\text{cm}^2\text{-hr}$ for Zn. For TCP, dC/dt , is $1.9 \times 10^{-3} \text{ mg}/\text{L}\text{-hr}$, and the resulting flux is $F = 2.4 \times 10^{-5} \text{ mg}/\text{cm}^2\text{-hr}$. The chemical analysis data are summarized in Table 8.5.2.1.1.

8.5.2.2 Determination of flat plate leaching test statistical variability

Triplicate samples were run through the flat plate tests on the standard asphalt (SACC). The average value, variance, standard deviation (SD), relative standard deviation (RSD) that is the method precision, deviation of measurement value from the average value (bias), and relative bias or percent error, for both zinc and 2,4,6-trichlorophenol are presented in Tables 8.5.2.2.1 and 8.5.2.2.2 for Zn and TCP, respectively. These results indicate that, based on single operator characteristics, the reproducibility was good for the flat plate tests for the standard asphalt. The relative standard deviations were generally under 10% unless near the detection limits for Zn and TCP. The ICP detection limit for Zn is about 20 parts per billion (ppb), and the GC flame ionization detector (FID) detection limit for TCP is about 10 ppb.

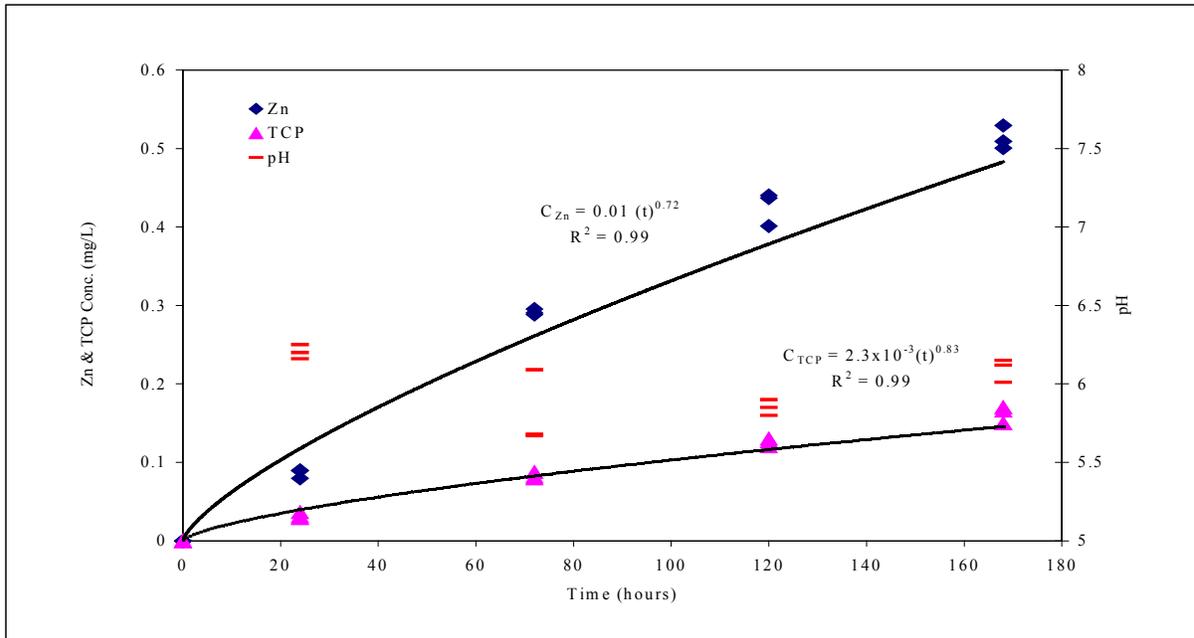


Figure 8.5.2.1.1. Zinc and TCP concentrations as a function of time for flat plate leaching of standard asphalt (SACC) (triplicate experiments).

Table 8.5.2.2.1. Standard asphalt (SACC) flat plate leaching test statistical variability for Zn.

Sample ID	Time hrs	Zn mg/L	Data Analysis					
			Average	Variance	(+/-)S.D*	RSD**	Bias***	% Error****
FP-ZN-TCP-1	6	0.043	0.039	0.000	0.008	19.991	0.004	9.985
FP-ZN-TCP-2	6	0.045	0.039				0.005	13.031
FP-ZN-TCP-3	6	0.030	0.039				-0.009	-23.017
FP-ZN-TCP-4	45.5	0.189	0.182	0.000	0.013	6.877	0.006	3.409
FP-ZN-TCP-5	45.5	0.168	0.182				-0.014	-7.916
FP-ZN-TCP-6	45.5	0.191	0.182				0.008	4.506
FP-ZN-TCP-7	73.5	0.267	0.268	0.000	0.013	4.696	0.000	-0.181
FP-ZN-TCP-8	73.5	0.255	0.268				-0.012	-4.603
FP-ZN-TCP-9	73.5	0.280	0.268				0.013	4.784
FP-ZN-TCP-10	97.5	0.328	0.326	0.001	0.025	7.610	0.002	0.495
FP-ZN-TCP-11	97.5	0.350	0.326				0.024	7.351
FP-ZN-TCP-12	97.5	0.301	0.326				-0.026	-7.846
FP-ZN-TCP-13	166.5	0.484	0.492	0.000	0.010	1.933	-0.009	-1.745
FP-ZN-TCP-14	166.5	0.490	0.492				-0.002	-0.333
FP-ZN-TCP-15	166.5	0.502	0.492				0.010	2.078
FP-ZN-TCP-16	196.5	0.545	0.519	0.001	0.023	4.382	0.026	4.973
FP-ZN-TCP-17	196.5	0.502	0.519				-0.017	-3.298
FP-ZN-TCP-18	196.5	0.511	0.519				-0.009	-1.675
FP-ZN-TCP-19	286.5	0.717	0.692	0.001	0.031	4.517	0.025	3.606
FP-ZN-TCP-20	286.5	0.702	0.692				0.010	1.460
FP-ZN-TCP-21	286.5	0.657	0.692				-0.035	-5.066

SD* : standard deviation

RSD* : relative standard deviation (SD/average)x100

Bias** : deviation of measurement value from the average value

% Error**** : relative Bias (Bias/average)x100

Table 8.5.2.2.2. Standard asphalt (SACC) flat plate leaching test statistical variability for TCP.

Sample ID	Time hrs	TCP mg/L	Data Analysis					
			Average	Variance	(+/-)S.D*	RSD**	Bias***	% Error****
FP-ZN-TCP-1	6	0.011	0.013	0.000	0.002	15.385	-0.002	-15.385
FP-ZN-TCP-2	6	0.015	0.013				0.002	15.385
FP-ZN-TCP-3	6	0.013	0.013				0.000	0.000
FP-ZN-TCP-4	45.5	0.057	0.054	0.000	0.003	5.623	0.003	4.908
FP-ZN-TCP-5	45.5	0.051	0.054				-0.003	-6.135
FP-ZN-TCP-6	45.5	0.055	0.054				0.001	1.227
FP-ZN-TCP-7	73.5	0.088	0.086	0.000	0.005	5.474	0.002	1.931
FP-ZN-TCP-8	73.5	0.081	0.086				-0.005	-6.178
FP-ZN-TCP-9	73.5	0.09	0.086				0.004	4.247
FP-ZN-TCP-10	97.5	0.102	0.103	0.000	0.004	3.936	-0.001	-0.649
FP-ZN-TCP-11	97.5	0.107	0.103				0.004	4.221
FP-ZN-TCP-12	97.5	0.099	0.103				-0.004	-3.571
FP-ZN-TCP-13	166.5	0.174	0.171	0.000	0.003	1.469	0.003	1.556
FP-ZN-TCP-14	166.5	0.169	0.171				-0.002	-1.362
FP-ZN-TCP-15	166.5	0.171	0.171				0.000	-0.195
FP-ZN-TCP-16	196.5	0.207	0.202	0.000	0.004	2.058	0.005	2.306
FP-ZN-TCP-17	196.5	0.201	0.202				-0.001	-0.659
FP-ZN-TCP-18	196.5	0.199	0.202				-0.003	-1.647
FP-ZN-TCP-19	286.5	0.261	0.265	0.000	0.005	1.934	-0.004	-1.633
FP-ZN-TCP-20	286.5	0.271	0.265				0.006	2.136
FP-ZN-TCP-21	286.5	0.264	0.265				-0.001	-0.503

*SD** : standard deviation

*RSD** : relative standard deviation (SD/average)x100

*Bias***: deviation of measurement value from the average value

*% Error***** : relative Bias (Bias/average)x100

8.5.2.3 Flat plate leaching tests at different solid-to-liquid ratios

Flat plate leaching tests at different solid-to-liquid ratios were conducted using the standard asphalt (SACC). Flat plate leaching from the SACC was modeled by modifying the standard flat plate procedure with varying solution volume. Flat plate tests were conducted at solid-to-liquid ratios of 2:1, 1:1, and 1:2. Figure 8.5.2.3.1 shows Zn leachate from the SACC at different solid-to-solution ratios. Zn leachate from the SACC is directly dependent on solid-to-liquid ratio. TCP concentrations at a solid:liquid ratio of 1:2 was below the GC detection limits and, therefore, no comparison was made (results not shown in figure).

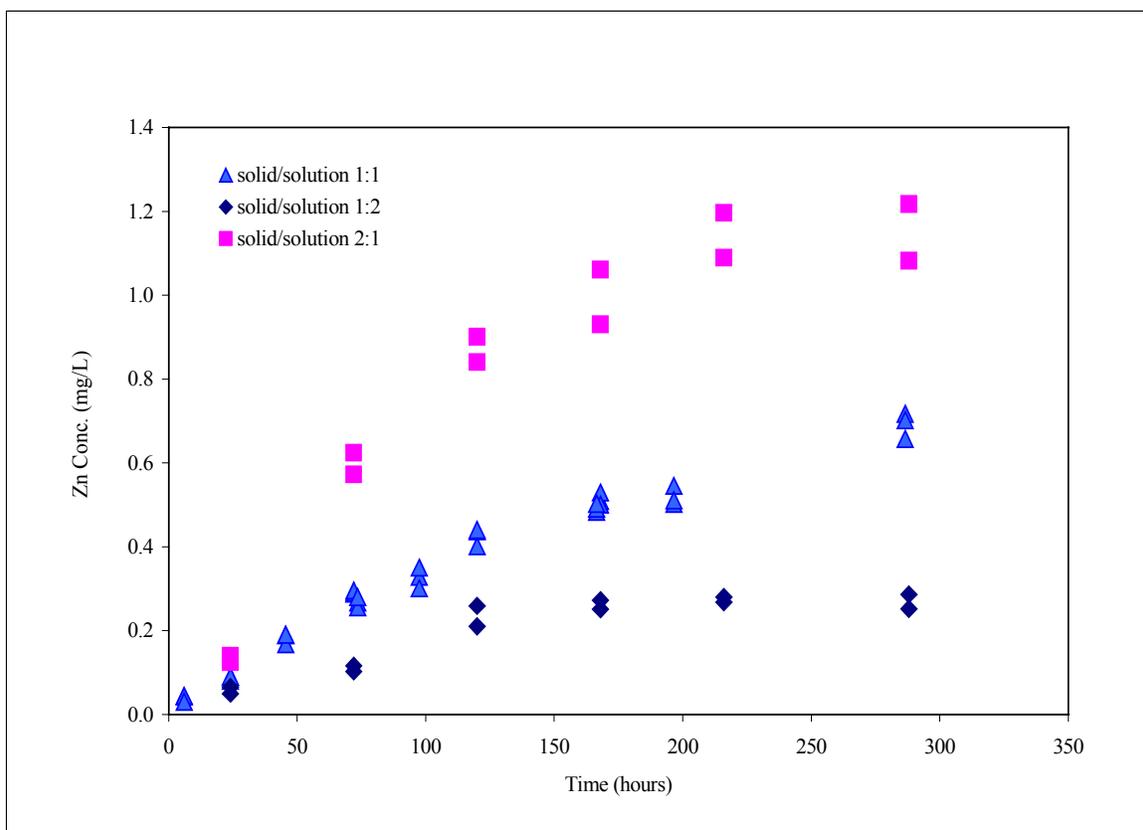


Figure 8.5.2.3.1. Flat plate leaching results for Zn from standard asphalt (SACC) at different solid-to-solution ratios, zinc leachate concentration as a function of time (triplicate experiments).

8.5.2.4 Effect of temperature in standard asphalt flat plate leaching

Temperature should have an effect on the leaching pattern of a waste due to its effects on solubility and reaction kinetics (Ham et al., 1979a,b). The effect of temperature on the dissolution rate will be determined by two opposing terms: the rate of lattice energy dissolution and the rate of ion solvation (charging of activated complexes with solvent molecules). While the solubilities of many inorganic salts increase with temperature, a number of compounds of interest in leachates (e.g., CaCO_3 , CaSO_4) decrease in solubility with increase in temperature (Lowenbach, 1978). In general, solubility increases with increasing temperature with a few notable exceptions, such as CaCO_3 , $\text{Ca}_3(\text{PO}_4)_2$, CaSO_4 , and FePO_4 , which are important in water chemistry (Snoeyink and Jenkins, 1980). Temperature also has a strong effect on both biological activity and organic reaction rates.

Generally, leaching tests have been conducted at room temperature. The effect of temperature on 4-inch thick by 4-inch diameter flat plate experiments was examined at 30°C and 4°C. As Figure 8.5.2.4.1 shows, Zn leachate increased with increasing temperature.

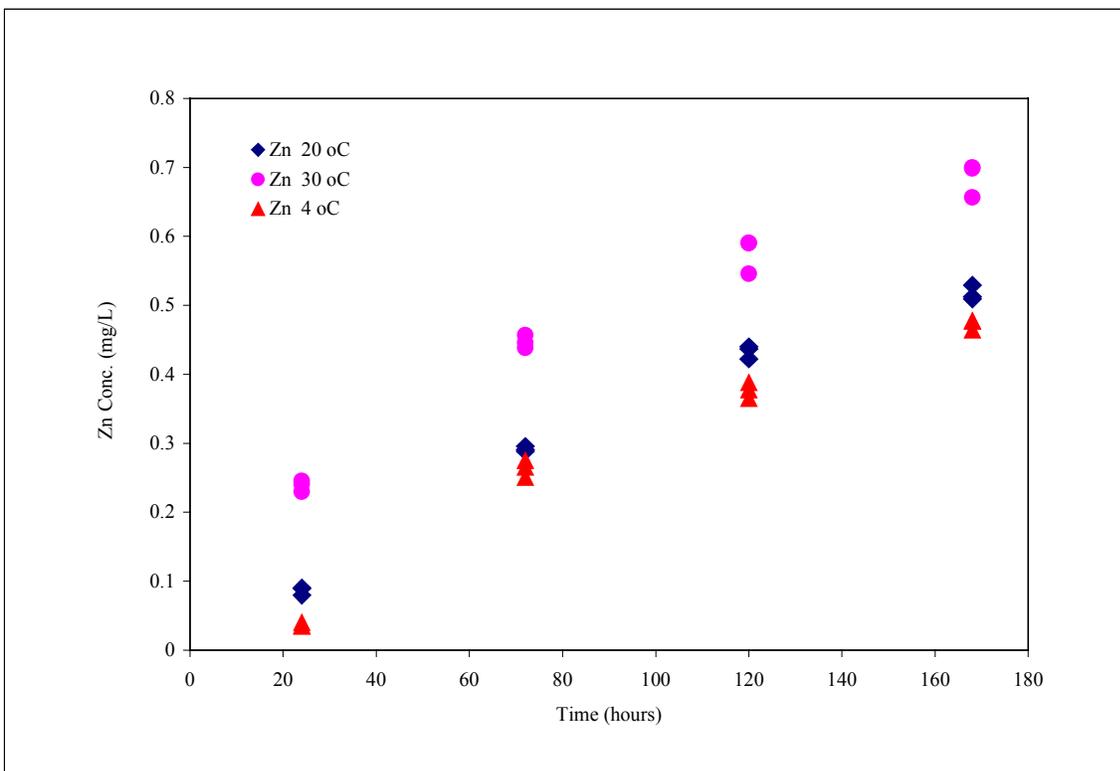


Figure 8.5.2.4.1. Effect of temperature on zinc concentrations as a function of time for flat plate leaching results for standard asphalt (SACC) (triplicate experiments).

8.5.2.5 Toxicity analysis

The 96-hour algal chronic toxicity test was performed on samples collected from flat plate leaching test for the standard asphalt (SACC). Results indicated very high toxicity for *Selenastrum capricornutum* (%EC50 <10) in 24-hour leachates. No significant increase in toxicity was observed with increase in leaching time (Figure 8.5.2.5.1). %EC50 values of 24, 72, 120, and 168-hour leachates ranged from 7.4 to 9.4% with overlapping confidence intervals indicating no significant change ($p > 0.05$) in toxicity after 24-hours of leaching. However, the chemistry of the leachates showed a gradual increase in Zn and TCP concentrations between 24 and 168-hour leachates. The concentration of Zn released in the leachates at 24-hr (0.08 – 0.09 mg/L) exceeded the EC50 of Zn for the algal test species (0.04 – 0.06 for *Selenastrum capricornutum*) and may thus have masked changes in toxicity as Zn concentrations increased.

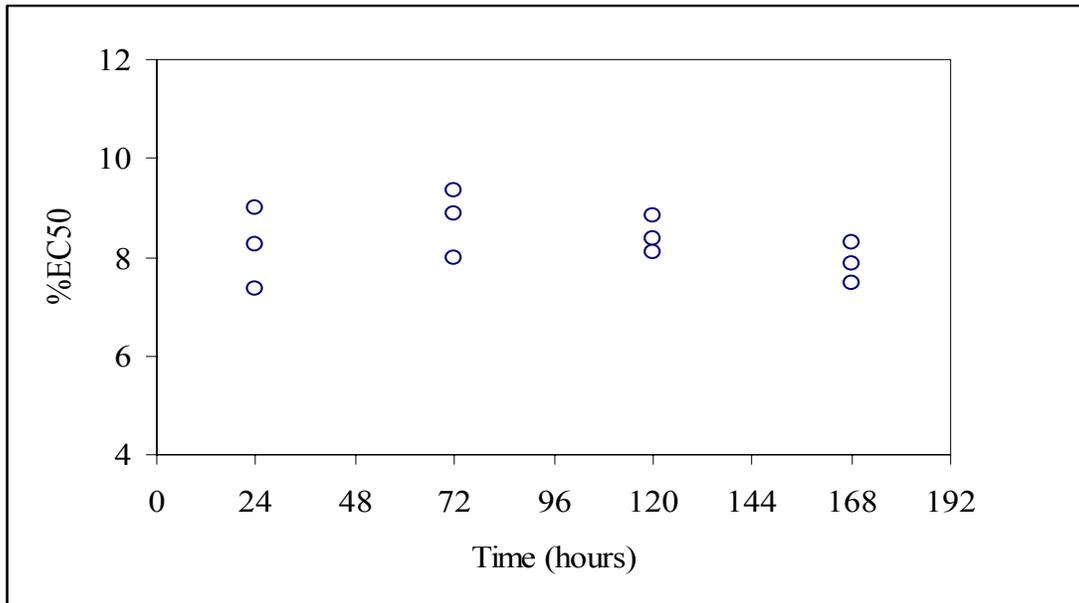


Figure 8.5.2.5.1. Algal %EC50 values as a function of leaching time for flat-plate leaching test of standard-asphalt (SACC) (triplicate experiments).

8.5.3 Standard Asphalt Leachate Soil Sorption Test

8.5.3.1 Chemical analyses

Standard asphalt (SACC) batch leachate solution was used to determine the sorption capacity of the two different soil materials (Sagehill and Woodburn). For the Woodburn soil, the range of solid to solution ratio was 5, 10, 20, 50, and 100 g/L, while for the Sagehill soil, the solid to solution ratio was 100, 200, 300, 400, and 600 g/L. Both soils removed zinc from the solution by adsorption even at the lowest solid to solution ratio (shown in Tables 8.5.3.2.2 and 8.5.3.2.4 in the next subsection). The average zinc concentration in the 24-hr control leachate for both soils was about 1.75 mg/L, which was reduced to about 0.11 and 0.07 mg/L at a 100 g/L soil-to-solution ratio, in the Woodburn and Sagehill soils, respectively. Therefore, only the TCP data were used to evaluate soil isotherm models for Woodburn and Sagehill soils.

Sorption characteristics on the two soils (Sagehill and Woodburn) for 2,4,6-TCP were analyzed and evaluated using three soil isotherm models: linear, Langmuir and Freundlich. Calculated values for K_f , N , and Q for Woodburn and Sagehill soil are presented in Tables 8.5.3.1.1 to 8.5.3.1.3. The high R^2 values of 0.78 for the Woodburn soil demonstrate a better fit to the sorption data by the Freundlich isotherm model (Figure 8.5.3.1.1).

The sorption capacity of the Sagehill soil is much less than that of the Woodburn soil, and data were collected at an insufficient range of TCP concentrations to confirm a mathematical fit of any of the three sorption equations (Figure 8.5.3.1.2). A detailed explanation of the isotherm

theory is included with the sorption protocols in Volume IV (Nelson et al., 2000b). The chemical analysis data are summarized in Table 8.5.1.1.1.

Table 8.5.3.1.1. Linear sorption distribution coefficient (K_d) for sorption of 2,4,6-TCP by two different soils.

Soil Type	K_d	R^2
Woodburn	5.5×10^{-2}	0.49
Sagehill	6.0×10^{-4}	0.03

Table 8.5.3.1.2. Langmuir sorption capacity (Q) and sorption constant (b) for sorption of 2,4,6-TCP by two different soils.

Soil Type	Q	b	R^2
Woodburn	2.9×10^{-2}	0.55	0.58
Sagehill	1.8×10^{-3}	6.2×10^{-1}	0.02

Table 8.5.3.1.3. Freundlich sorption constant (K_f) and intensity parameter (N) for sorption of 2,4,6-TCP by two different soils.

Soil Type	K_f	N	R^2
Woodburn	4.16×10^{-2}	0.21	0.78
Sagehill	6.0×10^{-4}	0.76	0.03

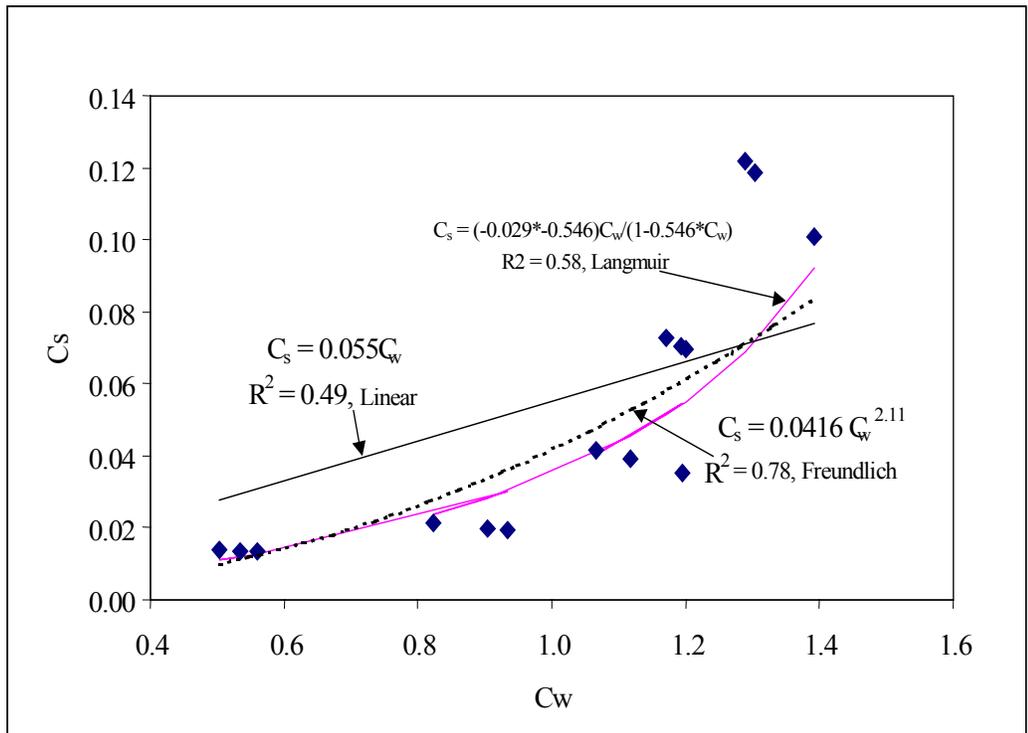


Figure 8.5.3.1.1. Isotherm sorption models (Freundlich, Langmuir, and linear) of 2,4,6,-TCP in standard asphalt (SACC) leachate for Woodburn soil.

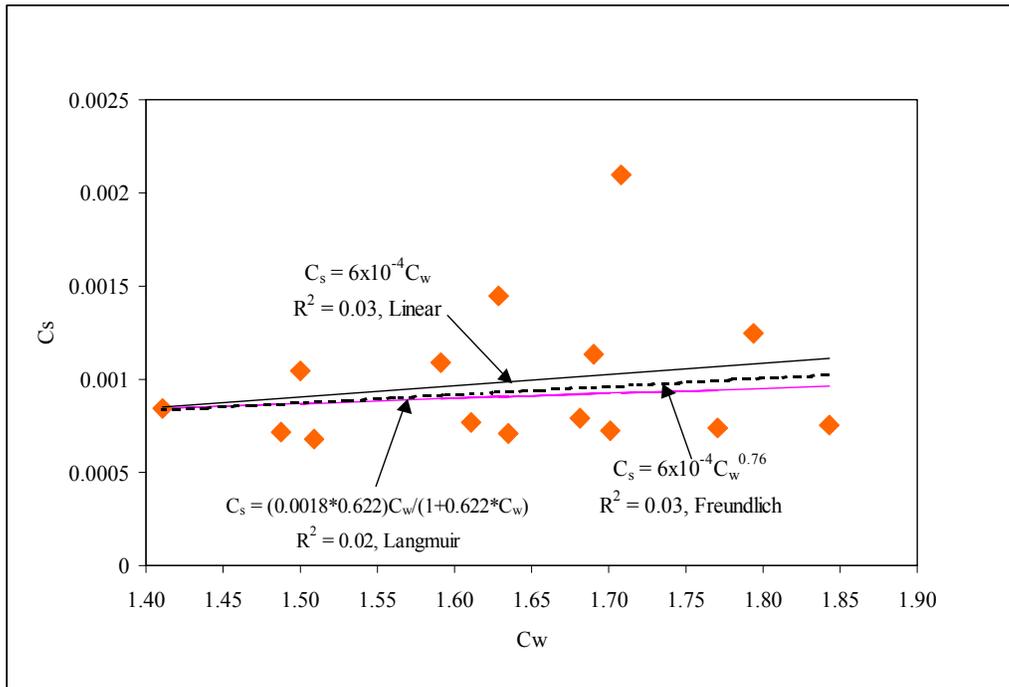


Figure 8.5.3.1.2. Isotherm sorption models (Freundlich, Langmuir, and linear) of 2,4,6-TCP in standard asphalt (SACC) leachate for Sagehill soil.

8.5.3.2 Determinations of soil sorption test statistical variability

Triplicate samples were run through the test series soil sorption tests on the standard asphalt (SACC). The average value, variance, standard deviation (SD), relative standard deviation (RSD), deviation of measurement value from the average value (bias), and relative bias or percent of error for both zinc and 2,4,6-trichlorophenol are presented in Tables 8.5.3.2.1 to 8.5.3.2.4. Zinc and TCP data indicate that, based on single operator characteristics, the soil sorption tests for standard asphalt data are acceptable with percent error of less than 5% and 7%, respectively.

Table 8.5.3.2.1. Standard asphalt (SACC) soil sorption test statistical variability of TCP on Woodburn soil.

Sample ID	Solid/Solution g/L	TCP mg/L	Data Analysis					
			Average	Variance	(+/-)S.D*	RSD**	Bias***	% Error****
Woodburn-1	5	1.393	1.328	0.003	0.056	4.222	0.064	4.823
Woodburn-2	5	1.305	1.328				-0.024	-1.800
Woodburn-3	5	1.288	1.328				-0.040	-3.024
Woodburn-1	10	1.200	1.188	0.000	0.015	1.289	0.012	1.044
Woodburn-2	10	1.193	1.188				0.005	0.397
Woodburn-3	10	1.171	1.188				-0.017	-1.441
Woodburn-1	20	1.066	1.126	0.004	0.065	5.800	-0.061	-5.379
Woodburn-2	20	1.196	1.126				0.069	6.144
Woodburn-3	20	1.118	1.126				-0.009	-0.766
Woodburn-1	50	0.904	0.887	0.003	0.057	6.408	0.017	1.878
Woodburn-2	50	0.824	0.887				-0.063	-7.137
Woodburn-3	50	0.934	0.887				0.047	5.259
Woodburn-1	100	0.559	0.532	0.001	0.028	5.254	0.027	5.088
Woodburn-2	100	0.504	0.532				-0.029	-5.406
Woodburn-3	100	0.534	0.532				0.002	0.317

*SD** : standard deviation

*RSD** : relative standard deviation (SD/average)x100

*Bias***: deviation of measurement value from the average value

*% Error***** : relative Bias (Bias/average)x100

Table 8.5.3.2.2. Standard asphalt (SACC) soil sorption test statistical variability of Zn on Woodburn soil.

Sample ID	Solid/Solution g/L	Zn mg/L	Data Analysis					
			Average	Variance	(+/-)S.D*	RSD**	Bias***	% Error****
Woodburn-1	5	0.230	0.238	0.000	0.007	3.087	-0.008	-3.162
Woodburn-2	5	0.245	0.238				0.007	3.005
Woodburn-3	5	0.238	0.238				0.000	0.157
Woodburn-1	10	0.175	0.166	0.000	0.009	5.422	0.009	5.536
Woodburn-2	10	0.157	0.166				-0.009	-5.300
Woodburn-3	10	0.166	0.166				0.000	-0.236
Woodburn-1	20	0.136	0.133	0.000	0.007	5.396	0.003	1.995
Woodburn-2	20	0.139	0.133				0.005	4.115
Woodburn-3	20	0.125	0.133				-0.008	-6.110
Woodburn-1	50	0.125	0.126	0.000	0.004	2.776	-0.002	-1.344
Woodburn-2	50	0.124	0.126				-0.002	-1.849
Woodburn-3	50	0.130	0.126				0.004	3.192
Woodburn-1	100	0.115	0.113	0.000	0.002	1.724	0.002	1.707
Woodburn-2	100	0.111	0.113				-0.002	-1.742
Woodburn-3	100	0.113	0.113				0.000	0.035

*SD** : standard deviation

*RSD** : relative standard deviation (SD/average)x100

*Bias***: deviation of measurement value from the average value

*% Error***** : relative Bias (Bias/average)x100

Table 8.5.3.2.3. Standard asphalt (SACC) soil sorption test statistical variability of TCP on Sagehill soil.

Sample ID	Solid/Solution g/L	TCP mg/L	Data Analysis					
			Average	Variance	(+/-)S.D*	RSD**	Bias***	% Error****
Sagehill-1	100	1.843	1.781	0.005	0.068	3.830	0.061	3.446
Sagehill-2	100	1.793	1.781				0.012	0.677
Sagehill-3	100	1.708	1.781				-0.073	-4.124
Sagehill-1	200	1.771	1.697	0.005	0.071	4.186	0.074	4.355
Sagehill-2	200	1.691	1.697				-0.006	-0.361
Sagehill-3	200	1.629	1.697				-0.068	-3.993
Sagehill-1	300	1.701	1.658	0.003	0.059	3.535	0.043	2.614
Sagehill-2	300	1.681	1.658				0.023	1.408
Sagehill-3	300	1.591	1.658				-0.067	-4.022
Sagehill-1	400	1.634	1.582	0.005	0.072	4.528	0.053	3.336
Sagehill-2	400	1.610	1.582				0.029	1.818
Sagehill-3	400	1.500	1.582				-0.082	-5.155
Sagehill-1	600	1.509	1.469	0.003	0.051	3.503	0.040	2.705
Sagehill-2	600	1.411	1.469				-0.058	-3.957
Sagehill-3	600	1.487	1.469				0.018	1.252

*SD** : standard deviation

*RSD** : relative standard deviation (SD/average)x100

*Bias***: deviation of measurement value from the average value

*% Error***** : relative Bias (Bias/average)x100

Table 8.5.3.2.4. Standard asphalt (SACC) soil sorption test statistical variability of Zn on Sagehill soil.

Sample ID	Solid/Solution g/L	Zn mg/L	Data Analysis					
			Average	Variance	(+/-)S.D [*]	RSD ^{**}	Bias ^{***}	% Error ^{****}
Sagehill-1	100	0.068	0.068	0.000	0.003	3.694	0.000	-0.460
Sagehill-2	100	0.066	0.068				-0.002	-3.442
Sagehill-3	100	0.071	0.068				0.003	3.903
Sagehill-1	200	0.062	0.063	0.000	0.002	3.379	-0.001	-1.951
Sagehill-2	200	0.066	0.063				0.002	3.902
Sagehill-3	200	0.062	0.063				-0.001	-1.951
Sagehill-1	300	0.061	0.060	0.000	0.001	2.310	0.000	0.739
Sagehill-2	300	0.059	0.060				-0.002	-2.589
Sagehill-3	300	0.061	0.060				0.001	1.850
Sagehill-1	400	0.056	0.054	0.000	0.002	4.419	0.002	3.948
Sagehill-2	400	0.055	0.054				0.000	0.826
Sagehill-3	400	0.052	0.054				-0.003	-4.774
Sagehill-1	600	0.031	0.033	0.000	0.002	5.570	-0.002	-6.125
Sagehill-2	600	0.034	0.033				0.002	4.761
Sagehill-3	600	0.033	0.033				0.000	1.364

SD^{}* : standard deviation

*RSD^{**}* : relative standard deviation (SD/average)x100

*Bias^{***}*: deviation of measurement value from the average value

*% Error^{****}* : relative Bias (Bias/average)x100

8.5.3.3 Toxicity Analyses

Samples from Woodburn and Sagehill soil sorption tests were analyzed for their capacity to reduce and/or remove toxicity of standard asphalt (SACC) leachate. Initially, SACC leachate (used as control leachate) exhibited %EC50 values of 2% and LC50 value of 50% for algae and Daphnia, respectively. After sorption with Woodburn soil, both algal and daphnia toxicity results indicated a significant reduction in toxicity at 5 g/L and 10 g/L soil to liquid ratio and complete removal of toxicity at 20 g/L soil to liquid ratio (Table 8.5.1.1.1). For Sagehill soil, complete removal of standard-asphalt leachate toxicity removal was observed at 100 g/L soil to liquid ratio for both the tested organisms.

8.5.4 Standard Asphalt Leachate Photolysis Test

8.5.4.1 Chemical analyses

To study the photochemical changes of standard asphalt (SACC) in the laboratory, the leachate was exposed to an artificial light source of about 30 Watts/m² in a 20°C constant temperature room. This light intensity is about one tenth the intensity of ambient sunlight. The control consisted of leachate under equivalent conditions without exposure to the light source and stored in 4°C. The results of the photolysis degradation of 2,4,6-TCP are shown in Figure 8.5.4.1.1.

Over 10 days, the 2,4,6-TCP decreased by about 50%, from 1.84 to 0.90 mg/L. No changes in zinc concentration were observed (Figure 8.5.4.1.1). As metals do not photochemically degrade, results confirm their conservation in the solution. Assuming a first order loss rate, the TCP data were modeled as:

$$C = C_0 e^{-k_p t} \quad (8.5.4.1.1)$$

where:

C = TCP concentration at time t;

C₀ = TCP initial concentration at time 0;

t = time; and

k_p = first-order photolysis rate constant, 1/time.

From the fitted equation $C_{TCP} = 1.81 e^{-0.003t}$ (Figure 8.5.4.1.1.), the first-order photolysis decay coefficient is determined by regression to be 3×10^{-3} /hr or 0.072/d. This rate coefficient corresponds to a half-life of about 13 days, indicating that photolysis will result in a significant environmental loss of TCP from the standard asphalt after prolonged exposure to light. The chemical analysis data are summarized in Table 8.5.1.1.1.

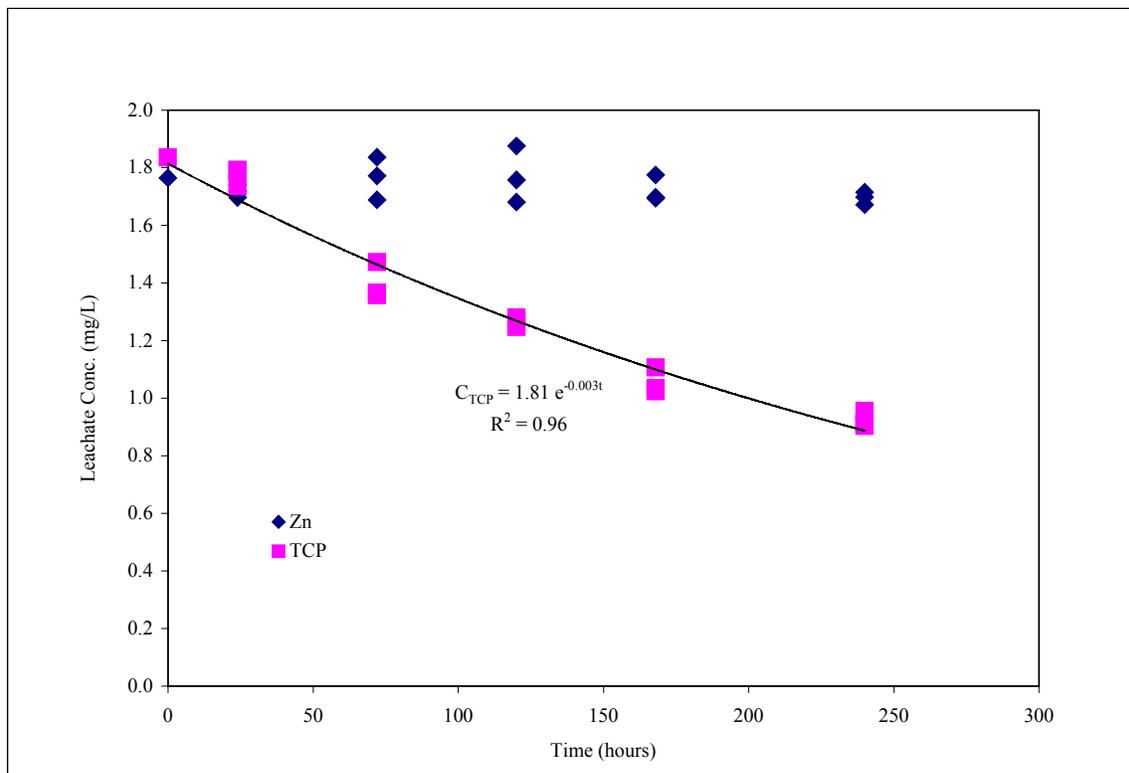


Figure 8.5.4.1.1. 2,4,6-TCP and Zn concentrations as a function of time for photolysis of standard asphalt (SACC) leachate (triplicate experiments).

8.5.4.2 Determinations of photolysis test statistical variability

Triplicate samples were run through the photolysis test on the standard asphalt (SACC). The average value, variance, standard deviation (SD), relative standard deviation (RSD), deviation of measurement value from the average value (bias), and relative bias or percent of error for both zinc and 2,4,6-trichlorophenol are presented in Tables 8.5.4.2.1 and 8.5.4.2.2. These results indicate that, based on single operator characteristics, the photolysis tests for standard asphalt data are acceptable with percent error of about 5%.

Table 8.5.4.2.1. Standard asphalt (SACC) leachate photolysis test statistical variability for Zn.

Sample ID	Time hrs	Zn mg/L	Data Analysis					
			Average	Variance	(+/-)S.D [*]	RSD ^{**}	Bias ^{***}	% Error ^{****}
PHOTO-Day1-1	24	1.719	1.719	0.000	0.021	1.251	0.001	0.031
PHOTO-Day1-2	24	1.740	1.719				0.021	1.235
PHOTO-Day1-3	24	1.697	1.719				-0.022	-1.266
PHOTO-Day3-1	72	1.836	1.766	0.005	0.074	4.196	0.071	4.012
PHOTO-Day3-2	72	1.772	1.766				0.006	0.346
PHOTO-Day3-3	72	1.689	1.766				-0.077	-4.359
PHOTO-Day5-1	120	1.758	1.772	0.010	0.098	5.528	-0.014	-0.772
PHOTO-Day5-2	120	1.876	1.772				0.104	5.873
PHOTO-Day5-3	120	1.681	1.772				-0.090	-5.101
PHOTO-Day7-1	168	1.697	1.722	0.002	0.046	2.675	-0.025	-1.472
PHOTO-Day7-2	168	1.775	1.722				0.053	3.088
PHOTO-Day7-3	168	1.694	1.722				-0.028	-1.615
PHOTO-DAY10-1	240	1.715	1.695	0.000	0.022	1.273	0.020	1.161
PHOTO-DAY10-2	240	1.672	1.695				-0.023	-1.361
PHOTO-DAY10-3	240	1.699	1.695				0.003	0.199

SD^{}* : standard deviation

*RSD^{**}* : relative standard deviation (SD/average)x100

*Bias^{***}*: deviation of measurement value from the average value

*% Error^{****}* : relative Bias (Bias/average)x100

Table 8.5.4.2.1. Standard asphalt (SACC) leachate photolysis test statistical variability for TCP.

Sample ID	Time hrs	TCP mg/L	Data Analysis					
			Average	Variance	(+/-)S.D [*]	RSD ^{**}	Bias ^{***}	% Error ^{****}
PHOTO-Day1-1	24	1.79	1.772	0.001	0.032	1.825	0.017	0.956
PHOTO-Day1-2	24	1.73	1.772				-0.037	-2.104
PHOTO-Day1-3	24	1.79	1.772				0.020	1.148
PHOTO-Day3-1	72	1.47	1.398	0.004	0.064	4.563	0.073	5.255
PHOTO-Day3-2	72	1.37	1.398				-0.032	-2.294
PHOTO-Day3-3	72	1.36	1.398				-0.041	-2.961
PHOTO-Day5-1	120	1.28	1.264	0.000	0.016	1.288	0.015	1.193
PHOTO-Day5-2	120	1.27	1.264				0.002	0.173
PHOTO-Day5-3	120	1.25	1.264				-0.017	-1.366
PHOTO-Day7-1	168	1.11	1.055	0.002	0.045	4.284	0.052	4.911
PHOTO-Day7-2	168	1.03	1.055				-0.020	-1.942
PHOTO-Day7-3	168	1.02	1.055				-0.031	-2.969
PHOTO-DAY10-1	240	0.95	0.924	0.001	0.027	2.941	0.031	3.347
PHOTO-DAY10-2	240	0.91	0.924				-0.011	-1.174
PHOTO-DAY10-3	240	0.90	0.924				-0.020	-2.172

SD^{}* : standard deviation

*RSD^{**}* : relative standard deviation (SD/average)x100

*Bias^{***}*: deviation of measurement value from the average value

*% Error^{****}* : relative Bias (Bias/average)x100

8.5.5 Standard Asphalt Leachate Volatilization Test

8.5.5.1 Chemical analysis

The volatilization experiments were conducted with 24-hr standard asphalt (SACC) batch leachate placed into 1-liter glass beakers. The beakers were placed in a 20°C controlled temperature room and the test solutions continuously sparged with air at a flow rate of 250 mL/min. Samples were taken daily from the glass beakers and analyzed for toxicity and chemical content. The solution volume was kept constant by adding distilled water after each sampling. The control consisted of leachate under equivalent conditions without sparging with air source and stored in 4°C. The results of the loss by volatilization of TCP from the leachate are shown in Figure 8.5.5.1.1. No changes in zinc concentration were observed (Figure 8.5.5.1.1), as metals do not volatilize. Results confirm their conservation in the solution. Over 10 days, 2,4,6-TCP decreased by about 28% from 1.68 to 1.20 mg/L.

The flux across the water-air interface is a first-order process, commonly assumed for environmental conditions. The TCP data were modeled as:

$$C = C_0 e^{-k_v t} \quad (8.5.5.1.1)$$

where:

C_0 = initial concentration of constituent at time $t=0$ (mg/L),

C = concentration of constituent at time t (mg/L), and

k_v = first-order volatilization rate constant (1/hr).

Using the fitted equation, $C_{TCP} = 1.72 e^{-0.0032t}$ (Figure 8.5.4.1.2.), an estimate of the first-order volatilization coefficient, $k_v = 3.2 \times 10^{-3}$ /hr or 0.077/d, will result in only slight volatilization losses over short time periods of exposure, but significant losses over long time periods.

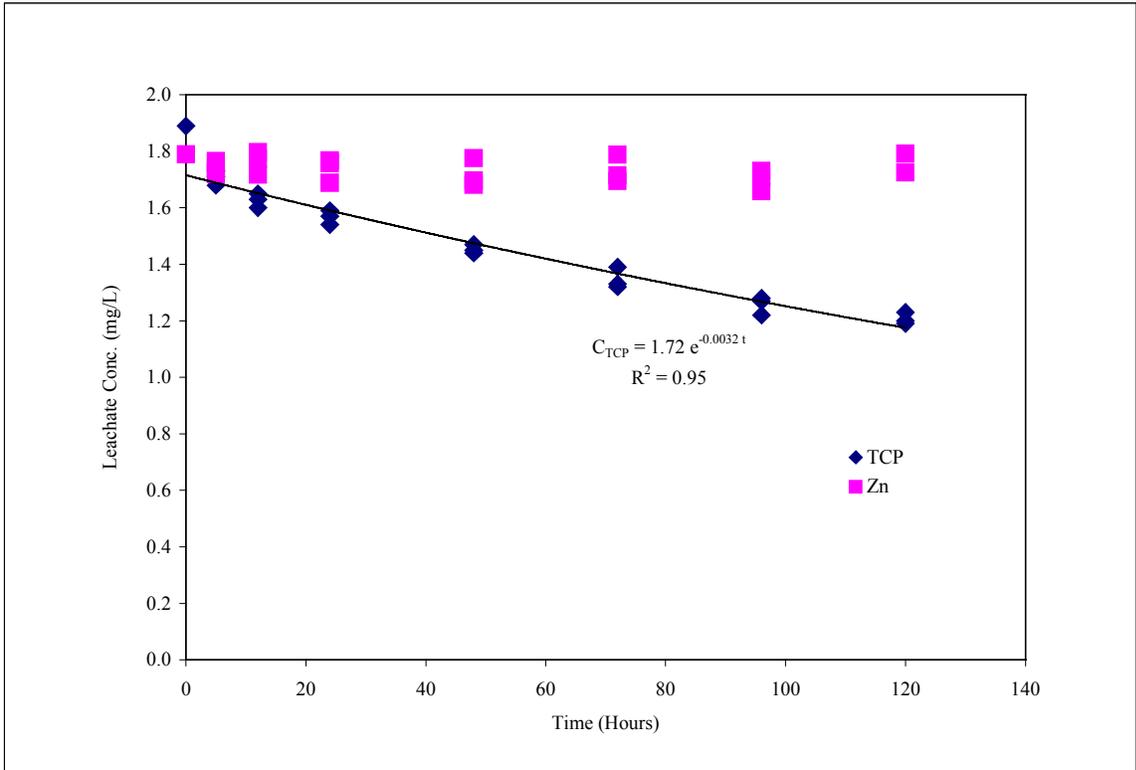


Figure 8.5.5.1.1. TCP and Zn concentrations as a function of time for volatilization in standard asphalt (SACC) leachate (triplicate experiments).

8.5.5.2 Determinations of volatilization test statistical variability

Triplicate samples were run through the test series volatilization tests on the standard asphalt (SACC). The average value, variance, standard deviation (SD), relative standard deviation (RSD), deviation of measurement value from the average value (bias), and relative bias or percent of error for both zinc and 2,4,6-trichlorophenol, are presented in Tables 8.5.5.2.1 and 8.5.5.2.2. These results indicate that, based on single operator characteristics, the volatilization tests for standard asphalt data are acceptable with percent error of less than 5%.

Table 8.5.5.2.1. Standard asphalt (SACC) leachate volatilization test statistical variability for Zn.

Sample ID	Time hrs	Zn mg/L	Data Analysis					
			Average	Variance	(+/-)S.D [*]	RSD ^{**}	Bias ^{***}	% Error ^{****}
LCH-VOL-1/1	5	1.765	1.742	0.001	0.023	1.311	0.023	1.349
LCH-VOL-1/2	5	1.719	1.742				-0.022	-1.269
LCH-VOL-1/3	5	1.740	1.742				-0.001	-0.080
LCH-VOL-12/1	12	1.717	1.762	0.002	0.041	2.302	-0.045	-2.532
LCH-VOL-12/2	12	1.796	1.762				0.035	1.968
LCH-VOL-12/3	12	1.772	1.762				0.010	0.564
LCH-VOL-Day1/1	24	1.689	1.738	0.002	0.043	2.478	-0.049	-2.843
LCH-VOL-Day1/2	24	1.758	1.738				0.020	1.142
LCH-VOL-Day1/3	24	1.768	1.738				0.030	1.701
LCH-VOL-Day3/1	48	1.681	1.718	0.003	0.050	2.939	-0.037	-2.133
LCH-VOL-Day3/2	48	1.697	1.718				-0.021	-1.219
LCH-VOL-Day3/3	48	1.775	1.718				0.058	3.352
LCH-VOL-Day5/1	72	1.694	1.732	0.002	0.049	2.843	-0.038	-2.195
LCH-VOL-Day5/2	72	1.715	1.732				-0.018	-1.016
LCH-VOL-Day5/3	72	1.788	1.732				0.056	3.212
LCH-VOL-Day7/1	96	1.705	1.698	0.001	0.037	2.150	0.007	0.416
LCH-VOL-Day7/2	96	1.659	1.698				-0.040	-2.328
LCH-VOL-Day7/3	96	1.731	1.698				0.032	1.912
LCH-VOL-Day10/1	120	1.725	1.754	0.001	0.033	1.908	-0.029	-1.633
LCH-VOL-Day10/2	120	1.791	1.754				0.037	2.097
LCH-VOL-Day10/3	120	1.746	1.754				-0.008	-0.463

SD^{}* : standard deviation

*RSD^{**}* : relative standard deviation (SD/average)x100

*Bias^{***}*: deviation of measurement value from the average value

*% Error^{****}* : relative Bias (Bias/average)x100

Table 8.5.5.2.2. Standard asphalt (SACC) leachate volatilization test statistical variability for TCP.

