CONTAMINATED SOILS

VOLUME 11

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Environmental Fate
Heavy Metals
MTBE
Radionuclides
Remediation
Sediments
Site Assessment

Edited by

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Contents

PART I: ENVIRONMENTAL FATE

PART II: HEAVY METALS

PART III: MTBE

PART IV: RADIONUCLIDES

PART V: REMEDIATION

PART VI: SEDIMENTS

PART IX: SITE ASSESSMENT

Forward

The Annual International Conference on Soils, Sediments and Water, held each year at the University of Massachusetts in Amherst, is one of the longest running conferences of its type in the world. From its beginnings as a focused meeting on petroleum contaminated soils during the mille-1980's, this conference has grown and broadened remarkably. The most recent iteration, conducted in October, 2005, marked the 21st annual meeting of this well-attended event that annually has drawn 800 to 9,000 participants. At least 40 states and 30 foreign countries have been represented during its history spanning more than two decades. To put this impressive longevity into perspective, recall that Back To The Future was at the movies in 1985, and it is sobering to recall that the first of these sessions followed close on the heels of the Bhopal tragedy in 1984.

One of the principal benefits and ongoing attractions attendant to a meeting such as this one is the opportunity to present, critique, debate and extend the work that we in the environmental field find so overwhelmingly important. Whether in the formal confines of the oral platform presentations, or the more informal dialogue held during the poster sessions, or even in those discussions conducted at dinner, we are reminded that there is always more to learn about how our colleagues and others view what we may take for granted every day. At these meetings, for example, engineers have the opportunity to speak freely to other engineers, to biologists, to geologists, to chemists, to agency representatives, and others in ways that frequently identify opportunities in the most unlikely of places.

Consider the breadth of coverage for the papers in this year's volume, which range from assessment and remediation of arsenic, dioxins and perchlorate, to the evaluation and correction of indoor radionuclide risks, to the application of several beneficial reuse projects involving valuable industrial byproducts. The broad spectrum of technical specialties and the impressive experience that comes to Amherst with the participants ensures every year a unique and practical blend of science, policy and philosophical views which cannot help but continue to open our eyes to new areas. It is a telling observation that very few participants come to this conference for a single year. Rather, it is much more common to learn of those who have attended repeatedly for many years, often in different professional positions, and with different views as their careers have progressed.

These Proceedings from the 2005 international conference, representing Volume 11 of this series, contain 24 technical papers that showcase the work of 80 different authors. This volume is organized into the following sections: Part I - Environmental Fate; Part II - Heavy Metals; Part III - MTBE; Part IV - Radionuclides; Part V - Remediation; Part VI - Sediments; and, Part VII - Site Assessment. The scientists, regulatory agency personnel, consultants, academicians and others who have prepared the manuscripts in this volume represent a very broad array of interests and technical disciplines that all are essential to responsible and effective environmental evaluation and decision-making. It is a pleasure to have the opportunity to introduce this newest contribution to a long-standing series. The editors, sponsors, and conference staff should be commended for their enthusiastic support and for the consistent quality of this important scientific event.

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In addition, we express our deepest appreciation to the members of the Scientific Advisory Boards. The tremendous success of the conference has been result of the dedication and hard work of our board members.

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PART I: Environmental Fate

Chapter 1

MODELING ZINC AND SODIUM CHLORIDE MIGRATION IN VADOSE ZONE SOILS BENEATH STORMWATER INFILTRATION DEVICES

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Abstract: Urbanization has been responsible for an increase in the amount of impervious surfaces, leading to an increase in stormwater runoff and a decrease in groundwater recharge. Stormwater runoff contains pollutants, such as nutrients, pathogens, heavy metals, solids, organic compounds, pesticides, and chlorides, which have greatly contributed to the degradation of receiving waters due to surface discharge of stormwater. This has prompted stormwater managers to consider implementing more infiltration practices into their designs. However, past studies have shown that infiltrating stormwater could contaminate the groundwater, and in some cases, contamination actually has occurred. Therefore, methods for easily predicting contamination potential need to be developed.

Stormwater pollutants interact with the soils in the unsaturated zone as they migrate towards the groundwater. The specific type of soil and its properties have a profound effect on the movement of water and pollutants. For this research, zinc and sodium chloride were chosen as the pollutants of interest because of their stormwater prevalence, solubility, and differing migration rates. Through the use of the SESOIL model, factors such as pollutant concentration, rainfall, vadose zone thickness, intrinsic permeability, organic content, and soil pH were evaluated to determine which ones likely have the greatest influence on pollutant migration. A factorial analysis (2^6 full factorial) was used to evaluate the effects of these factors on the maximum penetration depth of zinc and sodium chloride. High and low values for the factors were selected from the literature and the NRCS soils database. The pollutants were treated as separate ions (Zn^{+2}, Na^+, Cl^-), and the length of each simulation was set at one year. Results indicated that rainfall was a common factor controlling Zn^{+2}, Na^+, and Cl^- migration. Concentration was also influential in Zn^{+2} migration, while intrinsic permeability affected Na^+ and Cl^-.

Key words: infiltration, SESOIL, sodium chloride, stormwater, vadose zone, zinc

1. INTRODUCTION

Increased urbanization has caused an increase in impervious surfaces and has led to greater amounts of pollutants being deposited on the land surface. Impervious structures like roads, driveways, parking lots, sidewalks, and rooftops also reduce the area available for infiltration of rainfall and runoff, leading to an increase in runoff volume and peak flow. It has been determined that the most important hydraulic factors affecting urban runoff volume are directly connected impervious surfaces such as paved streets, driveways, parking areas draining to curb-and-gutter drainage systems, and roofs draining directly into a storm or combined sewer (Pratap, 2004 literature review). In addition, the increase in impervious pavement and increased surface discharge of stormwater has resulted in a major decrease in groundwater recharge. This has resulted in the accelerated depletion of groundwater resources, aquifer collapse, and the subsidence of the ground surface (Ku *et al.*, 1992; Detay *et al.*, 1997; Gobel *et al*, 2004).

1.1 Urban Runoff

Urban runoff consists of three different flow phases: dry-weather base flows, stormwater runoff, and snowmelt. Other sources of wastewater that enter the storm drainage system include non-stormwater flows, such as irrigation water from lawns, and inappropriate entries from sanitary sewers. The importance of each of the above flow phases depends upon many factors, with the two most important being season and land use. Seasonal factors like cold versus warm weather or dry versus wet weather are often not as critical as land use in determining the pollutant load in stormwater runoff. Pollutants such as nutrients, pathogens, heavy metals, solids, organic compounds, pesticides, and chlorides are present in stormwater runoff. Many critical source areas such as industrial manufacturing facilities, vehicle service stations, vehicle maintenance facilities, scrap yards, and various commercial developments have been identified. Generally, commercial and industrial facilities contribute a larger pollutant loading due to increased concentrations and to stormwater runoff for runoff volumes equal to that from typical residential developments. However, pollutant loadings from residential areas occasionally may exceed commercial and industrial facilities due to increased use of fertilizers and pesticides (Pratap, 2004 literature review).

Historically, one of the most popular ways of dealing with stormwater has been to divert it down a curb-and-gutter drainage system that eventually discharges into a stream, river, or lake. Curb-and-gutter drainage systems with outfalls in local surface receiving waters are commonly referred to as MS4s (Municipal Separate Storm Sewer Systems). This management strategy is integral to the idea of getting stormwater away from people as fast as possible. Usually, stormwater is a nuisance or "waste water" that no one wants to deal with, so the common practice has been to send it down a pipe and pass it downstream. Little consideration has been given to the pollutants in the stormwater that could become a serious environmental problem for the receiving water. Past studies have identified urban runoff as a major contributor to the degradation of many urban streams and rivers (Field and Turkeltaub, 1981; Pitt and Bozeman, 1982; Pitt and Bissonnette, 1984; Pitt *et al.*, 1996 which includes an extensive literature review).

In addition to stormwater, snowmelt is another type of urban runoff that contributes to environmental degradation. The main contaminants associated with snowmelt are the salts that are applied to pavements every year to prevent the bonding of ice with the pavement. There are several different types of salts that are currently used to melt ice and snow. These salts include sodium chloride, calcium chloride, magnesium chloride, and potassium chloride. Each of these salts contains the chloride ion known to be very mobile and conservative because it does not adsorb onto mineral surfaces or react readily with other chemicals (Novotny et al., 1999). Novotny *et al.* (1999) demonstrated that snowmelt runoff contains higher heavy metal concentrations, compared to non-winter runoff, likely due to the high chloride concentrations. This is because high chloride concentrations proportionally decrease the partition coefficients, causing more metals to be in a dissolved, and likely more toxic, form.

Because of receiving water degradation and the decrease in groundwater recharge, the current discussion is whether stormwater should be managed through infiltration, surface discharge, or a combination of the two. Lately, much consideration has been given to the practice of stormwater infiltration. Infiltration devices were once thought of as an effective way to promote groundwater recharge. However, Pitt *et al.* (1996) reported that previous research clearly proved that the potential for groundwater contamination exists as a result of stormwater infiltration. Pollutants are carried through the vadose zone by infiltrating stormwater, posing a threat to the groundwater. Other studies have also shown the contamination potential and that groundwater contamination has actually occurred (Mikkelsen *et al*., 1996; Barraud *et al*., 1999; Datry *et al*., 2003; Fischer *et al*., 2003). Stormwater managers are realizing that more infiltration is needed to sustain groundwater levels, but the problem of stormwater pollutants has become a major stumbling block.

1.2 The Vadose Zone

A very important component of the infiltration process is the vadose zone. It is characterized by unsaturated geologic material such as soil and rock. Because many different types of rocks exist in the subsurface as parent material for the soil, several types of soil also exist. These soils have been classified based on physical features and their formative processes. Several classification systems currently exist, and no single method is generally accepted. Despite the differing interpretations, each soil classification system agrees that sands, silts, and clays are the three basic size fractions of soil. Physical weathering processes in the vadose zone have combined these three soils in different proportions to create several unique types of soil (actually, tens of thousands of soil types have been identified). The specific type of soil ultimately depends on its percentage of sand, silt, or clay, which will differ depending on the specific soil classification system (Selker *et al*., 1999).

The rate of travel of water and pollutants through the vadose zone depends largely on the type of soil and its properties. While the mobility of inorganic pollutants, such as metals and organic, is also compound specific. Each type of pollutant will interact with the soil in its own way (Selker *et al*., 1999). For example, metals and microorganisms are more likely to adsorb, or stick, to soil particles than salts, which are known to be highly mobile (Pitt *et al*., 1996). It has already been discovered that soil characteristics such as organic content, pH, and permeability play an important role in pollutant movement. However, the extent of their role has not been determined because of the complexity of the vadose zone and large numbers and wide concentrations of pollutants found in stormwater.

1.3 Objectives

Many studies have shown that infiltrating stormwater has the potential to contaminate the groundwater. However, these studies do not clearly address the phenomena that cause the contamination potential to be lesser or greater for any given site. The research team believes that the soils in the vadose zone are the key to finding the answers as to why groundwater contamination occurs in one area and not in another when both areas are subject to the same pollutants with similar concentrations.

During the literature search to support this research, three main soil properties have been identified as potential controlling factors for pollutant migration: intrinsic permeability, organic content, and soil pH. Other factors beyond soil properties have an effect on pollutant movement and groundwater contamination as well. Three such factors include pollutant concentration, rainfall, and vadose zone thickness.

The objects of this research project were as follows:

- Firstly, to determine which controlling factors have the greatest influence on the movement of zinc and sodium chloride in the vadose zone beneath a typical infiltration device.

- Also, that the knowledge gained about the interactions between soil and pollutants could improve the siting and the design of infiltration devices to encourage groundwater recharge while reducing or preventing groundwater contamination.

As a first step towards achieving these goals, simulations of pollutant migration in the vadose zone using an appropriate computer model were performed. The computer model selected was SESOIL, a one-dimensional, unsaturated-zone model that has been widely used to predict pollutant movement in the vadose zone, typically as part of environmental risk assessments. SESOIL has never been applied to stormwater infiltration but an extensive model review indicated it was the best model to apply to this problem. It is believed that computer models, such as SESOIL, will become an integral part of stormwater management in the near future.

2. MATERIALS AND METHODS

2.1 Modeling Methodology

Because infiltrating stormwater could be a threat to groundwater quality, methods for easily predicting contamination potential need to be developed. Since pollutant fate and transport models have been proven to be very effective in predicting the migration of pollutants through the subsurface, the application of such models to stormwater management appears to be very feasible. The capabilities of many unsaturated-zone models were carefully reviewed in an attempt to find the most appropriate model. It was finally decided that the SESOIL model would be used to evaluate the fate and transport of stormwater pollutants.

SESOIL was chosen not only for its user-friendly nature, but also for the variability of the input values. The user can choose from several different contaminants and soil types as well as from a multitude of climate and soil data. This input data can also be modified to simulate almost any condition. The output data, which includes solid, liquid, and vapor phase pollutant concentrations, as well as graphs, can be easily interfaced with the majority of groundwater software (West, 2001). Since no computer software that specifically models infiltrating stormwater and its pollutants from the ground surface has been developed, SESOIL was selected as the best option for this research project.

SESOIL (Seasonal Soil compartment model) was developed in 1981 by Bonazountas and Wagner at Arthur D. Little, Inc. for the EPA's Office of Water and Office of Toxic Substances (OTS). It is a theoretically based model that uses mass balance and assumes equilibrium partitioning between phases. In order to simulate contaminant fate and transport, SESOIL uses three submodels: the hydrologic cycle, sediment washload cycle, and the pollutant fate cycle. The hydrologic cycle models the impact of rainfall, groundwater flow, surface runoff, capillary rise, soil moisture retention, infiltration, and evapotranspiration on the pollutant behavior. Next, the sediment washload cycle estimates the amount of erosion and sediment yield in predicting the amount of contaminant removed from the system. Finally, the contaminant fate and transformation model is derived through the use of the pollutant fate cycle. This cycle uses values from the hydrologic and sediment washload cycles in a mass balance approach to predict the final fate of the contaminant. SESOIL also considers the natural attenuation of compounds by applying degradative processes such as diffusion, volatilization, hydrolysis, adsorption, and biodegradation to its pollutant fate cycle (West, 2001).

Zinc (Zn^{2+}) and sodium chloride (NaCl) were chosen to be the pollutants of interest because of their prevalence in stormwater, solubility, and differing migration rates. Pitt *et al.*, (1996) state that Zn will adsorb to soil particles, even though it is considered one of the more mobile heavy metals, and that NaCl is highly mobile. Zn represents contaminants that are least likely to reach the groundwater, the heavy metals, while NaCl represents contaminants that have the greatest potential to impact the groundwater. Zn is most commonly used as an anti-corrosion agent. Metals, such as many found on vehicle exteriors, are galvanized/coated with Zn to prevent them from corroding (Pitt *et al*., 1996). NaCl is widely used to deice roads, parking lots, and sidewalks in cold weather climates (Novotny *et al*., 1999).

After learning the capabilities of SESOIL, a sensitivity analysis was performed. During the test simulations it was determined that the pollutants needed to be treated as separate ions (Zn^{+2}, Na^{+}, Cl^{-}). NaCl needed to be entered as Na^{+} and Cl^{-} because it dissociates in stormwater and its ions react differently with soil than would a neutral compound.

The experimental design selected for this research was a full factorial analysis. This type of experimental design allowed for the determination of which factor and interactions of the factors affected pollutant migration in a statistically significant manner. The modeling exercise would evaluate the effects of pollutant concentration, rainfall, vadose zone thickness, intrinsic permeability, organic content, and soil pH on the pollutant migration depth.

The factorial analysis requires that high and low values of each factor be selected. Pollutant concentrations were found in the literature, specifically in the NSQD (Pitt *et al*., 2004). Snowmelt concentrations were loaded onto the soil only during the typical snowmelt months, while it was assumed that Zn loading were independent of season. Rainfall high and low values were selected from SESOIL's climate database and corresponded to the average annual rainfall in West Palm Beach, Florida (high), and Phoenix, Arizona (low). Soils that matched the high and low parameter values were selected from the NRCS database built into SESOIL. The high and low values of the input parameters for the 2^6 factorial analysis for each ion are summarized in Table 1, while the specific soils chosen for this research are listed in Table 2.

Table 1. High and low values of the controlling factors

	Concentration (µg/g)			**Rainfall (cm)**
	Zn	**Na**	**Cl**	
Low	0.032	28	42	Phoenix: 6.71
High	2.1	1360	2040	W. Palm Beach: 153.59

	Vadose Zone Thickness (cm)	**Intrinsic Permeability (cm2)**	**Organic content (%)**	**pH**
Low	300	1.00 E-10	0.5	4.3 – 5.0
High	1200	1.00 E-7	3	7.2 – 8.0

Table 2. The relationship of actual soils to the controlling factors

Soil Name	**County**	**State**	**Soil Type**	**Intrinsic Permeability (cm^2)**	**Organic Content %**	**pH**
Julesburg	Logan	CO	Sandy Loam	High	High	High
Climara	Fresno	CA	Clay	Low	Low	High
Lewisville	Dallas	TX	Silty Clay	Low	High	High

Soil Name	County	State	Soil Type	Intrinsic Permeability (cm^2)	Organic Content %	pH
Pompano	Palm Beach	FL	Fine Sand	High	Low	High
Hazelton	Dauphin	PA	Ch. Loam	High	High	Low
Waynesboro	Coffee	TN	Clay Loam	Low	Low	Low
Charles	Cumberland	ME	Silt Loam	Low	High	Low
Lakewood	Ocean	NJ	Sand	High	Low	Low

3. RESULTS AND DISCUSSION

Results of the sensitivity analysis showed that the model was most sensitive to the number of sublayers in each layer of soil. The most realistic results were achieved by using the maximum number of sublayers (10). A result supported by the creators of SESOIL, Bonazountas and Wagner (West, 2001).

Once the simulations were completed, the data was analyzed to determine which factors and combinations of factors, had a statistically significant effect on pollutant migration. Factorial experiments can be analyzed in one of two ways: graphically or through the generation of probabilities showing that each factor and interaction were statistically significant. It had been planned to analyze the data with SYSTAT 11. However, compatibility issues with the software precluded its use.

Graphical analysis techniques were used instead. For the graphical analysis, "effect values" had to be calculated. Effect values are the differences between the average pollutant migration depth when the factor value is high and the average depth when the factor is low. These effect values are plotted on a probability plot after being ranked from lowest to highest calculated value. A straight line is fit through the majority of the data (see Figures 1, 2, and 3).

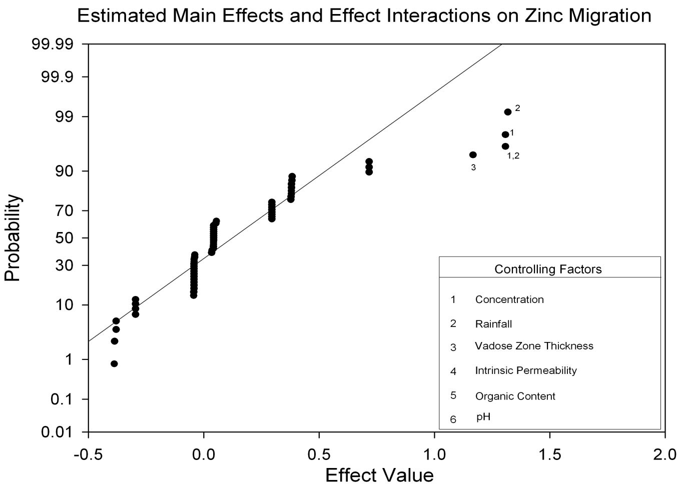

Figure 1.

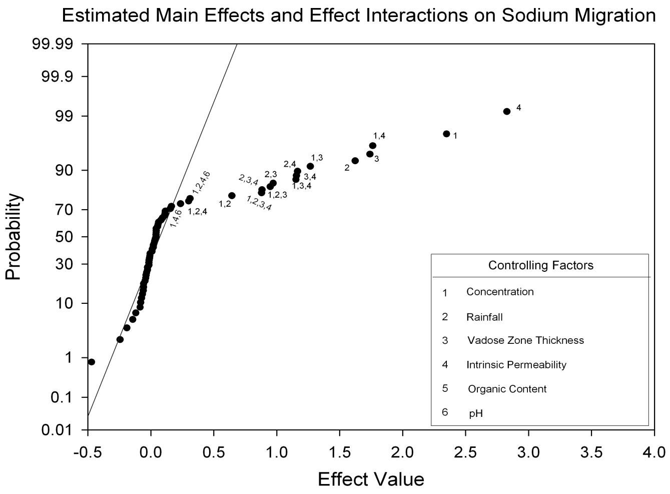

Figure 2.

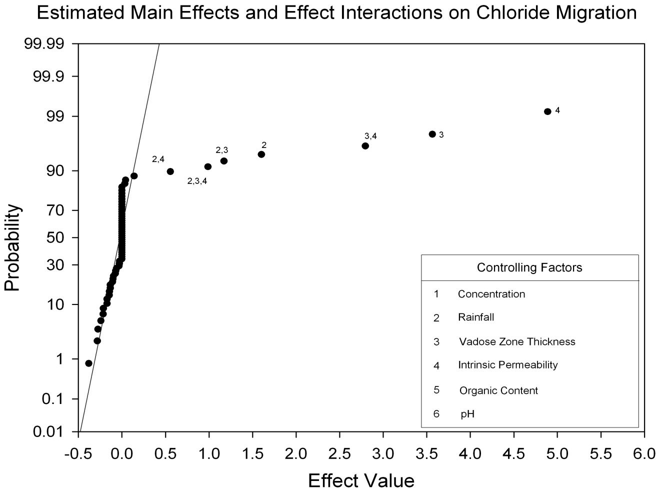

Figure 3.

Points falling off the line are the significant factors and interactions. Results indicated that rainfall was a common factor controlling Zn, Na, and Cl migration. Since the Zn and NaCl are assumed to dissolve in infiltrating stormwater, higher rainfall amounts would naturally allow the pollutants to migrate deeper in the vadose zone.

Results also showed that concentration was influential in Zn migration. Higher concentrations of Zn cause less adsorption to occur because the available sorption sites in the upper layers were filled before the zinc in the stormwater was completely removed. Once the maximum level of adsorption is reached in the upper soil layers, the remaining Zn will continue to migrate with the infiltrating water until available adsorption sites are reached.

Vadose zone thickness had a slight effect, but this likely is due to the way SESOIL calculates pollutant migration. SESOIL assumes that migration takes place within a specified volume of soil. A larger volume, with larger overall depths and a maximum of 10 sublayers, for example, will cause SESOIL to calculate a deeper migration. This is the primary reason that SESOIL consistently overpredicts migration depths. Vadose zone thickness is not a factor that controls migration, but needs to be considered when constructing infiltration devices. It is very likely that water tables 3m or less will be impacted by stormwater pollutant migration in a single season if the applications of road salt are sufficiently high.

Furthermore, since hydrolysis was not considered by the model due to the lack of hydrolysis constants, pH was not found to be a controlling factor in Zn migration. Zn is involved in hydrolysis reactions in soil, but the extent of these reactions is still not well understood. Because pH is believed to play a large role in Zn migration, further research should be done to experimentally derive neutral, acid and base hydrolysis constants.

It is well known that organic matter affects Zn migration. However, it is likely that the interaction between the low concentrations of Zn and comparatively low amounts of organic matter was not deemed significant by SESOIL. Since Zn concentrations in stormwater are usually very low, it could be possible that complexation reactions involving organic matter may be negligible.

The effect of rainfall and intrinsic permeability on Na migration was a very realistic result. Increased rainfall and soils that have a high permeability would naturally be expected to increase the mobility of Na. However, it is believed that SESOIL largely over-predicted the migration depth of Na. It is unlikely that NaCl would reach a deep water table within a year's time, especially in clayey soils. Based on what is known about the behavior of Na in soil, the migration depth of Na should have been somewhere between Zn and Cl. Sodium migration to depths of 12m in soils with high permeability may be possible after several years of NaCl deposition and high rainfall. The lack of K_d values for sodium was a main reason for the poor results.

The migration depth of Cl was the most realistic of the three pollutants based on pollutant migration literature. Chloride's non-reactive nature made its fate and transport very easy to model with SESOIL. However, chloride's migration depth of 12m in clayey soils in a one-year period is somewhat questionable. This result may realistically occur if the proper conditions existed. It would depend largely on the amount of rainfall, the permeability of the clay, and infiltration rates. Fortunately, the areas in the U.S. with the highest rainfall totals are tropical and typically do not use road salt due to the lack of wintertime icing.

This research not only demonstrated the feasibility of applying an unsaturated zone model to stormwater infiltration, but it also pointed out the informational gaps that need to be filled in order to move forward with this work. The most important pieces of information that need to be obtained are: pollutant input values, site-specific soil information, and stormwater influent and effluent data. Input values such as adsorption coefficients, hydrolysis rate constants, and stability constants, are needed for each pollutant of interest evaluated by SESOIL. Since these coefficients do not exist in the literature for each specific stormwater pollutant, they will have to be experimentally derived. Site-specific soil information is also very important because the extent of pollutant migration in the vadose zone mainly depends on the soil matrix and type of pollutant. Finally, actual stormwater influent and effluent data from infiltration devices is needed to make comparisons with the results of model simulations. Actual effluent stormwater concentrations can be compared to effluent concentrations simulated by SESOIL to determine the accuracy of the model's results.

Unfortunately, the vitally important influent, effluent, and soil data are not entirely available. The International Stormwater BMP Database does contain influent and effluent data for a few infiltration sites, but there is no specific information about the soils that lie beneath the infiltration devices. Therefore, the data sets are incomplete. This is illustrated in Table 3, which is a sample of grass filter strip water quality data found in the International Stormwater BMP Database. Because of this incompleteness, there is no real data to compare to SESOIL's results, thus making it difficult to determine the true accuracy of this model.

Table 3. Sample of grass filter strip water quality data obtained from the International Stormwater BMP Database

	Biofilter-Grass Strip US 183 at MoPac Grass Filter Strip Austin, TX		**Biofilter-Grass Strip Walnut Creek Veg. Buffer Strip Austin, TX**	
Analytical Parameter	**Inflow**	**Outflow**	**Inflow**	**Outflow**
Ammonia, Total as N (mg/L)	NA	NA	NA	NA
Arsenic, Dissolved (ug/L)	NA	NA	NA	NA
Arsenic, Total (ug/L)	NA	NA	NA	NA
BOD-5 (mg/L)	NA	NA	NA	NA
Cadmium, Dissolved (ug/L)	NA	NA	NA	NA
Cadmium, Total (ug/L)	NA	NA	NA	NA
Chromium, Dissolved (ug/L)	NA	NA	NA	NA
Chromium, Total (ug/L)	NA	NA	NA	NA
Chloride Dissolved in Water (mg/L)	NA	NA	NA	NA
COD (mg/L)	NA	39.67	NA	40.7
Conductivity at 25C (micromho)	NA	NA	NA	NA
Copper, Dissolved (ug/L)	NA	NA	NA	NA
Copper, Total (ug/L)	NA	NA	NA	NA
Fecal Coliform-FCAGAD/100 mL	NA	NA	NA	NA
Iron (mg/L)	NA	NA	NA	NA
Iron, Total (mg/L)	NA	867.7	NA	598
Lead, Dissolved (ug/L)	NA	NA	NA	NA
Lead, Total (ug/L)	NA	NA	NA	55.5
Nickel, Dissolved (ug/L)	NA	NA	NA	NA
Nickel, Total (ug/L)	NA	NA	NA	NA
Nitrate Dissolved (mg/L)	NA	NA	NA	NA
Nitrite Dissolved (mg/L)	NA	NA	NA	NA
Oil and Grease (mg/L)	NA	NA	NA	NA
Orthophosphates (mg/L)	NA	NA	NA	NA
pH Lab	NA	NA	NA	NA
Phosphorous, Total (mg/L)	NA	0.4467	NA	0.1489
Phosphates, Total (mg/L)	NA	NA	NA	NA
Total Dissolved Solids (mg/L)	NA	NA	NA	NA

	Biofilter-Grass Strip **US 183 at MoPac** **Grass Filter Strip** **Austin, TX**		**Biofilter-Grass Strip** **Walnut Creek** **Veg. Buffer Strip** **Austin, TX**	
Total Hardness CaCO3 (mg/L)	NA	NA	NA	NA
Total Kjeldahl Nitrogen (mg/L)	NA	NA	NA	1.452
Total Nitrogen (mg/L)	NA	1.677	NA	0.5938
Total Organic Carbon (mg/L)	NA	22.7	NA	NA
Total Suspended Solids (mg/L)	NA	37	NA	44.6
Total Volatile Solids (mg/L)	NA	NA	NA	NA
Turbidity, Lab (NTU)	NA	NA	NA	NA
Zinc, Dissolved (ug/L)	NA	NA	NA	NA
Zinc, Total (ug/L)	NA	17.33	NA	29.88

4. CONCLUSION

SESOIL is the most complete vadose zone model commercially available for performing this type of modeling. The maximum refinement of 10 sublayers should be used in the model in order to achieve the best results. Because SESOIL is a one-dimensional model, it likely over-predicted the migration depths. However, it is anticipated that the results illustrate the relative differences that would be seen in the field.

Results of the factorial analysis determined that Zn migration was controlled by rainfall and concentration, while Na migration was controlled by concentration and intrinsic permeability. Furthermore, Cl migration was affected by rainfall and intrinsic permeability. High rainfall amounts resulted in deeper migration in all soils types. The average maximum migration depths were 1.55m for Zn and 12m for NaCl. Based on model results, shallow groundwater (< 3m) will be rapidly and highly impacted by NaCl, but not by Zn. However, the potential for Zn contamination still exists and is more likely when the infiltration basin has been in operation for several years. It is highly unlikely that deep groundwater (> 12m) will be impacted by Zn, but will most likely be impacted by NaCl in areas of high rainfall in a short period of time.

Further research needs to be conducted to determine the long-term effects of these pollutants. We plan to run simulations that replicate 10 years of pollutant loading. Infiltration of stormwater pollutants in typical pollutant concentrations will be evaluated using long-term, actual stormwater data from several sites around the country (in the nine EPA rainfall zones) to qualitatively determine the influence of storm patterns on the migration of stormwater through the vadose zone. The idea of modifying SESOIL to handle multiple pollutants will also be explored. In order to produce more accurate results, soil column testing will be done to experimentally determine the needed input constants (based on actual stormwater concentrations). Once a better set of input values are generated, we hope to use SESOIL to model actual infiltration devices. Even though the lack of accurate data inputs hampered the modeling activity, the results do provide an idea of the direction for the next phase of this research.

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Chapter 2

FISH – USEFUL BIO-INDICATORS FOR EVALUATION OF CONTAMINATION IN WATER ECOSYSTEMS

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Abstract: Fish are one of the animal species used as an environmental bio-indicator. During the years 2002–2004, fish were taken from the Smradavka and Korycany water reservoirs located in the south-eastern Czech Republic. Seven fish species were monitored. Fish tissues were analyzed for both heavy metals and PCBs indicator congeners. Atomic absorption spectroscopy was used for heavy metals determination. High resolution gas chromatography was used for PCBs determination. The levels of particular trace elements ranged as follows (µg /kg fresh tissue): As 21.6–48.0, Cu 126–612, Ni 45–125, Pb 12.4–28.7 and Zn 3700–12500. Concentrations of cadmium were below the limit of determination (0.2 µg /kg) in all samples. The highest values (in µg /kg fresh tissue) were found for the PCB 153 congener in bream, eel and pike 12.5-22.5. The lowest concentration in all fish species was found for the PCB 52 congener 0.12-1.30. The sum of PCB indicator congeners ranged from 9.10 - roach to 53.9 - bream. The overall level of contamination in fish is low and the current limit for residues that is valid in the Czech Republic was not exceeded in any case.

1. INTRODUCTION

Fish are one of the animal species often used as an environmental bio-indicator to monitor a level of hydrosphere pollution. It is recommended that the monitoring of hydrosphere pollution should be as complex as possible, which means that the levels of xenobiotics should be known not only in water but also in sediments and tissues of animals considered to be bio-indicators. Monitoring studies of this kind are sometimes extended to phytoplankton and zooplankton (Zima and Vávrová, 1997). Fish are often screened for high-risk elements and/or also for various kinds of organic pollutants.

In their thorough monitoring studies aimed at marine fish, Voight, et al monitored the levels of high-risk elements in fish living in Finnish coastal waters, in the Baltic Sea and the offshore waters of western Estonia. (Voight, 1999, Zauke et al., 1999, Anonymous 2004). According to the available literature fresh-water fish have not been extensively used as a bio-indicator to evaluate a level of contamination in the fresh-water ecosystem.

Both the Ministry of the Environment and the Ministry of Agriculture of the Czech Republic evaluate contamination of fish annually, focussing particularly on the determination of high-risk elements, polychlorinated biphenyls and organic chlorinated insecticides. The current levels of particular pollutants are not too high and comply with both national and European limits; an increased level of pollution was found only as a consequence of ecological accidents (Anonymous 2004).

There are approximately one hundred PCBs congeners detected in environmental samples, of which about 50 are toxicologically and/or environmentally important. The maximum residual limit in particular commodities is given as the sum of seven PCBs indicator congeners (28, 52, 101, 118, 132, 153, 180). In addition, the congeners PCB 206 and PCB 209 are also monitored.

The hydrosphere probably contains the substantial part of PCBs present in the environment. Due to their hydrophobic behaviour and the ability to be kept in sediments and/or biota, they are detectable in all parts of hydrosphere even in areas where the contamination could be kept at the background levels (Niimi, 1996).

The load of sediments varies from several tenths of mg/kg up to tens of mg/kg depending upon the distance from contamination sources. Content in water organisms increases with their position in the food chain. Fish reflect the state of the pollution very well because of their limited ability to eliminate contaminants. Thanks to the stability of the PCBs and their lipophilic properties, they readily accumulate in fat tissue. The majority of PCBs congeners detected in fish tissues are penta- and/or hexachlorobiphenyls, especially the congeners PCB 118 and PCB 153 (Parte and Albaiges, 1994).

There have been two complex studies carried out in the Czech Republic dealing with the systematic monitoring of PCBs indicator congeners contents in fish (Vávrová et al., 2003, Svobodová et al., 2004).

2. MATERIALS AND METHODS

During the years 2002 – 2004, fish were taken from the Smradavka and Korycany reservoirs in order to find out whether fish can serve as a bio-indicator in the fresh-water ecosystem. Properly licensed workers complied with the law relating to the protection of animals against maltreatment. The following species of fish were taken: pike, zander, eel, carp, bream, roach, tench, and silver salmon.

2.1 Chemicals

All chemicals used for trace element determination were of Analytical Grade (Merck, Germany) except for HNO_3 (65%) which was additionally purified by sub-boiling distillation. In addition H_2SO_4 (96%, Suprapur, Merck Germany) and HCl (37%, Suprapur, Merck Germany) were used. All solutions were prepared using deionised water of specific resistance >0.4 MΩ. Standards of particular elements were prepared from commercial 1000 mg/L stock solutions (Analytika, Czech Republic). Standard reference materials DORM-2 and DOLT-2 (2Theta, Czech Republic) were used to check accuracy.

For determinations of PCBs, the following chemicals were used (Merck, Germany) anhydrous sodium sulphate, analytical grade, annealed in a muffle furnace at 650 °C for 4 h; sulphuric acid 96% (Suprapur, Merck); Florisil 60/100 mesh, cleaned and annealed at 600 °C; aluminium oxide, chromatography grade, cleaned and annealed at 400°C. Before use sorbents were activated in a hot-air drier at 130°C, 6 h. Furthermore, the following solvents and/or elution mixtures were used: n-hexane, isooctane (SupraSolv; Merck); n-hexane (Residue Analysis Grade); petroleum ether (boiling point 35 to 60 °C, pure) bi-distilled in a ground glass apparatus; diethyl ether (Analytical Grade) bi-distilled, peroxide-free, dried over anhydrous sodium sulphate; acetone (Residue Analysis Grade); n-hexane-diethyl ether (94+6), n-hexane-acetone (94+6). Standard solution of PCBs congeners Mix3 (Dr. Ehrenstorfer GmbH, Germany), standard reference material Chlorobiphenyls in Mackerel Oil, BCR No: 350 (Community Bureau of Reference, Belgium).

2.2 Pre-analytical and analytical procedure – determination of metals

Samples of fish tissues were wet digested using the mixture of nitric acid and sulphuric acid (26+1). The levels of lead, cadmium, copper and nickel were then determined using Graphite Furnace Atomic Absorption Spectrometry (GF-AAS). Zinc was determined by Flame Atomic Absorption Spectrometry (FAAS) and arsenic determined by Hydride Generation Atomic Absorption Spectrometry (HG-AAS). The instrument AAA Solar with appropriate accessories (Thermoelemental, UK) was used within the study. Limit of determination were 2 μg/ml for each particular element. The accuracy of the analysis was verified using standard reference materials.

2.3 Pre-analytical and analytical procedure – determination of PCBs

The complete procedure for the determination of PCBs is described in [8].

3. RESULTS AND DISCUSSION

The concentrations of trace metals found in fish muscles are summarized in Table 1 and Table 2. Mean values, standard deviations and ranges are given. In the Smradavka water reservoir (see Table 1), seven fish species (pike, zander, eel, carp, bream, roach and tench) were monitored. The number of fish samples in each group was different ranging between 6 (zander, tench) and 28 (eel). It can be seen that the level of contamination in fish taken from the Smradavka reservoir is low and that the current limit for residues, which is valid in the Czech Republic, was not exceeded in any case. Table 2 shows the average levels of heavy metals in muscle tissue of fish taken from the Korycany reservoir. Five fish species (pike, zander, eel, carp and silver salmon) were monitored. The number of fish in each group was different ranging between 6 (silver salmon) and 46 (eel). It follows from the values introduced in this table that the level of contamination in fish taken from the Korycany reservoir is very low and again the current limit for residues, which is valid in the Czech Republic, was not exceeded in any case.

Table 1. Content of heavy metals in muscle tissues of fish – reservoir Smradavka [μg/kg fresh tissue]

Elements		Pike N=13	Zander N=6	Eel N=28	Carp N=16	Bream N=12	Roach N=22	Tench N=6
As	mean	24.4	32.9	29.8	27.1	23.3	22.5	30.0
	range	19.8 – 27.6	29.8 – 37.8	24.5 – 37.2	23.2 – 29.8	18.2 – 29.5	15.3 – 29.6	27.9 – 32.3
	SD	2.35	2.94	3.40	1.92	3.94	4.02	1.62
Cd	mean	< 2	< 2	41.2	< 2	< 2	< 2	< 2
	range	n.e.	n.e.	20.0 – 70.0	n.e.	n.e.	n.e.	n.e.
	SD	n.e.	n.e.	17.1	n.e.	n.e.	n.e.	n.e.
Cu	mean	595	142	583	112	261	249	505
	range	533 – 658	127 – 158	463 – 712	86.0 – 126	215 – 302	196 – 287	482 – 528
	SD	37.9	12.5	65.2	12.9	26.0	21.6	16.2
Ni	mean	23.3	49.7	125	42.7	113	44.6	127
	range	17.5 – 34.5	39.0 – 66.0	89.0 – 184	25.3 – 38.3	85.0 – 158	28.0 – 70.0	104 – 142
	SD	3.93	10.1	23.0	14.1	22.7	11.3	14.7
Pb	mean	< 2	< 2	22.2	12.4	< 2	< 2	28.7
	range	n.e.	n.e.	12.0 – 32.0	10.4 – 19.6	n.e.	n.e.	24.0 – 33.0
	SD	n.e.	n.e.	5.59	2.25	n.e.	n.e.	3.50
Zn	mean	3264	5396	6960	7916	7886	2771	7889
	range	2335 – 4300	3597 – 6521	4968 – 12005	5998 – 10021	5987 – 10050	1998 - 4220	4295 – 12500
	SD	546	1098	1547	1229	1568	506	2780

N - number of analysed samples
SD - standard deviation
n.e. - not evaluated

Table 2. Content of heavy metals in muscle tissues of fish – reservoir Korycany [µg/kg fresh tissue]

Elements		Pike N=7	Zander N=8	Eel N=46	Carp N=13	Silver salmon N=6
As	mean	10.5	18.6	16.5	19.9	9.55
	range	<2 – 16.5	10.2 – 26.9	10.0 – 22.8	11.6 – 30.5	<2 – 14.6
	SD	1.55	2.12	2.08	3.65	1.16
Cd	mean	<2	<2	<2	<2	<2
	range	n.e.	n.e.	n.e.	n.e.	n.e.
	SD	n.e.	n.e.	n.e.	n.e.	n.e.
Cu	mean	142	217	212	245	168
	range	99 – 187	168 - 264	145 - 259	198 - 305	104 – 226
	SD	9.65	14.9	7.53	21.8	19.4
Ni	mean	65.5	75.4	66.9	60.9	38.2
	range	26.5 – 89.4	41.7 – 112.3	39.8 – 99.8	29.5 – 100.2	20.5 – 77 6
	SD	11.6	14.8	9.98	12.4	13.2
Pb	mean	<2	15.7	12.5	18.6	<2
	range	n.e.	<2 – 26.5	<2 – 18.6	14.3 – 26.7	n.e.
	SD	n.e.	9.62	6.55	8.65	n.e.
Zn	mean	1265	3015	2689	2998	987
	range	867 – 1665	2258 - 3612	2485 - 2998	2789 - 3351	712 - 1165
	SD	80.7	102	25.9	56.5	412

N- number of analysed samples
SD- standard deviation
n.e.- not evaluated

Levels of the most often-monitored risk elements such as cadmium and lead were even below the limit of determination in several cases. The lowest levels of all risk elements were found in pike (predatory fish) while the highest levels were detected in tench, which lives predominantly near to the bottom. The measured levels of risk elements were compared with the data published by the State Veterinary Administration of the Czech Republic (State Veterinary Administration of the Czech Republic 2002) and were significantly lower. However, it should be emphasized that the levels found in 2001 all over the Czech Republic were not high and that the hygienic limit was exceeded only once for arsenic (predatory fish – rainbow trout) and once for mercury (barbel).

The results of PCBs determinations are summarized in Table 3 (water reservoir Sradavka) and Table 4 (water reservoir Korycany). Average values and ranges in muscles of fish are given.

Table 3. Content of PCBs in muscle tissues of fish – reservoir Smradavka [µg/kg fresh tissue]

PCB congener		Pike N=5	Eel N=9	Bream N=7	Roach N=5	Carp N=9
28	mean	1.16	4.85	4.26	0.62	1.53
	range	0.36-1.82	0.88-13.25	0.42-7.35	0.35-1.05	0.78-3.03
52	mean	0.38	1.08	1.30	0.24	0.57
	range	0.23-0.86	0.33-3.25	0.10-3.86	0.08-0.52	0.22-0.78
101	mean	0.62	3.36	4.76	0.48	0.85
	range	0.18-0.98	0.60-9.56	0.21-7.98	0.26-0.82	0.79-0.83
118	mean	0.24	0.63	1.51	0.20	0.39
	range	0.11-0.51	0.37-1.12	0.19-3.68	0.10-0.48	0.33-0.92
138	mean	9.95	11.79	13.63	4.52	6.83
	range	2.48-19.10	5.70-23.14	2.72-24.11	1.04-9.85	4.56-9.88
153	mean	13.45	16.71	22.49	5.71	10.48
	range	3.27-24.66	8.26-31.40	3.96-44.65	1.43-12.52	6.36-14.99
180	mean	6.99	7.51	5.92	0.57	4.38
	range	1.38-13.59	2.93-17.65	1.12-15.72	0.15-2.52	2.43-8.28
∑ of congeners		32.79	45.93	53.87	12.34	25.03

N- number of analyzed samples

Table 4. Content of PCBs in muscle tissues of fish – reservoir Korycany [µg/kg fresh tissue]

PCB congener		Pike N=6	Eel N=8	Bream N=8	Roach N=6	Carp N=8
28	mean	0.71	3.09	3.15	0.36	1.02
	range	0.36-1.64	0.83-14.28	0.32-6.32	0.35-0.98	0.91-1.03
52	mean	0.21	0.83	1.06	0.14	0.37
	range	0.23-0.56	0.40-3.08	0.11-3.00	0.08-0.48	0.37-0.66
101	mean	0.39	2.94	3.85	0.29	0.62

PCB congener		Pike N=6	Eel N=8	Bream N=8	Roach N=6	Carp N=8
	range	0.18-0.95	0.60-9.36	0.31-7.76	0.26-0.61	0.79-0.83
118	mean	0.10	0.49	0.67	0.10	0.12
	range	0.11-0.36	0.37-0.98	0.19-3.35	0.10-0.32	0.33-0.34
138	mean	9.02	10.95	12.85	3.94	5.04
	range	2.48-19.07	5.70-23.06	2.72-23.97	1.04-9.62	4.56-9.18
153	mean	12.88	15.78	21.33	4.11	9.63
	range	3.17-24.00	8.26-31.40	3.96-44.29	1.44-12.36	6.56-14.28
180	mean	5.98	6.89	4.93	0.16	2.76
	range	1.36-13.19	2.80-17.25	1.01-11.72	0.65-5.52	2.43-6.28
∑ of congeners		29.29	40.97	47.84	9.10	19.56

N- number of analyzed samples

It follows from Table 3 and Table 4, that the Smradavka reservoir is more polluted than the Korycany reservoir (compare for example the sums of congeners. See also Figure 1). However, it should be noted that the Colorak Company, which uses Delor 106 in the production of paints is in the same region. Differences in concentrations in the Table 3 and Table 4 could be ascribed to the fact that the location of the Korycany reservoir is further from this source of contamination. In addition, illegal dumps were found in the vicinity of the Smradavka water reservoir, which was not the case for the Korycany. Although the differences found were not too extensive, nevertheless some additional work should be done in order to make reliable statistical evaluation. Whatever the cause, the levels of PCBs congeners in the reservoirs are higher than the background in the Czech Republic, where the sum of congeners ranges between 2 – 5 µg/kg of fresh tissue (State Veterinary Administration of the Czech Republic 2005).

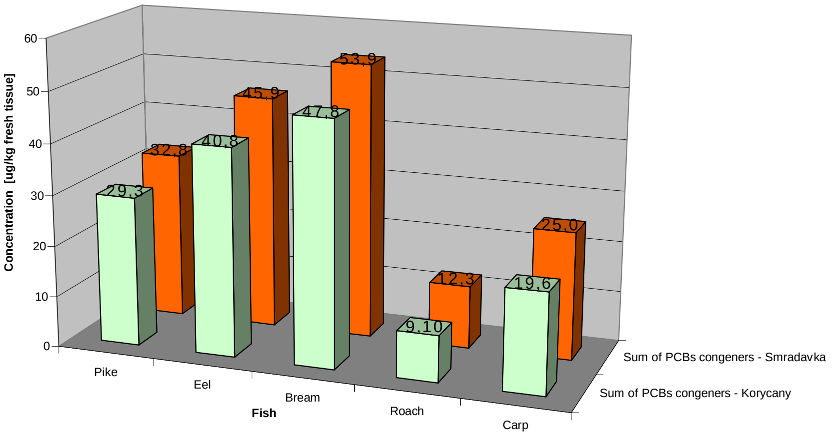

Figure 1. Comparison of the sum of PCBs indicator congeners found in the reservoir Korycany and Smradavka

4. CONCLUSION

Contents of heavy metals and PCBs indicator congeners were analyzed in fish tissues during the period 2002 – 2004. Heavy metals were determined by the AAS method, PCBs by the GC/ECD method. Variability of trace metals content was found regarding fish species. The results were compared with the legislation valid in the Czech Republic. It was found that the concentrations did not exceed the hygienic limits. Higher values of high-chlorinated congeners were found as a consequence of the use of Delor 103 in the Colorlak factory located in the vicinity. The source of higher values of PCB 28 congener could be a secondary contamination from air. It could be stated that transfer of PCBs into the food chain persists years after the production of paints containing PCBs was stopped.

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Chapter 3

ACHIEVEMENT OF A BENEFICIAL REUSE DESIGNATION FOR A SPECIALIZED HIGH VOLUME BYPRODUCT

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Abstract: The State of Florida encourages the recycling and reuse of a variety of materials, assuming that it can be accomplished in a manner that protects public health and the environment. A detailed technical and field evaluation was conducted on behalf of and in cooperation with a major municipal utility, to investigate the reuse potential of large volume byproducts from an electrical generating station which employs circulating fluidized bed (CFB) technology for combustion of coal and petcoke as fuel. In cooperation with FDEP, a 18 month field demonstration was conducted to assess stability, leachability, and runoff from one of the CFB byproducts ("EZBase™"). Pads (12 by 50 feet) were constructed of the compacted EZBase™ as well as of materials for which EZBase™ could be substituted (asphalt, limerock, concrete) and were designed to simulate proposed reuse scenarios. Shallow groundwater monitoring wells were installed immediately adjacent to the pads and were monitored monthly for a variety of constituents, in conjunction with surface water runoff samples collected during rainfall events, and soil samples adjacent to all of the pads.. Vanadium emerged as a substance of interest in both surface runoff and in soil, but vanadium was not detected in nearby groundwater wells. The groundwater, soil and storm water runoff data clearly demonstrated that the EZBase™ does not pose hazards to the environment, and demonstrated that the environmental fate of analytes in the byproduct is very similar to the other commonly used products in similar applications. A variety of potential risk-based reuse scenarios were proposed to the state environmental regulatory agency on the basis of human health and ecological considerations, including soil stabilization in environmental remediation applications, road bed and road surface projects, commercial/industrial site paving projects, and road right-of-way application. Toxicological, risk and engineering questions were satisfactorily addressed and approvals were granted for reuse of EZBase™ on a broad scale.

Key words: Beneficial reuse, recycling, circulating fluidized bed, field demonstration

1. INTRODUCTION

In November 1998, JEA, formerly known as the Jacksonville Electric Authority, submitted a permit application to the Florida Department of Environmental Protection (FDEP) for the repowering of two generating units at the Northside Generating Station (NGS). The centerpiece of the proposed repowering project entailed the conversion of two 1960s vintage oil-fired boilers to new, solid fueled state-of-the art circulating fluidized bed (CFB) boilers.

From the inception of the project through design and permitting, JEA expressed its intent to market and sell the byproduct from the CFB units for beneficial reuse. The byproduct from a solid fuel CFB plant is distinct from that of conventionally fired boilers (e.g., pulverized coal, fuel oil, etc.) because it is composed primarily of lime and gypsum, with less than 10 percent by weight being derived as ash from combustion of the fossil fuels. Accordingly, the byproduct from a CFB plant is not considered as an “ash” in the typical sense as the remnant material from conventionally-fired boilers. Over 90 percent of CFB byproduct is a result of the addition of limestone to the boilers to create thermal mass for the fluidized bed and to create the primary scrubbing medium for removal of sulfur gases. The resultant byproduct has excellent material properties that allow it to be used in numerous applications where lime, cement and concrete would otherwise be used.

Preliminary discussions with FDEP indicated that a designation of the byproduct for “beneficial use” was possible and, in fact, would be in alignment with stated Florida policy regarding recycling and reuse at both the State and Federal levels. However, other than for municipal solid waste incinerators (FDEP 2001), implementing procedures for acquiring the beneficial use designation were neither well-defined nor had been routinely received or reviewed by the FDEP since inception of the program. Thus, notwithstanding the clear direction in policy and statute, FDEP staff indicated that there were few examples of approved beneficial use applications to date. One option explored and eventually pursued was to have a relatively small area designed and permitted under the Chapter 62-701 FAC regulations as a solid waste management facility operationally concomitant with the CFBs coming on-line, to allow for storage of the byproduct while it was fully characterized and a market was developed. The decision to seek authorization under a Chapter 62-701 FAC permit (Class I landfill) was primarily based on the limited alternatives available for regulatory coverage of the byproduct storage area (BSA).

Based on the verified demand for uses of the byproduct in Florida and the designed limited capacity of the BSA, JEA approached both the Northeast District and the Solid Waste Offices of the FDEP headquarters in Summer 2003, to discuss how best to pursue expeditious review of and approval for the beneficial use of the JEA CFB byproducts. Numerous meetings were held with various FDEP personnel from both offices to seek input on the most effective method of providing the information needed for FDEP action on the request for beneficial use.

In order to encourage the implementation of recycling/reuse as a desired and desirable public policy, Florida has in place specific statutes. The criteria for judging whether industrial byproducts may obtain exemption from regulation as a solid waste for the purpose of safe and productive use are provided in Florida Statute §403.7045(1)(g), and are summarized as follows:

1. A majority of the industrial byproducts are demonstrated to be sold, used, or reused within 1 year;
2. The industrial byproducts are not discharged, deposited, injected, dumped, spilled, leaked, or placed upon any land or water so that such industrial byproducts, or any constituent thereof, may enter other lands or be emitted into the air or discharged into any waters, including groundwaters, or otherwise enter the environment such that a threat of contamination in excess of applicable Department air or water quality standards and criteria is caused; and,
3. The industrial byproducts are not hazardous wastes.

JEA's operation of the two CFB units at the NGS presently produces two marketable byproducts, both of which are exempt industrial byproducts:

- EZSorb™ is a sorbent byproduct consisting of either unhydrated bed or unhydrated fly ash and sold directly from the silos for a variety of uses where use of quick lime or Portland cement would be appropriate, such as to stabilize and strengthen soils in preparation for other construction activities, and to solidify soils at environmental remediation sites.

- EZBase™ is a sorbent byproduct consisting of hydrated mixed fly and bed ashes. Once removed from the boilers, the dry

> material enters a water hydration system and is sluiced into the BSA (Goodrich and Charhut, 2003), hence the identification as hydrated. The hydrated byproduct has materials properties that make it valuable for the beneficial uses as described in this report.

The byproducts subsequently have been trademarked as EZBase™ (hydrated sorbent mix of fly and bed ashes) and EZSorb™ (unhydrated sorbent byproduct of fly or bed ash).

2. MATERIALS AND METHODS

As part of the data gathering process for submittal of the beneficial use designation request to FDEP, a field study was conducted using the EZBase™ product in several applications typical of the market applications for which approval was to be requested. The purpose was to collect soil, groundwater and storm water runoff data for comparison between EZBase™ and similar materials for which EZBase™ would be a suggested replacement.

Test pads were constructed at the JEA Brandy Branch Generating Station located near Baldwin, FL (see Figure 1). The test pads were 12 feet wide by 50 feet long (nominal). The construction details for the test pads are shown in Figure 2 and were arranged as follows:

- Test Pad 1 was composed of 12 inches of compacted EZBase™ that was covered with a surface course of asphalt.
- Test Pad 2 was 12 inches of compacted EZBase™ alone, to compare the EZBase pads with commonly used road construction materials.
- Test Pad 3 was composed of limerock.
- Test Pad 4 was constructed of concrete.


Test Pads
Figure 1
Aerial of Brandy Branch with Test Pad Locations
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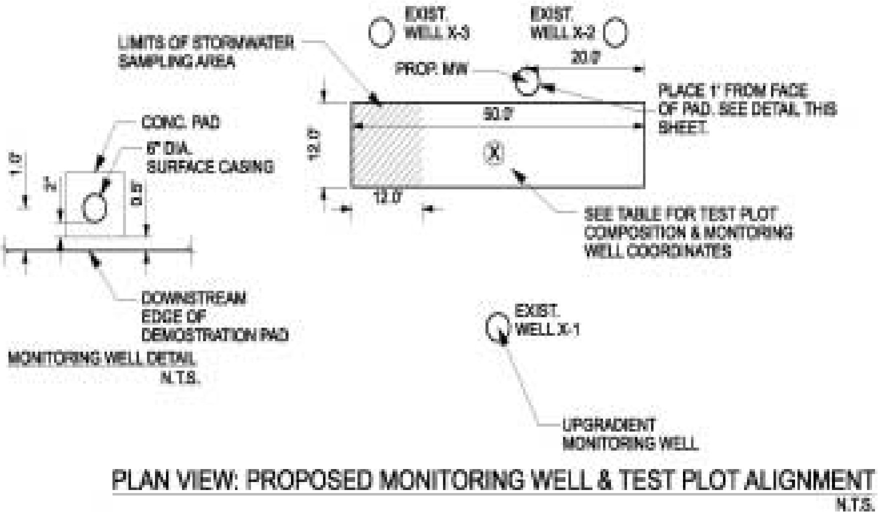
Figure 1.



TEST PLOT NUMBER (X)	TEST PLOT COMPOSITION
1	2.0" S-1 ASPHALT 12" HYDRATED ASH (COMPACTED IN 6" LIFTS)
2	12" HYDRATED ASH (COMPACTED IN 6" LIFTS)
3	12" COMPACTED LIMEROCK
4	12" CONCRETE (4,000 PSI MIXTURE)

Figure 2

JEA BENEFICIAL USE DEMONSTRATION
MONITORING WELL DESIGN & CONSTRUCTION SUMMARY
PROPOSED WELL INSTALLATION

Figure 2.

The EZBase™ used for the construction of the pads, as well as the limerock and concrete, were analyzed for metals, semivolatile and volatile organics. The synthetic precipitation leaching procedure (SPLP) also was performed on these samples for the same parametric coverage.

A portion of all test pads (12-ft. x 12-ft. section, approx.) was sloped to one end so that storm water runoff could be collected. Storm water runoff was collected and analyzed after each major storm event using a storm water sampler by Vortox. Storm water was collected after 11 rain events from late April to late June 2004.

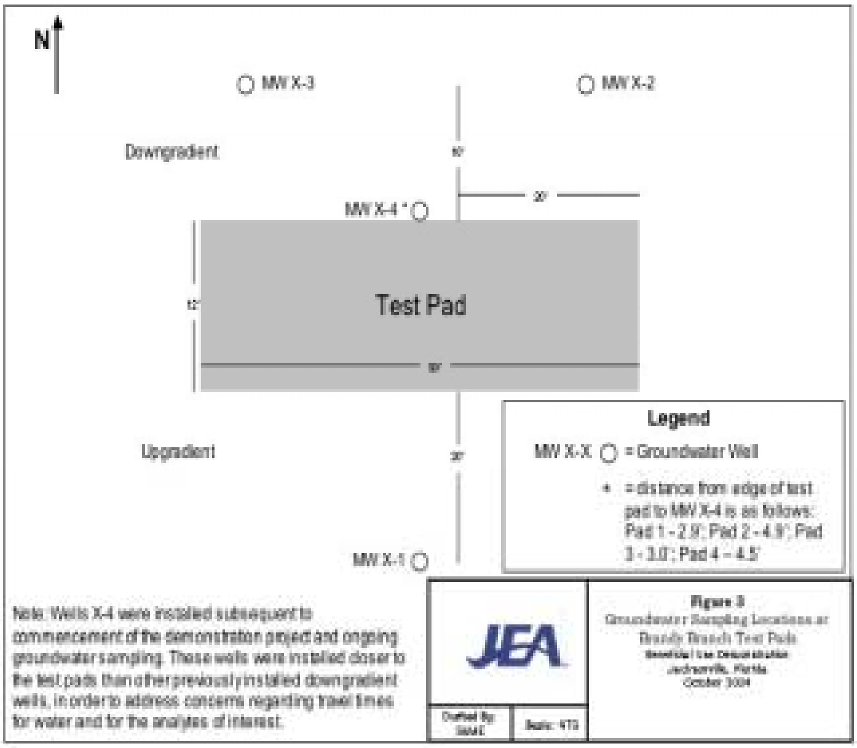
Soil surrounding the test pads was sampled at various locations approximately 15 months after installation of the test pads. The surface soil was sampled as well as 0.5 foot below ground surface (ft bgs), 1.0 ft bgs and 2.0 ft bgs. Both upgradient and downgradient soil samples were collected and analyzed for total metals (e.g., aluminum, antimony, arsenic, barium, boron, chromium, iron, lead, manganese, mercury, nickel, selenium, thallium and vanadium.)

Groundwater was monitored by installation of monitoring wells both upgradient ("background") and downgradient from the test pads. As shown in Figure 3, MW X-1 was the upgradient well and was located approximately 10 ft upgradient from each pad. MWX-2 and MW X-3 were approximately 10 feet downgradient from each pad. In addition, a nearer downgradient well was subsequently installed, about 3-4 feet from each pad (e.g., MW X-4; see Figure 3). The groundwater monitoring wells were sampled and analyzed approximately every four weeks for about 18 months for metals, mercury, semi-volatile organic compounds (SVOCs), volatile organic compounds (VOCs), radionuclides (gross alpha, uranium, Radium 226 and Radium 228), hardness, turbidity, pH and sulfates.

3. RESULTS

3.1 Materials of Construction

The chemical analysis of the EZBase™ used to build Test Pads 1 and 2 is shown in Table 1. As shown in Table 1, the maximum concentrations of analytes detected in the EZBase™ were compared with 100% and 50% of the residential, industrial and leachability-based soil guidance values of the Florida Department of Environmental Regulation (FDEP, 2005a), as recommended in the FDEP Reuse Documents. Arsenic, nickel, thallium and vanadium were the chemicals of concern in EZBase™, based on the comparisons with 100% of the values for residential exposure or for leachability.



Note: Wells X-4 were installed subsequent to commencement of the demonstration project and ongoing groundwater sampling. These wells were installed closer to the test pads than other previously installed downgradient wells, in order to address concerns regarding travel times for water and for the analytes of interest.

Figure 3
Groundwater Sampling Locations at Brandy Branch Test Pads
Beneficial Use Demonstration
Jacksonville, Florida
October 2004

Figure 3.

To assess the potential for leachability, the materials used to construct the test pads also were tested by the Synthetic Precipitation Leachability Procedure (SPLP). The SPLP concentrations were compared with both FDEP groundwater cleanup target levels [(GCTL) (FDEP, 2005a)] or the maximum contaminant level [(MCL)(FDEP, 1995)] and the FDEP Chapter 62-302 concentration for Class III freshwater (FDEP, 1996). As shown in Table 2, lead and Radium 226/228 were the only analytes with a maximum SPLP concentration that exceeded the surface water value. The maximum concentration of sulfates, chloromethane, methylene chloride, antimony, lead, molybdenum, vanadium and Radium 226/228 exceeded either the GCTL or the MCL.

3.2 Storm Water Runoff

The storm water runoff data were compared with the GCTL or MCL for groundwater and the Chapter 62-302 concentration for Class III freshwater. As shown in Table 3, the concentration of aluminum and iron in the storm water runoff exceeded both the groundwater and surface water values for <u>all</u> pads. Lead in the runoff from the EZBase™ pad marginally exceeded the MCL only on May 25, 2004 (e.g., 0.017 mg/L vs the MCL of 0.015 mg/L). The MCL for manganese of 0.05 mg/L also was exceeded in storm water runoff from the asphalt and limerock pads, as well as the rainwater control on two events.

Table 1. Analytical Data and Preliminary Screening Comparisons for EZBase Beneficial Use Demonstration JEA, Jacksonville, Florida, October 2004

	No. Positive/ Total No. of Samples	**95% UCL Conc. (mg/kg)**	**Maximum**	**FDEP RTLs (mg/kg)**					
				100% of Values			**50% of Values**		
				Residential	**Industrial**	**Leachability**	**Residential**	**Industrial**	**Leachability**
EPA METHOD 8260B (volatile organics)									
1,1-Dichloroethene	2/20	NC	0.02	95	510	0.06	47.5	255	0.03
EPA METHOD 8270C SIM (semi-volatile organics)									
Naphthalene	1/20	NC	0.018	55	300	1.3	27.5	150	0.65
Anions									
Chloride	15/15	NC	910	NF	NF	NF	NF	NF	NF
Sulfate	15/15	NC	37,000	NF	NF	NF	NF	NF	NF
Nitrate-N	0/10	NC	BDL	14,000	NA	SPLP	7,000	NA	SPLP
EPA METHOD 6010 (inorganics)									
Aluminum	23/23	17,504	23,800	80,000	NA	SPLP	40,000	NA	SPLP
Antimony	0/12	NC	BDL	27	370	5.4	13.5	185	2.7
Arsenic	22/22	5.4	8	2.1	12	29	**1.05**	**6**	14.5
Barium	21/22	74	96	120	130,000	1,600	**60**	65,000	800
Boron	22/22	112	154	7,900	200,000	SPLP	3,950	100,000	SPLP
Chromium	22/22	17	19	210	470	38	105	235	19
Iron	22/22	14,949	22,200	53,000	NA	SPLP	26,500	NA	SPLP
Lead	22/22	9.2	18	400	1,400	SPLP	200	700	SPLP
Manganese	21/21	61	72	3,500	43,000	SPLP	1,750	21,500	SPLP
Mercury	22/22	0.19	0.29	3	17	2.1	1.5	8.5	1.05

Nickel	22/22	515	710	**340****	35,000	**130**	**170**	17,500	**65**
Selenium	4/22	3.0	3.7	440	11,000	5.2	220	5,500	**2.6**
Sodium	20/21	928	1,100	NF	NF	NF	NF	NF	NF
Thallium	1/12	NC	9.1	**6.1**	150	**2.8**	**3.05**	75	**1.4**
Vanadium	22/22	2,814	4,100	**67****	10,000	**1,100**	**33.5**	5,000	**550**

Bold indicates that the maximum concentration exceeds the SCTL
** Direct exposure based on acute exposure considerations
SPLP (Synthetic Precipitation Leaching Procedure) SPLP test for leachability recommended
NA Not Applicable for this pathway at any concentration
NC Not calculated because an insufficient number of samples or positive results are available
☐ Preliminary Substances of Interest

RTL Reuse Target Levels (FDEP, 2001; FDEP, 2002; FDEP, 2003; FDEP, 2004; FDEP, 2005a)

Table 2. Comparison of Regulatory Values with SPLP Data for EZ Base Beneficial Use Demonstration JEA/Jacksonville, FL, October, 2004

Parameter	**95% UCL Concentration (µg/L)**	**Maximum Concentration (µg/L)**	**No. Positive/ Total No. of Samples**	**FDEP GCTL or MCL (µg/L)**	**Chapter 62-302 Class III, fresh (µg/L)**
SPLP, EPA METHOD 300					
Chloride	NC	20,000	1/1	250,000	NF
Sulfate [b]	NC	1,200,000	1/1	250,000	NF
Nitrates	NC	100	1/1	10,000	NF
SPLP, EPA METHOD 8260B					
Acetone	NC	560 Y	1/5	630	1,700
Chloromethane[b]	NC	3.3	1/11	2.9	NA
Methylene chloride [b]	NC	6.6	5/11	5	≤1,580
Toluene	NC	2.4	1/11	40*	NA
SPLP, EPA METHOD 6010					
Antimony [b]	NC	100	1/10	6	4,300
Barium	215	240	20/20	2,000	NA
Boron	NC	59	1/1	630	NF
Chromium	17	17	7/20	100	207
Lead [a,b]	NC	20	5/20	15	3.2
Molybdenum [b]	310	310	10/15	35	NA
Potassium	NC	24,000	10/10	NF	NF
Sodium	23,919	24,000	10/10	160,000	NA
Vanadium [b]	92	150	20/20	49	NA
Radionuclides					
Radium 226 (pCi/L) [a,b]	NC	4.24	5/10	5 (226+228) pCi/L	5 (226+228) pCi/L
Radium 228 (pCi/L) [a,b]	1.48	1.48	9/10	5 (226+228) pCi/L	5 (226+228) pCi/L
Uranium (µg/L)	NC	0.721	4/10	0.021	NA

FDEP GCTL- Florida Department of Environmental Protection Groundwater Cleanup Target Level, Table I, Chapter 62-777, Florida Administrative Code

SPLP- Synthetic Precipitation Leaching Procedure

Y The laboratory analysis was from an improperly preserved sample

* Secondary standard, based on taste and odor considerations

Shading indicates Preliminary Substances of Interest

NA Not Available

NC Not calculated because an insufficient number of samples or positive results is available.

Values for Lead were calculated based on a default hardness of 100 mg/L as $CaCO_3$.

[a] Selected based on comparison with surface water criteria.

[b] Selected based on comparison with groundwater criteria.

Table 3. Comparison of Storm Water Runoff Between Pads Beneficial Use Demonstration JEA/Jacksonville, Florida, October 2004

Analyte	Pad[1]	Statistic				CTL (mg/L)[2]	
		n/N[3]	Minimum[4]	Maximum[4]	Mean[4,5]	GW	SW
Aluminum	Asphalt	12/12	0.38	11	3.04	0.2	0.013
	EZBase	12/12	1.5	10	4.28		
	Limerock	10/11	<0.2	12	3.45		
	Concrete	11/11	0.04	9.6	3.47		
Antimony	Asphalt	0/4	<0.02	<0.02	--	0.006	4.3
	EZBase	0/4	<0.02	<0.02	--		
	Limerock	0/4	<0.02	<0.02	--		
	Concrete	0/4	<0.02	<0.02	--		
Arsenic	Asphalt	0/12	<0.008	<0.01	--	0.050	0.05
	EZBase	0/12	<0.008	<0.01	--		
	Limerock	0/11	<0.008	<0.01	--		
	Concrete	0/11	<0.008	<0.01	--		
Barium	Asphalt	5/12	<0.01	0.038	0.017	2	NP[6]
	EZBase	6/12	<0.01	0.023	0.014		
	Limerock	5/11	<0.01	0.033	0.015		
	Concrete	5/11	<0.01	0.022	0.012		
Boron	Asphalt	0/12	<0.05	<0.05	--	0.63	NP
	EZBase	0/12	<0.05	<0.05	--		
	Limerock	0/11	<0.05	<0.05	--		
	Concrete	0/11	<0.05	<0.05	--		
Chromium	Asphalt	1/12	<0.01	0.018	0.011	0.1	0.27
	EZBase	8/12	<0.01	0.034	0.014		
	Limerock	3/11	<0.01	0.032	0.014		
	Concrete	3/11	<0.01	0.025	0.014		
Iron	Asphalt	12/12	0.11	2.6	0.74	0.3	1.0
	EZBase	12/12	0.015	3.0	0.90		
	Limerock	11/11	0.12	3.3	1.24		
	Concrete	11/11	0.12	2.2	0.81		
Lead	Asphalt	4/12	<0.005	0.011	0.006	0.015	0.018
	EZBase	3/12	<0.005	0.017	0.006		
	Limerock	2/11	<0.005	0.007	0.005		
	Concrete	1/11	<0.005	0.0095	0.005		
Manganese	Asphalt	6/12	<0.01	0.100	0.028	0.050	NP
	EZBase	3/12	<0.01	0.027	0.014		
	Limerock	8/11	<0.01	0.055	0.024		
	Concrete	3/11	<0.01	0.027	0.012		
Mercury	Asphalt	0/12	<0.0002	<0.0002	--	0.002	0.000012
	EZBase	0/12	<0.0002	<0.0002	--		
	Limerock	0/11	<0.0002	<0.0002	--		
	Concrete	0/11	<0.0002	<0.0002	--		
Nickel	Asphalt	0/12	<0.02	<0.04	--	0.1	0.17
	EZBase	2/12	<0.02	0.056	0.036		

		Statistic				CTL (mg/L)[2]	
	Limerock	0/11	<0.02	<0.04	--		
	Concrete	0/11	<0.02	<0.04	--		
Selenium	Asphalt	0/12	<0.01	<0.01	--	0.05	0.005
	EZBase	0/12	<0.01	<0.01	--		
	Limerock	0/11	<0.01	<0.01	--		
	Concrete	0/11	<0.01	<0.01	--		
Sodium	Asphalt	2/12	<1.0	3.1	1.2	160	NP
	EZBase	12/12	11	180	62		
	Limerock	2/11	<1.0	2.1	1.2		
	Concrete	11/11	2.8	13	7.4		
Thallium	Asphalt	0/4	<0.01	<0.01	--	0.002	0.0063
	EZBase	0/4	<0.01	<0.01	--		
	Limerock	0/4	<0.01	<0.01	--		
	Concrete	0/4	<0.01	<0.01	--		
Vanadium	Asphalt	12/12	0.011	0.11	0.041	0.049	NP
	EZBase	12/12	0.097	0.31	0.160		
	Limerock	8/11	<0.01	0.034	0.016		
	Concrete	10/11	<0.01	0.073	0.020		
pH	Asphalt	11/11	4.63	9.65	7.49[7]	6.5-8.5	
	EZBase	11/11	5.54	9.67	8.54[7]		
	Limerock	10/10	7.77	8.76	8.53[7]		
	Concrete	10/10	6.65	10.4	8.31[7]		

1. Asphalt over EZBase (Pad 1); EZBase (Pad 2); Limerock (Pad 3); Concrete (Pad 4)
2. Cleanup Target Level (CTL) for groundwater (GW) and surface water (SW) per Chapter 62-777, F.A.C.
3. n/N = number of detections/number of samples
4. reported in mg/L, except pH reported in standard units (su)
5. If analyte detected at least once, then reporting limits used as discrete value in the calculation when less than value reported for other observations.
6. NP=not promulgated
7. median, not mean value reported
8. NC= not calculated

The storm water runoff from the EZBase pad also exceeded the MCL for sodium on one occasion. The GCTL of vanadium of 0.049 mg/L also was exceeded by the storm water runoff from the EZBase pad on most events and also by the runoff from the concrete pad after the rainfall event of 6/20/04. The pH of the storm water runoff from all four pads exceeded the groundwater and surface water regulatory values after most rainfall events.

3.3 Soil

None of the soil samples that were taken from areas near the test pads had concentrations of metals that exceeded either the residential or industrial soil cleanup target levels (SCTLs) established by FDEP (FDEP, 2005a).

There was one surface soil sample that was collected at the edge of the EZBase™ pad that had a vanadium concentration of 55 mg/kg, less than the SCTL of 67 mg/kg. Therefore, it appeared that vanadium that might be found in runoff from the EZBase™ pad was sequestered in the soil immediately adjacent to the pad. The transport of low concentrations of vanadium from the surface of the EZBase™ pad, followed by retention in the surficial-to-shallow portion of the soil column, conformed to observations made recently by Martin and Kaplan (1998). These authors hypothesized that the presence of aluminum and iron oxides and small amounts of clay minerals and organic matter were responsible for retention of the metals in the top 7.5 cm of soil.

The soil samples also were tested by SPLP. Essentially, the SPLP for all of the upgradient and downgradient samples exceeded the MCL for iron and aluminum. In addition, there were many of the samples, both upgradient and downgradient, that exceeded the MCL for lead (0.015 mg/L) and the GCTL for vanadium (0.049 mg/L). Neither lead nor vanadium was detected in any of the groundwater samples that were collected from either the upgradient or downgradient wells from any of the pads. Therefore, it did not appear that these SPLP results were a reflection of the effect of the pad materials on the surrounding soils.

3.4 Groundwater

Groundwater was tested for metals (including mercury), semivolatile organic compounds, volatile organic compounds, polycyclic aromatic hydrocarbons (PAHs), radionuclides, pH, sulfate, nitrate and chloride. The only analytes in groundwater that routinely exceeded MCLs were aluminum, iron, manganese and pH (see Table 4). Many of the upgradient and downgradient wells at all pads exceeded the MCL of 0.2 mg/L for manganese. All wells at all the pads exceeded the secondary MCL of 0.3 mg/L for iron. Many of the downgradient wells at all pads, with the exception of the downgradient wells of the concrete pad, exceeded the MCL of 0.05 mg/L for manganese. The pH of most of the wells exceeded the secondary standard of 6.5su to 8.5su.

There also were sporadic exceedances of the MCL for dibromochloromethane, bromodichloromethane, bromoform, benzene and PAHs in some of the wells during the process. However, the sporadic exceedances of these chemicals did not appear to be related to the test pads. Vanadium was not detected in any of the groundwater wells greater than the detection limit.

3.5 Risk Assessment

As part of the Beneficial Use Demonstration and Exemption Determination, potential human exposure scenarios and associated risk from contact with soil that may be impacted by the end-uses proposed were evaluated. Potential exposure to the uncompacted EZBase™ product itself also was evaluated.

For direct exposure to soil, the maximum reported concentrations in the top two feet (i.e., surface soils) were compared with the FDEP default residential and industrial soil SCTLs (FDEP, 2005a). None of the detected chemicals from any of the test pads exceeded either the default residential or commercial/industrial direct exposure SCTLs. This suggested that exposure to the soil immediately adjacent to the pads (or planned EZBase™ applications) presents an insignificant risk to humans even under an unrestricted 350 day per year residential scenario.

Based on the comparison of the results for the uncompacted EZBase™ with the commercial/industrial SCTLs, there are no constitutents of concern (COCs) for direct exposure. Potential direct exposure receptors based on a commercial/industrial scenario would be an indoor/outdoor maintenance worker, a JEA employee, a construction worker or an infrequent visitor/trespasser. However, since there were no COCs based on comparison with the commercial/industrial SCTLs, there would be no exposure of concern for these receptors. Although there are some COCs for consideration regarding leachability, the groundwater results at the site indicate that leachability also is not of concern for EZBase™ as it will be beneficially reused. The qualitative evaluation for exposure to soil is summarized in Table 5. The exposure assessment matrix for uncompacted EZBase™ is shown in Table 6.

Table 4. Comparison of Groundwater Data Between Pads

Analyte	MCL	Pad	Wells	n/N	Concentration Detected (mg/L)		
					Minimum	Maximum	Mean
Aluminum	0.2 mg/L	Asphalt	Upgradient	12/18 (12)	0.23	1.1	0.68
			Downgradient	26/34 (26)	0.21	5.2	0.79
		EZBase	Upgradient	7/17 (7)	0.25	7.4	2.8
			Downgradient	32/34 (32)	0.21	1.7	0.7
		Limerock	Upgradient	4/18 (3)	0.26	0.69	0.43
			Downgradient	24/35 (24)	0.21	3.1	0.73
		Concrete	Upgradient	14/17 (14)	0.24	4.5	1.06
			Downgradient	24/34 (24)	0.25	1.1	0.57
Iron	0.3 mg/L	Asphalt	Upgradient	19/19 (19)	2.5	7.8	3.8
			Downgradient	35/35 (35)	1.7	19	8.3
		EZBase	Upgradient	18/18 (18)	1.9	5.2	3.2
			Downgradient	37/37 (36)	0.08	39	13
		Limerock	Upgradient	18/18 (18)	1.6	3.7	2.2
			Downgradient	34/34 (33)	0.08	11	6.0
		Concrete	Upgradient	18/18 (18)	2.0	8.4	5.0
			Downgradient	35/35 (35)	1.8	16	6.9
Manganese	0.05 mg/L	Asphalt	Upgradient	11/11 (7)	0.034	0.15	0.07
			Downgradient	27/27 (27)	0.06	0.27	0.12
		EZBase	Upgradient	10/10 (10)	0.084	0.17	0.12
			Downgradient	27/27 (24)	0.041	0.22	0.09
		Limerock	Upgradient	10/10 (6)	0.02	0.11	0.06
			Downgradient	27/27 (16)	0.03	0.23	0.09
		Concrete	Upgradient	10/10 (10)	0.06	0.19	0.10

					Concentration Detected (mg/L)		
			Downgradient	27/27 (1)	0.02	0.11	0.04
pH	6.5-8.5 su	Asphalt	Upgradient	19/19 (17)	4.8	6.8	5.7
			Downgradient	35/35 (29)	5.2	7.21	5.9
		EZBase	Upgradient	18/18 (18)	5.2	6.1	5.4
			Downgradient	37/37 (33)	4.9	7.1	5.7
		Limerock	Upgradient	18/18 (14)	5.0	6.9	5.6
			Downgradient	34/34 (24)	5	7.2	5.8
		Concrete	Upgradient	18/18 (16)	5.8	7.4	6.1
			Downgradient	35/35 (29)	5.1	7.1	5.6

n/N = Number of detections/number of samples (Exceedances)

MCL= Maximum Contaminate Level, FDEP, 1995.

Table 5. Exposure Assessment Matrix for Soil Beneficial Use Demonstration JEA/ Jacksonville, Florida October 2004

Potential Receptor	**Exposure Pathway for Soil**				
	Commercial Parking Lot	**Road Bed**	**Soil Stabilization (Remedia-tion)**	**Residential Driveway**	**Covered Road**
Child Resident (0 to 6 yrs)	**NA**	**NA**	**NA**	4	2
Aggregate Resident (0 to 30 yrs)	**NA**	**NA**	**NA**	2	1
Commercial/Industrial (maintenance worker)	3	1	3	1	1
JEA Employee	1*	1*	1*	**NA**	**NA**
Transportation Personnel	1	1	1	**NA**	**NA**
Construction Worker	4*	4*	5*	3*	4*
Infrequent Visitor/ Trespasser	2	1	1	2	1

NA	Not Applicable. The exposure potential for the noted receptor/pathway combinations are not expected to be significant compared with the other combinations for those receptors.
Level 1	Minimal exposure potential with minimal exposure magnitude.
Level 2	Minimal exposure potential with moderate exposure magnitude.
Level 3	Moderate exposure potential with moderate exposure magnitude.
Level 4	High exposure potential with moderate exposure magnitude.
Level 5	High exposure potential with high exposure magnitude.
*	OSHA Regulations apply.

Table 6. Exposure Assessment Matrix for Uncompacted EZBase Beneficial Use Demonstration JEA/Jacksonville, Florida October 2004

Potential Receptor	**Exposure Pathway for Uncompacted EZBase**		
	Commercial Parking Lot	**Road Bed**	**Soil Stabilization (Remediation)**
JEA Employee	1*	1*	1*
Transportation Personnel	1	1	1
Construction Worker	4*	4*	5*
Infrequent Visitor/Trespasser	2	1	1

Level 1	Minimal exposure potential with minimal exposure magnitude.
Level 2	Minimal exposure potential with moderate exposure magnitude.
Level 3	Moderate exposure potential with moderate exposure magnitude.
Level 4	High exposure potential with moderate exposure magnitude.
Level 5	High exposure potential with high exposure magnitude.

* OSHA Regulations apply.

4. DISSCUSION

Based on the results of the demonstration project that have been outlined in this report, the FDEP issued a Beneficial Use Determination and designated the material as an industrial byproduct rather than a solid waste. In a letter to JEA dated July 25, 2005 (FDEP, 2005b), the FDEP indicated that the industrial byproduct could be used in the following applications:

1. Final top surface for roads, parking lots, lay down yards and similar industrial and commercial applications using compacted EZBase™ either alone or with stone (such as granite or limestone) or asphalt millings rolled into the top surface;
2. Compacted as a base course for civil applications in accordance with Florida Department of Transportation (FDOT) Standard Specification Section 200, where the EZBase™ will be covered with a friction surface (final top surface) such as asphalt or concrete or compacted EZBase™;
3. Stabilized base course (meeting compaction requirements) for civil applications in accordance with FDOT Standard Specification Sections 160 and 230, where a final top surface such as asphalt or concrete or compacted EZBase™ will be used;
4. Mixed with existing limestone base for civil applications in compliance with FDOT Standard Specification Section 210, where a final top surface such as asphalt or concrete or compacted EZBase™ will be used; and,
5. Used in stabilization processes for remedial projects where access controls (engineering and/or institutional) are in place and where the remedial project has been reviewed and approved by the Department.

5. CONCLUSION

JEA designed, installed and subsequently monitored a Beneficial Use Demonstration (BUD) project. FDEP staff at all levels offered strong encouragement to proceed with this field demonstration and provided valuable input on how best to capture appropriate data to accurately assess potential environmental impacts from the byproduct itself relative to other commodity construction products that the byproduct would displace. JEA has determined that both the legal/regulatory background of recycling/reuse policy and the marketing and the environmental data acquired during the BUD project support the conclusion that the sale of the byproducts from the

JEA Northside CFB project, as defined herein, for use in the demonstrated markets is protective of human health and the environment, especially when measured against the environmental impacts posed by the noted replacement materials currently-utilized for the associated construction applications.