Sample ID	Time hrs	TCP mg/L	Data Analysis					
			Average	Variance	(+/-)S.D [*]	RSD ^{**}	Bias ^{***}	% Error ^{****}
LCH-VOL-1/1	5	1.68	1.707	0.001	0.025	1.475	-0.027	-1.562
LCH-VOL-1/2	5	1.71	1.707				0.003	0.195
LCH-VOL-1/3	5	1.73	1.707				0.023	1.367
LCH-VOL-12/1	12	1.65	1.627	0.001	0.025	1.547	0.023	1.434
LCH-VOL-12/2	12	1.63	1.627				0.003	0.205
LCH-VOL-12/3	12	1.60	1.627				-0.027	-1.639
LCH-VOL-Day1/1	24	1.57	1.567	0.001	0.025	1.606	0.003	0.213
LCH-VOL-Day1/2	24	1.54	1.567				-0.027	-1.702
LCH-VOL-Day1/3	24	1.59	1.567				0.023	1.489
LCH-VOL-Day3/1	48	1.47	1.453	0.000	0.015	1.051	0.017	1.147
LCH-VOL-Day3/2	48	1.45	1.453				-0.003	-0.229
LCH-VOL-Day3/3	48	1.44	1.453				-0.013	-0.917
LCH-VOL-Day5/1	72	1.39	1.347	0.001	0.038	2.811	0.043	3.218
LCH-VOL-Day5/2	72	1.32	1.347				-0.027	-1.980
LCH-VOL-Day5/3	72	1.33	1.347				-0.017	-1.238
LCH-VOL-Day7/1	96	1.28	1.257	0.001	0.032	2.558	0.023	1.857
LCH-VOL-Day7/2	96	1.22	1.257				-0.037	-2.918
LCH-VOL-Day7/3	96	1.27	1.257				0.013	1.061
LCH-VOL-Day10/1	120	1.20	1.207	0.000	0.021	1.725	-0.007	-0.552
LCH-VOL-Day10/2	120	1.19	1.207				-0.017	-1.381
LCH-VOL-Day10/3	120	1.23	1.207				0.023	1.934

SD^{}* : standard deviation

*RSD^{**}* : relative standard deviation (SD/average)x100

*Bias^{***}*: deviation of measurement value from the average value

*% Error^{****}* : relative Bias (Bias/average)x100

8.5.6 Standard Asphalt Leachate Biodegradation Test

8.5.6.1 Chemical analysis

Biological degradation of the standard asphalt (SACC) leachate is shown in Figure 8.5.6.1.1. Over 10 days, the 2,4,6-TCP concentrations decreased by about 40% from 1.88 to 1.13 mg/L. The control consisted of leachate under equivalent conditions without sparging with air source and stored in 4°C.

Assuming a first order loss rate, the data were modeled again as:

$$C_{\text{TCP}} = 1.75 e^{-0.002 t} \quad (R^2 = 0.78) \quad (8.5.6.1.1)$$

For units of 2,4,6-TCP in mg/L and time in hours, a first-order biological decay coefficient, k_b , is indicated of $2 \times 10^{-3}/\text{hr}$ or $0.048/\text{d}$. This rate predicts that biodegradation will result in slow losses of the 2,4,6-TCP in natural environments.

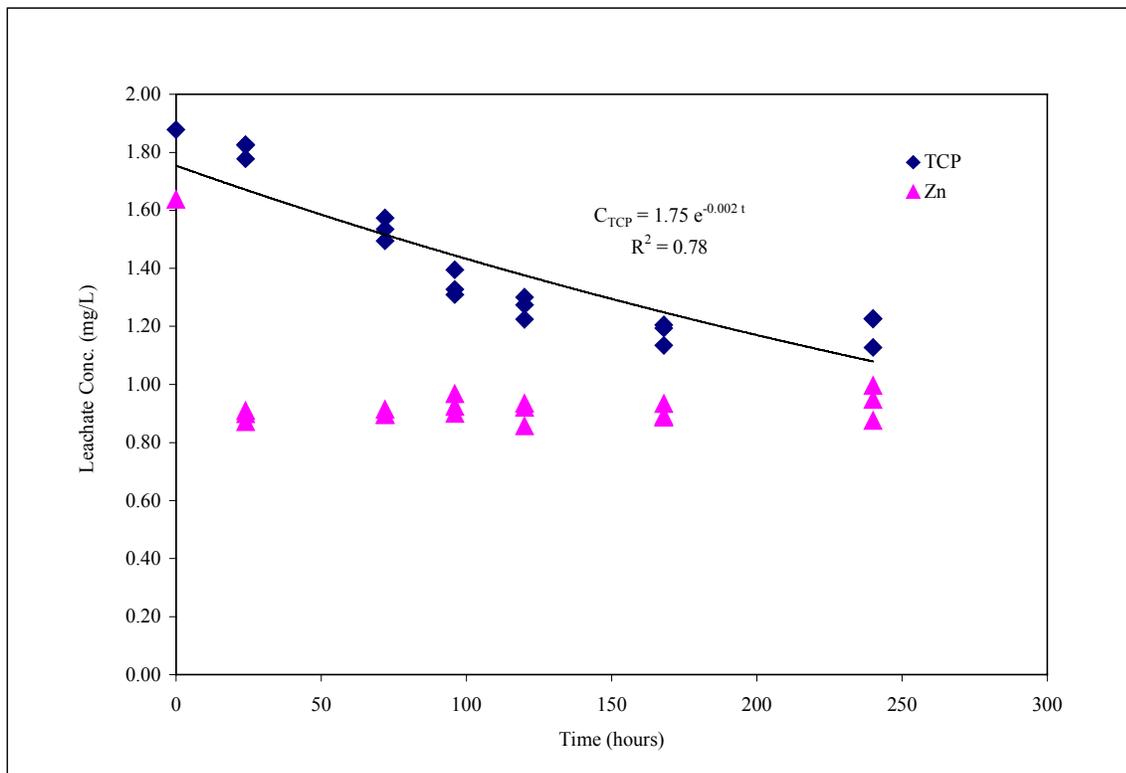


Figure 8.5.6.1.1. TCP and Zn concentration as a function of time for biodegradation in the standard asphalt (SACC) leachate (triplicate experiments).

8.5.6.2 Determinations of biodegradation test statistical variability

Triplicate samples were run through the biodegradation test series on the standard asphalt (SACC). The average value, variance, standard deviation (SD), relative standard deviation (RSD), deviation of measurement value from the average value (bias), and relative bias or percent of error for both zinc and TCP are presented in Tables 8.5.6.2.1 and 8.5.6.2.2. These results indicate that, based on single operator characteristics, the biodegradation tests for standard asphalt data are acceptable with percent error of less than 5%.

Table 8.5.6.2.1. Standard asphalt (SACC) leachate volatilization test statistical variability for Zn.

Sample ID	Time hrs	Zn mg/L	Data Analysis					
			Average	Variance	(+/-)S.D*	RSD**	Bias***	% Error****
TCP Day1-1	24	0.871	0.893	0.000	0.020	2.199	-0.022	-2.450
TCP Day1-2	24	0.899	0.893				0.006	0.647
TCP Day1-3	24	0.909	0.893				0.016	1.802
TCP Day3-1	72	0.896	0.902	0.000	0.010	1.135	-0.007	-0.721
TCP Day3-2	72	0.914	0.902				0.012	1.308
TCP Day3-3	72	0.897	0.902				-0.005	-0.586
TCP Day4-1	96	0.968	0.931	0.001	0.035	3.738	0.038	4.032
TCP Day4-2	96	0.900	0.931				-0.031	-3.349
TCP Day4-3	96	0.924	0.931				-0.006	-0.682
TCP Day5-1	120	0.921	0.905	0.002	0.041	4.557	0.017	1.859
TCP Day5-2	120	0.858	0.905				-0.047	-5.193
TCP Day5-3	120	0.935	0.905				0.030	3.334
TCP Day7-1	168	0.891	0.904	0.001	0.026	2.923	-0.013	-1.442
TCP Day7-2	168	0.934	0.904				0.030	3.364
TCP Day7-3	168	0.887	0.904				-0.017	-1.921
TCP Day10-1	240	0.948	0.940	0.004	0.061	6.507	0.008	0.879
TCP Day10-2	240	0.875	0.940				-0.065	-6.902
TCP Day10-3	240	0.997	0.940				0.057	6.023

*SD** : standard deviation
*RSD** : relative standard deviation (SD/average)x100
*Bias***: deviation of measurement value from the average value
*% Error***** : relative Bias (Bias/average)x100

Table 8.5.6.2.2. Standard asphalt (SACC) leachate biodegradation test statistical variability for TCP.

Sample ID	Time hrs	TCP mg/L	Data Analysis					
			Average	Variance	(+/-)S.D*	RSD**	Bias***	% Error****
TCP Day1-1	24	1.83	1.810	0.001	0.028	1.541	0.017	0.939
TCP Day1-2	24	1.78	1.810				-0.032	-1.779
TCP Day1-3	24	1.82	1.810				0.015	0.840
TCP Day3-1	72	1.57	1.534	0.002	0.040	2.589	0.040	2.583
TCP Day3-2	72	1.53	1.534				0.000	0.011
TCP Day3-3	72	1.49	1.534				-0.040	-2.594
TCP Day4-1	96	1.39	1.344	0.002	0.045	3.337	0.051	3.774
TCP Day4-2	96	1.33	1.344				-0.016	-1.218
TCP Day4-3	96	1.31	1.344				-0.034	-2.557
TCP Day5-1	120	1.30	1.267	0.001	0.038	3.034	0.034	2.690
TCP Day5-2	120	1.22	1.267				-0.042	-3.290
TCP Day5-3	120	1.27	1.267				0.008	0.600
TCP Day7-1	168	1.13	1.178	0.001	0.038	3.238	-0.044	-3.702
TCP Day7-2	168	1.19	1.178				0.016	1.394
TCP Day7-3	168	1.21	1.178				0.027	2.308
TCP Day10-1	240	1.23	1.194	0.003	0.057	4.797	0.034	2.838
TCP Day10-2	240	1.23	1.194				0.032	2.701
TCP Day10-3	240	1.13	1.194				-0.066	-5.539

*SD** : standard deviation
*RSD** : relative standard deviation (SD/average)x100
*Bias***: deviation of measurement value from the average value
*% Error***** : relative Bias (Bias/average)x100

8.5.7 Biological analyses of Photolysis, Volatilization and Biodegradation Samples

Degradation of toxic chemicals in the standard-asphalt leachates and thus reduction and/or removal of their toxicity were studied by conducting a battery of RRR processes such as photolysis, volatilization and biodegradation. 24-hour batch leachates of standard asphalt were used as the control for the RRR tests. An algal EC50 value of approximately 2% to 4% in photolysis, volatilization and biodegradation controls and a LC50 value of 50% for *Daphnia* were observed. Toxicity results of samples analyzed after these RRR processes did not indicate any significant change ($p > 0.05$) in toxicity for either algae or *Daphnia*. It should be noted that 24-hour batch leachates of SACC used in these tests have only Zn and TCP as their major chemical components. Although the RRR processes degraded and reduced the TCP concentration significantly, a similar effect was not observed for Zn. Figures 8.5.4.1.1, 8.5.5.1.1, and 8.5.6.1.1 clearly indicate that the initial Zn concentration of about 1.8 mg/L in photolysis and volatilization samples and 0.9 mg/L in biodegradation samples have not changed much to alter the toxicity of the standard-asphalt leachate. Comparison with published literature has shown that Zn can cause a significant effect at 0.06 mg/L and 0.56 mg/L for *S. capricornutum* and *D. magna* respectively. Thus, the standard-asphalt leachate toxicity remained about the same level even after the RRR processes.

8.6 SUMMARY AND CONCLUSIONS

QA/QC protocols were developed and validated for the leaching and RRR process tests for the “standard asphalt” (standard asphalt cement concrete, or SACC), which contains two model toxicants, one metal (zinc) and one organic (2,4,6-trichlorophenol, or TCP). This facilitates validation of this project’s new laboratory protocols when adopted by other labs.

A user’s manual describing the overall screening methodology and laboratory test protocols has been developed as an additional part of this task (Volume IV). This includes the overall screening methodology and contains detailed instructions for leaching and RRR process test methods and associated QA/QC protocols, as well as for biotoxicity tests and chemistry test methods and their associated QA/QC protocols. The manual is a stand-alone document to facilitate distribution to government agencies and other future users (Nelson et al., 2000b)

The selected toxicants, zinc and 2,4,6-TCP, are easily determined by common analytical methods and are of known toxicity in the standard toxicity tests using algae and daphnia.

Test statistics on triplicate samples were also developed. These are the average value, variance, standard deviation (SD), relative standard deviation (RSD, which is the method precision), deviation of measurement value from the average value (bias), and relative bias or percent of error for both zinc and 2,4,6-trichlorophenol. Test statistics form an integral part of the QA/QC protocols.

Degradation of toxic chemicals in the standard-asphalt leachates and thus reduction and/or removal of their toxicity were studied by conducting a battery of RRR processes such as photolysis, volatilization and biodegradation. Results indicate that, based on single operator

characteristics, the volatilization, photolysis, and biodegradation tests for the standard asphalt data are acceptable with percent error of less than 5%.

Table 8.5.1.1.1. Task 7 Summary data for chemical and toxicity analyses.

TASK 7: COMPARISON OF LABORATORY TEST PROTOCOLS WITH EPA PROTOCOLS AND DETERMINATION OF TEST STATICAL VARIABILITY.										
Sample ID	Test Conditions	Time (hr)	Chemistry Test Results							Final pH
			TCP (mg/L)	Al (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Zn (mg/L)	
	Standard Asphalt Batch Leaching at Different Solid/Solution Ratio									
1	RATIO 1:0.5	2:1	14.96	0.951	181.606	13.434	24.130	102.159	12.039	8.39
2	RATIO 1:0.5	2:1	14.58	0.891	179.876	12.784	22.990	101.096	13.879	8.42
3	RATIO 1:0.5	2:1	14.12	0.911	182.006	12.985	25.005	104.157	14.344	8.3
4	RATIO 1:1	1:1	7.55	0.582	99.605	6.068	10.062	55.961	7.219	8.05
5	RATIO 1:1	1:1	7.11	0.577	98.032	5.698	10.116	53.946	7.098	8
6	RATIO 1:1	1:1	7.21	0.628	102.238	6.281	9.876	56.004	7.302	8.01
7	RATIO 1:4	1:4	1.87	0.299	25.989	1.392	2.090	10.213	1.830	7.23
8	RATIO 1:4	1:4	1.79	0.234	26.003	1.422	2.111	10.036	1.857	7.13
9	RATIO 1:4	1:4	1.84	0.277	27.983	1.354	2.101	10.112	1.906	7.25
10	RATIO 1:8	1:8	0.902	0.250	8.474	0.555	0.807	4.549	0.905	7.64
11	RATIO 1:8	1:8	0.895	0.223	8.005	0.568	0.799	4.705	0.889	7.56
12	RATIO 1:8	1:8	1.23	0.265	8.978	0.595	0.838	4.663	0.923	7.67
13	RATIO 1:20	1:20	0.344	1.014	5.039	0.295	0.479	3.302	0.357	7.56
14	RATIO 1:20	1:20	0.396	1.332	5.567	0.289	0.457	3.788	0.388	7.49
15	RATIO 1:20	1:20	0.308	1.036	5.000	0.267	0.506	3.687	0.408	7.51

Table 8.5.1.1.1. Task 7 Summary data for chemical and toxicity analyses (cont.).

TASK 7: COMPARISON OF LABORATORY TEST PROTOCOLS WITH EPA PROTOCOLS AND DETERMINATION OF TEST STATICAL VARIABILITY.									
Sample ID	Test Conditions	Time (hr)	Tox Lab ID	Toxicity Results			Chemistry Results		
				Algal Toxicity			TCP (mg/L)	Zn (mg/L)	Final pH
				Concentration as % Elutriate					
				%EC ₅₀ or %LC ₅₀	Lower 95% C.L.	Upper 95% C.L.			
	Flat Plate Zn & TCP Standard Asphalt								
1	FP-ZN-TCP-1	6	NA	NA	NA	NA	0.024	0.011	6.55
2	FP-ZN-TCP-2	6	NA	NA	NA	NA	0.021	0.015	6.54
3	FP-ZN-TCP-3	6	NA	NA	NA	NA	0.028	0.013	6.66
4	FP-ZN-TCP-4	45.5	NA	NA	NA	NA	0.075	0.057	6.72
5	FP-ZN-TCP-5	45.5	NA	NA	NA	NA	0.078	0.051	6.74
6	FP-ZN-TCP-6	45.5	NA	NA	NA	NA	0.118	0.055	6.55
7	FP-ZN-TCP-7	73.5	NA	NA	NA	NA	0.150	0.088	6.61
8	FP-ZN-TCP-8	73.5	NA	NA	NA	NA	0.153	0.081	6.6
9	FP-ZN-TCP-9	73.5	NA	NA	NA	NA	0.175	0.09	6.64
10	FP-ZN-TCP-10	97.5	NA	NA	NA	NA	0.190	0.102	6.67
11	FP-ZN-TCP-11	97.5	NA	NA	NA	NA	0.192	0.107	6.67
12	FP-ZN-TCP-12	97.5	NA	NA	NA	NA	0.186	0.099	6.73
13	FP-ZN-TCP-13	166.5	NA	NA	NA	NA	0.336	0.174	6.58
14	FP-ZN-TCP-14	166.5	NA	NA	NA	NA	0.350	0.169	6.71
15	FP-ZN-TCP-15	166.5	NA	NA	NA	NA	0.326	0.171	6.82
16	FP-ZN-TCP-16	196.5	NA	NA	NA	NA	0.391	0.207	6.84
17	FP-ZN-TCP-17	196.5	NA	NA	NA	NA	0.388	0.201	6.84
18	FP-ZN-TCP-18	196.5	NA	NA	NA	NA	0.362	0.199	6.84
19	FP-ZN-TCP-19	286.5	4237401	2.3	2.0	2.6	0.450	0.261	6.88
20	FP-ZN-TCP-20	286.5	4237402	1.9	1.7	2.2	0.465	0.271	6.86
21	FP-ZN-TCP-21	286.5	4237403	2.1	1.9	2.3	0.423	0.264	6.88

Table 8.5.1.1.1. Task 7 Summary data for chemical and toxicity analyses (cont.).

TASK 7: COMPARISON OF LABORATORY TEST PROTOCOLS WITH EPA PROTOCOLS AND DETERMINATION OF TEST STATICAL VARIABILITY.									
Sample ID	Test Conditions	Time (hr)	Tox Lab ID	Toxicity Results			Chemistry Results		
				Algal Toxicity			TCP (mg/L)	Zn (mg/L)	Final pH
				Concentration as % Elutriate					
				%EC ₅₀ or %LC ₅₀	Lower 95% C.L.	Upper 95% C.L.			
Flat Plate Standard Asphalt Leaching @ Different Solid/Solution Ratio									
1	FPR-DAY1-1 at 1:2 Ratio	1:2	24	NA	NA	NA	NA	0.049	6.32
2	FPR-DAY1-2 at 1:2 Ratio	1:2	24	NA	NA	NA	NA	0.065	6.29
3	FPR-DAY3-2 at 1:2 Ratio	1:2	72	NA	NA	NA	NA	0.103	6.31
4	FPR-DAY3-1 at 1:2 Ratio	1:2	72	NA	NA	NA	NA	0.116	6.82
5	FPR-DAY5-1 at 1:2 Ratio	1:2	120	NA	NA	NA	NA	0.210	6.81
6	FPR-DAY5-2 at 1:2 Ratio	1:2	120	NA	NA	NA	NA	0.259	6.63
7	FPR-DAY7-1 at 1:2 Ratio	1:2	168	NA	NA	NA	NA	0.272	6.15
8	FPR-DAY7-2 at 1:2 Ratio	1:2	168	NA	NA	NA	NA	0.251	6.37
9	FPR-DAY9-1 at 1:2 Ratio	1:2	216	NA	NA	NA	NA	0.280	6.19
10	FPR-DAY9-2 at 1:2 Ratio	1:2	216	NA	NA	NA	NA	0.268	6.22
11	FPR-DAY12-1 at 1:2 Ratio	1:2	288	NA	NA	NA	NA	0.286	6.17
12	FPR-DAY12-2 at 1:2 Ratio	1:2	288	NA	NA	NA	NA	0.252	6.10
13	1/2FPR-DAY1-1 at 2:1 Ratio	2:1	24	NA	NA	NA	NA	0.126	6.27
14	1/2FPR-DAY1-2 at 2:1 Ratio	2:1	24	NA	NA	NA	NA	0.140	6.36
15	1/2FPR-DAY3-1 at 2:1 Ratio	2:1	72	NA	NA	NA	NA	0.572	6.30
16	1/2FPR-DAY3-2 at 2:1 Ratio	2:1	72	NA	NA	NA	NA	0.624	6.16
17	1/2FPR-DAY5-1 at 2:1 Ratio	2:1	120	NA	NA	NA	NA	0.840	6.85
18	1/2FPR-DAY5-2 at 2:1 Ratio	2:1	120	NA	NA	NA	NA	0.901	6.50
19	1/2FPR-DAY7-1 at 2:1 Ratio	2:1	168	NA	NA	NA	NA	0.931	5.94
20	1/2FPR-DAY7-2 at 2:1 Ratio	2:1	168	NA	NA	NA	NA	1.061	6.05
21	1/2FPR-DAY9-1 at 2:1 Ratio	2:1	216	NA	NA	NA	NA	1.196	6.16
22	1/2FPR-DAY12-1 at 2:1 Ratio	2:1	216	NA	NA	NA	NA	1.089	6.12
23	1/2FPR-DAY122 at 2:1 Ratio	2:1	288	NA	NA	NA	NA	1.217	6.52
24	1/2FPR-DAY9-2 at 2:1 Ratio	2:1	288	NA	NA	NA	NA	1.082	6.15
25	FP-ZN-TCP-1 at 1:1 Ratio	1:1	24	NA	NA	NA	NA	0.080	6.10
26	FP-ZN-TCP-2 at 1:1 Ratio	1:1	24	NA	NA	NA	NA	0.089	5.99
27	FP-ZN-TCP-3 at 1:1 Ratio	1:1	24	NA	NA	NA	NA	0.090	6.70
28	FP-ZN-TCP-1 at 1:1 Ratio	1:1	72	NA	NA	NA	NA	0.288	6.65
29	FP-ZN-TCP-2 at 1:1 Ratio	1:1	72	NA	NA	NA	NA	0.291	6.65
30	FP-ZN-TCP-3 at 1:1 Ratio	1:1	72	NA	NA	NA	NA	0.296	6.68
31	FP-ZN-TCP-1 at 1:1 Ratio	1:1	120	NA	NA	NA	NA	0.437	6.17
32	FP-ZN-TCP-2 at 1:1 Ratio	1:1	120	NA	NA	NA	NA	0.401	6.45
33	FP-ZN-TCP-3 at 1:1 Ratio	1:1	120	NA	NA	NA	NA	0.440	6.52
34	FP-ZN-TCP-1 at 1:1 Ratio	1:1	168	NA	NA	NA	NA	0.509	6.65
35	FP-ZN-TCP-2 at 1:1 Ratio	1:1	168	NA	NA	NA	NA	0.529	6.30
36	FP-ZN-TCP-3 at 1:1 Ratio	1:1	168	NA	NA	NA	NA	0.500	6.50

Table 8.5.1.1.1. Task 7 Summary data for chemical and toxicity analyses (cont.).

TASK 7: COMPARISON OF LABORATORY TEST PROTOCOLS WITH EPA PROTOCOLS AND DETERMINATION OF TEST STATICAL VARIABILITY.									
Sample ID	Test Conditions	Time (hr)	Tox Lab ID	Toxicity Results			Chemistry Results		
				Algal Toxicity			TCP (mg/L)	Zn (mg/L)	Final pH
				Concentration as %					
				Elutriate					
%EC ₅₀ or %LC ₅₀	Lower 95% C.L.	Upper 95% C.L.							
Long-Term and Short-Term Batch Leaching									
1	TCP-ZN-1 3 HR	3	4241401	5.5	4.2	6.4	0.084	0.741	5.40
2	TCP-ZN-2 3 HR	3	4241402	4.8	3.6	5.4	0.081	0.700	5.40
3	TCP-ZN-3 3 HR	3	4241403	5.2	4.2	6.0	0.088	0.708	5.50
4	TCP-ZN-1 8 HR	8	4241404	3.2	2.4	4.1	0.305	1.427	6.00
5	TCP-ZN-2 8 HRS	8	4241405	3.4	2.6	4.2	0.312	1.249	6.04
6	TCP-ZN-3 8 HRS	8	4241406	3.0	2.0	4.1	0.348	1.305	6.07
7	TCP-ZN-1 29 HRS	29	4241407	2.1	1.5	2.9	1.000	1.598	6.03
8	TCP-ZN-2 29 HRS	29	4241408	2.5	1.9	3.1	1.040	1.513	6.06
9	TCP-ZN-3 29 HRS	29	4241409	2.7	2.1	3.5	1.090	1.468	6.07
10	TCP-ZN-1 72 HRS	72	4242401	2.4	1.9	3.1	1.370	1.776	6.1
11	TCP-ZN-2 72 HRS	72	4242402	2.6	2.0	3.2	1.380	1.809	6.08
12	TCP-ZN-3 72 HRS	72	4242403	2.0	1.4	2.6	1.320	1.698	6.1
13	TCP-ZN-1 5 DAYS	120	4242404	2.3	1.7	2.9	1.560	1.905	6.2
14	TCP-ZN-2 5 DAYS	120	4242405	2.2	1.6	2.8	1.480	1.854	6.17
15	TCP-ZN-3 5 DAYS	120	4242406	1.9	1.4	2.4	1.610	1.806	6.21
16	TCP-ZN-1 7 DAYS	168	4243401	2.3	1.6	2.8	1.490	1.862	6.24
17	TCP-ZN-2 7 DAYS	168	4243402	1.8	1.2	2.4	1.530	1.873	6.25
18	TCP-ZN-3 7 DAYS	168	4243403	1.9	1.3	2.4	1.490	1.766	6.27
19	TCP-ZN-1 10 DAYS	240	4243404	NA			1.560	1.907	6.39
20	TCP-ZN-2 10 DAYS	240	4243405	NA			1.440	1.85197	6.40
21	TCP-ZN-3 10 DAYS	240	4243406	NA			1.390	1.9808	6.42
Standard Asphalt Leachate Photolysis									
								1.719	
1	PHOTO-Day1-1	24	4245401	4.2	3.6	4.8	1.79	1.740	5.66
2	PHOTO-Day1-2	24	4245402	2.4	1.7	3.1	1.73	1.697	5.67
3	PHOTO-Day1-3	24	4245403	3.6	3.0	4.2	1.79	1.836	5.64
4	PHOTO-Day3-1	72	4246401	2.4	2.7	3.1	1.47	1.772	5.60
5	PHOTO-Day3-2	72	4246402	3.1	2.6	3.6	1.37	1.689	5.59
6	PHOTO-Day3-3	72	4246403	3.5	2.9	4.0	1.36	1.758	5.62
7	PHOTO-Day5-1	120	4246404	3.4	2.9	3.9	1.28	1.876	5.90
8	PHOTO-Day5-2	120	4246405	3.4	2.9	4.0	1.27	1.681	5.87
9	PHOTO-Day5-3	120	4246406	3.2	2.5	3.9	1.25	1.697	5.96
10	PHOTO-Day7-1	168	4246407	4.1	3.5	4.7	1.11	1.775	5.42
11	PHOTO-Day7-2	168	4246408	4.1	3.5	4.7	1.03	1.694	5.48
12	PHOTO-Day7-3	168	4246409	4.2	3.6	4.7	1.02	1.715	5.55
13	PHOTO-DAY10-1	240	4247401	4.2	3.6	4.7	0.95	1.672	6.14
14	PHOTO-DAY10-2	240	4247402	4.3	3.8	4.9	0.91	1.699	5.97
15	PHOTO-DAY10-3	240	4247403	4.5	4.1	5.0	0.90		5.96

Table 8.5.1.1.1. Task 7 Summary data for chemical and toxicity analyses (cont.).

TASK 7: COMPARISON OF LABORATORY TEST PROTOCOLS WITH EPA PROTOCOLS AND DETERMINATION OF TEST STATICAL VARIABILITY.									
Sample ID	Test Conditions	Time (hr)	Tox Lab ID	Toxicity Results			Chemistry Results		
				Algal Toxicity			TCP (mg/L)	Zn (mg/L)	Final pH
				Concentration as %					
				Elutriate					
%EC ₅₀ or %LC ₅₀	Lower 95% C.L.	Upper 95% C.L.							
Standard Asphalt Leachate Volatilization									
1	LCH-VOL-1/1	5	N/A	NA	NA	NA	1.68	1.765	NA
2	LCH-VOL-1/2	5	N/A	NA	NA	NA	1.71	1.719	NA
3	LCH-VOL-1/3	5	N/A	NA	NA	NA	1.73	1.740	NA
4	LCH-VOL-12/1	12	N/A	NA	NA	NA	1.65	1.717	NA
5	LCH-VOL-12/2	12	N/A	NA	NA	NA	1.63	1.796	NA
6	LCH-VOL-12/3	12	N/A	NA	NA	NA	1.60	1.772	NA
7	LCH-VOL-Day1/1	24	4246410	2.5	2.1	2.9	1.57	1.689	5.73
8	LCH-VOL-Day1/2	24	4246411	4.3	3.8	4.8	1.54	1.758	5.78
9	LCH-VOL-Day1/3	24	4246412	2.5	2.0	2.9	1.59	1.768	5.8
10	LCH-VOL-Day3/1	72	NA	NA	NA	NA	1.47	1.681	NA
11	LCH-VOL-Day3/2	72	NA	NA	NA	NA	1.45	1.697	NA
12	LCH-VOL-Day3/3	72	NA	NA	NA	NA	1.44	1.775	NA
13	LCH-VOL-Day5/1	120	4247404	4.1	3.5	4.6	1.39	1.694	6.06
14	LCH-VOL-Day5/2	120	4247405	3.0	2.6	3.4	1.32	1.715	6.06
15	LCH-VOL-Day5/3	120	4247406	3.1	2.6	3.6	1.33	1.788	6.04
16	LCH-VOL-Day7/1	168	NA	NA	NA	NA	1.28	1.705	NA
17	LCH-VOL-Day7/2	168	NA	NA	NA	NA	1.22	1.659	NA
18	LCH-VOL-Day7/3	168	NA	NA	NA	NA	1.27	1.731	NA
19	LCH-VOL-Day10/1	240	4247407	2.7	2.2	3.2	1.20	1.725	5.84
20	LCH-VOL-Day10/2	240	4247408	3.9	3.5	4.4	1.19	1.791	5.92
21	LCH-VOL-Day10/3	240	4247409	4.0	3.4	4.6	1.23	1.746	5.98
Standard Asphalt Leachate Woodburn Soil Sorption									
Solid/Solution (g/L)									
1	Woodburn-1	5	4249404	12	11	12	1.393	0.230	6.29
2	Woodburn-2	5	4249405	15	NCL	NCL	1.305	0.245	6.30
3	Woodburn-3	5	4249406	14	13	14	1.288	0.238	6.32
4	Woodburn-1	10	4249407	54	48	60	1.200	0.175	6.35
5	Woodburn-2	10	4249408	51	46	54	1.193	0.157	6.39
6	Woodburn-3	10	4249409	56	52	60	1.171	0.166	6.36
7	Woodburn-1	20	4249410	NTE			1.066	0.136	6.38
8	Woodburn-2	20	4249411	NTE			1.196	0.139	6.36
9	Woodburn-3	20	4249412	NTE			1.118	0.125	6.37
10	Woodburn-1	50	4249413	NTE			0.904	0.125	6.45
11	Woodburn-2	50	4249414	NTE			0.824	0.124	6.46
12	Woodburn-3	50	4249415	NTE			0.934	0.130	6.49
13	Woodburn-1	100	4249416	NTE			0.559	0.115	6.54
14	Woodburn-2	100	4249417	NTE			0.504	0.111	6.56
15	Woodburn-3	100	4249418	NTE			0.534	0.113	6.57

Table 8.5.1.1.1. Task 7 Summary data for chemical and toxicity analyses (concluded).

TASK 7: COMPARISON OF LABORATORY TEST PROTOCOLS WITH EPA PROTOCOLS AND DETERMINATION OF TEST STATICAL VARIABILITY.									
Sample ID	Test Conditions	Time (hr)	Tox Lab ID	Toxicity Results			Chemistry Results		
				Algal Toxicity			TCP (mg/L)	Zn (mg/L)	Final pH
				Concentration as % Elutriate					
				%EC ₅₀ or %LC ₅₀	Lower 95% C.L.	Upper 95% C.L.			
Standard Asphalt Leachate Volatilization									
Standard Asphalt Leachate Sagehill Soil Sorption									
1	Sagehill-1	100	4249422	NTE			1.843	0.068	6.88
2	Sagehill-2	100	4249423	NTE			1.793	0.066	6.90
3	Sagehill-3	100	4249424	NTE			1.708	0.071	6.91
4	Sagehill-1	200	4249425	NTE			1.771	0.062	7.04
5	Sagehill-2	200	4249426	NTE			1.691	0.066	7.05
6	Sagehill-3	200	4249427	NTE			1.629	0.062	7.08
7	Sagehill-1	300	4249428	NTE			1.701	0.061	7.19
8	Sagehill-2	300	4249429	NTE			1.681	0.059	7.26
9	Sagehill-3	300	4249430	NTE			1.591	0.061	7.20
10	Sagehill-1	400	4249431	NTE			1.634	0.056	7.25
11	Sagehill-2	400	4249432	NTE			1.610	0.055	7.29
12	Sagehill-3	400	4249433	NTE			1.500	0.052	7.30
13	Sagehill-1	600	4249434	NTE			1.509	0.031	7.39
14	Sagehill-2	600	4249435	NTE			1.411	0.034	7.36
15	Sagehill-3	600	4249436	NTE			1.487	0.033	7.40
Standard Asphalt Leachate Biodegradation									
Time (hrs)									
1	TCP Day1-1	24	4248401	2.0	1.4	2.6	1.83	0.871	6.83
2	TCP Day1-2	24	4248402	2.3	1.6	2.8	1.78	0.899	6.80
3	TCP Day1-3	24	4248403	2.6	2.0	3.2	1.82	0.909	6.82
4	TCP Day3-1	72	NA	NA	NA	NA	1.57	0.896	NA
5	TCP Day3-2	72	NA	NA	NA	NA	1.53	0.914	NA
6	TCP Day3-3	72	NA	NA	NA	NA	1.49	0.897	NA
7	TCP Day4-1	96	NA	NA	NA	NA	1.39	0.968	NA
8	TCP Day4-2	96	NA	NA	NA	NA	1.33	0.900	NA
9	TCP Day4-3	96	NA	NA	NA	NA	1.31	0.924	NA
10	TCP Day5-1	120	4248407	3.0	2.0	4.1	1.30	0.921	6.90
11	TCP Day5-2	120	4248408	1.9	1.4	2.4	1.22	0.858	6.91
12	TCP Day5-3	120	4248409	2.2	1.6	2.8	1.27	0.935	6.92
13	TCP Day7-1	168	NA	NA	NA	NA	1.13	0.891	6.89
14	TCP Day7-2	168	NA	NA	NA	NA	1.19	0.934	6.88
15	TCP Day7-3	168	NA	NA	NA	NA	1.21	0.887	6.89
16	TCP Day10-1	240	4249419	2.1	1.5	2.9	1.23	0.948	6.91
17	TCP Day10-2	240	4249420	3.4	2.6	4.2	1.23	0.875	6.92
18	TCP Day10-3	240	4249421	1.8	1.2	2.4	1.13	0.997	6.91

CHAPTER 9
TASK 8: LEACHING METHODS COMPARISON STUDY

9.1 INTRODUCTION

Asphalt products often are among the typical leachate or runoff products that should be of concern at a construction site. Crumb rubber asphalt cement (CR-AC), Portland concrete cement (PCC) and municipal incinerator bottom ash (MSWIBA) are among the materials used for highway construction and repair (C&R). These materials were among those studied under this National Cooperative Highway Research Program (NCHRP) project. The leachate from in-place construction and repair materials will migrate into the unsaturated and saturated soil below the highway, thereby posing a potential threat to groundwater and surface water.

Leaching is the process by which contaminants are transferred from a stabilized solid matrix to a liquid medium, such as water (LaGrega et al., 1994). In recent years, it has been shown conclusively that the total concentration of contaminants in a waste material is not correlated with release to the environment. The chemical form of contaminants in the matrix and the distribution over different solid phases in the material largely dictates the availability for leaching and the potential for release through external influences. Under environmental conditions, the availability for leaching is more relevant for environmental assessment purposes than the total concentration (van der Sloot, 1991).

Many leaching tests have been developed with their own purposes in assessing environmental impacts. Comparison is made between the distilled water leaching method of this project and EPA's standard leaching methods to compare leachate strengths by each method. In this study, two US EPA leaching tests, the Toxicity Characteristic Leaching Procedure (TCLP) and the Synthetic Precipitation Leaching Procedure (SPLP), and the NCHRP distilled water leaching method of this project were used to evaluate the leachability of five different materials.

The objectives of this study were to: 1) determine and compare the leachability of specific metals from highway construction materials using TCLP, SPLP and NCHRP methods; 2) evaluate the mobility of specific metals as a function of pH; 3) compare the regular NCHRP (24-hour leaching) and modified NCHRP (18-hour leaching) methods.

9.2 LITERATURE REVIEW

9.2.1 Leaching Processes

Leaching is an environmentally important process of dissolution of minor components from a solid matrix (Bodek et al., 1988). How is material leached from a stabilized mass? As the leachate passes through and around the stabilized mass, the sample contaminants are transferred to the leachant (leaching or extraction fluid). This may occur as contaminants are dissolved into the leachant, washed from the surfaces of the stabilized material, or as contaminants diffuse from within the stabilized mass to the leachant. Numerous examples of leaching processes occur in reactions of water with soils, man-made solid wastes, different types of ash from power plants burning fossil fuels, and in reactions of waters with nuclear fuel wastes. For a trace component X residing in a solid matrix M, one process of dissolution may involve transfer of X from a virtually insoluble matrix (Bodek et al., 1988). In this case, a solid MX loses component X, becoming solid M in the process:



Most inorganic systems exhibit surface charge along fracture and cleavage surfaces due to the rupture of bonds. When such systems are brought into contact with water, these compounds absorb water molecules, which can then dissociate and form ions. Dissociation occurs until the equilibrium is established. A possible mechanism for the dissolution of a solid consists of: 1) an initial diffusion of the ion or molecule from a kink site; 2) the ion or molecule may diffuse to a still less stable site or to the bulk of the solution; or 3) by bulk diffusion. Experimental studies show that the steps 1) and 2) are the rate-determining steps rather than step 3) (Lowenbach, 1978).

Transfer of a component of a solid phase to solution takes place if the chemical potential of this component in the solid is greater than its chemical potential in solution. The chemical potential of a component is the driving force responsible for its transfer from a phase where the chemical potential is higher to a phase where the chemical potential is lower. Equilibrium corresponds to an equality of the chemical potentials of the component in the two phases (Bodek et al., 1988). As the system approaches equilibrium the transfer of mass from the solid phase to the solution phase slows down. The final equilibrated mass distribution between the two phases describes the equilibrium condition (van der Sloot et al., 1997).

The rate of leaching in a closed system is a measure of the mass of a solid transferred to a volume of solution in a unit of time. The rate of increase in solute concentration during leaching indicates in a general way that the rate of dissolution may depend on the solute concentration in solution and it may vary with time t ; it also depends on such environmental parameters as the temperature, pressure, and ionic strength of the solution (Bodek et al., 1988).

$$dC/dt = f(C, t, \text{environmental parameters}) \quad (9.2.1.2)$$

According to Walton (1967), dissolution is nearly always controlled by the rate of diffusion of the species away from the solids. Accordingly, a first-order rate law is followed.

$$dC/dt = k(C^*-C) \quad (9.2.1.3)$$

where:

C^* = the saturation concentration, and

k = first order rate constant (1/time).

On occasion the rate of dissolution of the substance may be affected by the formation of surface complexes. Thus, the leachability is dependent upon the physical and chemical properties of both the stabilized material and the leachant (LaGrega et al., 1994).

This study focuses specifically on the leaching of highway-related construction and repair materials. At present, substantial quantities of quarried materials such as gravel, sand, clay, and limestone are used in engineering road works. However, due to the limited natural resources of the mentioned materials, studies on the possible replacement of the natural resources with waste products are being conducted (van Houdt et al., 1991).

Rankers and Hohberg (1991) carried out leaching tests using fly ash and mortar. Fly ash has long been used as a concrete additive or cement component. Two fly ashes were selected for use in the tests: a bituminous fly ash approved as a concrete additive (SFA) and a fly ash from municipal waste incineration (MVA). Mortar mixtures were prepared according to German Industry Standard (DIN, *Deutsche Industrie Normen*). Mixture A is a reference mixture containing no fly ash. Mixture B contains SFA and Mixture C contains MVA, with 20% replacement of cement by fly ash. The test procedure is simple: 100 g of specimen material are placed in a 2 L polyethylene bottle and 1 L of demineralized water is added. The bottle is agitated for 24 hrs and the specimen is filtered through a 0.45 μm membrane filter. The liquid to solid ratio is 10. Table 9.2.1.1 shows the results of the tests.

Table 9.2.1.1. Results of concrete mortar leaching test (Rankers and Hohberg, 1991).

Sample	pH	Cr (mg/L)	Cu (mg/L)	Zn (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)
Cement	12.8	<0.05	<0.05	<0.02	78	751	879
SFA	10.4	0.2	<0.05	0.02	38	56	242
MVA	10.8	0.1	<0.05	0.10	2539	4536	1162
Mix. A	12.7	<0.05	<0.05	<0.02	22	130	714
Mix. B	12.1	<0.05	<0.05	<0.02	25	153	421
Mix. C	12.3	<0.05	<0.05	<0.02	58	146	363

Appraisal of the environmental impacts of materials that contains fly ash on the basis of a single leaching test is not feasible. However, all contaminant concentrations in the leachates are below the permissible limit prescribed by the German Drinking Water Order and below the regulatory level in the TCLP extract. Only the concentration of chromium in the leachate from the SFA exceeded the MCL (maximum contaminant level) standard established by the US EPA (EPA On-line 810-F-94-001, 1999a).

9.2.2 Factors Affecting Metal Leaching

Factors affecting metal leaching can be divided into physical, chemical and biological factors. The latter can generally be translated into chemical factors such as pH effects, the generation of dissolved matter or the development of reducing conditions (van der Sloot et al., 1997).

Typical physical factors that influence leachate are particle size or surface area exposed to leaching, homogeneity or heterogeneity of the solid matrix in terms of mineral phases, leaching time, flow rate of the leachant, and temperature.

Typical chemical factors that influence leachate are pH of the solution, complexation with inorganic or organic compounds, potential leachability of constituents, redox (oxidation-reduction) conditions of the material or that imposed by the surroundings.

9.2.2.1 pH

Many metals exhibit a marked increase in solubility at both low and high pH values, for example, lead and zinc. Other constituents may exhibit maximum solubility at neutral pH values, for example, oxyanions such as vanadate and molybdate, or show no dependence on pH, for example, sodium and chloride (van der Sloot et al., 1997). The initial pH of the leachant and the equilibrium pH may differ widely, particularly if the liquid-to-solid ratio (L/S) is low and the solid phase dominates the system. At high L/S ratios the solution may become more important. In systems open to the atmosphere the pH can be strongly affected by uptake of CO₂ from the air.

The pH can also be influenced by biological factors. This pH effect can be caused indirectly by formation of carbon dioxide through biological degradation of organic matter. In general, pH may affect dissolution in two principal ways: alteration of simple solution equilibrium and direct participation in redox reactions. An example of dissolution by the first mechanism is the following (Lowenbach, 1978):



However, in the presence of acid the following action takes place:



Thus, a sparingly soluble salt in a neutral solution may be completely dissolved in a sufficiently acidic one. The pH of natural leachate is principally controlled by low molecular weight organic acids (principally acetic, propionic, butyric, and valeric acid) and carbon dioxide, which result from the anaerobic degradation of organic material in the landfill.

Bulchholz and Landsberger (1995) examined the leaching of metals from a municipal solid waste incinerator ash. They determined that the pH of the leaching fluid is the single greatest factor governing the concentration of metals in solution. They considered the US EPA Toxicity Characteristic Leaching Procedure (TCLP) to be extremely conservative because of its low pH. The pH helps to solubilize inorganic materials that, along with the high volatile acid concentrations, produce a high ionic strength (Ham et al., 1979a,b). Several of the factors that

affect the leaching are linked, as complexation with either inorganic or organic complexing agents is often strongly pH dependent (WASCON, 1991; Gomez and Lejeune, 1987; van der Sloot, 1996; IAWG, 1997). Change in redox conditions will in several cases result in a change in pH (van der Sloot et al., 1994). And re-precipitation and sorption are to a large extent a function of pH. This leads to the conclusion that release as a function of pH is a very common leaching characteristic with which many aspects of leaching can be correlated (van der Sloot et al., 1997).

9.2.2.2 Chemical complexation

Coordination compounds, or *complexes*, consist of one or more central atoms or central ions, usually metals, with a number of ions or molecules, called *ligands*, surrounding them and attached to them (Snoeyink and Jenkins, 1980). In the presence of specific complexing agents, constituents that would otherwise not be soluble under the conditions in the leachant can be mobilized and reach concentrations far exceeding the equilibrium concentration of mineral phases present in the system. A common example of such inorganic complexation is the mobilization of cadmium by the formation of mobile anionic CdCl_4^{2-} complexes (van der Sloot et al., 1997). According to Snoeyink and Jenkins (1980), when any of the constituent ions of a solid participate in complex formation following dissolution, there will be an increase in the solubility of the solid. For cadmium hydroxide the formation of hydroxocadmium (II) complexes increases the solubility by approximately 14 percent. As the pH increased, the various complex forms become more dominant; at lower pH values they are not present in significant concentrations. Many different ligands, both organic and inorganic, can complex metals and leach them from industrial wastes. Organic compounds containing nitrogen, oxygen, or sulfur in the proper configuration can be strong complexers (Ham et al., 1979). In systems containing degradable organic matter the complexation of metals with dissolved organic carbon (DOC) is also well known in several matrices (Belevi, 1993; McCarty and Zachara, 1989).

An important characteristic of organic compounds that function as ligands is their ability to form water-soluble and water-insoluble complexes with metal ions. Of special concern is the formation of water-soluble metal-organic complexes with toxic metals, which may increase the concentrations of these constituents in leachate to levels far in excess of their normal solubilities (Lowenbach, 1978).

For the complex-formation reactions between metal ions (M) and organic ligands (L):



The equilibrium constants (or stability constants) are:

$$K = [\text{ML}]/[\text{M}][\text{L}] \quad (9.2.2.2.2)$$

In general, a metal ion will coordinate with more than one ligand and form complexes in a stepwise manner, e.g., Cu^{2+} , $\text{Cu}(\text{NH}_3)^{2+}$, $\text{Cu}(\text{NH}_3)_2^{2+}$, $\text{Cu}(\text{NH}_3)_3^{2+}$, $\text{Cu}(\text{NH}_3)_4^{2+}$, for which equilibrium constants are defined for each step as above. Furthermore, the concentration of species complexed in solution will be pH dependent since the ligands are generally acids or bases in their own right and thus dissociate according to the equilibrium:



Natural leachate systems, even though well buffered, are considerably more complex since there are numerous ligands of differing complexing ability competing for coordination of a large variety of metals. Generally, complexes with monodentate ligands are usually less stable than those with multidentate ligands, and metal ions can be buffered by adding appropriate ligands to a metal ion solution (Lowenbach, 1978).

9.2.2.3 Leaching media composition

The leaching media composition prior to waste contact is one of the key variables in a leaching test. For a mono-landfill, distilled, deionized water or a synthetic rainwater can be used as a representative extractant or solvent. A waste that released large amounts of an undesirable parameter under acidic leaching conditions should not be landfilled with acid or acid producing wastes. A waste containing small amounts of a leachable basic salt will raise the pH of a distilled water leachant, and only materials that are soluble in basic solutions will be found in the leachate. Conversely, use of a synthetic municipal leachant, which is heavily buffered, or an acid leaching solution, will probably neutralize the basic salt while maintaining an acidic pH. In the first case (distilled water), the waste controls the pH of the solution, while in the second case (buffered leachate), the leaching media is the controlling factor (Ham et al., 1979).

Demineralized water is the most common leaching fluid (leachant) used. In soil studies mild salt solutions are used to assess mobilization of labile bound species and more aggressive leachants, such as EDTA and acetic acid, are applied to extract trace metals in soil (van der Sloot et al., 1997).

9.2.2.4 Redox potential

The redox potential in a system is important, as the absence of oxygen leads to formation of different chemical phases with significantly different solubilities compared to oxidized conditions. The formation of very insoluble metal sulfides is a clear example of such phases (van der Sloot et al., 1997). In leaching and extraction tests, the role of redox changes is often neglected (van der Sloot et al., 1994). Although much more difficult to conceptually model, the redox environment of the system is also important (Lowenbach, 1978).

9.2.2.5 Major elements chemistry

The role of major elements in leaching from the wide range of materials is insufficiently addressed when the leaching behavior of materials is assessed. This is largely caused by the regulatory requirements, which only specify the analysis of potentially hazardous elements. The major element chemistry largely dictates the leachate composition and controlling conditions, such as pH and redox, and controls the trace and minor element leachability. For example aluminum is the third most abundant element found on the earth's crust, 8.2% (weight basis). High aluminum levels have been found in some regions of the brains of patients who died of Alzheimer's disease (Csuros, 1994).

Aluminum is less toxic to humans at low concentrations, and the quantities of dissolved aluminum in water are normally very low. Sodium aluminate (NaAlO_2) or aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$, alum) are soluble, and these aluminum compounds are hydrolyzed in water and converted to aluminum hydroxide ($\text{Al}(\text{OH})_3$), a gelatinous precipitate with a high surface area that helps to remove the color and colloids when the suspension is filtered (O'Neill, 1993).



The most important forms of dissolved aluminum are Al^{3+} , $\text{Al}(\text{OH})_2^+$, and $\text{Al}(\text{OH})_4^-$. Each species predominates over a certain pH range. The cation Al^{3+} predominates in many solutions where pH values are <4.0 . At pH values around 5-6, $\text{Al}(\text{OH})_2^+$ predominates. Around pH 6.0, aluminum solubility reaches a minimum. Above neutral pH, the predominant dissolved form of aluminum is the anion $\text{Al}(\text{OH})_4^-$ (Bodek et al., 1988). Below a pH value of approximately 6.5, the large, highly charged polymeric species such as $\text{Al}_{13}(\text{OH})_{34}^{5+}$ and $\text{Al}_7(\text{OH})_{17}^{4+}$ may control $\text{Al}(\text{OH})_3(\text{s})$ solubility in recently precipitated aluminum solutions (Snoeyink and Jenkins, 1980).

9.3 TCLP, SPLP, AND NCHRP LEACHING METHODS COMPARISON

9.3.1 TCLP Method

The 1984 amendments to the Resource Conservation and Recovery Act (RCRA) required that the U.S. Environmental Protection Agency (EPA) restrict the land disposal of hazardous wastes. The Toxicity Characteristic Leaching Procedure (TCLP) is a regulatory test developed to address a congressional mandate to identify additional characteristics of wastes that may pose a threat to the environment. The TCLP method has been promulgated for use in determining specific treatment standards associated with the land disposal restrictions of RCRA (Bricka et al., 1992). The TCLP method evaluates metal mobility in a sanitary landfill. This method is the only leaching procedure approved for characterizing hazardous waste under RCRA.

When RCRA was initially promulgated, a procedure called the Extraction Procedure Toxicity (EP) was required for testing the characteristics of a waste to leach toxic constituents at hazardous concentrations. This procedure required that the waste be leached in an acetate solution (essentially at pH 5) for 24 hours. Since the TCLP was first published in 1986, it has undergone several modifications (Bricka et al., 1992).

Leaching tests using lightweight aggregate from wastes were carried out by Krol et al. (1991). The lightweight aggregate, which is used in the construction industry, is produced by the *Neutralysis* process, which mixes municipal solid waste, liquid waste and clay in a rotating kiln system. The following leaching test procedures was undertaken on *Neutralysis* lightweight aggregate:

- The TCLP, EPA Method 1311
- A distilled water extraction test (ASTM D3987)
- A 10% (vol/vol) nitric acid extraction test using the same liquid to solid ratio (20:1) as the TCLP

Table 9.3.1.1 summarizes the metal concentrations found in leachates obtained by TCLP, water, and nitric acid extraction of aggregate samples. Analyses of TCLP leachate have shown that in all cases the TCLP leachate was substantially below the US EPA TCLP criteria. The margin by which the aggregate passes the TCLP test suggests that the leachability of the regulated heavy metals is environmentally acceptable.

Table 9.3.1.1. Leachate concentrations (mg/L) obtained using TCLP, water and nitric acid extraction of aggregate (Krol et al., 1991).

Metal	TCLP	Water	Nitric acid	US EPA TCLP criterion
As	0.015	0.012	<0.1	5.0
Ba	0.21	0.02	not measured	100.0
Cd	<0.01	<0.01	<0.003-0.01	1.0
Cr	<0.01	<0.01	0.03-0.22	5.0
Cu	1.29	<0.01	0.83-5.4	none
Zn	0.32	0.03	0.39-0.58	none

9.3.2 SPLP Method

The question of how to assess the risks associated with groundwater contamination from soils containing toxic substances or wastes disposed of in a monofill environment was also a critical issue for the EPA. A major limitation of using EPA methods 1310 (EP) and 1311 (TCLP) is the fact that the sanitary landfill co-disposal scenario does not apply to contaminated soils or wastes disposed of in a monofill environment. If these methods are used to assess sites for cleanup purposes, the acetic acid leaching fluid could selectively solubilize toxicants and incorrectly classify the soil or waste as hazardous when, in fact, no mobilization (leaching) would be expected to occur in the environment (Chiang et al., 1989). EPA method 1312, the Synthetic Precipitation Leaching Procedure (SPLP), was developed to evaluate the potential for leaching metals into ground and surface waters. This method provides a more realistic assessment of metals mobility under actual field conditions, i.e., what happens when it rains (or snows).

The extraction fluid is intended to simulate precipitation. East of the Mississippi River the fluid is slightly more acidic at pH 4.20, reflecting the air pollution impacts of heavy industrialization and coal utilization. A pH of 5.00 is used west of Mississippi reflecting less industrialization and smaller population densities. The SPLP is a method of choice when evaluating fate and transport of metals in a properly engineered solid-waste land disposal facility from which municipal solid waste is excluded (Alforque, 1996).

9.3.3 NCHRP Method

The NCHRP leaching procedure was developed to assess the environmental impact from highway construction and repair (C&R) materials used in the highway construction system. The NCHRP leaching procedure uses distilled water that emulates uncontaminated precipitation contacting materials surfaces with subsequent release of constituents by dissolution and partitioning processes. The increased utilization of chemically complex C&R materials and various waste materials has resulted in the need to develop this new leaching process (NCHRP method). In

addition, the NCHRP evaluation methodology assesses environmental impact with aquatic toxicity tests in conjunction with direct chemical determinations, necessitating use of a leaching solution that itself is nontoxic to aquatic organisms.

9.4 EXPERIMENTAL METHODS AND MATERIALS

9.4.1 Experimental Approach

The primary objective of this task is to compare the concentrations of leachates using three different leaching procedures. Five different materials were selected. In order to meet the objectives of this task, batch reactor experiments were conducted under uniform conditions for each material and extraction fluid. Preliminary experiments were conducted with each extraction fluid at varying concentrations and final pH. Since the choice of the extraction fluid in the TCLP procedure depends on the physical and chemical properties of the materials, all of the materials to be leached were crushed to the same size (smaller than 1 cm in their narrowest dimension) and pH values were measured. Before adding the material to the TCLP and SPLP extraction fluid, the pH of the extraction fluid was measured. If the extraction fluid did not meet the required range of pH, the extraction fluid was discarded and new extraction fluid was prepared. For the NCHRP procedure, the pH of the distilled water extraction fluid was not measured. Because distilled water is unbuffered, the pH of the extraction fluid is largely determined by materials leached into the solution.

According to the TCLP and SPLP procedure, the filter should be washed with nitric acid before measuring the concentration of the metals. Preliminary tests for the difference between using filters with and without acid washing were made. There was no difference between the concentration of the leachate filtered with acid-washed filters and that of the leachate filtered without acid-washed filters.

All leachates were analyzed within two hours after filtering so the leachates need not be stored with refrigeration. Since the materials yielded no liquid when subjected to pressure filtration, all materials were assumed to be 100% solids by the EPA procedure.

9.4.2 Materials

More than 90% of pavements in our transportation network are constructed from asphalt concrete. The wide application of asphalt has also invited the use of a large number of asphalt additives. One of these additives is crumb rubber. Crumb Rubber Asphalt Concrete (CR-AC) is used in highway construction in Florida, Texas, California, and Arizona, and was evaluated as a “non-fill” material, i.e., as a pavement material, in this study. Two types of CR-AC were used: CR-AC (type I) consisted of hot mixed asphalt that was transported from Mississippi and rubber that was manufactured by the Rouse plant (80 mesh). CR-AC (type II) used the same asphalt, but different rubber, which was manufactured by the BASF plant. The rubber used in type II passes a 40-mesh sieve. These two materials are black, but type II was more sticky and lost part of its original color after leaching.

Portland cement concrete (PCC) is also widely used in transportation networks. PCC is a primary construction material in pavement, bridges, over-passes, and similar vital structures in our highway systems. Plasticizers are sometimes mixed with the PCC to improve the concrete properties. Two types of PCC were used in this study: PCC with (w/) plasticizer and PCC without (w/o) plasticizer. PCC w/ plasticizer was slightly finer than the PCC w/o plasticizer. Approximately 2-3% plasticizing admixtures are added to a batch of PCC. The main ingredients of the plasticizer are the lignosulfates, lignosulfonic acid, sulfonated naphthalene, sulfonated melamine and zinc salt. The mixture proportions of PCC are shown in Table 9.4.2.1.

Table 9.4.2.1. The mixture proportions of PCC.

Material	Quantity (kg/m ³)
Cement (ASTM Type I/II) ¹	275
Coarse Aggregates (washed) ^{2, 3}	1025
Fine Aggregate (washed) ^{2, 3}	865
Water	155
Plasticizer (when added)	1000 mL per 100 kg of cement

¹Cement manufacturer: Tilbury

²Aggregate manufacturer: Morse Brothers (Oregon, Willamette Valley)

³Uncrushed river gravel, maximum size: 25 mm

The MSWIBA aggregate consisted of MSWIBA and aggregate. MSWIBA is a New England municipal solid waste incinerator bottom ash, and the aggregate is manufactured by Morse Brothers (Willamette Valley near Corvallis, Oregon). MSWIBA contains a wide mixture of metallic contaminants and is extensively discussed in Volume II (Eldin et al., 2000).

9.4.3 Apparatus and Equipment

- 1) Orion pH meter (Model 701 A)
- 2) End-over-end sample tumbler (internally padded with foam pads, Rota-Tox, 8- sample tumbler)
- 3) Millipore glass filter system (47mm diameter)
- 4) Balance (Mettler Toledo AG 104)
- 5) 2.2L extraction vessel made of borosilicate glass (Nalgene)
- 6) 2L leachate container made of glass (Pyrex)
- 7) 0.6 – 0.8 µm glass fiber filter (Whatman GF/C)
- 8) Inductively coupled plasma atomic emission spectrometer (ICP – AES, Varian Liberty Model 160)

9.4.4 Analytical Methods

9.4.4.1 pH measurement

The pH was measured electrometrically using a research grade electrode Ag/AgCl and pH meter (Orion Model 701A). The system was calibrated daily using pH 7 buffer solutions.

9.4.4.2 ICP measurements

Metal concentrations in the leachate were determined using the ICP-AES method (inductively coupled plasma-atomic emission spectroscopy, Varian Liberty Model 160, see Volume IV).

9.4.5 Extraction Fluids

In the TCLP method, one of the two extraction fluids is selected to extract the solid waste sample. The type of extraction fluid is determined in an initial test on the waste and the waste's alkalinity. The initial test is carried out as follows:

1. Weigh out a small subsample of the solid phase of the waste, reduce the solid to a particle size of approximately 1 mm in diameter or less.
2. Transfer 5.0 grams of the solid phase of the waste to a 500-mL beaker
3. Add 96.5 mL of reagent water to the beaker, cover with a watch glass, and stir vigorously for 5 minutes. Measure and record the pH. If the pH is <5.0, use extraction fluid 1.
4. If the pH is >5.0, add 3.5 mL 1N HCl, heat to 50°C, and hold at 50°C for 10 minutes. Record the pH. If the pH is <5.0, use extraction fluid 1. If the pH is >5.0, use extraction fluid 2.

Since the initial pH values of the CR-AC, PCC with (w/o) plasticizer, and MSWIBA were above 5.0, and the pH values after adding HCl were below 5.0 (Table 9.4.5.1), extraction fluid 1 was used in the TCLP tests for these materials.

Table 9.4.5.1. The pH for materials before and after addition of HCl

	Initial pH	pH after adding HCl
CR-AC	8.8	1.9
PCC w/ and w/o	11.5	4.2
MSWIBA	9.5	1.5

Extraction fluid 1 is prepared using 5.7 mL glacial acetic acid and 64.3 mL of 1N NaOH to the 1L of distilled water and the pH of this fluid will be 4.93 ± 0.05 . Extraction fluid 2 is an acetic acid solution with a pH of 2.88 ± 0.05 .

In the SPLP method, one of the two extraction fluids is used. Extraction fluid 1 is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids to distilled water until the pH is 4.20 ± 0.05 . This fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes and wastewaters. Extraction fluid 2 is made by adding the same acids until pH is 5.00 ± 0.05 , and this fluid is used to determine the leachability of soil from a site that is west of the Mississippi River. Extraction fluid 1 was used in this study as this is a more rigorous leaching test. In the NCHRP method, distilled deionized water was used as the extraction fluid.

The TCLP and SPLP procedures require that the particle size of the solids be small enough to pass a 9.5-mm standard sieve. All the materials larger than 9.5-mm were crushed with mortar-and-pestle.

ACS reagent grade chemicals were used in all tests. Distilled deionized water (DDW; Barnstead Nano Pure II deionizer) was used in the preparation of all solutions. 2.2-L bottles made of borosilicate glass (Nalgene) were used as extraction vessels. All bottles were washed in an acid bath, acetone, liquid soap, and distilled water prior to use.

9.4.6 TCLP, SPLP and NCHRP Extraction Methods

In the TCLP test method, the material is crushed to a particle size smaller than 9.5 mm in diameter. The crushed material is mixed with extraction fluid 1 or fluid 2 (above), in a liquid to solid weight ratio of 20:1, and the reactor sealed with paraffin paper. For each run, three reactors were used and agitated in a rotary extractor for a period of 18 hours at 30 RPM. After 18 hours of agitation, the reactors were removed from the tumbler and the sample was filtered through a 0.6-0.8 micrometer acid-rinsed glass fiber filter (EPA On-line SW-846 Methods, 1999). The filtrates were collected in glass bottles. The leachates were analyzed for fifteen metals of concern using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

The SPLP method is similar to the TCLP method except that the acetic acid buffer extraction fluid has been replaced by a dilute nitric acid/sulfuric acid mixture, which has a pH value of 5.0 (EPA On-line SW-846 Methods, 1999b).

The NCHRP extraction method was developed during this NCHRP project. In the NCHRP method, distilled water is used as the extraction fluid and crushed material is added into the extraction fluid at a liquid to solid ratio of 4:1. Extraction takes place over a period of 24 hours, with agitation. After 24 hours of agitation, the sample is filtered through a 0.45-micrometer filter paper. Chemical analyses of the filtered extract are then conducted using the ICP-AES to determine the concentration of the inorganic constituents. For this study comparing the leaching methods, the above “regular” NCHRP method was modified. The extraction time was reduced to 18 hours and a liquid to solid ratio of 20:1 instead of 4:1 ratio was used as in the TCLP and SPLP methods. The same filtration procedure as the TCLP or SPLP was also used for the NCHRP method. Comparisons between regular and modified NCHRP method were made to see the differences in the leachate concentrations between these methods, which are discussed in Section 9.5.6. But references to the “NCHRP Method” in the forthcoming discussion refer to the modified NCHRP method, unless otherwise qualified.

9.5 RESULTS AND DISCUSSION

9.5.1 Reproducibility

Triplicates were run through the test series on most materials. The mean value, standard deviation, and relative standard deviation (RSD) for major elements of five materials are presented in Table 9.5.1.1. The deviations include errors due to material subsample difference, test procedures, and analytical procedures. To compare meaningfully the precision

(reproducibility) of the three methods, it is important to control the variance caused by the inherent difference between the three methods (Kimbrough and Wakakuwa, 1992).

The results from each method were checked to see if the triplicate met the control limits for each element of EPA SW 846 test methods. A control limit of $\pm 20\%$ RPD (relative percent difference) or within the documented historical acceptance shall be used for sample values greater than ten times the instrument detection limit (EPA, SW-846 On-line test methods for evaluating solid waste physical/chemical methods, <http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm>, 1999). The elements that have concentrations below the instrument detection limit or no value were not included for reproducibility.

Generally, the reproducibility was good. As shown in Table 9.5.1.1, the relative standard deviations were generally under 20% unless near the detection limit. When the concentration of a metal in the leachate was high, then the reproducibility of that element was better. The RSD for calcium and sodium was near or under 10%, while the RSD for barium and strontium ranges from 5% to over 100%. That means that precision or reproducibility drops at the lower metal concentrations due to the instrumental detection limit.

The TCLP method showed better precision than the other two methods. The SPLP method has the lowest RSD, which reflects the difficulties of adjusting the initial extraction fluid to pH 4.2, because the SPLP extraction fluid was not buffered.

When comparing the RSD in terms of materials, MSWIBA has the highest RSD. The reason why the MSWIBA has the highest RSD is its lower homogeneity when preparing subsamples.

Table 9.5.1.1. Comparison of the average, SD, and RSD values for major elements for TCLP, SPLP, and NCHRP (modified) methods for triplicate samples.

material	element	TCLP			SPLP			NCHRP		
		average	S.D	RSD	average	S.D	RSD	average	S.D	RSD
CR-AC (type I)	Al	1.03	0.06	6.10	0.72	0.03	4.03	0.81	0.30	36.56
	Ba	0.288	0.018	6.084	0.007	0.003	43.301	0.005	0.003	69.282
	Ca	83.71	4.71	5.63	19.80	1.80	9.11	23.32	2.79	11.80
	K	3.50	0.29	8.28	1.53	0.21	13.67	1.57	0.18	11.84
	Mg	3.54	0.40	11.15	0.08	0.01	15.84	0.05	0.02	32.16
	Na	80.63	0.79	0.98	2.50	0.29	11.54	2.84	0.53	11.70
	Sr	0.81	0.11	13.76	0.07	0.01	7.41	0.06	0.01	11.11
CR-AC (type II)	Al	2.24	0.10	4.40	0.70	0.08	10.96	0.66	0.05	8.14
	Ba	0.152	0.004	2.653	0.002	0.002	124.90	0.005	0.003	69.282
	Ca	382.02	24.92	6.52	19.80	1.80	9.11	23.32	2.79	11.98
	K	0.27	0.06	21.65	B.D	-	-	B.D	-	-
	Mg	7.06	0.19	2.69	0.14	0.01	4.94	0.13	0.01	5.69
	Na	76.15	0.54	0.71	0.10	0.01	7.37	0.07	0.01	9.47
	Sr	0.43	0.03	7.48	0.04	0.01	18.43	0.03	0.00	15.95
PCC w/o plasticizer	Al	2.62	0.04	1.60	2.68	0.03	0.99	2.65	0.03	1.04
	Ba	0.268	0.006	2.058	0.088	0.004	4.006	0.076	0.009	11.842
	Ca	774.45	15.12	1.95	354.50	36.27	10.23	335.81	13.88	4.13
	K	7.37	0.39	5.28	5.24	0.05	0.88	4.37	0.26	6.03
	Mg	0.11	0.05	47.49	B.D	-	-	B.D	-	-
	Na	117.26	0.69	0.59	5.93	0.13	2.23	5.80	0.27	4.65
	Sr	0.80	0.03	3.92	0.51	0.02	3.14	0.44	0.03	7.68
	Cr	0.04	0.01	10.42	0.02	0.00	15.00	0.02	0.00	24.17
PCC w/ plasticizer	Al	3.38	0.21	6.09	2.77	0.08	3.05	3.02	0.07	2.37
	Ba	0.276	0.022	7.838	0.125	0.005	4.116	0.203	0.003	1.242
	Ca	558.15	0.03	0.01	343.34	7.21	2.10	668.95	4.80	0.72
	K	6.24	0.06	0.95	4.73	0.13	2.78	4.00	0.05	1.12
	Mg	0.03	0.01	29.34	B.D	-	-	B.D	-	-
	Na	81.92	0.81	0.99	5.57	0.13	2.38	4.95	0.11	2.24
	Sr	0.72	0.03	3.48	0.48	0.01	1.87	0.61	0.00	0.41
MSWIBA	Al	13.56	2.43	17.90	9.98	0.35	3.51	12.96	1.53	11.82
	Ba	0.285	0.046	16.106	0.036	0.002	4.283	0.055	0.027	48.754
	Ca	126.55	19.38	15.31	36.45	3.17	8.71	45.41	21.52	47.39
	K	12.90	1.23	9.52	7.14	0.44	6.13	9.36	3.94	42.11
	Mg	12.96	0.99	7.63	0.60	0.16	26.28	0.92	0.26	28.26
	Na	120.72	0.37	0.30	26.15	1.29	4.92	23.92	2.30	9.61
	Sr	0.58	0.07	11.11	0.19	0.01	4.99	0.17	0.08	48.66

9.5.2 Statistical Comparison of Metals Leachate for CR-AC, PCC, and MSWIBA for TCLP, SPLP, and NCHRP Methods

The statistical methodology for comparing several means is called analysis of variance, or simply ANOVA. ANOVA uses an F-statistic and its p-value (computed probability of Type I error) to evaluate the null hypothesis that all of several population means are equal (Moore and McCabe, 1996). This test compares mean concentrations obtained by the three procedures (TCLP, SPLP, modified NCHRP) and does not account for differences that might be due to experimental error – but the latter are small, as shown earlier in Table 9.5.1.1. The results for this comparison are shown in Table 9.5.2.1. This test is a function of the variance of the data obtained with each method. When the variance is larger in one method (method 1) than in the other method (method 2), then the method having larger variance may show no significant difference, while the method having smaller variance may show significant difference. In other words, a large variance makes it hard to separate methods on the basis of a difference in mean values. These results are based on the 95% confidence limit ($\alpha=0.05$, a fixed Type I error). That is, the computed p-value must be less than 5% for a difference in means to be considered significant.

Generally, higher concentrations of metals were leached by the TCLP method than by the other two methods (SPLP and NCHRP) based on the 95% confidence limit. For CR-AC (type I), the TCLP method shows a significant difference from the SPLP and NCHRP methods for all metals with the exception of aluminum in CR-AC (type I) and PCC w/o plasticizer. A few metals (e.g., K and Sr in PCC) have significantly different concentrations for all three methods, but in most cases, the concentrations obtained by SPLP and NCHRP are not significantly different. And in two cases (Al and K in MSWIBA leachate), there is no significant difference between NCHRP leachate and either TCLP or SPLP even though the latter two procedures generated statistically different concentrations. And there is only one instance in which the NCHRP leachate (Ca for PCC w/plasticizer) is higher than both other methods.

Table 9.5.2.1. ANOVA test results for major elements comparing TCLP, SPLP, and NCHRP leaching methods.

material	element	TCLP	SPLP	NCHRP
CR-AC (type I)	Al	A	A	A
	Ba	A	B	B
	Ca	A	B	B
	K	A	B	B
	Mg	A	B	B
	Na	A	B	B
	Sr	A	B	B
CR-AC (type II)	Al	A	B	B
	Ba	A	B	B
	Ca	A	B	B
	Mg	A	B	B
	Na	A	B	B
	Sr	A	B	B
PCC w/o plasticizer	Al	A	A	A
	Ba	A	B	B
	Ca	A	B	B
	K	A	B	C
	Na	A	B	B
	Sr	A	B	C
	Cr	A	B	B
PCC w/ plasticizer	Al	A	B	B
	Ba	A	C	B
	Ca	B	C	A
	K	A	B	C
	Na	A	B	B
	Sr	A	C	B
MSWIBA	Al	A	B	AB
	Ba	A	B	B
	Ca	A	B	B
	K	A	B	AB
	Mg	A	B	B
	Na	A	B	B
	Sr	A	B	B

Notes:

Means with the same letter are not significantly different.

The order of concentration from largest to smallest is: A>B>C

AB means not significantly different from either A or B even though A and B are significantly different from each other.

Confidence limit: 95%

9.5.3 Graphical Comparison of Metals in Leachates from CR-AC, PCC, and MSWIBA for TCLP, SPLP, and NCHRP Methods

9.5.3.1 Crumb rubber asphalt concrete (CR-AC)

The concentrations of the metals in the CR-AC that were released in the TCLP, SPLP, and NCHRP extractions are summarized in Figures 9.5.3.1.1 to 9.5.3.1.4. As illustrated in these figures, the TCLP leachate contained higher concentrations than the SPLP and NCHRP leachate, and there was no significant difference of concentration between the SPLP and NCHRP leachates. Even though the aluminum concentrations in TCLP leachate in CR-AC (type I) seem higher than those in SPLP and NCHRP, those values do not provide a statistically significant difference. Among the elements whose concentration was above the detection limit, only the aluminum concentrations in CR-AC (type I) were not significantly different among those three methods.

The significant differences seen in the metals concentrations in the CR-AC leachates can be largely attributed to pH influences. The final pH of the TCLP leachate was low (pH 5.0-5.6) while that of the SPLP and NCHRP were high (pH 9.9 - 10.3). The TCLP extraction fluid has higher buffering capacity than the SPLP and NCHRP extraction fluids. For all metals, e.g., Ca and Mg, comparison of the three extraction fluids procedures shows that the TCLP fluid extracts more of the metals than do the SPLP and NCHRP fluids. This can be explained by the pH effect (Table 9.5.3.1.1), that is, a lower pH (pH about 5) provides higher dissolution of metals. The higher concentration of sodium in the TCLP leachate for CR-AC as well as PCC and MSWIBA was due to sodium in the extraction fluid, which was prepared by adding sodium hydroxide and acetic acid into distilled water. For CR-AC the final pH of the leachate varies depending on reactions of the leaching fluid with the material being tested.

Table 9.5.3.1.1. Final pH values for CR-AC materials for the three leaching methods.

Material	TCLP	SPLP	NCHRP
CR-AC	4.97-5.06	10.17-10.28	9.97-10.26

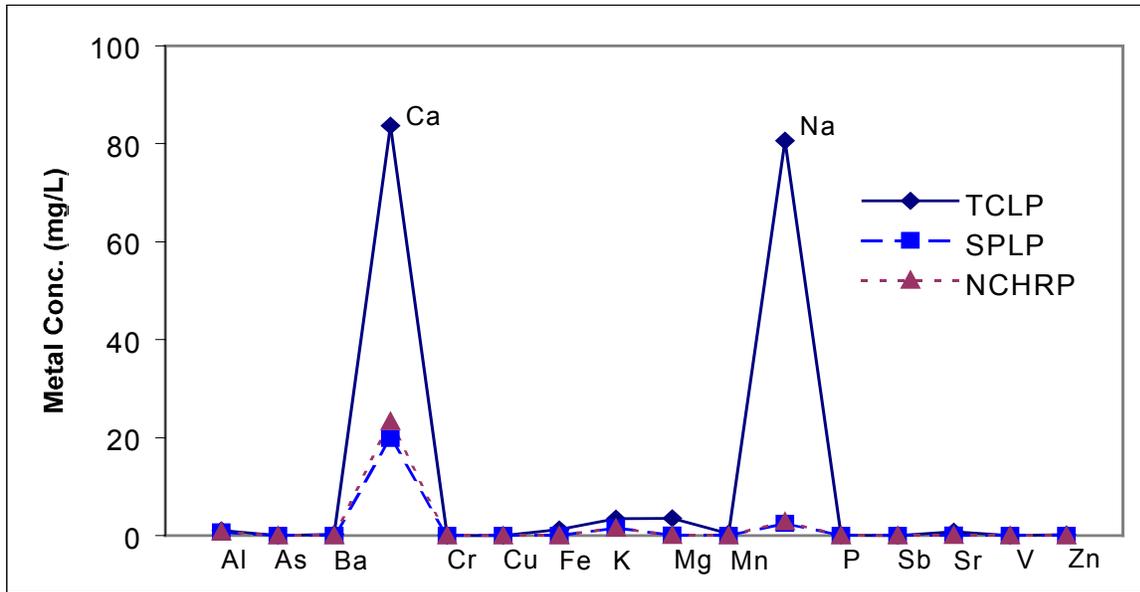


Figure 9.5.3.1.1. Extracted metals from CR-AC (type I) using three extraction fluids, TCLP, SPLP, and NCHRP procedures.

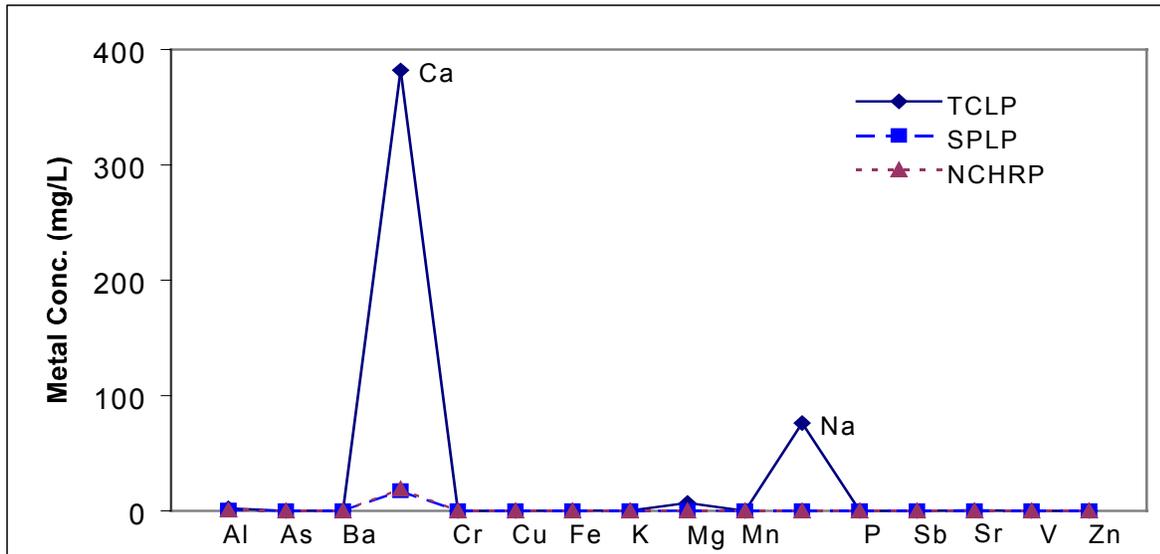


Figure 9.5.3.1.2. Extracted metals from CR-AC (type II) using three extraction fluids, TCLP, SPLP, and NCHRP procedures.

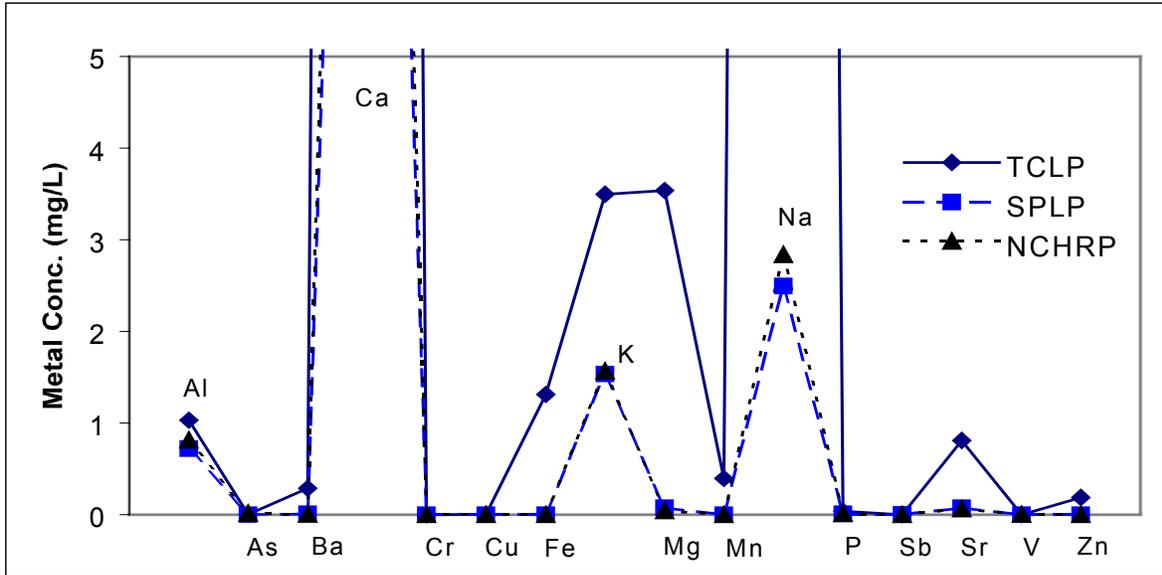


Figure 9.5.3.1.3. Extracted metals from CR-AC (type I) using three extraction fluids, TCLP, SPLP, and NCHRP.

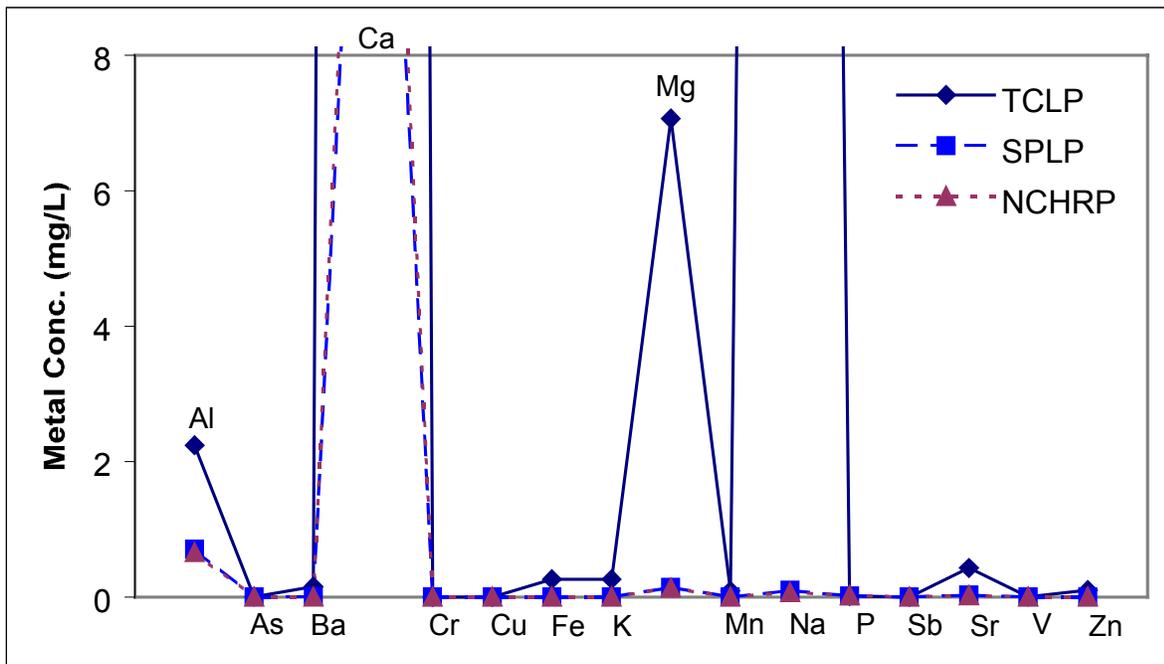


Figure 9.5.3.1.4. Extracted metals from CR-AC (type II) using three extraction fluids, TCLP, SPLP, and NCHRP procedures.

9.5.4 PCC With and Without Plasticizer

The concentration of the metals in the PCC with (or without) plasticizer that were released in the TCLP, SPLP, and NCHRP extractions are summarized in Figures 9.5.4.1 to 9.5.4.4. As illustrated in those figures, TCLP extract contained higher concentrations of most metals except for calcium. Comparing the concentrations of SPLP and NCHRP extracts, the SPLP extract had higher concentrations of potassium and strontium for PCC w/o plasticizer, while the NCHRP extract had higher concentrations of barium, calcium, and strontium. The final pH of the extracts is shown in Table 9.5.4.1. Results of TCLP, SPLP, and NCHRP extraction data for the PCC are given in the summary Table 9.5.3.1.1.

The reason why the TCLP leachate had higher concentrations for some metals could not be explained by pH difference, as leachate pH (Table 9.5.4.1) does not correspond with concentrations of metals for PCC leachates. The presence of acetic acid in the TCLP extract may help metal complexation as seen in the PCC w/ plasticizer leachate.

Table 9.5.4.1. Final pH of leachates from PCC.

	TCLP	SPLP	NCHRP
PCC w/o plasticizer	11.1-11.3	11.4	11.3
PCC w/ plasticizer	11.4	11.3	11.3-11.4

Although differences were small, there was also no clear explanation as to why the SPLP leachate contained higher metals concentrations for PCC w/ plasticizer than did the NCHRP leachate, and why the NCHRP leachate contained higher metals concentrations for PCC w/o plasticizer than did the SPLP leachate. Solution pH value might contribute to the differences among concentrations for some metals between SPLP and NCHRP leachates.

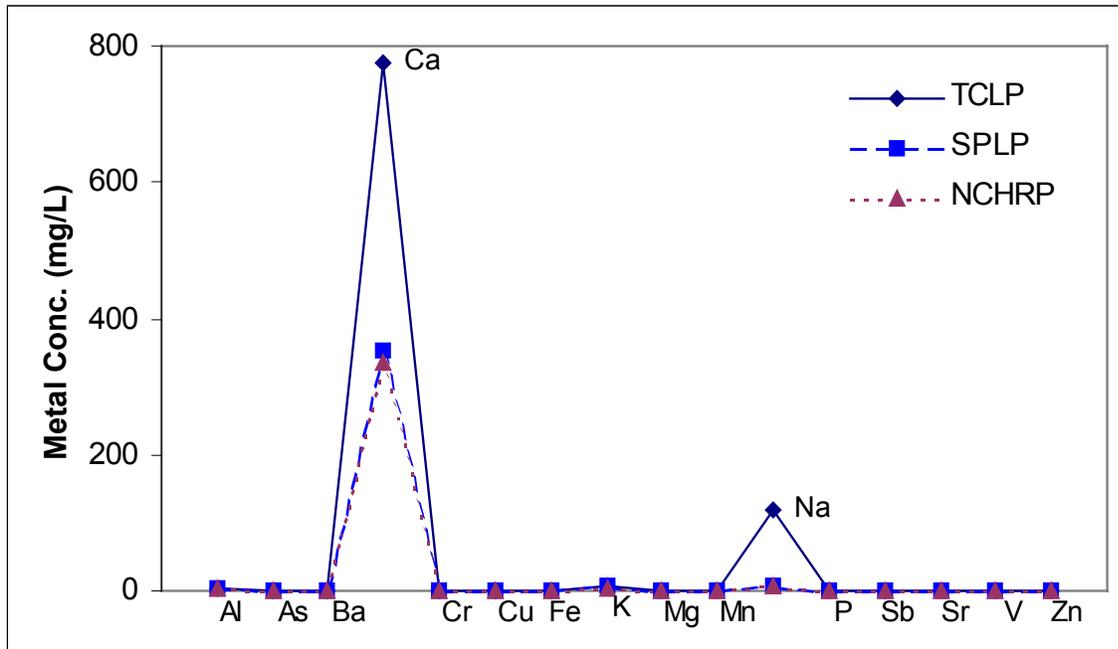


Figure 9.5.4.1. Extracted metals from PCC-without-plasticizer using three extraction fluids, TCLP, SPLP, NCHRP procedures.

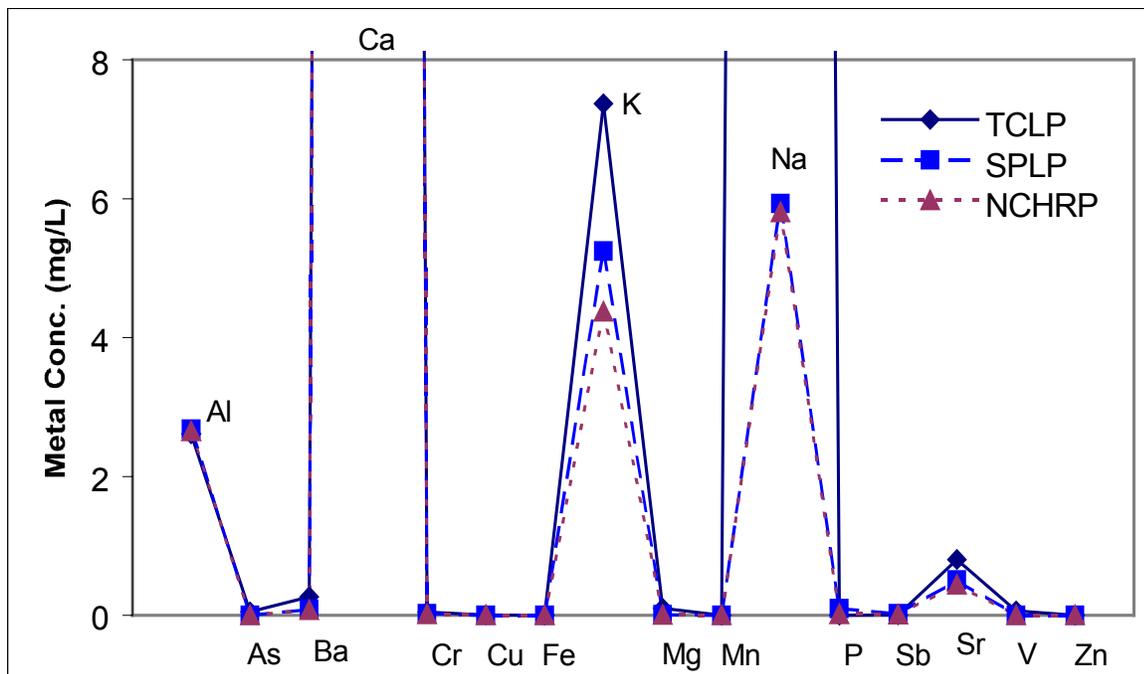


Figure 9.5.4.2. Extracted metals from PCC-without-plasticizer using three extraction fluids, TCLP, SPLP, NCHRP procedures (compressed scale).

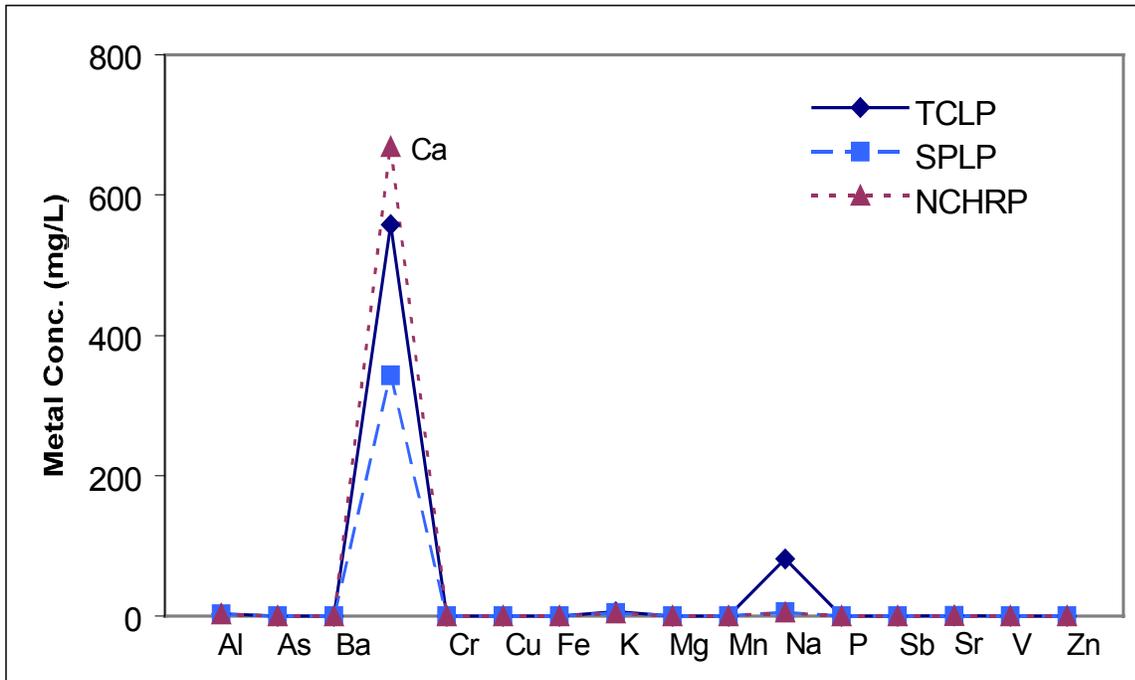


Figure 9.5.4.3. Extracted metals from PCC-with-plasticizer using three extraction fluids, TCLP, SPLP, and NCHRP procedures.

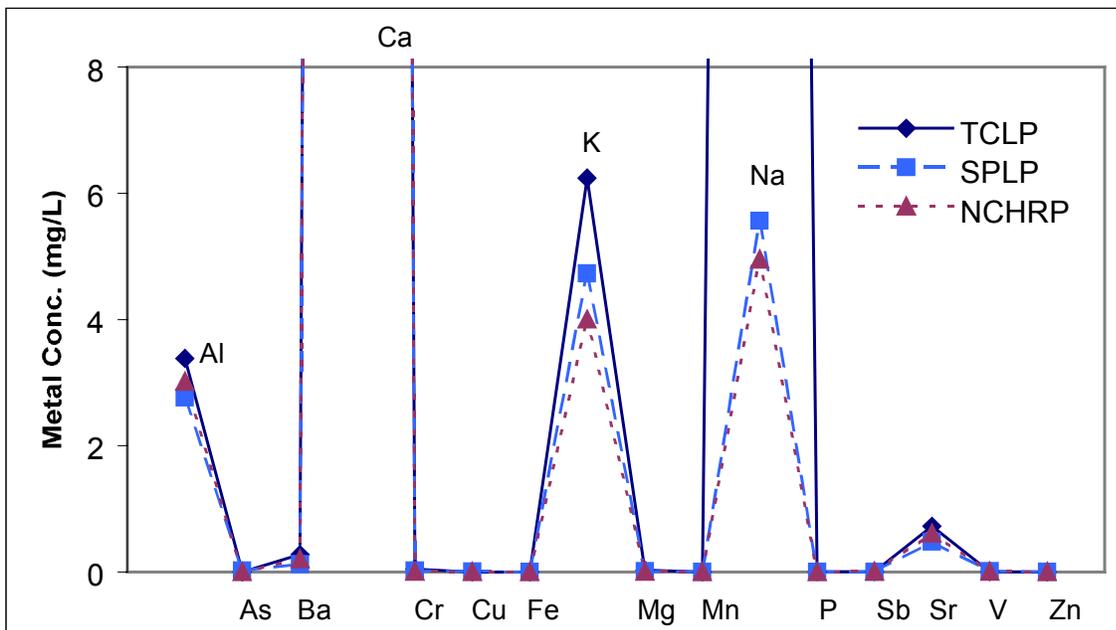


Figure 9.5.4.4. Extracted metals from PCC-with-plasticizer using three extraction fluids, TCLP, SPLP, and NCHRP procedures (compressed scale).

9.5.5 MSWIBA Aggregate

9.5.5.1 Leaching results

The concentrations of the metals in the MSWIBA aggregate mix are summarized in Figures 9.5.5.1.1 and 9.5.5.1.2. The TCLP leachate contained higher concentrations for all metals than did the SPLP and NCHRP leachates. As with CR-AC, pH and metal complexation with acetate contributed to the different concentrations. Similarly as for CR-AC, a lower pH (Table 9.5.5.1.1) for the TCLP leachate provides higher dissolution of metals

Table 9.5.5.1.1. Final pH values for MSWIBA aggregate for the three leaching methods.

Material	TCLP	SPLP	NCHRP
MSWIBA	5.1	9.2-9.5	8.9-9.0

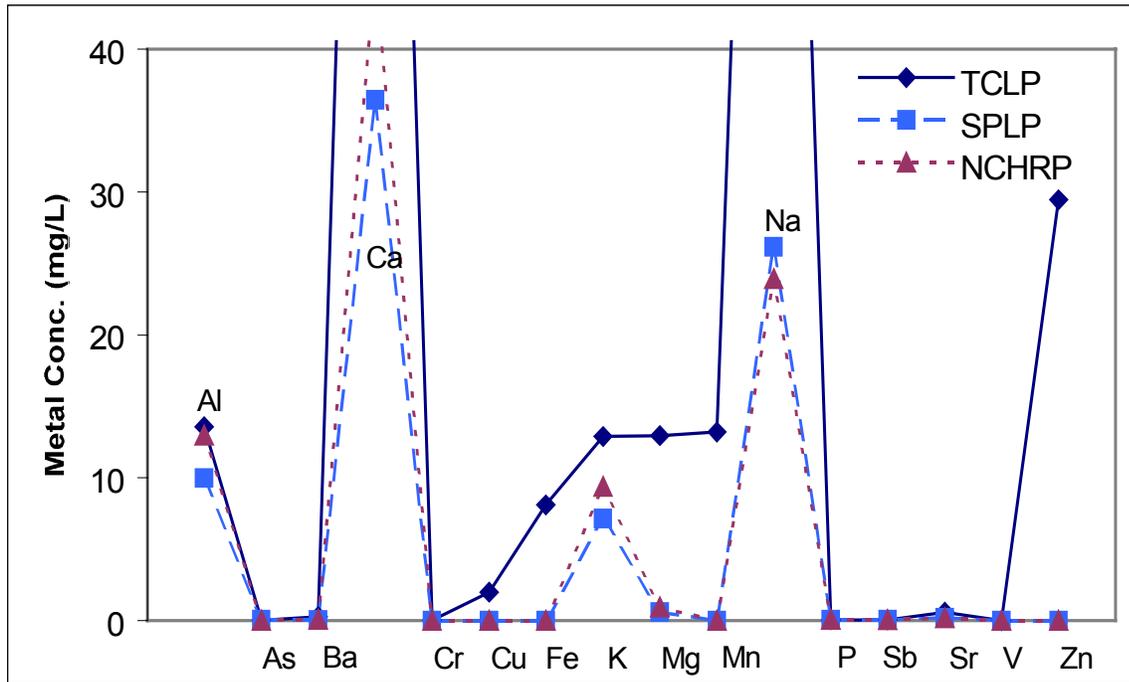


Figure 9.5.5.1.1. Extracted metals from MSWIBA using three extraction fluids, TCLP, SPLP, and NCHRP procedures.

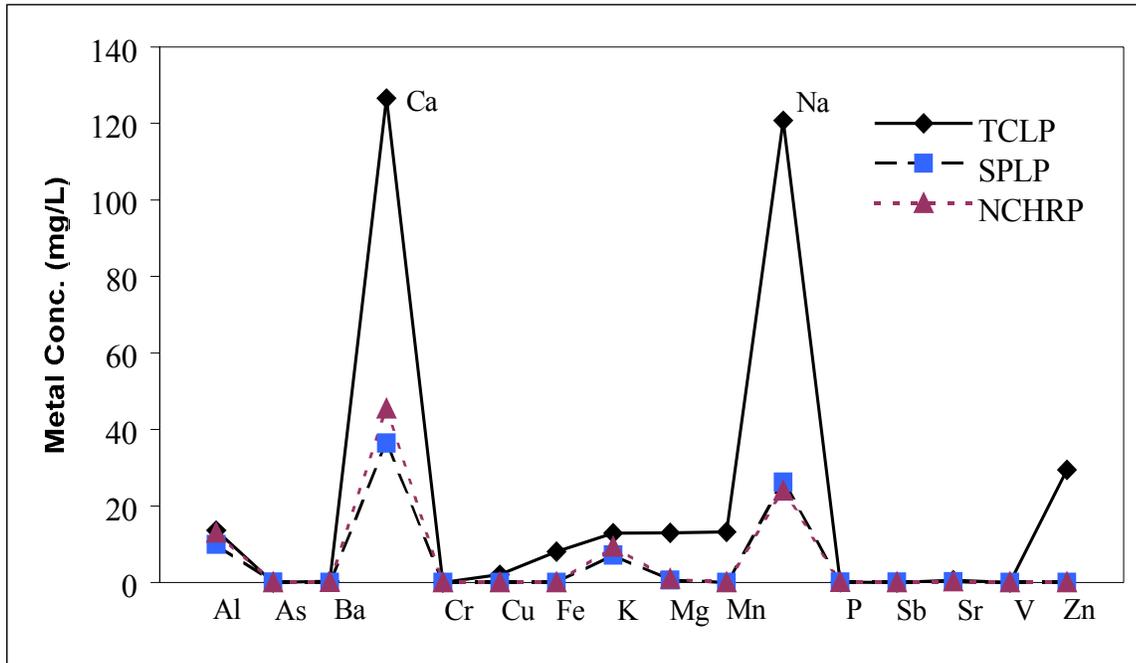


Figure 9.5.5.1.2. Extracted metals from MSWIBA using three extraction fluids, TCLP, SPLP, and NCHRP procedures (expanded scale).

9.5.5.2 Effect of pH on MSWIBA leachate

Buchholz and Landsberger (1995) examined leaching of metals from a municipal solid waste incinerator ash. They determined that the pH of the leaching fluid is the greatest factor governing the concentration of metals in solution. In order to study the effect of pH on leachate metals concentrations, several extraction fluids were prepared by adding nitric acid into distilled water. MSWIBA aggregate was used as the material. Leaching time, solid to liquid ratio, and temperature were the same for the leachates. Only the amount of the added 1 N nitric acid was different for each sample. The initial pH of the extraction fluid and the final pH of the leachates are shown in Table 9.5.5.2.1.