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Chapter 4

INFLUENCE OF AGING IN SOIL ON THE DERMAL PENETRATION OF HEXAVALENT AND TRIVALENT CHROMIUM

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Abstract: Sensitive individuals may develop allergic contact dermatitis (ACD) from exposure to chromium contaminated soil. However, health risk assessments often do not consider the amount of metal in soil that is absorbed by the body (bioavailability). Instead, they rely on the total concentration of metal that can be extracted from soil by rigorous procedures. This practice can overestimate health risks and soil remediation goals because metals can be sequestered in soil with time ("aging") thereby decreasing bioavailability. In this study, the effects of aging in soil on the dermal penetration of trivalent chromium as chromium chloride or hexavalent chromium as sodium chromate were evaluated in two soils – Atsion and Keyport. Dermal penetration was measured *in vitro* through dermatomed pig skin by Teflon flow-through diffusion cell methodology. After four months in soil, the dermal penetration of both species was decreased by 93 - 96% relative to pure chromium (without soil). While an aging effect was prominent for Cr (III) in the Atsion soil, surface adsorption was important in the Keyport soil. The dermal penetration of Cr (VI) was similar in both soils after aging. The data suggest that soil cleanup levels for chromium based on the ACD health endpoint will be dependent on soil type and time in soil.

Key words: heavy metals, skin, matrix and time effects, risk assessment

1. INTRODUCTION

Risk assessment and the evaluation of remediation needs of metal contaminated soils are usually based on the acid-soluble metal content of soil (Turpeinen *et al.*, 2003). Previously, we showed that the dermal penetrations of arsenic, mercury, and nickel were significantly decreased by 95-98% with time in soil ("aging") compared to the pure metals (without soil) (Abdel-Rahman *et al.*, 2005). Furthermore, the bioaccessibility of soil-aged chromium was reduced by 50-82% in simulated gastric fluid (Skowronski *et al.*, 2001). Therefore, the amount of a metal that is absorbed from soil by the body (bioavailability) is important because it can improve the accuracy of risk assessment which can result in the establishment of more realistic remediation goals. This study will focus on the dermal penetration of chromium in soil

Chromium can enter the environment by natural processes as well as from human activities (Palmer and Wittbrodt, 1991). In the environment, chromium occurs primarily in the trivalent state [Cr (III)] or in the hexavalent form [Cr (VI)]. The environmental behavior and toxicity of chromium are largely a function of its oxidation state. Hexavalent chromium compounds (mainly chromates and dichromates) are strong oxidizers, more toxic, highly soluble, and more mobile in soil/water systems than trivalent compounds. The trivalent state is generally considered to be the stable form of the two species (Losi *et al.*, 1994).

Sensitive individuals can develop allergic contact dermatitis (ACD) from exposure to chromium. Once an individual is sensitized to chromium, a subsequent exposure to the allergen above a threshold level will elicit dermatitis (Polak, 1983). The response resembles a "poison oak" hypersensitive reaction. Symptoms include erythema, edema, and small vesicles (Ackerman, 1978; Adams, 1990). The most widely accepted study to determine the minimum elicitation threshold (MET) for Cr (VI) is the study by Nethercott *et al.* (1994). Results from patch test studies on 54 Cr (VI) sensitized volunteers indicated that about 0.089 µg Cr (VI)/cm^2 skin was required to elicit ACD in 10% of the volunteers. Because Cr (VI) compounds generally penetrate skin faster than Cr (III) compounds, they are more likely to produce a skin response in sensitized subjects (Samitz *et al.*, 1967). However, Cr (III) is considered to be the actual cause of allergic contact sensitization since only Cr (III) is capable of forming covalent bonds with skin proteins which is a precondition for immunogenicity (Mali *et al.*, 1966; Polak *et al.*, 1973; Hansen *et al.*, 2003). After Cr (VI) diffuses into the skin, it is reduced to Cr (III) which then complexes with protein to form the complete antigen thereby causing the immune response (Samitz and Katz, 1964; Samitz *et al.*, 1967, 1969; Polak *et al.*, 1973). The reducing capacity of the skin, however, is limited (1 mg/g skin) as shown by Samitz and Katz (1964).

ACD is often associated with occupational exposures to numerous materials and processes, including chrome plating baths, chrome colors and dyes, cement, leather tanning agents, wood preservatives, anticorrosive agents, welding fumes, and textiles (Polak *et al.*, 1973; Burrows and Adams, 1990; USEPA, 2004). In addition to individuals who are exposed to chromium either occupationally or in consumer products, there are several groups within the general population who have a greater probability of elevated chromium exposure. These groups include people who live in proximity to sites where chromium was manufactured or processed, sites where chromium was disposed, or near one of the United States Environmental Protection Agency's (USEPA's) National Priorities List (NPL) hazardous waste sites where chromium has been identified in environmental media (ATSDR, 2000a). Currently, there are 1,778 hazardous waste sites on the NPL that have been identified as being contaminated with chromium (ATSDR, 2003). About 210 sites in New Jersey were confirmed as contaminated with chromite ore processing residue (COPR) (NJDEP, 2005). More than 2 million tons of the waste was used as fill material in construction sites in Hudson County (NJDEP, 1997). Total chromium concentrations in COPR measured at these sites ranged from 5 to 11,800 ppm and Cr (VI) concentrations ranged from < 0.5 to 780 ppm (ESE, 1989). Since many of the contaminated sites have been developed for housing, schools, playgrounds, and commercial establishments, there is substantial opportunity for human exposure to chromium at these sites (Snyder *et al.*, 1997).

Historically, the inhalation and ingestion pathways have driven chromium-related risk assessments at contaminated sites in the United States (Horowitz and Finely, 1993). However, the NJDEP developed a soil cleanup approach based on elicitation of ACD by Cr (VI). The risk assessment subgroup of the NJDEP Chromium Workgroup conducted benchmark dose modeling of the 10% MET data from Nethercott *et al.*'s study (1994). A $BMDL_{10}$ (i.e., the lower 95% confidence limit on the dose corresponding to a 10% response among sensitized individuals) of 0.08 $\mu g/cm^2$ for Cr (VI) was determined by the risk assessment subgroup. The USEPA's suggested average soil adherence value of 0.2 mg soil/cm^2 skin (USEPA, 2003) and an assumed dermal bioavailability of Cr (VI) of 100% together with the $BMDL_{10}$, were used to calculate a soil cleanup value of 400 ppm for Cr (VI). This cleanup level was originally proposed in 1998 and recommended in a recent report by the NJDEP Chromium Workgroup (NJDEP, 2005). NJDEP's recommended soil cleanup level for Cr (VI) is very similar to that of Nethercott *et al.* (1994) (450 ppm) who applied the same soil adherence factor and assumed bioavailabiltiy to their 10% MET. The Massachusetts Department of Environmental Protection (MADEP) has also recommended a soil standard for Cr (VI) based on ACD as the health endpoint (Zewdie, 1998). However, the MADEP used a soil adherence factor of 0.51 mg soil/cm^2 skin according to a previous USEPA guidance (USEPA, 1996) in their calculation. Although the 10% MET and the assumed bioavailability were identical to that used by Nethercott *et al.* (1994*)*, the utilization of a higher soil adherence factor resulted in a more conservative estimate of soil cleanup (170 ppm). Horowitz and Finley (1993) estimated the bioavailability of Cr (VI) from soil by extracting COPR with human sweat. At a COPR concentration of 1240 ppm, less than 0.1% of the Cr (VI) in the COPR sample was extracted by sweat. They concluded that COPR concentrations greater than or equal to 1200 ppm Cr (VI) would be protective of 99.9% of the general population (Horowitz and Finely, 1994). From the above studies, it can be seen that the use of different soil adherence values and assumed bioavailability can lead to a large variation in soil cleanup levels for chromium.

There are many studies in the scientific literature on the amount of Cr (III) and Cr (VI) that penetrated human and/or animal skin (Mali *et al.*, 1963; Spruit and van Neer, 1964; Wahlberg and Skog, 1965; Samitz *et al.*, 1967; Wahlberg, 1970; Lidén and Lundberg, 1979; Baranowska-Dutkiewicz, 1981; Gammelgaard *et al.* 1992; Corbett *et al.*, 1997). To the best of our knowledge, there are no studies that examined the dermal bioavailability of Cr (III) or Cr (VI) from soil. Furthermore, many of the studies to predict the bioavailability of chemicals in soil are based on soils that are freshly spiked in the laboratory with chemical prior to conducting the bioavailability experiments. However, chemicals in contaminated soils may have been in the soil for days, weeks, or even years (i.e., aged). Compared to newly contaminated soil, a further reduction in bioavailability may be seen due to aging. Therefore, the objective of this study was to investigate the effects of aging in soil as well as soil type on the dermal penetration of trivalent and hexavalent chromium and to evaluate their impact on health risk and soil cleanup levels.

2. MATERIALS AND METHODS

2.1 Chemicals

Chromium-51 as chromium chloride (588.9 mCi/mg specific activity, 99.9% purity) or as sodium chromate (477.6 mCi/mg specific activity, 99.9% purity) was purchased from New England Nuclear (NEN) Life Science Products, Boston, MA.

2.2 Soils

Studies were performed on two different soils that were selected after discussions with soil scientists on the characteristics of various soils. Both are representative of soil types widely distributed in the United States. The Atsion soil consists of 90% sand, 8% silt, 2% clay, 4.4% organic matter; has a pH of 4.2; and was collected from the Cohansey sand formation near Chatsworth in south central New Jersey. Atsion soil is formed in Atlantic Coastal plain sediments of New Jersey and New York. Similar soil is found extensively in Maryland, Virginia, North and South Carolina, Alabama, Georgia, and Florida (USDA, 1977). The Keyport soil contains 50% sand, 28% silt, 22% clay, 1.6% organic matter; has a pH of 5.0; and was collected from the Woodbury formation near Moorestown in southwestern New Jersey. Keyport soil is found in New Jersey, Delaware, Maryland, and Virginia, with similar soils occurring as far southwest as Texas (USDA, 1972). The majority of the soil particles were 50-250 μm in size. Organic matter content was measured by a modified Walkley & Black (1934) dichromate oxidation method. Soil analyses were performed by the Soil Testing Laboratory at Rutgers Cooperative Extension Resource Center, Rutgers University, New Brunswick, NJ.

2.3 Chemical Aging in Soil

Radiolabeled chemicals were added to each of the soils that had been previously autoclaved and hydrated to 11% with sterile distilled-deionized water. This is the maximum amount of water that could be used to lightly moisten the soils without there being an excess of water when the chemicals were added to the soils. Each chemical was added to soil at a ratio of 300 ng to 1 g of soil. After the chromium compounds were mixed thoroughly with the soils to ensure uniform distribution of chemical, treated soils were added to Teflon-sealed vials and stored in the dark at room temperature for 4 months.

2.4 Animal Model

Whole pig skin was obtained from the costo-abdominal areas of euthanized (40-60 lb) male Yorkshire pigs (Cook College Farm, Rutgers University, New Brunswick, NJ). Research has shown that chemical penetration of human skin is similar to that of the pig or monkey, and much slower than that of the rat or rabbit (Bartek *et al*. 1972; Paustenbach, 2000). The pig has been widely accepted as an animal model for studying human percutaneous absorption of a large variety of chemicals under various experimental conditions (Bartek *et al*., 1972; Reifenrath and Hawkins, 1986; Qiao *et al*., 1993) because of the well documented histological (Monteiro-Riviere and Stromberg, 1985), physiological, biochemical, and pharmacological similarities between pig skin and human skin (Qiao and Riviere, 2000). Skin was transported to the laboratory and viability maintained in ice-cold HEPES buffered (25 mM) Hank's balanced salt solution (HHBSS), pH 7.4, containing gentamycin sulfate (50 mg/l) (Collier *et al*., 1989) after which it was immediately prepared for diffusion cells according to Bronaugh and Stewart (1985).

2.5 *In Vitro* Dermal Penetration Studies

Excised skin was cut to a thickness of 200 µm with a dermatome (Padgett Electro-Dermatome Model B, Padgett Instruments Inc., Kansas City, MO) and circular pieces were mounted into Teflon flow-through diffusion cells (Crown Bio Scientific, Inc., Somerville, NJ). The exposed skin surface area (0.64 cm^2) was maintained at a temperature of 32^oC. The dermal side of each skin sample was perfused with HHBSS containing 10% fetal bovine serum (Sigma/Aldrich, St. Louis, MO) at a flow rate of 3 ml/h and aerated continuously with oxygen (Collier *et al*., 1989). Chemical was applied to the surface of the skin either alone in 5 µl of 0.01 M sodium phosphate buffer, pH 6.8, immediately after the addition of 30 mg soil, or after aging in 30 mg of each of the two soils. The chemical dose was 15.5 ng/cm^2 skin while the elemental dose was 5 ng/cm^2. Although the data on freshly spiked soil can overestimate the dermal penetration of a chemical that has been in the same soil for a longer period of time, the data on freshly spiked soil are important because it can be used to predict the risk from newly contaminated sites and to calculate the percent decrease in the dermal penetration of soil-aged chemical versus chemical in freshly contaminated soil. A low dose of chromium was used in this study because low doses of chromate or dichromate may be more effective in producing sensitization than high ones. A low dose penetrates only into the skin where it is retained by skin and can induce sensitization whereas a high dose is transported through the skin into the circulatory blood supply (Mali *et al.,* 1964; Polak *et al*., 1973). Also, it has been concluded that Cr (VI) should not exceed 1 ppm (equivalent to 0.01 $\mu g/cm^2$ skin) in household products such as laundry detergents, to prevent elicitation of ACD (Basketter *et al*., 2003).

Receptor fluid (perfusate) was collected in scintillation vials containing 10 ml of Formula-989 liquid scintillation cocktail (Packard Instruments Co., Inc., Meriden, CT) up to 16 h postdosing. Loosely adsorbed chemical was washed from the skin surface with soap and water (once with 1 ml of a 1% aqueous soap solution and twice with 1 ml of distilled-deionized water). Skin samples were completely solubilized in Solvable (Packard) for 8 h at 50^oC to determine the quantity of the chemical remaining in skin. Radioactivity in all samples was counted by liquid scintillation spectrometry (LS 7500, Beckman Instruments, Inc., Fullerton, CA). Sample quench was corrected by using the H-ratio method. Total penetration is defined as the sum of chemical in receptor fluid and skin.

2.6 Statistical Analysis

All data were reported as the mean ± standard error of the mean (SEM) and expressed as percent of the applied initial dose. Statistical differences between treatment groups were determined by one-way analysis of variance (ANOVA) with Scheffe's test except for the soil comparisons which were performed by Student's independent t-test. The level of significance was $p < 0.05$.

3. RESULTS AND DISCUSSION

When Cr (III) was aged in the Atsion soil, the amount of trivalent chromium that penetrated skin was significantly decreased compared to Cr (III) without soil or Cr (III) in brief contact with soil (Table 1). Furthermore, a significantly lower percentage of soil-aged trivalent chromium was observed in receptor fluid (0.5% of the initial dose) versus pure Cr (III) (2%) or Cr (III) in freshly treated soil (1.3%). While 34% of pure trivalent chromium was detected in skin, the amount decreased to 13% of the initial dose after Cr (III) was in contact with the Atsion soil for 16 h. A further reduction to 1.9% was observed after aging in the Atsion soil. Most of the total penetration of Cr (III) after each of the treatments was due to Cr (III) in skin. Total penetration decreased from 36% to 14% when the Atsion soil was freshly spiked with Cr (III) relative to pure Cr (III). For aged Cr (III), total penetration (2.4%) was significantly reduced versus pure Cr (III) or Cr (III) in freshly spiked soil. The data for skin wash correlated well with the results for total penetration. The majority of the dose for pure Cr (III) (64%) was washed from the surface of the skin. When the Atsion soil was freshly spiked with Cr (III), there was more radioactivity in the skin wash (83%)

than from pure Cr (III). The amount of radioactivity in the skin wash was even greater after aging (97%).

Table 1. Effect of Aging on the Dermal Penetration of Trivalent Chromium in Atsion Soil

	Pure	Freshly Spiked Soil	Aged in Soil
Receptor Fluid	2.0 ± 0.2 [a]	1.3 ± 0.2 [b]	0.5 ± 0.1 [c]
Skin	33.6 ± 2.4	12.8 ± 2.5 [b]	1.9 ± 0.3 [c]
Total Penetration	35.6 ± 2.4	14.1 ± 2.4 [b]	2.4 ± 0.2 [c]
Skin Wash	63.9 ± 4.1	83.1 ± 2.6 [b]	97.1 ± 0.2 [c]

[a] Mean ± SEM of percent initial dose for n = 10-14 replicates per treatment from three pigs administered $CrCl_3$

[b] Significantly different from pure ($p< 0.05$, ANOVA)

[c] Significantly different from pure and freshly spiked soil ($p< 0.05$, ANOVA)

The dermal penetration of Cr (III) into receptor fluid after aging in the Keyport soil (Table 2) was similar to that in the Atsion soil. Percent initial dose decreased from 2% for pure Cr (III) to 1.4% for Cr (III) in freshly spiked Keyport soil, and then to 0.6% for aged Cr (III). For freshly treated soil, the quantity of radioactivity was almost the same in receptor fluid (1.4%) and skin (1.6%). However, after aging, there was twice as much radioactivity in skin (1.2%) than in receptor fluid (0.6%). Total penetration decreased from 36% for pure Cr (III) to 3% and 1.8%, respectively, for Cr (III) in freshly treated soil and Cr (III) aged in soil. While there was an additional 12% decrease in the dermal penetration of Cr (III) in the Atsion soil after aging, there was only a 1% more decrease in dermal penetration in the Keyport soil. The remaining non-absorbed Cr (III) was detected in the skin wash fraction.

Table 2. Effect of Aging on the Dermal Penetration of Trivalent Chromium in Keyport Soil

	Pure	Freshly Spiked Soil	Aged in Soil
Receptor Fluid	2.0 ± 0.2 [a]	1.4 ± 0.2 [b]	0.6 ± 0.1 [c]
Skin	33.6 ± 2.4	1.6 ± 0.2 [b]	1.2 ± 0.2 [b]
Total Penetration	35.6 ± 2.4	3.0 ± 0.3 [b]	1.8 ± 0.2 [b]
Skin Wash	63.9 ± 4.1	96.0 ± 0.4 [b]	97.6 ± 0.3 [b]

[a] Mean ± SEM of percent initial dose for n = 10-14 replicates per treatment from three pigs administered $CrCl_3$

[b] Significantly different from pure ($p< 0.05$, ANOVA)

[c] Significantly different from pure and freshly spiked soil ($p< 0.05$, ANOVA)

The total penetration of pure Cr (VI) (33.5% of the initial dose, Table 3) was almost the same as that of Cr (III) (35.6%, Table 1). Wahlberg and Skog (1965) also reported that there were no statistical differences in the dermal absorption of trivalent and hexavalent chromium compounds by guinea pigs at low concentrations (0.017-0.239 M) but at higher concentrations (0.261-0.398 M), sodium chromate penetrated skin more quickly than chromium chloride. Also, according to Samitz *et al.* (1967), chromium chloride penetrated isolated human skin almost exactly as potassium dichromate. It is believed that the dermal penetration is the same between Cr (III) and Cr (VI) because several studies have shown that the hexavalent species is reduced in skin to the trivalent form at low doses (Samitz and Katz, 1964; Samitz *et al.*, 1967, 1969; Polak *et al.*, 1973).

Table 3. Effect of Aging on the Dermal Penetration of Hexavalent Chromium in Atsion Soil

	Pure	Freshly Spiked Soil	Aged in Soil
Receptor Fluid	0.8 ± 0.1 [a]	0.8 ± 0.1	0.3 ± 0.03 [c]
Skin	32.7 ± 2.4	3.3 ± 0.5 [b]	0.9 ± 0.2 [b]
Total Penetration	33.5 ± 2.2	4.1 ± 0.6 [b]	1.3 ± 0.2 [b]
Skin Wash	66.5 ± 2.1	92.3 ± 1.8 [b]	98.0 ± 0.2 [c]

[a] Mean ± SEM of percent initial dose for n = 8-11 replicates per treatment from three pigs administered Na_2CrO_4

[b] Significantly different from pure ($p < 0.05$, ANOVA)

[c] Significantly different from pure and freshly spiked soil ($p < 0.05$, ANOVA)

The Atsion soil significantly decreased the dermal penetration of Cr (VI) into receptor fluid to 0.3% of the initial dose after aging relative to pure Cr (VI) and Cr (VI) in brief contact with soil (0.8% each) (Table 3). Like pure trivalent chromium, a large percentage of hexavalent chromium alone was found in skin (33%). Consequently, the total penetration of pure Cr (VI) was also high (34%). The Atsion soil decreased skin radioactivity to 3.3% after 16 h and to 0.9% after 4 months. The total penetration of Cr (VI) in newly contaminated soil (4.1%) and the three-fold decrease after aging (1.3%) were significantly lower than for pure Cr (VI). The bulk of the dose for pure Cr (VI) was found in the skin wash (66%). For the soil treatments, 92-98% of the dose was washed from the skin.

The results for Cr (VI) in the Keyport soil (Table 4) indicated that aged Cr (VI) was significantly decreased in the receptor fluid (0.4% of initial dose) versus pure Cr (VI) (0.8%) and Cr (VI) in freshly treated soil (0.6%). However, the difference in skin radioactivity between Cr (VI) in freshly spiked soil (2.2%) and aged Cr (VI) (0.8%) was not significant as it was between either soil treatment and pure Cr (V1) (33%). Likewise, total penetration was greater for pure Cr (VI) (34%) than for hexavalent chromium in newly treated soil (2.8%) or aged Cr (VI) (1.2%). After either time in soil, the skin wash contained more of the chromium dose (96-98%) than the skin wash from the pure treatment (66%). Thus, significant soil matrix effects were observed for Cr (VI) in either of the freshly spiked soils versus their respective pure counterparts.

Table 4. Effect of Aging on the Dermal Penetration of Hexavalent Chromium in Keyport Soil

	Pure	Freshly Spiked Soil	Aged in Soil
Receptor Fluid	0.8 ± 0.1 [a]	0.6 ± 0.04 [b]	0.4 ± 0.03 [c]
Skin	32.7 ± 2.4	2.2 ± 0.5 [b]	0.8 ± 0.1 [b]
Total Penetration	33.5 ± 2.2	2.8 ± 0.6 [b]	1.2 ± 0.1 [b]
Skin Wash	66.5 ± 2.1	96.4 ± 0.6 [b]	98.0 ± 0.2 [b]

[a] Mean ± SEM of percent initial dose for n = 9-14 replicates per treatment from three pigs administered Na_2CrO_4

[b] Significantly different from pure ($p < 0.05$, ANOVA)

[c] Significantly different from pure and freshly spiked soil ($p < 0.05$, ANOVA)

A comparison of the dermal penetration of Cr (III) and Cr (VI) between the two soils is presented in Figure 1. The dermal penetration of Cr (III) in freshly treated Keyport soil was significantly lower than in the Atsion soil. Furthermore, the dermal penetration of Cr (III) in the Atsion soil only reached the level in the Keyport soil after aging. This was expected because the organic matter content in the Atsion soil is almost three-fold higher than in the Keyport soil. The data indicate that in the Atsion soil, Cr (III) initially adsorbed to the surface of freshly spiked soil particles but then slowly diffused into the soil over several months and became less bioavailable than non-aged Cr (III). It has been suggested that slower absorption and increased resistence to desorption of some metals may be due to diffusion through the intraparticle micropores of soil organic matter (Yin *et al*., 1997; Strawn and Sparks, 2000). On the other hand, adsorption of Cr (III) to the Keyport soil occurred rapidly in the first 16 hr after treatment. The similarity in the decrease in the dermal penetration of Cr (III) in freshly spiked Keyport soil and after aging suggests that trivalent chromium binds predominately to the surface of the Keyport soil. Therefore, while an aging effect was prominent for Cr (III) in the Atsion soil, surface adsorption was important in the Keyport soil. Several investigators have demonstrated that Cr (III) is rapidly and strongly adsorbed to soil by iron and manganese oxides, clay minerals, and sand (Schroeder and Lee, 1975; Bartlett and Kimble, 1976a; Korte *et al*., 1976; Griffin *et al*., 1977; Rai *et al*., 1984; Dreiss, 1986; Stanin, 2005). About 90% of Cr (III) is adsorbed by clay minerals and iron oxides within 24 h. Stewart et al.'s (2003a) study comparing the bioaccessibility of Cr (III) aged in 35 soils, revealed that soils with higher quantities of clay, inorganic carbon, higher pH, and higher cation exchange capacity generally sequestered more Cr (III).

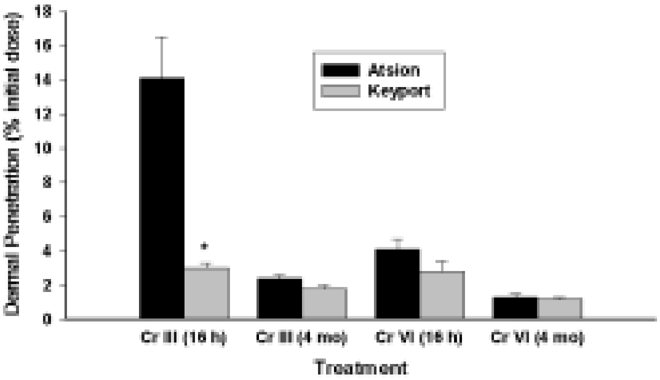

Figure 1. Influence of soil type on the dermal penetration of trivalent and hexavalent chromium. Values (means ± SEM) represent the total penetration expressed as percent of initial dose. The asterisk denotes a significant difference from Atsion soil. Values were considered significant when p was less than 0.05 (Student's independent t-test.).

For Cr (VI), there were no significant differences in dermal penetration between the two soils either as freshly spiked or aged (Figure 1). At low concentrations of Cr (VI), adsorption increases as pH decreases no matter what the sorbent (Griffin *et al*., 1977; Bartlett and Kimble, 1979; Rai *et al*., 1984; Stanin, 2005). This would explain why the adsorption of Cr (VI) decreased similarly in the two freshly spiked acidic soils. Cr (VI) can also be reduced to Cr (III) in acidic soils in the presence of electron donors like soil organic matter, ferrous iron, and reduced sulfur compounds (Bartlett and Kimble, 1976b; Palmer and Puls, 1994; Jardine *et al*., 1999; Kotas and Stasicka, 2000; Wielinga *et al*. 2001). For soils (pH range 4-7), Stewart *et al.* (2003b) reported that the reduction of Cr (VI) to Cr (III) was nearly complete after 200 days aging. In the present study, less aging time (120 days) suggests that Cr (VI) may not have been competely reduced to Cr (III).

In addition to the percent bioavailability, the amount of soil that adheres to skin is another critical factor in setting ACD-based soil concentrations (Horowitz and Finley, 1994). The soil load (amount of soil deposited per

cm^2 of skin) that was used in this study (47 mg/cm^2), was based on soil adherence amounts reported in the literature. Measurements of soil loadings on the skin of volunteers revealed that actual loadings can range from less than 0.01 to more than 100 mg/cm^2 (Kissel *et al*., 1996). Soil load depends on soil properties, occupational and recreational activities, and different parts of the body (Kissel *et al*., 1996, 1998; Holmes *et al*., 1999). However, Yang *et al*. (1989), Duff and Kissel (1996), and Roy and Singh (2001) showed that only chemical in the monolayer of soil which is in contact with the skin surface is likely to be absorbed by skin. Their studies indicated that increasing the soil load decreased the percent of the applied dose of chemical absorbed. More recently, Touraille *et al*. (2005) demonstrated that for a relatively short exposure period (8 h), soil loading in excess of that required to produce a monolayer of particles did not change the amount of chemical absorbed. When exposure time was increased to 24 h, absorption increased with soil loading (5-148 mg/cm^2).

Horowitz and Finley (1994) recommended that for sites where the soil properties are well characterized, it would be appropriate to ensure that the soil adherence factor reflects these properties. For example, although Wester *et al.* (1993) used a soil loading of 40 mg/cm^2 in their arsenic studies, the soil load probably represented only slightly more than monolayer coverage because a very coarse grain size was used (Duff and Kissel, 1996). Moreover, the risk assessment subgroup of the NJDEP Chromium Workshop noted that the soil loading/adherence factor (0.2 mg/cm^2) recommended by the USEPA in their Risk Assessment Guidance for Superfund, Part E (RAGS Part E) (USEPA, 2003), was originally intended to address systemic (i.e., whole body) exposure and was expressed as a weighted average of soil on the entire exposed skin surface. Thus, the weighted average reflects exposed areas of the body with little or no soil loading as well as areas with much greater loading. ACD, however, is not a classic systemic response, but results from absorption of an allergen across a relatively small and localized area of skin. Therefore, the RAGS Part E factor may underestimate the soil loading/adherence factor on the discrete skin surfaces with the heaviest soil contact and use of this factor may overestimate the resulting ACD soil cleanup value (NJDEP, 2005).

In conclusion, the data indicate that at a low dose, the dermal bioavailability of either trivalent or hexavalent chromium was significantly decreased (93-96%) by soil adsorption and aging in soil depending on the soil type. Since less chromium was bioavailable in soil, assuming 100% bioavailablility will overestimate the health risk. As a result, recently proposed soil cleanup standards based on ACD as the health endpoint may be too conservative. Although the reducing capacity of the skin will also prevent absorption of Cr (VI) into the systemic circulation at a low dose, very high concentrations of Cr (VI) in solution are known to damage skin stratum corneum (the "barrier layer" or the outermost surface of the epidermal layer of skin) (ATSDR, 2000b). For soil that is heavily contaminated with Cr (VI), the reducing capacity of the soil and the skin may be exceeded. Therefore, any damage to the stratum corneum by Cr (VI) may facilitate penetration of Cr (VI) into the dermis where it can enter the systemic circulation via the capillaries of the dermis. In that case, systemic effects may be more important than ACD as the health endpoint for setting soil cleanup standards for dermal exposure. More extensive research should be conducted to address the issue of dose as well as soil load and exposure time on the dermal bioavailability of hexavalent chromium.

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PART II: HEAVY METALS

Chapter 5

CONTAINING ARSENIC-ENRICHED GROUNDWATER TRACING LEAD ISOTOPIC COMPOSITIONS OF COMMON ARSENICAL PESTICIDES IN A COASTAL MAINE WATERSHED CONTAINING ARSENIC-ENRICHED GROUND WATER

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Abstract: Arsenical pesticides and herbicides were extensively used on apple, blueberry, and potato crops in New England during the first half of the twentieth century. Lead arsenate was the most heavily used arsenical pesticide until it was officially banned. Lead arsenate, calcium arsenate, and sodium arsenate have similar Pb isotope compositions: $^{208}Pb/^{207}Pb = 2.3839\text{-}2.4722$, and $^{206}Pb/^{207}Pb = 1.1035\text{-}1.2010$. Other arsenical pesticides such as copper acetoarsenite (Paris green), methyl arsonic acid and methane arsonic acid, as well as arsanilic acid are widely variable in isotope composition. Although a complete understanding of the effects of historical use of arsenical pesticides is not available, initial studies indicate that arsenic and lead concentrations in stream sediments in New England are higher in agricultural areas that intensely used arsenical pesticides than in other areas. The Pb isotope compositions of pesticides partially overlap values of stream sediments from areas with the most extensive agricultural use.

The lingering effects of arsenical pesticide use were tested in a detailed geochemical and isotopic study of soil profiles from a watershed containing arsenic-enriched ground water in coastal Maine. Acid-leach compositions of the soils represent lead adsorbed to mineral surfaces or held in soluble minerals (Fe- and Mn-hydroxides, carbonate, and some micaceous minerals), whereas residue compositions likely reflect bedrock compositions. The soil profiles contain labile Pb (acid-leach) showing a moderate range in $^{206}Pb/^{207}Pb$ (1.1870-1.2069), and $^{208}Pb/^{207}Pb$ (2.4519-2.4876). Isotope values vary as a function of depth: the lowest Pb isotope ratios (e.g., $^{208}Pb/^{206}Pb$) representing labile lead are in the uppermost soil horizons. Lead contents decrease with depth in the soil profiles. Arsenic contents show no clear trend with depth. A multi-component mixing scheme that included lead from the local parent rock (Penobscot Formation), lead derived from combustion of fossil fuels, and possibly lead from other anthropogenic sources (e.g., pesticides), could account for Pb isotope variations in the soil profiles. In agricultural regions, our preliminary data show that the extensive use of arsenical pesticides and herbicides can be a significant anthropogenic source of arsenic and lead to stream sediments and soils.

Key words: lead, arsenic, pesticides, New England, Maine, watershed, ground water, anthropogenic, soils, bedrock, Penobscot Formation, lead isotopes, sources, minerals

1. INTRODUCTION

Extensive application of arsenical pesticides and herbicides on apple, blueberry, and potato crops in New England during the first half of the twentieth century may have significantly contributed arsenic, lead, and other metals to the surface environment, and particularly to orchard soils (Veneman et al., 1983; Chormann, 1985; D'Angelo et al., 1996; Robinson and Ayuso, 2004). These metal-enriched soils can influence the composition of ground water. Lead arsenate, calcium arsenate, and sodium arsenate were the most important pesticides and herbicides, and among the three, lead arsenate was the most extensively applied pesticide (Peryea, 1998) in apple orchards. Copper acetoarsenite (Paris green) was also used throughout the region (Shepard, 1939; Veneman et al., 1983; Peryea, 1998).

Before 1914 the U.S. imported most metallic arsenic from Germany (e.g., Smith, 1945). From 1914 to about 1930 the bulk of the arsenic production in the U.S. (marketed for commercial applications as As_2O_3, arsenic trioxide, or white arsenic) was derived as a metallurgical by-product of the smelting of copper, lead, and gold. Arsenic trioxide was used in the production of fertilizers, herbicides, and insecticides (Kirk-Othmer Encyclopedia of Chemical Technology, 1992; Ullman's Encyclopedia, 1998), or if transformed to arsenic acid, used in the manufacture of chromated copper arsenate, a preservative of wood products (Mineral Commodities Summary, 2004). A few companies accounted for the bulk of U.S. arsenic production in the first half of the twentieth century: American Smelting and Refining Co., ASARCO (both copper and lead smelting in several domestic plants), Anaconda Copper Co. (copper smelting), U.S. Smelting Co. (lead smelting), and various minor producers. Notably, from 1974 to 1985, the domestic supply of arsenic was controlled by ASARCO, and since 1985 by imports primarily from China, Chile, and Mexico (Mineral Commodities Summary, 2004). Arsenic metal is also used for solders, ammunition, anti-friction additive to bearings, and in the computer and electronics industry for semiconductors (Mineral Commodities Summary, 2004).

Lead isotope compositions are useful to investigate the sources and mobility of lead, and by inference, other geochemically similar metals. Biological, physical and chemical processes in the near surface environment do not disturb the lead isotope signatures. Also, natural (rock-derived) and anthropogenic metal sources commonly have diagnostic lead isotope values so that the variations in soils, sediments, and other near-surface materials can be used to evaluate the various contributions from different point sources. Anthropogenic metal sources are related to a wide range of long-lived industrial and urban activities (e.g., burning of fossil fuels, mining and metal alloy industries, smelting, manufacturing, wood preservation, glass and ceramics industries, sewage, etc.), as well as agricultural activities (e.g., pesticides, herbicides, fertilizers, feed additives) that can result in a wide and overlapping range of isotope compositions.

Certain areas in New England have ground water wells supplied by bedrock aquifers that are anomalously rich in arsenic (Marvinney et al., 1994; Peters et al., 1999; Ayotte et al., 2003). Within one of these areas, we selected a small watershed near Northport, coastal Maine (Fig.1), which is the focus of extensive geological studies on processes leading to arsenic mobilization and ground water enrichment (Horesh, 2001; Ayuso and Foley, 2002; Foley et al., 2004a; Lipfert and Reeve, 2004; Lipfert et al., in press). Our primary objective is to test, using the isotopes of lead, whether the effects of arsenical pesticide use can be discerned from those of other potential natural and anthropogenic sources.

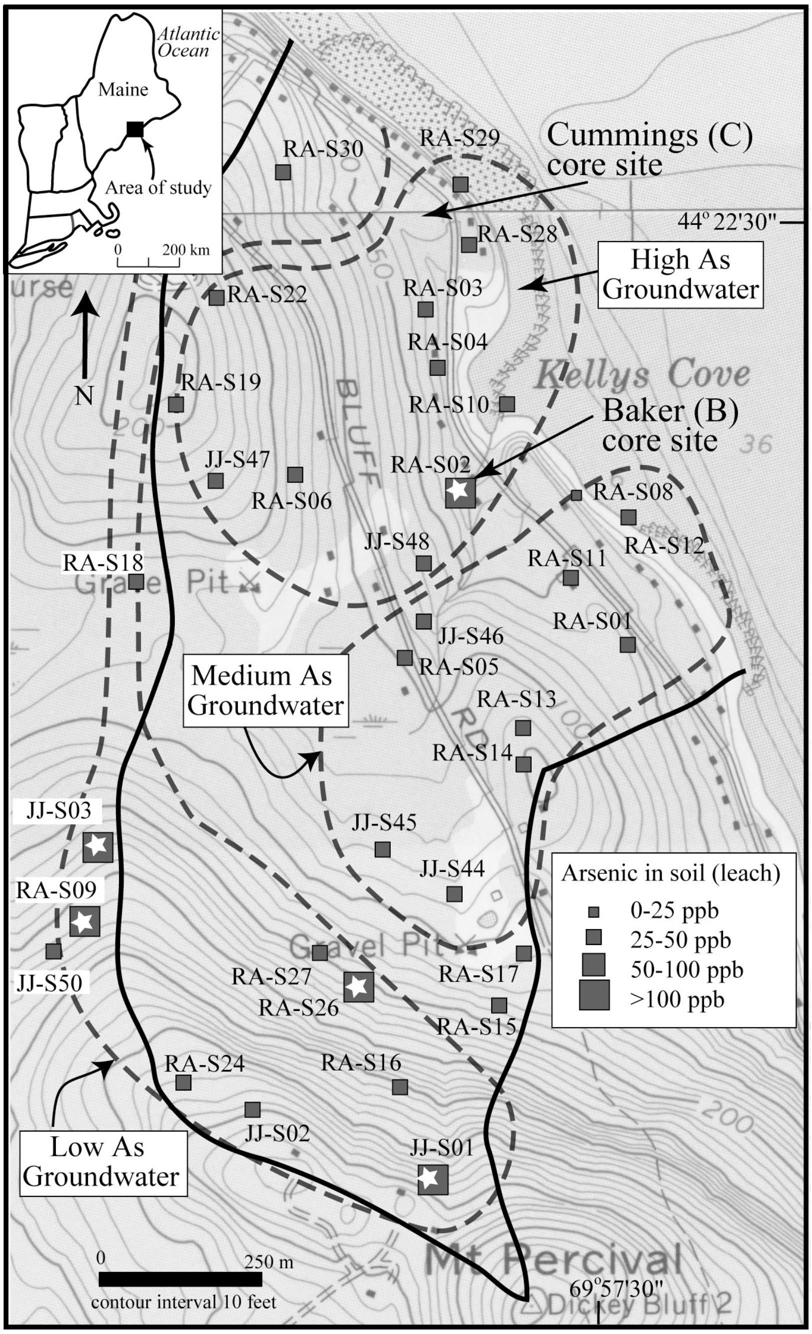

Figure 1. Map showing locations of sites (squares) used for the soil profiles and boreholes (C, and B), and contents of arsenic in the leach fractions of the top layer of the soil profiles. Squares with stars denote samples used for the Pb isotope study; other squares are locations of

profiles used in a geochemical study (Ayuso, unpublished data). Dashed lines enclose areas containing wells characterized by Lipfert and Reeve (2004), and Lipfert et al. (in press) as containing high-arsenic ground water (As > 1.3 µmol/L), medium arsenic ground water, and low arsenic ground water in the Mount Percival recharge area (most wells have < 0.13 µmol/L). Solid line encloses the drainage basin in this study.

1.1 Previous Work

Robinson and Ayuso (2004) used spatial statistical tests and lead isotope tracers to measure the influence of arsenical pesticide use on stream sediment chemistry in New England. Agricultural census data for the first half of the twentieth century were evaluated to determine an agricultural index that identified areas inferred to have used arsenical pesticides extensively. Factor analysis on metal concentrations in ~1600 stream sediment samples were grouped according to their agricultural index value. Pb and As contents were correlated, and the contents of these elements were found to be higher in areas that had higher agricultural index values. Lead isotope compositions of stream sediments from a range of agricultural-index settings mostly overlapped the isotopic range of bedrock sulfides and their weathering products. A few of the stream sediments representing high agricultural-index settings were more radiogenic than the geologic background values and were mostly attributed to lead from industrial uses (atmospheric deposition). In this previous study, no lead isotope data were available for herbicides and pesticides for comparison, but Robinson and Ayuso (2004) speculated that the more radiogenic sediments collected from high-agriculture index settings may have included Pb and As from the arsenical pesticides.

1.2 Geologic Setting

The predominant regional rock type in the Northport area is the rusty-weathering iron-sulfide-rich rocks of the Lower Ordovician Penobscot Formation (Stewart, 1998). The upper part of the formation consists of abundant pelitic beds (with sandy siltstone layers), containing coarse-grained andalusite produced by regional metamorphism. Limestone and calcareous sandstone are rare in the study area. Diorite dikes and muscovite granite pods and dikes are present locally. The formation is well exposed at higher elevations in the Northport area where it is thinly covered by a layer of glacial sediments (till) scavenged from the underlying rocks by the Late Wisconsian Laurentide ice sheet (e.g., Hunter and Smith, 2001). Glaciomarine sediments were deposited as ice withdrew at about 14,000 and 12,200 yr B.P. in the coastal lowlands of eastern Maine, (Dorion et al., 2001). Till deposits predominate in the watershed and consist of a scrambled mixture of clay, silt, sand, cobbles and boulders.

Ayuso and Foley (2002, 2004) and Foley et al. (2004a), building on pioneering studies by Horesh (2001), and Lipfert and Reeve (2004), identified several generations of arsenic- and lead-bearing metal sulfides and secondary minerals in the Penobscot Formation. The early generation of sulfide minerals (including arsenic-rich pyrite and pyrrhotite) likely formed by diagenesis. A later sulfide and oxide mineral population including galena, pyrite, arsenopyrite, iron-oxide minerals, and As-sulfides, formed as a result of Silurian metamorphic and igneous events affecting the Penobscot Formation. In addition, secondary oxide and sulfate minerals (e.g., Fe-hydroxides, anglesite, As-oxides, and As-jarosite) were produced from recent weathering of the till and pedogenic processes. Foley et al. (2004a) concluded that low-temperature oxidation and decarbonation reactions involving the later group of arsenic-bearing minerals in contact with local ground water, could have accounted for the bulk of the As contributed to the regional ground water.