Table 9.5.5.2.1. Initial and final pH of MSWIBA leachate.

	pH before leaching	pH after leaching
Sample #1	1.8	2.0
Sample #2	2.0	3.8
Sample #3	2.5	4.3
Sample #4	2.56	4.5
Sample #5	2.62	5.5
Sample #6	2.71	6.8

The leached metals concentrations for the different final pH values are shown in Figures 9.5.5.2.1 and 9.5.5.2.2. As shown in these figures, the lower the pH of the extraction fluid, the more metals are extracted. This is consistent with the fact found in the literature that inorganic components are generally more readily leached in acidic than in neutral or slightly basic solutions (Ham et al., 1979a,b; Krol, 1981). TCLP leachates for CR-AC and MSWIBA aggregate, which have lower final pH values than the other leachates, therefore extract more metals than do the leachates for the other two methods. One conspicuous exception to the general trend is the high concentration of zinc in the solution of pH 3.8, which must be due to the non-homogeneity of the sample.

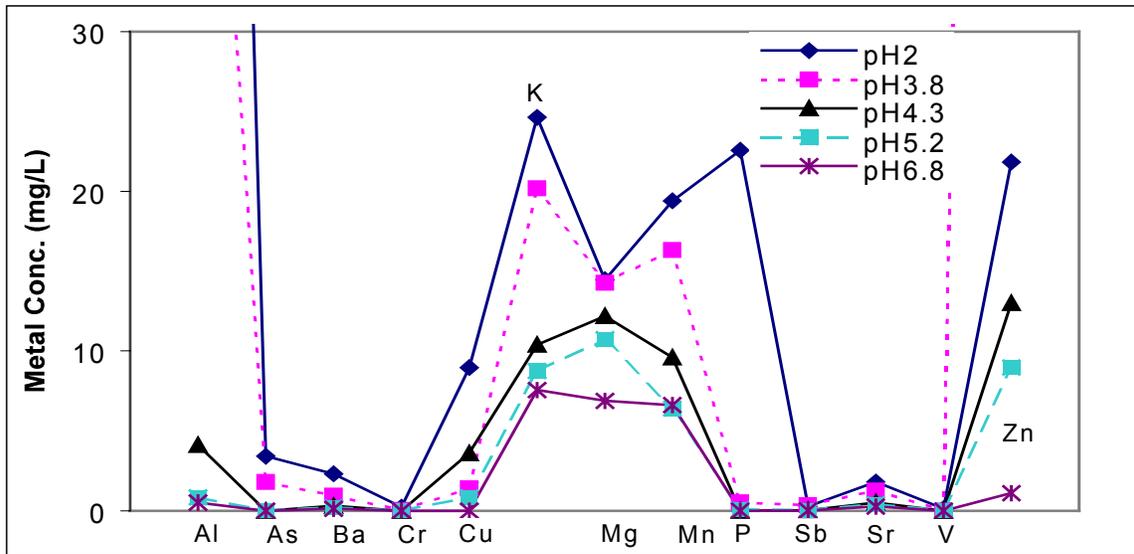


Figure 9.5.5.2.1. Concentration of leachate from MSWIBA as a function of pH.

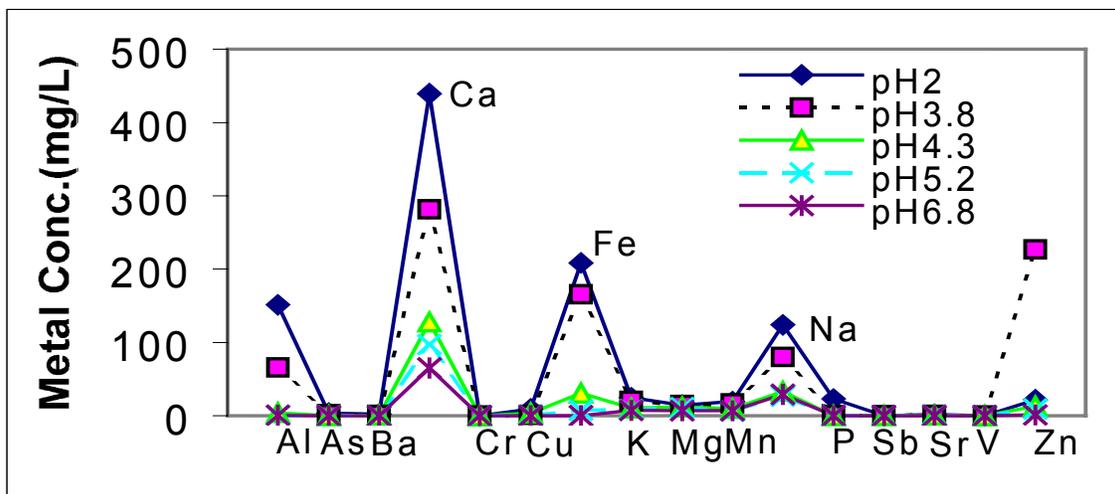


Figure 9.5.5.2.2. Concentration of leachate from MSWIBA as a function of pH (expanded scale).

Even though the pH value of the leachate is the most important factor in leaching metals into the solution, the phenomena of the leaching system are not so simple. Other important factors are the buffering capacity and complexation of the metals. To compare the effects of these factors on the leaching capacity of the solution, two different extraction fluids, which have the same final pH, were used. One extraction fluid (TCLP) was prepared as usual by adding acetic acid and sodium hydroxide into distilled water, and the other extraction fluid was prepared by adding nitric acid into the distilled water as in the SPLP procedure. The initial pH of the TCLP fluid was 4.93 and that of the modified SPLP fluid was 2.60 in order to achieve the same final pH values in the extraction fluids. MSWIBA aggregate was used as the test material.

The results are shown in the Figure 9.5.5.2.3. Generally the leachate of the TCLP method contained higher metals concentrations than the modified SPLP leachate. This means that even though the final pH of the leachates are the same (final pH value 5.1), the TCLP extraction fluid can form complexes with the metals and thus increase their solubility compared to the modified SPLP fluid.

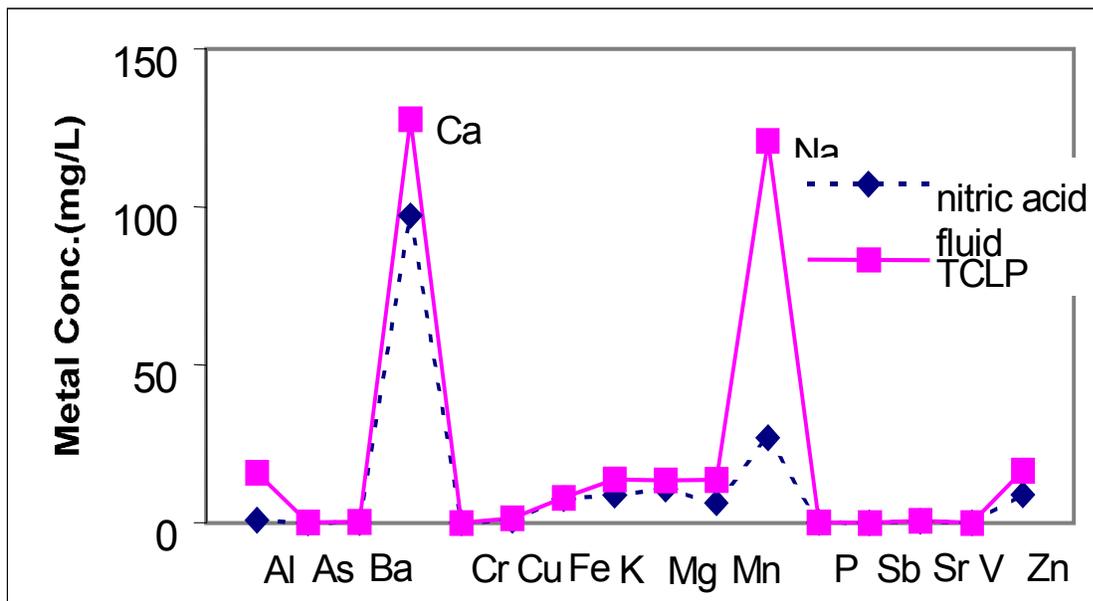


Figure 9.5.5.2.3. Comparison of the concentration of two leachates from MSWIBA aggregate, both of which have the same final pH.

9.5.6 Comparison of regular and modified NCHRP Methods

In this study the NCHRP method was modified in order to be more comparable to the two EPA leaching methods. Both the leaching time and the solid-to-liquid (S/L) ratio were modified as shown in Table 9.5.6.1.

Table 9.5.6.1. Comparison of leaching time and S/L ratio for regular and modified NCHRP procedures.

	Regular NCHRP	Modified NCHRP
Leaching time	24 hrs	18 hrs
Solid to liquid ratio	1:4	1:20

Since the solid-to-liquid ratio was not the same for these methods, a comparison of the leachates was made based on both concentration and released metal per mass of sample added. The release of a metal per unit mass of material for each of the tests was calculated using Equation 9.5.6.1:

$$\text{released mass (mg / kg)} = \frac{(\text{concentration, mg / L}) (\text{leachate volume, L})}{(\text{weight of solid in test, g})(1 \text{ kg} / 1000\text{g})} \quad (9.5.6.1)$$

Figures 9.5.6.1 and 9.5.6.2 show that the concentrations of metals were higher in the regular NCHRP leachate than in the modified NCHRP leachate. Since the solid-to-liquid ratio is higher in the regular NCHRP than in the modified NCHRP, it takes less time to reach higher concentrations, although time to reach the equilibrium state between the leachate and solid phase should be the same in the regular and modified methods. Thus, if the leachate did not reach the equilibrium state, the regular NCHRP method should contain higher concentrations of metals than the modified method. If solubility controls a metal's concentration, under equilibrium conditions the concentration of that metal in the leachates for the two methods should theoretically be the same. The reason why the concentration of aluminum in the modified NCHRP method is higher than in the regular NCHRP method could not be explained directly, although a solubility limitation is apparent.

Comparison of the two methods based on the released mass is shown in Figures 9.5.6.3 and 9.5.6.4. Considering the higher solid-to-liquid ratio in the modified method, for some metals more is leached (based on mass) in the modified NCHRP. Solubility limitations may be responsible for greater specific mass of metals leached in the lower S/L ratio of the modified NCHRP method.

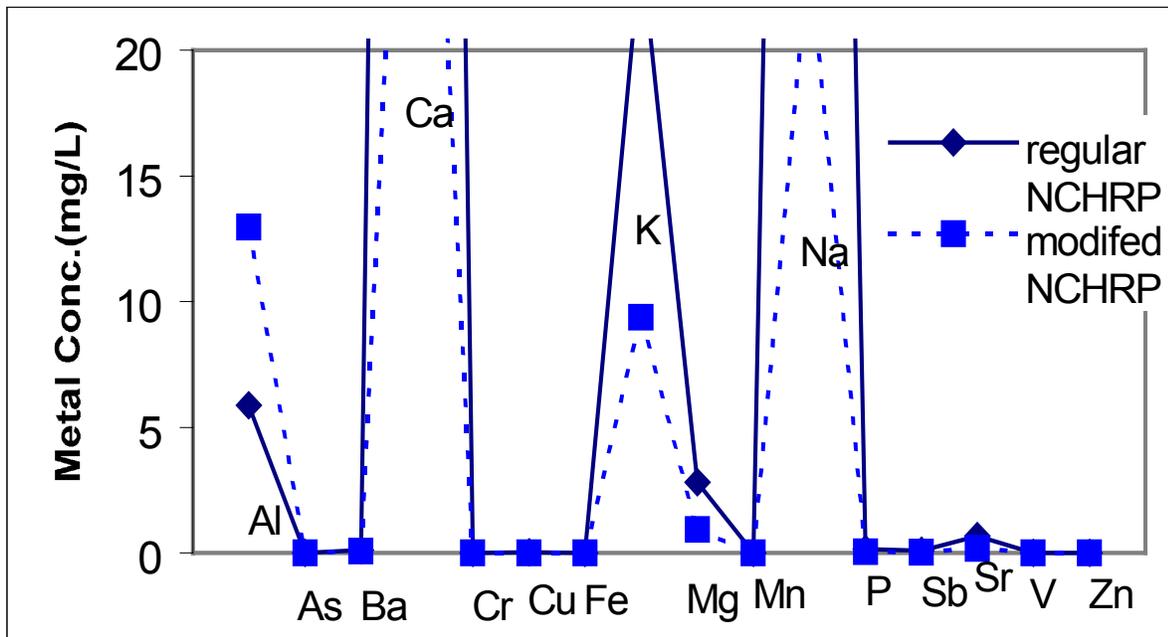


Figure 9.5.6.1. Comparison of concentration between regular NCHRP and modified NCHRP methods.

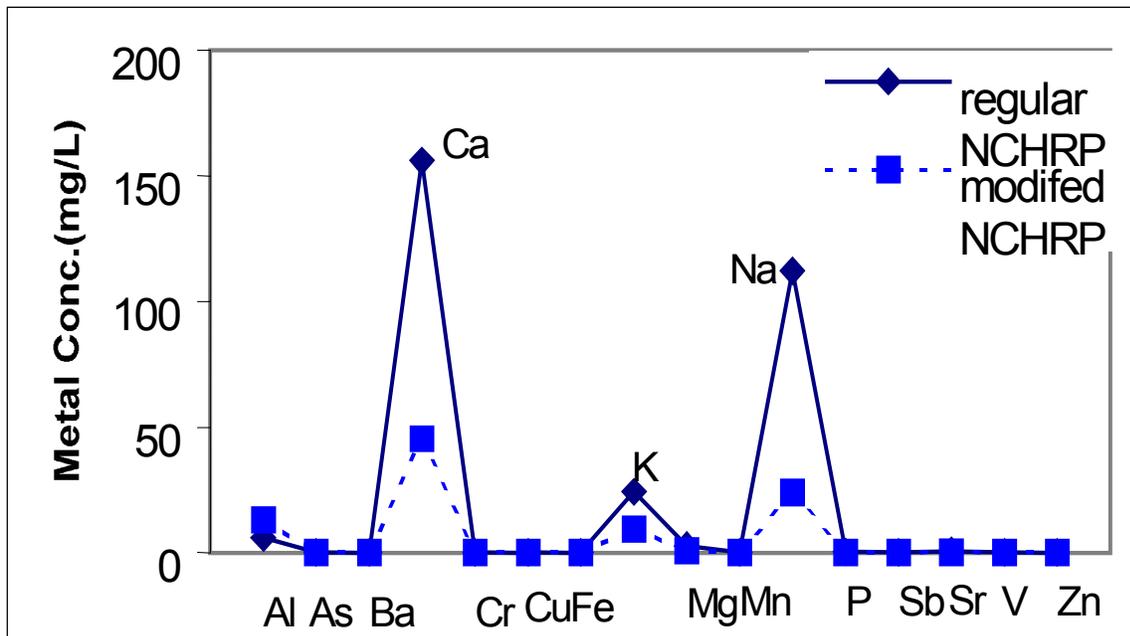


Figure 9.5.6.2. Comparison of concentration between regular NCHRP and modified NCHRP methods (expanded scale).

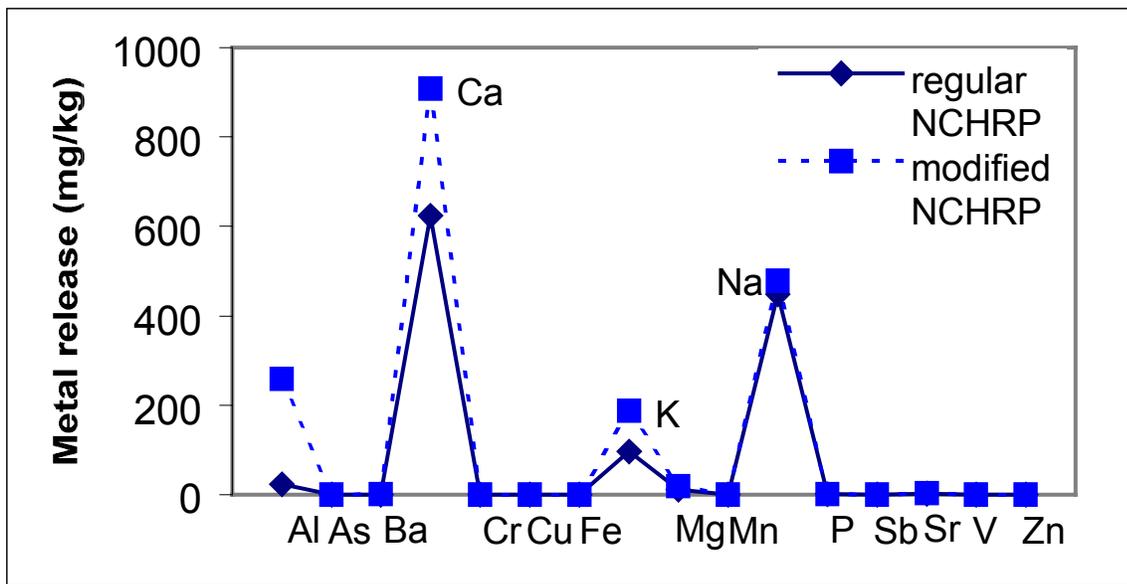


Figure 9.5.6.3. Comparison of metals released per unit mass between regular NCHRP and modified NCHRP methods.

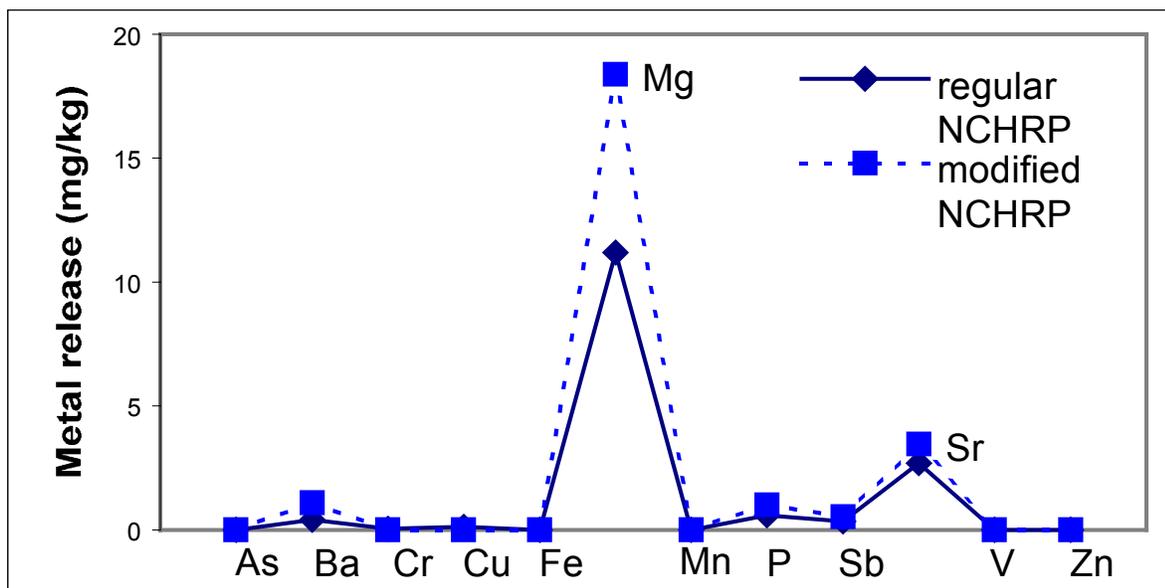


Figure 9.5.6.4. Comparison of metals released per unit mass between regular NCHRP and modified NCHRP methods (expanded scale).

9.5.7 Mechanisms Controlling Major Elements Leaching

To better understand mechanisms controlling metals leaching, two comparisons were made using the results reported above. The influence of pH on leaching was investigated using MSWIBA aggregate and a distilled water extraction with varying nitric acid additions to produce a range of leachate final pH values. Metals leached using the TCLP, SPLP, and modified NCHRP extraction methods were also directly compared for five construction and repair materials. Results are discussed for aluminum and calcium elements in the leachates.

9.5.7.1 Aluminum

Figure 9.5.7.1.1 shows the leachability (concentration) of aluminum as a function of pH for MSWIBA aggregate. The aluminum concentration increases as pH is decreased below 4, and decreases above pH 4 to the lowest concentrations in the range of pH 5 to 7. Aluminum solubility in Figure 9.5.7.1.1 compares more closely to that of aged precipitated $\text{Al}(\text{OH})_3(\text{s})$ than for freshly precipitated $\text{Al}(\text{OH})_3(\text{s})$ (Snoeyink and Jenkins, 1980). The pH range of lowest concentration of soluble Al for thermodynamically stable aged $\text{Al}(\text{OH})_3(\text{s})$ is 5 to 7, while that of freshly precipitated $\text{Al}(\text{OH})_3(\text{s})$ is 6 to 8. This is consistent with the mineral form of aluminum present in the MSWIBA aggregate. In spite of the low aluminum concentration near pH 5 to 6 in Figure 9.5.7.1.1, this leachate still contained a higher aluminum concentration than did the leachates of the SPLP and modified NCHRP methods, whose leachates have pH values near 10 (Figure 9.5.7.1.2). The formation of a soluble complex with acetate in the TCLP solution may have contributed to the greater leachability of aluminum by this procedure ($\log K = 2.4$ for aluminum acetate stability constant, Morel and Hering, 1993).

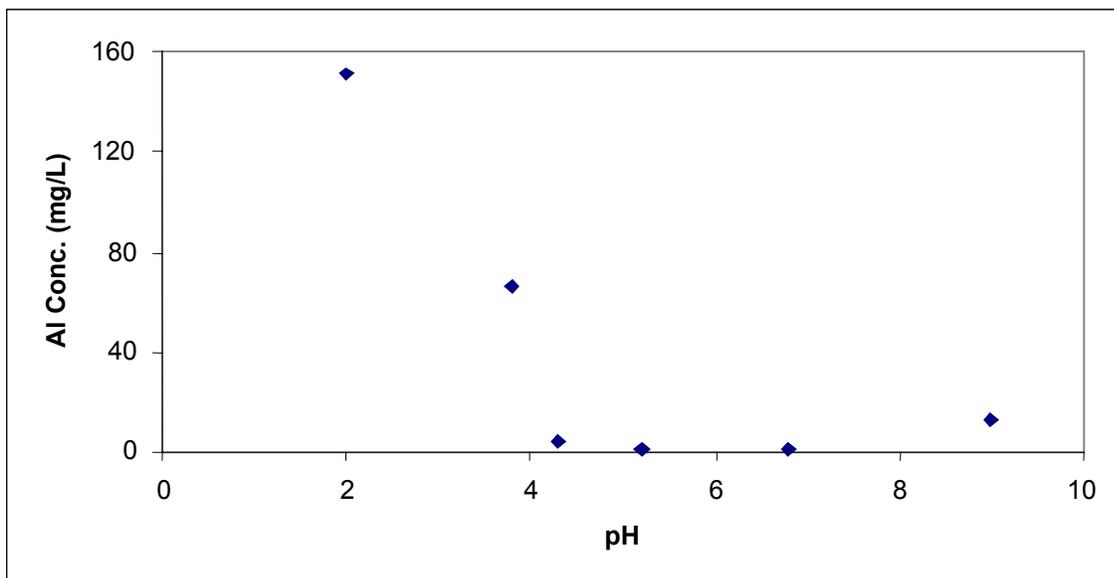


Figure 9.5.7.1.1. Leaching of aluminum from MSWIBA aggregate as a function of pH.

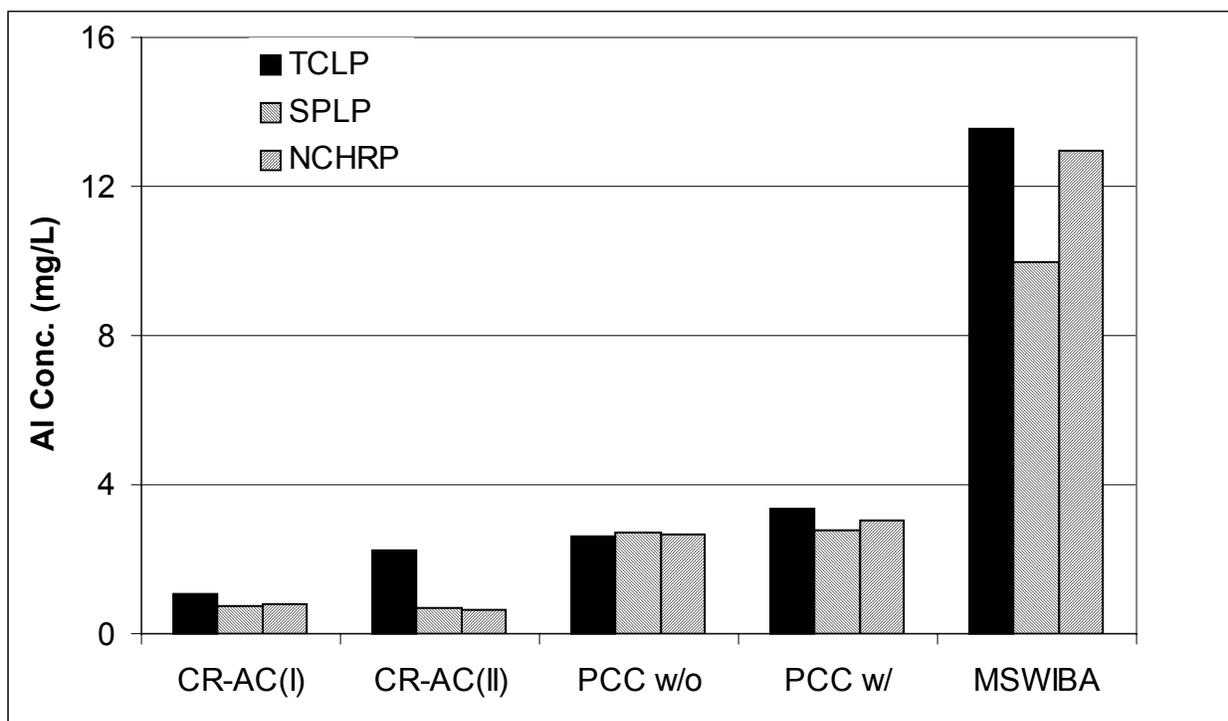


Figure 9.5.7.1.2. Aluminum concentrations using three extraction fluids for five C&R material assemblages.

9.5.7.2 Calcium

Calcium concentration in leachate from MSWIBA decreases as pH increases, which means that calcium is leached more easily in acid than in alkaline solutions (Figure 9.5.7.2.1). The main reason why the TCLP leachates contained higher calcium concentrations for CR-AC and MSWIBA is that the pH values of the TCLP leachates (pH 5-5.5) are lower than those of SPLP or modified NCHRP leachates (pH \approx 10). Since PCC is a more alkaline material than CR-AC and MSWIBA, the TCLP extraction fluid for PCC lost its buffering capacity and the final pH of the three methods is almost the same (pH 11.2-11.4). The reasons why the TCLP leachate for PCC without plasticizer and the modified NCHRP leachate for PCC with plasticizer have higher calcium concentrations could not be directly explained. Even though the calcium ion forms several kinds of complexes with CO_3^{2-} , its possibility of complexation is rare in a closed system. The formation of weak complexes with acetate in the TCLP solution also contributes to higher concentrations of calcium in TCLP leachates (log K = 1.1 for calcium acetate stability constant, Morel and Hering, 1993).

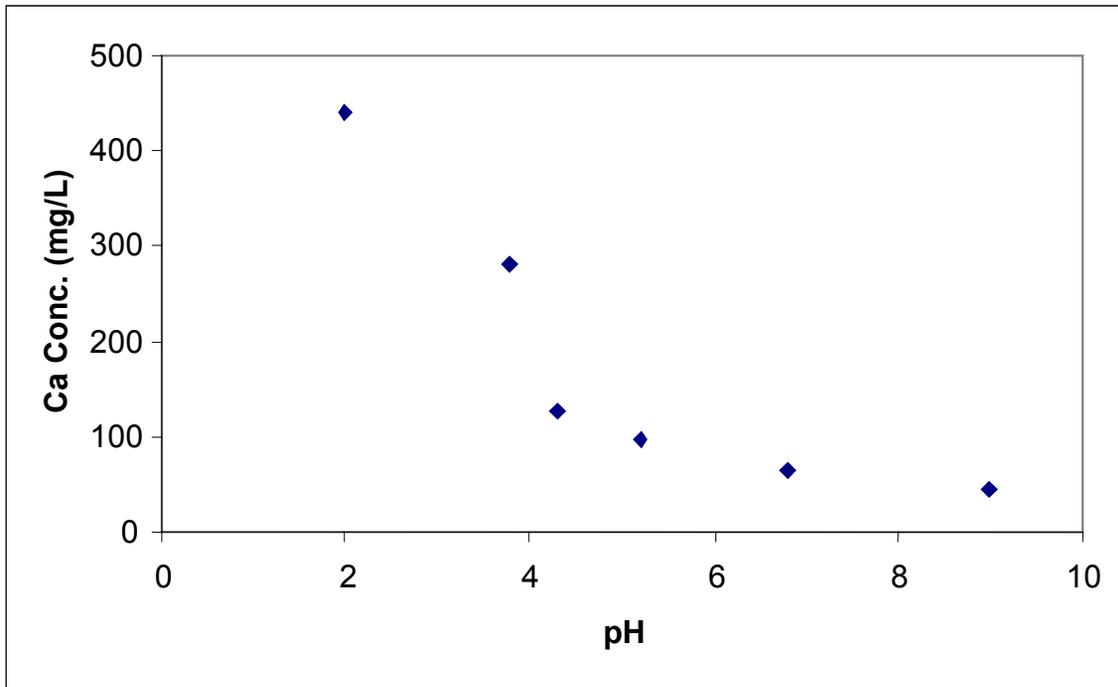


Figure 9.5.7.2.1. Leaching of calcium from MSWIBA as a function of pH.

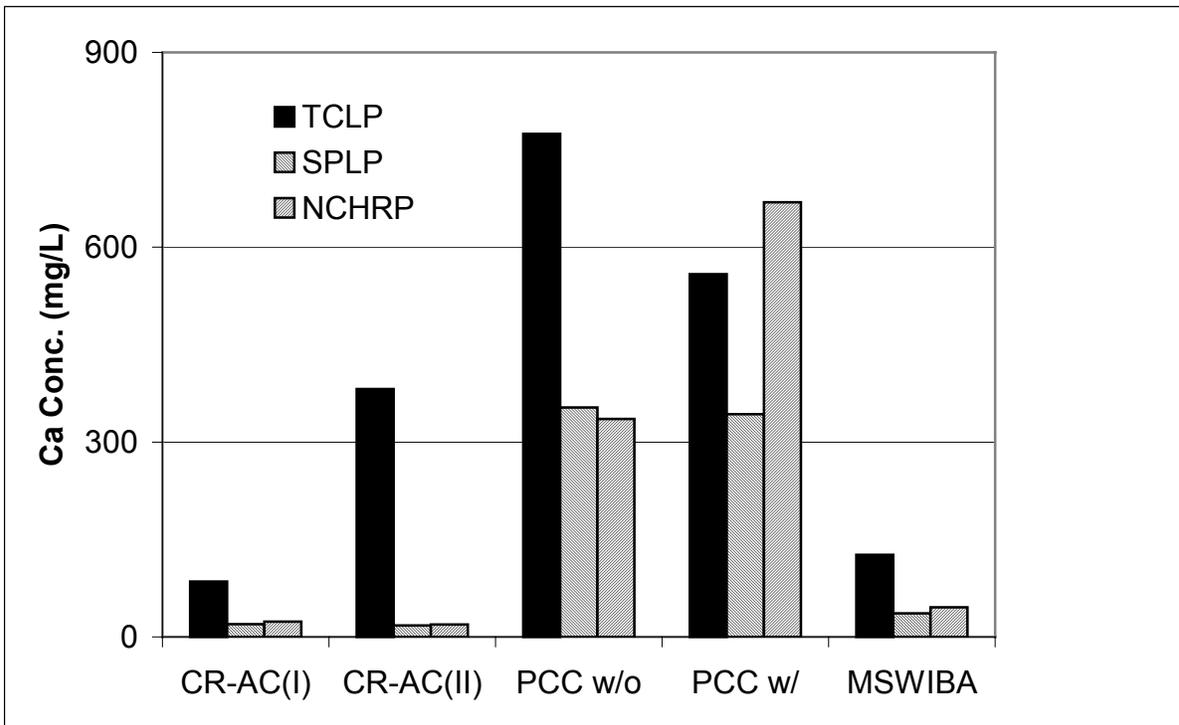


Figure 9.5.7.2.2. Calcium concentrations using three extraction fluids for five C&R material assemblages.

9.6 CONCLUSIONS

The leaching behavior of highway construction and repair (C&R) materials is important in order to understand the transport of metals in the environment. Leaching of C&R materials is a complex phenomenon in which many factors influence the release of specific metals from the materials. Because extensive analysis of the leachates from these materials could be very time consuming, standard procedures have been developed to assess leaching conditions in selected environments.

This study was conducted to compare the results of the TCLP, SPLP and NCHRP (modified) leaching methods. A comparison was made of the concentrations of metals in the different test leachates from five different C&R materials. The influence of pH on leaching and the difference between the regular and modified NCHRP methods were also studied. Based on the results of this study, the following conclusions were drawn and observations made:

Generally, the TCLP was a more aggressive leaching procedure than the SPLP and modified NCHRP procedures. The TCLP leachate generally contained higher metal concentrations than the SPLP and NCHRP leachates for the five C&R materials. The difference in metals concentrations in the CR-AC (type I, II) and MSWIBA aggregate leachates for the three extraction methods can be attributed to lower leachate pH values and higher metal solubility by complexation with acetate. Acetate metal complexation in PCC leachates likely explains why the TCLP leachate contained higher metals concentrations although at the same pH range as the SPLP and NCHRP methods.

When comparing the test results by ANOVA based on 95 % confidence limit, there was a significant difference of concentrations between the TCLP and the other two methods, SPLP and modified NCHRP. Test results for the SPLP and NCHRP methods were generally not significantly different.

Generally, the reproducibility was good for multiple samples in all three methods. The relative standard deviation (RSD, standard deviation/mean) values of metals concentrations in the leachate are generally under 20 % unless near the metals detection limit. MSWIBA aggregate had the highest RSD values due to the lower homogeneity of the material.

More metals are generally extracted as the final pH value of the leachate solution decreases. The inorganic components (metals) are generally more readily leached in acidic than in neutral or slightly basic solutions.

Generally, higher concentrations of metals were leached in the regular NCHRP method than in the modified NCHRP method, and concentrations were proportional to the mass of C&R material present. For some metals, more were leached in the modified NCHRP method in terms of specific mass released (per unit mass of C&R material), which implies possible solubility limitations for those metals.

9.7 RECOMMENDATIONS

There are a number of different types of leaching tests. A number of parameters can be varied in each test, for example, S/L ratio and composition of leachant (leaching or extraction fluid). Which leaching method is the most appropriate to apply for the highway C&R materials? The TCLP method was designed to model the leaching environment found in actively decomposing municipal landfills. Since most construction materials will not be subject to these leaching conditions, the TCLP does not represent a realistic case for highway situations. The selection of the extraction fluid should be based on the objectives of the test.

This study was done based on the 15 selected compounds that would most likely be extracted from the highway C&R materials. Even though some elements don't have EPA regulatory levels in TCLP extracts, the concentrations of the other elements, which have regulatory levels, were below the regulation limits. Regulatory limits for some elements such as aluminum, which showed high concentrations in all three methods and may exhibit toxicity, may need to be established in TCLP extracts.

The modified NCHRP method was equivalent in leaching aggressiveness to the SPLP method for the C&R materials tested. The moderate acidity of the SPLP leaching fluid is generally overwhelmed by the acid-base characteristics of the C&R material, leading to very similar final leachate pH values for the modified NCHRP and SPLP methods. It thus appears that the regular NCHRP method, which uses distilled water as the leaching fluid, is suitable for assessing the environmental leaching characteristics of highway C&R materials.

Table 9.5.3.1.1. Task 8: Summary data for chemical analyses.

Task 8: Leaching Methods Comparison Study																			
Sample ID	Test Conditions	Leaching Method	Chemistry Test Results																
			Al (mg/L)	As (mg/L)	Ba (mg/L)	Ca (mg/L)	Cr (mg/L)	Fe (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)	P (mg/L)	Sb (mg/L)	Sr (mg/L)	V (mg/L)	Zn (mg/L)	pH
Crumb Rubber Asphalt Mix. (CRAC)																			
1	CRAC Type I	EPA-TCLP	0.964	BD	0.270	80.27	BD	BD	1.185	3.173	3.087	0.353	79.78	0.024	BD	0.827	BD	0.181	4.97
2	CRAC Type I	EPA-TCLP	1.088	BD	0.288	89.08	BD	BD	1.368	3.728	3.713	0.424	80.90	0.041	BD	0.912	BD	0.196	5.05
3	CRAC Type I	EPA-TCLP	1.045	BD	0.305	81.80	BD	BD	1.388	3.594	3.816	0.411	81.31	0.045	BD	0.691	BD	0.192	5.06
1	CRAC Type I	EPA-SPLP	0.702	BD	BD	17.88	BD	BD	BD	1.331	0.089	BD	2.27	0.022	BD	0.068	BD	BD	10.17
2	CRAC Type I	EPA-SPLP	0.710	BD	BD	20.06	BD	BD	BD	1.522	0.070	BD	2.40	BD	BD	0.077	BD	BD	10.28
3	CRAC Type I	EPA-SPLP	0.756	BD	BD	21.46	BD	BD	BD	1.750	0.067	BD	2.82	BD	BD	0.078	BD	BD	10.22
1	CRAC Type I	OSU-NCHRP	0.604	BD	BD	20.24	BD	BD	BD	1.381	0.063	BD	2.28	BD	BD	0.058	BD	BD	9.97
2	CRAC Type I	OSU-NCHRP	0.680	BD	BD	24.03	BD	BD	BD	1.752	0.036	BD	3.34	BD	BD	0.060	BD	BD	10.25
3	CRAC Type I	OSU-NCHRP	1.152	BD	BD	25.69	BD	BD	BD	1.566	0.039	BD	2.90	BD	BD	0.071	BD	BD	10.26
1	CRAC Type II	EPA-TCLP	2.135	BD	0.157	353.80	BD	BD	0.297	0.330	6.846	0.096	75.78	0.028	BD	0.394	BD	0.106	5.51
2	CRAC Type II	EPA-TCLP	2.331	0.057	0.150	401.00	BD	BD	0.245	0.217	7.157	0.085	75.90	0.039	BD	0.446	BD	0.106	5.60
3	CRAC Type II	EPA-TCLP	2.252	0.032	0.150	391.25	BD	BD	0.247	0.253	7.190	0.090	76.76	BD	BD	0.453	BD	0.103	5.53
1	CRAC Type II	EPA-SPLP	0.615	BD	BD	15.64	BD	BD	BD	BD	0.149	BD	0.10	0.011	BD	0.038	BD	BD	9.98
2	CRAC Type II	EPA-SPLP	0.741	BD	BD	17.93	BD	BD	BD	BD	0.143	BD	0.10	0.017	BD	0.028	BD	BD	9.83
3	CRAC Type II	EPA-SPLP	0.755	BD	BD	18.92	BD	BD	BD	BD	0.135	BD	0.09	0.030	BD	0.028	BD	BD	9.80
1	CRAC Type II	OSU-NCHRP	0.603	BD	BD	17.26	BD	BD	BD	BD	0.138	BD	0.08	0.038	BD	0.026	BD	BD	9.82
2	CRAC Type II	OSU-NCHRP	0.658	BD	BD	19.01	BD	BD	BD	BD	0.127	BD	0.06	BD	BD	0.021	BD	BD	9.93
3	CRAC Type II	OSU-NCHRP	0.710	BD	BD	20.95	BD	BD	BD	BD	0.124	BD	0.07	0.046	BD	0.029	BD	BD	10.05
Potland Cement Concrete (PCC)																			
1	PCC w/plasticizer	EPA-TCLP	3.338	BD	0.258	558.19	0.044	BD	BD	6.177	0.042	BD	81.43	BD	BD	0.697	0.002	BD	11.47
2	PCC w/plasticizer	EPA-TCLP	3.201	BD	0.300	558.12	0.046	BD	BD	6.293	0.024	BD	82.86	BD	BD	0.747	0.007	BD	11.43
3	PCC w/plasticizer	EPA-TCLP	3.606	BD	0.270	558.14	0.047	BD	BD	6.255	0.029	BD	81.47	BD	BD	0.719	0.017	BD	11.40
1	PCC w/plasticizer	EPA-SPLP	2.747	-0.006	0.129	347.71	0.019	0.003	BD	4.744	0.007	BD	5.440	BD	BD	0.484	0.019	BD	11.27
2	PCC w/plasticizer	EPA-SPLP	2.694	0.015	0.126	347.30	0.021	0.002	BD	4.597	0.012	BD	5.554	BD	BD	0.485	0.005	BD	11.30
3	PCC w/plasticizer	EPA-SPLP	2.859	0.068	0.119	335.02	0.022	0.003	BD	4.860	0.020	BD	5.704	BD	BD	0.469	0.011	BD	11.30
1	PCC w/plasticizer	OSU-NCHRP	2.936	BD	0.205	668.64	0.010	BD	BD	4.053	0.008	BD	5.08	BD	BD	0.615	0.004	BD	11.32
2	PCC w/plasticizer	OSU-NCHRP	3.075	BD	0.203	673.90	0.004	BD	BD	3.966	0.007	BD	4.89	BD	BD	0.610	0.008	BD	11.38
3	PCC w/plasticizer	OSU-NCHRP	3.033	BD	0.200	664.30	0.008	BD	BD	3.992	0.006	BD	4.89	BD	BD	0.613	0.011	BD	11.40

Table 9.5.3.1.1. Task 8: Summary data for chemical analyses (concluded).

Task 8: Leaching Methods Comparison Study																			
Sample ID	Test Conditions	Leaching Method	Chemistry Test Results																
			Al (mg/L)	As (mg/L)	Ba (mg/L)	Ca (mg/L)	Cr (mg/L)	Fe (mg/L)	Cu (mg/L)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)	P (mg/L)	Sb (mg/L)	Sr (mg/L)	V (mg/L)	Zn (mg/L)	pH
Potland Cement Concrete (PCC)																			
1	PCC w/plasticizer	OSU-NCHRP	2.936	BD	0.205	668.64	0.010	BD	BD	4.053	BD	BD	5.08	BD	BD	0.615	BD	BD	11.32
2	PCC w/plasticizer	OSU-NCHRP	3.075	BD	0.203	673.90	BD	BD	BD	3.966	BD	BD	4.89	BD	BD	0.610	0.008	BD	11.38
3	PCC w/plasticizer	OSU-NCHRP	3.033	BD	0.200	664.30	0.008	BD	BD	3.992	BD	BD	4.89	BD	BD	0.613	0.011	BD	11.40
1	PCC w/o plasticizer	EPA-TCLP	2.572	0.121	0.264	783.953	0.047	BD	BD	7.322	0.161	BD	117.450	BD	BD	0.825	0.100	BD	11.09
2	PCC w/o plasticizer	EPA-TCLP	2.621	BD	0.265	757.021	0.039	BD	BD	6.999	0.067	BD	116.497	BD	BD	0.768	0.051	BD	11.3
3	PCC w/o plasticizer	EPA-TCLP	2.655	BD	0.274	782.382	0.047	BD	BD	7.773	0.086	BD	117.829	BD	BD	0.820	0.041	BD	11.23
1	PCC w/o plasticizer	EPA-SPLP	2.653	BD	0.084	313.102	0.023	BD	BD	5.194	BD	BD	5.799	BD	0.016	0.490	0.012	BD	11.37
2	PCC w/o plasticizer	EPA-SPLP	2.706	BD	0.091	369.724	0.017	BD	BD	5.251	BD	BD	6.063	0.130	0.027	0.521	BD	BD	11.39
3	PCC w/o plasticizer	EPA-SPLP	2.684	BD	0.088	380.684	0.020	BD	BD	5.285	BD	BD	5.920	0.171	0.026	0.512	BD	BD	11.41
4	PCC w/o plasticizer	EPA-SPLP	2.645	BD	0.094	381.624	0.012	BD	BD	5.864	BD	BD	9.067	0.149	0.020	0.496	BD	BD	11.29
5	PCC w/o plasticizer	EPA-SPLP	2.808	BD	0.079	343.752	0.008	BD	BD	5.476	BD	BD	8.457	0.270	BD	0.480	BD	BD	11.33
6	PCC w/o plasticizer	EPA-SPLP	2.819	BD	0.076	331.619	0.009	BD	BD	5.628	BD	BD	9.069	0.403	0.023	0.466	BD	BD	11.29
1	PCC w/o plasticizer	OSU-NCHRP	2.617	BD	0.085	351.828	0.020	BD	BD	4.669	BD	BD	6.103	BD	BD	0.479	BD	BD	11.34
2	PCC w/o plasticizer	OSU-NCHRP	2.670	BD	0.076	328.324	0.013	BD	BD	4.178	BD	BD	5.581	BD	0.017	0.420	BD	BD	11.35
3	PCC w/o plasticizer	OSU-NCHRP	2.656	BD	0.067	327.285	0.014	BD	BD	4.259	BD	BD	5.724	BD	BD	0.421	BD	BD	11.28
MSWIBA Asphalt Mix.																			
1	MSWIBA asphalt	EPA-TCLP	13.706	BD	0.234	145.25	0.022	2.452	8.968	13.427	13.590	11.632	120.33	BD	0.030	0.631	BD	12.794	5.07
2	MSWIBA asphalt	EPA-TCLP	15.918	BD	0.298	127.84	0.028	1.534	7.883	13.771	13.471	13.557	121.06	0.092	0.061	0.611	BD	16.563	5.10
3	MSWIBA asphalt	EPA-TCLP	11.069	BD	0.323	106.56	0.019	2.008	7.457	11.494	11.820	14.384	120.76	BD	0.045	0.510	BD	59.066	5.10
1	MSWIBA asphalt	EPA-SPLP	9.836	BD	0.036	38.32	BD	BD	0.010	7.595	0.419	BD	27.58	0.095	0.058	0.201	0.008	BD	9.48
2	MSWIBA asphalt	EPA-SPLP	9.716	BD	0.037	38.24	BD	BD	BD	7.104	0.702	BD	25.80	BD	0.060	0.190	0.014	BD	9.22
3	MSWIBA asphalt	EPA-SPLP	10.374	BD	0.034	32.78	BD	BD	0.011	6.722	0.682	BD	25.08	BD	0.060	0.182	0.006	BD	9.24
1	MSWIBA asphalt	OSU-NCHRP	14.692	BD	0.044	40.42	BD	0.010	BD	7.528	1.012	BD	24.47	0.076	0.027	0.156	BD	BD	8.97
2	MSWIBA asphalt	OSU-NCHRP	11.798	BD	0.035	26.83	BD	BD	BD	6.673	0.625	BD	21.40	BD	0.029	0.099	BD	BD	8.98
3	MSWIBA asphalt	OSU-NCHRP	12.377	BD	0.085	68.98	BD	BD	BD	13.890	1.118	BD	25.89	BD	0.020	0.265	BD	BD	8.89

CHAPTER 10

FATE AND TRANSPORT MODELING

10.1 INTRODUCTION

The majority of time spent on Phase III model development was dedicated to programming. The remainder of the time included enhancement of the numerical methods employed in the model, other model calculations, and development of a user's guide (Volume V of this report series). The final, Phase III, version of the fate and transport model is named IMPACT in the text that follows and in the user's guide.

Four limitations of the Phase II version of the Model were addressed by the following enhancements:

- numerical method accounts for desorption of material;
- the user has the option of using long-term hydrologic data;
- there is a decrease in the source term concentration with time; and
- layered soils may be simulated.

A final major modification is the inclusion of Phase III data in the modeling parameters (drying and wetting cycles, leaching scale effects, etc.). A significant portion of the modeling effort has been to expand the flexibility of the model to allow modeling of other construction and repair (C&R) materials that do not have the necessary parameters available for runs with the model.

The development of the model and its theoretical components are explained in Volume II of this report series (Eldin et al., 2000). This Chapter 10 should be considered as a supplement to Volume II. In addition, details of the numerical method used to solve the advection dispersion equation and the other calculations used in the model are contained in Appendix A. This is included because (1) it was a primary focus of the modeling effort, and (2) so that the calculations can be understood by anyone using the model. It is hoped that this will have two important outcomes. The first is that an understanding of the calculations employed in the model will allow the end user to have a closer understanding of what the model is capable of and its limitations. The second is that, by including the appendix on the numerical methods, it provides the opportunity for anyone to examine the calculations without needing to access the Visual Basic for Applications (VBA) code contained in the Excel spreadsheet release of the model.

An additional purpose of this chapter is to describe tests of the model using laboratory column study data from Task 1. That is, model calculations are compared against laboratory breakthrough curves in Section 10.5.

In this chapter the term 'increment' is used to refer to a period of time for which calculations are performed. An increment is equal to one hour or the duration of the storm, whichever is less, for a single event model run, or equal to the time interval of the time series of hydrologic data in a long term run.

10.2 MODEL OVERVIEW

10.2.1 Model Components

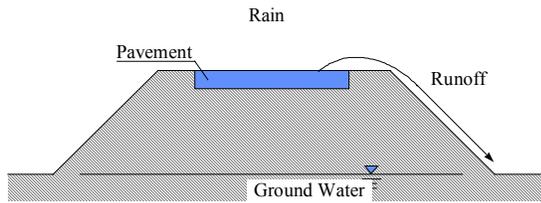
The model consists of two components: 1) data retrieval, and 2) fate and transport model. Data retrieval includes all summary data (e.g., EC50, LC50, chemistry samples) collected during Phases I, II, and III of the project. The fate and transport model itself is constructed to simulate any of six reference environments shown in Figure 10.2.1.1. In addition to these six reference environments, lateral transport of solute may be simulated, as shown in Figure 10.2.1.2. After the user selects a combination of reference environment and C&R material, the model first calculates the source-strength (leaching) rates for generation of constituents transported into the removal/reduction/retardation (RRR) model section. This section incorporates the effects of relevant environmental factors on the leachate. Note that the user may supply his/her own parameters for the C&R material; it is not necessary to simulate only the materials studied during this project.

Both sections utilize the laboratory findings (or user-supplied data) and are supported by the extensive database of laboratory data collected as part of this project. These results are included with the model in summarized tabular form in an Excel spreadsheet format. The data are the main support for the modeling effort and are presented in such a way that they are easily searchable by C&R material tested and by the tests run.

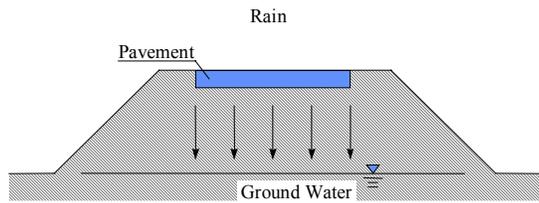
Primary model output consists of concentrations and loads into the underlying aquifer for the simulated reference environment. Flows rates, water volumes, and aquatic toxicity estimates are also provided. If the surface or subsurface runoff itself is the primary water volume of interest, then the concentration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

10.2.2 Software Requirements

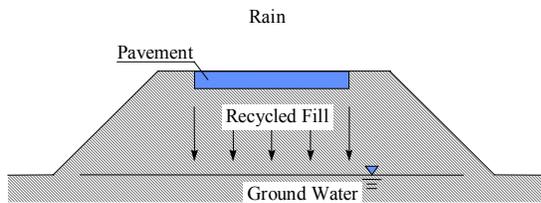
The fate and transport model is incorporated into a Microsoft Excel '97 spreadsheet. This version of Excel must be run under the Windows 95/97/98/2000/NT operating system. Excel is one of the most widely used spreadsheet programs available and contains useful tools for both the modeler and model user. The code for running the model has been written in Visual Basic for Applications (Lomax, 1998; Dictor, 1999), which Microsoft has incorporated into Excel '97 as the primary macro language. Visual Basic for Applications (VBA) allows the developer to interface with Excel data, functions, and routines using a recognized industry standard development tool, the Visual Basic language. Microsoft Excel '97 is the only software required to run the model, but this implies that at least minimal Excel proficiency is a requirement for the user.



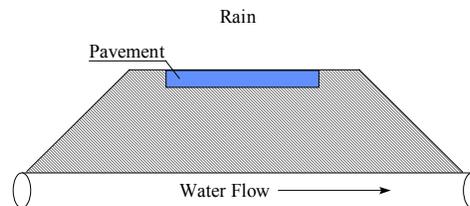
Description:Runoff from impermeable highway surface or bridge.
Pathways:Surface flow
Primary Processes:Photolysis, Volatilization
Source Term Model Parameter:Maximum leaching capacity (leachate extraction), Flat Plate Leaching (typical value)



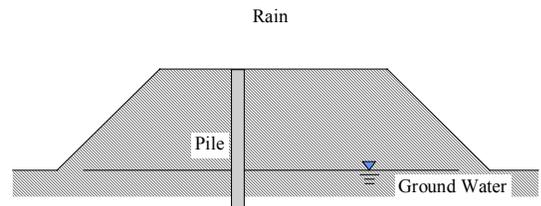
Description:Runoff through permeable highway surface.
Pathways:Subsurface, Surface flow
Primary Processes:Sorption, Biodegradation, Photolysis, Volatilization
Source Term Model Parameter:Maximum leaching capacity (leachate extraction), mass transfer rate (column test)



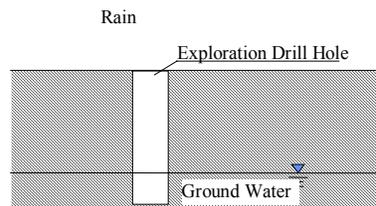
Description:Runoff through permeable highway surface.
Pathways:Subsurface flow
Primary Processes:Sorption, Biodegradation
Source Term Model Parameter:Maximum leaching capacity (leachate extraction), mass transfer rate (flat plate leaching)



Description:Culvert
Pathways:Surface flow
Primary Processes:Sorption, Photolysis, Volatilization
Source Term Model Parameter:Maximum leaching capacity (leachate extraction), Mass transfer rate (flat plate leaching)



Description:Piling
Pathways:Subsurface flow
Primary Processes:Sorption, Biodegradation
Source Term Model Parameter:Flat Plate leaching mass transfer rate (flat plate leaching)



Description:Bore Hole.
Pathways:Subsurface flow
Primary Processes:Sorption, Biodegradation
Source Term Model Parameter:Maximum leaching capacity (leachate extraction), Mass transfer rate (flat plate leaching)

Figure 10.2.1.1. Highway reference environments for fate and transport model application.

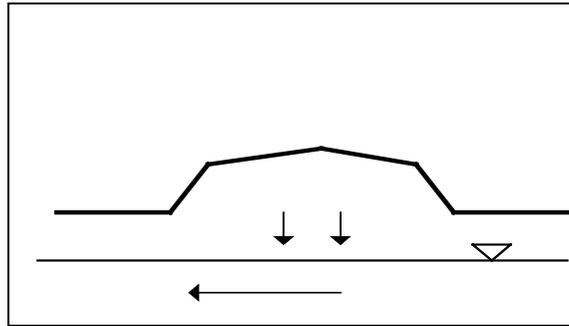


Figure 10.2.1.2. Schematic of permeable highway surface infiltration moving downward to water table, followed by lateral migration to left.

10.2.3 Some Key Assumptions

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

10.2.4 Some Key Limitations

- The model cannot simulate heterogeneous or structured soils, except for layering.
- The model cannot simulate preferential flow.
- The model does not simulate changes in the soil moisture content.
- The model cannot simulate chemical reactions (other than sorption and biodegradation), such as precipitation or complex formation.
- Leaching rates for large highway surfaces are mostly extrapolated from small (76 cm²) flat plate studies in the laboratory. Similar extrapolation occurs for column studies of fill materials.

10.2.5 Source Term Section

The determination of source terms is the first major component of the transport model. Source terms provide the loadings of the contaminant that are subject to advective-dispersive transport as well as for RRR parameters. Determination of the source term depends on the actual field situation (reference environment) that is to be modeled. The leaching tests conducted in the laboratory (short-term batch, long-term batch, column leaching, and flat plate leaching tests) are the primary determining factors in source term definition. Certain situations and materials dictate that laboratory data obtained from a particular test may be more applicable to that situation than other data. For example the source term for a material used as a deck sealer, where contact may occur mostly on the surface of a roadway, is best estimated by the flat plate leaching test.

Section A.3 of Appendix A details the transformation of rainfall data to flow and concentrations (time, flow, and concentration) at the boundary between the highway reference environment and the surrounding soil or adjacent receiving water.

10.2.6 Removal/Reduction/Retardation Section

The second major model section employs the laboratory analyses of the effects of environmental factors to simulate the fate and transport of a leached material. The four primary tests run in the laboratory (soil sorption, photolysis, biodegradation, and volatilization) are coupled with transport equations to provide predictions for concentration, load, and aquatic toxicity. The effect of each environmental factor must be coupled with the conditions present in the reference environment to be modeled. Three of the environmental factors are functions of time: photolysis, biodegradation, and volatilization. Once a functional relationship for the results of these tests is found in the model and/or input by the user, the resulting equations can be superimposed on the time dependent leaching functions, on each other, or on any of the environmental factors tested. They can be used where leaching and environmental factors are concurrent or where an initial concentration is subjected to RRR processes after leaving the site of leaching. Soil sorption information allows prediction of the sorption potential of the leachate and its toxic constituents. Results of the sorption testing give values that are dependent on soil type and concentration. Rapid equilibrium is assumed; hence, sorption computations are not a function of time and are applicable to situations where the material is passed through a soil matrix.

10.3 PHASE III PROGRAMMING CHANGES

The major Phase III programming changes to the model are discussed below. Greater detail on using the new options is provided in the user's manual (Volume V).

10.3.1 New Forms

Most of the dialogue boxes in the previous version of the model have been replaced with \ forms (interactive VBA "boxes" with "controls" for user response) in the new version. For example, dialog boxes for soil parameters for each of the six reference environments have been replaced with a single form. All of the navigation code has been replaced. The forms in Excel '97 allow some of the code to be included in the forms themselves, which has simplified the programming in the modules for the individual reference environments. The code used to navigate through the model is now much simpler, more robust, and easier to follow. The new forms are shown in the user's manual.

10.3.2 Phase III Database and Parameters

The data summary tables from the Phase III testing have been added to the model. The modeler now has the option of accessing test results for all tasks completed in this latest phase of testing.

The data from Phase III have been incorporated into the model parameters. The additional model parameters are essentially the addition of Portland cement concrete or PCC (with plasticizer) to the available materials for modeling and expanded sorption isotherms for the toxic components of ACZA. The data for these parameters were taken from Tasks 4 and 5, respectively.

The data from Tasks 2, Confinement Effects, showed little difference in the leaching of confined versus unconfined materials. The results support the continued use of leaching data from Phase II of the project. The results from Task 3, Scale Effects, also supported use of data from Phase II. There was very little difference in the flux of leachate from flat plat materials of different sizes. Task 6, Aging Effects, did not demonstrate any discernable effects between the leachate of aged materials and the leachate of the same materials that did not undergo the aging processes. All of these results indicate that no changes were needed to the basic model formulation of leaching.

10.3.3 Numerical Methods

The new numerical method (Discussed in Appendix A.5) now includes desorption and dispersion in the solution of the advection-dispersion equation. There are also checks on the time step for the explicit finite difference scheme using the stability condition (Roache, 1972):

$$\Delta T \leq \frac{1}{\frac{2D_1}{\Delta z^2} + \frac{V_p}{\Delta z}} \quad (10.3.3.1)$$

where:

D_1 = hydrodynamic dispersion coefficient, m^2/s ,

ΔT = time step, s,

Δz = distance step, m, and

V_p = pore velocity, m/s.

The pore velocity is the velocity at which a solute is advected through the porous media. Larger values for dispersion result in smaller time steps to meet the stability criteria, which increases the model run times. The coefficient of hydrodynamic dispersion can be expressed in terms of three components (Freeze and Cherry, 1979; Fetter, 1999)

$$D_1 (L^2/T) = \alpha_1 (L) \times V_p (L/T) + D^* (L^2/T) \quad (10.3.3.2)$$

where:

α_1 = dispersivity, m, and

D^* = coefficient of molecular diffusion, m^2/s .

The dispersivity is a characteristic property of the porous medium. The effects of dispersion are calculated from the dispersivity parameter entered by the model user and the pore velocities of the leachate during the model run. Mechanical dispersion (proportional to pore velocity) is typically much larger than molecular diffusion, unless the pore water velocities are very small (see Section 2.4.1). Since this model is for vertical infiltration, the molecular diffusion is considered negligible compared to the mechanical dispersion. Guidelines for the choice of dispersivity are included in model help screens.

The effect of dispersion depends a great deal on the sorption isotherm parameters used in the model run. Most of the materials in the model sorb strongly to the soil, which has the effect of limiting the dispersion of the solute. A high sorption capacity tends to adsorb material at the solute front, which prevents spreading of the solute. When the sorption capacity is low, high dispersion can greatly increase the penetration of a solute into the soil during a model run. Varying the dispersion (actually the dispersivity) by a factor of 100 for model runs for arsenic (using Langmuir and Freundlich isotherms) had minimal effect on the concentration profiles in the soil. Varying the dispersivity over a similar range (0.001 to 0.1m) when using a linear distribution coefficient of 0.01 mL/mg caused the solute to penetrate three times as far with the higher dispersivity.

10.3.4 Long Term Runs

The input options for rainfall data have been modified to allow the modeler to use historic long-term hydrologic data. The model has a routine capable of reading data and converting it to a format for use in the model. The two available formats are based on hourly and 15-min

precipitation data available from the National Weather Service, National Climatic Data Center in Asheville, NC. These formats are described in Appendix A.

10.3.5 Decay in Source Term

Both the single event and long-term event options include decay in the source term concentration. For the single event option the time increment is set to 1 hour and in the long-term option the time increment is set to the same increment as the hydrologic data. The source term concentration is recalculated for every time increment during the model run. The calculation methods employed are detailed in Appendix A, Section A.3.2.

10.3.6 Model Outputs

The model outputs have been updated in the Model Results worksheet and in the new Aquifer Inputs sheet. Outputs in the model results sheet have been modified to reflect single event or long-term model runs. Two new outputs to the model results have been added: mass calculations for the amount of sorbed and dissolved solute in the soil at the end of the run. The calculations for the results reported in the Model Results worksheet are now based on mass inputs into the soil column and aquifer rather than the calculated retardation coefficient as in the previous version of the model. The new calculations are detailed in Section A.7 of Appendix A.

Calculations for the mass loading into the aquifer are performed at the end of every increment. The outputs for each time increment are displayed in the Aquifer Inputs worksheet. The order of appearance (from left to right) is: time (hours), total mass input to the aquifer (mg or mmol), total volume of contaminated water into the aquifer (L), concentration of the water entering the aquifer (mg/L or mmol/L), the EC50(%) based on the current concentration, the average concentration to the aquifer (mg/L or mmol/L), and finally the EC50(%) based on the average concentration. Four (nearly) evenly spaced time increments are graphed in the Model Results chart (from the data in the Model Results worksheet) showing the concentration profile in the soil. The Aquifer Inputs chart graphs the mass loading to the aquifer and the EC50(%) based on the average concentration. This chart is blank unless some of the contaminant reaches the aquifer. Further information is included in the user's manual on reading the model results.

10.3.7 Access to Model Parameters

The new Model Parameters form allows the user access to all the laboratory parameters to be used in the model run. The modeler can input his or her own values for any of the parameters. This is designed to allow for the modeling of other materials not included in the model database or to adapt model parameters to different types of soils not included in the model. Manual entry, as opposed to selection from a drop down list, is also an input option on the Model Parameters form. Any time manual entry of values is allowed there is the potential for "crashes" due to entry of improper values or characters. All the variable entry options that allow manual input have checks to ensure that the values entered are acceptable for use in the model calculations.

An option allowing the modeler to select the number of nodes used in the model run has also been added. The intent is to allow an increase in the number of nodes for runs with deeper vadose zones or a decrease in the number of nodes for shallow soil depths. This option allows for control over the nodes spacing, which will affect the run times. For faster runs times the node spacing can be increased, which decreases the number of calculations to be performed during the run.

10.3.8 Groundwater Transport

The groundwater transport option has been changed to work with all the reference environments, except the impermeable environment. This option models the flux of leachate, from the bottom of the soil column, into the unit width (one meter) of the underlying aquifer. The source material is a one-meter width of pavement, culvert, or fill material for the permeable, culvert, or fill environments, respectively. The source material for the piling and bore hole environments is a single pile or bore hole. The calculations for the groundwater transport option are explained in Section A.8 of Appendix A.

10.3.9 Additional Help Menus

A help menu has been added to the Soil Parameters form to guide the model user in selecting a dispersivity coefficient that is used in the dispersion calculations. Another help menu has been added to the Model Parameters form that provides information on the parameters that can be changed by the modeler in this form.

10.3.10 Langmuir Isotherm

The Langmuir isotherm is now an option in the Soil Parameters form. This isotherm allows for direct solution of the dissolved and sorbed solute after a change in mass at a node calculated from the finite difference method employed in the model. Please see Section A.5 of Appendix A for more detail on the method. Langmuir isotherms have been plotted for arsenic, copper, and zinc used in modeling AZCA. Langmuir isotherms have been added, where possible, for all other materials.

10.3.11 Model Restructuring

The last major change to the model was restructuring the reference environment modules, adding two new modules, and slightly rearranging the order of progression through the model code. The numerical methods that were previously included in every reference module have been moved to one separate numerical module that is called from the reference modules. This is also true for the long-term module, which reads and transforms long-term hydrologic data into a series of

values that can be used by the model. Further details on the model code are provided in the user's manual.

The revised program flow is show in Figure 10.3.11.1.

10.4 NUMERICAL METHODS AND CALCULATIONS

The explicit finite difference method used to solve the advection-dispersion equation and the other model calculations are explained in Appendix A.

10.5 MODEL VERIFICATION

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

10.5.1 Available Column Studies

In Task 1, Confirmation of Phase II Methodology, AZCA and 2,4,6-TCP leachates were used in column studies with Sagehill and Woodburn soils. Not all of the individual metal species (Cu and Zn) reached a breakthrough concentration high enough in all of the column studies to be useful for comparison with model results. Although arsenic was available for model comparisons in the 50 mm Woodburn soil column, it was not run, as studies utilizing longer columns were available. The column studies used for comparison with the breakthrough curves predicted by the model are listed in Table 10.5.1.1.

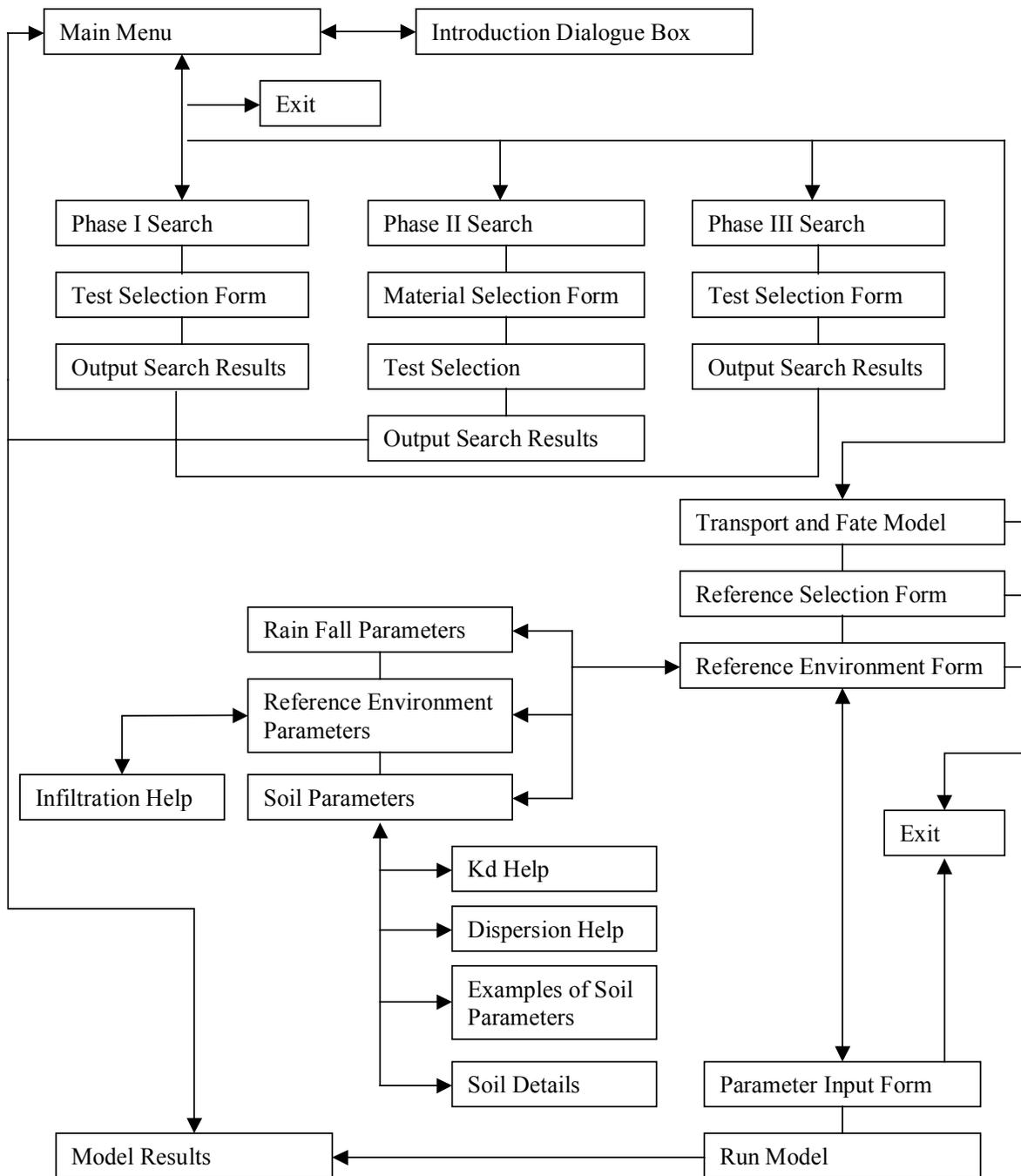


Figure 10.3.11.1 Model flow chart.

Table 10.5.1.1. Column studies used for comparison with model results.

ACZA Column Comparisons				TCP Column Comparisons	
Sagehill	As	Cu	Zn	Sagehill	
50 mm	yes	yes	yes	110 mm	yes
110 mm	yes	no	no		
Woodburn				Woodburn	
50 mm	no	yes	yes	50 mm	yes
110 mm	yes	no	no		
200 mm	yes	no	no		

10.5.2 Modeling Parameters

For meaningful comparison of model outputs to data from column studies, the parameters used in a run of the model must reflect the actual conditions in the column as closely as possible. Modeling parameters for the soil sorption isotherms were obtained from analyzing laboratory sorption data as part of Phase III, Task 5. The remaining modeling parameters used reflect the physical parameters of the soil columns and the physical properties of the soils used as closely as possible.

Data from Task 5 of the Phase III testing were analyzed to give Freundlich and Langmuir soil sorption isotherms for ACZA leachate in both Sagehill and Woodburn soils. Individual isotherms for arsenic, copper, and zinc were obtained.

The Freundlich isotherms are derived from the sorption data by plotting the sorbed concentration (mg/g) versus the concentration of material remaining in solution (mg/L). The coefficient and the exponent of a power fit of the plotted data points correspond directly to the Freundlich coefficient (K_f) and exponent (N) used in the Freundlich isotherm,

$$C_s = K_f \times C^N \quad (10.5.2.1)$$

where:

C_s = concentration sorbed (mg solute / g soil),

C = concentration in solution (mg solute / L solution),

K_f = Freundlich coefficient (L solute / g soil when $N = 1$), and

N = exponent.

When C_s and C are plotted on log scales, parameters N and K_f may be determined from the slope and intercept, respectively. The units for the Freundlich sorption isotherm in the model are mmol/g and mmol/L for the sorbed and dissolved forms, respectively. The data analysis for the sorption isotherms and leachate concentration for the model verification were done in units of milligrams rather than millimoles for ease of comparison with the column study data. The units of the isotherm constants were then changed when incorporated into the final version of the model.

The Langmuir isotherm formulation is

$$C_s = \frac{\alpha \times \beta \times C}{1 + \alpha \times C} \quad (10.5.2.2)$$

where:

C_s = concentration sorbed (mg solute / g soil)

C = concentration in solution (mg solute / L solution)

α = adsorption constant related to the binding energy (L / mg)

β = maximum sorption capacity of the soil (mg / g)

The Langmuir isotherm is obtained by plotting C/C_s versus C , as shown in Figure 10.5.2.1. The slope is equal to $1/\beta$ and the intercept is equal to $1/\alpha\beta$ (Fetter, 1999).

All but one of the isotherm analyses gave reasonable data fits. The only problem was the Langmuir isotherm for zinc in the Woodburn soil. In an effort to obtain useable parameters for α and β in the Langmuir isotherm the following rationale was employed. The constant β represents the maximum sorption capacity of the soil, so mass balance data from the column study just prior to switching to deionized water (i.e., just prior to the desorption phase of the experiment) were used for the following calculation. The mass influx to the column was known from the volume of infiltrating leachate multiplied by the concentration. The mass of zinc out of the column was estimated from analysis of the effluent and extrapolating the concentrations between the samples taken at certain time intervals. From these values, the mass remaining in the soil column could be estimated. The average concentration in solution in the soil column was estimated by averaging the influent and effluent concentrations at the time the mass balance data were used. This estimated concentration multiplied by the pore volume gave the mass in solution, which, when subtracted, left an estimate of the mass sorbed to the soil. Dividing this quantity by the mass of soil in the column gave an estimate for β (mg solute / g soil). For sorption data points near the origin, $1 \gg \alpha \times C$. Plotting points near the origin, assuming that $1 \gg \alpha \times C$, gives a slope of $\alpha \times \beta$. Dividing this value by the estimate for β gave an estimate for α . These estimated parameters are listed in Table 10.5.2.1.

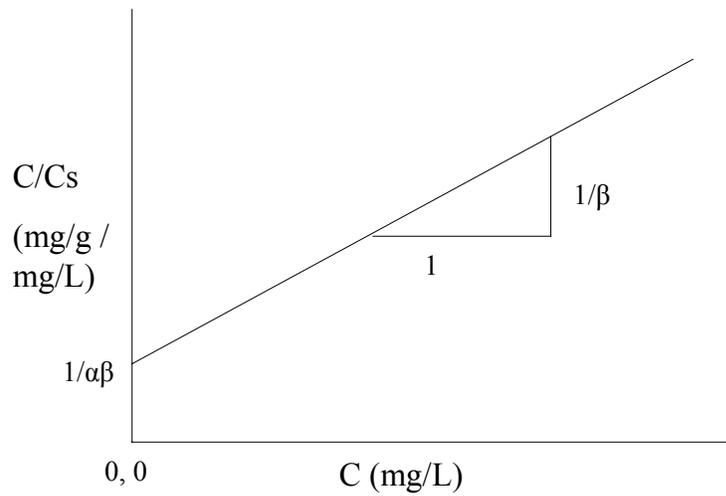


Figure 10.5.2.1. Data analysis for Langmuir isotherm.

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

The plots of the sorption data for arsenic, copper, and zinc for Sagehill and Woodburn soils are shown in Figures 10.5.2.2 – 10.5.2.7. Sorption data are obtained in the laboratory by mixing different amounts of soil and water and observing equilibrium concentrations. In two cases, data points obtained by mixing 10 grams soil per liter of solution were omitted from the Langmuir fit for arsenic in Sagehill soil (Figure 10.5.2.2) and for the Langmuir fit for copper in Woodburn soil (Figure 10.5.2.5) to get a better fit for the data ($R^2 \approx 0.6 - 0.7$ rather than $0.1 - 0.2$).

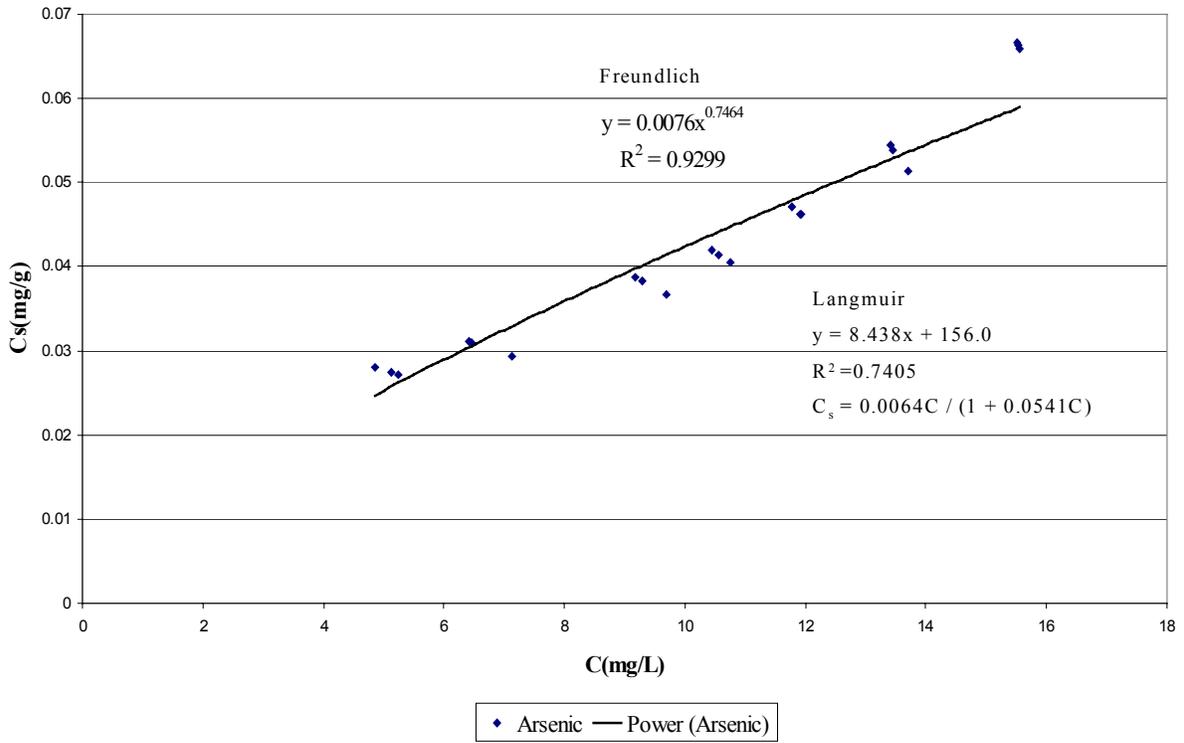


Figure 10.5.2.2 Arsenic sorption data for Sagehill soil.

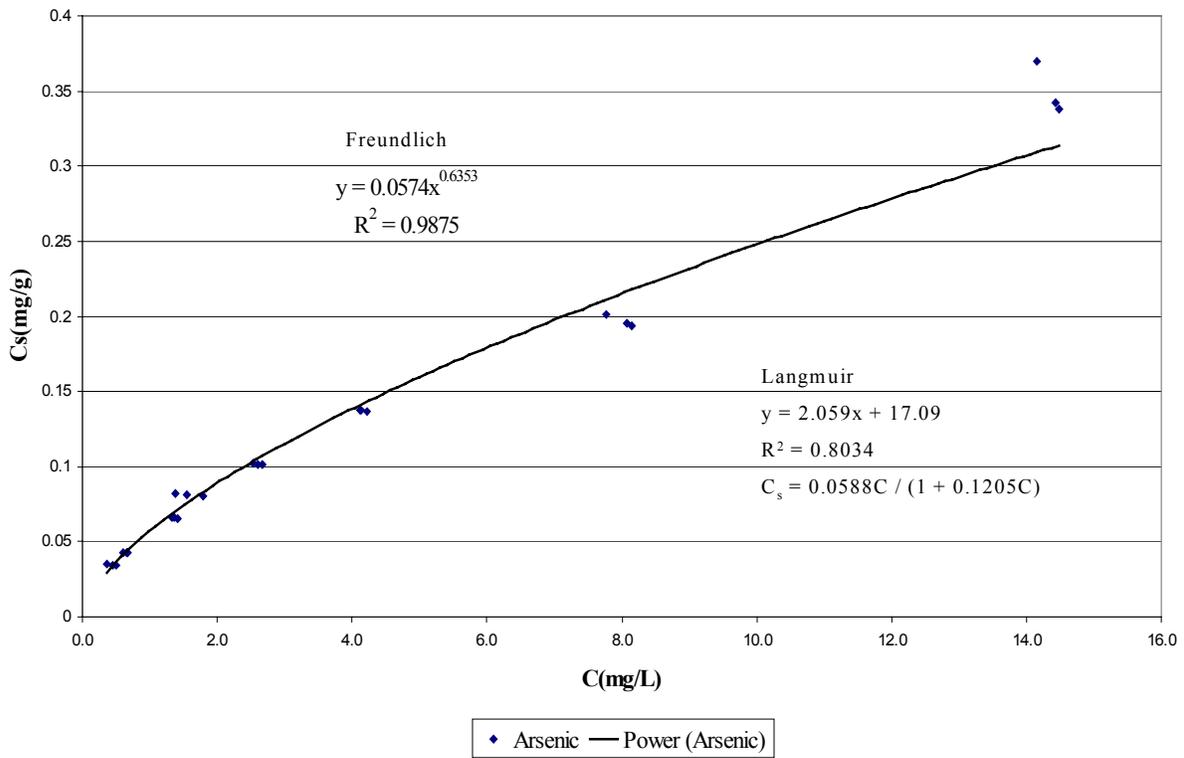


Figure 10.5.2.3 Arsenic sorption data for Woodburn soil.

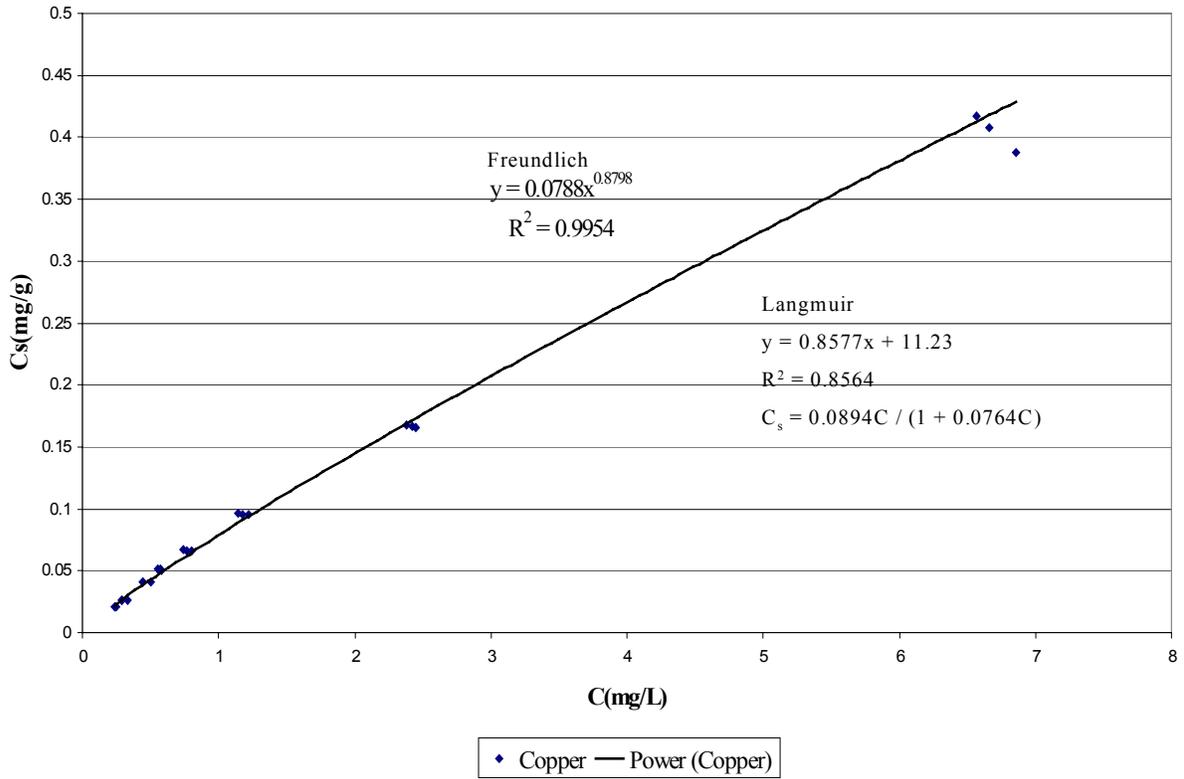


Figure 10.5.2.4 Copper sorption data for Sagehill soil.

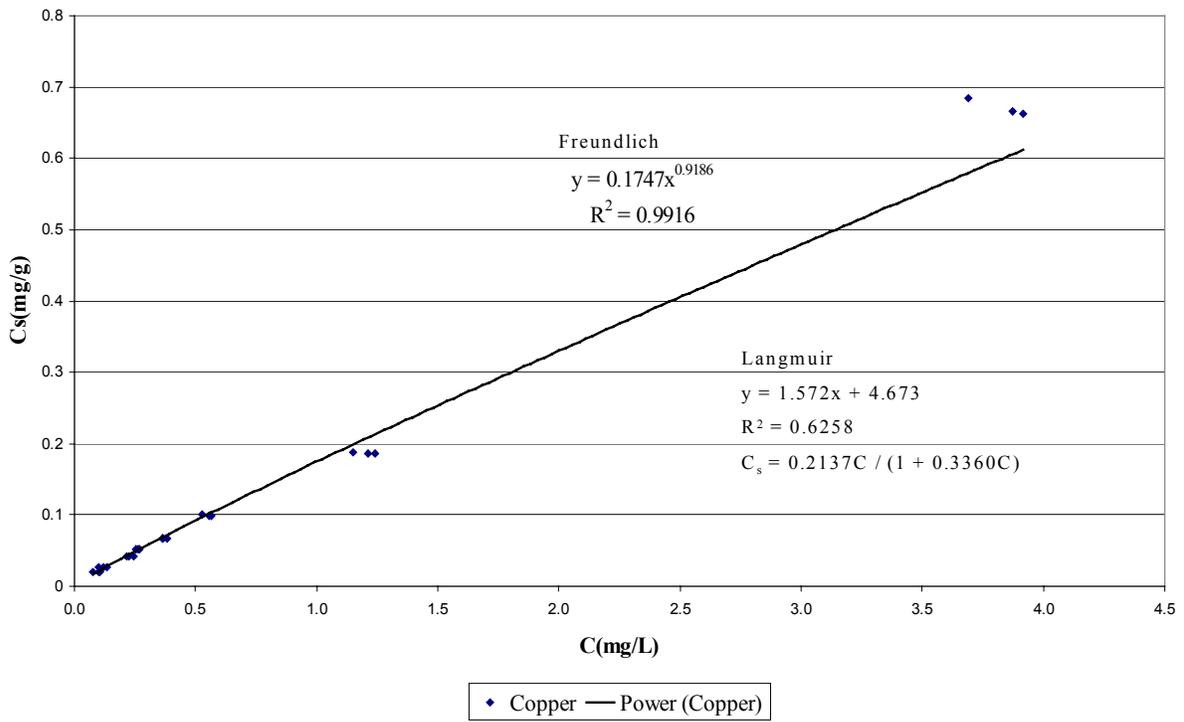


Figure 10.5.2.5 Copper sorption data for Woodburn soil

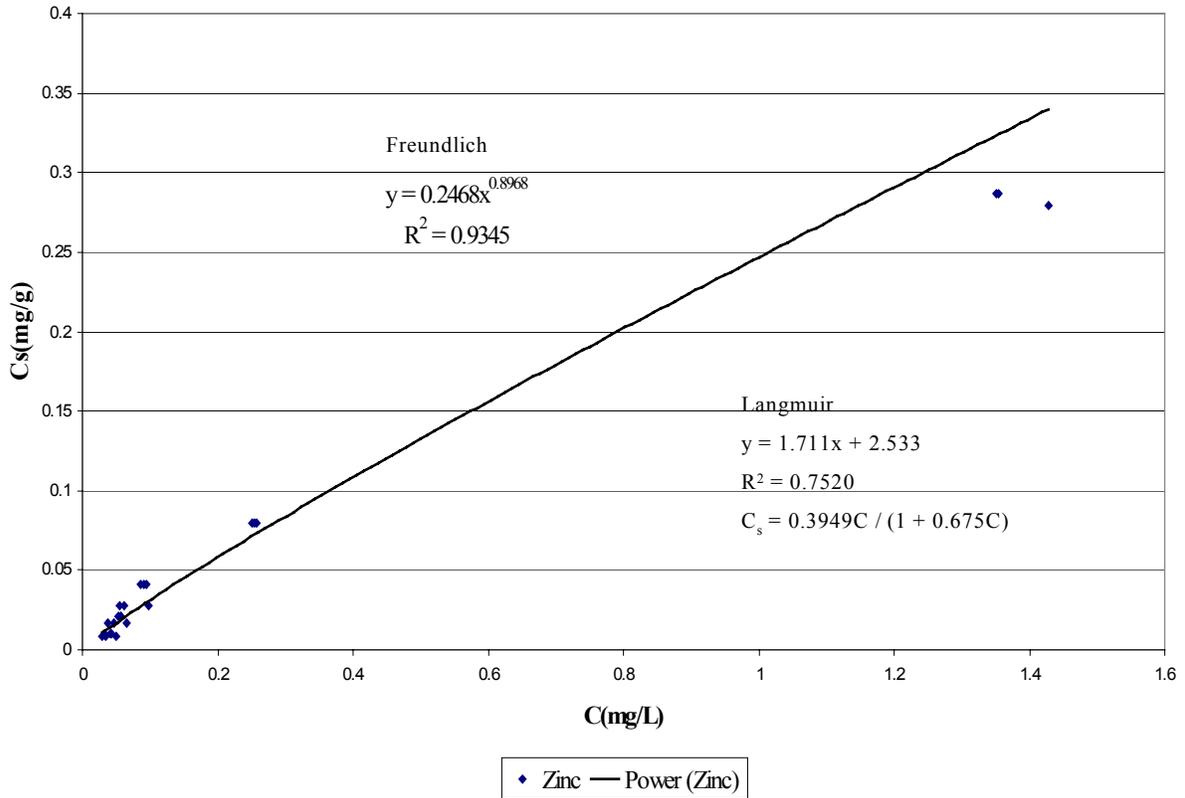


Figure 10.5.2.6 Zinc sorption data for Sagehill soil.

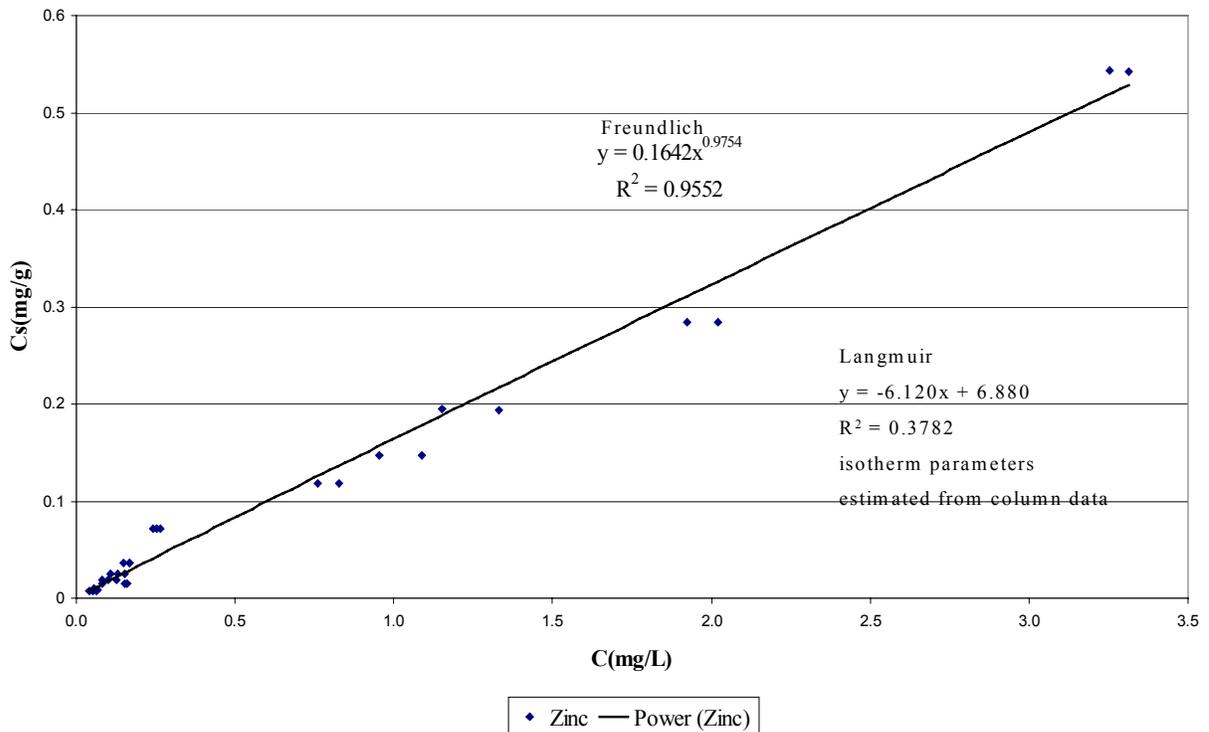


Figure 10.5.2.7 Zinc sorption data for Woodburn soil.

Table 10.5.2.1 Modeling parameters used for column comparisons.

Modeling Parameters		ACZA Column Studies					TCP Column Studies		
		Sage Hill		Woodburn			Soil	Sage Hill	Woodburn
Soil									
column length	50 mm	110 mm		50 mm	2 - 110 mm	200 mm	column length	110 mm	50 mm
porosity	0.37	0.37		0.49	0.52	0.43	porosity	0.50	0.40
bulk density	1.67	1.66		1.59	1.24	1.50	bulk density	1.33	1.58
Leachate					Leachate				
As Source Conc (mg/L)	27.65	27.65		27.65	29.74	29.74	TCP Source Conc (mg/L)	2	2
Cu Source Conc (mg/L)	26.43	26.43		26.43	23.00	23.00			
Zn Source Conc (mg/L)	10.46	10.46		10.46	9.87	9.87			
Column Data					Column Data				
length (mm)	50	110		50	110	200	length (mm)	110	50
volume (ml)	24.6	54.0		24.6	54.0	98.2	volume (ml)	54.0	24.6
pore volume (ml)	9.1	20.1		12.1	28.7	42.7	pore volume (ml)	27.0	9.8
flow rate (ml/hr)	10.0	10.0		10.0	10.0	10.0	flow rate (ml/hr)	10.0	10.0
seepage velocity (mm/hr)	55.1	54.6		41.3	38.3	46.8	seepage velocity (mm/hr)	40.7	51.0
duration of run (hours)	500	460		320	480	650	duration of run (hours)	58	150
Csource -> zero @ (hours)	373.3	402.5		264	307.9	597.2	Csource -> zero @ (hours)	52.7	103
Freundlich Isotherm					Freundlich Isotherm				
Kf	0.0076	0.0788	0.247	0.0547	0.175	0.164	Kf	0.00071	0.0226
N	0.7464	0.880	0.897	0.635	0.919	0.975	N	0.794	0.583
Langmuir Isotherm					Langmuir Isotherm				
Alpha (L/mg)	0.0541	0.0764	0.675	0.121	0.336	2.86	Alpha (L/mg)	0.290	1.66
Beta (mg/g)	0.119	1.17	0.585	0.486	0.636	0.324	Beta (mg/g)	0.0032	0.035

Finally, parameters used in the model runs are shown in Table 10.5.2.1. The values in this table are the measured values of soil properties, solute concentrations in the leachate used for the study, physical parameters of the columns, and isotherm parameters from the sorption data analysis.

In all of the column studies a leachate of constant concentration (the second row of data in Table 10.5.2.1) is pumped into the soil column at a flow rate of 10 mL/hr. After the breakthrough concentrations reached a significant level the influent is switched to deionized water for the desorption phase of the column study.

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

10.5.3 Model Verification Runs

The code of the IMPACT model was adapted to be able to mimic the column studies. The solute concentrations, duration of the model run, seepage velocity, and the time at which the influent

concentration was changed to zero were set equal to the times of the actual column studies. The contact time in the model was set to zero so the time of the model outputs would coincide with the time of the column studies. The model depth was set equal to the length of the columns. The soil physical parameters were entered in the Soil Parameters form, and the isotherm parameters were entered using the Parameters Input form. The dispersivity was set to one tenth the lengths of the columns being modeled as suggested in the dispersivity help form. After entering all the parameters for the Task 1 column study being duplicated, the model was run. Each scenario was run twice, once using Freundlich isotherm parameters and once with the Langmuir parameters.

The data in the Aquifer Inputs sheet were used for comparison with the column data. The data in the column entitled 'Concentration of Water Entering Aquifer (mg/L)' were divided by the influent concentration to give (C/C_0) , a value ranging from zero to one. The values from the real column studies were plotted along with the data from both model runs.

10.5.4 Model Verification Results

The graphs of the results for all ten column comparisons (4 As, 2 Cu, 2 Zn, 2 TCP) between model results and column study data are shown in Figures 10.5.4.1 – 10.5.4.10.

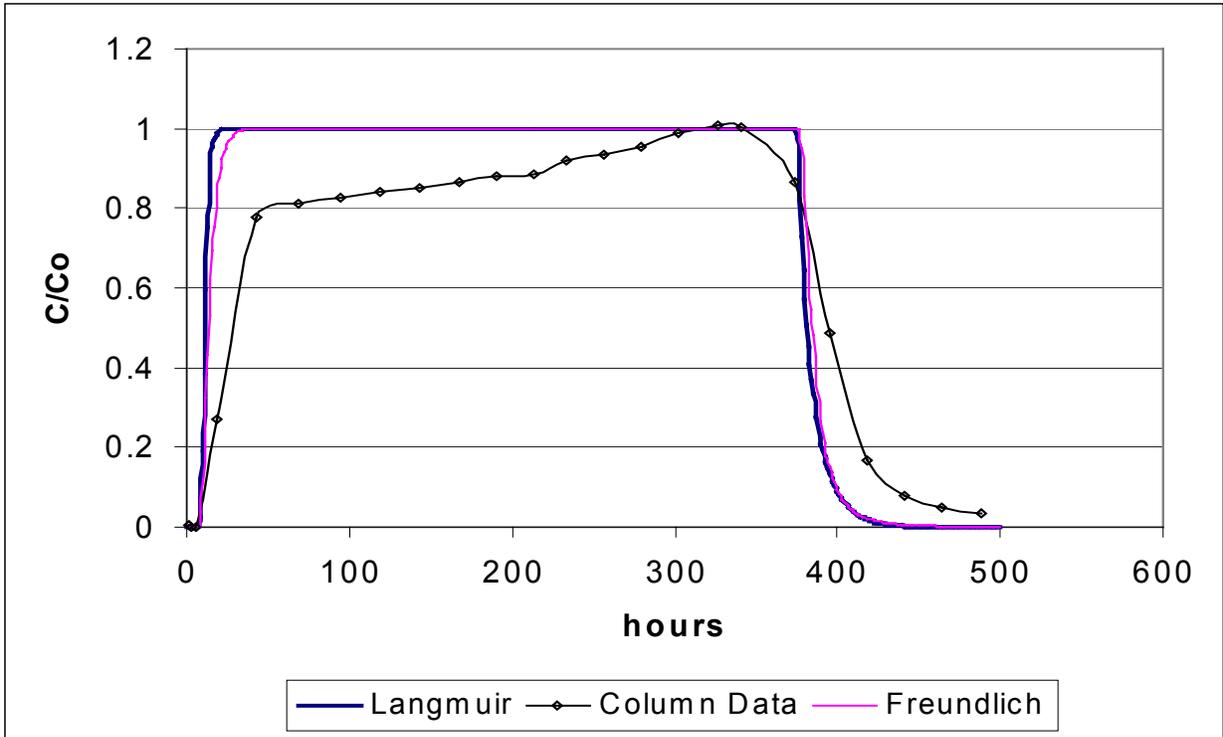


Figure 10.5.4.1 Data for 50mm column comparison arsenic in Sagehill soil.

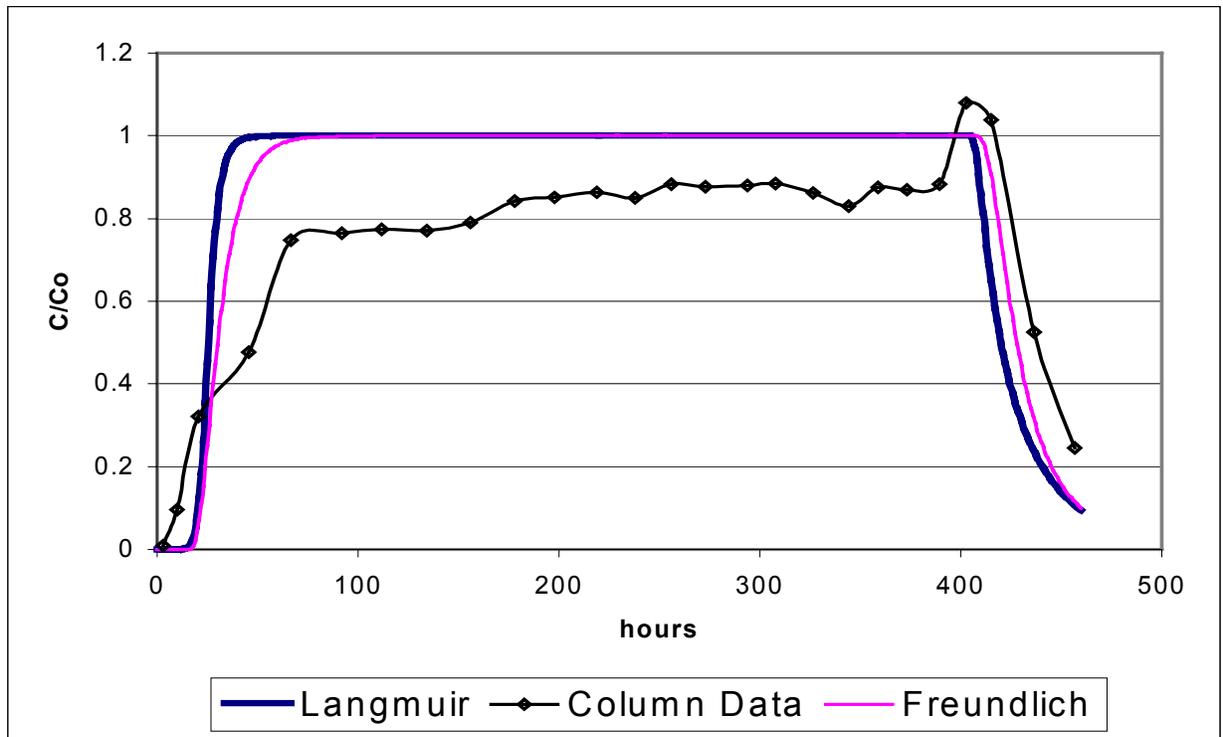


Figure 10.5.4.2 Data for 110mm column comparison arsenic in Sagehill soil.