1.3 Soil Types in the Northport Area

The major protolith of the soils in this portion of coastal Maine is glacial till, but marine and lacustrine sediments can be locally important. The predominant soil type in the watershed belongs to the Peru-Marlow-Brayton association (Fig. 2), which is found along the coast and consists of deep, nearly level to steep soils that range from well drained to poorly drained; the soils developed in predominantly moderately coarse-textured compact glacial till (Hedstrom and Popp, 1981). Another soil type in the watershed, one that is somewhat less extensively developed is the Boothbay-Swanville-Lyman association (Hedstrom and Popp, 1981), generally found landward from the Peru-Marlow-Brayton soil association. The Boothbay-Swanville-Lyman soil association has moderately well-drained to poorly drained soils that formed in marine and lacustrine sediments. The Boothbay-Swanville-Lyman soil association also includes excessively drained soils in moderately coarse-textured glacial till (Hedstrom and Popp, 1981). Glaciofluvial sediments, organic material, and alluvium may also constitute significant components in the soils.

The soil profiles typically contain unstratified clay to boulder-sized constituents (generally up to about 10 cm). The soil, till and other near-surface materials generally make up a relatively thin (<1.5 m thick) layer that overlies bedrock. A predominantly local provenance for the glacial till is likely, on the basis of the types and amounts of pebbles and cobbles. Organic-rich and irregularly bedded layers dominate the top of the profiles, extending to a depth of about 8-12 cm. Intensely weathered, saprolitized, and disaggregated, rusty-weathering sulfidic schistose bedrock was encountered at many sites at the bottom of the profiles (~ 60 cm). The large pebbles and boulders in the intermediate depth intervals were rusty-weathered sulfidic schist, in addition to minor granite, mafic rocks, and quartzite.

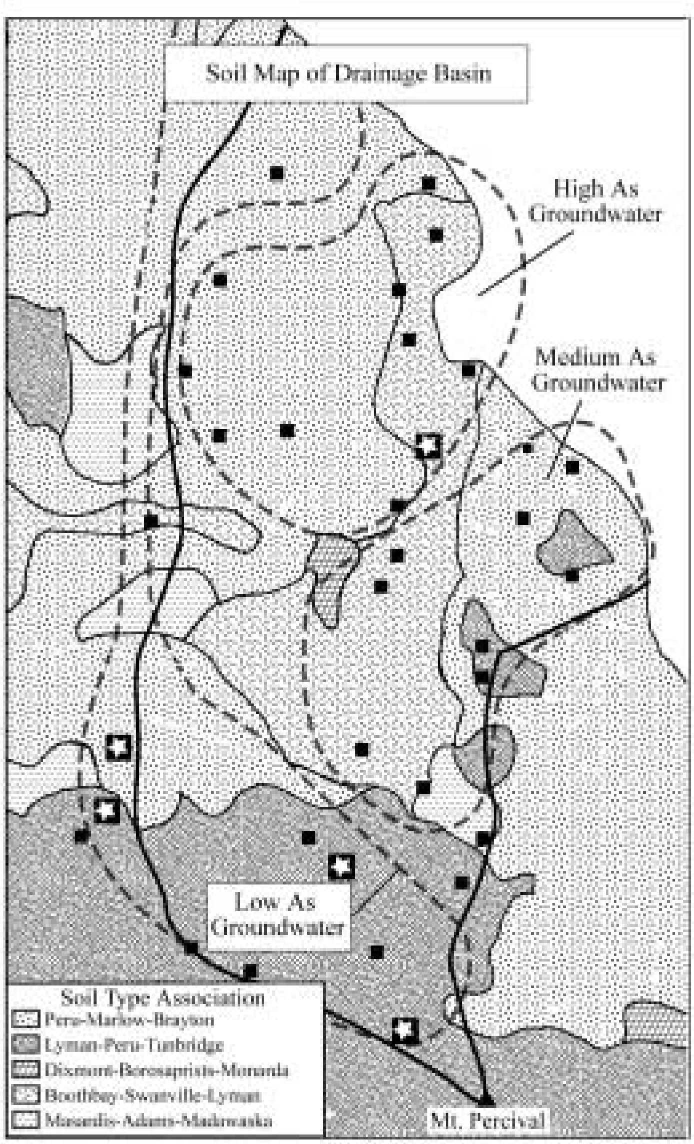

Figure 2. Map of the drainage basin showing generalized distribution of the soil type associations (modified from Hedstrom and Popp, 1981) Symbols as in Figure 1

Abrupt color changes were found locally, and color variations in the dominant soil association are characterized by a surface layer of dark brown soils with fine sandy loam at the top (~10-15 cm thick), overlying a layer of gray to orange-brown fine sandy loam (~4-7 cm). Deeper in the profiles, the subsoils ranged from dark orange-brown silty to sandy loam to gray and green-brown pebbly to sandy loam (~25-35 cm). The profiles were usually dug shallower than about 1m, and ended below the subsoils in a dense layer (substratum) of disaggregated schist and gneiss fragments or intensely weathered bedrock. Locations dug at higher elevations (Mount Percival area, Figs. 1-2) were characterized by abundant outcrop and consisted of soils and tills shallowly underlain by bedrock. In the predominant soils, permeability above the substratum and bedrock is moderate. In the spring, the water table is commonly perched above the substratum and bedrock (Hedstrom and Popp, 1981).

Soil profiles of the Northport area contain various silicate, carbonate, oxide, and rare sulfide minerals, as identified by petrography, X-ray diffraction, and electron microprobe analysis (Foley et al., 2004a). The tills also have abundant organic constituents at the top of the profiles. The soils display several horizons that characteristically reflect the general incorporation of organic material and the effects of weathering. The silicate mineralogy is dominated by quartz, feldspar, and mica, including sericite and chlorite. Our studies suggest that Fe-hydroxides are the predominant secondary minerals in the profiles and underlying bedrock (Ayuso and Foley, 2002; Foley et al., 2004a; Foley, unpublished data). In general, the Fe and Fe-Mn oxyhydroxide minerals occur throughout the till profiles, although they are most abundant in the upper depth intervals, particularly below the organic layer. Rare sulfide minerals include pyrrhotite, greigite, sphalerite, galena, djurlite, and arsenopyrite. Carbonate (calcite manganoan siderite) and Fe-bearing phosphate minerals also occur.

1.4 Sampling of Soil Profiles

Soil profiles at five sites were used for the lead isotope study, and these represent a subset of 34 sites (Fig. 1) that have been investigated for an ongoing geochemical study. Pits approximately 30-40 cm in diameter were hand dug in the midsummer to expose profiles, free of forest litter, to depths of at least 60 cm. Five or six samples (about 150-500 g) were obtained, spaced approximately 10 cm apart, in order to select representatives of the morphological variations in the soils and tills.

Samples from the top of the profiles are from the uppermost surface layers of the soils, as characterized by color (e.g., most are dark brown), particle size and morphology (silt or sandy loam). Most soils in the area exhibited contrasting color and compositional features distinguishing the soils, subsoils, and lower horizons. The surface layer was clearly evident in the watershed (mostly representative of the A1 horizon, and in some cases the Ap soil horizon; Hedstrom and Popp, 1981). This topmost layer is at or near the surface and consists of humified organic matter and minerals, and may include a plowed surface horizon that is part of the underlying, mineral horizon (B). Bedrock was often found at depths of less than 60 cm.

1.5 Analytical Techniques

The pesticides were dissolved in dilute HNO_3 and this solution was passed through Pb exchange columns using normal elution protocols (Ayuso et al., 2004a). Isotopic compositions were measured using a Finnigan-MAT 262 thermal ionization mass spectrometer (TIMS). Mass fractionation was monitored by frequent analysis of the NIST-SRM 981 standard. Lead blanks during the course of the study were less than 50 nanograms and thus are not significant compared to the lead abundances in the samples. A mass fractionation correction of about 0.1% per *amu* was applied to all samples. Maximum analytical uncertainties (± 2 standard error of the mean) are as follows: $^{206}Pb/^{204}Pb < 0.005$, $^{206}Pb/^{207}Pb < 0.00007$, and for $^{208}Pb/^{207}Pb < 0.00006$. Table 1 summarizes the Pb isotope data for the pesticides determined in this study and from a preliminary report (Ayuso et al., 2004b).

Soil samples were air-dried and prepared for lead isotope analysis using 50-100 mg of the <0.2 mm size fraction. Sulfides, Fe-hydroxides, and other secondary minerals in the Penobscot Formation can be used to monitor the composition of labile Pb and provide the means to discriminate labile (anthropogenic) lead from lead inherited from the parent rocks and sulfides. A cool and mild acid leach (1.5N HCl+3N HNO_3) was used to attack the secondary minerals. This solution likely reflects the labile Pb (e.g., Erel et al., 1997) captured in the Fe-hydroxide, carbonate, or organic materials, or other secondary minerals (clays). These minerals can contain lead, arsenic, (and other elements) derived from outside of the watershed. Mixed solutions of HF- HNO_3 were used for final dissolution of the residual fractions. Table 2 summarizes the Pb isotope data for the leach fractions of the soil horizons (together with Pb and As contents); Table 3 shows equivalent data for the residues.

Trace element compositions and mineralogy of the soils and Penobscot Formation were obtained by various analytical techniques including XRD, XRF, ICP-MS, and INAA. Table 4 is a summary of the trace element data for the leach aliquots obtained on the soils in the Pb isotope study, and for the Penobscot Formation.

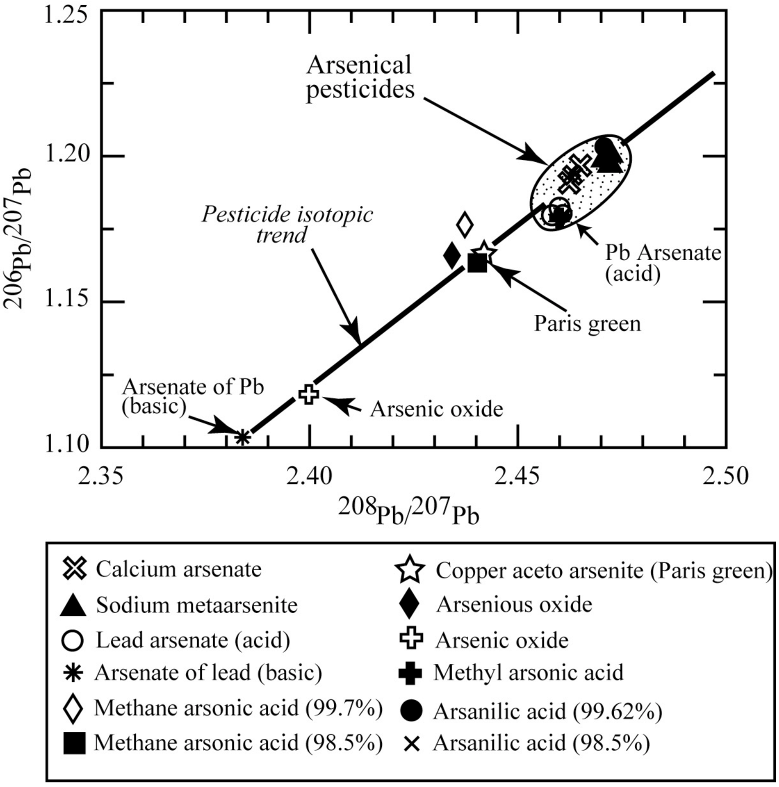

Figure 3. ^{206}Pb/^{207}Pb vs. ^{208}Pb/^{207}Pb plot showing the compositions of arsenical pesticides, herbicides and feed additives.

2. RESULTS

A preliminary assessment of lead isotopic signatures of the arsenical pesticides shows that considerable diversity in values exists (Table 1, Fig. 3). The pesticides range in values of ^{206}Pb/^{207}Pb = 1.1035-1.2010, ^{208}Pb/^{207}Pb = 2.3839-2.4722, and ^{206}Pb/^{204}Pb = 17.070-18.761. The pesticides plot along a trend for values of ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb (Fig. 3). Some of the pesticides show large isotope differences even for similar compounds. For example, lead arsenate (acid form) (^{206}Pb/^{204}Pb = 18.395) is significantly more radiogenic than lead arsenate (basic form) (^{206}Pb/^{204}Pb = 17.070), consistent with a different source of lead used in their manufacture. Table 1 also shows lead isotope compositions of widely used feed additives used to promote swine and poultry growth.

The three most common arsenical pesticides used in New England (lead arsenate-acid form, calcium arsenate, and sodium arsenate) have similar isotope signatures. As a group, they are somewhat more radiogenic than other pesticides (Fig. 3). Contrasting lead isotope values produced by different companies characterize arsenious oxide and arsenic oxide and both are less radiogenic than the more commonly used pesticides in New England (Fig. 3). Other compounds such as methyl arsonic acid and methane arsonic acid (and copper acetoarsenite or Paris green) have lead isotope signatures that are intermediate between lead arsenate and arsenious oxide.

Table 1. Lead isotopic compositions of pesticides, herbicides, and feed additives

Compound name as labeled and purity (if known)	Formula	Manufacturer and date (if known)	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Pesticides and herbicides used in New England					
Calcium arsenate	$Ca_3(AsO_4)_2$	Pfaltz and Bauer Inc., 1981	18.617	1.19345	2.46316
Calcium arsenate	$Ca_3(AsO_4)_2$		18.620	1.19350	2.46320
Calcium arsenate	$Ca_3(AsO_4)_2$	Pfaltz and Bauer Inc., 1981?	18.615	1.19343	2.46314
Sodium metaarsenite (98.0%)	$NaAsO_2$	Aldrich Chemical Co.	18.759	1.20102	2.47212
Sodium metaarsenite (98.0%)	$NaAsO_2$		18.755	1.20100	2.47209
Sodium metaarsenite (98.0%)	$NaAsO_2$		18.761	1.20104	2.47215
Lead arsenate (acid) (91.6%)	$PbHAsO_4$	Pfaltz and Bauer Inc., 1976	18.395	1.18026	2.46083
Lead arsenate (acid) (91.6%)	$PbHAsO_4$		18.393	1.18024	2.46080
Lead arsenate (acid) (91.6%)	$PbHAsO_4$		18.398	1.18029	2.46086
Acme arsenate of lead (basic)	$Pb_5OH_9(AsO_4)_3$	PBI/Gordon Corp., Acme Quality Paints	17.070	1.10352	2.38394
Acme arsenate of lead (basic)	$Pb_5OH_9(AsO_4)_3$	(from H. Evans, USGS), 1950?	17.075	1.10354	2.38397
Acme arsenate of lead (basic)	$Pb_5OH_9(AsO_4)_3$		17.068	1.10348	2.38390
Copper acetoarsenite (90.0%)	$C_4H_6As_6Cu_4O_{16}$	Sherwin-Williams Co., Paris green, 1985	18.153	1.16649	2.44191
Copper acetoarsenite (90.0%)	$C_4H_6As_6Cu_4O_{16}$		18.149	1.16644	2.44185
Copper acetoarsenite (90.0%)	$C_4H_6As_6Cu_4O_{16}$		18.161	1.16652	2.44197
Other pesticides and herbicides					
Arsenous oxide	As_2O_3	Union Mechling Co. (from J. Ayotte, USGS)	18.153	1.16587	2.43421
Arsenic oxide (99.95%)	As_2O_3	Aldrich Chemical Co.	17.342	1.11826	2.39982
Methyl arsonic acid (99.9%)	CH_5AsO_3	Ricerca Inc., 1993	18.381	1.17881	2.46001
Methane arsonic acid (99.7%)	CH_5AsO_3	Vineland Chemical Co., 1978	18.333	1.17644	2.43727
Methane arsonic acid (98.5%)	CH_5AsO_3	Vineland Chemical Co., 1982	18.042	1.16337	2.44030
Feed additives (poultry and swine growth)					
Arsanilic acid (99.62%)	$C_6H_8AsNO_3$	Fleming Labs Inc., 1990	18.754	1.20321	2.47068
Arsanilic acid (99.86%)	$C_6H_8AsNO_3$	Fleming Labs Inc., 1990	18.411	1.17985	2.46093

Soil profiles from the Coastal Maine watershed (Fig. 2) were selected to test whether the effects of arsenical pesticide use in the area could be discerned from other potential natural and anthropogenic lead sources. Soil profiles of 48 samples (leach and residues) show a moderate range in ^{208}Pb/^{207}Pb = 2.4519-2.4876, and ^{206}Pb/^{204}Pb = 18.583-18.836 and ^{206}Pb/^{207}Pb = 1.1870-1.2069 (Table 2 and Fig. 4). Leach fractions are lowest in ^{208}Pb/^{207}Pb for the uppermost soils (surface layers within 10 cm from the surface), in contrast to the values obtained deeper in the profiles (up to about 50 cm from the surface) so that the profiles are stratified isotopically (Fig. 4F). Labile Pb isotope compositions are not homogeneous at 20-30 cm. Soil and glacial processes controlling the dissolution and re-precipitation of secondary minerals did not homogenize the lead, similar to results obtained on temperate forest near-surface tills (Emmanuel and Erel, 2002). Compositions of the residues range in ^{206}Pb/^{207}Pb = 1.2056-1.2328, ^{208}Pb/^{207}Pb = 2.4661-2.5000, and ^{206}Pb/^{204}Pb = 18.831-19.303 and are distinctly more radiogenic than the leach fractions (Table 2, Fig. 4).

Table 2. Pb isotope compositions and contents of Pb and As in leach samples from soil profiles, Northport area, coastal Maine

Leach sample/horizon	Pb (ppb) average (range)	As (ppb) average (range)	$^{206}Pb/^{204}Pb$ average (range)	$^{206}Pb/^{207}Pb$ average (range)	$^{208}Pb/^{207}Pb$ average (range)
0-10 cm, all sites	296 (76-606)	372 (35.1-3960)			
0-10 cm, isotope study	252 (76-606)	985 (40.3-3960)	18.655 (18.601-18.751)	1.19577 (1.19046-1.20111)	2.46014 (2.45188-2.46186)
JJ-ME-02-S01A	86.5	70.5	18.751	1.20111	2.46280
JJ-ME-02-S03A	606	696	18.601	1.19046	2.45188
RA-ME-02-S02A	76	40.3	18.621	1.19465	2.45896
RA-ME-02-S09A	366	159	18.619	1.19274	2.45518
RA-ME-02-S26A	124	3960	18.685	1.19989	2.46186
10-20 cm, all sites	42.3 (20.4-29.8)	170 (9.4-2030)			
10-20 cm, isotope study	42.3 (20.4-29.8)	639 (17.6-2030)	18.704 (18.603-18.774)	1.19854 (1.19351-1.20252)	2.46847 (2.46314-2.47236)
JJ-ME-02-S01B	20.4	57.1	18.716	1.19964	2.47119
JJ-ME-02-S03B	112	1040	18.603	1.19351	2.46314
RA-ME-02-S02B	22.3	17.6	18.661	1.19564	2.46488
RA-ME-02-S09B	29.8	47.7	18.774	1.20252	2.47236
RA-ME-02-S26B	27.1	2030	18.766	1.20138	2.47079
20-30 cm, all sites	26.4 (11.9-47.4)	874 (47.1-2150)			
20-30 cm, isotope study	25.9 (11.9-47.4)	702 (14.2-2150)	18.734 (18.583-18.836)	1.19418 (1.18703-1.20355)	2.47669 (2.47327-2.48761)
JJ-ME-02-SO1C	20.35	48	18.742	1.19957	2.47456
JJ-ME-02-SO3C	47.35	1250	18.583	1.19038	2.47400
RA-ME-02-S02C	24.1	14.2	18.752	1.19038	2.47400
RA-ME-02-S09C	26	47.05	18.757	1.20355	2.47327
RA-ME-02-S26C	11.85	2150	18.836	1.18703	2.48761
30-40 cm, all sites	29.1 (9.6-65.9)	843 (34.1-1860)			

Leach sample/horizon	Pb (ppb) average (range)	As (ppb) average (range)	$^{206}Pb/^{204}Pb$ average (range)	$^{206}Pb/^{207}Pb$ average (range)	$^{208}Pb/^{207}Pb$ average (range)
30-40 cm, isotope study	27.7(9.60-65.9)	678 (16.0-1860)	18.741 (18.731-18.822)	1.20048(1.19147-1.20685)	2.47232(2.46895-2.47630)
JJ-ME-02-SO1D	17.85	34.1	18.730	1.19960	2.47418
JJ-ME-02-SO3D	65.85	1440	18.596	1.19147	2.46588
RA-ME-02-S02D	22.4	16	18.753	1.20253	2.46895
RA-ME-02-S09D	22.9	37.95	18.802	1.20197	2.47628
RA-ME-02-S26D	9.62	1860	18.822	1.20685	2.47630
40-50 cm, all sites	16.9 (12.2-19.7)	716 (48.9-1780)			
40-50 cm, isotope study	19.0 (12.2-27.5)	577 (17.8-1780)	18.902 (18.733-18.810)	1.20780 (1.19128-1.23280)	2.47812 (2.46994-2.49296)
JJ-ME-02-S01E	17.5	48.9	18.733	1.20106	2.47354
JJ-ME-02-S03E	18.2	979	18.762	1.19123	2.46994
RA-ME-02-S02E	27.5	17.8			
RA-ME-02-S09E	19.7	57.5	19.303	1.23280	2.49296
RA-ME-02-S26E	12.2	1780	18.810	1.20613	2.47605

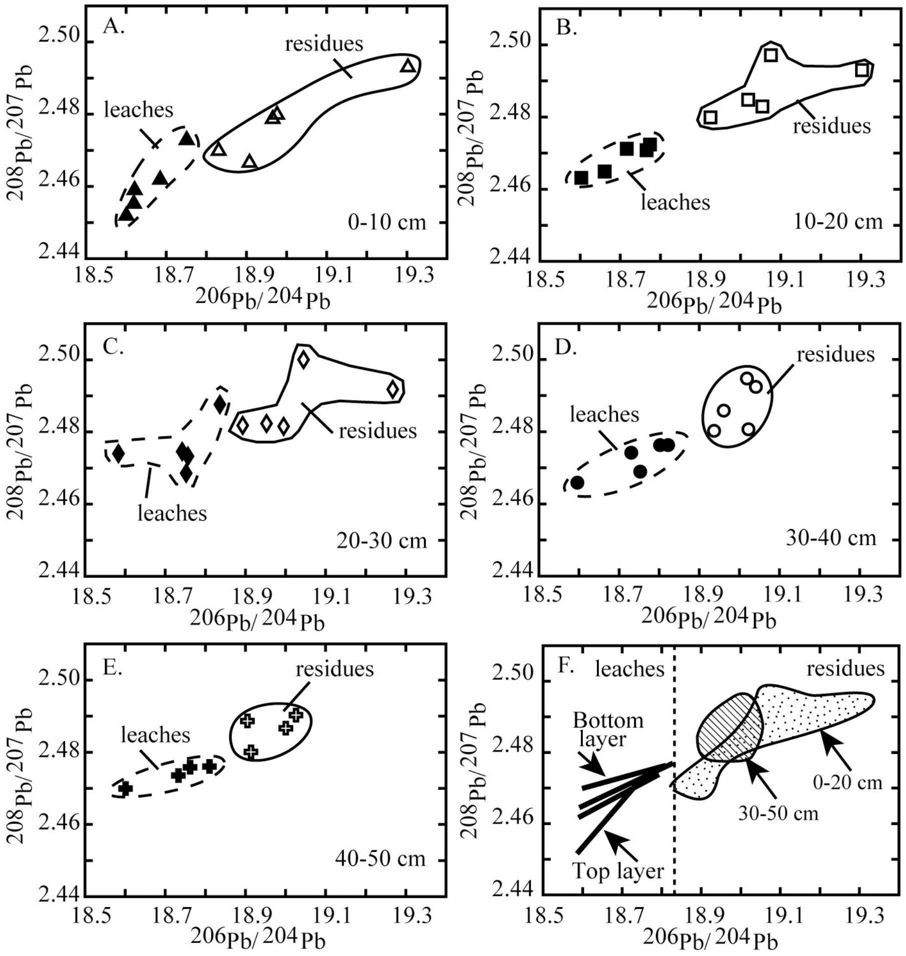

Figure 4. ^{208}Pb/^{207}Pb vs. ^{206}Pb/^{204}Pb plots showing the acid-leach and the residue fractions at different depth intervals. A) 0-10 cm. B) 10-20 cm. C) 20-30 cm. D) 30-40 cm. E) 40-50 cm. F) Summary plot showing estimated trends of the leach fractions and the fields for the residue fractions. The leach fractions (labile lead) are shown by lines of decreasing slope as a function of depth. The residue fractions (silicate lead) are more homogeneous in the deeper portion (>30 cm) of the profiles.

Pb and As contents of the bulk soil samples in the watershed show a wide range (Table 3). The content of Pb is highest in the surface layer (average ~36 ppm). As shows no systematic trend with depth (~176 ppm at the top). Variations in the contents of Pb and As in the leach fractions of the depth intervals (Table 2) show that Pb contents decrease with depth (average = 252 ppb in the surface soil to 19 ppb in the bottom horizon). Average As contents, however, show no clear trend, averaging 985 ppb in the uppermost soil surface layer, and 577 ppb in the bottom horizon. The leach fractions are also most variable for Pb and As in the soil surface layer (Pb ~76 ppb to ~606 ppb; As ~40 ppb to ~3900 ppb). Average contents of C_{total} (surface soil = 6.17 wt.%, bottom horizon = 1.73 wt.%) and pH (surface soil = 4.55, bottom horizon = 5.11) show consistent differences as a function of depth. The values for S_{total}, however, show no clear trend along the profiles (surface soil = 0.03%, bottom horizon = 0.02%) (Ayuso, unpublished data).

Table 3. Pb isotope compositions and contents of Pb and As in residue (bulk) samples from soil profiles, Northport area, coastal Maine

Residue (bulk) sample/horizon	Pb (ppm) average (range)	As (ppm) average (range)	$^{206}Pb/^{204}Pb$ average (range)	$^{206}Pb/^{207}Pb$ average (range)	$^{208}Pb/^{207}Pb$ average (range)
0-10 cm, all sites	35.9 (23.7-59.6)	176 (37.9-517)			
0-10 cm, isotope study	33.7 (23.7-59.6)	144 (13.9-517)	18.916 (18.831-18.976)	1.20958 (1.20560-1.21375)	2.47517 (2.46654-2.48104)
JJ-ME-02-S01A	23.7	102	18.900	1.21075	2.48104
JJ-ME-02-S03A	59.6	37.9	18.831	1.20597	2.46982
RA-ME-02-S02A	24.6	13.9	18.965	1.21182	2.47863
RA-ME-02-S09A	30.0	48.1	18.908	1.20560	2.46654
RA-ME-02-S26A	30.5	517	18.976	1.21375	2.47984
10-20 cm, all sites	22.8 (15.0-37)	62.7 (9.9-606)			
10-20cm, isotope study	18.7 (15.0-22.1)	172 (13.0-606)	19.075 (18.925-19.303)	1.22054 (1.21182-1.23280)	2.48753 (2.47863-2.49296)
JJ-ME-02-S01B	15.0	109	19.054	1.21817	2.48291
JJ-ME-02-S03B	17.4	71.2	19.303	1.23280	2.49296
RA-ME-02-S02B	20.2	13	19.076	1.22230	2.49712
RA-ME-02-S09B	18.7	61.1	19.019	1.21515	2.48477
RA-ME-02-S26B	22.1	606	18.925	1.21428	2.47989
20-30 cm, all sites	21.8 (16.6-24.3)	221 (62.0-657)			
20-30 cm, isotope study	20.9 (16.9-23.2)	183 (32.0-657)	19.031 (18.893-19.267)	1.21812 (1.21042-1.23151)	2.48750 (2.48156-2.50001)
JJ-ME-02-SO1C	16.6	97.0	18.893	1.21042	2.48182
JJ-ME-02-SO3C	23.0	68.0	19.267	1.23151	2.49179
RA-ME-02-S02C	16.9	32.0	19.045	1.21853	2.50001
RA-ME-02-S09C	24.3	62.0	18.953	1.21285	2.48233
RA-ME-02-S26C	23.5	657.0	18.995	1.21728	2.48156
30-40 cm, all sites	21.9 (20.5-23.2)	203 (55.0-616)			
30-40 cm, isotope study	20.9 (16.9-23.2)	170 (34-616)	18.996 (18.937-19.041)	1.21571 (1.21163-1.21884)	2.48674 (2.48024-2.49473)
JJ-ME-02-SO1D	22.1	83	18.961	1.21393	2.48585
JJ-ME-02-SO3D	23.2	55	19.041	1.21884	2.49242
RA-ME-02-S02D	16.9	34	19.019	1.21659	2.49473
RA-ME-02-S09D	20.5	61	18.937	1.21163	2.48024

Residue (bulk) sample/horizon	Pb (ppm) average (range)	As (ppm) average (range)	$^{206}Pb/^{204}Pb$ average (range)	$^{206}Pb/^{207}Pb$ average (range)	$^{208}Pb/^{207}Pb$ average (range)
RA-ME-02-S26D	21.9	616	19.022	1.21755	2.48068
40-50 cm, all sites	19.1 (8.9-47.1)	225 (59.0-640)			
40-50 cm, isotope study	18.9 (8.9-28.9)	192 (59-640)	18.961 (18.905-19.026)	1.21392 (1.20992-1.21774)	2.48641 (2.48008-2.49028)
JJ-ME-02-S01E	25.1	83	19.026	1.21774	2.49028
JJ-ME-02-S03E	8.9	118	19.001	1.21648	2.48665
RA-ME-02-S02E	19.1	60			
RA-ME-02-S09E	12.8	59	18.914	1.21154	2.48008
RA-ME-02-S26E	28.9	640	18.905	1.20992	2.48864

Variations in trace element contents of the sulfidic Penobscot Formation reflect the range from pelite-dominated to sandy silts, and broad variability in contents of sulfide minerals (Table 4). Fe_2O_3, Al_2O_3, MgO, and CaO contents, for example, vary widely (Ayuso, unpublished data). Although the outcrop and drill core samples have similar compositional features, arsenic contents can differ widely (Table 4). Whole-rock samples from drill core are somewhat depleted in lead (average ~17 ppm) and enriched in arsenic (average ~83 ppm), compared to the outcrop samples (average Pb ~29 ppm; average As ~28 ppm) (Table 4).

Table 4. Average of selected trace element compositions of the soil horizons (leach fractions), and the Penobscot Formation (whole rocks), Northport area

Soils	0-10	10-20	20-30	30-40	40-50	Penobscot Formation (ppm)	
(ppb)	cm	cm	cm	cm	cm	outcrops (n=9)	cores (n=19)
As	372	170	874	843	716	28.2	82.6
Pb	296	42.3	26.4	29.1	16.9	28.8	17.15
Be	12.0	17.4	22.7	23.1	20.5	3.44	nd
Sb	10.3	6.98	5.32	5.37	6.27	0.37	0.5
Hg	bdl	1.19	1.08	bdl	bdl	9.32	bdl
Bi	bdl	bdl	0.84	0.75	0.907	0.35	0.4
Se	42.2	65.4	29.0	24.0	17.0	0.58	0.7
Tl	1.60	2.18	1.97	2.17	2.01	1.49	1.3
Sc	nd	nd	138.5	118.8	132	18.3	18.9
V	308	294	270	256	244	179	115
Ni	261	236	63.6	79.5	325	39.9	576.1
Co	463	632	1031	1338	1355	8.75	24.9
Cr	131	167	151	135	88.2	98.8	2404
Ga	18.0	12.4	10.4	13.0	11.4	26.9	25
Ge	1.37	1.65	1.22	1.067	1.60	2.27	1.9
Cu	24.5	17.1	24.2	16.1	13.2	29.9	30.8
Zn	934	832	865	734	644	105.5	119.8
Mo	10.0	6.4	4.16	4.17	4.75	5.43	5.8
Sn	4.88	3.36	2.66	2.98	1.54	3.58	8.7
W	10.4	11.1	12.38	9.3	5.4	1.63	4.5
Cd	18.9	17.6	16.4	16.3	13.5	9.32	nd

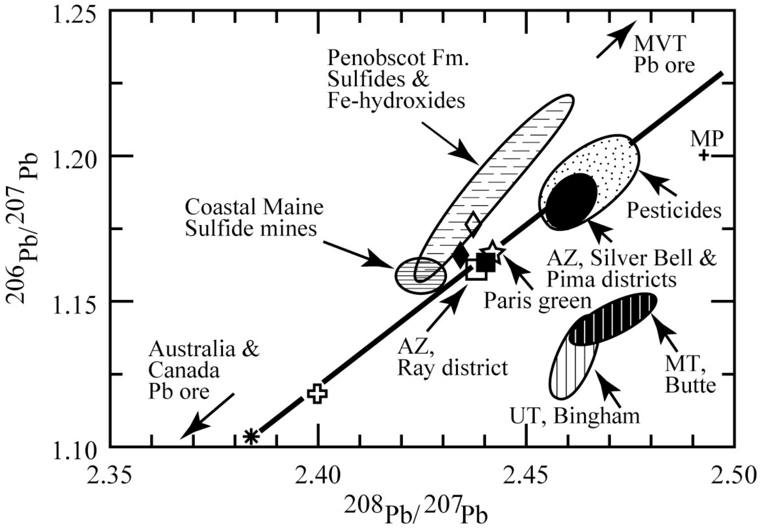

Figure 5. $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ plot showing the field of arsenical pesticides and herbicides, mining districts from the southern portion of the Southeast Arizona terrane (Arizona, Pima, and Ray), and other districts in Montana (Butte), and Utah (Bingham) likely used in the production of arsenic trioxide. Lead isotope data for porphyry copper deposits in Arizona are from Bouse et al. (1999), porphyry copper deposits in Montana are from Murthy and Patterson (1961), and in Utah are from Stacey et al. (1968). Also shown are compositions of Mississippi Valley type (MVT) ore deposits (Doe and Delevaux, 1972), Pb ore from Mexico and Peru (Chow et al., 1975), shown as MP, and Pb ore from Australia and Canada (Cumming and Richards, 1975). The figure also shows the field of galena and other sulfide minerals from massive sulfide deposits from coastal Maine (Foley et al., 2004b), sulfides at various stages of weathering and secondary Fe-hydroxides (representative of the natural background compositions) in the Penobscot Formation (Ayuso and Foley, 2002). Symbols are given in Figure 3.

3. DISCUSSION

The lead isotope signature of arsenic trioxide (As_2O_3), starting material for the manufacture of the arsenical pesticides, will closely reflect the composition of the sulfide minerals (e.g., arsenian sulfides such as arsenopyrite, and arsenian pyrite) used during the smelting of copper, lead, and gold ore. Production data for the major manufacturers of arsenic trioxide from the 1920s to the 1980s, and isotope data in the literature show that the sulfide ores used in the production of arsenic trioxide had substantial isotope differences (Fig. 5). Also, as a group, the arsenical compounds have distinctive lead isotope signatures that in some cases can be uniquely traced to domestic industrial arsenic trioxide suppliers in the U.S. and to sulfide ores from specific mining districts. This information can be useful to constrain the possible provenance of the individual pesticides. In the case of lead arsenate (acid form), calcium arsenate, and sodium arsenate, the lead isotope compositions closely match those of sulfides from porphyry copper deposits from southeastern Arizona, specifically from the Pima and Silver Bell districts (Bouse et al., 1999). Notably, other major historical producers of arsenic trioxide (e.g., Anaconda Copper Co., U.S. Smelting Co., Jardine Mining Co.) used sulfide ore during their smelting operations that differed greatly from southeastern Arizona because of the different rock ages and metallogenic settings. For example, the porphyry deposits from Montana and Utah (Stacey et al., 1968; Murthy and Patterson, 1961) have higher ^{208}Pb/^{207}Pb and lower ^{206}Pb/^{207}Pb than ores from southeastern Arizona (Fig. 5). Sulfides from the northern domain of southeastern Arizona (e.g., Ray district) also produced ore that is isotopically distinct and is similar to the composition of Paris green (copper acetoarsenite). Other pesticides that plot along the pesticide isotope trend of Fig. 3 reflect lead sources having much lower values of ^{208}Pb/^{207}Pb, and ^{206}Pb/^{207}Pb than the mines of southeastern Arizona.

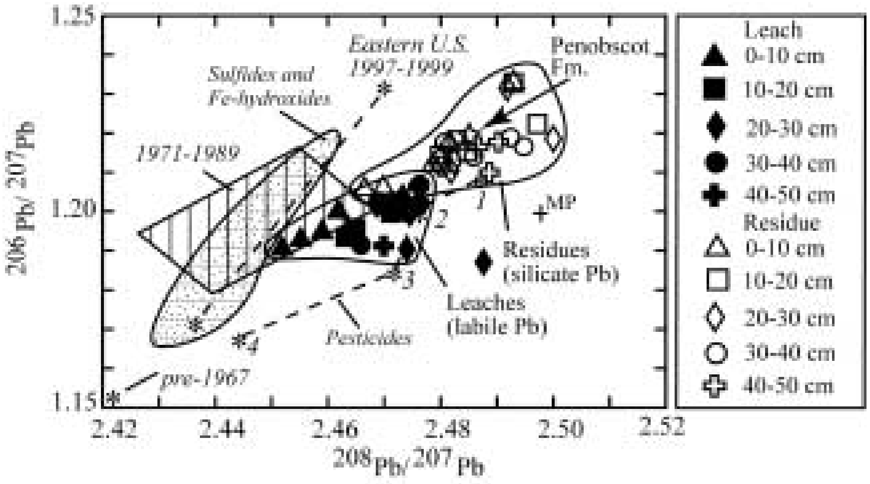

Figure 6. ^{206}Pb/^{207}Pb vs. ^{208}Pb/^{207}Pb plot of lead arsenate (#1), sodium metarsenite (#2), calcium arsenate (#3), and Cu-acetoarsenite as (#4), compositions of the soil profiles, average composition of the Penobscot Fm., generalized field for sulfides and Fe-hydroxides from the Penboscot Fm. (Foley et al., 2004a), and U.S. aerosols (1971-1989 (Rosman et al., 1994) and a dashed line representing the range for atmospheric Pb in the Eastern U.S. for 1997-1999 (Bollhöfer and Rosman, 2001). MP, lead from Mexico and Peru. See text for additional explanation and references.

3.1 Pb and As in the Soil Profiles

We now turn to the question of whether the contributions of the arsenical pesticides can be distinguished from the effects of anthropogenic lead derived from fossil fuel combustion in the Northport watershed area. A fundamental step toward determining the ultimate source of lead (and by inference other elements) depends on accurately assessing the contributions from all of the possible natural and anthropogenic point sources.

Baseline concentrations of arsenic in U.S. near-surface till are ~7.4 mg kg^{-1} (Shacklette et al., 1971), although concentrations can vary broadly because of the heterogeneous distribution of sulfide minerals and redox conditions. Soils that have not been greatly disturbed retain arsenic and lead near the top of the soil horizon, suggesting that metal migration is not significant (Veneman et al., 1983; Peryea, 1998). The soil profiles show considerable Pb isotope variations from top to bottom. Leach fractions are lowest in $^{208}Pb/^{207}Pb$ in the surface soil layer, 10 cm from the surface, but there is no clear isotope gap that can be used to distinguish a limit for the possible effects of near- surface contaminants such as industrial lead from atmospheric deposition versus lead derived from weathering of bedrock. The dominant source of anthropogenic lead is industrial emissions involving combustion of alkyl-lead gasoline additives (Chow et al., 1975) distributed by long-range atmospheric transport (e.g., Nriagu and Pacyna, 1988) producing heavily polluted soils enriched in lead, with possible associated enrichments in As, Zn, and Cd (e.g., Steinnes et al., 1989). A direct relation between the Pb contents, Pb isotope variations, and As contents remains equivocal. Perhaps this reflects the contrasting solubilities of Pb (low solubility at high soil pH) and As (complexing and solubility contrasts with pH) in the near-surface layers, and the various effects of mechanical disturbance (tillage, and digging) near the surface (Peryea, 1998).

Compared to the Pb isotope values of lead arsenate, calcium arsenate, and sodium arsenate pesticides, isotope compositions of industrial lead in the 1960s to the 1980s are somewhat shifted toward lower values of $^{208}Pb/^{207}Pb$ relative to $^{206}Pb/^{207}Pb$ (Fig. 6). Mississippi Valley type (MVT) deposits contain generally radiogenic lead (high values of $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ in Fig. 5; Doe and Delevaux, 1972) and provided most of the lead ore used for industrial applications in the U.S., and for gasoline additives from about 1964 to 1976 (Rosman et al., 1994). From ~1930 to 1970, the period of most intensive application of pesticides in New England, anthropogenic lead throughout the U.S. was primarily derived from combustion of alkyl-lead gasoline additives and with input of lead to the atmosphere ($^{206}Pb/^{207}Pb$ ~1.23 and $^{208}Pb/^{207}Pb$ ~2.46: Chow et al., 1975). Because the supply of lead changed from domestic to foreign sources, $^{206}Pb/^{207}Pb$ in aerosols and gasoline evolved from ~1.15 in the mid-1960s (Erel et al., 1997) to ~1.22 in the 1970s and early 1980s (Figs. 5-6). Values of ^{206}Pb/^{207}Pb decreased after 1976 (Rosman et al., 1994), partly as a result of decreasing gasoline consumption, lead recycling, and imports from Australia, Canada, Mexico, and Peru (Graney et al., 1995; Bollhöfer and Rosman, 2000, 2001). By 1997-1999 (Fig. 6), eastern U.S. aerosols were less radiogenic than values measured in alkyl-lead in the 1970s (Bollhöfer and Rosman, 2001).