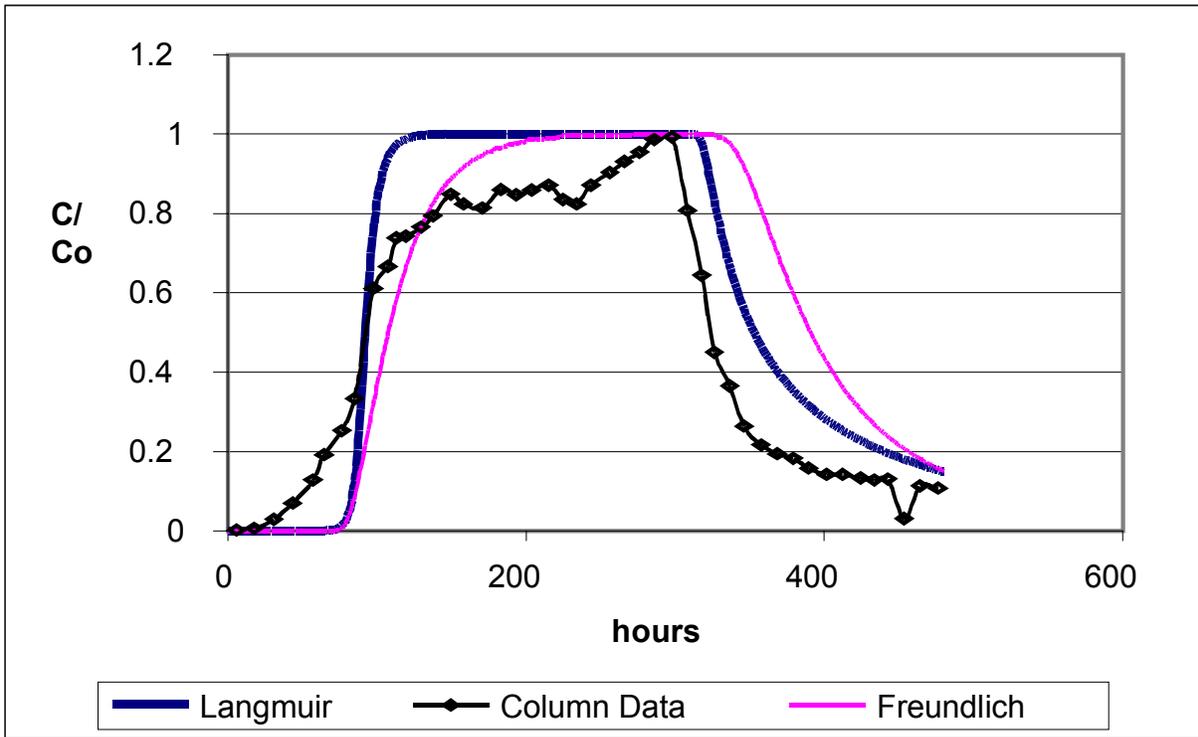


Figure 10.5.4.3 Data for 110mm column comparison arsenic in Woodburn soil

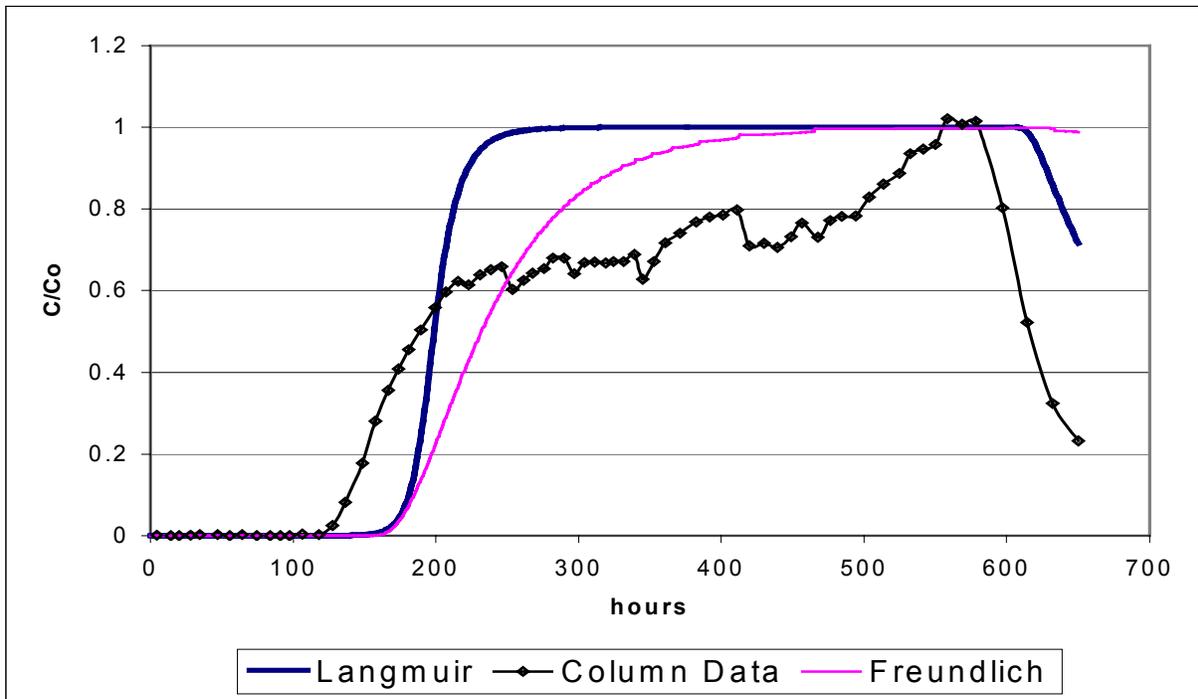


Figure 10.5.4.4 Data for 200mm column comparison arsenic in Woodburn soil.

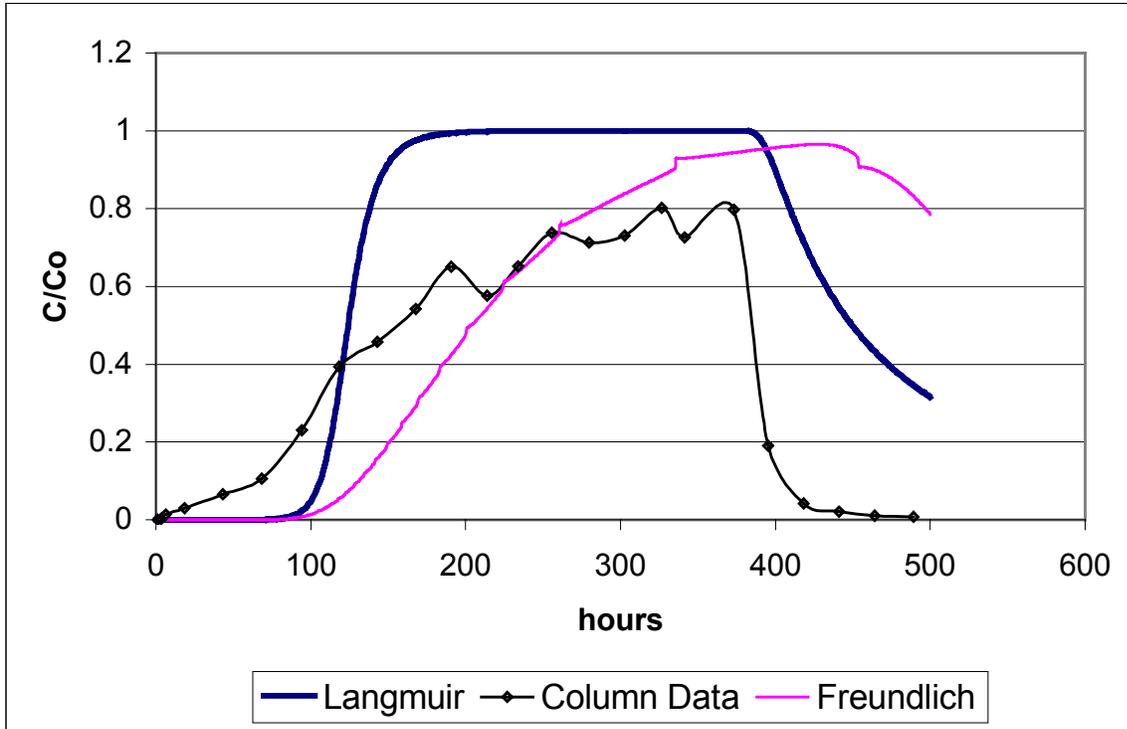


Figure 10.5.4.5 Data for 50mm column comparison copper in Sagehill soil.

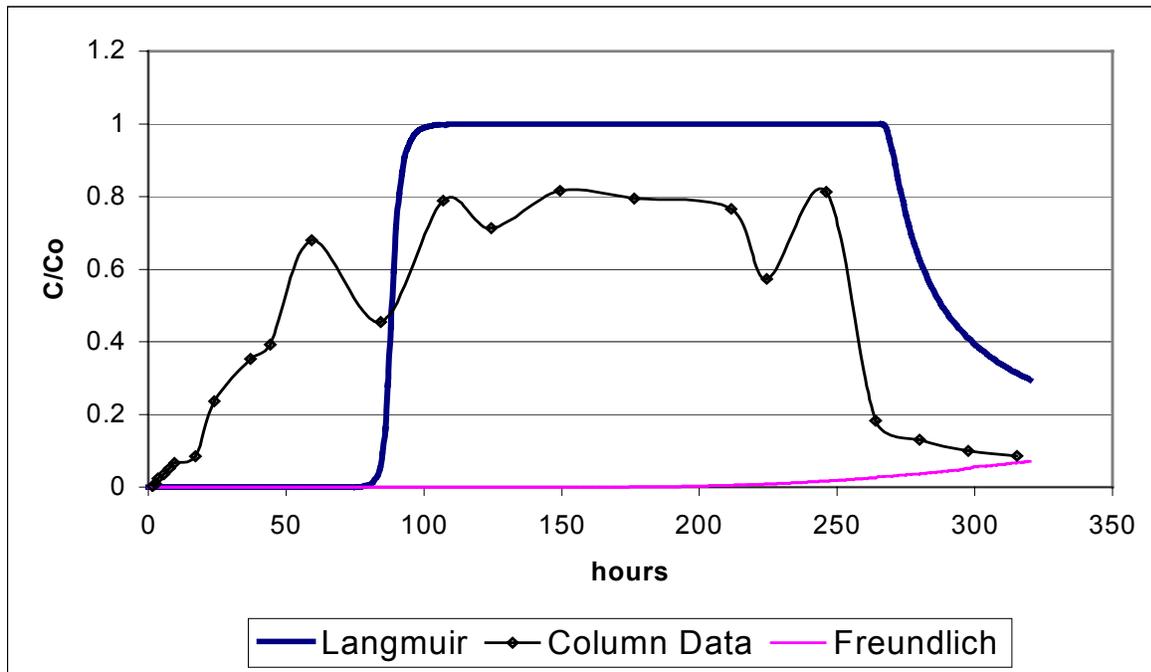


Figure 10.5.4.6 Data for 50mm column comparison copper in Woodburn Soil

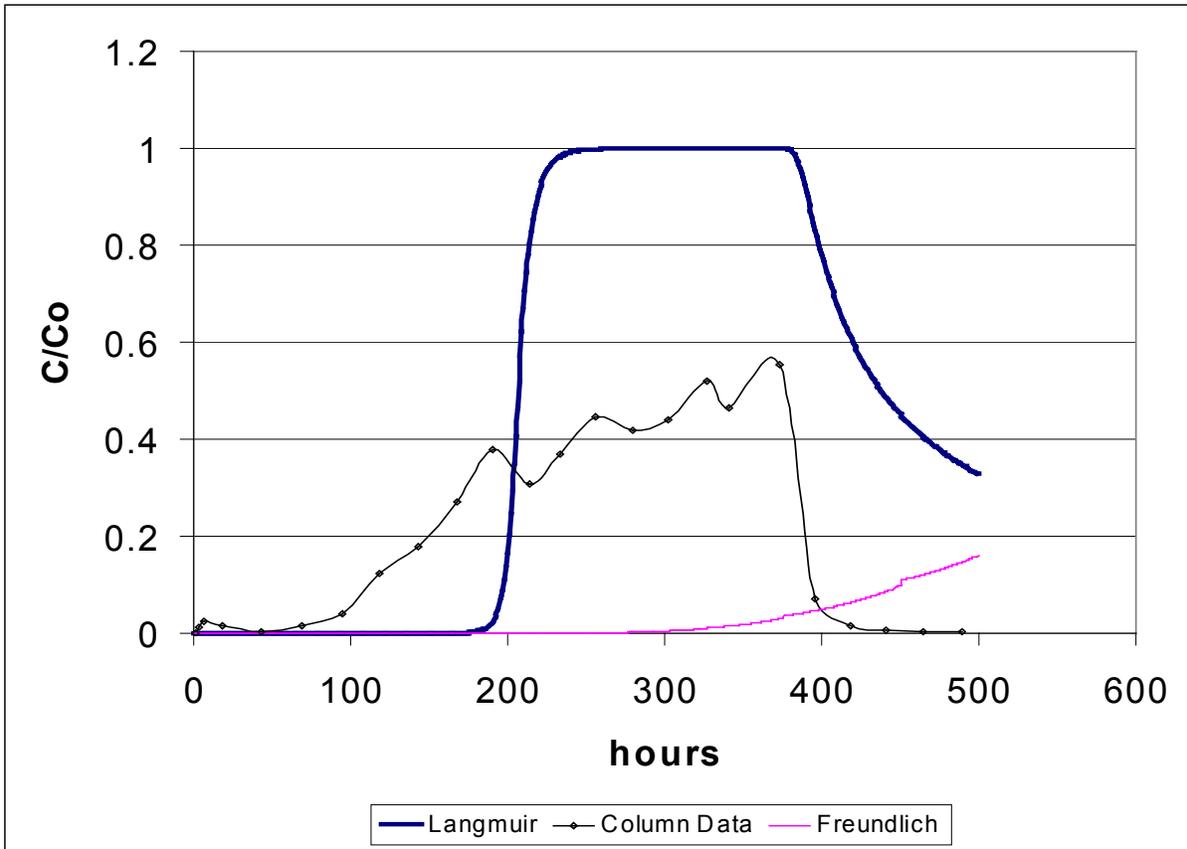


Figure 10.5.4.7 Data for 50mm column comparison zinc in Sagehill soil.

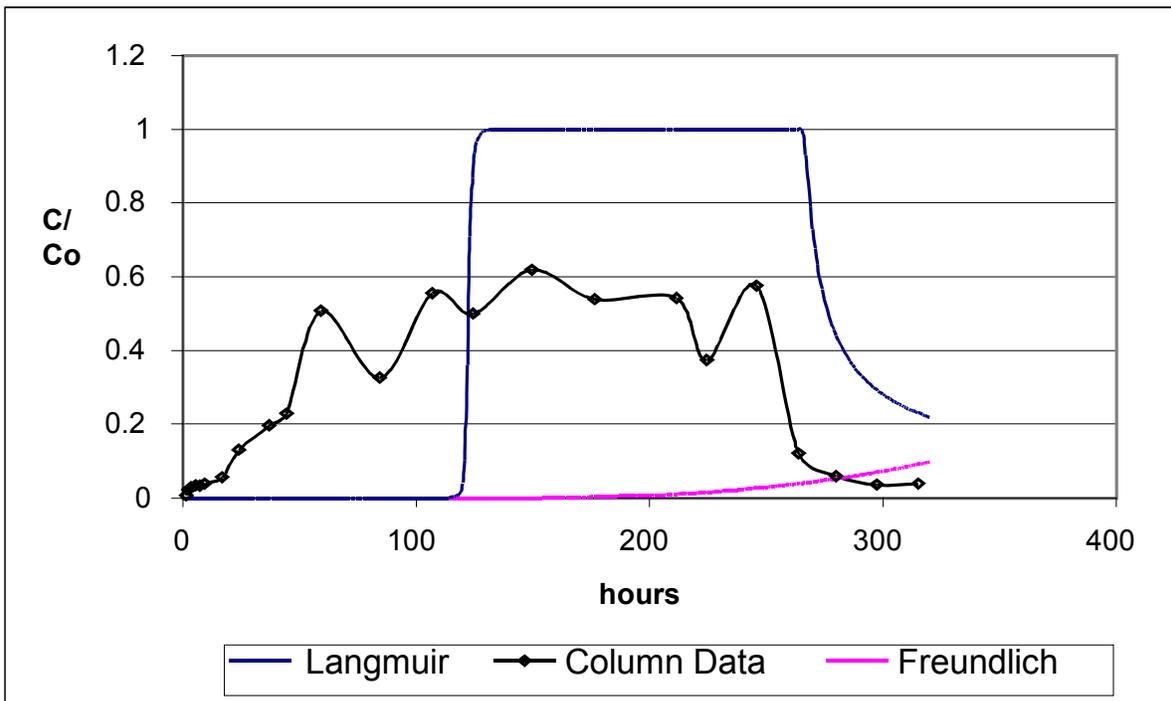


Figure 10.5.4.8 Data for 50mm column comparison zinc in Woodburn soil.

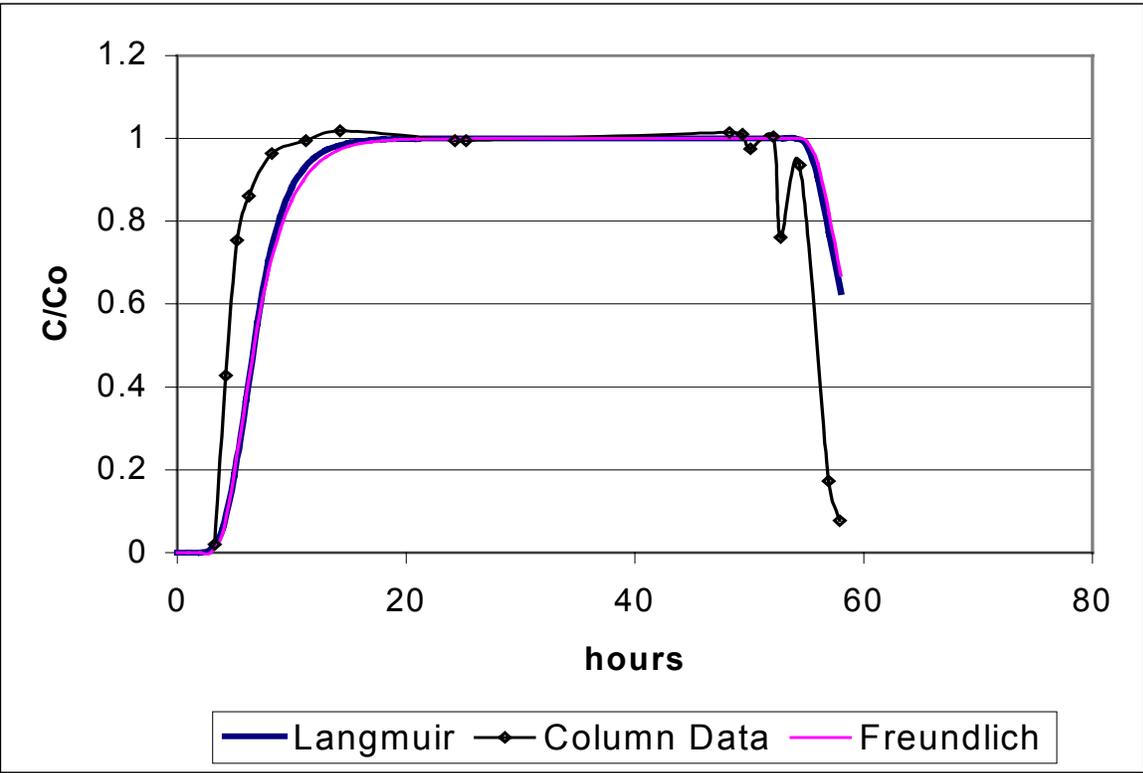


Figure 10.5.4.9 Data for 110mm column comparison TCP in Sagehill soil.

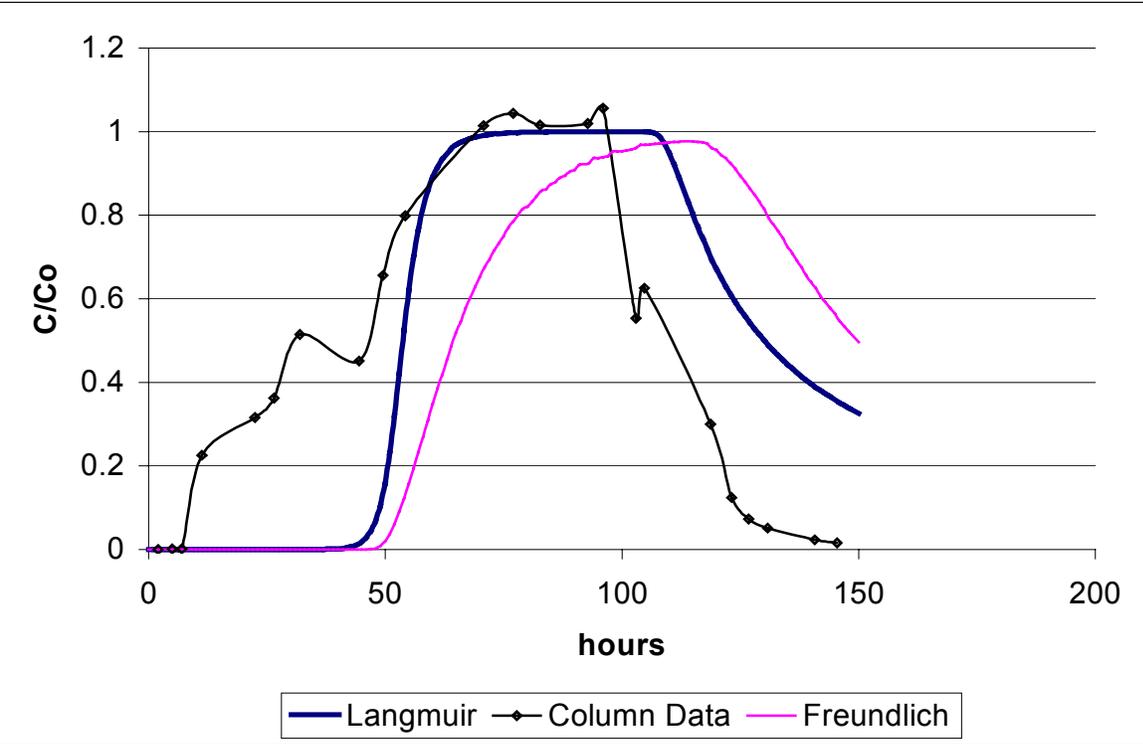


Figure 10.5.4.10 Data for 50mm column comparison TCP in Woodburn soil.

10.5.5 Discussion of Model Verification Results

The model comparisons for arsenic and 2,4,6-TCP gave good results for the Sagehill soil and fairly close results for the Woodburn soil. The model results using the Langmuir isotherm for copper gave C/Co estimates that were around 20% high for both soils. The model runs for copper with the Freundlich isotherm produced mixed results. The fit for the Sagehill soil was mediocre. The time to arrival of the solute front was delayed by about 80% and the decrease in concentration was even more delayed. The results for copper using the Freundlich isotherm with the Woodburn soil were extremely poor, as were the results using the Freundlich isotherm for zinc in both soils. The results for zinc using the Langmuir isotherm were poor for both soils. The time to breakthrough for both runs was much longer than the column study and both model runs overestimated the concentration by about 50%.

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

Table 10.5.5.1 Comparison of modeled leachate concentrations with available concentrations in the sorption data.

Compound or Element modeled	Maximum concentration in solution of sorption data points Sagehill Soil (mg / L)	Maximum concentration in solution of sorption data points Woodburn Soil (mg / L)	Concentration of leachate modeled in column comparisons (mg / L)
2,4,6 TCP	1.90	1.00	2.00
Arsenic	18.24	14.48	29.74
Copper	6.86	3.92	23.00
Zinc	1.43	0.76	10.46

The lack of sorption data in the range of concentrations being modeled appears to result in high estimates of the parameters used in the sorption isotherms (for copper and zinc), which in turn result in high estimates of the mass of material being sorbed by the soil. The high estimates of the sorption parameters accounts for the delay in the time for the solute front to arrive in the model calculations. This results in a somewhat delayed time of arrival for model runs using the Langmuir isotherm and the extremely delayed times with the Freundlich isotherm. Figures 10.5.4.11 and 10.5.4.12 help illustrate the differences observed in model runs with the different sorption isotherms.

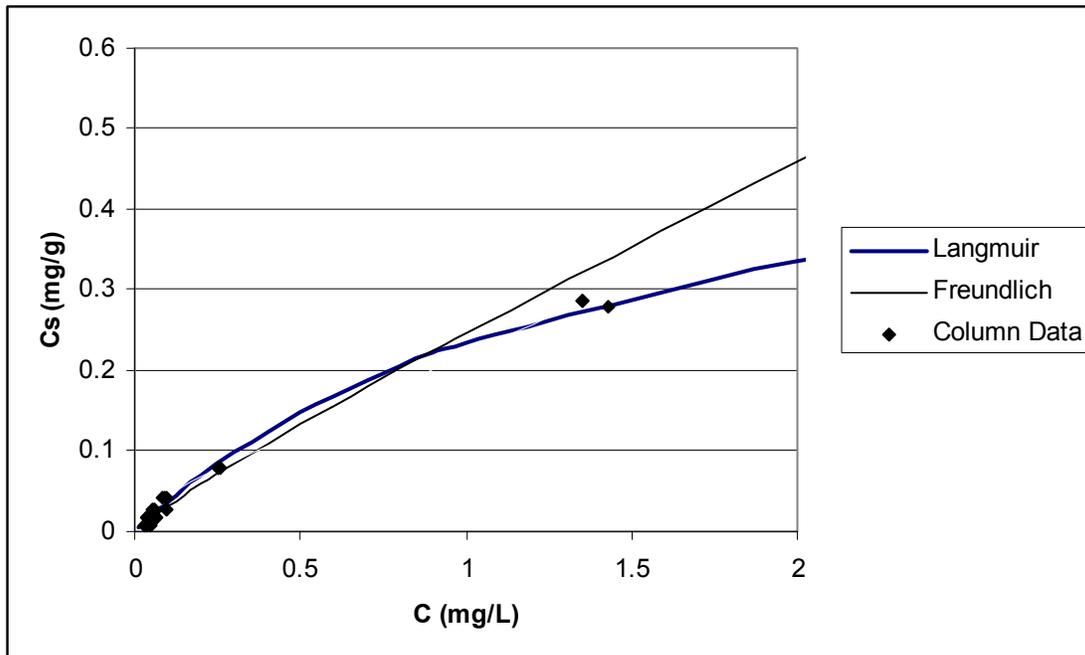


Figure 10.5.4.11 Langmuir and Freundlich isotherm comparison with sorption data for zinc in Sagehill soil

Figure 10.5.4.11 shows the Langmuir and Freundlich isotherms with the sorption data from laboratory experiments used to calculate the isotherms. The highest concentration in solution is 1.4 mg/L after sorption by the soil sample (details of the sorption studies can be found in Nelson et al., 2000c). Due to the nature of the isotherms the predicted sorbed concentrations begin to diverge near the upper limit of the sorption data, but the difference is not large. The predicted sorbed concentrations are 0.284 mg/g for the Langmuir isotherm and 0.334 mg/g for the Freundlich isotherm (or 18% higher than the Langmuir isotherm). This difference is not terribly significant at a dissolved concentration of 1.4 mg/L, but the concentration of zinc in the column study using Sagehill soil was 10.46 mg/L. Figure 10.5.4.12 expands the x-axis to include the concentration of zinc used in the column study.

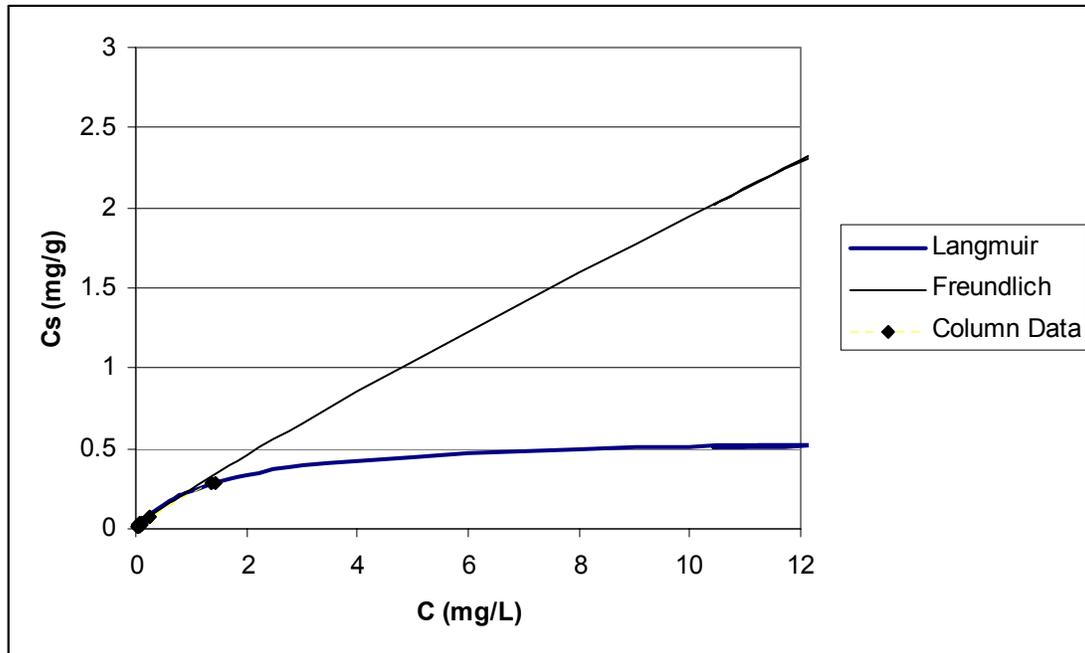


Figure 10.5.4.12 Langmuir and Freundlich isotherm comparison with sorption data for zinc in Sagehill soil

At the concentration of 10.46 mg/L used in the column study, the Langmuir isotherm predicts a sorbed concentration of 0.513 mg/g while the Freundlich isotherm predicts 2.04 mg/g of zinc will be sorbed by the soil. This is nearly 400% (398) higher than the sorbed concentration predicted by the Langmuir isotherm. The Langmuir isotherm resulted in a model run that overestimated the time required for the solute front to reach the end of the soil column. The factor of four difference predicted by the Freundlich isotherm for the sorbed concentration results in the model predicting a drastic difference in the time required for breakthrough of the solute to occur. This same phenomenon applies to the two other column studies (both copper and zinc in the 50 mm Woodburn column study) with drastically delayed times for solute breakthrough. The limited range of concentrations available in the sorption studies contributes to the overestimation of sorbed concentrations with the Freundlich isotherm. The nature of the isotherm itself contributes to the problem as well. The isotherm is a power fit of the sorption data and therefore does not reach a maximum sorbed concentration. Sufficiently large concentrations in the sorption data would help attenuate this problem by eliminating the large extrapolation needed to predict sorbed concentrations at the dissolved concentrations used in the column studies. While this may account for the large time delays for the solute front to reach the end of the soil columns when modeling with the Freundlich sorption isotherms, it does not explain the large difference between the C/C_0 concentrations predicted by model runs with the Langmuir isotherms.

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

phases, 3) bound to reducible phases (Fe and Mn oxides), 4) bound to organic matter and sulfides, and 5) detrital and lattice metals (Ma and Rao, 1997). Four of these possible reaction mechanisms can result in copper and zinc being bound to the soil matrix in a fashion that may not be reversible over the limited duration for desorption in the column studies.

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

Mass balances performed on the influent and effluent in the column studies demonstrate that significant amounts of the zinc and copper remain sorbed to the soil. Estimated amounts of sorbed material remaining in the columns after flushing with deionized water until the effluent concentration approached zero are shown in Table 10.5.5.2. The input values are the total mass of each metal into the column over the time of the test. The mass sorbed is the amount not accounted for in the effluent from the columns.

Table 10.5.5.2 Residual amounts of metals in the soil columns.

Sagehill 50 mm column					
As Input	Cu Input	Zn Input	Sorbed As	Sorbed Cu	Sorbed Zn
mg	mg	mg	mg	mg	mg
94.35	90.15	35.73	16.83 (18%)	48.60 (54%)	27.06 (76%)
Woodburn 50 mm column					
As Input	Cu Input	Zn Input	Sorbed As	Sorbed Cu	Sorbed Zn
mg	mg	mg	mg	mg	mg
68.00	64.98	25.75	12.41 (18%)	25.39 (39%)	14.79 (57%)

Regardless of the cause for the majority of copper and zinc to be irreversibly sorbed, the breakthrough of these metals cannot be modeled under the assumption that the sorption isotherms are reversible. Reversible sorption is one of the assumptions of the model. It is possible that the copper and zinc are not irreversibly sorbed, but that desorption is rate limited. This still contradicts an assumption of the model that the sorbed and dissolved concentrations of a solute are in equilibrium. The result is that the model is conservative in computing total desorption in a time span comparable to that required to sorb the material during the hydrologic event. Estimations of breakthrough curves in the case of column comparisons (or mass loading to an aquifer in real world simulations) exceed the actual results by a factor of about 20 to 50% (for the model runs using the Langmuir isotherm), and this discrepancy increases for larger model depths. In reality, some additional desorption will occur with time, but probably not all. That is, especially for metallic cations, some permanent sorption in the soil matrix is probable, as described earlier.

In spite of the disappointing results for copper and zinc, the comparisons of model predictions to column data still support the use of the model as a screening tool. Results for arsenic and TCP were good. In comparisons utilizing the Langmuir isotherm, the model results were good for arsenic and TCP, fair for copper, and poor for zinc. Model results using the Freundlich isotherm were good for arsenic and TCP, but very poor for copper and zinc. This is likely due in part to the complexities of the sorption of metallic species discussed previously. This may also be because the range of concentration data in the sorption studies for arsenic and TCP were relatively close to the concentrations used in the column studies, while the ranges in the copper and zinc sorption studies were much lower than the concentrations in the column studies (Table 10.5.5.1). The lack of sophistication of the model can be offset by a modeler familiar with transport and fate phenomena able to make educated deductions about how real-world complexities will affect the results predicted by the model. This shortcoming in model results for copper and zinc is more a function of the limited sorption data than the numerical methods of the model.

10.6 DOCUMENTATION

A user's manual has been prepared that provides an inexperienced modeler with the necessary skills and information to be able to use IMPACT. Sufficient detail has been provided to support the experienced modeler as well. Background information is provided on the transport and fate processes incorporated into the model and the estimation of parameters to be used in the model.

Good references for fate and transport parameters include Mills et al. (1985) and Bowie et al. (1985). Hydrologic parameters can be found in references such as Chow (1959), Bedient and Huber (1992) and Maidment (1993).

The user's manual is released as Volume V in this series of reports (Hesse et al., 2000).

10.7 CONCLUSIONS

The transport and fate model developed during this project does a good job of simulating the transport of solutes in the soil that do not undergo reactions other than reversible sorption and biodegradation. Despite the program's inability to model other chemical reactions or complexity in the soil environment that can affect solute transport, it can still prove to be a useful tool for a modeler with an understanding of the processes at work. The modeler needs to have an understanding of how real world complexities, which the model cannot simulate, differ from the model assumptions and apply her or his experience and good judgment in estimating their effects on the results output by the model.

The model is only as good as the parameters input to it, the applicability of the model assumptions and limitations (listed in Sections 10.2.3 and 10.2.4), and how the model results are interpreted and used. Of primary importance for modeling parameters is the sorption isotherm (and the supporting data) and of secondary importance are the physical properties of the soil. It is

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

CHAPTER 11

TASK 10: EVALUATION OF FIELD DATA

11.1 INTRODUCTION

The NCHRP Review Panel collectively has knowledge of and access to various data sets that might be useful for future verification of the model. For Task 10, Panel members have proposed data sets about which they have some knowledge. More detailed information may or may not be readily available, and has been supplied by the NCHRP Panel member if he/she has it. The purpose of this task is then to determine whether individual data sets so offered are suitable for model testing. Model testing as such has not been performed under this task. But the results will be valuable for future efforts at verification of model performance and documented applicability to the “real world” and the engineering workplace.

Criteria used to evaluate a proposed data set include but are not limited to the following:

- Are rainfall, runoff, and water quality data available?
- Are toxicity data available?
- Are hydrographs and pollutographs available or just total flow volumes and loads?
- Are subsurface water samples available?
- Are the data in computerized form?
- Is there an adequate physical description of the site, including maps, plans, dimensions, elevations, photos, drainage design, etc.?
- Can the soils be characterized by type, bulk density, organic carbon content, hydraulic conductivity, etc.?
- Does the site consist of new highway material or is it an operational site that includes the complication of traffic-induced water quality constituents?
- Is there information about the composition of the pavement (if paved), e.g., what waste materials are incorporated, if any? Is similar information available about the composition of pilings, culverts, sealers, etc., that is, about whatever reference environment best characterizes the site?
- Is there a report describing the study that included the data collection effort?

It is too much to expect that all the information listed above would be available for practically any site, but not all is required for most model applications. This task is being used to determine if there are sites that can at least minimally be used for model testing and evaluation. Essential missing information not available upon request to the responsible agency might still be estimated based on library research and the use of engineering judgment where necessary. In this way, “less than perfect” data sets might still be useful for model evaluation.

11.2 BRIEF SUMMARY

Several locations suggested by NCHRP Review Panel members were investigated for possible application of the NCHRP Model. Most of them were found to be unsuitable, primarily because they focused on a single scientific aspect, such as sorption, or they did not correspond to one the model reference environments. A further complication is that some literature was incomplete,

e.g., in the form of unsigned letters, undated proposals, memos, etc. Still others focused on transport of road salting chemicals, not included in this NCHRP study. The relatively few studies of possible usefulness are discussed below.

No field sites were found that contained enough information to exercise the model. The field studies were either at too large a scale (e.g., Cape Cod) or lacking information about inflow concentrations (e.g., northwestern Indiana). But a few studies are discussed below because they relate to the work of this study and because at some time in the future, additional information might be gathered that would allow the NCHRP Model to be applied.

The most likely possibilities for model applications outside of data generated from within this NCHRP project are laboratory column studies conducted elsewhere. Four such studies are reported herein, but there are likely many in the gray literature (e.g., theses).

During the course of this NCHRP study, many other possible data sources were proposed by Panel members. These were all investigated to the extent of the writers' available resources and the outcomes have been reported to the Panel in a separate communication. This is because all the remainder of the proposed field locations are based on either anecdotal information or miscellaneous printed matter that cannot be referenced. The Project Team's summary of this review is provided at the end of this chapter.

11.3 FIELD STUDIES

11.3.1 Cape Cod, Massachusetts

The purpose of this study was to examine the transport and dispersion of solutes in a sand and gravel aquifer (LeBlanc et al., 1991). The work was done by the USGS at a site near the Massachusetts Military Reservation (formerly Otis Air Force Base). A pulse injection into the aquifer was performed in July 1985. Bromide was used as the non-reactive tracer, and lithium fluoride and molybdenum bromide as reactive tracers. The movement of the tracers was monitored for two years in three dimensions down-gradient for distances up to 280 meters with multi level samplers. The lithium and molybdenum clouds were retarded much more than the bromide in the feldspar/quartz sands.

The scale of application of this study is much larger than the scale of the NCHRP Project modeling and reference environments. Furthermore, the NCHRP Model is one-dimensional and with a simplified mechanism for generation of flow. It is not suitable for modeling the Cape Cod data. The USGS is currently applying (circa 1998) their work to transport of solutes in a sewage plume at the Massachusetts Military Reservation.

11.3.2 Bairstow Landfill, Indiana

Measurements were made by the USGS (Bayless et al., 1998) at the Bairstow landfill in northwest Indiana, primarily on leachates from blast furnace slag. In wells in blast furnace slag the pH was 11+. Below the blast furnace slag there was a lake bed sand/glacial till aquifer, which is about 20-30 feet thick where measurements were made. Up gradient, this aquifer had a

pH of about 7. Underneath the blast furnace slag there was a well about 1 foot into the sand/till that showed a pH of about 9. A well about 20 feet into the till had a pH of about 7. The magnitude of groundwater flow in the aquifer/till is unknown and hence how much reduction of pH is due to dilution versus neutralization. However, it is assumed that the blast furnace slag continues to be leached by rainfall but perhaps at a decreasing rate. The USGS in their studies showed that as the pH changed various ions changed valence, etc.

This study includes good chemistry data but it is primarily a leaching study; there is no monitoring of concentrations at the top of the fill. It might serve as test of subsurface model component if pH can be related to concentration of surrogate chemicals. This in turn might require a speciation model, not currently a component of the NCHRP model.

11.3.3 Interstate Highways in Indiana

The Indiana Department of Transportation sponsored studies by Purdue University to investigate runoff from drainage from highway fills that include recycled concrete (Wukasch and Siddiqui, 1996). High pH values caused some vegetation kills and clogging at drains. Alkalinity and pH were measured at drains along three Indiana interstate highway segments, with a goal of determining appropriate treatment measures for high pH. The data might resemble the “fill” reference environment for the NCHRP model and also provide some leaching data for concrete to be compared to NCHRP laboratory results. But the data as presented in the report are insufficient to test the model directly.

11.3.4 Other Field Studies

Some other field studies reviewed relate to the general theme of this NCHRP project, but are not suitable modeling candidates. Leaching from shredded waste tires implanted in two Minnesota roadway sub-grades is compared with leaching from laboratory studies of leaching from “pure” shredded tires by Twin City Testing Corporation (1990). The field sites generally showed lower concentrations of metals and organics, but the study concluded that the use of waste tires as sub-grade materials should be limited to the non-saturated zone in roadways. Two studies characterize calcareous tufa originating from slag in highway embankments (Gupta et al., 1994; Boyer, 1994). McBride et al. (1999) present metals concentrations in leachate from a sludge-amended soil near Cornell University. These studies are listed not as likely candidates for testing of the NCHRP Model but rather as typical of many similar investigations in the literature.

11.4 LABORATORY STUDIES

11.4.1 University of Tennessee Column Studies

Smoot et al. (1997) of the University of Tennessee present data similar to Phase III column studies of NCHRP project; however, enough detail for modeling awaits completion of a masters thesis by A. Turpin (scheduled for completion in 2000). The purpose is to study ion removal in soils to be used as infiltration beds in stormwater infiltration ponds. Each of 60 simulated storms consisted of adding 6 liters to each of three columns. The columns were 3-inch diameter. The peat content (dry) of each column was: 415 grams in column 1 and 421.5 grams in column 2

(column 3 had carbon and no peat). The thesis should provide the detailed concentration vs. time (or pore volume) needed for model simulation.

11.4.2 Washington State University Column Studies

The Washington State University (WSU) column studies were conducted for a similar reason as those at the University of Tennessee: to investigate the suitability of certain soils in Washington State for use in stormwater infiltration ponds (Hathorn and Yonge, 1996). Simulated stormwater was placed in the top 90 cm of a 180 cm long, 30 cm diameter PVC column. Natural soils were placed in the bottom 90 cm and sorption of metals (Cd, Cu, Pb, Zn) was studied as the “stormwater” drained by gravity through the soils. Generally, metals removal increased with organic carbon content of the soils. With some additional information, these data might be used to test the NCHRP model similarly to Phase III column studies. One other plus is that Oregon State University provided some toxicity evaluations for some of the leachate provided by WSU. This is the only study for which toxicity data might be available in the same way they are for OSU experiments.

11.4.3 Other Column Studies

There are likely very many column studies reported in the literature that might be useful for NCHRP Model testing, but the writers have not attempted an extensive literature review since the original thrust of this Task 10 was to investigate field sites. However, two additional studies will be mentioned. Chichester and Landsberger (1996) investigated the leaching behavior of 33 elements in municipal solid waste fly ash. The fly ash sample was leached using double deionized water in a column apparatus. Camobreco et al. (1996) studied the transport of metals through soil columns in a study of movement of metals contained in sewage sludge, and their laboratory study complements the field study of McBride et al. (1999). Both column studies show break-through curves that might be useful for model comparisons.

11.5 SUMMARY

None of the field studies discussed above include comprehensive enough measurements or are focused enough on the strict highway environment to be useful for testing of the NCHRP Model. There are a considerable number of studies (referenced in Volume II of this study, Eldin et al., 2000) related to nonpoint source runoff from operational highways. Generally, these studies cannot be used to test the leaching component of the NCHRP Model because of the mixture of possible source mechanisms. Although it is possible that some soil sorption data might be found, the uncontrolled nature of these studies is much less preferable to the controlled studies conducted during this NCHRP Phase III work at OSU and possibly other column test studies listed above. Other soil migration data, such as the northern Indiana USGS studies, typically are lacking some key element necessary for the model, such as the groundwater flow rate or the “entering” concentration of material through a soil layer.

The other problem with using field data is that many of the data are not taken in the immediate highway environment such that they may be represented by one of the reference environments present in the NCHRP Model. It still may be possible to find some groundwater transport measurements that the NCHRP Model could possibly simulate, but in most cases, a much better

option would be to use a conventional groundwater quality model for this purpose and not try to “stretch” the capabilities of what was designed as a screening model for the immediate highway environment.

CHAPTER 12 SUMMARY AND CONCLUSIONS

12.1 PHASE III RESEARCH SCOPE

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

Phase I focused on a broad screening of common C&R material to identify the extent of the problem and to guide the succeeding phases. Phase II focused on analysis of leaching characteristics of C&R materials, full development of a predictive computer model, and the validation of the overall evaluation methodology. Phase III has focused on additional laboratory testing to validate modeling assumptions, to expand the current data base, and to compare laboratory testing and leaching methodologies with conventional EPA procedures. The predictive model itself has been enhanced and documented.

Phase III work was broken down into ten separate tasks. Tasks 1 – 8 dealt with verification and refinement of the laboratory testing methodology, while tasks 9 and 10 involved enhancements to the computer fate and transport model and evaluation of data set requirements to run the model.

In Task1, **Confirmation of Phase II Methodology**, confirmation of the Phase II methodology was examined at laboratory scale by linkage of leachate generation to soil columns to represent the impermeable highway, piling, and fill reference environments. Full confirmation of the Phase II methodology was not possible at the laboratory scale due to constraints on the size of flat-plates that can be tested resulting in limitations on the volume of leachate that can be generated for RRR testing. Because of these constraints, the methodology was tested in relation to RRR processes in soil columns using leachate generated by the short-term batch leaching procedure.

Task 2 is titled **Leaching From Flat Surfaces With and Without Soil Confinement**. Under field conditions, environments exist in which a flat, impermeable surface is buried in soil, and thus leaching occurs under confined conditions (soil is packed against flat surface). The Phase II methodology does not directly address leaching under these conditions, but implicitly assumes that leaching flux is not affected by confined conditions. The purpose of Task 2 was to confirm whether leachate flux from flat, impermeable surfaces is affected under confined conditions. These conditions are relevant to the reference environments of piling, fill, and culverts.

Task 3 is titled **Effect of Scale On Flat-Plate Leachate Composition**. An assumption of the flat-plate leaching test is that the contaminant flux from the C&R material surface is directly proportional to surface area and thus scaleable to field conditions. However, testing at the laboratory scale because of various scale effects can poorly represent field results. Determining

scale effects is difficult because of the problems associated with preparation and handling of large test specimens. The research approach involved conducting flat plate experiments with samples of varying size. All other variables including leaching solution, testing time, and C&R material were held constant. The objective of Task 3 was to determine whether scale effects exist for chemical leaching with water in the flat-plate leaching test of highway C&R materials.

In Task 4, **Tests of Portland Cement and Portland Cement Concrete (PCC) With and Without Plasticizer**, Tilbury cement PCC (with and without plasticizer admixture) was subjected to the complete Phase II testing methodology to determine leachate characteristics and parameters for the removal/reduction/retardation (RRR) factors in the fate and transport model. Laboratory tests included batch and long-term leaching, flat plate leaching, and sorption to Sagehill and Woodburn soils. Photolysis, volatilization, and biodegradation tests were performed on the leachate and on separately prepared solutions of the plasticizer.

In Task 5, **Determine a Range of Typical Adsorption and Desorption Parameters for C&R Materials on Sand and Gravel Utilized in Unbound Pavement Layers and Shoulders**, typical adsorption and desorption parameters for C&R materials were determined for a range of soils and of sand and gravel materials of varying physical and chemical characteristics. Results of laboratory adsorption experimental data were expressed in isotherms as mass adsorbed per unit mass dry solids (C_s) versus the concentration of the constituent (C) in solution. Equilibrium isotherm models were used to determine the maximum adsorption and desorption capacities and distribution coefficients from the experimental data. By gaining an understanding of these factors, conclusions can often be drawn about the impact of sorption on the movement and distribution of contaminants in the subsurface. Failure to account for sorption can result in significant underestimation of the mass of a contaminant at a site and of the time required for it to move from one point to another.

Task 6 is titled **Aging Effects In C&R Materials**. The effect of exposure time to the environment for highway materials has been termed aging. Environmental factors that could affect materials include time for solid or crystalline formation, exposure to air/oxygen, exposure to heat, and wet/dry cycles. In this task, the effect of aging was measured with flat plate experiments using open graded asphalt concrete (AC) amended with selected C&R materials. The various forms of aging were tested using Strategic Highway Research Program (SHRP) protocols and compared to the results for “new” amended AC. The forms of aging evaluated were the effect of heat, the effect of oxygen, the effect of exposure time, and the effect of wet and dry cycles of exposure.

In Task 7, **Comparison of Laboratory Test Protocols with EPA Protocols, Determination of Test Statistical Variability, and Preparation of User's Manual**, confirmation was obtained that the project's standard testing methods and QA/QC protocols are consistent with published EPA methods and protocols by undertaking a thorough review and comparison between the project's methods/protocols and those of EPA. For leaching and environmental effects (RRR) processes, new test methods were developed as a part of this research, and thus no standard accepted procedures exist from EPA or other agencies. Standard QA/QC protocols specific to these tests had been developed. In this task, the laboratory testing methods and QA/QC protocols for the leaching and RRR process tests were thus developed, refined and validated. As

a part of this process, replicate testing on all methods was performed to define the variability and degree of confidence of the results using statistically determined parameters (coefficient of variation, precision). To do this, a standard asphalt, called “standard asphalt cement concrete” (SACC), was developed that contains two model toxicants, one metal (zinc) and one organic (TCP).