The natural geochemical cycle of lead has also been greatly disturbed by a variety of anthropogenic inputs. These include emissions from industrial plants and ore smelters (Graney et al., 1995; Dunlap et al., 1999; Ayuso et al., 2001; De Vivo et al., 2001; Tarzia et al., 2002), effects of urbanization (Hopper et al., 1991; Erel et al., 1997; Hansman and Koppel, 2000; Teutsch et al., 2001), and by other human activities which emit metals (As, Sb, Cd, Se, Hg, etc.) into the atmosphere and surface environment (e.g., Steinnes et al., 1992). However, little arsenic is thought to be contributed to surface and ground water bodies by precipitation, unless a major source of arsenic exists locally (Smedley and Kinniburgh, 2002). Extensive pesticide use in agricultural lands can significantly increase the amount of anthropogenic lead because of reaction of surface water runoff with contaminated soils (e.g., Erel and Patterson, 1994; Kober et al., 1999). Lead isotope compositions of stream sediments inferred to have the highest intensity of pesticide use show considerable overlap in Pb isotope compositions with the arsenical pesticides (Robinson and Ayuso, 2004; Ayuso, unpublished data).

The Pb isotope trend from top to bottom of the soil profiles indicates that compositions of U.S. aerosols (industrial lead) overlap the leach fractions of the surface soil layers (Fig. 6). The data suggest the profiles are influenced by Pb isotope contributions from the youngest aerosols (1997-1999), perhaps generally decreasing in a trend from the top layer to the bottom layer. The Fe-hydroxides also overlap in composition with the leach fractions at the top of the profiles (Fig. 6). This feature agrees with studies showing that in temperate forest soils, the Fe-hydroxides have a high affinity for lead (Emmanuel and Erel, 2002). Lead residence in water (Jaffe and Hites, 1986) and in such temperate forest floors is also thought to be short, probably less than 80 yr (e.g., Miller and Friedland, 1994; Erel et al., 1997). Arsenic, as in the case of lead, also has a strong preference for Fe-hydroxides under surface conditions (e.g., Korte and Fernando, 1991).

Leach fractions from deeper in the soil profiles (>10 cm) are somewhat shifted from the field of aerosols and gasoline, and the field of the Fe-hydroxides toward higher values of ^{208}Pb/^{207}Pb and towards the field of the arsenical pesticides (Fig. 6). Higher values of ^{208}Pb/^{207}Pb than the Fe-hydroxides and pesticides in deeper portions of the soil profiles may indicate a more prominent role for imported lead sources (Peruvian and Mexican Pb ores), or a natural source that has not yet been identified (Fig. 6).

The lead arsenate-acid form, calcium arsenate, and sodium arsenate pesticides do not have a sufficiently distinct Pb isotope range that would allow quantification of their contribution to the anthropogenic lead in the soils. Average compositions of the top layers of the profiles, however, plot as a cluster, intermediate to the rock-derived and anthropogenic point sources, and consistent with the idea that labile Pb reflects involvement of several natural and anthropogenic components (Fig. 7). This figure shows the average compositions of the top layer of the soils (A1 and Ap horizons) used in the isotope study, the top layer of soils for all sites in the geochemical study, as well as that of the 40-50 cm layer (near the bottom of the profiles). Also shown are average isotope compositions of the top layers in areas of the watershed identified as containing high-As ground water, and the top layers in the area identified as the water recharge zone (Lipfert and Reeve, 2004; Lipfert et al., in press). The soil field essentially encloses the total isotope variation of the profiles in the watershed. For the purpose of illustrating possible combinations of point sources that may have contributed anthropogenic lead to the soils, representative compositions of aerosols and gasoline are shown from pre-1967 to 1999. Qualitative mixing schemes can be devised to explain the observed isotope variations in the soils involving lead from arsenical pesticides, Fe-hydroxides and sulfides, and aerosols (Fig. 7). A mixing scheme is illustrated that involves goethite with a high Pb content (Pb~492 ppm; As~4490 ppm), goethite with a low Pb content (Pb~10 ppm; As~14 ppm), and lead arsenate. Only the sample representing the average composition of the lowest soil horizon plots outside of the mixing triangle, adjacent to the average composition of the Penobscot Formation. Similar mixing schemes involving sulfides (e.g., pyrite, Pb ~22-330 ppm; As ~30-1290 ppm) in the Penobscot Formation, and lead from aerosols would also overlap the data for the soils. The exact role of the pesticides is difficult to evaluate quantitatively due to the inherent isotopic variability of the arsenic-bearing ore used in the production of the pesticides, and a lack of information about the identity, dates, and amounts of pesticide applied in the area.

This study was carried out to test whether Pb isotope compositions of in the soils and tills can be linked to use of arsenical pesticides, other anthropogenic point sources, and likely parental rocks (Penobscot Formation). The lead isotope data indicate that a derivation of Pb in soil and till profiles from the local country rocks remains the best explanation of the lead isotope compositions, and is the most likely primary source of arsenic in local ground water. Contribution of Pb from combustion of fossil fuels is likely, especially at the top of the profiles. A major addition of lead from arsenical pesticides is possible but cannot be proven at this time.

The most important natural source of lead (and by inference arsenic) is likely derived from the breakdown of sulfide-bearing bedrock during glaciation and subsequent weathering of the oxidation zone overlying the ground water (Ayuso and Foley, 2002, 2004; Foley et al., 2004a). Decomposition of the sulfide minerals as a result of fluid migration leached and oxidized bedrock and soils, producing Fe-hydroxides and other secondary minerals. As-bearing sulfides (e.g., pyrite and arsenopyrite), for example, would have been converted to limonite, goethite, and secondary sulfide minerals which captured lead (and by inference arsenic) in the original sulfide minerals. Subsequent reduction of secondary mineral phases is thought to release metals into the ground water (e.g., As: Matisoff et al., 1982; Stuben et al., 2003).

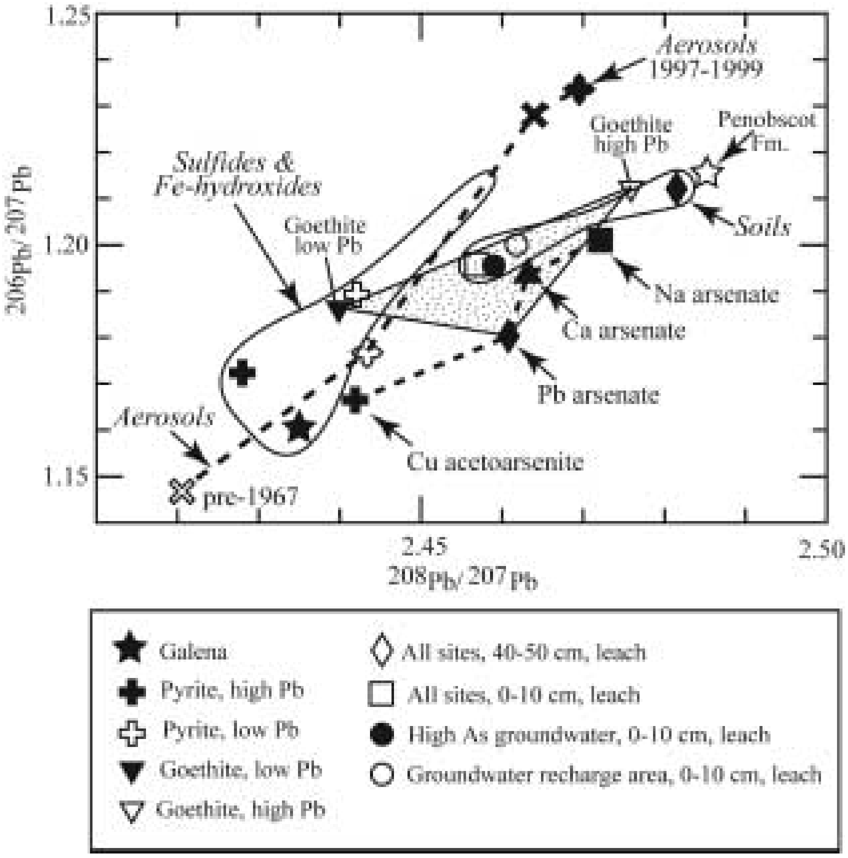

Figure 7. ^{206}Pb/^{207}Pb vs. ^{208}Pb/^{207}Pb plot showing the lead isotopic compositions of lead arsenate, sodium metarsenite, calcium arsenate, and Cu-acetoarsenite (dashed line connects average compositions), and a field for soils that includes the average compositions of the top layer of the soils (roughly equivalent to the A1 and Ap horizons), the top layer of soils for all sites in the geochemical study, and the average compositions of the deep layer at 40-50 cm (near the bottom of the profiles). Also shown are the isotope compositions of the top layers in

areas within the watershed containing wells with groundwater characterized as high-As type, and the top layer in the area identified as the water recharge zone (Lipfert and Reeve, 2004; Lipfert et al., in press). Lead isotope compositions of U.S. aerosols and gasoline produced since the 1960s vary widely and the figure shows estimated compositions starting pre-1967 to about 1999 (sources of data include Chow et al., 1975; Nriagu and Pacyna, 1988; Bollhöfer and Rosman, 2000, 2001; Rosman et al., 1994; Erel et al., 1997; Sturges and Barrie, 1987, and references therein).

4. CONCLUSIONS

Although the predominant source of arsenic and metals to most soils and sediments in New England is sulfide-rich rock, the extensive application of arsenical pesticides and herbicides (lead arsenate, calcium arsenate, and sodium arsenate, and others) on apple, blueberry, and potato fields may have been a significant anthropogenic source of arsenic and lead. The main objective of this work was to determine the lead isotopic compositions of commonly used pesticides, such as lead arsenate, sodium metarsenite, and calcium arsenate, in order to assist in future isotopic comparisons and to better establish this anthropogenic source of Pb. The pesticides plot along a linear trend in isotope diagrams, for example, in values of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$.

Pb isotope compositions of near-surface soil and till profiles in coastal Maine were measured in an area known to have ground water with anomalously high arsenic contents to determine the source of the Pb and by inference, provide constraints on possible sources of As. Labile Pb from the soils and tills shows a moderate range in isotope values, distinctly less radiogenic than the residue fractions. Leach fractions are lowest in values of $^{208}Pb/^{207}Pb$ in the soil surface layers. Acid-leach compositions represent lead that is loosely bound in minerals (Fe- and Mn-hydroxides, carbonate, and micaceous minerals), and likely approximate the composition of Pb available to the regional ground water. The profiles show that average Pb and As contents are generally highest in the surface soil layer. Pb isotope and other geochemical data show that a contribution of Pb from the local country rocks to the soil and till profiles remains the best explanation for the lead isotope compositions. Contribution of lead from combustion of fossil fuels is likely (especially at the top of the profiles).

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Chapter 6

HEAVY METAL IMMOBILIZATION IN GROUNDWATER BY *IN SITU* BIOPRECIPITATION: COMMENTS AND QUESTIONS ABOUT EFFICIENCY AND SUSTAINABILITY OF THE PROCESS

In situ bioprecipitation of heavy metals by sulfate reducing bacteria: understanding and stimulating the process

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Abstract: About 45% of site contamination is caused by heavy metals. Metals are spread in the environment by mining activities, surface treatment and non- ferrous processing. As heavy metals can not be degraded, the only existing risk-reducing removal measures are removal or immobilization (leading to bioavailability reduction). Next to the often used but expensive pump and treat technologies, heavy metals can be immobilized by inducing sulfate reducing bacteria (SRB) to transform the sulfates that are very often present in groundwater (due to the metal mining or processing activities), into sulfides. These sulfides will precipitate the metals as insoluble metal sulfides. Several studies have demonstrated the feasibility of this *In Situ* Bioprecipitation Process (ISBP) for the removal of heavy metals from groundwater as well at lab scale (batch and column tests) as at field scale. However, some questions arise concerning the continuation of the process, and the efficiency and the sustainability of the precipitates. The study, based on more than 10 different studies, all done by the same authors, on different groundwaters and aquifer samples, will try to answer these questions.

The presentation gives an overview of the guidelines necessary for a correct and successful bioprecipitation process with stable metal sulfide precipitates. It pays attention to the influence of the carbon source on the complexing of the metals and the efficiency of the induction of the bioprecipitation process, the possible negative influence of acetate inhibition, the influence on the competence between sulfate reducers and methanogenic bacteria and the influence of low pH on the ISBP. The results will allow the correct implementation of the ISBP with an eye on the longevity and sustainability of the process and present the ISBP as a much more sustainable alternative to the pump and treat technology as a remediation measure for heavy-metals contaminated groundwaters.

Key words: heavy metals, in situ bioprecipitation, sulfate reducing bacteria

1. INTRODUCTION

Most heavy metals exist naturally in the earth's crust at trace concentrations, sufficient to provide living systems with essential nutrients but too low to cause toxicity. Since the industrial revolution, pollution by heavy metals has substantially increased through industrial effluents and landfill leaching, mining activities, fertilizer and pesticide use in agriculture, the burning of waste and fossil fuels, and municipal waste treatment. Since heavy metals cannot be degraded, they are persistent and accumulate over time in the environment, including the food chain. Among the heavy metals cadmium, copper, lead, mercury, nickel and zinc, together with metalloid arsenic, are considered the most hazardous (Cameron, 1992). Because of their threat to human health, and the extent of the problems related to both natural and anthropogenic contamination by heavy metals and metalloids, major efforts are undertaken to develop remediation technologies – based either on physical or chemical principles, or on biological processes – for the treatment of metal-contaminated soils, sediments and groundwater. Conventionally, heavy metal pollution in soils and waters is removed by methods based on physical and/or chemical processes (Mulligan *et al.*, 2001). Pump and treat, using precipitation or flocculation techniques followed by sedimentation and disposal of the resulting contaminated sludge is frequently used for treating heavy metal contamination in water. Other methods for heavy metal removal from water involve ion exchange, reverse osmosis and microfiltration. For the *in situ* treatment of groundwater, a reactive barrier may be installed which removes the heavy metals either by chemical means, i.e. reduction by ferrous iron, or by biological means (Benner *et al.*, 2002; Nyman *et al.*, 2002; Scherer *et al.*, 2000). Due to the fact that conventional methods are often expensive, lack specificity or may even give rise to more environmental problems, alternative cost-effective technologies, generally based on biological processes using microorganisms and/or higher organisms, such as plants, are being developed as treatment alternatives. Overall, bacteria can adopt two major strategies for heavy metal tolerance. In some bacteria, metal tolerance is the outcome of their metabolism or is an intrinsic property related to their cell wall structure or the presence of extra-cellular polymeric substances. Other bacteria have developed specific resistance mechanisms to protect themselves against the toxic effects of heavy metals. These mechanisms include active transport, mediated by efflux pumps, intra- and extracellular sequestration, enzymatic transformation to other, less toxic chemical species by redox reactions, methylation, or alkylation/ dealkylation, and reduction in the sensitivity of cellular targets to metal ions (Gadd, 1992). Precipitation of metals as metal sulfides or phosphates is an alternative way of increasing the resistance of microorganisms to metals. Sulfate-reducing bacteria (SRB) couple the oxidation of organic compounds or molecular H_2 with the reduction of sulfate as an external electron acceptor under anaerobic conditions, a process known as dissimilatory sulfate reduction (Barton and Tomei, 1995). Once sulfide is formed, it readily reacts with the heavy metals to form metal sulfide (MeS) precipitates, resulting in a lower sulfide concentration and a reduced metal toxicity. These MeS precipitates exhibit extremely low solubility and are relatively stable in environments under low redox conditions (Hao, 2000). Moreover, hydrogen sulfide can reduce soluble toxic metals, often to less toxic or less soluble forms (Tebo, 1995).

In our laboratory, the *In Situ* Bioprecipitation Process (ISBP) by Sulfate Reducing Bacteria (SRB) was investigated for metals as Cu, Zn, Cd, Ni, Co, Fe, Cr, and As. The first field tests showed that ISBP is feasible as a strategy for sustaining groundwater quality (Geets et al., 2003; Ghyoot et al., 2004). However, the effect of some factors such as the choice of electron donor, the frequency of the electron donor injection, the soil type, the pH increase due to molasses fermentation, on ISBP still have to be elucidated. Therefore, an overview of the application of ISBP for the removal of heavy metals from groundwater will be presented based on several other publications and many feasibility tests performed for different industrial clients. The results comprise studies of more than 10 different sites with different aquifer compositions, different concentrations of heavy metals and other components, different physico-chemical parameters etc. The different parameters determining the quality, efficiency and sustainability of ISBP will briefly be discussed.

2. RESULTS AND DISCUSSION

The following section presents and discusses the effect of 1) type and concentration of electron donor, 2) sulfate concentration, 3) pH, 4) redox potential, 5) structure microbial community, and 6) soil type on *In situ* bioprecipitation (ISBP) by sulfate reducing bacteria (SRB) for the removal of heavy metals from groundwater. In addition, the importance of the stability of these metal-sulfide precipitates in ISBP will also be investigated and discussed.

2.1 Effect of type and concentration of electron donor on ISBP

A wide range of carbon sources has been proved to be useful in ISBP, varying from expensive and pure substrates such as ethanol (Kalyuzhnyi et al., 1997), lactate (Hammack et al., 1992), and hydrogen (Van Houten et al., 1994) to economically more favorable waste products with or without enrichment with pure substrates or inoculation with monocultures or media containing SRBs (manure, sludge, soil) (Maree et al., 1987; Annachhatre et al., 2001; Prasad et al., 1999). Acetate, a rather cheap carbon source can also be used. However only few SRBs, like *Desulfobacca* (Elferink et.al.,1999), *Desulfobacter* (Skerman et. al., 1980) and *Desulfovibrio* can assimilate this carbon source. Thus, using acetate as single electron donor can lead to very long induction periods: in some cases more than 150 days were necessary to start the sulfate reduction process. Therefore, a combination of electron donors that easily induce the process, such as lactate and molasses, together with a cheap carbon source, such as ethanol and acetate, is suggested.

Next to its difficult assimilation, Caplice et al. (1999) and Diels et al. (2005d) observed that high acetate concentrations can inhibit the sulfate reduction process. The direct antimicrobial effects of organic acids including lactic, acetic and propionic acids, which may be produced by lactic acid bacterial fermentation of foods, are well known. The antagonism is believed to result from the action of the acids on the bacterial cytoplasmic membrane which interferes with the maintenance of membrane potential and inhibits active transport, and may be mediated both by dissociated and undissociated acids. The antimicrobial activity of each of the acids at a given molar concentration is not equal. Acetic acid is a greater inhibitor than lactic acid and can inhibit yeasts, moulds and bacteria. This is one of the supposed reasons for the temporary decrease in the sulfate reduction process observed in reactors and passive treatment systems. On the other hand, too high concentrations of an electron donor can also lead to methanogenic conditions (Diels et al., 2005d). In some cases, high gas production and an absence metal precipitation process was observed. Hence, carbon source concentration plays an important role also. This is especially problematic in the case of carbon source injection. Temporarily high concentrations of electron donor can be present in the injection well resulting in methane production. Also, in the case of molasses, high concentrations could induce a pH decrease due to fermentation processes resulting in metal release from the aquifer into the groundwater.

Several carbon sources were used in a two-step system. Molasses (and other waste products) or polylactate (on the market under the name of HRC®) must first be fermented into small volatile fatty acids and hydrogen gas. The hydrogen gas, and also in some cases the fatty acids, serve as an electron donor. In experiments where the ISBP-stimulating effect of molasses and HRC® were compared, results indicated that the molasses did not work for a long time. Pulles et al. (2004) noted that the sulfate reduction process is not always stable. It starts quickly, drops down, then starts again. Presumably some sugars in the molasses are degraded too quickly and take some time to generate new useful electron donors. In addition, care must be taken that the fermentation process has not started already in the stock recipient. The ISBP-stimulating effect of the polylactate, however, lasted much longer (evaluation is still going on). Slow-release compounds have the advantage of removing all the oxygen very efficiently and in so doing decrease the redox potential and negate the need for regular injection. The slow release compounds seem to last for at least 6 months (study is on-going) and so can be used as a long-lasting electron donor source resulting in a more stable ISBP.

Vanbroekhoven et al. (2005) also showed in a column set-up that initially molasses induced the ISBP-process very quickly, but subsequently failed to maintain the sulfate reduction even as metal concentrations quickly increased in the molasses column's effluent. By contrast, the HRC® and lactate gave rise to a more continuous process. However, a difference could be observed between the HRC®-induced process and the lactate-induced process. In the latter, a mixture of nitrogen and phosphorus was added together with the lactate which noticeably sustained the process, indicating that nutrients and perhaps also micro-elements are necessary to keep the process on track in the long term. Janssen et al. (2004) mentioned the need for SRB medium to induce the Sulfate Reducing Bacteria (SRBs).

The way the electron donor is added to the aquifer also has an effect on ISBP. In all the former experiments, the electron donor was added to the batch flasks with aquifer and groundwater or was pumped continuously with the groundwater through the columns. A new series of tests was performed by pumping just groundwater over columns, filled with aquifer (Vanbroekhoven et al., unpublished). Some centimeters above the inlet an injection of molasses or HRC® was done in single stages. After the first injection with HRC®, the redox turned negative and stayed negative in contrast to the molasses column where after a while the redox increased again. In both columns, the pH decreased first and increased afterwards to a pH of more than one unit higher than the original groundwater pH. Sulfate decreased better in the HRC® column compared to the molasses column. Also, the formation of black iron sulfides could be better observed in the HRC® column. And Zn removal went more quickly with HRC®. Indeed, 10 days after injection, Zn was removed by 100%. In the case of the molasses column, 53 days after the second carbon source injection, Zn removal started to decrease. Therefore, ISBP was not only stimulated faster by the HRC® than by the molasses but was also more stable in function of time.

High molasses concentrations also lead to the complexation of chromium (III) and hence its solubilization (Diels et al. 2005a). It appears that chromium (VI) can be reduced very easily by several electron donors. However, in certain cases the chromium (III) stayed in solution due to complexation with some compounds of the carbon source, indicating that increasing concentrations of molasses (but also protamylasse) decreased the precipitated chromium (III) concentration especially at the rather low pH of 6. However, chromium (III) precipitation could be improved by increasing the pH up to 8.

2.2 Effect of sulfate concentration on ISBP

The concentration of sulfate is important in relation to the electron donor. If the sulfate concentration is low (< 100 mg SO_4^{2-}/L, the sulfate-reducing process will not start unless a sulfate-reducing inoculum is added. Further, at low sulfate concentrations the sulfate reduction could only be started if hydrogen was added as electron donor. Diels et al. (2005d) showed the removal of Zn from a groundwater at a sulfate concentration of 74 mg SO_4^{2-}/L. In two conditions the sulfate-reducing strain *Desulfovibrio desulfuricans* Dd8301 was added and only then Zn removal occurred. The same paper shows an ISBP-process at a sulfate concentration of 506 mg SO_4^{2-}/L. In this case, the Zn is also removed without addition of *D. desulfuricans* Dd8301.

2.3 Effect of pH on ISBP

Sulfate-reducing bacteria can be induced at a pH between 4 and 8. At neutral pH, SRBs from different origins could be detected (Groudev et al., 2005). Temminghof et al. (2005) noted that at a location in The Netherlands (Dieren), at an initial pH of 3.9, the ISBP process could only be started after addition of an SRB inoculum. At low pH levels, only *Desulphotomaculum* and *Desulphosporosinus* could be detected (Geets et al., 2005). Similarily, Johnson (personnal communication) suggested that at low pH, *Desulphosporosinus* and *Desulphotomaculum* were observed always.

2.4 Effect of redox potential on ISBP

A redox potential < -200 mV is necessary to induce the SRBs. Temminghof et al. (2005) used Na_2S to reduce the Eh. Diels et al. (2005b) used other redox manipulating compounds like Zero Valent Iron, Na_2S to decrease the Eh especially in the case of low pH.

2.5 Effect of the structure of the microbial community on ISBP

Competition between sulfate-reducing bacteria and iron-reducing bacteria is also of high importance in ISBP. The energy benefit of sulfate-reducing bacteria is only -0.10 kcal/mol e, while it is -10.49 kcal/mol e for iron-reducing bacteria. The ΔG for chromate-reducing bacteria is also -10.76 kcal/mol e. It was frequently observed that when the redox potential could not be decreased to low values, denitrifying or iron-reducing bacteria were observed to be active. At very low metal concentrations, denitrifying conditions, induced for instance with acetate as electron donor, lead to very good Cd and Zn removal. This process turned out to be a natural attenuation process that can occur in diffusely polluted areas (Seuntjens et al., 2005) when some organic carbon degradation products are available. Also, under conditions of iron reduction, some metals seem to be removed from the groundwater due to the co-precipitation processes. Arsenic in particular can be removed or immobilized in this way.

The correct microbial population has to be stimulated before ISBP can occur. Molecular biology is an excellent field for the identification of SRBs and study of their diversity. Either 16S rRNA gene-based primers can be used, or *dsr*-based (dissimilatory sulfite reductase) primers. It could be concluded that only by using *dsr*-based DGGE, could a real biodiversity be observed (Geets et al. 2005).

2.6 Effect of the soil type on ISBP

The soil composition influenced ISBP. Comparative tests on groundwater obtained from sandy and clay layers from the same site indicated that both aquifer compositions lead to the induction of the metal precipitation process. However, ISBP in the sandy aquifer seemed to be induced at a much faster rate than in the clay aquifer. This is presumably due to the limited diffusion of electron donor in the clay system. At the moment tests are being conducted in a gravel aquifer (Vanbroekhoven et al., unpublished).

When heavy metals have been immobilized by ISBP, it is also important to study the stability of the metal-sulfide precipitates. This can be done by sequential extraction (Tessier et al., 1979). A detailed study is presented by Diels et al. (2005c) and a summary of some results is given below.

An aquifer from a non-ferrous contaminated site was used in a column study. Groundwater from the site containing *in situ* concentrations of Cd, Zn, Co and Ni, was pumped over the aquifer loaded columns during a two-year period. The columns were treated with different electron donors including molasses, and lactate. Besides lactate, lactate-containing additional nutrients N and P (a mixture of ammonium nitrate and orthophosphate) were added in order to avoid nutrient limitation for the SRB population. A column without electron donor was operated also. This column was representative of the Natural Attenuation process (NA). In the electron-donor amended columns, redox potential decreased to -250 mV, the initial pH of about 4 went up to 6 and most of the metals were removed. In the NA column, almost no metals were removed. Different carbon sources like molasses, HRC® and lactate (with or without N/P nutrients) promoted sulfate reduction within eight weeks, with average sulfate-removal efficiencies of 50%. At the same time, substantial removal of Cd, Zn (at least 75%) and Co (at least 45%) took place, whereas attenuation of Ni was getting into its stride.

In the following weeks, molasses failed in maintaining sulfate reduction, and metal concentrations quickly increased in the column's effluent. After 15 weeks, the sulfate reduction process in the HRC® amended column also showed a decreasing efficiency in metal removal, whereas the ISBP process seemed to be stable in the lactate-amended columns (Vanbroekhoven et. al., 2005). At T2, after two years of operation, the columns were stopped and samples were taken at four places (C1, C2, C3 and C4) in the column. C1 is the inlet of the column and C4 the outlet. C2 – C3 are intermediate. Different extractions were made in order to define the speciation of the metal: Leachable fraction (extraction with water), exchangeable fraction (extraction with $MgCl_2$), carbonate fraction (extraction with sodium acetate), Fe-Mn oxide fraction or reducible fraction (extraction with $NH_4OH.HCl$), organic or oxidizable fraction (extraction with NH_4-acetate) and the residual fraction. The sum of all the fractions was made and compared with a second sample treated by *aqua regia* in order to control the mass balance. It turned out that the mass balance was relatively satisfactory considering that the aquifer was not homogeneously contaminated.

During the two-year groundwater pumping, metals were continuously fed to, and precipitated on, the aquifer resulting in a large difference (increase of metal deposition) between T0 and T2. The metal concentrations were highest at the inlet (C1) of the column where oxygen was first consumed and the redox potential decreased. In the fractions of the columns taken at T2, leachable, exchangeable and carbonate fractions are decreased compared to the original situation T0. This indicates that all the metals moved into a more tightly bound precipitate. Nearly all the metals are found in the reducible (Fe-Mn oxide) and mostly in the oxidizable fraction (organic). In fact, the metal sulfide precipitates are expected in the oxidizable fraction.

Table 1 presents a comparison of the results of the sequential extraction for the columns operated under natural attenuation condition or with molasses or lactate as electron donor. To the lactate column, the nutrients N and P were added also. The leachable and exchangeable fractions are stable in the NA column and are reduced in the molasses and lactate columns. However, the reduction is always higher in the lactate column compared to the molasses column. The same is true for the carbonate fractions, but the differences are smaller. It is also observed that the Zn is precipitated in the reducible fraction and that the highest amount can be recovered from the oxidizable fraction (ZnS). However Ni can be recovered in the reducible, and mostly in the oxidizable, fraction in the lactate-amended column. Only very small amounts of Ni could be recovered from the aquifer of the molasses-amended column. For Ni, a large difference is observed between the use of molasses and lactate as electron donors. Lactate always tends to precipitate the metals in a more stable form and this especially true for Ni. Ni removal and stable precipitation is rather low in the case of molasses-amended columns and optimal conditions could only be obtained with lactate.

In conclusion, we can say that the group IIb elements Zn and Cd were both precipitated in the presence of all the carbon sources. For Ni and Co, both transition metals and those belonging to group VIII, only the addition of lactate resulted in the formation of a good and stable bioprecipitate while both these elements did not or hardly precipitate in the presence of molasses. In some further studies, sequential extractions were performed under aerobic or anaerobic conditions. These two methods performed on a same aquifer sample showed one big difference: the aquifer material sequentially extracted under aerobic conditions gave a rather large metal carbonate fraction in some cases. The anaerobic treated aquifer did not show a carbonate fraction. This difference still needs further research and elaboration (Vanbroekhoven et al. unpublished).

In another study concerning the stability of metal-sulfide complexes, some aquifer material was studied by Scanning Electron Microscopy. First a separation method was developed in order to enrich the fine precipitates. In the enriched samples, a metallic layer was observed on the sand particles. After EDAX evaluation, Zn and S were detected at equimolar concentrations indicating the presence of ZnS. As these tests were performed on aquifer samples from batch experiments, the precipitates were rather small and below the detection level for X-ray diffraction analysis. The following study will focus on the metal precipitates of the previously mentioned columns (after a two-year operation).

Table 1. Sequential extraction for Zn and Ni from aquifer derived material from columns operated with molasses or lactate as electron donor compared to natural attenuation

	Zn (mg/kg dm)			**Ni (mg/kg dm)**		
	NA	**Molasses**	**Lactate N/P**	**NA**	**Molasses**	**Lactate N/P**
Leachable						
T0	227	227	227	81	81	81
C1 (T2)	267	71	16	93	77	103
C2 (T2)	306	80	1	111	75	35
C3 (T2)	292	77	1	108	75	12
C4 (T2)	293	42	2	107	76	10
Exchangeable						
T0	809	809	809	22	22	22
C1 (T2)	763	262	45	23	23	81
C2 (T2)	890	308	0	31	37	46
C3 (T2)	828	281	0	62	46	19
C4 (T2)	720	155	0	21	39	17
Carbonate						
T0	93	93	93	22	22	22
C1 (T2)	119	51	83	23	23	81
C2 (T2)	124	38	9	31	37	46
C3 (T2)	191	41	6	62	46	19
C4 (T2)	75	20	2	21	39	17
Fe-Mn oxide						
T0	144	144	144	5	5	5
C1 (T2)	189	689	445	189	11	126
C2 (T2)	199	625	430	7	11	95
C3 (T2)	198	572	381	7	12	39
C4 (T2)	265	423	228	26	16	32
Organic						
T0	69	69	69	3	3	3
C1 (T2)	69	3153	2652	4	6	3425
C2 (T2)	83	2783	1594	5	7	1706
C3 (T2)	91	1536	684	5	10	794
C4 (T2)	99	2647	1217	8	44	530

3. CONCLUSIONS

This paper focused on the further development of ISBP combined with other techniques for the removal of heavy metals from groundwater. Special attention was given to the longevity and sustainability of the process.

Parameters as pH, redox potential, carbon source and sulfate concentration seem to play an important role in the induction of the sulfate-reduction process. On the other hand, the selection of the electron donor seemed to be important in order to sustain the process. Presumably combinations of electron donors must be selected in order to induce and to keep the process going. Agathos et.al.(2005) also suggested electron donor combination to sustain the dehalogenation process. They suggested inducing the process with lactate as it induced a broad sample of dehalogenating bacteria. Later on the process could be kept going on by adding the much cheaper carbon source methanol. Some experiments also showed that the presence of trace elements can become necessary in order to make the process sustainable. Some first results indicated that the addition of a nitrogen and phosphorous source in combination with lactate kept ISBP much more stable. Perhaps in the long run other metals or elements can become limiting too. On the other hand, the mineral aquifer can probably be a source of the slow release of micro-elements.

The comparison between the regular injection of electron donor and the slow-release based processes also needs to be evaluated. Initial tests currently underway indicate no difference between continuous injection and slow release systems. However, the regular injection of an electron donor has some drawbacks. It is laborious and even when fully automated needs maintenance. In addition, the regular injection of a carbon source into an injection or monitoring well, creates the risk of bacterial growth on the housing of the injection well and can lead to biofouling and blocking of the filters. On the other hand, slow release compounds are more expensive but need only be injected once or twice a year by a push system (e.g. by a Geoprobe system) and carry no risks of clogging or biofouling. A comparative study on the effects of fast- and slow-release compounds on ISBP is underway and results will be available at the beginning of 2006 (Vanbroekhoven et al., unpublished). Tests, performed with single injections of molasses and HRC®, showed that metals could be precipitated in both cases. However, the frequency of injections necessary to keep the system under operation was much higher for molasses than in the case with HRC®.

Another intriguing point is the different behavior of Cd-Zn at one end and Ni-Co at the other. In the experiments performed up until now the Cd- and Zn-precipitates are stronger and more stable compared to the Ni- and Co-precipitates. Further investigations are underway in order to find out if the unstable behavior of Ni and Co precipitates is temporary rather than continuous. Some studies indicate that metal sulfide formation processes tend to transform from an amorphous state to a more crystalline state making the precipitate much more stable. One such study is planned and already started and will give a final answer on the sustainability of ISBP. It will be necessary to convince authorities about the final usefulness of this risk-reduction process.

As many sites are contaminated by several metals (anions and cations or radionuclides) by activities such as non-ferrous metals processing, surface treatment and mining activity (including also coal mining in some cases), pump and treat can not always deliver an economically acceptable solution. Therefore the development of *in situ* technology is becoming critical. The results and problems encountered up to now show that in many cases the combination of different more passive systems (e.g. also in combination with wetlands) will be necessary. The use of the *in situ* bioremediation process, whether or not combined with other passive systems such as wetlands, PRBs, etc., will allow an economically acceptable management of risks related to metals and acid spreading into the environment from large contaminated sites (e.g. mining sites). Pump and treat technology can be useful in source removal whereas the passive-treatment systems will be more applicable for the diffuse pollution of affected sites.

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Chapter 7

MICROBES AND ARSENIC CONTAMINATION OF GROUNDWATER IN MAINE: IS THERE A LINK?

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Abstract: High arsenic concentrations occur naturally in groundwater in some locations and can result in serious health effects when the groundwater is used as a drinking water supply. The effects have been well documented in Bangladesh, where millions of people have been exposed to unacceptably high arsenic concentrations since the 1970s and serious health impacts, such as cancer, have emerged. Here in the USA, there are several problem areas, among them, parts of Maine. In 2001, an isolate named NP4, later identified by 16S rRNA sequencing as a member of the genus *Sulfurospirillum*, was obtained from a contaminated well in Northport, Maine. The well is among a cluster of wells with very high arsenic concentrations, and with no known anthropogenic sources of arsenic. At the time of sampling, the total arsenic concentration in the water was 1400 ppb. The presence of NP4 in groundwater, and its ability to reduce arsenate as well as a variety of other electron acceptors, including Fe(III) and Mn(IV), prompted a fluorescence *in situ* hybridization (FISH) study to determine its prevalence in the environment. Well water was taken from wells in the Northport area and in the Branch Lake area of Ellsworth, Maine, where the groundwater has much lower concentrations of arsenic, but with some readings still higher than the drinking water standard of 10 ppb. In the Northport area, NP4 accounted for as much as 16% of the total suspended bacterial population. While NP4 as a percentage of total bacterial numbers does not correlate with total As concentrations in groundwater, it does correlate with As(III). A positive correlation was also found between *Geobacter*, a genus that includes many iron-reducing bacteria, and total arsenic. These results indicate that microorganisms may be important in arsenic mobilization and speciation in groundwater.

Key words: Arsenic, groundwater, arsenate reduction, iron reduction, *Geobacter*, *Sulfurospirillum*

1. INTRODUCTION

Drinking water is probably the most important source of arsenic in humans who are not occupationally exposed (Matschullat, 2000; Smedley and Kinniburgh, 2002), and a causal link between arsenic exposure in drinking water and cancer has been made (USEPA, 1998). Surface and groundwater may be contaminated with arsenic through human activities such as mining, wood preservation and agricultural use of arsenic compounds among others (Smith et al., 1998; Smedley and Kinniburgh, 2002). Naturally high arsenic levels also occur in waters affected by geothermal activity and in groundwater where aquifer materials contain arsenic (Smedley and Kinniburgh, 2002). Notably, in China, Taiwan, Bangladesh, and India, large populations have been exposed to high arsenic concentrations in drinking water, which has resulted in mass chronic arsenic poisoning with devastating health consequences (e.g. USEPA, 1998; Mukhopadhyay et al., 2002). Many other countries, including the United States, are also affected by high arsenic concentrations.

Parts of eastern New England, including regions in Maine, have groundwater with elevated levels of arsenic. The USGS has conducted two major surveys of the area and found that high groundwater arsenic correlates with calcareous metasedimentary bedrock (Ayotte et al., 1999; Ayotte et al., 2003). In Northport, Maine, the arsenic concentration in groundwater from some wells exceeds 1000 $\mu g\ l^{-1}$. Since the bedrock at the site is enriched with arsenic and local surface water is not contaminated, the source of arsenic is thought to be natural (Lipfert et al, 2005).

At publicly owned treatment facilities in the United States, the arsenic concentration must be monitored and maintained below the maximum contaminant level (MCL) of 10 $\mu g\ l^{-1}$. Arsenic can be removed from drinking water by a variety of means, including adsorption, ion exchange and reverse osmosis (USEPA, 2000). Water treatment can therefore reduce arsenic to acceptable levels if an uncontaminated source is not available. Where water is self-supplied, however, there is no testing or treatment requirements, and users may be unaware that they are consuming dangerously high levels of arsenic. In Maine, nearly half of the population relies on private wells for drinking water, and up to 13% of these wells contain arsenic above the 10 $\mu g\ l^{-1}$ MCL (Loiselle, et al. 2002). A better understanding of arsenic cycling in the subsurface is needed to develop management tools and direct resources to education and outreach activities in areas that are likely to be affected by high arsenic concentrations.

Microorganisms can potentially affect arsenic speciation and mobility in a number of ways. They may act directly on an arsenic species, either oxidizing As(III) or reducing As(V). As(III) oxidation by chemolithotrophs has been reported in surface water fed by geothermal sources (e.g. Wilkie and Hering 1998, Langner et al. 2001). As(V) reduction can be mediated by detoxification systems like the *ars* operon (Rosen 2002), or by arsenate-respiring microorganisms. Arsenate respiring bacteria have been isolated from an array of environments (see Oremland and Stolz, 2005). Since the form of arsenic affects its toxicity and mobility in the environment, these microbial activities could affect both the environmental concentration and effects of arsenic. Microorganisms may also affect arsenic indirectly, by altering or solubilizing minerals or surface sites that bind arsenic, resulting in its release into the water. Since ferric iron is common and binds arsenic strongly, iron reducers, like those from the genus *Geobacter*, could affect arsenic mobility indirectly. In areas where arsenic is present in aquifer materials, any of these activities might affect arsenic levels in groundwater.

As a first step in determining the effects of microorganisms on arsenic mobility, water from a high arsenic well in Northport, Maine was incubated with added arsenic and a carbon source. An arsenate-respiring isolate was obtained and characterized. Respiration reactions where arsenate is used as the terminal electron acceptor result in the formation of As(III), which is the more toxic form of arsenic (Newman et al. 1998, Stolz and Oremland 1999, Smedley and Kinniburgh 2002). These reactions might also result in greater arsenic mobility under some conditions. The prevalence of these microorganisms in groundwater was determined by fluorescence *in situ* hybridization (FISH) to determine if they were likely to have an effect on groundwater chemistry. The prevalence of microorganisms from the genus *Geobacter*, which are iron-reducing bacteria that could affect arsenic mobility indirectly, was also determined.

2. MATERIALS AND METHODS

2.1 Sampling

Water samples were taken from University of Maine Geology Department research well Baker # 39 located in Northport, Maine (Lipfert et al. 2005) from a depth of 30 m for the enrichment and isolation. Water was collected via sterile tygon tubing fed through a peristaltic pump. After pumping for 20 minutes, 25 ml samples were pumped into sterile, nitrogen-purged 30 ml serum bottles and crimp sealed. These samples were amended with 10 mmol l^{-1} sodium acetate and 1 mmol l^{-1} sodium arsenate upon return to the laboratory. Later transfers were made into media containing lactate instead of acetate. The arsenic concentration in the groundwater samples measured by ICP (APHA 1998) was 1446 $\mu g\ l^{-1}$.

For FISH and chemical analyses, 12 samples were either taken from boreholes as described above, or from outside taps prior to any treatment at private residences. Conductivity was measured with a Hach CO150 meter, pH, and temperature were monitored using a Hach EC20 meter until readings stabilized prior to taking samples. For total arsenic, 25 mL samples were filtered through a 0.45 mm syringe filter and acidified to 0.2 M nitric acid. For arsenite, 25 mL samples were acidified with hydrochloric acid to a concentration of 0.05%, and passed through a BioRad™ laboratories AG 1-X8 resin Poly-Prep 0.8 x 4 cm column prior to nitric acid addition. Five hundred milliliters of sample from each site was taken for analysis via the FISH method in sterile, N_2-flushed bottles and 3.7 % formaldehyde was added. All samples were kept on ice until they reached the lab and stored at 4 ^{o}C until analysis.

2.2 Isolation and culture conditions

Strict anaerobic procedures were followed at all times when handling these organisms (Breznak and Costilow 1994). Headspaces of all vessels were flushed with filtered N_2 gas prior to dispensing media or cultures. The defined media used to grow NP4 is described elsewhere (Weldon and MacRae, 2005). When solid media was required for colony isolation, 2% washed agar was added to the media and the cultures were serially diluted in agar deeps. Colonies were picked using a sterile, stretched Pasteur pipette and transferred to fresh liquid media.

2.3 Electron donor and acceptor surveys

For electron donor/carbon sources, arsenate was added to serum bottles containing defined media to a final concentration of 1 mmol l^{-1} and the following carbon sources were added to separate serum bottles to a final concentration of 10 mmol l^{-1}: acetate, acetate + H_2, butyrate, citrate, ethanol, formate, fumarate, glucose, glycerol, lactate, methanol, pyruvate, and succinate. At intervals, samples were withdrawn and monitored for the reduction of arsenate to arsenite and growth of NP4. NP4 was transferred into fresh media with each electron donor twice prior to being scored positive for its use. For electron acceptors, the media was prepared with 10 mmol l^{-1} lactate or formate. The following TEAs were added to a final concentration of 10 mmol l^{-1}: Na_2SeO_4, Na_2SO_3, MnO_2, $NaNO_2$, $NaNO_3$, Na_2SO_4, $Na_2S_2O_3$, Fe(III) prepared by neutralizing $FeCl_3$ with NaOH. For O_2, 10 mL air was included in the headspace. Sodium arsenate was added at 1 mM to prevent toxicity. NP4 growth and lactate consumption were monitored over time. Selenate, manganese and Fe(III) reduction also produced color changes. The results were confirmed using formate as C source.

2.4 Analyses

Arsenite, arsenate, lactate and acetate concentrations were quantified over time using a Hewlett Packard model 1050 High-Performance Liquid Chromatography (HPLC) with a diode array UV detector (Culbertson et al. 1988, as modified by Laverman et al. 1995). The HPLC was fitted with a Bio-Rad HPX-87H organic acid column and a Phenomenex SecurityGuard column with carbo-H+ inserts. The mobile phase was 5 mmol l^{-1} sulfuric acid delivered at 0.2 mL min^{-1}. Injections (35 µL) were made onto the column, and the run time was 80 minutes. The detector was set at 192 nm for arsenate species and 220 nm for carbon species.

The headspace of culture bottles was analyzed for CO_2, CH_4, and H_2 by gas chromatography. Samples (500 µL) were withdrawn from the headspace and the gases were separated using a GOW Mac 600 series gas chromatograph with a TCD detector and a Carboxen 1000 column. The run program was: 35 ^{o}C for 5 min, then a 20 ^{o}C min^{-1} ramp to 225 ^{o}C. The balance gas was argon at a 30 ml min^{-1} flow rate.

For growth experiments, cell density was monitored using acridine orange (AO) direct counts (Murray and Robinow 1994). Stained cells were counted using a Nikon Eclipse E400 epifluorescence microscope with a Chiu Technical Corporation Mercury-100W lamp and a FITC-acridine orange filter set.

Metals in the groundwater samples were measured via Inductively Coupled Plasma-Atomic Emission Spectometry (ICP-AES) using a Perkin-Elmer Optima 3300XL axial view ICP-AES (US EPA, 1996).

2.5 Polymerase Chain Reaction (PCR) and Sequencing

PCR amplification of the 16S rRNA was carried out using the primers 27F: 5'- AGAGTTTGATCATGGCTCAG (bacterial) or 530F: 5'-GTGCAAGCAGCCGCGG (universal) and 1492R: 5'-GGTTACCTTGTTACGACTT (Lane 1991; Giovannoni 1991) and the Qiaquick-purified product (Qiagen) was sequenced. The sequence was submitted to Genbank and assigned the accession number AY756183. BLASTn was used to determine phylogeny (Altschul et al., 1997).

2.6 Fluorescence *in situ* Hybridization (FISH)

The FISH method was modified from Karner et al. (2001) as described in (Weldon and MacRae 2005). Briefly, 3.7% formaldehyde fixed cells were filtered through 0.2 μm filters (Nucleopore) and placed in a humidified chamber with 100 μl 50% formamide buffer and 4 μl 1 mg ml^{-1} IDT® FAM labeled NP4-specific (5'-TATCGCTTCTCTTTGTCCTAGCCA) or *Geobacter* specific (5'- TACCCGCRACACCTAGT) probe. The hybridization temperature was 75 °C, and the wash temperature was 55 °C. The samples were viewed by epifluorescence microscopy as for the AO counts. The DAPI counterstain was viewed with a DAPI/Hoechst filter set.

3. RESULTS

Enrichment cultures made from the groundwater samples were tested for arsenate reduction by As(III) production. Significant concentrations of As(III) were observed in transfers into media containing 1 mmol l^{-1} arsenate and lactate, but not in acetate media, or in media containing 5 or 10 mmol l^{-1} arsenate. To isolate colonies, the enrichment cultures in which arsenate reduction was observed were serially diluted and inoculated into agar shake tubes containing minimal media prepared with 2% agar. Attempts to grow these organisms on plates were unsuccessful. Small, diffuse, white colonies appeared in media containing 10 mmol l^{-1} lactate and 1 mmol l^{-1} arsenate. Colonies were picked and transferred to fresh liquid media. The colony isolation was repeated, and microscopic examination showed a single, gram negative curved rod or S-shaped, motile cell type. Cells were able to grow at temperatures as low as 4 °C.

Sequencing of the PCR-amplified partial 16S rRNA gene, obtained using bacterial primers, yielded a 1342 base sequence, which was submitted to Genbank and assigned the accession number AY756183. Blastn analysis showed that this isolate has no identical matches in the database, and clusters within the ε-Proteobacteria. NP4 are closely related to several *Sulfurospirillum* species, among them, species that have been shown to respire arsenate and chlorinated solvents (Stolz et al. 1999, Luijten et al. 2003).

The range of electron acceptors that NP4 can use, based on growth in media containing 10 mmol l^{-1} lactate and a variety of electron acceptors at 10 mmol l^{-1}, are shown in Table 1. Growth was confirmed by growth on formate media, since NP4 could not grow on this carbon source alone. NP4 can grow anaerobically at the expense of a variety of electron acceptors, but cannot use oxygen.

The results of the carbon and electron donor survey are also shown in Table 1. In addition, NP4 was tested for growth in the absence of an electron acceptor on the carbon sources it could use. NP4 could not grow on formate or pyruvate in the absence of an added electron acceptor, but could grow on lactate, though more slowly than with an electron acceptor, and on fumarate alone.

Comparison of FISH prevalence data and water chemistry at the sampling sites yielded interesting results. Linear regression analyses of NP4 prevalence vs concentration for iron and total arsenic showed no relationship (r^2 = 0.01 and 0.29, respectively), but NP4 prevalence did correlate with arsenite (r^2 = 0.86). *Geobacter* was strongly positively related to total arsenic (r^2 = 0.74) and had somewhat weaker correlations with arsenite (r^2 = 0.63) and iron (r^2 = 0.54).

Table 1. Growth of NP4 on different electron acceptors and carbon sources

Electron Acceptor	**Lactate use and Growth**	**Carbon source**	**Reduction of As(V) and Growth**
Arsenate	+	Acetate	-
Fe(III)	+	Acetate + H2	-
Fumarate	+	Butyrate	-
Mn(IV)	+	Citrate	-
Nitrate	+	Ethanol	-
Nitrite	-	Formate	+
Oxygen	-	Fumarate	+
Selenate	+	Glucose	-
Sulfate	-	Glycerol	-
Sulfite	+	Lactate	+
Sulfur	+	Methanol	-
Thiosulfate	+	Pyruvate	+
		Succinate	-

4. DISCUSSION

The results in Table 1 show that NP4 can grow anaerobically at the expense of several different electron acceptors. In the absence of an electron acceptor, it can grow at the expense of fumarate or lactate, but overall appears to have a fairly restricted organic carbon substrate usage profile. The electron acceptor usage of NP4 invites speculation on what it might be doing in the groundwater environment. Since it can reduce As(V), it could have a direct impact on arsenic speciation in groundwater. Its ability to reduce the solid phase electron acceptors Fe(III) and Mn(IV),both of which can bind arsenic, indicates that it could also cause release of arsenic from subsurface materials by indirect means. The ability of NP4 to reduce sulfur compounds and to ferment some organic carbon substrates provides alternative modes of growth such that NP4 could also exist in the subsurface without affecting arsenic cycling in the groundwater at all.

Since NP4 accounted for up to 16% of the total population in some Northport groundwater samples, it could have a significant impact on water chemistry at those sites. NP4 (as a percentage of the total microbial population) correlated strongly with the arsenite concentration in Northport groundwater but not with either iron or total arsenic. These results suggest that NP4 does not control the total arsenic concentration, but it might indeed be reducing As(V) in groundwater and adversely affecting the water quality *in situ*. The lack of correlation with iron suggests that NP4 is probably not an important iron reducing bacterium in this system.

The presence of As(III) in groundwater is problematic for a number of reasons. The primary reason for concern is that As(III) is more toxic than As(V) (Newman et al. 1998, Stolz and Oremland 1999, Smedley and Kinniburgh 2002). There is more controversy over the issue of mobility. This issue is discussed in some detail by van Geen et al. (2004), but under field conditions As(III) is often reported to be more mobile (e.g. Newman et al. 1998, Bose and Sharma 2002, Smedley and Kinniburgh 2002, Islam et al. 2004). As(III) is also more difficult to remove from water using typical treatments such as ion exchange columns, adsorption columns and reverse osmosis (Kartinen and Martin 1995, USEPA 2000, Ning 2002). Removal of As(III) typically requires the addition of an oxidation step to improve performance. Regardless of the mobility issue, then, reduction of As(V) in groundwater, which NP4 appears to contribute to, results in a degradation of water quality through an increase in arsenic toxicity, and increased cost and difficulty of treatment.

The correlation between *Geobacter* prevalence and total arsenic suggests that iron reduction controls arsenic mobility in this system. This has also been reported elsewhere (e.g. Islam et al., 2004; van Geen et al., 2004; Horneman et al., 2004). *Geobacter* species are able to use solid phase electron acceptors such as iron(III) oxides but are not known to reduce arsenate (Nevin and Lovely, 2000). They could thus contribute to the release of arsenic by solubilizing As-bearing iron minerals in the bedrock or iron based surface coatings that adsorb arsenic. If this is the case, the weaker correlation between *Geobacter* and iron requires further examination. This could either mean that *Geobacter* species are not the only important iron reducers in the system or that insoluble Fe(II) products such as magnetite, siderite or vivianite, are being formed. If arsenic concentration is controlled by *Geobacter* through the availability of Fe(III) binding sites, our results support the latter interpretation, however the data are not conclusive.

The weak correlation between *Geobacter* and As(III) is interesting. Since no *Geobacter* species are currently known to be able to reduce arsenate, the correlation could indicate that the activity of *Geobacter* is required for NP4 to act. One mechanism that would be consistent with this interpretation is that NP4 can only use soluble As(V) and thus requires *Geobacter* to release arsenic before it can be reduced.

A prerequisite for the activity of both of these populations is anaerobic conditions. Organic carbon is often the driver for the generation of reducing conditions in groundwater. NP4 also requires an organic carbon source for growth and arsenate reduction. This is generally the case for reduction of Fe(III) binding sites as well. Organic carbon availability could thus be a factor that limits these activities in the subsurface. The sources of TOC *in situ* and potential effects of land use and management in affected areas should be investigated with these activities in mind.

In conclusion, *Sulfurospirillum* species NP4 is a unique arsenate respiring microorganism from high arsenic, but otherwise uncontaminated groundwater at Northport, Maine. Based on correlations between population prevalence and groundwater chemistry, it appears that NP4 affects the speciation but not the overall concentration of arsenic. Members of the *Geobacter* genus may control arsenic release at the site.

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Chapter 8

TREATMENT OF HEAVY METALS IN STORMWATER RUNOFF USING WET POND AND WETLAND MESOCOSMS

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Abstract: Urban stormwater runoff is being recognized as a major source of pollutants to receiving waters and a number of recent investigations have evaluated stormwater runoff quality and best management practices to minimize pollutant input to receiving waters. Particle-bound contaminants are widespread in the urban environment causing impairment to urban water bodies such as streams and lakes. Non-point sources significantly contribute to this impairment, which occur in a variety of urban media. Trace elements associated with stormwater runoff are one group of contaminants identified in urban aquatic sediments (Van Metre and Mahler, 2003). In the aquatic environment, heavy metals are distributed among water-soluble species, colloids, suspended matter and sedimentary phases; deposition-mobilization processes play an important role in influencing the concentration of metals in water and sediments (Filgueiras et al., 2004). The primary objectives of this research are to investigate the particulate association (20 to 0.4 µm) of heavy metals in stormwater runoff generated from parking lots and rooftops, to assess the removal of particulate-bound and soluble heavy metals by wet pond and cattail wetland mesocosms, and to examine any seasonal variability. The secondary objective is to study the solid-phase fractionation of these heavy metals in wetland sediments by selective sequential extraction procedures for a qualitative assessment of heavy metal bioavailability. Early studies investigated the relative removal of heavy metals in stormwater in different particulate size classes using structural best management practices. The following heavy metals were investigated: Aluminum (Al), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Lead (Pb), and Zinc (Zn). Preliminary results for the sampling events conducted in April and June 2005 are presented in this paper.

Key words: urban stormwater runoff, heavy metals, retention ponds, constructed wetlands, suspended particulates.

1. INTRODUCTION

Urban stormwater discharge during wet-weather flows is a major contributor to the pollution of many receiving waters (Lee et al., 2004; Nordeidet et al., 2004). Impervious surfaces have long been implicated in the decline of watershed integrity in urban and urbanizing areas (Bannerman et al., 1993; Brattebo and Booth, 2003). The chemical composition of urban runoff is influenced by watershed characteristics such as land use, traffic volume, and percent impervious cover. Heavy metals are of particular interest in stormwater runoff due to their toxicity, ubiquitousness, and to the fact that they do not degrade in the environment. The sources of heavy metals in urban stormwater runoff are numerous and the release of metals into the environment is governed by several complex mechanisms (Davis et al., 2001). Generally speaking, heavy metals are dominated by discharges from impervious areas such as highways, road surfaces, and roofs (Nelson and Booth, 2002; Van Metre and Mahler, 2003; Chang et al., 2004; Nordeidet et al., 2004). These metals are either dissolved in the stormwater or are bound to particulates; the degree of binding is a function of pH, average pavement residence time and the nature and quantity of solids present (Sansalone and Buchberger, 1997). This partition between the solid and aqueous phase has a major effect on the occurrence, transport, fate, and biological effects of heavy metals in aquatic systems (Ran et al., 2000). A significant portion of the heavy metals in stormwater is associated with suspended particulate materials that vary from coarse (>75 μm) and fine particulates (<75 to 1 μm), to colloids (<1μm) (Sansalone, 2003).

Research investigations on stormwater runoff increasingly focus on evaluating stormwater runoff quality and the effectiveness of adopting stormwater best management practices (BMPs) to minimize pollutant input to receiving waters. Most pollutants in urban runoff, including heavy metals, are in particulate form, or, are bound to particulates and tend to settle out of the water column and accumulate in sediments (Campbell, 1994). Sedimentation is believed to be the primary means by which vegetated control facilities and other BMPs improve runoff quality (Mazer et al., 2001). One widely adopted method is to treat a large volume of stormwater in a detention pond, as this allows the pollutants to separate out prior to its controlled release to a local water course. This helps to reduce the heavy metal load associated with particulate matter (Yousef et al., 1990; Hares and Ward, 1999; Pontier et al., 2001). Constructed ponds used as stormwater treatment facilities aim at reducing the levels of suspended solids and heavy metals (Persson and Wittgren, 2003). The use of constructed wetlands to treat wastewater and other sources of water pollution is another valuable and appropriate technology to be used alone or in combination with other systems. The long-term efficiency and sustainability of these systems is critically dependent on an integrated understanding of their biological, chemical, and hydrological processes (Shutes, 2001). Heavy metals in stormwater can be removed by specially constructed wetlands and filtration systems; both natural and constructed wetlands have been used for the treatment of road runoff (Farm, 2002). Heavy metals such as Zn, Pb, and Cu showed a significant reduction in wetlands (Walker and Hurl, 2002). The differences in removal observed for different metals in wetlands could be due to various factors such as organic matter (Wood and Shelley, 1999) and redox potential (Walker and Hurl, 2002). In wetland BMPs, in addition to sedimentation, macrophytes could provide a major removal mechanism by providing sites for metal precipitation and/or sedimentation. Above-ground plant parts (stems, stolons, leaves) are thought to induce sedimentation of particulates and their sorbed pollutants; plant roots stabilize sediment deposits and prevent sediment re-suspension (Mazer et al., 2001). Emergent plants such as the common reed (Phragmites australis) and reed mace (Typha latifolia) have been shown to effectively remove particulate and soluble heavy metals in wetland BMPs (Ellis et al., 1994; Mungur et al., 1995; Shutes et al., 1999; Shutes, 2001; Sriyaraj and Shutes, 2001).

Relatively little work has been done on the use of wetland BMPs for the treatment of heavy metals in stormwater runoff and the solid-speciation study of metals in wetland BMPs is lacking (Lim et al., 2001). Since metals are primarily removed due to suspended solids removal in stormwater BMPs, the geochemical partitioning of metals should be an important consideration for BMP selection (Lee et al., 2004). Information on the particulate association of heavy metals in stormwater is a fundamental requirement prior to using wetland and wet pond BMPs for treatability studies of heavy metals in stormwater runoff. Previous studies on the use of these structural BMPs for the treatment of heavy metals in stormwater have not focused on either the lower or upper practical size limit for the removal of particulate-bound heavy metals, and this investigation will address this growing research need. Sedimentation has been recognized as the principal process in the removal of heavy metals from stormwater in pond BMPs (Bavor et al., 2001), and in natural as well as constructed wetlands (Walker and Hurl, 2001). However, due to the presence of extensive vegetation, constructed wetlands may be more effective in removing both coarse and fine particulate-bound pollutants, possibly due to phytological uptake, sequestration processes, and vegetation-aided precipitation of coarse and fine suspended solids (Bavor et al., 2001). Heavy metals accumulated in sediments have the potential to produce toxic effects in benthic invertebrates and aquatic microorganisms, both in wetlands (Wood and Shelley, 1999) as well as ponds (Karouna-Renier and Sparling, 2001). In order to evaluate the possible toxicity or risk of environmental pollution of heavy metals present in sediments, it is imperative to assess the types of association between heavy metals and the sediment solid phase. The geochemical forms of particulate heavy metals allow a qualitative assessment of metal lability/stability, metal bioavailability and toxicity, and ultimately the potential for environmental degradation of receiving water bodies; these properties are strongly related to the type of metal-particle binding as well as to the chemical nature of the binding particles (Garnaud et al., 1999). This is precisely the reason why chemical speciation of heavy metals in sediments by selective extraction procedures is important to evaluate their mobility and the potential for bioavailability (Gumgum and Ozturk, 2001; Jong and Parry, 2004). For the purposes of this investigation, sediments are defined as those mineral and organic materials situated beneath the aqueous layer of the cattail wetland mesocosm. The sequential chemical fractionation procedure recommended by the Standards, Measurements and Testing Programme (SM&T) (formerly known as the Bureau Commun de Reference, BCR) of the European Commission will be used in this project and will yield four "operationally" defined species: (i) Water soluble, exchangeable, and carbonate bound; (2) Fe-Mn oxide bound; (3) organic matter and sulfide bound; and, (4) residual (Davidson et al., 1994; Rauret et al., 1999).

1.1 Objectives

The proposed investigation has the following objectives:

(1) Characterize the particulate association of select heavy metals (Cu, Zn, Pb, Cr, Fe, Al, and Mn) in stormwater runoff, between 20 and 0.4 um, generated from parking lots and roof-runoff;
(2) Evaluate the effects of two types of structural BMPs (cattail wetland and wet pond) on the removal of particulate-bound and soluble heavy metals from stormwater;
(3) Examine if the distribution of heavy metals in stormwater particulates exhibits a seasonal variability, and determine the effects of BMP type, water column chemistry as well as season on the removal of dissolved and particulate heavy metals in BMP mesocosms.
(4) Assess the chemical associations between heavy metals and wetland sediments by selective sequential chemical fractionation techniques

[BCR procedure, (Rauret et al., 1999)] and thereby predict heavy metal mobility and toxicity.

2. STUDY SITE AND EXPERIMENTAL DESIGN

The two environmental systems tested in this project are wet pond and cattail wetland BMP mesocosms for the treatment of particulate–associated heavy metals in stormwater. To perform this investigation, urban stormwater runoff generated from a parking lot and rooftop of a county college campus (9.75 acres) next to the U.S. EPA's Urban Watershed Research Facility (UWRF) in Edison, NJ, (Figure 1) were sampled and analyzed prior to, and after passing through two circular BMP mesocosms, designed and constructed at UWRF, Edison, NJ. The two mesocosms were of the same size and with two different BMP treatments: (i) constructed wetland, vegetated with cattails, and (ii) wet, retention pond.

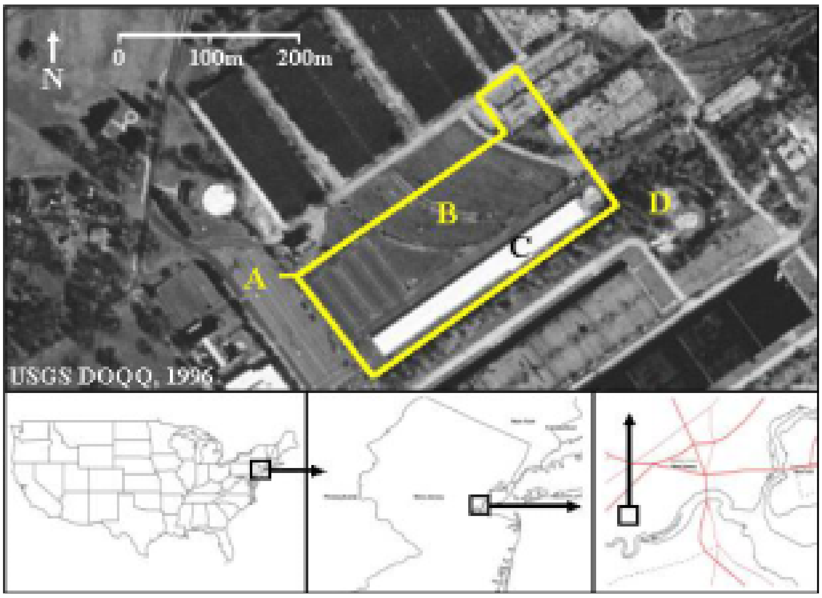

Figure 1. Map of study area, Edison, NJ. A – drainage area; B – location of the outfall

Stormwater runoff from the college campus was collected from an outfall near the UWRF and stored onsite. The stormwater was then routed to a smaller supply tank and then distributed to the two mesocosms by a "simulated" event, which is best described as follows: In a "simulated" event, adequate volume of gravity-fed stormwater was routed to each of the two mesocosms. The detention time of a "simulated" event was 24 h conforming to general recommended detention time guidelines for stormwater BMPs. In order to assess seasonal variability, this investigation comprises the study of eight separate storm events (two rain events per season – spring, summer, fall, and winter) out of which three stormwater sampling events (two events in spring and one event in summer 2005) have been completed to date. Wetland sediment was sampled prior to the stormwater sampling events and the results are awaited. Between storm event "simulations", the mesocosms were operated under semi-continuous flow-through, regulated by a float valve connected to a tap water supply line (Nietch, 2002). Yellow Springs Instruments (YSI) data sondes were installed in the mesocosms and the control tank to monitor water quality parameters (pH, dissolved oxygen (DO), temperature, conductivity and oxidation-reduction potential (ORP) on a 12-min time step before, during, and after experimental events to assess the temporal variation and the dynamics of mesocosm-to-mesocosm water chemistry.

Stormwater from the outfall, storage tank, supply tank, and stormwater effluents from the retention pond, cattail wetland mesocosms, and one control tank were sampled using various techniques (flow-weighted, time-weighted, and grab) and analyzed during every storm sampling event. The addition of a control tank will help understand changes in stormwater chemistry in the mesocosms with time and also the relative differences in the heavy metals removal in the pond and wetland BMPs. In order to understand the particulate association of heavy metals, the samples were sequentially filtered through five different pore sizes - 20 μm, 10, 5, 1, and 0.4 μm using Millipore polycarbonate membrane filters. The unfiltered and the filtered samples were analyzed for major physico-chemical parameters: pH, ORP, total suspended solids (TSS), and total organic carbon, (TOC). The unfiltered samples were additionally analyzed for particle size distribution (PSD). Cations (Na, K, Ca, Mg) were analyzed in unfiltered samples and in samples filtered through 0.4 μm, while chloride and sulfate were determined in samples filtered through 0.4 μm. The seven heavy metals - Cu, Zn, Pb, Cr, Fe, Al, and Mn were analyzed in unfiltered and filtered stormwater samples and effluents from the two mesocosms and the control tank. Results from these analyses will help in evaluating the relative changes in particulate heavy metal distribution that occur in stormwater stored and routed through the wet pond and cattail mesocosms. Cleaning of samplers, sample containers, sampling, subsampling, and filtration of stormwater samples were done in accordance with U.S. EPA recommended procedures and UWRF standard operating procedures (SOP) developed for stormwater analysis. All the selected analytes in stormwater were determined using Standard Methods (APHA, 1998) and U.S. EPA-approved/recommended techniques (U.S. EPA, 1983; 1985).

3. PRELIMINARY RESULTS AND DISCUSSION

3.1 Characterization of parking lot and roof runoff

The preliminary characterization of stormwater runoff from two sampling events conducted in spring 2005 showed that the pH of unfiltered stormwater was neutral (7.41) in the outfall (Table 1). With regard to the mesocosms, pH was a little higher (7.58) in retention pond effluent when compared to wetland (7.22). However, the redox potentials of the two systems were quite similar as seen from the unfiltered effluents (635.5 and 616.2 mV, respectively) and did not vary considerably from the outfall (672.1 mV). Organic carbon in runoff was mostly dissolved (TOC 18.67 and DOC 18.1 mg/l).

Table 1. Physicochemical characteristics of urban stormwater runoff

Sample	**pH**	**Temp °C**	**ORP (mV)**	**TOC (mg/l)**	**DOC (mg/l)**	**SO42- (mg/l)**	**Cl- (mg/l)**	**Na (mg/l)**	**K (mg/l)**	**Mg (mg/l)**	**Ca (mg/l)**
Outfall	7.41	22.6	672.1	25.4	22.1	30.5	335.3	152.7	3.47	7.26	48.1
Storage	7.19	20.1	646.7	18.4	17.5	22.6	232.6	103.8	2.42	5.29	34.9
Supply	7.47	20.5	600.7	18.4	16.9	22.8	229.3	105.8	2.47	5.33	35.3
Ret. (wet) pond	7.58	19.8	635.5	9.95	9.65	18.2	89.2	52.4	2.28	6.15	26.6
Wetland	7.22	20.6	616.2	12.6	12.3	21.7	141.4	81.1	3.38	7.76	34.9
Control	7.39	21.3	583.8	15.7	15.3	22.2	226.2	108.3	2.44	5.41	36.2

Results presented for pH, Temp., ORP, TOC, DOC, and anions are mean values for $n = 3$

Results presented for cations are mean values for $n = 6$ (unfiltered $n = 3$; filtered $n = 3$)

3.2 Heavy metals partitioning in urban stormwater runoff

Heavy metals concentration in parking lot and roof runoff increased between the two events conducted in April and June, 2005, with a concomitant increase in TSS (Table 2), and this was more pronounced for Al (8-fold increase), Fe (7-fold increase) and Zn (6-fold increase) respectively (Figure 2). Most of the metals studied (Cu, Zn, Fe, Mn, and Al) were routinely detected in the runoff; Pb and Cr were detected sporadically, and especially in the second event. It was also seen from these events that both Al and Fe are particulate-bound and Mn remained dissolved (< 0.4 μm) in stormwater. Also, Cu and Zn were mostly soluble during the first event (71.9 % and 66.4 % soluble, respectively). However, during the second event, Cu and Zn were bound to particulates (83.7% and 82.6 % respectively) predominantly (Figure 3) compared to their soluble species. This was consistent with the observation of a 6-fold increase in TSS in the runoff during the second sampling event, i.e. it increased from 24.2 mg/l to 152.0 mg/l. The increase in TSS during June could be attributed to the rain event itself in that it was characterized by thunderstorms and heavy precipitation following a prolonged dry spell that resulted in a higher washing off of heavy metals and suspended solids in runoff. There was a wide variation in Zinc and TSS concentrations between outfall and the supply tank from where it was routed to the mesocosms. The relationships between the quantitative values for the various metals were investigated. Manganese exhibited reasonable associations with Cu ($r^2 = 0.665$, $P < 0.05$) and Zn ($r^2 = 0.792$, $P = 0.0175$) during the first event; Cu and Fe were strongly correlated ($r^2 = 0.955$, $P < 0.001$) during the second event (Figures 4, 5, 6). However, no significant relation was observed between TSS and heavy metals during the two events. Additional sampling and monitoring events will provide a better insight into these heavy metal associations in stormwater runoff.

Table 2. TSS and heavy metals concentrations in parking lot and roof runoff

Heavy Metal	**Conc. (mg/l) - April'05**	**Conc. (mg/l) - June'05**
Al_{tot}	0.405 (0.597)	3.06
Cr	NA	0.0115 (0.522)
Cu_{tot}	0.0157 (0.205)	0.041 (0.361)
$Cu_{0.4}$	0.0110 (0.241)	0.0063 (0.158)
Fe_{tot}	1.19 (0.375)	7.92 (0.366)
$Fe_{0.4}$	0.243 (0.021)	0.774 (0.022)
Mn_{tot}	0.311 (0.315)	0.739 (0.036)
$Mn_{0.4}$	0.317 (0.145)	0.533 (0.163)

Heavy Metal	**Conc. (mg/l) - April'05**	**Conc. (mg/l) - June'05**
Pb_{tot}	0.008*	0.0307 (0.391)
Zn_{tot}	0.043 (0.507)	0.258 (0.084)
$Zn_{0.4}$	0.030 (0.696)	0.044 (0.279)
TSS	24.2 (0.92)	152.0 (0.398)

Results presented are mean values for *n* = 9 (outfall, storage, and supply tanks); R.S.D values are given in parenthesis

$_{tot}$ – unfiltered sample

$_{0.4}$ – sample filtered through 0.4 µm membrane filter

* possible analytical error

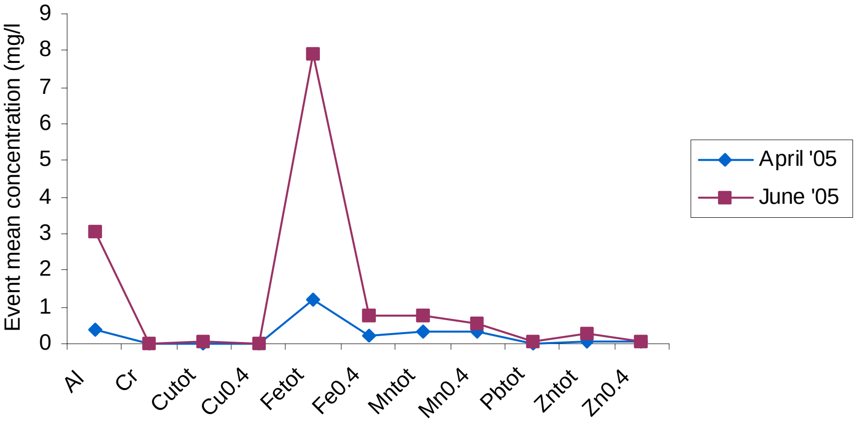

Figure 2. Heavy metal concentrations in stormwater runoff from roof and parking lot

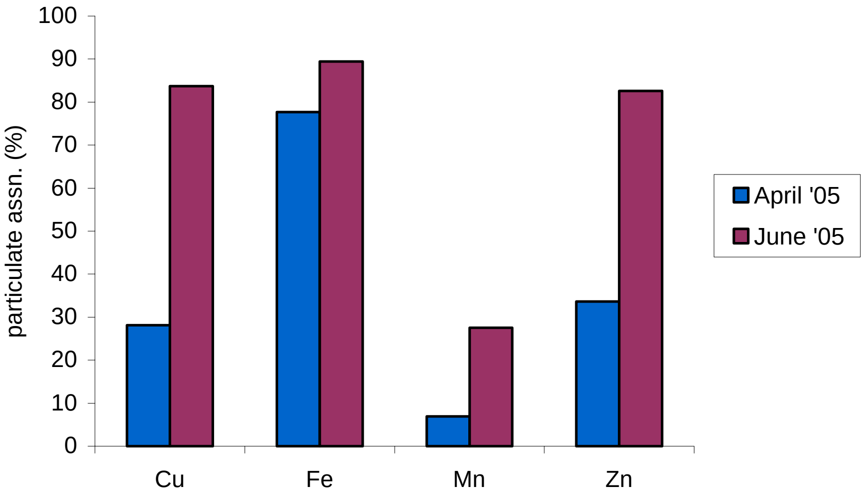

Figure 3. Particulate associations of heavy metals in urban stormwater runoff

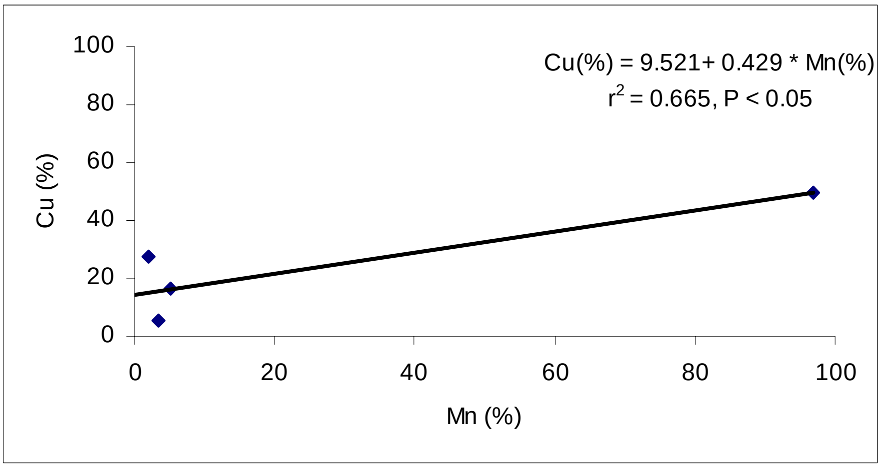

Figure 4. Cu vs. Mn in urban stormwater runoff

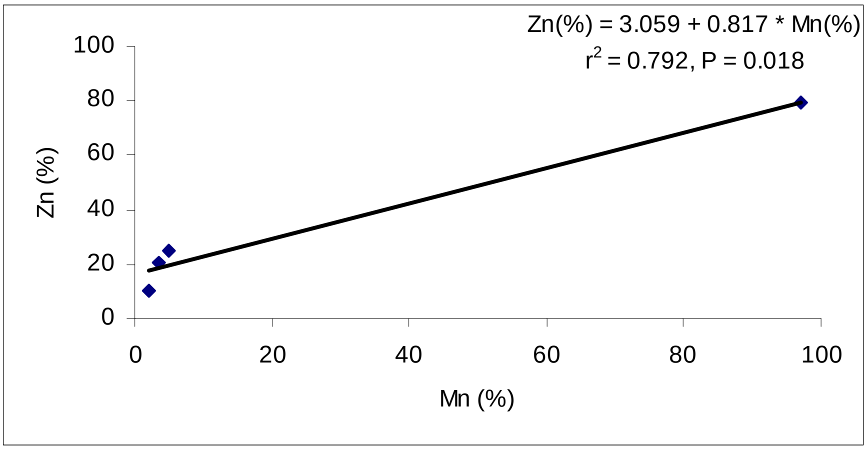

Figure 5. Zn vs. Mn in urban stormwater runoff

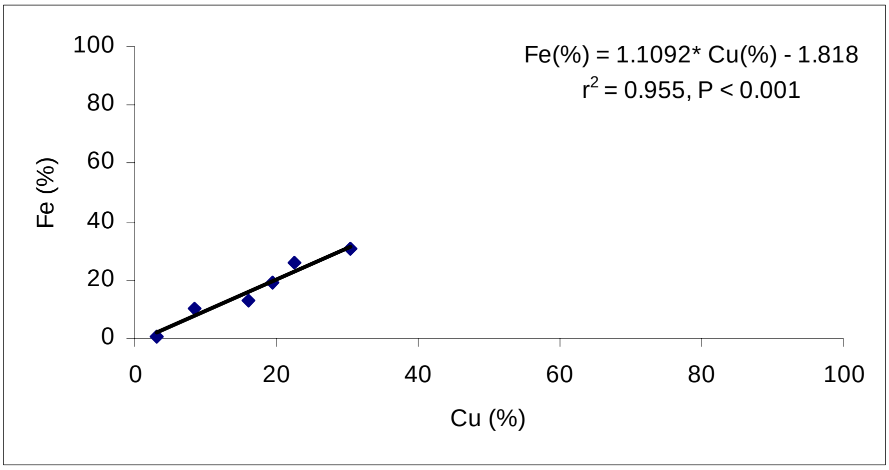

Figure 6. Fe vs. Cu in urban stormwater runoff

3.3 Changes in retention (wet) pond and wetland mesocosm chemistry during storm events

The various physico-chemical parameters measured *in situ* in the mesocosms and the control tank during the two spring sampling events are shown in Table 3. Changes in mesocosm chemistry observed using the YSI sondes in the two mesocosms (approx. 72 h) and in the control tank (approx. 48 h) are shown for the April sampling event in Figure 7. The temperature increased between two sampling events and the wetland temperature was lower than the retention pond during both events. Wetland pH did not vary much between the events compared to the retention pond where the pH decreased by more than 1 unit in the second event. The lower values for these various parameters in the wetland could be attributed to several factors, the most important of these being the dead biomass resulting in a shallow water depth, and growing vegetation. The diurnal variations of these parameters in the two BMPs are shown for one sampling event (April ’05) in Figures 8, 9, and 10. It is expected that results from the remaining sampling and monitoring events of these systems would lead to a better understanding of the chemistry in these BMPs during a storm event.

Table 3. YSI monitoring data in retention pond and wetland mesocosms

	April’05			**June’05**		
	Ret.pond	**wetland**	**control**	**Ret.pond**	**wetland**	**control**
Temp °C	14.7	12.4	14.4	26.4	23.3	25.7
pH	8.61	6.83	7.31	7.37	6.73	7.01
DO (mg/l)	0.12	5.39	8.16	3.78	4.28	3.93
Cond. (mS/cm)	0.281	0.431	0.613	0.511	0.662	0.970
ORP (mV)	329.2	531.6	243.3	341.2	153.5	367.8

Results presented are mean values of 72 h monitoring data.