A user’s manual describing the overall screening methodology and laboratory test protocols (Environmental Impact Of Construction And Repair Materials on Surface and Ground Waters, Final Report, Volume IV: Laboratory Protocols, Nelson et al., March 2000b) has been developed as an additional part of this task. This covers the overall screening methodology and contains detailed leaching and RRR process test methods and associated QA/QC protocols, and in addition includes the biotoxicity tests and the chemistry test methods and associated QA/QC protocols. The manual has been prepared and bound as a stand-alone document to facilitate distribution to government agencies and other future users.

In Task 8, **Leaching Methods Comparison Study**, comparison is made between the distilled water leaching procedure of this study (short-term [24-hr] batch leaching procedure) and EPA's standard TCLP test (Toxicity Characteristic Leaching Procedure; EPA Method 1311) and SPLP test (Synthetic Precipitation Leaching Procedure; EPA Method 1312). A carefully controlled laboratory comparison study was conducted of leaching results from the distilled water and EPA procedures applied to C&R materials assemblages. Leaching results included, as applicable, inorganic compounds (primarily metals), organic compounds, leachate TOC, and solution pH. Comparison between methods was made by statistical techniques.

In Task 9, **Model Enhancement**, the computer fate and transport simulation model developed in Phase II, which operated on a simple storm-event basis, was enhanced to account for presumed decrease in release of constituents with flushing time and for the possibility of desorption along the subsurface pathway. One of the principal changes to the model was to include a continuous simulation option. The simulation follows the pathway of the water to the site boundary, including the possibility of lateral groundwater flow. Sensitivity analyses were made and documented for user guidance, and the knowledge base for model parameters was expanded. Additional minor improvements and changes have been made. The database portion of the model has been updated to encompass all results of Phases I and II as well as any new information from Phase III. The model has been tested on a limited basis using experimental data from Task 1, in order to document model capabilities and prepare examples for documentation for the end user. More extensive applications could follow as a future additional work item from the data set evaluation of Task 10. A formal User’s Manual (Environmental Impact of Construction and Repair Materials on Surface and Ground Waters, Final Report, Volume V, IMPACT, User’s Guide, Hesse et al., 2000) was prepared for model dissemination.

For Task 10, **Data Set Assessment**, the NCHRP Review Panel members proposed data sets for which they had detailed information. This information (and as much of the data as feasible) was transmitted to the project team for evaluation. The team then determined whether individual data sets so offered were suitable for model testing. Model testing as such was not performed under this task. But the results will be valuable for future efforts at verification of model performance and documented applicability to the “real world” and the engineering workplace.

12.2 PHASE III CONCLUSIONS

The following conclusions resulted from Task 1, **Confirmation of Phase II Methodology**.

Soil columns are able to effectively represent retardation and removal of leachate constituents by adsorption and biodegradation processes.

For ACZA leachate, the mixture of metals (As, Cu, Zn) was differentially retarded by soil. Arsenic, present as the oxyanion arsenate (AsO_4^{3-}), was the least retarded, followed by copper (Cu^{2+}) and zinc (Zn^{2+}). It is hypothesized that copper was retarded less than zinc due to possible soluble complexation with organic compounds, either from ACZA leachate (50-150 mg/L TOC) or from the soil organic matter (approximately 400-650 mg/L TOC after column break-in period).

TCP leachate in soil columns exhibited retardation by sorption and removal by biodegradation processes. Sorption of TCP was reversible, and TCP was desorbed from the soil columns when flushed with deionized water.

Soil column mass balances showed that sorbed concentrations of ACZA metals and TCP at saturation (C_s values) were equivalent to those predicted for isotherms derived from batch reactor data for the Woodburn soil, but 2-4 times greater for Sagehill soil.

For the ACZA leachate, arsenic, being more weakly sorbed, was more rapidly desorbed, followed by Cu and Zn, when soil columns were flushed with deionized water.

Overall, soil column studies on ACZA and TCP leachates confirmed the importance of sorption and biodegradation processes as components of the full C&R materials leachate evaluation methodology.

The following conclusions resulted from Task 2, **Leaching From Flat Surfaces With and Without Soil Confinement**.

The effect of confinement on leaching was tested with an embedded pile in a soil column under confined and unconfined conditions. Clean sand packed around the pile was used to test the effect of soil confinement on leaching rate, while large glass beads (for mixing control) around the test materials served as the no-confinement control. Distilled water was pumped through the column, and contaminants were leached from the outer surface of the embedded piles into the flowing water and through the packing materials (sand or beads). Sand serves as the confining soil but is a weak adsorbent, thus allowing leached constituents to elute from the column for measurement. For the unconfined surface, the column is packed with large glass beads (marbles) for flow and mixing control (to avoid turbulent eddies and axial mixing not present in the sand-packed column). Adsorption to the glass beads is expected to be negligible due to the small total surface area and weak adsorption affinity. The tests were conducted with two C&R materials in piling configurations, PCC with plasticizer in poured columns, and wood posts preserved with ACZA.

For most tests, concentrations of leachate constituents (e.g., As, Cu, and Zn for ACZA-treated wood posts) increased initially at a somewhat greater rate for the unconfined pile compared to the confined pile, but reached the same final concentrations. Overall, results of metals in leachates from the ACZA-treated wood posts and PCC piles show that the rates of leachate released from impermeable surfaces, such as piling, fill, and culverts, are largely unaffected under confined conditions.

The following conclusions resulted from Task 3, **Effect of Scale On Flat-Plate Leachate Composition**.

Flat plate experiments with samples of varying size were conducted under controlled conditions such that other variables, including leaching solution composition, testing time, and C&R material, were held constant. The objective of Task 3 was to determine whether scale effects exist for chemical leaching with water in the flat-plate leaching test of highway C&R materials. The flat plates were made of a municipal solid waste incinerator bottom ash (MSWIBA, from New England) asphalt cement mix (MSWIBA-AC). MSWIBA-AC leachates have demonstrated toxicity in Phase I-II testing and contain a mixture of both metals and organic compounds. Flat plate samples made of a MSWIBA asphalt cement mix (MSWIBA-AC) were tested in three sizes that yielded surface area ratios of 1 to 2.25 to 18.55.

Results of metals and TOC in leachates from flat plate specimens of varying size show that the contaminant flux from the three different flat-plates is directly proportional to surface area, and thus is scaleable to field conditions. However, testing at a laboratory scale can poorly represent field results because of the possibility of a non-homogeneity in a small-sized (e.g., 4-inch cylinder) flat plate.

The tests just described were conducted at the same ratio of elution volume to surface area for the three different size flat plates. Additional tests conducted under this task and during Task 8 show that concentration decreases inversely and linearly as this ratio increases. That is, the greater the volume of water relative to the leaching area, the lower the concentration. This validates one assumption of the fate and transport model.

The following conclusions resulted from Task 4, **Tests of Portland Cement and Portland Cement Concrete (PCC) With and Without Plasticizer**.

Both PCC-with and without-plasticizer leachates showed high levels of calcium (~700 mg/L) and significant levels of aluminum (2-5 mg/L) in them. PCC-with-plasticizer had slightly higher levels of TOC compared with PCC-without-plasticizer.

Algal growth inhibitory effects by PCC leachates were attributed to phosphorus limitation and coprecipitation due to high levels of calcium and aluminum at alkaline pH. The higher inhibitory effect exhibited by PCC-with-plasticizer leachate compared with PCC-without-plasticizer could be due to the additive effect of plasticizer along with calcium and aluminum.

In batch sorption studies, Woodburn soil showed greater sorption capacity for calcium than Sagehill soil. Similarly, Woodburn soil showed greater removal of toxicity than Sagehill soil. In

addition, aluminum and TOC were released from Woodburn and Sagehill soils to the PCC leachates, and thus a simple relationship for aluminum and TOC sorption could not be derived from sorption studies.

No substantial change in organics was observed due to photolysis of PCC leachates. Toxicity results also indicated no significant change ($p > 0.05$) between controls and photolysis samples.

In general there was a good correspondence between the toxicity and chemistry data of the PCC leachates generated during the leaching and RRR processes testing methodology.

The following conclusions resulted from Task 5, **Determine a Range of Typical Adsorption and Desorption Parameters for C&R Materials on Sand and Gravel Utilized in Unbound Pavement Layers and Shoulders.**

Different soils and sand/gravels were used to adsorb the constituents of ACZA leachate, namely arsenic, copper and zinc. Using the adsorption data, isotherms were constructed for the different materials. From a comparison of the distribution coefficients, it was found that zinc was the most strongly adsorbed followed by copper and then by arsenic.

Arsenic adsorption is relatively lower because the pH of the leachate was around 6.5-7.0 in the case of soils, and 8.8-9.0 in the case of sand/gravels. Arsenic adsorption is higher at lower pH and decreases as pH is increased (being an oxyanion). At higher pH values, the surface hydroxyl groups are deprotonated resulting in an increased negative charge on the soil, and this reduces the adsorption potential of arsenic on the soils.

Copper adsorption was found to be lesser when compared to that of zinc. Although the literature suggests that copper is more strongly bound than zinc, the presence of high amounts of soluble organic matter in both the leachate and the soils (particularly Woodburn) are possible reasons for the reversed trend. Since copper forms soluble organo-metal complexes preferentially over soil adsorption complexes, this results in fewer copper ions available for adsorption onto soil sites. Evidence for this hypothesis was seen in the decreased partition coefficients for the sand/gravel materials (which contain much smaller quantities of organic matter) compared to soils.

Zinc was found to be adsorbed the most, by all the materials. Since zinc has a weaker tendency to form organic complexes preferentially over adsorption onto soil inorganics, its adsorption was less affected by the varying amount of organic materials present.

Amongst the soils, Woodburn adsorbed all metals highest, followed by Sagehill soil. The sand/gravel mixtures adsorbed the metals the least, although all three still adsorbed some. This is reasonable based on the composition of the individual materials (lower organic matter content and lower clay and silt fractions).

The following conclusions resulted from Task 6, **Aging Effects In C&R Materials.**

Short-term aging (135°C for 4-hours) did not show any significant change in both toxicity and

chemistry. Long-term aging (85°C for 30-days), however exhibited significant reduction in algal toxicity after 360- and 720-hours of aging.

No simple relationship was observed between the toxicity reduction in aged samples and chemical components. TOC levels in aged samples remained largely unchanged even after 30-days of oxidation under 10 atm pressure. Apparently, during the aging process, either aluminum speciation changes (e.g., formation of inorganic or organic soluble complexes) or the effects of oxidation and volatilization reduced the toxicity of leachable soluble organic compounds without affecting the TOC substantially.

MSWIBA-asphalt leachates generated from wet and dry cycle tests had aluminum levels ranging from ~3 mg/L to 25 mg/L. Results indicated a significant correlation ($p < 0.01$) between %EC50 values and aluminum levels in MSWIBA-asphalt leachates.

A similar trend in the reduction of toxicity for both “wet” cycle (continuous leaching without dry exposure) and “wet and dry” cycle tests (with intermittent exposure to dry air) was observed. This consistent pattern in toxicity reduction with increasing wetting hours both in samples with and without intermittent exposure to dry air strongly agreed with leaching behavior of chemical components (aluminum and TOC in particular) as well.

Comparing “wet and dry” cycle and “wet” cycle only indicated that the leaching of chemical components from MSWIBA-asphalt occurs simply as function of wet-weather hours regardless of interruptions by dry weather. This confirms an important modeling assumption.

The following conclusions resulted from Task 7, **Comparison of Laboratory Test Protocols with EPA Protocols, Determination of Test Statistical Variability, and Preparation of User's Manual**.

A method of incorporating toxic substances into a standard asphalt (standard asphalt cement concrete, or SACC) was developed that generates acceptable toxic leachate concentrations. The selected toxicants were easily determined by common analytical methods and are of known toxicity in the standard toxicity tests using algae and daphnia. The toxicants were zinc as the metal, as it is already a reference toxicant, and 2,4,6-trichlorophenol (TCP) as the organic compound, which besides being readily determined by gas chromatography, undergoes the degradation processes of volatilization, photolysis, and biodegradation. The SACC was formulated as a typical ODOT assemblage with the inclusion of Zn and TCP as toxic materials. Both Zn and TCP are added in chemical forms that are soluble when leached into distilled water. Zn and TCP concentrations in 24-hr leachate, using the laboratory testing protocols (Volume IV, Nelson et al., March 2000b), were about 1.7 and 1.8 mg/L, respectively. These concentrations were high enough to cause toxicity for *S. capricornutum* and *D. magna*. Equilibrium (batch leaching) and non-equilibrium tests (flat plate surface leaching) and removal/reduction/retardation (RRR) processes were conducted on SACC leachate to simulate the full range of leaching processes anticipated for C&R materials.

Batch and flat leaching results for Zn and TCP from SACC were similar to typical results for C&R materials in terms of leaching rates during the 24 hr short-term test and the resulting fitting model

equations. The batch leaching tests simulated equilibrium leaching behavior, whereas flat plate tests provided cumulative release data that described leaching rates (concentration vs. time) under conditions of constant surface renewal.

Soil sorption results for SACC leachate showed that zinc was nearly completely adsorbed to both Woodburn and Sagehill soils. TCP adsorption was higher on Woodburn soil with high organic matter content than on Sagehill soil, showing similar results to those of typical C&R materials.

Results of removal/reduction/retardation (RRR) processes for SACC leachate again showed similar behavior to that of C&R materials. No changes in zinc concentration were observed, as metals do not undergo removal through RRR processes, confirming their conservation in the solution, while 2,4,6-TCP concentrations during the test period decreased by about 28% from 1.68 to 1.20 mg/L.

Degradation of TCP in SACC leachate by RRR processes indicated an algal EC50 value of about 2% to 4% and a daphnia LC50 value of 50% in photolysis, volatilization and biodegradation controls. Toxicity results of samples analyzed after these RRR processes did not indicate any significant reduction ($p > 0.05$) in toxicity for either algae or daphnia. The 24-hour batch leachates of SACC used in these tests have both Zn and TCP as their major chemical components. Although the TCP concentration is reduced significantly, Zn is unaffected, thus resulting in little change in toxicity.

Test statistics on triplicate samples for the leaching and RRR process tests were also developed and validated. The average value, variance, standard deviation (SD), relative standard deviation (RSD) which is the method precision, deviation of measurement value from the average value (bias), and relative bias or percent of error, for both zinc and 2,4,6-trichlorophenol were presented. These results indicate that, based on single operator characteristics, the long-term and short-term batch leaching and RRR process tests, standard asphalt data are acceptable with less than 5 percent error.

The following conclusions resulted from Task 8, **Leaching Methods Comparison Study**.

Generally, the Toxicity Characteristic Leaching Procedure (TCLP) was a more aggressive leaching procedure than the Synthetic Precipitation Leaching Procedure (SPLP) and the modified NCHRP procedure. The TCLP leachate generally contained higher metal concentrations than the SPLP and NCHRP leachates for the five C&R materials tested. The difference in the concentrations in the crumb rubber asphalt concrete (CR-AC, types I and II) and MSWIBA aggregate leachates can be attributed to pH influence and metal complexation. The TCLP leachate from PCC contained higher concentrations that could not be explained clearly, but one possibility is that the TCLP extraction fluid may increase metal complexation in PCC leachates.

When comparing the test results by ANOVA based on 95 % confidence limit, there was a significant difference of concentrations between the TCLP and the other two methods, SPLP and modified NCHRP. However, concentrations obtained by the SPLP and modified NCHRP methods were generally not significantly different.

Generally, the reproducibility was good for multiple samples in all three methods. The RSD values of metals concentrations in the leachates are generally under 20 % unless near the metals detection limit. MSWIBA aggregate had the highest RSD values due to the lower homogeneity of the material.

More metals are generally extracted as the final pH value of the leachate decreases. The inorganic components (metals) are generally more readily leached in acidic than in neutral or slightly basic solutions.

Generally, more metals (concentration basis) were leached in the regular NCHRP method (higher solid-to-liquid, or S/L, ratio) than in the modified NCHRP method in terms of concentrations, but more metals were leached in the modified NCHRP method in terms of mass of release per mass of C&R material.

The following conclusions resulted from Task 9, **Model Enhancement**.

The NCHRP fate and transport model was enhanced to include the effects of desorption, long-term simulation (using standard National Weather Service hourly and 15-minute rainfall formats), and reduction of leaching concentrations with time. In addition, many less significant changes were made to improve model usability, including the option for the user to enter all leaching data from his/her own sources and not be bound to only the C&R materials tested in this project. The model, named "IMPACT," is written as an Excel spreadsheet macro in the Visual Basic for Applications language and is documented separately (Volume V, User's Guide, IMPACT, Hesse et al., 2000).

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

The model was compared with Task 1 soil column breakthrough curves for ACZA and TCP. Freundlich and Langmuir isotherms were derived from data from Task 5 or earlier Phase II data, if the earlier data were the only data available. Problems were encountered in that most isotherm data were collected in a range of dissolved concentrations much less than the range of ACZA and TCP concentrations flowing into the upstream end of the columns. Hence, there was uncertainty about the sorption capacity that should be input to the model.

TCP breakthrough was simulated reasonably well in both the Woodburn and Sagehill soils. The copper, zinc and arsenic within the ACZA leachate were not well simulated, with copper and zinc the worst. Computed breakthroughs tended to be "early" and the ratio of effluent concentration to influent concentration, C/C_0 , was higher than observed in the laboratory, partly

because several laboratory column tests never experienced complete breakthrough ($C/C_0 = 1$). In addition to the lack of good isotherm data, copper and zinc can undergo complex chemical reactions in natural soils; these are not simulated in the NCHRP model.

The consequence for the modeler is that the model is conservative in that it computes breakthrough, followed by total desorption (in a time span comparable to that required to sorb the material during the hydrologic event). Breakthrough times for the column comparisons generally occurred faster in the model than in the laboratory columns, and this discrepancy increases for larger model depths. Furthermore, the model simulates reversible sorption, during which all sorbed material is eventually desorbed. In reality, some additional desorption will occur with time in the columns or in the real highway environment, but probably not all. That is, especially for metallic cations, some permanent sorption in the soil matrix is probable.

Comparisons of model predictions to column data still support the use of the model as a screening tool. Results for arsenic were fair and for TCP were good. In all comparisons, the model estimated solute concentrations equal to or exceeding actual concentrations in solution, which is supporting evidence that the model predictions are a good representation of a worst-case scenario. The results emphasize the need for a model user to have some experience with the phenomena being simulated in order to interpret the results properly.

The following conclusions resulted from Task 10, **Data Set Assessment**.

None of the field studies discussed in Chapter 11 (Task 10) include comprehensive enough measurements or are focused enough on the strict highway environment to be useful for testing of the NCHRP Model. There are a considerable number of studies (referenced in Volume II of this study, Eldin et al., 2000) related to nonpoint source runoff from operational highways. Generally, these studies cannot be used to test the leaching component of the NCHRP Model because of the mixture of possible source mechanisms. Although it is possible that some soil sorption data might be found, the uncontrolled nature of these studies is much less preferable to the controlled studies conducted during this NCHRP Phase III work at OSU and possibly other laboratory column test studies discussed in Chapter 11. Soil migration data from the field typically are lacking some key element necessary for the model, such as the groundwater flow rate or the “entering” concentration of material through a soil layer.

The other problem with using field data is that many of the data are not taken in the immediate highway environment such that they may be represented by one of the reference environments present in the NCHRP Model. It still may be possible to find in an existing study some groundwater transport measurements that the NCHRP Model could possibly simulate, but in most cases, a much better option would be to use a conventional groundwater quality model for this purpose and not try to “stretch” the capabilities of what was designed as a screening model for the immediate highway environment.

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APPENDIX A MODEL CALCULATIONS

A.1 INTRODUCTION

The vast majority of Phase III model development has been programming. The calculations for flow and leaching around the reference environments are essentially the same as in the Phase II version of the model (Eldin et al., 2000). The calculations for model results, and the numerical method for solving the advection-dispersion equation are new. Also new to this version of the model are the decay in the source term concentration with time and the option of using a time series of rainfall data as input. This appendix is intended to explain the calculations performed by the model. Knowing the details of model computations will allow for a more educated interpretation of the model results by the end user. This appendix explains the transformation of rainfall data to a time series of flows and concentrations at the model boundary (interface between the reference environment and the surrounding soil or surface drainage), the numerical method used to solve the advection-dispersion equation in the highway grade, the calculations for the model output, and groundwater transport.

The equations demonstrating the calculations in this appendix have been taken directly from the programming code. All of the variables used in Excel closely resemble their English counterparts. These are defined in Table A.1.1.

In this appendix the term ‘increment’ is used to refer to a period of time for which calculations are performed. An increment is equal to a one-hour period for a single event model run or equal to the time interval (15 min or 1 hour) for the time series of hydrologic data in a long term run.

Table A.1.1. Definition of variables used in example calculations

Variable in code	Definition of Variable	Units
a	constant (coefficient) used to fit the leaching data	mg/L hr (if b = 1)
aAlpha	conveyance factor used in Manning’s equation	no units
aAreaofFlatPlate	surface area of flat plates used in laboratory testing	m ²
aAreaforLeaching	surface area of material available for leaching	m ²
aAreaofPile	cross sectional area of pile or bore hole	mm ³
aAreaNode	cross sectional area of node	m ²
aAtox	constant (coefficient) used to fit the toxicity data	L/mg (if bBTox = 1)
b	constant (exponent) used to fit the leaching data	no units
bBtox	constant (exponent) used to fit the toxicity data	no units
bBulkdensity	bulk density of the soil	g/L
cCoefficient	coefficient used to find % of rain infiltrating in permeable environment	
cColumnDiameter	diameter of lab column used for leaching data	mm
cColumnLength	length of lab column used for leaching data	mm
cColumnPoreVolume	pore volume of lab column used for leaching data	cm ³

Table A.1.1. Definition of variables used in example calculations (Cont.)

Variable in code	Definition of Variable	Units
cConcEst	estimate of concentration in iteration	mg or mmol/L
cConcNew	concentration at a node at end of a time step	mg or mmol/L
cConcOld	concentration at a node from previous time step	mg or mmol/L
cConcSorbEst	estimate of sorbed concentration used in iteration	mg or mmol/g
cConcSorbNew	concentration sorbed at a node at end of a time step	mg or mmol/g
cConcSorbOld	conc. sorbed at a node from previous time step	mg or mmol/g
cContactLength	height of culvert	mm
cContactTime	contact time of infiltrating water with material	hr
cContactTimeOutside	contact time of infiltrating water with culvert	hr
cContactWidth	inside width of culvert	mm
cCrackArea	area of cracks in permeable pavement	m ²
cCrackSourceConc	conc. of water infiltrating through pavement	mg or mmol/L
cCrackTime	time of contact with cracks	hr
dDataDepth	depth of rainfall of the N th increment	mm
dDataFlowRate	flow rate of leachate of the N th increment	m ³ /hr
dDataHours	end time of the N th increment from start time of run	hr
dDataSourceConc	concentration of leachate of the N th increment	mg or mmol/L
dDegrade	biodegradation rate	hr ⁻¹
dDeltaConc	change in concentration over a time step	mg or mmol/L
dDeltaConcdt	rate of change of concentration over a time step	mg or mmol/L hr
dDeltaMass	change in mass at a node over a time step	mg or mmol
dDeltaMassAdve	change in conc. at a node due to advection	mg or mmol/L
dDeltaMassDegr	change in conc. at a node due to biodegradation	mg or mmol/L
dDeltaMassDisp	change in conc. at a node due to dispersion	mg or mmol/L
dDeltaT	duration of a time step in finite difference calcs.	hr
dDeltaZ	distance between node in model	mm
dDepth	depth of rain for an increment	inches
dDepthRainTotal	total depth of rain	mm
dDepthTotal	cumulative depth of infiltrating water in fill envr.	mm
dDFofcConcEstDC	parameter used in Newton Raphson iteration	no units
dDiameterofInfluence	diameter of area affected by leaching for piling or bore hole reference environments	mm
dDiameterPile	diameter of piling or bore hole	mm
dDispersivity	property of soil used to calculate the dispersion	m
fFillThickness	thickness of fill in the fill environment	mm
fFlowRate	flow rate of infiltrating water	mm/hr
fFlowTime	time for infiltration through fill environment	hr
fFofcConcEst	parameter used in Newton Raphson iteration	no units
gGroundWaterVel	seepage velocity of flow in aquifer	mm/hr
hHead	difference in water surface elevation of aquifer	m
hHydraulicCond	maximum flow rate through soil	mm/hr
iInfiltrationRate	rate of infiltration of rainfall	mm/hr

Table A.1.1. Definition of variables used in example calculations (Cont.)

Variable in code	Definition of Variable	Units
iInitialTime	cumulative time of leaching prior to an increment	hr
iInitialVolume	volume of water infiltrating through pavement	m ³
kKf	coefficient of Freundlich isotherm	L/g (when nN = 1)
lLambdaPhoto	first order rate constant for photodegradation	hr ⁻¹
lLambdaVolatile	first order rate constant for volatilization	hr ⁻¹
lLangAlpha	alpha constant from Langmuir isotherm	L/mg
lLangBeta	beta constant from Langmuir isotherm	mg/g
lLeachateConc	concentration of leachate reaching aquifer	mg or mmol/L
lLeachateVolume	volume of leachate reaching aquifer	L
lLength	length of culvert	m
lLinearDegRate	linear degradation rate	mg or mmol/L hr
M	coefficient for overland flow in Manning's equation	no units
mManning	Manning's coefficient	no units
mMassIntoAquifer	cumulative mass leached into the aquifer	mg or mmol
mMassIntoSoil	cumulative mass leached into the soil	mg or mmol
mMassNode	mass at node used to calculate dissolved and sorbed concentrations	mg or mmol
mMassNodeEst	estimate of mass at node used in iteration	mg or mmol
mMassNodeNew	mass at node at end of time step	mg or mmol
mMassNodeOld	mass at a node from previous time step	mg or mmol
mMaxFlowLeachate	max. flow of leachate around pile or bore hole	m ³ /hr
mMixedConc	concentration after mixing in groundwater transport	mg or mmol/L
mModelDepth	depth of vadose zone in the model	m
nN	exponent used in Freundlich isotherm	no units
nNodeSpacing	spacing between nodes in the model	mm
nNumberOfEvents	number of increments of rainfall in long term runs	no units
	or number of hours of single event run	no units
nNumberOfNodes	number of nodes used in finite differences method	
nNumberOfTimes	number of calculation iterations during an increment	no units
pPavementThickness	thickness of pavement in permeable environment	m
pPercentMixing	percent of aquifer flow mixing with leachate	percent
pPerpDist	perpendicular distance to boundary	m
pPileDepth	depth of pile or bore hole	m
pPileSeepageVelocity	seepage velocity around pile or bore hole	mm/hr
pPoreVolume	pore volume of column used for fill leaching	cm ³
pPorosity	fraction of pore spaces in the soil	no units
rRainDuration	duration of single rain event	hr
rRainIntensity	intensity of rainfall event	mm/hr
rRainVolume	volume of rainfall falling on pavement surface	m ³
rRetardation	retardation factor for solute during model run	no units
rRoadArea	area of pavement intercepting rainfall	m ²
sSeepageVelocity	seepage velocity of the water through the soil	mm/hr

Table A.1.1. Definition of variables used in example calculations (Cont.)

Variable in code	Definition of Variable	Units
sSourceConc	concentration of leachate during an increment	mg or mmol/L
sSourceMass	mass leached from the fill during an increment	mg
sSourceSourceConc	concentration of leachate from pavement surface	mg or mmol/L
sSurfaceLength	length of path for surface flow	m
sSurfaceTime	time of surface flow for an increment	hr
tTime	total time for infiltration of rainfall	hr
tTimeIncrement	length of time of long term rainfall data	hr
tTimeStep	length of time for finite difference calculations	hr
tTimetoAquifer	time for solute from leachate to reach aquifer	hr
tTotalContactTime	total time for leaching	hr
vVel	seepage velocity for the N th increment	mm/hr
vVolContWaterIntoAquifer	volume of contaminated water into aquifer	L
vVolumeofFlatPlate	volume of flat plate in laboratory experiments	m ³
vVolumeGroundWater	volume of ground water mixing with leachate flowing into aquifer	L
vVolumeofFlatPlate	volume of the flat plates used in laboratory testing	m ³
vVolumeofLeachate	volume of leachate for the N th increment	m ³
vVolumeNode	volume of each node	L
wWidthPavement	width of road above the fill environment	m

A.2 BOUNDARY CONDITIONS

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

$$sSeepageVelocity(mm/hr) = \frac{dDataFlowRate (m^3/hr) \times 1000 (mm/m)}{aAreaNode (m^2) \times pPorosity} \quad (A.2.1)$$

This is analogous to setting the seepage velocity to the infiltration rate divided by the porosity for all the reference environments except piling and bore hole. For the piling and borehole reference environments it is assumed that the water in contact with the material for leaching flows at the hydraulic conductivity of the soil. The area of effect for leaching is a function of the infiltration rate and hydraulic conductivity as can be seen in Section A.3.2.1 for the borehole and piling environments. For these reasons the flow rate of contaminated water is not necessarily a function of the infiltration rate, so the above method is used to calculate the seepage velocity.

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

$$\text{Mass Flux into Soil (mg/hr)} = \text{Seepage Velocity (mm/hr)} \times \text{Node Area (m}^2\text{)} \times \text{Source Conc (mg/L)} \quad (\text{A.2.2})$$

The boundary for the soil-aquifer interface is also a flux boundary condition. This means that the mass flux into and out of the soil environment is only due to advection and the flux due to dispersion is zero. This is done by setting the derivative of the concentration gradient ($\partial^2 C / \partial z^2$) to zero. The mass flux out of the soil column and into the aquifer is described by Equation A.2.3.

$$M A \text{ (mg/hr)} = \text{Seepage Velocity (mm/hr)} \times \text{Node Area (m}^2\text{)} \times \text{Conc (boundary node) (mg/L)} \quad (\text{A.2.3})$$

Where M A = the mass flux into the aquifer (or next soil layer if the layering option is used).

A.3 MODEL COMPUTATIONS

A.3.1 Precipitation Calculations

If the type of run is a "Single Event" then the time increment is set to 1 hour, and the number of increments is equal to the number of hours of rain

$$n\text{NumberOfEvents} = r\text{RainDuration (hr)} \quad (\text{A.3.1.1})$$

The hydrologic event is divided into smaller increments to allow for a decrease in the source concentration with time. An hour is the chosen increment of time because it is an easy value to work with and the leaching tests are conducted in increments of hours so the unit of time coincides with the data analysis. For long-term runs the time increment is set to match the increment of the long-term data, and the number of increments is extracted from the long-term data selected for the run.

$$r\text{RainIntensity (mm/hr)} = \frac{r\text{RainDepth (mm)}}{r\text{RainDuration (hr)}} \quad (\text{A.3.1.2})$$

The infiltration rate is then set to the rain intensity.

$$i\text{InfiltrationRate (mm/hr)} = r\text{RainIntensity (mm/hr)} \quad (\text{A.3.1.3})$$

or to the saturated hydraulic conductivity, whichever is less. The variable dDataHours is set as the end time for each increment from the start of the run. This is done to facilitate the use of the dDataHours variable to track time for the output of model results. The variable dDataDepth is set to the depth of rain for each increment. While dDataDepth is the same for each increment in the single run and dDataHours is equal to the number of the increment,

these variables are tracked for consistency with the long-term runs. This allows the same calculations to be performed with the series of data (single or long-term runs) for the leaching and the numerical methods.

For the long-term runs the rainfall data must first be extracted from the data file and then converted to the same series of values: the time of the end of the increment (relative to the start of the run), dDataHours and the amount of rain during the increment dDataDepth. There are two types of long-term precipitation data commonly used in the U.S.: “Release B Condensed,” a format no longer available from the National Climatic Data Center since it is not Y2K compliant, and “NCDC” (format TD 3240 for hourly data and TD 3260 for 15-min. data). Since many users will have “Release B Condensed” data, both options are included in the Model.

Example of the ‘Release B Condensed’ data format:

8,971,6,21,"HT",5 – this line gives the date (06/21/1971) for the following data

9,14,15,0,"A","0" – rainfall data for the 14th hour 15th minute 0 depth

9,15,0,40,"A","0" – rainfall date for the 15th hour 0 minutes 0.40” depth

Example of the ‘NCDC’ data format:

15M07357002QPCPHI19711100250040045000020 0100000010 0900000010 2500000040

15M07357002QPCPHI19711100270041315000010 1400000010 1630000010 2500000030

For the NCDC format data for each day are on the same line, and “hour 25” gives the daily total. While the code to read this data format differs from that for the ‘Release B Condensed’ format, the methods for converting the data from the file to the series data, dDataDepth and dDataHours, are the same.

For each increment the date is converted into a useable form and compared to the start date of the model run to find the number of days since the run began. The hours and minutes of the increment are then converted into a decimal number of hours, e.g., the 14th hour 15th minute becomes 14.25.

$$dDataHours(hr) = \text{The number of days} \times 24 + \# \text{ of hours} + tTimeIncrement \quad (A.3.1.4)$$

This then gives the end time of the increment relative to the start of the run. The end time is used, because this variable will be used to track mass loading into the aquifer with time in the ‘Aquifer Inputs’ worksheet.

The depth for the increment is then converted from hundredths of inches to millimeters and stored in the depth variable.

$$dDataDepth(mm) = \frac{dDepth(\text{hundredths of inches})}{100(\text{hundredths/inch})} \times 25.4(\text{mm/inch}) \quad (A.3.1.5)$$

This then provides a series of variables for time and depth for each increment for the long-term data.

Now that the series of rainfall data is the same for all possible run and data types the dDataDepth variable is limited to the depth of rain able to infiltrate through the pavement for the Fill and Permeable environments. The dDataDepth variable is then limited to the depth of rainfall that can infiltrate through soil during the increment by comparison with the hydraulic conductivity.

$$\text{If } \frac{\text{dDataDepth(mm)}}{\text{tTimeIncrement(hr)}} > \text{hHydraulicCond (mm/hr)} \quad (\text{A.3.1.6})$$

$$\text{Then } \text{dDataDepth(mm)} = \text{hHydraulicCond (mm/hr)} \times \text{tTimeIncrement(hr)} \quad (\text{A.3.1.7})$$

The depth of rainfall is never limited in this manner for the Impermeable environment, because all runoff (leachate) directly enters the receiving body of water.

A.3.2 Leaching Calculations

The leaching calculations can vary depending on the reference environment. The methods for each environment are demonstrated below.

A.3.2.1 Borehole and piling environments

In this section the word “pile” is used to represent both a pile or borehole environment. For each increment the area for active leaching area around the pile is first calculated. It is assumed, for the calculation, that the area of influence surrounding the pile equals the area of the pile. If the hydraulic conductivity is greater than the rain intensity (dDataDepth/ tTimeIncrement) then the following equation is used to set the diameter of influence.

$$\text{dDiameterofInfluence (mm)} = \frac{\left[\text{dDiameterPile (mm)} \times \left(\frac{\text{hHydraulicCond (mm/hr)}}{\text{(dDataDepth(mm) / tTimeIncrement (hr))} \right)^{1/2} \right]}{\left[-1 + \left(\frac{\text{hHydraulicCond (mm/hr)}}{\text{(dDataDepth (mm) / tTimeIncrement (hr))} \right) \right]^{1/2}} \quad (\text{A.3.2.1.1})$$

If the Rain Intensity equals the Hydraulic Conductivity or if the Diameter of Influence calculated from Equation A.3.2.1.1 is greater than 1 meter, then diameter of influence is set to 1 meter.

The leaching data are fit using the equation

$$\text{Concentration (mg or mmol/L)} = a \times \text{Time (hrs)}^b \quad (\text{A.3.2.1.2})$$

The “a” coefficient of the leaching function has units of mg or mmol / L × hr^{-b}, while the b parameter is dimensionless. The concentration of the leachate for the nth increment is equal to the change in concentration on the curve (Figure A.3.2.1.1) between the leaching time prior to the nth increment and the leaching time including the nth increment.

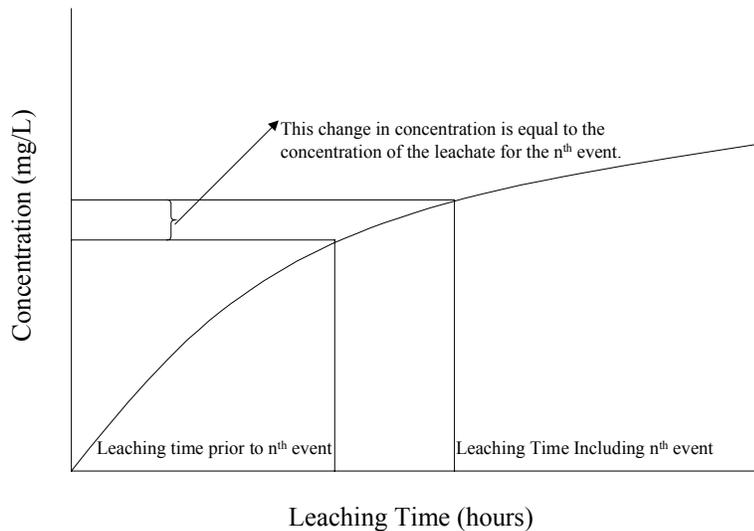


Figure A.3.2.1.1 Points for concentration calculations for nth increment.

Once the diameter of influence has been found for all rain increments then the volume of contaminated water and concentration are calculated. The seepage velocity along the pile is assumed to be equal to the hydraulic conductivity for all increments. It is calculated from

$$p\text{PileSeepageVelocity (mm/hr)} = \frac{h\text{HydraulicCond (mm/hr)}}{p\text{Porosity}} \quad (\text{A.3.2.1.3})$$

The contact time of the water with the pile is then found from.

$$c_{\text{ContactTime}} (\text{hr}) = \frac{p_{\text{PileDepth}} (\text{m}) \times 1000 (\text{mm/m})}{p_{\text{PileSeepageVelocity}} (\text{mm/hr})} \quad (\text{A.3.2.1.4})$$

Then the area for leaching is found from

$$a_{\text{AreaforLeaching}} (\text{m}^2) = \frac{p_{\text{PileSeepageVelocity}} (\text{mm/hr}) \times t_{\text{TimeIncrement}} (\text{hr}) \times \pi \times d_{\text{DiameterPile}} (\text{mm})}{100000 \text{ mm}^2 / 1 \text{ m}^2} \quad (\text{A.3.2.1.5})$$

The volume of contaminated water for the increment is given by

$$v_{\text{VolumeofLeachate}} (\text{m}^3) = p_{\text{PileSeepageVelocity}} (\text{mm/hr}) \times (t_{\text{TimeIncrement}} (\text{hr}) \times \dots \\ \dots \left[\left(\frac{d_{\text{DiameterofInfluence}} (\text{mm})}{2} \right)^2 \times \pi - a_{\text{AreaofPile}} (\text{mm}^2) \right] \times \frac{1 \text{ m}^3}{10^9 \text{ mm}^3} \quad (\text{A.3.2.1.6})$$

The flow rate of contaminated water for each increment is calculated to track the mass input into the soil column.

$$d_{\text{DataFlowRate}} (\text{m}^3/\text{hr}) = \frac{v_{\text{VolumeofLeachate}} (\text{m}^3)}{t_{\text{TimeIncrement}} (\text{hr})} \quad (\text{A.3.2.1.7})$$

The concentration of contaminated water for each increment is found by first calculating the concentration for the cumulative wet time (leaching time + nth increment on curve above) for the material that is being leached. Then the concentration is calculated for the previous leaching time (leaching time prior to nth increment on curve above) is subtracted from the concentration calculated at the cumulative wet time.

$$s_{\text{SourceConc}} (\text{mg/L}) = \left(\frac{v_{\text{VolumeofFlatPlate}} (\text{m}^3)}{v_{\text{VolumeofLeachate}} (\text{m}^3)} \right) \times \left(\frac{a_{\text{AreaforLeaching}} (\text{m}^2)}{a_{\text{AreaofFlatPlate}} (\text{m}^2)} \right) \times \dots \quad (\text{A.3.2.1.8}) \\ \dots a \times (c_{\text{ContactTime}} + t_{\text{TotalContactTime}} (\text{hr}))^b$$

$$s_{\text{SourceConc}} (\text{mg/L}) = s_{\text{SourceConc}} (\text{mg/L}) - \left(\frac{v_{\text{VolumeofFlatPlate}} (\text{m}^3)}{v_{\text{VolumeofLeachate}} (\text{m}^3)} \right) \times \left(\frac{a_{\text{AreaforLeaching}} (\text{m}^2)}{a_{\text{AreaofFlatPlate}} (\text{m}^2)} \right) \times \dots \\ \dots a \times (c_{\text{ContactTime}} + t_{\text{TotalContactTime}} (\text{hr}))^b \quad (\text{A.3.2.1.9})$$

The value for the concentration of contaminated water for each increment is then stored in the variable `dDataSourceConc` and the time tracking variable is stepped up for the current increment.

$$t_{\text{TotalContactTime}}(\text{hr}) = n_{\text{NumberOfEvents}} \times t_{\text{TimeIncrement}}(\text{hr}) + c_{\text{ContactTime}}(\text{hr}) \quad (\text{A.3.2.1.10})$$

A.3.2.2 Culvert environment

Two sets of concentration data are calculated for the culvert environment. The first is for the leaching of material by groundwater flow from the outside of the culvert. This leachate infiltrates through the vadose zone. The other leachate is from the inside of the culvert, which is discharged directly into a receiving body of water. The source concentration for the leachate from the outside of the culvert is found as follows for each increment. The variables `a` and `b` are the coefficient and exponent of the leaching function respectively.

$$s_{\text{SeepageVelocity}}(\text{mm/hr}) = \frac{\left(\frac{d_{\text{DataDepth}}(\text{mm})}{t_{\text{TimeIncrement}}(\text{hr})} \right)}{p_{\text{Porosity}}} \quad (\text{A.3.2.2.1})$$

$$c_{\text{ContactTimeOutside}}(\text{hr}) = \frac{c_{\text{ContactLength}}(\text{mm})}{s_{\text{SeepageVelocity}}(\text{mm/hr})} \quad (\text{A.3.2.2.2})$$

$$v_{\text{VolumeofLeachate}}(\text{m}^3) = \frac{d_{\text{DataDepth}}(\text{mm})}{1000(\text{mm/m})} \times l_{\text{Length}}(\text{m}) \times \frac{c_{\text{ContactWidth}}(\text{mm})}{1000(\text{mm/m})} \quad (\text{A.3.2.2.3})$$

$$d_{\text{DataFlowRate}}(\text{m}^3/\text{hr}) = \frac{v_{\text{VolumeofLeachate}}(\text{m}^3)}{t_{\text{TimeIncrement}}(\text{hr})} \quad (\text{A.3.2.2.4})$$

The calculation to find the source concentration for the increment is analogous to that for the borehole or pile reference environments. The source concentration calculated for the leaching time prior to the increment is subtracted from the source concentration for the total leaching time as is shown in equations A.3.2.1.8 and A.3.2.1.9. After calculating the source concentration for the increment, the counter for leaching time is stepped up as shown in equation A.3.2.1.10.

A similar process is used to find the concentration in water leaving the inside of the culvert. First the normal depth inside the culvert is found, for the estimated discharge rate, using Manning's equation. Once the normal depth is calculated the source concentration for flow through the culvert is calculated in the same way as for flow outside the culvert.

A.3.2.3 Fill environment

Once the time and depth variables have been determined for all rain increments, the infiltrating water is limited according to the infiltration method chosen. For method 1 the infiltrating water is limited to a fraction of the rainfall intensity, method 2 limits the infiltrating water to a maximum value.

method 1:

$$\text{If } \frac{d\text{DataDepth (mm)}}{t\text{TimeIncrement (hr)}} > i\text{InfiltrationRate (mm/hr)} \quad (\text{A.3.2.3.1})$$

$$\text{Then } d\text{DataDepth} = i\text{InfiltrationRate (mm/hr)} \times t\text{TimeIncrement (hr)} \quad (\text{A.3.2.3.2})$$

method 2:

$$d\text{DataDepth (mm)} = d\text{DataDepth (mm)} \times c\text{Coefficient} \quad (\text{A.3.2.3.3})$$

The rate of infiltration of water is then limited to that which can infiltrate through the soil by comparison with the hydraulic conductivity.

$$\text{If } \frac{d\text{DataDepth (mm)}}{t\text{TimeIncrement (hr)}} > h\text{HydraulicCond (mm/hr)} \quad (\text{A.3.2.3.4})$$

$$\text{Then } d\text{DataDepth (mm)} = h\text{HydraulicCond (mm/hr)} \times t\text{TimeIncrement (hr)} \quad (\text{A.3.2.3.5})$$

The leaching data are plotted versus the pore volumes of infiltrating water for the fill environment (Figure A.3.2.3.1).

$$\text{Mass (mg)} = a \times \text{pore volumes}^b \quad (\text{A.3.2.3.6})$$

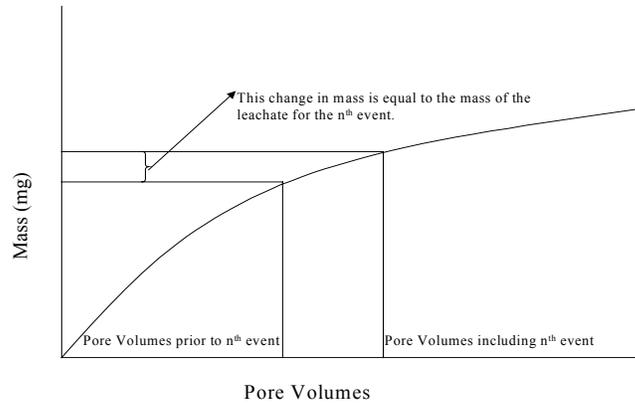


Figure A.3.2.3.1. Points for mass calculations for n^{th} increment.

To find the source concentration for each increment in the fill environment the mass leached prior to the current rainfall increment is subtracted from the total mass leached after the increment. This is the same process as in the piling reference environment only with mass instead of concentration.

The pore volumes are calculated from the rainfall prior to the current increment.

$$p\text{PoreVolume} = \frac{d\text{DepthTotal}(\text{mm}) \times w\text{WidthPavement}(\text{m}) \times 1(\text{m}) \times 10000(\text{cm}^2 / \text{m}^2)}{10(\text{mm} / \text{cm}) \times c\text{ColumnPoreVolume}(\text{cm}^3)} \quad (\text{A.3.2.3.7})$$

Then the mass leached prior to the increment.

$$s\text{SourceMass}(\text{mg}) = a \times p\text{PoreVolume}^b \quad (\text{A.3.2.3.8})$$

The depth of rain is increased to include the current rainfall increment, and Equation A.3.2.3.7 is recalculated for the current increment. The mass leached for the increment is then found by

$$s\text{SourceMass}(\text{mg}) = a \times p\text{PoreVolume}^b - s\text{SourceMass}(\text{mg} - \text{prior to event}) \quad (\text{A.3.2.3.9})$$

The final source concentration is equal to the mass leached, normalized for the column volume, divided by the volume of leachate for the increment.

$$sSourceMass (mg) = sSourceMass (mg) \times \frac{fFillThickness (mm) \times wWidthPavement (m) \times 1(m) \times 10^6 (mm^2 / m^2)}{((cColumnDiameter (mm) / 2)^2 \times \pi \times cColumnLength)} \quad (A.3.2.3.10)$$

$$dDataFlowRate (m^3/hr) = \frac{dDataDepth (mm) \times wWidthPavement (m) \times 1(m)}{tTimeIncrement (hr) \times 1000 (mm/m)} \quad (A.3.2.3.11)$$

$$dDataSourceConc (mg/L) = \frac{sSourceMass (mg)}{dDataFlowRate (m^3/hr) \times 1000 (L/m^3) \times tTimeIncrement (hr)} \quad (A.3.2.3.12)$$

A.3.2.4 Impermeable environment

The first step in computing the source concentration for a pavement environment consists of finding the time required for runoff to occur. The equation used is a combination of Manning's equation and the equation for a kinematic wave. Detailed development of the following equation used in the Visual Basic for Applications (VBA) code can be found in Quigley (1998) and Eldin et al. (2000).

$M = 5 / 3$ – coefficient for overland flow from Manning's equation.

$$aAlpha = \frac{1}{mManning} \times sSlope^{0.5} \text{ - conveyance factor} \quad (A.3.2.4.1)$$

$$sSurfaceTime (hr) = \frac{M}{(M+1)} \times \left(\frac{sSurfaceLength (m)}{aAlpha} \right)^{(1/M)} \times \left(\frac{dDataDepth (mm)}{tTimeIncrement (hr) \times 1000 (mm/m)} \right)^{(1/M-1)} \quad (A.3.2.4.2)$$

The volumes of rain and flow rate for each increment are found from the following equations.

$$rRainVolume (m^3) = \frac{dDataDepth (mm)}{1000 (mm/m)} \times rRoadArea (m^2) \quad (A.3.2.4.3)$$

$$dDataFlowRate (m^3/hr) = \frac{rRainVolume (m^3)}{tTimeIncrement (hr)} \quad (A.3.2.4.4)$$

The amount of time leaching has occurred is found from

$$iInitialTime(hr) = \text{the Number of the Event (I in the code)} \times tTimeIncrement(hr) \quad (A.3.2.4.5)$$

The final concentration of solute in the runoff is found using a finite difference method that accounts for leaching, photodegradation, and volatilization. Coefficients a and b are the constants used in the fit of the leaching equation. The programming loop is:

For tTimeNode = 1 To nNumberNodes + 1

$$dDeltaConc(mg/Lhr) = a \times b \times (tTime + iInitialTime(hr))^{(b-1)} + \dots \dots sSurfaceSourceConc(mg/L) \times (iLambdaPlato + iLambdaVolatile(hr^{-1})) \quad (A.3.2.4.6)$$

$$dDeltaConc(mg/L) = dDeltaConc(mg/Lhr) \times dDeltaTime(hr) \quad (A.3.2.4.7)$$

$$sSurfaceSourceConc(mg/L) = sSurfaceSourceConc(mg/L) + dDeltaConc(mg/L) \quad (A.3.2.4.8)$$

$$tTime(hr) = tTime(hr) + dDeltaTime(hr) \quad (A.3.2.4.9)$$

Next Time Node

The final concentration in the runoff is adjusted for the laboratory scaling, and the value for the source concentration is stored in the tracking variable dDataSourceConc.

$$sSourceConc(mg/L) = \frac{vVolumeofFlatPlate(m^3)}{rRainVolume(m^3)} \times \frac{rRoadArea(m^2)}{aAreaofFlatPlate(m^2)} \times sSurfaceSourceConc(mg/L) \quad (A.3.2.4.10)$$

A.3.2.5 Permeable environment

The concentration of solute in the surface runoff is calculated in the same manner as in the impermeable reference environment. The calculations for the concentration of solute in the flow through cracks are similar to those for the surface flow. First the rate of infiltration through the pavement is calculated. The infiltration rate through the cracks is set to a maximum infiltration rate or to a percent of the rainfall depending on the method selected by the modeler. If the maximum infiltration rate method is selected the infiltration rate is calculated by

$$iInfiltrationRate(mm/hr) = \frac{dDataDepth(mm)}{tTimeIncrement(hr)} \quad (A.3.2.5.1)$$

and does not exceed the maximum infiltration rate selected by the modeler.