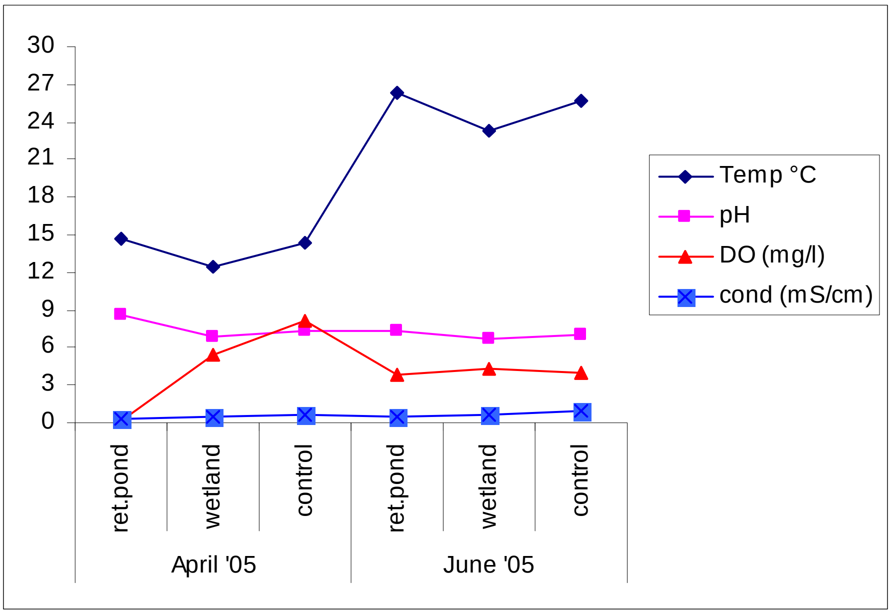

Figure 7. YSI monitoring in retention pond and wetland mesocosms

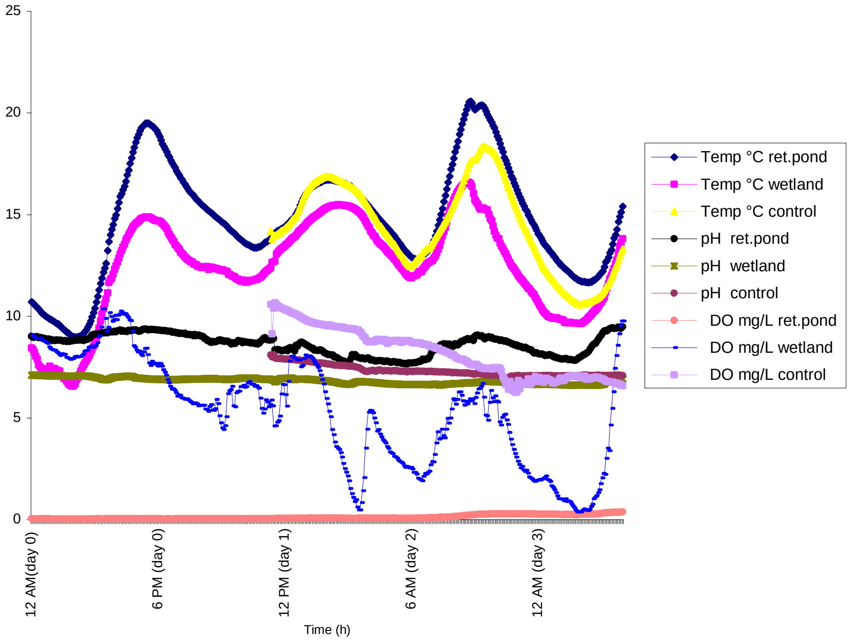

Figure 8. Variation in Temperature, pH, and DO in retention pond and wetland mesocosms

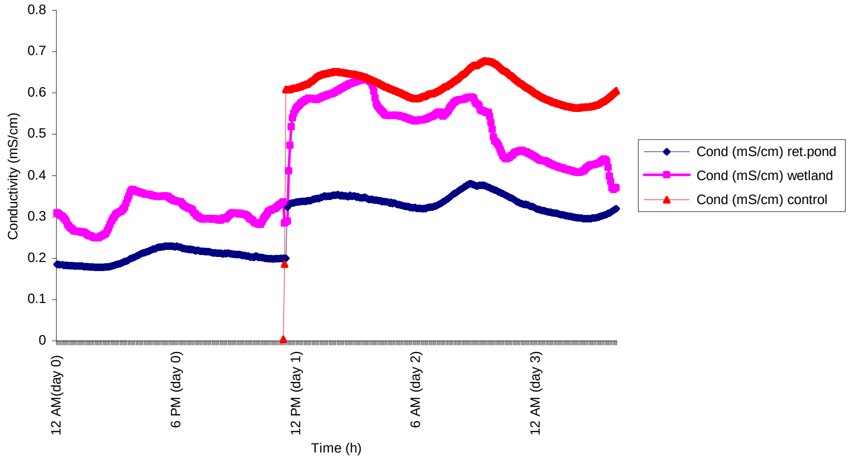

Figure 9. Variation in conductivity in retention pond and wetland mesocosms

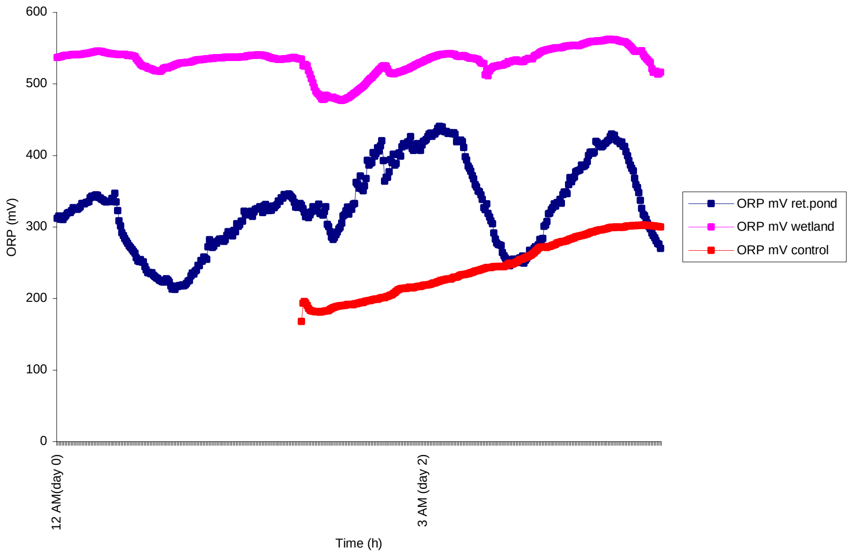

Figure 10. Variation in ORP in retention pond and wetland mesocosms

3.4 Heavy metals removal from stormwater runoff in retention (wet) pond and wetland BMP mesocosms

Preliminary results showed that Fe and Al were primarily particulate bound (> 20 µm); Mn was mostly in the soluble fraction (<0.4 µm); and Cu and Zn were primarily associated with fine particulates (1 – 10 µm) as well as in the dissolved fraction (<0.4 µm) in stormwater runoff. TSS increased during the June event and a size-partitioning study showed that there was a significant increase in fine particles <20 µm in runoff compared to the first event (Figure 11). The association of heavy metals with fine particulates (10 – 5 µm increased in the second event (Figure 12). This clearly showed that the nature of the storm event, and the antecedent conditions, both of which are highly variable, largely influence the solids and heavy metals concentrations and the particulate associations of the latter in urban stormwater runoff. However, no discerning relationship between heavy metals and TSS loads could be determined from studying only two events that were highly variable.

The concentrations of heavy metals in the influent runoff and the composite effluents from the retention pond and wetland are shown in Figure 13. The effects of the two BMP mesocosms on heavy metals removal from urban stormwater runoff are shown in Table 4. Paired t-tests showed that there was no significant in Cu loads in stormwater runoff between the two events. The attenuation of Cu concentrations was significant in both retention pond ($P = 0.013$) and wetland ($P = 0.047$) during the first event. In the case of Fe, the difference in concentration in runoff varied significantly between events ($P < 0.05$) and reduction in Fe loads was significant for both mesocosms ($P < 0.05$) in the second event. Unfortunately, there were some errors in the ICP measurement of Fe during the first event leading to a few questionable results and as a result, parametric tests could not be verified for the April event. Al concentration varied significantly between April and June ($P < 0.05$) and was attenuated considerably ($P = 0.027$) on passing through the retention pond. The 24-h detention appeared to effectively result in a 100% removal of Al, which was all particulate-bound, in the wetland due to sedimentation; Al was not detected in the wetland effluent during these events. As for Zn and Mn, no significant variation in runoff concentrations was seen between the two events was observed. While individual BMPs were seen to be effective in removing heavy metals from runoff, the two events were insufficient to suggest the effect of different BMP treatment; there were no significant statistical observations to verify if the two treatments differed significantly from each other in removing heavy metals from stormwater runoff. It is hoped that a much clearer insight on these could be gained with additional sampling events, which are underway.

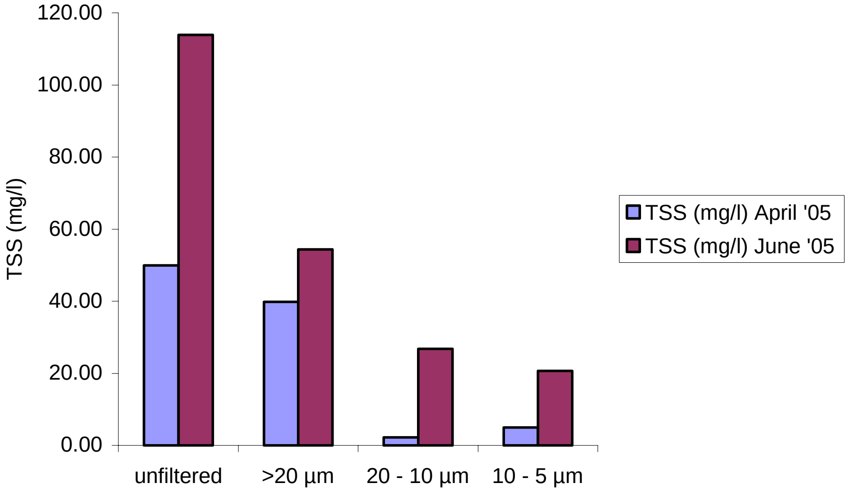

Figure 11. Variation in TSS in stormwater runoff

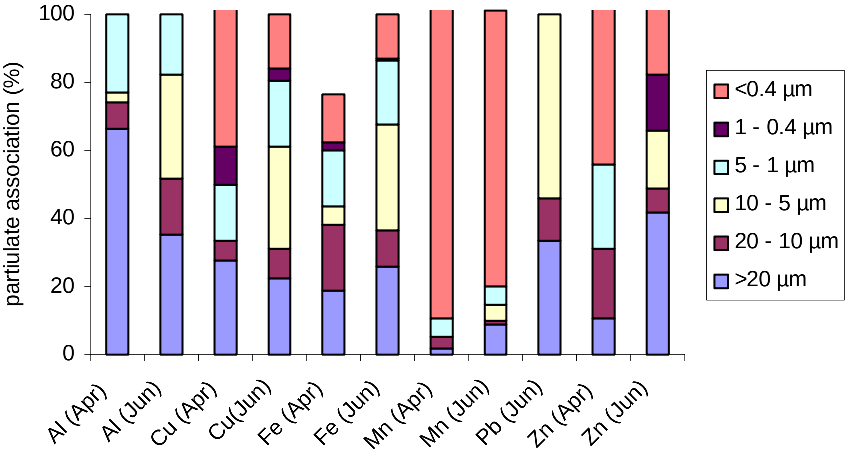

Figure 12. Size partitioning of heavy metals in urban stormwater runoff

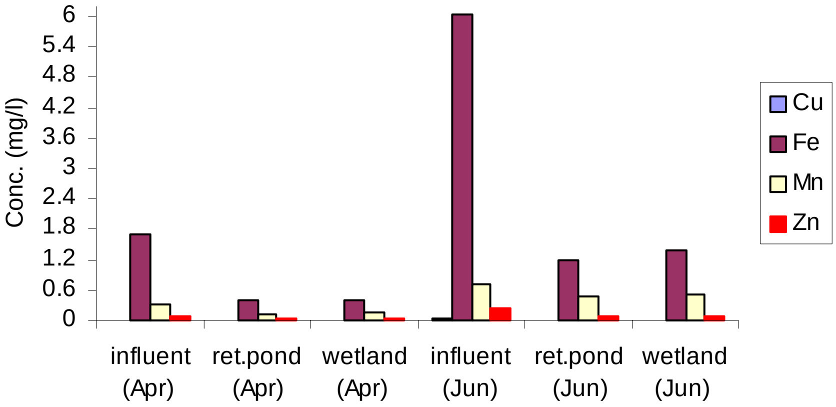

Figure 13. Concentrations of heavy metals in the influent (runoff) and mesocosm effluents

Table 4. Removal of heavy metals in stormwater runoff in retention pond and wetland mesocosms

	Influent (mg/l)	**Retention Pond**			**Cattail wetland**		
		Effluent conc. (mg/l)	**Redn in conc. (mg/l) in**	**Redn. (%)**	**Effluent conc. (mg/l)**	**Redn in conc. (mg/l) in**	**Redn. (%)**
April'05							
Al	0.684	0.113	0.571	83.5	NA	0.684	100.0
Cu	0.018	0.007	0.011	61.1	0.006	0.012	66.7
Fe	1.693	0.386	1.31	77.2	0.378	1.32	77.7
Mn	0.298	0.107	0.191	64.1	0.148	0.15	50.3
Zn	0.068	0.050	0.018	26.5	0.054	0.014	20.6
June'05							
Al	2.18	0.254	1.93	88.3	NA	2.18	100.0
Cu	0.031	0.006	0.025	80.6	0.005	0.026	83.9
Fe	6.06	1.38	4.68	77.2	1.08	4.98	82.2
Mn	0.726	0.469	0.257	35.4	0.526	0.200	27.5
Pb	0.024	NA	0.024	100.0	NA	0.024	100.0
Zn	0.233	0.073	0.16	68.7	0.069	0.164	70.4

Results presented are mean values for $n = 3$.

4. CONCLUSION

Structural BMPs such as retention ponds and cattail wetlands are effective in attenuating heavy metal loads in urban stormwater runoff and result in improving the quality of receiving waters. The overall efficiency and effectiveness of these systems largely depend on the proper design, monitoring practices, and maintenance of these systems. By conducting this heavy metals research under controlled meso-scales, these treatment methods can be better evaluated, and the various factors causing variability in these systems can be better understood. Heavy metal concentrations in stormwater and their associations with fine particulates (20 – 0.4 µm) are largely influenced by the nature of the storm event and antecedent conditions. Preliminary results from the mesocosm investigation conducted at UWRF, Edison, NJ clearly showed that Fe and Al are particulate-bound (> 20 µm), Mn remains soluble (<0.4 µm), and Cu and Zn tend to associate with fine particulates (10 – 1 µm) and also remain dissolved in urban stormwater runoff. The spring sampling events showed that wetland and cattail BMP mesocosms are effective in attenuating Cu, Zn, Al and Fe in runoff. A greater understanding of the seasonal variability in heavy metals concentration in urban stormwater runoff is expected from the remaining sampling events. From the entire investigation, notable differences are expected between the two BMP treatment types in the removal of heavy metals from urban stormwater runoff generated from roof and parking lot.

DISCLAIMER

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Chapter 9

COPPER, CHROMIUM AND ARSENIC IN SOIL AND PLANTS NEAR COATED AND UNCOATED CCA WOOD

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Abstract: For many years, Chromated Copper Arsenate (CCA) was widely applied as a wood preservative, and though its use for most residential uses has been phased out, concerns about CCA leaching into soil from existing structures remain. In this study, we determined the effects of coating CCA wood on reducing such leaching. Ten boxes were constructed, six of which were coated with opaque film forming (FF) or penetrating finishes (PF), filled with soil, and weathered for two years. The soil was periodically sampled up to two years, and then romaine lettuce, arugula, basil and chives were grown under greenhouse conditions in these boxes. After two years, average amounts of arsenic (As) in the soil 2 cm from the CCA wood was 29 mg/kg, dry weight, 27 from wood coated with PF finishes and six in those coated with FF finishes. Soil As in all samples 6 cm from the wood were near the background value of 3.4. The average amount of As in arugula grown 2 cm from the edge of the CCA wood was 60 mg/kg, dry weight, 61 in wood coated with PF finishes and 24 in those coated with FF finishes. Similarly, in chives the amounts were 75 in CCA, 75 in PF, 12 in FF, in lettuce they were 5 in CCA, 5 in PF, in 1.4 FF and in basil they were 6 CCA, 10 PF, 3 FF. The amounts of As in plants grown in the control boxes were all <1. Compared to uncoated CCA wood, there was no reduction in As in plants grown along the edge of CCA wood coated with penetrating finishes, while the reduction in plant As ranged from 50-84% in plants grown next to the opaque finished wood. The reduction in arsenic in samples grown 6 cm from the wood compared to 2 cm from the wood ranged from 55-84%. The amounts of arsenic in the arugula and chives exceed the British limit for plant As of 1 mg/kg (fresh weight). As a result, gardeners should avoid growing certain vegetables in soils near CCA wood.

Key words: Arsenic, CCA wood, plant uptake, soil, coating

1. INTRODUCTION

For many years, chromated copper arsenate (CCA) was the predominant formulation used in the pressure-treatment process to preserve wood from decay and insect damage. A number of investigations, however, have shown that varying amounts of CCA can be dispersed from the wood by leaching, erosion, weathering, decay and physical dislodgement (Belluck et. a*l*. 2003; Lebow 1996; Stilwell and Gorny 1997; Stilwell et *al*. 2003; Lebow et *al*. 2000; Stilwell and Graetz 2001; Weis and Weis 2002; Townsend et *al*. 2003; Zagury et *al*. 2003). The potential environmental problems associated with this dispersal resulted in a phase out of its use in the US for most residential applications effective January 2004 (Fed Reg. 2002). However, CCA wood produced prior to the phase out is expected to remain in service for many years (Solo-Gabriele and Townsend 1999), and its use is still permitted for many applications outside the residential setting, such as, utility poles and docks.

One major application for this wood was in situations involving soil contact, including raised-bed gardens, fence posts, and utility poles. Rahman et al. (2004) has shown that Cu, Cr, and As from CCA wood used to construct raised garden beds diffuse into the soil. Elevated levels of these elements in soils near CCA wood stakes and utility poles have also been reported (Zagury et *al*. 2003; Lebow et *al.* 2004). Recent reports have also shown that As levels in plants increased when grown in soils near CCA wood (Shiralipour 2004; Rahman et al. 2004; Cao and Ma 2004).

A promising treatment for minimizing CCA dispersal is to coat the wood with a paint, stain, sealer or varnish, thus forming a barrier between the wood and the environment. These finishes may contain water repellents to prevent water penetration or may provide a physical barrier by way of film formation. Much of the information on coatings for CCA wood focuses on the durability of the finish to withstand weathering in a given application (Williams 1999). A limited number of studies have been conducted to assess the ability of finishes to reduce metal dispersal (Kizer 1987; Reidel 1991; Cooper et *al*. 1997; Stilwell 1998; Lebow et *al*. 2002; Lebow et *al*. 2003, US EPA 2005). These studies have shown that finishes can reduce the dispersal of the preservative by 50-90%. Film-forming finishes tend to be the most effective barriers but they are not preferred in situations where they can chip and flake. A recent study by the US EPA on finishes applied to CCA wood found that, after one year of weathering, certain penetrating finishes were nearly as effective as the film-forming finishes in reducing surface available As (US EPA 2005).

In this study, we tested the use of coatings to prevent preservative dispersal from CCA wood in a soil environment, by coating boxes made from this wood with various finishes, both film-forming (FF) and penetrating finishes (PF), filling them with soil, and weathering them for two years. During this time, the soil was sampled periodically and after two years, plant uptake of arsenic was determined by growing romaine lettuce, arugula, basil and chives in these boxes under greenhouse conditions. Preliminary results on the first phase of this study have been reported earlier (Stilwell et *al.* 2005).

2. EXPERIMENTAL

A total of 10 boxes (27x28x14 cm) were constructed, eight using 3x15 cm CCA boards, one using an alternative preservative containing copper and quaternary ammonia (ACQ), and one control using untreated pine. The bottom of each box was constructed using 1 cm thick untreated plywood, with nine drainage holes (0.5 cm dia.). The CCA containing boxes were constructed using 2.5 m x 3 cm x 15 cm pine boards, purchased at a lumber yard, nominally treated with 6.4 kg/m^3 of CCA preservative by Universal Forest Products. The boards originated from three sets, and though differences in the treatment level in the wood between sets from the nominal amounts (mg/kg) of 1840 (Cu), 3120 (Cr) and 2800 (As) were observed, there was no correlation between bulk levels in the wood compared to the amounts leached into the soil (Stilwell et al., 2005). The ACQ wood contained 3073±58 (Cu), <20 (Cr), and <20 (As) (mg/kg), while the control wood and the plywood contained <20 mg/kg Cu, Cr, and As. All of the boards appeared new and were stored indoors until use.

Each paint or stain was applied in two coats. As shown in Table 1, the coatings consisted of oil-based, semi-transparent stains (two brands, one with and the other without alkyd resin ingredients), water-based coatings (two brands, one with a penetrating alkyd/acrylic formulation), an acrylic solid color deck stain, and a polyurethane enamel. Two of the boxes made from CCA wood were left uncoated, as were the control box and the box made using the ACQ preserved wood.

Table 1. Description of Coatings

Coating/Box #	Coating*	Base	Color	Cover
1	None			
2	Sealant	Water	Clear	Clear
3	Stain	Oil	Grey	Semi
4	Sealant	Oil	Clear	Clear
5	Stain	Oil	Gray	Semi
6	Solid Stain	Water	White	Opaque
7	Solid Enamel	Oil	Grey	Opaque

Coating/Box #	Coating*	Base	Color	Cover
8	None			
9	ACQ wood			
10	Untreated Pine			

** Brand and Code: Coating 2, Behr, 300 with alkyd and acrylics; 3, Behr 1-765 deck and siding stain; 4, Thompson's; 5 Olympic, 53178 deck stain with alkyds; 6, Olympic, 53097 acrylic deck stain; 7, Sapolin, 40-9309 polyurethane floor and deck enamel.*

The boxes were filled with a mixture of 90% soil (sandy loam) and 10% compost (by volume) and placed out to weather. The soil properties and sampling procedures are detailed in Stilwell et al. (2005). Briefly, after 107 days of weathering, the soil was sampled using a 2.2 cm diameter soil corer, at 0-3 cm from the wood to the box bottom, taking one sample from each of the four sides, 5 cm from the left corner. The procedure was repeated after 365, 547 and 731 days of weathering, except that the samples were taken 22 (day 365), 9 (day 547) and 14 cm (day 731) from the left corner of each side. Also on day 731, a soil sample was taken at the center of each of the four sides, 6 cm from the edge and one was taken at the center of each box. Inverted plastic test tubes were inserted to fill the void caused by the soil removal after sampling. Natural rainfall supplied most of the water, but in times of drought, the soil in the boxes was watered at a rate of about 2-3 cm per week (1 cm per application).

Elemental analysis of the soil and wood composite samples was determined, following nitric acid digestion, using a Thermo Jarrell Ash ICP-AES Atom Scan 16 atomic spectrometer (Stilwell and Graetz 2001). In samples containing low arsenic (<0.1 mg/l in solution) the more sensitive technique of graphite furnace atomic absorption (GFAA) was employed using a Perkin Elmer 5100 instrument.

After two years of weathering, arugula (*Eruca sativa, rocket)*, romaine lettuce (*Lactuca sativa*), sweet basil (*Ocimum basilicum)*, and chives (*allium schoenoprasum*) were grown in these boxes in a greenhouse. The seeds were germinated in 1.2x1.2x2.6 plugs in a starter tray filled with growth media. After germination and sprouting (14 days lettuce and arugula, 21 days chives and basil) the seedlings were transplanted into the box soil. The arugula seedlings were planted, equally spaced, 2 cm from the box edge, four along one side and three along an adjacent side. Two seedlings were also planted, equally spaced, 8 cm from the edge of the two sides and one seedling was placed in the center of box. The lettuce seedlings were planted similarly along the remaining two sides, three seedlings 2 cm from the edge per side, and one seedling on each side, 8 cm from the edge. The chives and basil were planted in the corners of each box and with each type on opposite sides. Water was supplied as needed, typically 1 liter per box every other day. On seven occasions fertilizer was added to the water at a rate of 30 mg/l

N/P/K. Over the growing period approximately 300 mg of P was added to the approximately 10 kg of soil.

The entire plants were harvested after 21 days of growth for the lettuce and arugula, and after 28 days for the chives and basil, by cutting them off within 1 cm of the soil line. The arugula plants harvested along each box edge and 8 cm from each box edge were composited, forming four composites and one center plant sample per box. The lettuce plants along each edge were similarly composited, along with the two lettuce plants grown 8 cm from the edges, forming three composites per box. The basil and chives harvested from the box corners were combined, forming one composite of basil and one of chives per box. All the plants were rinsed with distilled water, dried at 80^{o} C for 10 hours in paper bags, crushed and transferred to polypropylene containers. For percent moisture determination, the lettuce and arugula plants along one edge of each box were weighed prior to compositing, and three composites of the chives and basil were weighed right after harvest. The percent moisture in the plants were, arugula, 91.4 ± 0.3 (n=10), lettuce, 92.9±0.5 (n=10), basil, 90.1±0.3 (n=3), and chives 89.8±0.4 (n=3). The percent moisture in these plants were in close agreement to those reported by the USDA (2005), arugula 91.7%, lettuce 94.6%, basil 91.0%, and chives 90.6%.

The plant tissue was analyzed by weighing 0.2-0.4 g of dried plant material into 50 ml plastic containers, adding 5 ml of conc. nitric acid, and digesting in a hot block (Digi-Prep Ms, SCP Science, Champlain NY) at 115^{o} C for one hour. After adding distilled deionized water to the 50 ml mark, the plant digests were analyzed for copper, chromium, and arsenic, as described above.

Statistical analysis was carried out by using the analysis of variance (ANOVA) utility in Microsoft Excel 2003.

3. RESULTS AND DISCUSSION

3.1 Arsenic Leached

The average soil arsenic levels next to the wood over time for different treatments are given in Figures 1 and 2. The results from the uncoated CCA boxes (Box 1 and 8) were combined (n=8) in computing the averages for each weathering time period. All other averages were an individual box (n=4). Arsenic levels in the soil samples from the uncoated CCA boxes increased with time of weathering (Figure 1). Furthermore, the average arsenic level in soil samples taken from the uncoated boxes, after 365 days of weathering, exceeded the State of Connecticut limit of 10 mg/kg (State of

CT 1996). The results in Figure 2 show that after 731 days of weathering, As in soil from the uncoated CCA boxes was not significantly different (p=0.43) from the As levels in soils from boxes coated with the penetrating finishes (coatings 2-5). The lowest soil As levels were from boxes coated with opaque finishes. These levels, 6.8±0.6 (coating 6) and 4.6±1.5 (coating 7) mg/kg As, though elevated with respect to the As in soils from the control box (3.0 ± 0.2 mg/kg) maintained a level below the 10 mg/kg State of Connecticut limit throughout the two-year period. The amounts of As in the soil next to the wood after two years of weathering, 29±7 mg/kg, was within the range of 12-56 mg/kg As found in soil next to CCA wood in a survey of six raised garden beds by Rahman et al. (2004).

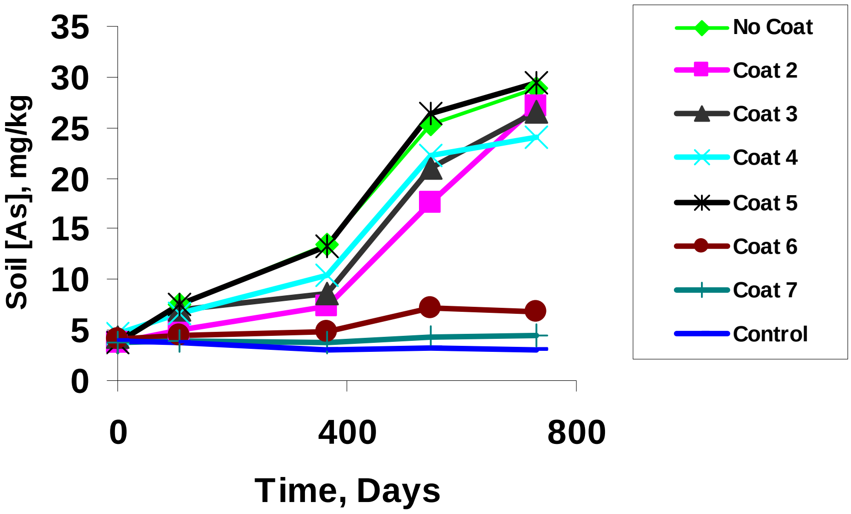

Figure 1. Comparison of soil arsenic versus time for different wood coatings (see Table 1)

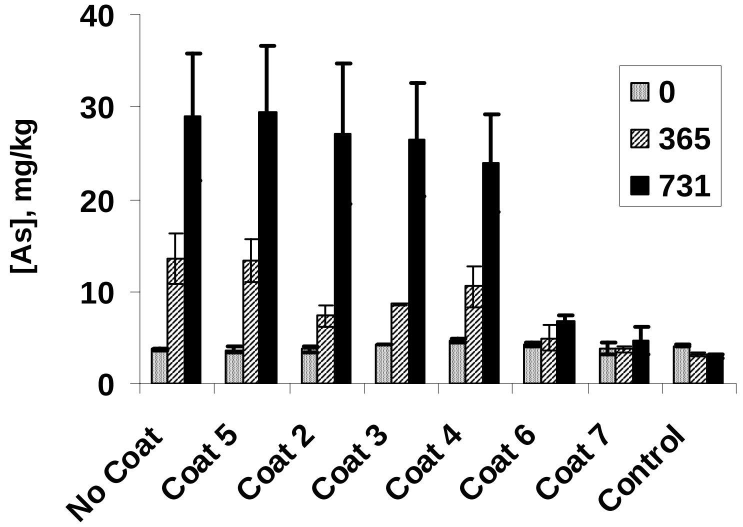

Figure 2. Average soil arsenic after 0, 365, and 731 days of weathering, ranked by coating effectiveness (107 and 547 day data omitted for clarity)

The percent reduction in soil As with different finishes and weathering time is given in Figure 3. The percent reduction was calculated by subtracting the amount of arsenic in soil from the control box from that in soil from each coated box, and dividing this by the difference between the arsenic in soils from uncoated boxes and the control boxes, i.e. 100*(Coat Value-Control Value)/(No Coat Value-Control Value). The opaque acrylic finish (#6) reduced the arsenic level by about 80% while the polyurethane based finish (#7) was around 95% effective over the entire two-year time. Opaque finishes were also found to be the most effective coating to reduce arsenic dislodged from surfaces (Kizer 1987; Stilwell 1998). The oil-based, deck and siding stain (#3), the sealant with alkyd and acrylics (#2) and the oil-based sealant (#4) were less effective and reduced the arsenic level by only 30-60%. In addition, the barrier appears to be breaking down after 1.5 years of weathering for these finishes (#2-4) since the percent reduction in soil arsenic was noticeably diminished compared to the one-year values (figure 3). The oil-based stain (#5) which had no apparent effect on arsenic leaching in this soil environment was found earlier to reduce arsenic dislodged from surfaces (Stilwell 1998).

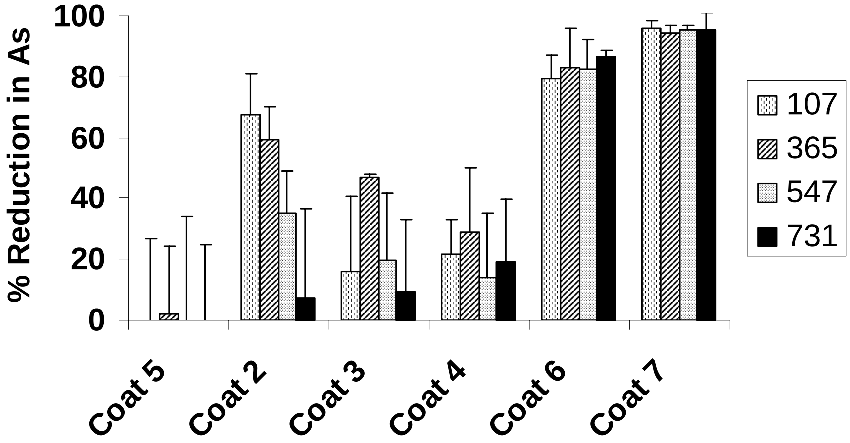

Figure 3. Percent reduction in soil arsenic levels with coating after 107, 365, 547, and 731 days of weathering

Shown in Figure 4 is the relationship between soil As and distance from the box edge. The concentrations of As in soil 6 cm away from the edge of the boxes is significantly less than the levels in soil next to wood. The average arsenic in all samples 6 cm from the box edge were at most 0.7 mg/kg higher than the average of 3.1±0.2 mg/kg in the control soils samples taken at this time. At the box center (13 cm), As levels in all treatments were within 0.3 mg/kg of the control except for Box 4 sample which was 0.6 mg/kg higher. Thus, beyond 6 cm from the edge of the wood the soil arsenic levels is reduced to well within 1 mg/kg of background levels of 3-4 mg/kg in this type of soil. This immobilization of As by the soil is likely due to the presence of Fe and clay which are known to fix As (Lebow 1996). Lateral decreases in soil As, reaching background levels within 15-130 cm from the CCA wood, has also been observed next to raised beds (Rahman et al. 2004), fences (Shiralipour, 2004), and traffic sound barriers (Stilwell and Graetz, 2001).

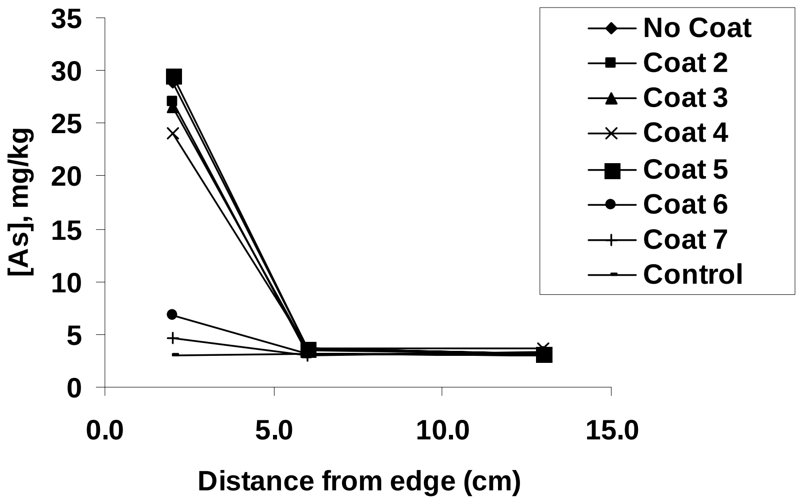

Figure 4. Soil arsenic with distance from box edge after 731 days of weathering

3.2 Copper and Chromium Leached

The average copper levels in soils from various treatments are given in Figure 5. The copper in the soil samples next to uncoated CCA wood increased modestly, from 23 mg/kg initially, to 36 mg/kg after two years of weathering, a 55% increase over the two-year period. The increase in copper in soils next to wood coated with the penetrating finishes increased to a lesser extent, from 16% (coat 4) to 35% (coat 2), while the copper in soils next to wood coated with the film-forming finishes (coat 6&7) increased the least, 10-15%, over the two-year period. In contrast, the copper in soil samples next to the ACQ treated wood increased from 24±0.5 mg/kg, to 80±25 after two years (Figure 5), a greater than three-fold increase. The greater copper content in the soils next to the ACQ wood is due in part to the fact that the ACQ wood contained about 2.3 times more copper than the CCA wood, 3073±58 mg/kg in the ACQ wood compared to 1360±370 mg/kg in the CCA wood. However, the copper content in the soil samples next to the ACQ wood increased over the weathering time to 56 mg/kg, about a factor of four, over the average 13 mg/kg increase in soil copper next to CCA wood. This increase is higher than the 2.3 expected from the difference in concentrations between the two materials, suggesting a faster leaching rate in the ACQ wood than in the CCA wood, consistent with the findings of Stook et al. 2005. The copper in soil samples away from the wood (6 and 13 cm) were all within 2 mg/kg of the background value of 23 mg/kg.

The average chromium levels in the soil for different treatments exhibited only limited increases compared to the pre-weathering values. For example, the increase in the soil Cr in the uncoated wood treatment increased from the initial value of 10±2 mg/kg, to 12±2 (day=107), 13±1 (day 365), and 13±2 (day 547) and 13.6 (day 731). Due to these small increases in soil Cr, coupled with the variation in baseline Cr (range 9-11 mg/kg) we could not evaluate the effects of coatings on Cr leaching.

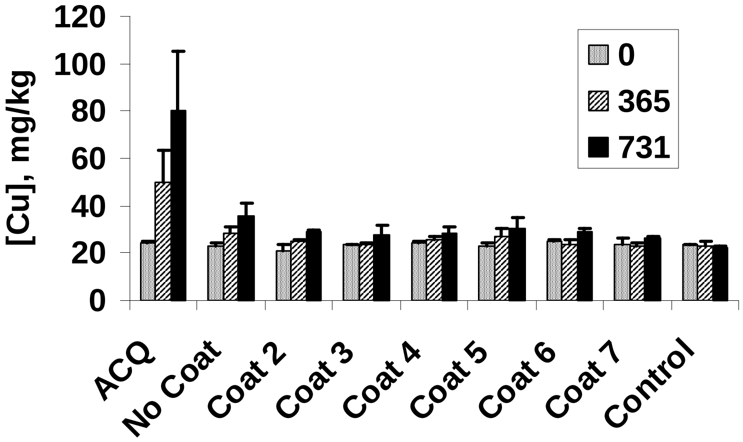

Figure 5. Average soil copper after 0, 365, and 731 days of weathering (107 and 547 day data omitted for clarity)

3.3 Plant Uptake

The amounts of As in the plants and soil at the box edges, with finish type, are shown in Table 2. Average amount of As in the soil next to the box edges was 29±7 mg/kg next to uncoated CCA wood, 27±6 next to wood with PF coatings and only 6±2 next to wood with FF finishes. Average amounts of As (mg/kg, dry weight) in arugula grown 2 cm from the CCA wood was 60±0.1 (4 composites), 61±13 (8 composites) from wood coated with PF finishes and 24±7 (4 composites) in those coated with FF finishes. Similarly, the amounts in chives were, 75 (CCA), 75 (PF), 12 (FF); lettuce 5 (CCA), 5 (PF), 1.4 (FF); basil 6 (CCA), 10 (PF), 3 (FF). The amounts of As in plants grown in the control boxes were all <1 mg/kg. Clearly, there was no reduction in plant As when plants were grown next to the non-opaque finished wood, while the reduction in plant As ranged from 50-84% in plants grown next to the opaque finished wood. The amounts of arsenic in the arugula and chives grown in the CCA boxes exceeded the British limit for plant As (Thornton 1994) of 1 mg/kg on a fresh weight basis (10-14 mg/kg dry weight basis).

Table 2. Arsenic (mg/kg, dry weight basis) in soil and plants next to CCA and control wood boxes coated with penetrating (PF) or film forming (FF) finishes.

Finish	**Soil**	**Arugula**	**Chives**	**Basil**	**Lettuce**
None	29 ± 7	60 ± 0.1	75 ± 19	6 ± 2	4.9 ± 0.6
PF	27 ± 6	61 ± 13	75 ± 24	10 ± 3	4.8 ± 0.5
FF	5.7 ± 1.6	24 ± 7	12 ± 3	3 ± 0.3	1.4 ± .25
Control	3.0 ± 0.2	0.5 ± 0.2	<0.2	0.9 ± 0.7	0.2 ± 0.01

The amounts of As in the soil and in plants grown with distance from the edge of the box and type of finish are shown in Figure 6. Although the plant As followed the trends in soil As, and the amounts of As in plants grown 6 cm from the box edge compared to 2 cm from the edge were lowered by 55 to 84%, these amounts were well above the background levels in plants grown in the control soil. Furthermore, the As levels in arugula plants grown in the box center (13 cm from the edges) did not decrease significantly from the levels in plants grown 6 cm from the edge. Also, the As in the arugula plants grown 13 cm from the edge in the CCA boxes, ranging from 7 to 18 mg/kg, was significantly above the 0.5 mg/kg As levels in arugula plants grown in the control boxes, even though the soil As in the center of the box was at or near background. This increase in uptake of As in the plants probably results from root growth into areas of As contamination (Miliss et *al*., 2004).

Evidence suggesting that the As originating from the CCA wood was generally more available to plants is shown by a comparison of the uptake factors, given in Figure 7. The uptake factor is the dry-weight concentration of plant As divided by the soil As. The uptake factor in arugula (2.4 ± 0.7) and chives (2.6 ± 0.7) is greater than one, showing that these plants actually concentrate the As from the CCA soil, but not in the control soil, where the uptake factor is much less (0.14 ± .04 arugula; <0.06, chive). In lettuce this effect is less pronounced (0.21 ± 0.08, CCA soils, <0.06, control soils), and in basil there is no difference (0.4 ± 0.1, CCA; 0.3 ± 0.2 control). Increased plant availability of As in CCA soil was also noted by Cao and Ma (2004). They determined that the percentage of water soluble As in the soil, the fraction available for plant uptake, was much higher in CCA contaminated soils (3-14%) than in uncontaminated soils (<1%). The continuous leaching of a fresh supply of As from the wood may also account for the increased phytoavailabilty. Jacobs et al. (1970), found that the extraction of As in

NH4Cl, which is related to the plant As, decreased substantially over a six month aging period compared to As freshly spiked into soils.

The significant accumulation of As in plants reported here is consistent with recent reports showing increased As in plants when grown in soils near CCA wood (Cao and Ma 2004; Rahman 2004; Shiralipour 2004). Cao and Ma (2004) determined the As levels in carrots and lettuce grown in pots containing CCA contaminated soil (27 and 43 mg/kg As). The amounts of As in the lettuce, which ranged from 4-32 mg/kg dry weight, and in carrots which ranged from 9-44 mg/kg, increased by a factor of 2-10 with the addition of phosphorus, and decreased by 80% or more with the addition of biosolid amendments. They concluded that growing vegetables in soils near CCA-treated wood may pose a risk of As exposure. Rahman et al. (2004) conducted a similar study using CCA contaminated soil (40-50 mg/kg As) from raised beds that were at least 10 years old. The As content in carrots, spinach, buckwheat and beans grown in pots containing the CCA soil ranged from an average of 0.32 mg/kg dry weight (bean pods) to 3 mg/kg in unpeeled carrots. In plants grown in control soil, taken 1.5 m from the beds, the As was <0.1 mg/kg except in unpeeled carrots where it was 0.2-0.3. Shiralipour (2004) grew lettuce and turnip in pots containing soils taken 0 to 135 cm from a fence constructed using CCA wood. The As decreased from 31 mg/kg in soils taken directly under the fence to 1.3 mg/kg in soils 135 cm from the fence. The As in the plants grown in soil taken under the fence ranged from 3 mg/kg dry weight in carrot leaf to 6 mg/kg in lettuce leaf and turnip root. There was around a 50-70% reduction in plant As in plants grown in soils taken 15 cm from the fence and when grown in soils 30-45 cm from the fence the plant As was indistinguishable from background levels. The large variability in the plant As in these studies could be partly due to differences in plant species and soil properties.

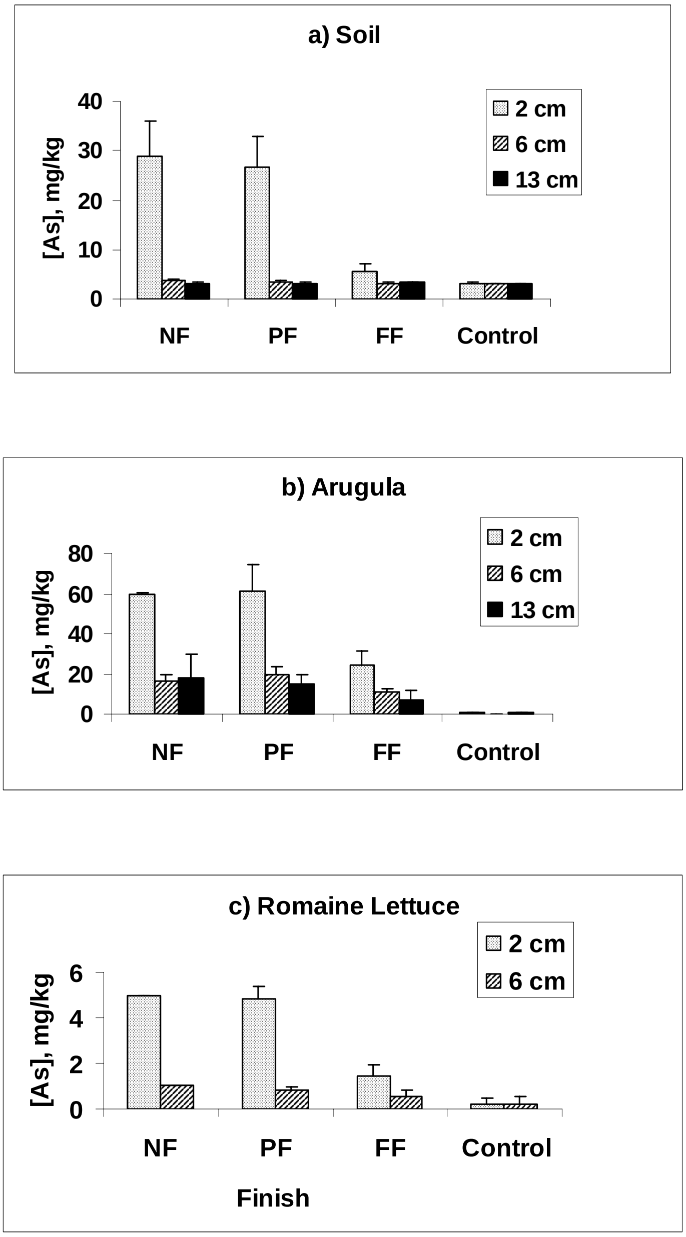

Figure 6. Soil and plant As with distance from edge of box and type of finish. a) Soil, b) Arugula, c) Romaine lettuce (NF= No Finish, PF= Penetrating Finish, FF= Film Forming finish).