For the coefficient method the infiltration rate is set by

$$iInfiltrationRate(mm/hr) = \frac{dDataDepth(mm)}{tTimeIncrement(hr)} \times cCoefficient(\%) \quad (A.3.2.5.2)$$

The time for flow through the cracks is found from

$$cCrackTime(hr) = \frac{pPavementThickness(mm)}{iInfiltrationRate(mm/hr)} \quad (A.3.2.5.3)$$

A finite difference method is used for leaching during crack flow that is analogous to the leaching for surface flow, as shown in the impermeable environment, without photodegradation or volatilization.

The concentration is then corrected for surface area and volume differences in the laboratory and the field.

$$cCrackSourceConc(mg/L) = \frac{vVolumeofFlatPlate(m^3)}{iInfiltrationVolume(m^3)} \times \frac{cCrackArea(m^2)}{aAreaofFlatPlate(m^2)} \times cCrackSourceConc(mg/L) \quad (A.3.2.5.4)$$

The source concentration to be used in the finite difference method is found by adding the concentration of the crack flow and surface flow. It is assumed that the infiltrating water leaches mass from both the pavement surface and cracks.

$$sSourceConc(mg/L) = (cCrackSourceConc(mg/L) + sSurfaceSourceConc(mg/L)) \quad (A.3.2.5.5)$$

The concentration and flow rates to be used are then transferred to the tracking variables dDataSourceConc and dDataFlowRate.

A.4 MODEL PARAMETER CALCULATIONS

At this point in the model four parameters have been calculated for each rainfall increment. These are: the time for the increment (dDataHours) (measured relative to the start time), the depth of infiltrating water (dDataDepth), the flow of contaminated water (dDataFlowRate), and concentration of contaminant in the water (dDataSourceConc). Prior to running the numerical method the model parameters must be calculated. The number of nodes for the model is retrieved from the value selected by the modeler on the Parameters Form. The model depth is calculated from

$$mModelDepth (mm) = (dDepthtoWater (m) - \text{Depth of reference environment material}(m)) \times 1000(mm/m) \quad (A.4.1)$$

The node spacing is then calculated by

$$dDeltaZ(mm) = \frac{mModelDepth (mm)}{(nNumberofNodes-1)} \quad (A.4.2)$$

To find the cross sectional area of each node it is necessary to know the maximum flow of leachate that the model will need to handle. This is found with the equation below for the pile and bore hole environments

$$mMaxFlowLeachate(m^3/hr) = pPileSeepageVelocity(mm/hr) \times pPorosity \times \dots \quad (A.4.3)$$

$$\dots \left(\left(\frac{dDiameterofInfluence (mm)}{2} \right)^2 \times \pi - aAreaofPile(mm^2) \right) \div 10^9 mm^3 / m^3$$

To be able to conduct that amount of flow the cross sectional area of the node must then be equal to

$$aAreaNode(m^2) = \frac{mMaxFlowLeachate(m^3/hr)}{(hHydraulicCond(mm/hr))} \times 1000(mm/m) \quad (A.4.4)$$

The node volume is then given by

$$vVolumeNode(L) = aAreaNode(m^2) \times nNodeSpacing(mm) \times \frac{1000(L/m^3)}{1000(mm/m)} \quad (A.4.5)$$

Units of liters for the node volume facilitate the calculations of mass loading into the aquifer given by $C (mg/L) \times \text{Node Volume} (L) \times \text{porosity}$ for each time step.

Two conditions must be met for the numerical method to be run. First the leachate must demonstrate toxicity when infiltrating through the selected soil or the linear isotherm must be selected. Second the piling or borehole cannot penetrate beyond the vadose zone. If the first condition is not met the model run ends with a message box explaining why no further calculations had been performed. If the first condition is met, but not the second then the model skips the numerical method for the infiltration through the soil and outputs results for the leachate entering the aquifer directly.

A.5 FINITE DIFFERENCE METHODS

A.5.1 Solution for Mass at a Node

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

C = concentration (mass/volume)
D_l = longitudinal dispersion coefficient
V_p = pore velocity in soil (length/time) (Darcy velocity/ porosity)
S = sorption (mass sorbed/mass soil)
ρ = bulk density of soil (mass/volume)
η = porosity of soil (fraction of pore space)
t = time increment
Cr_{xn} = biological or chemical reaction other than sorption

$$\frac{\partial C}{\partial t} = \frac{D_l \partial^2 C}{\partial z^2} - \frac{V_p \partial C}{\partial z} - \frac{\rho \partial S}{\eta \partial t} + \frac{\partial C_{rxn}}{\partial t} \quad (\text{A.5.1.1})$$

The solution method for the AD (advection-dispersion) equation needs to be computationally efficient to allow long term runs (using real hydrologic data) on home or office personal computers. Two numerical options were considered for its solution. Finite element methods divide the overall spatial domain into a series of smaller finite domains termed finite elements, with the unknown function, C(z,t), represented by an interpolating polynomial, which is continuous with its derivatives, within the specified element (Lapidus and Pinder, 1982). Finite element methods are more flexible in representing two and three-dimensional geometries but hold no particular advantage over finite difference methods for one-dimensional systems. Finite difference methods represent the domain of interest by a set of evenly-spaced points (nodes), with the derivatives of the AD equation simulated as difference equations. Different options for the difference representations can be derived by expansion of the derivatives using a Taylor series (Lapidus and Pinder, 1982). Generally, finite difference formulations are straightforward representations of the governing partial differential equation and were chosen for IMPACT due to their simplicity and well-known properties. An explicit formulation was used in order to handle the nonlinear sorption isotherms more easily. The explicit solution is thus subject to a stability criterion (explained in Section A.6) that limits the size of the computational time step (Roache, 1972).

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

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

Often the equation is rearranged so the change in sorption and concentration with time are on the same side of the equation. This allows the separation of the sorption term into a term involving the retardation factor as follows. Rearranging Equation A.5.1.1,

$$\frac{\partial C}{\partial t} \left[1 + \frac{\rho \partial S}{\eta \partial C} \right] = \frac{D_1 \partial^2 C}{\partial z^2} - \frac{V_p \partial C}{\partial z} + \frac{\partial C_{rxn}}{\partial t} \quad (\text{A.5.1.2})$$

where R_d (retardation coefficient) is given by

$$R_d = \left[1 + \frac{\rho \partial S}{\eta \partial C} \right] \quad (\text{A.5.1.3})$$

the AD equation becomes

$$\frac{\partial C}{\partial t} = \frac{\frac{D_1 \partial^2 C}{\partial z^2} - \frac{V_p \partial C}{\partial z} + \frac{\partial C_{rxn}}{\partial t}}{R_d} \quad (\text{A.5.1.4})$$

The R_d term can be calculated based on the derivative ($\delta S / \delta C$) of the isotherm used to fit the sorption data. (e.g., Freundlich $S = K_f C^N$ and $\delta S/\delta C = K_f N C^{N-1}$). This works well **if there is not any solute sorbed to the soil**, but when solute is sorbed this will change the equilibrium and the retardation factor. Instead of recalculating the retardation coefficient or using iterative methods, an alternate rearrangement of the AD equation allows a more direct solution, described below.

In order to solve for the change in mass sorbed to the soil (δS) it is necessary to keep track of mass sorbed in the soil at each node. It is easy enough to calculate δS , and if there is no need to calculate R_d , then just δS and δC can be calculated. Thus, taking the AD equation with time dependent changes in sorption and concentration on the same side of the equation.

$$\frac{\partial C}{\partial t} + \frac{\rho \partial S}{\eta \partial t} = \frac{D_1 \partial^2 C}{\partial z^2} - \frac{V_p \partial C}{\partial z} + \frac{\partial C_{rxn}}{\partial t} \quad (\text{A.5.1.5})$$

Multiplying each side of the equation by the porosity, η , and the volume of a representative node, V_{node} , used in the finite difference approximations gives

$$V_{\text{node}} \left[\frac{\eta \partial C + \rho \partial S}{\partial t} \right] = V_{\text{node}} \eta \left[\overset{\text{dispersion}}{\frac{D_l \partial^2 C}{\partial z^2}} - \overset{\text{advection}}{\frac{V_p \partial C}{\partial z}} + \overset{\text{reaction}}{\frac{\partial C_{\text{rxn}}}{\partial t}} \right] \quad (\text{A.5.1.6})$$

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

Backwards-difference approximations for $\delta C / \delta z$ (“upwind differencing”) are used because the change in concentration at a node due to advection is a function of the concentration in solution at the node and the concentration in solution at the adjacent node (‘upwind’) from which the water is advecting (Smith, 1985).

$$\frac{\partial C}{\partial z} \cong \left[\frac{C(i) - C(i-1)}{\Delta z} \right] \quad (\text{A.5.1.7})$$

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

$$\frac{\partial^2 C}{\partial z^2} \cong \left[\frac{C(i+1) - 2C(i) + C(i-1)}{\Delta z^2} \right] \quad (\text{A.5.1.8})$$

and biodegradation reactions are simulated with

$$\frac{\partial C}{\partial t} \cong -K_{\text{bio}} C \quad (\text{A.5.1.9})$$

This allows for the direct solution in the change in mass at a node for a given time step. Once the mass at a node is known the concentrations sorbed and in solution can be found for the sorption isotherm used. Once the sorbed and dissolved are known, the change of mass at the node can be found for the next time step. This process is repeated for the desired duration of the simulation.

A.5.2 Calculations of Sorbed and Dissolved Concentrations

A.5.2.1 Parameters

When using linear or Langmuir isotherms for sorption the concentrations in solution and sorbed to the soil can be found directly (without iteration). The Freundlich isotherm requires an iterative procedure to solve for the respective concentrations at the node. This is done as

follows for each isotherm once the mass at each node has been found from the solution to the modified AD equation.

For all sorption isotherms

C_s = concentration sorbed (mg/kg)

C = concentration in solution (mg/L)

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

Vol_{Node} = Node Volume

Soil Parameters

η = porosity

ρ = bulk density of soil (kg/L)

The mass at the node is equal to the mass sorbed and the mass in solution at the node.

The mass sorbed is given by the sorbed concentration \times the bulk density \times Vol_{Node}, while the mass in solution is given by the dissolved concentration \times porosity \times Vol_{Node}

$$\text{Mass}_{\text{node}} = V_{\text{node}} [C_s \times \rho + C \times \eta] \quad (\text{A.5.2.1.1})$$

A.5.2.2 Linear isotherm

A linear relationship between the sorbed and dissolved concentration is:

$$C_s = K_d \times C \quad (\text{A.5.2.2.1})$$

where:

K_d = linear distribution coefficient (L/kg).

Using Equation A.5.2.1.1 for the mass at a node and substituting for C_s gives

$$\text{Mass}_{\text{node}} = V_{\text{node}} [K_d \times C \times \rho + C \times \eta] \quad (\text{A.5.2.2.2})$$

Solving for C gives

$$C = \frac{\text{Mass}_{\text{node}}}{V_{\text{node}} [K_d \times \rho + \eta]} \quad (\text{A.5.2.2.3})$$

Then the sorbed concentration can be found from the linear isotherm.

A.5.2.3 Freundlich isotherm

The functional relationship between sorbed and dissolved concentrations shown below is known as a Freundlich isotherm (Fetter, 1993):

$$C_s = K_f \times C^N \quad (\text{A.5.2.3.1})$$

where:

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

When this formulation is included in Equation 5.2.1.1, an iterative solution is required to solve for C (after which C_s is determined from Equation A.5.2.3.1). A first estimate for C and C_s is found by increasing the estimate for C by a small increment, calculating C_s , and comparing the mass accounted for by the estimate to the known mass at the node. Once the estimate accounts for an amount of mass equal to or slightly greater than the mass at the node, the Newton-Raphson iterative technique (Chapra and Canale, 1985) is used to solve for the sorbed and dissolved concentration. This is shown in the programming code in section A.6.

A.5.2.4 Langmuir isotherm

The following functional relationship between sorbed and dissolved concentration is known as a Langmuir isotherm (Fetter, 1993):

$$C_s = \frac{\alpha \times \beta \times C}{1 + \alpha \times C} \quad (\text{A.5.2.4.1})$$

where:

α = absorption constant related to binding energy (L/mg), and
 β = maximum amount of solute that can be absorbed by the soil (mg/g).

Using the equation for the mass at a node and substituting for C_s gives

$$\text{Mass}_{\text{node}} = V_{\text{node}} \left[\left(\frac{\alpha \times \beta \times C}{1 + \alpha \times C} \right) \times \rho + C \times \eta \right] \quad (\text{A.5.2.4.2})$$

Equation A.5.2.4.2 can be rearranged as follows

$$\eta \alpha C^2 + C(\eta + \alpha \beta \rho - \alpha C_{\text{mass}}) - C_{\text{mass}} = 0 \quad (\text{A.5.2.4.3})$$

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

Then the quadratic Equation A.5.2.4.3 can be solved for C , with:

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

$$c = -C_{mass}$$

$$C = \frac{-b + (b^2 - 4ac)^{0.5}}{2a} \quad (A.5.2.4.4)$$

The solution for the concentration is given by

$$C = \frac{-(\eta + \alpha\beta\rho - \alpha C_{mass}) + ((\eta + \alpha\beta\rho - \alpha C_{mass})^2 - 4\eta\alpha - C_{mass})^{0.5}}{2\eta\alpha} \quad (A.5.2.4.5)$$

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

The calculations for the parameters of the numerical scheme are discussed in section A.4. The parameters are the node spacing, the node area, and the node volume. Once these fixed parameters are found for the model, the numerical method is run for each rainfall increment.

A.6 PROGRAMMING CODE FOR FINITE DIFFERENCE METHODS

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

Outer loop is run for each increment.

For K = 1 To nNumberOfEvents

Set seepage velocity for the increment based on depth of rainfall, which has been limited to that which can infiltrate.

sSeepageVelocity = (dDataDepth (K) / tTimeIncrement) / pPorosity

Set time increment to amount of time necessary for advection of leachate between node in finite difference scheme.

dDeltaT = dDeltaZ / (sSeepageVelocity)

Limit the iteration time steps (DeltaT) to the length of increment (Time Increment) in case of small seepage velocities possible in pile or bore hole environments.

If dDeltaT > tTimeIncrement Then dDeltaT = tTimeIncrement

Limit the iteration time steps (DeltaT) to the stability criterion where the stability criterion is given by $\Delta t \leq 1/(2D_l/\Delta z^2 + V_p/\Delta z)$

If $d\Delta T > ((d\text{Dispersivity} \times 1000 \times s\text{SeepageVelocity}) / d\Delta Z^2) + s\text{SeepageVelocity} / d\Delta Z)^{-1}$ Then
 $d\Delta T = ((d\text{Dispersivity} \times 1000 \times s\text{SeepageVelocity}) / d\Delta Z^2) + s\text{SeepageVelocity} / d\Delta Z)^{-1}$

End If

Set the number of times to iterate for the rainfall increment.

$n\text{NumberofTimes} = \text{Int}(t\text{TimeIncrement} / d\Delta T) + 1$

Define initial concentration at first nodes based on the source concentration calculated for the increment. (See Section A.3)

$c\text{ConcNew}(1) = d\text{DataSourceConc} (K)$

$c\text{ConcOld}(1) = d\text{DataSourceConc} (K)$

Define initial Darcy velocity at each node.

For I = 1 To (nNumberofNodes + 1)

$v\text{Vel} (I) = s\text{SeepageVelocity}$

Next I

Begin finite difference procedure.

This loop runs the finite difference procedure for each time step or the rainfall increment duration.

For tTimeStep = 1 To (nNumberofTimes)

This loop calculates the new sorbed and dissolved concentrations for each node, except the first node, which is set to the boundary conditions for the increment.

For I = 2 To nNumberofNodes

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

$\delta C / \delta Z = (c\text{ConcOld} (I) - c\text{ConcOld} (I - 1)) / (\Delta Z)$

$\delta^2 C / \delta Z^2 = (c\text{ConcOld} (I + 1) - 2 \times c\text{ConcOld} (I) + c\text{ConcOld} (I - 1)) / (d\Delta Z^2)$

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

Change in mass due to dispersion

$d\Delta\text{MassDisp} (I) = d\text{Dispersivity} \times 1000 \times v\text{Vel}(I) \times \delta^2 C / \delta Z^2 \times d\Delta T$

$d\Delta\text{MassAdve} (I) = -v\text{Vel}(I) \times \delta C / \delta Z \times d\Delta T$

$d\Delta\text{MassDegr}(I) = (d\text{DegrRate} \times c\text{ConcOld} (I) + l\text{LinearDegRate}) \times d\Delta T$

$d\Delta\text{Mass}(I) = (d\Delta\text{MassDisp} (I) + d\Delta\text{MassAdve} (I) + d\Delta\text{MassDegr}(I)) \times p\text{Porosity} \times v\text{VolumeNode}$

$m\text{MassNodeNew} (I) = m\text{MassNodeOld}(I) + d\Delta\text{Mass} (I)$

Use selected isotherm to find new concentration in solution from sorption and soil equilibrium.

If mMassNodeNew (I) > 0 Then

If Isotherm = "Linear" Then

$$cConcNew(I) = mMassNodeNew(I) / (vVolumeNode \times (pPorosity + Kd \times bBulkdensity))$$

$$cConcSorbNew(I) = kKd \times cConcNew(I)$$

End If

If Isotherm = "Freundlich" Then

Find maximum possible concentration in solution, used for beginning estimate.

$$cConcMax = mMassNodeNew(I) / (vVolumeNode \times pPorosity)$$

cConcEstCounter = 0 - counter for initial estimate

mMassNodeEst = 0 - counter for initial estimate

This is to find a good first estimate for the Newton-Raphson iteration below.

Do Until Mass Node Est > mMassNodeNew (I)

$$cConcEstCounter = cConcEstCounter + 0.01$$

$$cConcEst = cConcEstCounter \times cConcMax$$

$$cConcSorbEst = kKf \times (cConcEst^{nN})$$

$$mMassNodeEst = vVolumeNode \times (pPorosity \times cConcEst + bBulkdensity \times cConcSorbEst)$$

Loop

Newton-Raphson iteration for estimate of the concentration.

Do Until $0.9995 \times mMassNodeNew(I) < mMassNodeEst < 1.0005 \times mMassNodeNew(I)$

FofcConcEst - function of estimated C

$$fFofcConcEst = (bBulkdensity \times Kf \times (cConcEst^{nN})) + (pPorosity \times cConcEst) - (mMassNode(I) / vVolumeNode)$$

Df(C)/DC - rate of change of estimate w/ concentration

$$dDFofcConcEstDC = (bBulkdensity \times kKf \times nN \times (cConcEst^{nN-1})) + pPorosity$$

$$cConcEst = cConcEst - (fFofcConcEst / dDFofcConcEstDC)$$

$$cConcSorbEst = kKf \times (ConcEst^{nN})$$

$$mMassNodeEst = vVolumeNode \times (pPorosity \times cConcEst + bBulkdensity \times cConcSorbEst)$$

Loop

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

$$cConcNew(I) = cConcEst$$

$$cConcSorbNew(I) = kKf \times cConcEst^{nN}$$

End If

If Isotherm = "Langmuir" Then

$$a = (pPorosity \times ILangAlpha \times vVolumeNode)$$

$$b = vVolumeNode \times pPorosity + ILangAlpha \times ILangBeta \times bBulkdensity \times vVolumeNode - ILangAlpha \times mMassNodeNew(I)$$

$$c = - mMassNodeNew(I)$$

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

$$cConcSorbNew(I) = (ILangAlpha \times ILangBeta \times cConcNew(I)) / (1 + ILangAlpha \times cConcNew(I))$$

End If

If the mass at the node was not greater than zero then set concentrations equal to zero.

Else

$$cConcNew(I) = 0$$

$$cConcSorbNew(I) = 0$$

End If

Next I – begin calculations for next node number

The following mass and volume calculations are completed for every time step.

Track mass into soil from flux across model boundary, the conversion factors 1m/1000mm x 1m³/1000L cancels out.

$$mMassIntoSoil = mMassIntoSoil + (sSeepageVelocity \times aAreaNode \times pPorosity \times dDeltaT \times dDataSourceConc(K))$$

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

$$vVolumeofLeachate = vVolumeofLeachate + dDataFlowRate(K) \times dDeltaT$$

Track mass introduced into aquifer from flux across model boundary.

$$mMassIntoAquifer = mMassIntoAquifer + (sSeepageVelocity \times aAreaNode \times pPorosity \times dDeltaT \times cConcOld(nNumberofNodes))$$

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

If cConcOld(nNumberofNodes) > 0.000001 Then

$$vVolContWaterIntoAquifer = vVolContWaterIntoAquifer + (sSeepageVelocity \times aAreaNode \times pPorosity \times dDeltaT)$$

End If

Transfer concentration values for next set of calculations.

For I = 2 To (nNumberofNodes + 1)

$$cConcOld(I) = cConcNew(I)$$

$cConcSorbOld(I) = cConcSorbNew(I)$
 $Mass\ Node\ Old(I) = mMassNodeNew(I)$
Track time to reach aquifer - if this occurs during run
 If $cConcOld(nNumberofNodes + 1) > 0.000001$ And $tTimetoAquifer = 0$ Then ...
 ... $tTimetoAquifer = tTimeStep \times dDeltaT + (increment\ # - 1) \times tTimeIncrement$

Next I

Iterate through steps for individual increment.

Next tTimeStep

Track rain depth for retardation calculation.

$dDepthRainTotal = dDepthRainTotal + dDataDepth(K)$

Calculate retardation factor if solute reaches aquifer.

If $tTimetoAquifer > 0$ Then $rRetardation = dDepthRainTotal / mModelDepth$

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

Next K - iterates through all increments

A.7 MODEL OUTPUT CALCULATIONS

The Phase II version of the Model outputs relating to mass calculations, such as Percent Reduction in Mass Due to Sorption and Total Mass Reaching Aquifer for Increment, were based on the retardation coefficient for the run. In the final version of the model there are variables in the finite difference method that track all the mass leached into the soil and all the mass leaching into the aquifer. At the end of the run the mass in the soil and mass in solution are calculated. These parameters are now used for the calculations previously based on the retardation coefficient. For example the percent reduction in mass due to sorption used to be calculated by $(1 - (1 / Retardation)) \times 100$ and is now found from $(Mass\ Sorbed\ (mg) / mMassIntoSoil\ (mg)) \times 100$.

The Aquifer Inputs worksheet tracks several parameters related to the mass input into the aquifer. These parameters are the time (hr) of the inputs, the total mass input (mg), total volume of contaminated water (L), the concentration of the water entering the aquifer at that time (mg/L), the EC50(%) based on the current concentration, the average concentration of the contaminated water (mg/L), and the EC50(%) based on the average concentration of contaminated water reaching the aquifer.

The time is tracked from the time of the increment and the contact time during the leaching process.

$$tTime(hr) = cContactTime(hr) + dDataHours(hr) \quad (A.7.1)$$

Four variables track the mass and volume of contaminated water into and out of the soil column. The mass into the aquifer is tracked by summing the mass output from the last node of the model.

$$mMassIntoAquifer(mg) = mMassIntoAquifer(mg) + (sSeepageVelocity(mm/hr) \times aAreaNode(m^2) \times \dots \\ \dots pPorosity \times dDeltaT(hr) \times cConcOld(mg/L @ last node) \times \frac{1000(L/m^3)}{1000(mm/m)}) \quad (A.7.2)$$

If the mass is present at the last node, the volume of contaminated water is tracked by

$$vVolContWaterIntoAquifer(L) = vVolContWaterIntoAquifer(L) + \dots \\ \dots (sSeepageVelocity(mm/hr) \times aAreaNode(m^2) \times pPorosity \times dDeltaT(hr) \times \frac{1000(L/m^3)}{1000(mm/m)}) \quad (A.7.3)$$

The current concentration of water entering the aquifer is equal to the concentration at the last node that advects into the aquifer over the time step. The average concentration (mg/L) is found by dividing the total mass input by the total volume of contaminated water reaching the aquifer. Finally the EC50(%) values for the current and average concentrations are calculated from the equation for the laboratory data for the surrogate used to track toxicity for the given material. aAtox and bBtox are the coefficients used in the fit of the laboratory data.

$$1/EC50 = (aAtox \times mMixedConc(mg \text{ or } mmol/L))^{bBtox} \quad (A.7.4)$$

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

$$mMassIntoSoil(mg) = mMassIntoSoil(mg) + (sSeepageVelocity(mm/hr) \times aAreaNode(m^2) \times \dots \\ \dots pPorosity \times dDeltaT(hr) \times dDataSourceConc(mg/L) \times \frac{1000(L/m^3)}{1000(mm/m)}) \quad (A.7.5)$$

The volume of leachate is tracked in a similar manner.

$$v\text{Volumeofleachate(L)} = v\text{VolumeofLeachate(L)} + (s\text{SeepageVelocity(mm/hr)} \times a\text{AreaNode(m}^2) \times \dots \\ \dots p\text{Porosity} \times d\text{DeltaT(hr)} \times \frac{1000(\text{L/m}^3)}{1000(\text{mm/m})})$$

(A.7.6)

A.8 GROUNDWATER TRANSPORT CALCULATIONS

The groundwater transport model is coupled with all of the reference environments except the impermeable module. The leachate from the impermeable module is considered to enter surface water flow and is therefore not considered for groundwater transport.

The groundwater transport models a unit width (meter) of aquifer flow. The material considered for leachate per meter width of aquifer is a one meter width of pavement, culvert, or fill for the permeable, culvert, or fill reference environments, respectively. For the piling and borehole reference environments a single piling or borehole is considered per meter width of the aquifer.

The groundwater velocity is calculated using the change in water surface elevation over the distance from the reference environment to the boundary for the groundwater transport. The change in the water surface elevation is the head. It is used in the equation below

$$g\text{GroundWaterVel(mm/hr)} = \frac{h\text{Head(m)}}{p\text{PerpDist(m)}} \times \frac{h\text{HydraulicCond(mm/hr)}}{p\text{Porosity}} \quad (\text{A.8.1})$$

The time required for any leachate flowing into the to reach the boundary is given by

$$t\text{TimetoArrive(hr)} = \frac{p\text{PerpDist(m)} \times 1000(\text{mm/m})}{g\text{GroundWaterVel(mm/hr)}} \quad (\text{A.8.2})$$

The volume of groundwater flow for possible mixing is given by multiplying the total flow by the percent of flow considered for mixing entered by the model user.

$$v\text{VolumeGroundWater(L)} = f\text{FlowRate(m}^3/\text{hr)} \times t\text{TimeIncrement(hr)} \times p\text{PercentMixing(\%)} \times 1000(\text{L/m}^3) \quad (\text{A.8.3})$$

A diluted concentration is then calculated for the mixing of the leachate with the groundwater flow

$$m\text{MixedConc(mg or mmol/L)} = \frac{l\text{LeachateConc(mg or mmol/L)} \times l\text{LeachateVolume(L)}}{l\text{LeachateVolume(L)} + v\text{VolumeGroundWater(L)}} \quad (\text{A.8.4})$$

The EC50(%) is calculated for the diluted leachate

$$EC50(\%) = ((aAtox \times mMixedConc(\text{mg or mmol/L})^{bBtox}) \times 100(\%))^{-1} \quad (\text{A.8.5})$$

where aAtox and bBtox are the coefficients from the fit of the laboratory toxicity data.

$$1/EC50 = (aAtox \times mMixedConc(\text{mg or mmol/L})^{bBtox}) \quad (\text{A.8.6})$$

A.9 CODE

As mentioned earlier, the code is written in Visual Basic for Applications and included in the Excel spreadsheet that constitutes the model. The entire code may be viewed by keying Tools/Macro/Visual Basic Editor in the Excel program. Many comments are included in the code, similar to those in italics provided above.

APPENDIX B

QUALITY ASSURANCE AND QUALITY CONTROL RESULTS

B.1 INTRODUCTION

It is critical to have a well-established quality assurance (QA) program for any laboratory testing. The evaluation methodology developed by Oregon State University (OSU) for the environmental impact assessment of C&R materials included leaching and RRR tests accompanied by chemical and toxicological (specifically aquatic toxicity) analyses. The QA/QC program established for satisfactory laboratory performance and to ensure reproducibility of good quality data is discussed in detail in Volume IV (Nelson et al., 2000b). In the following sections, a summary discussion of the QA/QC results for the entire duration of the NCHRP 25-9 study is given.

B.2 QA/QC IN TOXICITY TESTING

The OSU Ecotoxicology Laboratory QA Program is discussed in detail in Volume IV (Nelson et al., 2000b). Standardized QA requirements were established for toxicity testing, with a number of quality assurance elements being incorporated from U.S. EPA standard protocol documents including U.S. EPA, 1989a, 1993, and 1994. This QA program was followed consistently throughout the entire NCHRP 25-9 study. Also, supplementary studies using 2,4,6-trichlorophenol were performed to validate the OSU Ecotoxicology Laboratory QA program. In general, QA practices for leachates generated from construction and repair materials consist of all aspects of the test that affect data quality: (1) material sampling and handling, (2) quality of the test organisms, (3) condition of the equipment, (4) test conditions, (5) instrument calibration, (6) replication, (7) use of reference toxicants, (8) test validity, and (9) documenting satisfactory laboratory performance. Among these, laboratory practices followed in evaluating the quality of test organisms, test reproducibility and test validity (using negative and positive controls respectively) during all three phases of NCHRP 25-9 studies are discussed in the following sections.

Reference Toxicants: A reference toxicant serves as a positive control. A reference toxicant is used to 1) ensure quality of test organisms, 2) ensure comparability of data on national scale, and 3) to demonstrate the ability of laboratory personnel to obtain consistent, precise results with given test organism and protocol.

At least one acceptable reference toxicant test per month and per each test method was run to demonstrate a satisfactory laboratory performance. The same test method (reference toxicant, dilution water, data analysis etc.) was followed for all three phases of NCHRP 25-9 study. Control charts (mean charts) are established for each reference toxicant-test, species-protocol combination. These are used to track reference toxicant results over time with respect to established upper and lower warning limits to allow immediate identification of out-of-control conditions. The outliers, which are values

falling outside the upper and lower limits, and trends of increasing and decreasing sensitivity are readily identified.

A zinc chloride reference standard is used as the reference toxicant for algae. The choice of this reference toxicant in the OSU laboratory is based on the advice from toxicologists of the Hazardous Waste Assessment Team, U.S. EPA, Corvallis, Oregon. A control chart was prepared by plotting the successive EC50 value and examined to determine if the results are within the prescribed limits. In fact, a running plot for the *S. capricornutum* EC50 values was maintained for the entire duration of the NCHRP 25-9 study from successive tests with the given reference toxicant (Figure B.2.1). A mean EC50 value of 0.056 mg/L at coefficient of variation of 8.3% was obtained indicating excellent agreement with literature values cited in Miller et al. (1985) and Novak (1990).

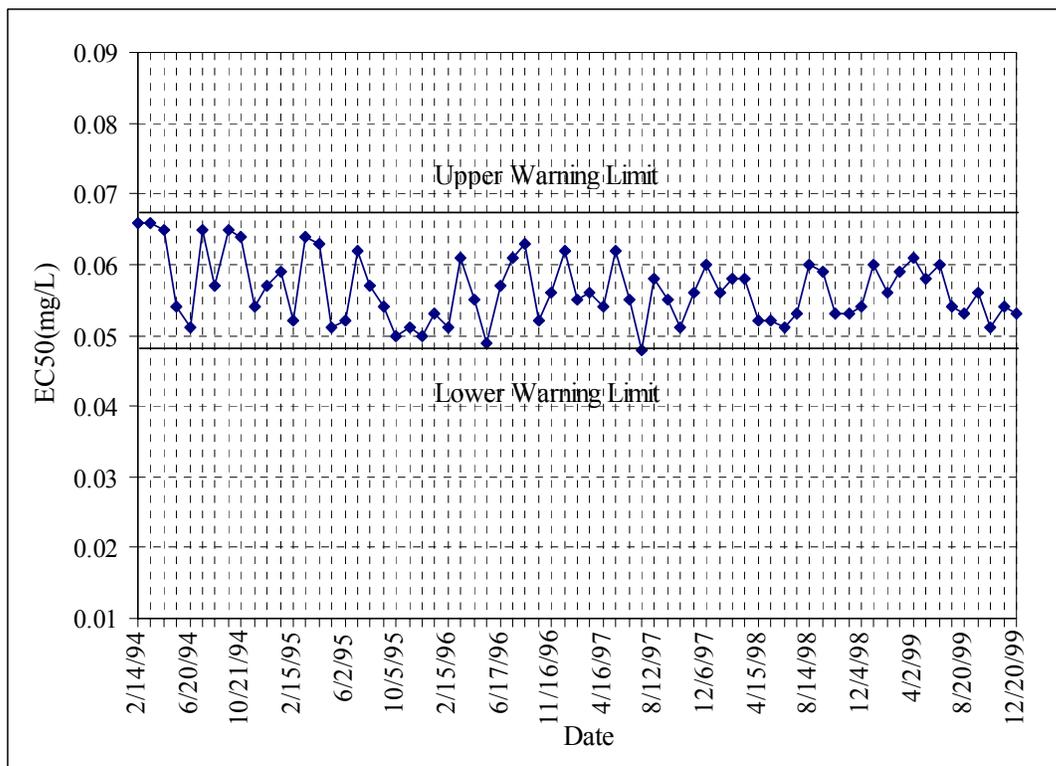


Figure B.2.1. *Selenastrum capricornutum* reference toxicant ($ZnCl_2$) control chart for duration of NCHRP Project 25-9.

For *D. magna* acute toxicity test, a $CuSO_4$ reference toxicant was used based on the standard method EPA/4-85/013. This reference toxicant and instructions are acquired from Quality Assurance Branch, Environmental Monitoring Systems laboratory, U.S. EPA, Cincinnati, Ohio. A similar control chart for the $CuSO_4$ reference toxicant tests performed for the entire duration of NCHRP 25-9 study was prepared (Figure B.2.2). A mean LC50 value of 0.059 mg/L was obtained which is well within the acceptable range of 0.016 mg/L to 0.2 mg/L (U.S. EPA, 1989b). A coefficient of variation of 7.5% was

observed indicating excellent reproducibility of reference toxicant data. Cumulative trends of toxicity values observed from both reference toxicant control charts maintained for the entire duration of NCHRP 25-9 study indicate the ability of laboratory personnel to obtain consistent, precise results with the given test organisms and test protocols. Furthermore, the coefficient of variation of LC50 and EC50 values obtained in these series of tests clearly demonstrates the overall laboratory performance as highly satisfactory.

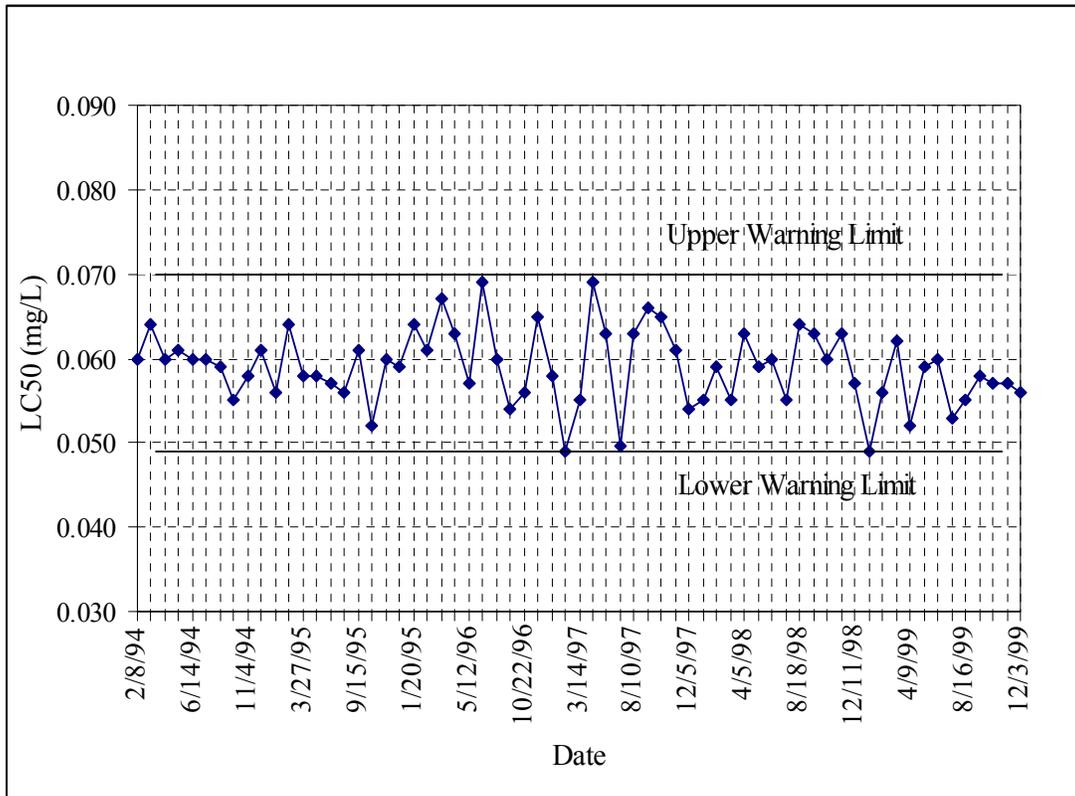


Figure B.2.2 *Daphnia magna* reference toxicant (CuSO₄) control chart for duration of NCHRP Project 25-9.

Acceptability of test results: Negative controls in a toxicity tests are used to confirm the absence or discover the presence of any toxicant in the test that will amplify the effect of toxicants on test organisms. They are used to monitor the health of test organisms and, in some bioassays (such as the algal chronic toxicity test), allow for comparison of yields between test concentrations. They are also the diluents for the toxicity bioassays. They should duplicate all test conditions and should not be toxic to the test organisms. Acceptability of bioassay test results is based on the negative control yields. Thus, negative controls are part of every single test conducted in the ecotoxicology laboratory.

For the 96-hour *S. capricornutum* chronic toxicity test, 100% algal assay medium (culture medium for algae) serves as the negative control. The *S. capricornutum* chronic toxicity test is considered valid only if there are 10^6 cells/mL in the negative controls at 96-hours. For the *D. magna* acute toxicity test, well water with adjusted hardness of 80-100 mg/L (growth medium for *D. magna*) serves as the negative control. The *D. magna* static acute toxicity test is considered valid only if the daphnids survival is at least 90%. The negative controls of algal as well as daphnia tests almost always passed the acceptability criteria. In a few cases, where the controls did not pass, a scrutiny of test data on test conditions (pH, dissolved oxygen, temperature) and organism culture was conducted and possible source of defects examined. Often, these tests were repeated with a different batch of tests organisms.

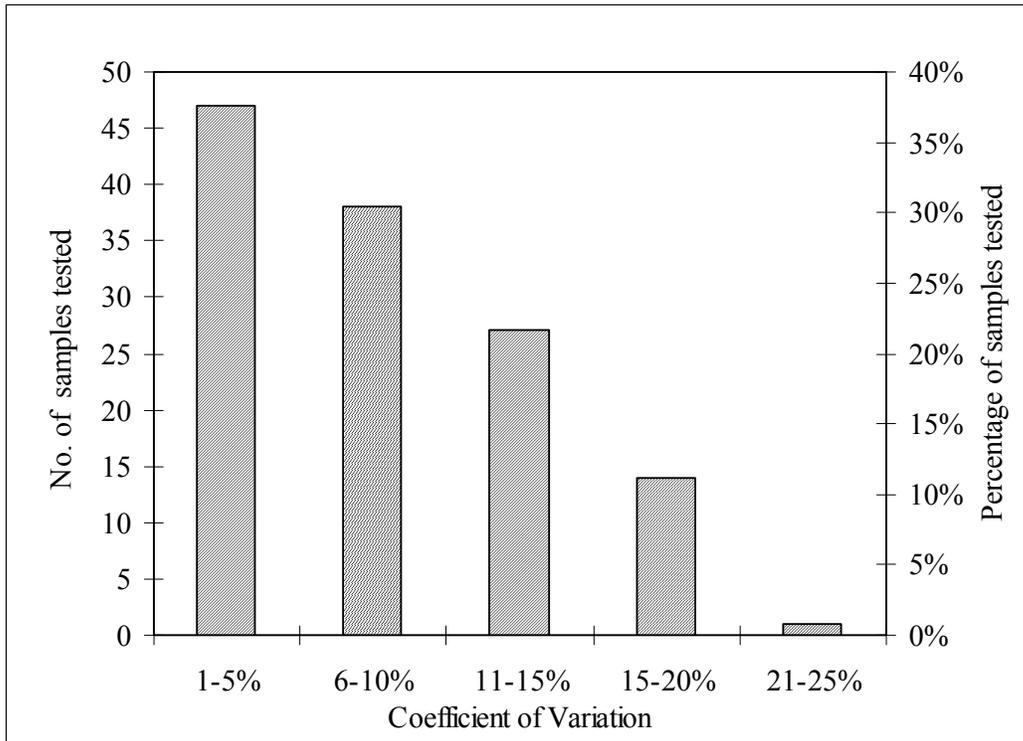


Figure B.2.3 Coefficient of variation in algal cell yields of split samples from a series of 127 algal chronic toxicity tests.

Precision: Algal cell yields from a series of 127 algal chronic toxicity tests performed during the 2,4,6 TCP methodology validation study are discussed here as an example to demonstrate the reproducibility of laboratory toxicity results. A coefficient of variation of 30% [where $\% CV = (\text{standard deviation} / \text{mean}) \times 100$] was used to judge acceptable reproducibility or precision of toxicity results (Environment Canada, 1990). The coefficient of variation of algal cell yields in three replicates (i.e., split samples) of negative controls from each of 127 tests was evaluated. Algal cell yields from a total of 381 (127×3) samples were used in this analysis. About 67% of the CV values fell within 1-10% range, showing excellent reproducibility in the toxicity test results (Figure

B.2.3). Almost all the rest of CV values fell within 1-20% range. Only one CV value fell above 20%, but even this is well within the acceptable limit of 30%. Overall, a good reproducibility in split samples was demonstrated by laboratory toxicity results.

Summary: For laboratory toxicity testing, a QA/QC program to ensure generation of good quality data was developed and maintained for the entire duration of NCHRP 25-9 study. The QA/QC results were observed to be consistent for all three phases of this study. Results from standard reference toxicants tests and built-in checks on test validity (negative controls) and reproducibility (coefficient of variation) are discussed in this section. Over all, these QA/QC results demonstrate satisfactory laboratory performance on health and sensitivity of test organisms, test validity, data reproducibility and the ability of laboratory personnel to obtain consistent, precise results with given test organism and test protocol.

B.3 QA/QC IN CHEMISTRY TESTING

B.3.1 Objectives and Instruments

The quality assurance program for chemical analysis was designed to ensure and document an acceptable level of quality of data and to ensure the proper documentation of all pertinent procedures and transactions related to the generation of the data.

The principal objectives were:

1. Process, store, and analyze samples using acceptable and standardized procedures.
2. Adequately maintain and document data quality.
3. Report results completely and correctly.
4. Maintain security of samples and data at all times.

For chemical analyses the period of 1993 – 95, different instruments were used for metallic element analyses (ICP-AES in the OSU College of Oceanography) and organic analyses (GC/MS HP 5890) than were used later in the project, but each instrument had its own valid QA/QC program. For the period of 1996-1999 for chemical analyses, a new ICP-AES (Varian Liberty 150) and GC/MS (HP 6890/5973) were used with different QA/QC programs from the previous instruments. No changes with time were observed for chemical analysis data as shown in the laboratory database. The reader should understand that if standard, documented QA/QC procedures are followed for the sophisticated chemical instruments discussed below, it is not possible for there to be variations over time. All project chemical analysis QC data are stored in worksheets along with test data, and they are available for review.

B.3.2 Inorganic Analyses

Chemical Interference: Chemical interference was minimized by careful selection of operational conditions (incident power, plasma observation position, etc.). Chemical interference was highly dependent on the sample matrix and element of interest.

Calibration Standards: Mixed calibration standards were prepared by combining the appropriate volumes of the metal stock solutions in 1-L volumetric flasks; simple dilution calculations were used to determine the required standard volumes. Before preparing mixed standards, each stock solution was analyzed separately to determine possible spectral interference. Mixed standards solutions were stored in polyethylene bottles. Calibration standards were verified for stability by using quality control standards. A two point standard curve was performed each time the system was calibrated.

Calibration Blank: A calibration blank was prepared using 1% vol/vol nitric acid (GFS Chemicals single distilled) in double distilled water. This blank was also used, along with the two mixed standard solutions, each time the system was calibrated.

Instrument Check Standard: Instrument check standards were prepared from the same quality control (QC) standard solutions used for the calibration standard, provided by the Varian Company. These check standards were prepared at a different concentration than the calibration standards and with the same acid matrix.

Instrument Calibration: The instrument calibration was set up according to the manufacturer's recommended procedure. The instrument was allowed to warm up for 15 min, after which an optical alignment was performed using the Hg lamp. The alignment of the plasma torch and spectrometer entrance slit was checked. The instrument was calibrated with the prepared calibration standards and blank. Each standard or blank was aspirated for a minimum of 15 seconds after it reached the plasma, before beginning signal integration. The QC standard was used before analyzing samples. A check was made to ensure that concentration values obtained did not deviate from the actual values by more than $\pm 2\%$.

B.3.3 Organic Analyses

Gas Chromatographic Procedures: Determination of target analytes by the GC procedure was required to meet the criteria detailed in the following sections, as judged by the operator and the QA supervisor.

Standard curve:

Run a 4-point standard curve along with an internal standard solution. For each compound calculate response factors (RF) for each concentration. Determine the linear range of each compound. The linear range is that over which the CV is less than 20%.

Using the data that are within the linear range, plot a standard curve of area of the chromatogram vs. concentrations for each compound, and determine the slope and coefficient for each. The R^2 values exceed 0.9995 in all cases.

Calculate the mean and standard deviation of the internal standard chromatogram areas from the standard curve data. The coefficient of variation (CV) should be less than 12%.

Routine quality control procedures for the GC:

Each analytical batch must contain:

A 4-point standard curve (including a reagent blank). Start with the blank and move up in concentration. The range of the standard curve should bracket all the unknown samples. Samples that fall outside the range of the standard curve should be rerun.

A method blank. This is distilled water treated exactly the same way that a sample is treated. For example, if the experimental method consists of taking a 15-mL sample out of a filtered leachate, the method blank will be 15 mL of filtered DI (deionized) water.

Run a number of blind standards. Report the concentration of each compound. Values must be within $\pm 15\%$ of actual value.

GC/MS QA Program: Determination of target analytes by the SIM GC/MS (HP 5890/1000) procedure (a program that compares sample results to a library to obtain a match) was required to meet the following criteria as judged by the operator and the QA supervisor.

The GC/MS procedure must be operating within the control limits for precision, accuracy, sensitivity and chromatographic performance and must pass autotune requirements.

The calibration standards accompanying the analyses must yield relative response factors (RRF) for each analyte that are within 15% of the running average RRF from the last multilevel and subsequent single calibration sequences.

The calibration standards accompanying the analyses must yield “q” values (ratios of relative ion abundances) within 10% of the expected values, i.e., those derived from previous analyses of chemical standards.

The recoveries of surrogate standards in the sample must be greater than 20%.

The range of surrogate recoveries in a sample must be less than 25%; a disproportionately high or low recovery is indicative of enrichment discrimination and may mean that the

use of one or more of the surrogates for purposes of quantification has been compromised.

The relative retention times of the analytes must be within 0.01 RRT (relative response time) units of the current calibration standard.

The “q” value (comparison of the analyte relative ion abundances with that of the standard) for each analyte must be 80% or greater of that of the calibration standards. If any analyte concentration exceeds the upper limit of the calibration range by greater than 30%, the analysis must be repeated on an appropriate dilution of the sample. Documentation of autotune, calibration, surrogate recoveries, “q” values and RRTs must accompany each set of analyses.

Calibration of and quantification by GC/MS procedures were conducted according to the following guidelines.

After autotune criteria have been met and prior to analysis of samples, the GC/MS procedure will be calibrated using a series of standards containing all target compounds, surrogate and injection internal standards. The amount of target compounds injected will range from about 5 times the lower limit of instrumental sensitivity to 500 times this limit; this results in a range of about 500 pg to 50 ng. These amounts correspond to approximately 5 to 5000 ng/g (ppb) in a 5-gram sample if 1/100 of the sample is injected (e.g., 2 µL to 2.0 mL will be made). Concentrations of the surrogate standards in the sample will normally be in the range of 200-500 ppb, and the injection internal standard will be added to the analyte solution at about this same level. This corresponds to 1-2 ng of each surrogate compound injected during GC/MS analysis for an analyte solution at 200 µL, or 100-200 pg for a 2-mL analyte solution volume.

TOC QA program: Sample handling, machine maintenance, and overall operating procedures for the Total Organic Carbon (TOC) analyzer (model DC-190) was in accordance with those procedures specified by the manufacturer (Rosemount Analytical, Inc., Dohrmann Division) as well as in Standard Methods 505A: *Organic Carbon (Total): Combustion-Infrared Method*. This method is suitable for liquid samples having a TOC \geq 1 mg/L. The analyzer determines TOC by calculating the difference between the measured total carbon (TC) and inorganic carbon (IC) content of a sample. Generally, the automatic sampler, rather than manual injection, can be utilized in sample analysis.

Prior to analyzing the daily samples, the operator should clean the system with a series of acid and distilled water rinses. Once the distilled water gives a TC measurement of \leq 0.5 mg/L, then the system is ready to run samples. If this cannot be achieved, then a second rinse at a higher furnace temperature (900°F) is conducted. This usually cleans out the system, and the furnace is brought back to the normal operating temperature (680°F).

The system is calibrated daily by analyzing a standard solution of a known TC concentration. The standard was prepared according to the methods specified by the

manufacturer and by Standard Methods. Some systems require a standard curve to be developed; however, the model used for this project requires just one standard concentration for calibration.

B.4 QA/QC IN LEACHING AND RRR PROCESS TESTING

A description of the development and validation of the laboratory testing methods and QC protocols for the leaching and RRR process tests conducted in this project is provided in Chapter 8 of this Volume III. As a part of this process, replicate testing was performed on all methods to define the variability and degree of confidence of the results using statistically determined parameters (coefficient of variation, precision). To do this, a “standard asphalt” (standard asphalt cement concrete, or SACC) was developed that contains two model toxicants, one metal (zinc) and one organic (TCP). The SACC is used as a standard by which other researchers may evaluate project protocols and hence perform their own QA/QC.

Triplicate samples were run through a series of leaching and RRR processes for the standard asphalt (SACC). The average value, variance, standard deviation (SD), relative standard deviation (RSD), which is the method precision, deviation of measurement value from the average value (bias), and relative bias or percent of error, for both zinc and 2,4,6-trichlorophenol are presented in Chapter 8, Tables 8.5.1.3.1 and 8.5.1.3.2, respectively. These results indicate that, based on single operator characteristics, the long-term and short-term batch leaching tests for standard asphalt data are acceptable with less than 5 percent error.