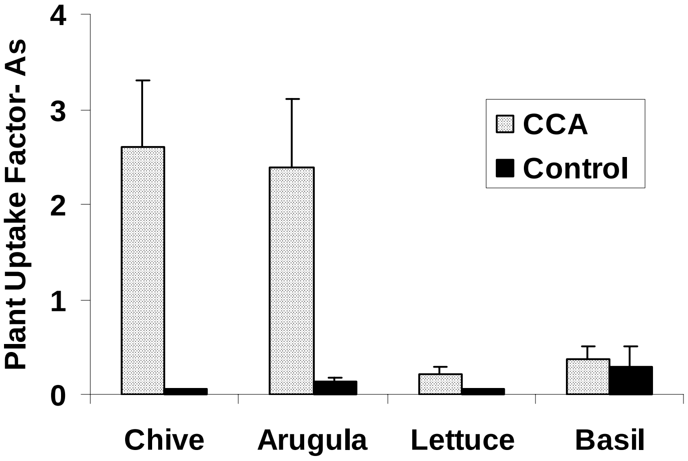

Figure 7. Plant uptake factor for As ([As]plant/[As]soil) in plants grown in soil 2 cm from the wood.

Differences in uptake of As by plant species was demonstrated by Thornton (1994). Thornton determined the As content in vegetables grown in garden soils contaminated with As from mining activity in south-west England. The As uptake was highest in lettuce and lowest in beans. Plant uptake was found to increase with increasing phosphorus in the soil and decreased with increasing iron content, presumably due to competitive sorption reactions between phosphorus and arsenic in the soil and with precipitation reactions with iron to form insoluble iron arsenates. Other studies on plant uptake of arsenic under laboratory conditions (Burlo et al., 1999; Carbonell-Barrachina et al., 1999; Cox et al., 1996; Onken and Hossner, 1995) have confirmed that arsenic levels in plant tissue are dependent on the type of plant, the part of the plant (root vs. shoot), the concentration and form of arsenic in the soil and in the soil solution, and the amounts of phosphorus and iron in the soil.

The copper and chromium contents were also determined in the plants. The Cr content in all of the plant tissue samples were below the detection limit of 3 mg/kg. The Cu content in plants grown in soils next to the CCA wood were not any different than the amounts in plants grown in the control box. There was, however, a slight increase in the Cu content of arugula plants grown next to the ACQ wood. In these samples the Cu content in plants grown 2 cm and 6 cm from the ACQ was 16±2 (n=2) and 14.2±1.3 (n=2) mg/kg, respectively, compared 10.2±1.0 (n=5) in the plants grown in the control soil. The average Cu content (mg/kg) in all of plant tissue samples (excluding the arugula grown in the ACQ box) was 5.8±1.1 (n=30), lettuce; 10.4±1.2 (n=45), arugula; 6.2±1.2 (n=10) chives, and 11.9±1.4 (n=10) basil.

4. CONCLUSIONS

Over the two-year weathering period the As levels in soils within 2 cm of the uncoated CCA wood increased from 3.7±0.1 to 29±7 mg/kg. Moreover, within one year of weathering, the arsenic next to uncoated CCA wood increased to levels that not only exceeded the State of Connecticut limit of 10 mg/kg, but which were also on the upper bounds of As limits (2-26 mg/kg) set by other local, state and federal government agencies (Belluck et *al*. 2003). This contamination, however, appears to be localized to soil within a few cm of the CCA wood. Soil samples, taken 6 and 13 cm from the box edge after two years of weathering, were at, or near background levels for As.

Only minor increases in the copper and chromium content occurred in the soil next to CCA wood over this two-year period. The relatively minor increases in Cu, and Cr, reflects one, the relatively low amount of Cu in the wood, and two, the lower leaching rate of Cr (Lebow 1996; Stilwell and Gorny 1997). All of the copper levels in the soil samples from all treatments were much less than the State of CT limit of 2500 mg/kg (State of CT 1996). In no case did the Cr level approach the State of CT limit of 100 mg/kg (hexavalent Cr) or 3900 for trivalent Cr (State of CT 1996).

Opaque coatings formulated using acrylics or polyurethane when applied to CCA wood reduced the migration of arsenic from the wood into the surrounding soil by 80% to 95%, which kept the As levels in the soil below the regulatory limit over the entire two-year weathering period. Other coatings, either oil- or water-based, but with clear or semi-transparent coverage, while initially reducing the arsenic migration up to 60%, did not appear to exhibit any protective properties after two years of weathering. Clearly, the film-forming opaque finishes are effective in reducing leaching and dislodgeable arsenic from CCA treated wood. The penetrating semi-transparent and transparent finishes, though useful in above ground situations, proved to be very limited when used in contact with soil.

The plant uptake of As followed the order Chives > Arugula > Basil > Lettuce. Compared to plants grown next to uncoated CCA wood, there was no reduction in plant As when grown along the edge of CCA wood coated with penetrating finishes, while in plants grown next to opaque finished wood the reduction in plant As ranged from 50-84%. The As reduction in plants grown 6 cm from the wood compared to 2 cm from the wood ranged from 55-84%. The amounts of arsenic in the arugula and chives were significant and exceeded the British limit for As in edible plants of 1 mg/kg, fresh weight basis (10-14 mg/kg, dry weight basis). The As in the basil was near the limit and the lettuce plants were all below the limit.

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PART III: MTBE

Chapter 10

MTBE: COVERAGE FOR THIS "SPREADING" PROBLEM

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Abstract: Environmental professionals need to understand the legal issues involving MTBE-related claims and insurance coverage. Legal actions involving MTBE contamination are on the rise. Throughout the United States, litigation has included MTBE claims based on negligence, conspiracy, property damage and product liability. In April 2002, for example, after an 11–month trial brought by a California public utility against MTBE producers, oil refineries and gasoline retailers, a jury found that gasoline containing MTBE was a defective product and decided in favor of large awards to plaintiffs. As a possible harbinger of what is to come, a number of law firms now include information relating to MTBE on their websites.

As MTBE–based claims increase, disputes concerning insurance coverage for those claims will also most assuredly increase. This presentation will provide a framework for helping to determine how insurance policies cover MTBE–related claims. For example, if government requirements to use MTBE result in legal actions relating to substances or commercial products exempted from Superfund liability, can insurance companies successfully deny coverage based on a pollution exclusion?

Standard liability insurance forms generally provide coverage for damage to the environment arising from MTBE. First, the large majority of jurisdictions that have addressed the issue of the "legal obligation to pay" hold that amounts paid to address government mandates in administrative enforcement actions are amounts which the policyholder "is legally obligated to pay as damages." Therefore, costs to investigate and remediate MTBE contamination in response to a government directive should be construed "as damages" which a policyholder is legally obligated to pay. Second, environmental contamination arising from gasoline containing MTBE is "property damage" and courts uniformly hold so. Such damage generally is to the property of a third–party because most states designate groundwater as a resource held in trust for all people so actual or potential threats to groundwater from MTBE are considered damage to the property of another. Third, "property damage" takes place or "triggers" coverage as long as the gasoline spill or leak was released into the environment at least, in part, during the policy period(s) at issue.

To deny insurance coverage for MTBE–related environmental damages, the insurance companies have (with varying degrees of success) relied upon: (1) the "expected or intended"/no "occurrence" defense; and (2) various forms of "pollution" exclusions. Policyholders should be sure this fine print actually applies before taking "no coverage" for an answer. While coverage for MTBE–related liabilities will not come easily, policyholders and environmental professionals need to know what evidence is necessary to support a claim for MTBE coverage.

Key words: MTBE; Insurance Coverage; CERCLA; Pollution Exclusion.

1. INTRODUCTION

Legal actions involving MTBE contamination are on the rise. Throughout the United States, litigation has included MTBE claims based on negligence, conspiracy, property damage and product liability. In April 2002, for example, after an 11–month trial brought by a California public utility against MTBE producers, oil refineries and gasoline retailers, a jury found that gasoline containing MTBE was a defective product and that Lyondall Chemical Co., a manufacturer of MTBE, and Shell Oil Co., a refiner, acted maliciously by withholding information about MTBE's potential hazards. As a result, in August 2002, Shell agreed to pay $28 million as part of an out–of–court settlement, bringing the total settlement in that action to over $69 million. As evidence of the increasing notoriety of MTBE and as a possible harbinger of what is to come, a number of plaintiff personal injury law firms now include information relating to MTBE on their websites.

As MTBE–based claims increase, disputes concerning insurance coverage for those claims will also most assuredly increase. Environmental professionals – and their legal counsel – need to understand the legal and insurance coverage implications of their work and the reports they generate in order to avoid liability themselves and effectively identify issues for their clients. This article provides a framework for helping to determine how insurance policies cover MTBE–related claims.

2. BACKGROUND

Most petroleum products are exempted from the reach of Superfund liability. See 42 U.S.C. § 9601(14) (exempting petroleum from the CERCLA/Superfund definition of "hazardous substance"). The law is set up this way for two basis reasons. First, petroleum is a naturally occurring substance. It would be ludicrous to have to treat the La Brea tar pits as a Superfund site. Second, petroleum hydrocarbon products occupy a unique position in the global social and economic order.

What happens, however, when the government requires that you mix petroleum with something else? The mixture may hurt people or property. But if government requirements result in legal actions relating to substances exempted from Superfund liability, can your insurance company deny coverage based on a so–called absolute or total polluter's exclusion?

Methyl tertiary butyl ether ("MTBE"), a substance almost exclusively used as a fuel additive in gasoline, is one of a group of chemicals commonly known as "oxygenates" – they raise the oxygen content and burning efficiency of petroleum hydro carbons. MTBE has been used in domestic gasoline at low levels since 1979 to replace lead as an octane enhancer. Since 1992, MTBE has been used at higher concentrations in some gasoline to fulfill the oxygenate requirements set by Congress in the 1990 Clean Air Act Amendments. MTBE is currently added to about 87% of the gasoline that is marketed, sold and used in the United States.

MTBE's expanded use has caused increasing problems related to environmental liabilities for damage or injury. The principal source of MTBE contamination is leaking underground fuel storage tanks (commonly known as "USTs"): The chemical properties of MTBE cause any of its spills and leaks to travel faster and further than other components of gasoline.. The ultimate health impacts of exposure to MTBE have not fully been determined. It is a known animal carcinogen, however, and has been identified as a possible human carcinogen.

3. ANALYSIS

3.1 Cleanup For MTBE Contamination Should Trigger Insurance Coverage Under the Insuring Agreement

The plain meaning of the insuring agreement of the standard–form comprehensive general liability insurance policy indicates that the defense and indemnity obligations of the insurance company are triggered by third–party liability claims alleging property damage. MTBE contamination caused by a spill or storage tank leak routinely gives rise to such claims.

First, the large majority of jurisdictions that have addressed the issue of the "legal obligation to pay" hold that amounts paid to address government mandates in administrative enforcement actions are amounts which the policyholder "is legally obligated to pay as damages." Thus, costs to investigate and remediate MTBE contamination in response to a government directive should be construed "as damages" which a policyholder is legally obligated to pay. Second, environmental contamination arising from gasoline containing MTBE is "property damage" and courts uniformly hold so. Such damage generally is to the property of a third–party because most states designate groundwater as a resource held in trust for all people so actual or potential threats to groundwater from MTBE are considered damage to the property of another. Third, "property damage" takes place or "triggers" coverage as long as the gasoline spill or leak was released into the environment at least, in part, during the policy period at issue.

3.2 Various Exclusions Relied Upon By the Insurance Industry

To deny insurance coverage for MTBE–related environmental damages, the insurance industry has (with varying degrees of success) relied upon the following three exclusions/defenses to coverage: (1) the "expected or intended"/no "occurrence" defense; and (2) various forms of so–called polluter's exclusions.

3.2.1 "Expected Or Intended" Defense

Based upon the typical "occurrence" definition, insurance companies routinely argue that coverage for "environmental" liabilities is barred because the policyholder "expected or intended" the property damage. There is a split of authority on the standard of proof applicable to this defense. Most courts hold that the relevant standard is a subjective one, i.e., the policyholder or, more often, company management must actually expect or intend the specific property damage and the resulting harm for coverage to be avoided. Some courts, however, hold that the relevant standard is an objective one, i.e., irrespective of the policyholder's actual knowledge or intent, coverage is barred only if the policyholder reasonably should have expected that property damage would take place. Whatever standard may be applied, as long as the MTBE contamination was not intended, expected or reasonably should have been expected, the "expected or intended" defense should not preclude coverage for MTBE–related events and, accordingly, insurance companies have had marginal success with this defense.

3.2.2 The Various So–Called Polluter's Exclusions

3.2.2.1 The Qualified Exclusion – 1970-1985

From the early 1970's through approximately 1985, most general liability insurance policies contained a qualified polluter's exclusion which purported to exclude coverage for "releases" and "discharges" of "pollutants" unless they were "sudden and accidental." The primary dispute over this "clarification" on coverage centers on whether the word "sudden" means "unexpected," or always includes a temporal element requiring that a covered claim arise out of an event which is "abrupt, immediate, or of short duration." Some courts have held that the uncertainty alone creates an ambiguity favoring policyholders. Other courts have looked to contemporaneous statements to insurance regulators at the time the purported exclusion was introduced by the insurance industry. Irrespective of the interpretation or legal theory, an unintentional spill resulting in MTBE contamination should not be excluded under the "sudden and accidental" pollution exclusion. If a court reads a temporal component into the exception, however, then damage occurring over an extended period of time, such as a slow leak from an UST, may not be covered even if the pollution is unexpected and unintended.

Based on the insurance industry's representations to regulators that this exclusion would only bar intentional pollution, a number of courts throughout the country have rejected the insurance industry's attempts to escape environmental liabilities. The most comprehensive analysis of the history of the insurance industry's efforts to secure regulatory approval for the "sudden and accidental" pollution exclusion as a mere "clarification" (not a "restriction" which would have required premium adjustment) is set forth in the New Jersey Supreme Court's decision in Morton International, Inc. v. General Accident Insurance Co. The Morton court, applying a theory known as "regulatory estoppel," held that the standard form "sudden and accidental" polluter's exclusion does not bar insurance coverage except when the policyholder intentionally discharges a known pollutant. Accordingly, for a variety of reasons, many state courts have rejected exclusion of coverage for environmental liability pursuant to the "sudden and accidental" polluter's exclusion.

Another area of contention concerns whether the particular injury producing agent is a “pollutant.” Although there are no decisions resolving application of the so–called “sudden and accidental” polluter's exclusion to MTBE contamination, an argument could be made that because MTBE is a useful, environmentally friendly product, it is not a “pollutant,” “irritant,” or “contaminant” and, therefore, is not excluded under the “sudden and accidental” polluters exclusion. Such an argument has been accepted by some courts for gasoline itself as well as for lead paint, which is merely paint plus a paint additive – lead. If these useful products are not “pollutants,” the useful gasoline additive MTBE should likewise not be deemed a “pollutant.”

3.2.2.2 The So-Called “Total” Or “Absolute” Exclusions 1985 – Present

From approximately 1985 forward, the insurance industry will also rely upon the so–called “absolute” or the more recent “total” pollution exclusions to exclude coverage for MTBE contamination. These exclusions removed the “sudden and accidental” language. The main areas of litigation involve: (1) the term “pollutant;” which is the same as discussed previously; and (2) whether there has been an “actual, alleged or threatened discharge, dispersal, seepage, migration, release or escape” of the purported “pollutant.”

As litigation surrounding the scope of environmental coverage mushroomed in the 1980’s, the insurance industry, through the Insurance Services Office (“ISO”), an insurance industry trade organization which drafts and revises standard–form liability insurance policies and endorsements, drafted another pollution exclusions: first, the “absolute” pollution exclusion and then the “total” pollution exclusion. ISO specifically crafted these exclusions to exclude liability for CERCLA–directed cleanup of damage to the natural environment. Courts generally have recognized that many of the key terms in the so–called absolute pollution exclusion – “release,” “disposal,” and “escape” – are environmental terms of art; indeed, many are key defining terms for the imposition of liability under CERCLA. See, e.g., 42 U.S.C. § 9607(a).

When these newer exclusions were introduced, the insurance industry made clear that they were designed to address environmental issues arising out of federal environmental laws, i.e., regular, long–term industrial pollution. For instance, at a 1985 hearing before the Texas State Board of Insurance, representatives of the insurance industry stated that the so–called absolute exclusion was not intended to bar coverage in all instances. These representatives discussed several examples of passive pollution which were not intended to be barred from coverage, including leaking USTs. In fact, the Liberty Mutual Insurance Company representative stated specifically that the manufacturer of leaking USTs should not lose coverage for “pollution”:

> You can read today’s CGL [Comprehensive General Liability] policy and say that if you insure a tank manufacturer whose tank is put in the ground and leaks, that leak is a pollution loss. And the pollution exclusion if you read it literally would deny coverage for that. I don’t know anybody that’s reading the policy that way.

Moreover, as discussed above, to the extent MTBE is a useful, governmentally required additive to petroleum products expressly exempted from the ambit of environmental law under CERCLA/Superfund, it does not fit within the definition of pollutant. Whether this distinction is accepted by a court, the mere fact that reasonable people disagree, can be used as evidence of an ambiguity in favor of the policyholder.

Thus, policyholders should be able to hold the insurance industry and Congress to their words: pollution exclusions should not apply in the normal circumstances that would give rise to “releases” or “dispersals” of MTBE into the environment, in part, because MTBE is a required additive to a ubiquitous product which is not a hazardous substance as the term is defined under federal and state law.

4. CONCLUSION

While coverage for MTBE–related liabilities will not come easily, policyholders and the environmental professionals they rely upon should be heartened by the fact that strong evidence and arguments exist to support a claim for MTBE coverage. You are entitled to the coverage you pay for, especially when an insurance company engages in revisionist underwriting after the fact. MTBE, as a government-mandated product, should be encompassed within that coverage.

Chapter 11

AN ESTIMATE OF THE NATIONAL COST FOR REMEDIATION OF MTBE RELEASES FROM EXISTING LEAKING UNDERGROUND STORAGE TANK SITES

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EXECUTIVE SUMMARY

The intent of this paper is to provide a balanced, scientific approach to estimating the national cost for remediation of methyl tertiary butyl ether (MTBE) releases from existing leaking underground storage tank (LUST) sites. A draft version of this paper was distributed to a limited number of external peer reviewers, who subsequently participated in expert panel discussions to finalize the paper. Panelists included members of state and federal regulatory agencies, including the U.S. Environmental Protection Agency, Office of Underground Storage Tanks (EPA OUST) and local professors. Through this limited peer review process, we received suggestions related to clarifying the scope and context of this study, and providing additional detail for our calculations and analysis. These suggestions are incorporated into this paper. The result is an estimated $2.0 billion for the remediation of MTBE releases from existing LUST sites. A sensitivity analysis, which was added to our research as a result of the peer review process, presents a discussion of cost variations that could result from altering our baseline assumptions.

The $2.0 billion cost estimate is based on the number of existing LUST sites maintained in published databases, and the average cost of addressing the MTBE portion of those sites. This is a total cost estimate, not adjusted for historic or future dollar values. The approach we derived for this cost estimate accounted for several factors, such as the fraction of LUST site releases that contain MTBE, and the portion of ongoing remediation that is already complete. To clarify the context of this estimate, we focused exclusively on the remediation of MTBE releases associated with LUST sites. As recorded by the EPA OUST in the database of existing LUST sites, the types of releases include tank overflows and leaks from pressure-relief valves, dispensers, piping networks, and other equipment typically associated with UST systems. The "UST site" is the area impacted by the release, including soil and groundwater in the immediate vicinity of the release, as well contaminant plumes emanating from the release. This may also include plumes that have impacted nearby water supplies, such as domestic wells or source-water aquifers. The remediation cost associated with these releases and areas encompasses costs ranging from initial site assessment to remediation and closure.

Insufficient information was available to reliably estimate and quantify potential remediation costs for new LUST site releases beyond EPA's current database. According to annual EPA reports, the number of new confirmed LUST site releases projected in the UST Corrective Action Measures dataset has decreased between 1992 (57,641 new sites) and 2004 (7,848 new sites). It is likely that new MTBE sites will be identified as requiring remediation in the future. However, the pace of site closures will likely outpace the identification of new sites, as reflected in EPA OUST data trends.

Beyond the potential continuation of a decreasing trend for new LUST sites, the unit cost per site could also change, resulting in increased or decreased costs. Factors that could increase the unit cost per site include more aggressive regulatory standards, the reopening of previously closed sites, or inflation. Factors that could contribute to a unit-cost decrease include more rapid response, improvements in remediation strategy, compliance, and system optimization, improved zoning laws to lessen the impact of site releases, and market consolidation to improve the efficiency of site management and remediation through economies-of-scale.

In addition to published literature on key aspects of estimating MTBE impacts from LUST site release, there is some published data on potential impacts to water supplies. EPA (2005) data indicate that less than 0.4% of community water supply systems report MTBE at concentrations greater than 5 parts per billion (ppb). As previously noted, the unit cost data compiled for our calculations may include costs for remediation of nearby water supplies, if they were impacted by a LUST site release. Regardless of a water supply's proximity or association with a nearby LUST site release, we have not quantified a collective differential cost for water supplies that are impacted by MTBE.

An additional point of clarification is the handling of non-LUST sites in general. As described, our cost estimate includes LUST site remediation, spanning from initial reporting and assessment, to remediation and closure. Incidental releases from non-LUST systems, such as motors, salvage yards, or roadways are not included in EPA's database of existing LUST sites (EPA OUST, 2004). Similarly, a complete inventory of LUSTs that contain heating oil, diesel, or other non-gasoline products may not be fully captured in EPA's database. The national cost contributions from these other sources, which are expected to be minimal in comparison to reported LUST sites, were not available for us to include quantitatively in this paper.

This research yields an estimated value of $2.0 billion for the remediation of MTBE releases from existing LUST sites, across the nation. The National Cost Equation (NCE) developed through this research was used to estimate this cost. The NCE was populated with a series of input parameters obtained from a thorough review of available published data sources, supplemented by internal ENSR data. Each data source was assigned a reliability index based on the comprehensiveness of the underlying dataset. A distribution of possible results was generated using 100,000 iterations of a Monte-Carlo procedure, which consisted of the mid-range values for each data source, matched with the associated source reliability index. The statistical distribution of the mid-range values yields a median value of $2.0 billion.

To provide context, the following chart illustrates the estimated fraction of MTBE-related costs relative to the overall costs associated with existing LUST sites. Similar to the Monte-Carlo procedure implemented to estimate the MTBE-related national cost of $2.0 billion, 100,000 iterations of the Monte-Carlo procedure were used to generate a distribution of overall LUST site costs. The mid-range input values yield a median cost of $17.8 billion for the remediation of existing LUST sites, irrespective of MTBE. The $2.0 billion MTBE-related fraction accounts for approximately 11% of this national cost.

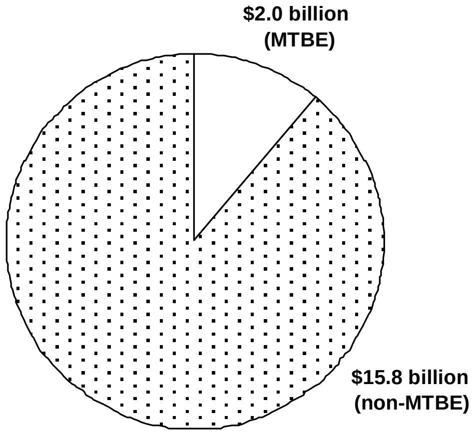


Figure 1. Remediation Costs for Existing LUST Site Releases

Assumptions contributing to the $2.0 billion national estimate are explored in the sensitivity analysis provided in the paper. As shown, by changing selected inputs into the NCE calculation, one can generate an array of associated results. We consider our baseline assumptions (resulting in the $2.0 billion median value) to be the most balanced and representative set of assumptions, based on our review of the source data. These variations are exploratory in nature, to provide practitioners with a sense of how the median value may change if key assumptions are altered.

Overall, the national cost estimated through this research relies heavily upon the available published data sources. Some uncertainties are reflected in the statistical distribution of our NCE calculation. Other limitations and uncertainties have been discussed qualitatively in this section. Despite the variability and limitations of this research topic, the methodology applied is appropriate for the wide range of reported data, and very limited datasets. This work can be expanded upon as desired, to further reduce uncertainties and continue to improve the precision of a national cost estimate.

1. INTRODUCTION

The focus of this paper is to establish a well-documented estimate of the national cost for remediation of methyl tertiary butyl ether (MTBE) releases from existing leaking underground storage tank (LUST) sites. This cost estimate is based on the number of existing LUST sites maintained in published databases, and the average cost of addressing the MTBE portion those sites. Adjustments were necessary to account for several factors, such as the fraction of LUST site releases that contain MTBE, and the portion of ongoing remediation that is already complete. To clarify the context of this cost estimate, we considered all releases from existing LUST sites, regardless of the source of the release or the area potentially impacted. For example, the types of LUST site releases reported by the U.S. Environmental Protection Agency (EPA) Office of Underground Storage Tank (OUST) "backlog" database (EPA OUST, 2004) include: releases from tank overflows and leaks, pressure-relief valves, dispensers, piping networks, and other equipment typically associated with UST systems. The EPA database encompasses plumes that are associated with LUST site releases, which may include impacted water supplies if they are associated with an adjacent LUST site release. An additional point of clarification is use of the term "remediation." Sources reviewed consider remediation costs to encompass site assessment and other costs associated with investigating and closing a LUST site release.

A draft version of this paper was completed on June 14, 2005 and provided to three expert panels for discussion from June 21 through 23, 2005. Panelists included members of state and federal regulatory agencies, including the EPA OUST and local professors. Through this limited peer review process, we received suggestions related to clarifying the scope and context of this study, and providing additional detail for our calculations and analysis. These suggestions are incorporated into this paper, and a sensitivity analysis (provided in Section 6) presents a discussion of cost variations that could result from altering our assumptions.

1.1 Background

Underground storage tanks (USTs) are typically used to store petroleum products at service stations, fueling depots, industrial facilities, commercial operations and residential properties. Releases from these tanks to the environment can occur through tank or piping leaks, overfill incidents or spills. As a result of historic releases, soil and groundwater can be impacted, creating a potential need for environmental remediation. After environmental impacts have been identified, an assessment of the necessity and degree of remediation typically begins with a comparison of chemical concentrations in the environment to regulatory standards and a risk-based evaluation (evaluating the risks associated with the presence of contaminants in the environment based on potential receptors of the contaminants). If remediation is necessary, it can be accomplished through either passive measures, such as monitored natural attenuation, or active measures, such as groundwater treatment.

MTBE is an additive in gasoline that has been used as an octane booster since 1979. The Clean Air Act (CAA) in 1990 increased the use (and concentration) of MTBE in gasoline. This increase was necessary to meet the requirements for refiners to produce oxygenated gasoline with reduced ozone precursor emissions. In 1995, the federal Reformulated Gasoline (RFG) program was introduced mandating the use of oxygenated gasoline in some major metropolitan areas. According to the United States (U.S.) Energy Information Administration (U.S. Department of Energy) report of March 2005, approximately 34% of all gasoline sold in the U.S. is reformulated or oxygenated.

Understanding the potential costs and funding sources associated with MTBE releases from existing LUST sites can be a complex endeavor. According to the EPA LUST Trust Fund (2004), an estimated 4% of LUST cases have no identified responsible party, thus public funding is necessary for their assessment and remediation. The remaining 96% of LUST cases are typically paid for by potentially responsible parties (PRP), trust funds, and other funding sources.

1.2 Approach

Many technical papers and presentations that estimate factors contributing to MTBE remediation costs have been produced over the past decade, particularly during the past three years. For this particular research effort, we combined the information from these references and developed a Nationwide Cost Equation (NCE) to estimate a national cost for remediation of MTBE releases from existing LUST sites. Our equation relies on input variables (equation parameters), which were developed from published data sources and data compiled from our internal LUST project databases, and assigned reliability indices to account for the variation in quality or reliability between different data sources.

Published data sources researched for this work included public databases, regulatory and public agency sources, technical papers and presentations. Sources were evaluated to determine applicability to the input parameters used in the NCE. Those sources with pertinent information were then further screened to exclude sources published prior to 1998, thus focusing the research on the most current information. Sources were further evaluated to determine if duplicate root sources were used (sources that rely on the same data).

Most of the published data sources used in the calculations were identified by searching references listed in the web pages of the U.S.

Environmental Protection Agency (EPA) and other agencies and consortiums, such as the New England Interstate Water Pollution Control Commission (NEIWPCC). Other sources of published data include ENSR's internal library. ENSR's internal project data was also used as described in Section 4.

1.3 Report Organization

The remainder of this paper presents the draft findings of our research. We intend to solicit input via peer reviews and panel discussions relative to our derivation of the NCE and our selection and application of input parameters for that equation. This paper is organized as follows:

1. Introduction
2. Derivation of Nationwide Cost Equation (NCE)
3. NCE Input Variables
4. ENSR Internal Data
5. Statistical Analysis
6. Sensitivity Analysis
7. Results and Discussion
8. References

1.4 Report Limitations

To clarify the context of our research, we focused primarily on existing LUST site releases, which is consistent with EPA's reported "backlog" database (EPA OUST, 2004). Existing LUST site releases were the focus of our research because EPA and several other entities routinely track LUST site release data, which is considered to be reliable and well-quantified. A "LUST site release" encompasses any area where environmental media is impacted. Sources of LUST site releases include tanks, pipelines, dispensers, and other potential equipment associated with UST systems. The remediation of LUST site releases includes the immediate release area, which may include impacts to adjacent properties and adjacent drinking water supplies.

As this estimate reflects the potential remediation costs for the existing backlog of LUST site releases that contain MTBE, consideration must be given to conditions that can change over time, and variables that are difficult to quantify. The following considerations are briefly discussed below:

- Potential identification of new sites in the future
- Potential changes in the cost of remediation
- Allocation of remediation funding
- Potential impacts to water supplies
- Potential releases from non-LUST sites

According to annual EPA reports, the number of new confirmed LUST site releases projected in the UST Corrective Action Measures dataset has decreased between 1992 (57,641 new sites) and 2004 (7,848 new sites). It is likely that new MTBE sites will be identified as requiring remediation in the future. However, the pace of site closures will likely outpace the identification of new sites, as reflected in EPA data. The trend of new LUST sites is shown in Figure 2, which is based on the most recent EPA published data, reported for the period between 1992 and 2004.

Beyond the potential continuation of a decreasing trend for new LUST sites, the unit cost per site could also change, resulting in increased or decreased costs. Factors that could increase the unit cost per site include more aggressive regulatory standards, the reopening of previously closed sites, or inflation. Factors that could contribute to a unit-cost decrease include more rapid response, improvements in remediation strategy, compliance, and system optimization, improved zoning laws to lessen the impact of site releases, and market consolidation to improve the efficiency of site management and remediation through economies-of-scale.

Cost impacts to potable water supplies as a result of MTBE impacts from LUST site releases are reported in some published sources. EPA (2005) data indicate that on a nationwide basis, less than 0.4% of community water supply systems report MTBE at concentrations greater than 5 parts per billion (ppb). As previously noted, the unit cost data compiled for our calculations includes costs for remediation of adjacent drinking water supplies, if they were impacted by the LUST site release. Regardless of a water supply's proximity or association with a nearby LUST site release, we have not quantified a collective differential cost for water supplies that are impacted by MTBE.

An additional point of clarification is the handling of non-LUST sites in general. As described, our cost estimate includes costs spanning from initial reporting and assessment, to remediation and closure. Our cost estimate also encompasses impacted media, whether at the source of the release or at a downgradient receptor. However, incidental releases from non-LUST systems, such as motors, salvage yards, or roadways are not included in EPA's database of existing LUST sites (EPA OUST, 2004). Similarly, a complete inventory of LUSTs that contain heating oil, diesel, or other non-gasoline products may not be fully captured in EPA's database. The national cost contributions from these other sources, which are expected to be minimal in comparison to reported LUST sites, were not available for us to include quantitatively in this paper.

Overall, the national cost estimated through this research relies heavily upon the available published data sources. Some uncertainties are reflected in the statistical distribution of our NCE calculation. Other limitations and uncertainties have been discussed qualitatively in this section. Despite the limitations outlined above, the methodology applied is appropriate for the wide range of reported data, and very limited datasets. The statistical distribution can be reduced and the precision of a final result can be improved though the inclusion of additional information as it becomes available.

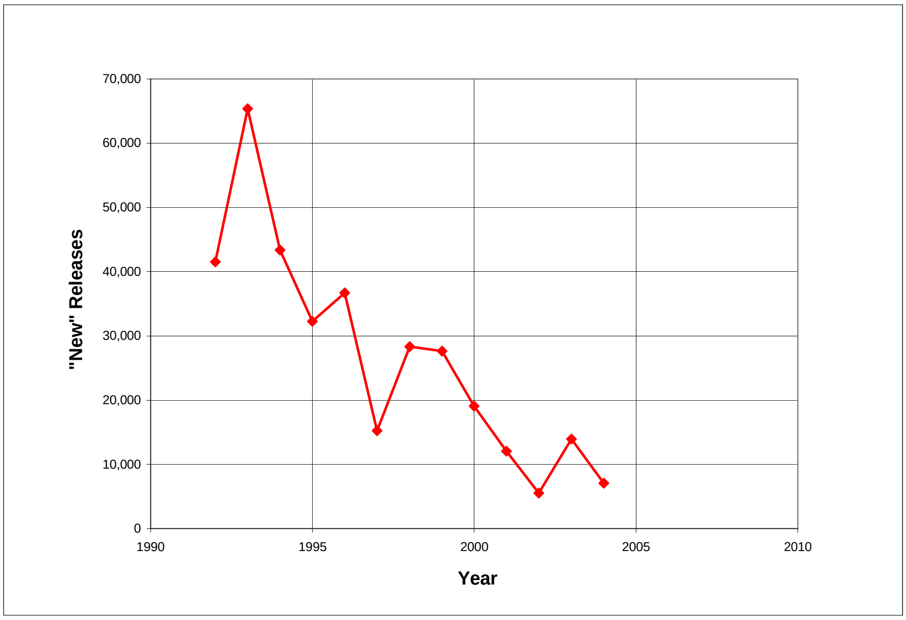


Figure 2. Trend of New LUST Site Releases

2. DERIVATION OF NATIONWIDE COST EQUATION (NCE)

This section presents the equation used to estimate the nationwide cost for MTBE remediation. Factors contributing to remediation costs associated with LUST site releases have been estimated in a variety of published sources; however, none of the sources reviewed presents a complete set of parameters and an associated nationwide cost. In addition, the reported cost factors reviewed vary widely among the published sources. For example, some sources evaluate costs associated with LUST site remediation in only one state, which could bias the cost data. Other sources do not account for costs already incurred for completed or ongoing remediation. By recognizing the importance of these and other variables in developing a national cost of MTBE remediation of existing LUST site releases, we derived an equation that considers the key parameters necessary for cost estimation. Our equation, which we refer to as the "Nationwide Cost Equation" (NCE), is relatively simple, but requires that each input parameter be critically selected and evaluated to account for uncertainties and potential bias.

In reviewing available published data sources and ENSR internal data, we catalogued information pertaining to 27 separate parameters (labeled as "A" through "AA" during our research). The parameters ranged from the number of active USTs estimated by EPA, to the frequency of MTBE detected at LUST site releases reported by NEIWPCC. In reviewing this multitude of somewhat mismatching information, we derived the following NCE, which relies upon a set of independent input variables:

$$NCE = (H + G*AA) * K * S$$

In this equation, parameters AA and K are input variables obtained directly from source data, and are referred to as input variables. Parameters H, G, and S are derived values from combinations of other input variables (C, D, E, O and Q). The following two tables (Tables 1 and 2) provide definitions of these parameters, sorted by whether they are input variables or derived values. Further descriptions of the input variables (refer to Table 1), as well as data sources and selected values, are provided in Section 3 and summarized in Table 3.

Table 1. Input Variables

Parameter Definition	Parameter
Number of confirmed LUST site releases	C
Number of LUST site releases with remediation initiated	D

Parameter Definition	**Parameter**
Number of closed LUST site releases	E
Fraction of LUST site releases with MTBE	K
Remediation cost per LUST site	O
Fraction of LUST remediation costs due to MTBE	Q
Fraction of effort not yet incurred for ongoing LUST remediation	AA

Table 2. Derived Values

Parameter Definition	**Parameter**	**Equation**
Remediation LUST site backlog *(all open LUST site releases maintained in EPA database)*	F	C-E
Number of LUST site releases where remediation has not been initiated *(open sites, remediation not initiated)*	H	C-D
Number of LUST site releases where remediation is ongoing *(open sites, remediation initiated)*	G	F-H (or D-E)
Differential MTBE remediation cost per LUST site *(cost attributable to MTBE portion of remediation)*	S	O * Q

3. NCE INPUT VARIABLES

As introduced in Section 2, the NCE we derived for cost calculation consists of seven independent input variables, which are used to quantify subsequent derived variables. For each of the input variables used in the NCE calculation, we researched information available from published data sources, as well as ENSR internal data. Table 3 presents the input variables (and parameter designations) defined in Section 2. A description of each is provided in the following subsections along with information about the data sources used to develop the parameter values.

Table 3. Summary of Input Variables

Input Variables (Parameter Designation)
Number of confirmed LUST site releases (Parameter C) *(all open and closed sites)*
Number of LUST site releases with remediation initiated (Parameter D) *(total of sites with remediation ongoing and sites with remediation completed)*
Number of closed LUST site releases (Parameter E) *(sites with remediation completed)*
Fraction of LUST site releases with MTBE (Parameter K) *(fraction of sites with MTBE)*
Remediation cost per LUST site (Parameter O) *(total remediation cost for either MTBE or non-MTBE sites)*
Fraction of LUST remediation costs due to MTBE (Parameter Q) *(fraction of MTBE portion of site remediation costs, for sites with MTBE)*
Fraction of effort not yet incurred for ongoing LUST remediation (Parameter AA) *(fraction of remediation remaining for sites with remediation in progress)*

3.1 Number of Confirmed LUST Site Releases (Parameter C)

This parameter represents the total number of reported LUST site releases, since reports of such incidents have been required. The intent of this category is to account for verifiable release incidents regardless of remediation status, site status (closed or open), number of tanks, or size of the release. Although reportable conditions vary by state, a “LUST site release” is typically considered to be the reported discovery of a leaking tank, failed tightness test, or the detection of petroleum constituents in drinking water, soil, air, groundwater or surface water that stems from a LUST system. The source of environmental impact can include tanks, piping, dispensers, surface spills, or other tank-related incidents. The designation of a LUST site release does not exclude impacts to adjacent receptors; however, many LUST site releases impact nearby drinking water supplies. This parameter is not adjusted for whether particular releases contain MTBE; all LUST site releases that are reported are included.

3.1.1 EPA OUST (2004)

The U.S. Environmental Protection Agency, Office of Underground Storage Tanks issues periodic updates to a database of LUST site releases. Attachment 1 of the most recent publication, “UST Corrective Measures for the End of the Year FY2004,” provides a table of state-by-state total for several statistics as of September 30, 2004, including the “number of confirmed releases.” The value used for this parameter is 445,002, which includes all 50 U.S. states; however, it excludes U.S. territories and tribal lands.

3.1.2 EDR (2005)

Environmental Data Research maintains a database of state-by-state inventory of reported LUST site releases, based on searches of state regulatory agency databases for each state (excluding Kentucky where there was no reported data). ENSR contracted EDR to obtain the most current database information, as of April 2005, for the 49 states with information. Summing the data reported by EDR yields a value of 539,623 existing LUST site releases.

3.1.3 GAO (2002)

The U.S. General Accounting Office prepared a "Testimony to Congress on "MTBE Contamination from Underground Storage Tanks." The testimony includes the following statement: "States reported to EPA that as of the end of 2001, they had completed cleanups at 64 percent (267,969) of the 416,702 known releases at tank sites and had begun some type of cleanup action for another 26 percent (109,486), as Figure 4 illustrates." Based on this information, a value of 416,702 was used for this parameter.

3.1.4 ENSR Trust Fund Records (2005)

ENSR submitted a questionnaire to state agency trust fund programs, for the third and fourth quarter of 2004. This questionnaire resulted in state-by-state statistics, including number of LUST site releases, which were compiled for this parameter. This yields a total value of 507,243 existing LUST site releases for this parameter.

3.2 Number of LUST Site Releases with Remediation Initiated (Parameter D)

This parameter is the number of confirmed LUST site releases where remediation has been initiated, as defined by EPA (EPA OUST, 2004). As defined by EPA, the reported value includes the following actions: management of contaminated soils, removal of non-aqueous phase liquid (NAPL), management or treatment of dissolved-phase contamination, monitoring for natural attenuation (soil or groundwater), or evaluation of site and determination by a regulatory agency that no further remediation is necessary. It is important to note that EPA defines this parameter as including sites with ongoing remediation, as well as sites that are closed (EPA OUST, 2004). EPA does not delete closed sites from this reported value.

3.2.1 EPA OUST (2004)

Attachment 1 of this publication provides the state-by-state total of the "number of cleanups initiated," as of September 20, 2004. The value used for this parameter (410,689) includes the total from all 50 U.S. states, excluding U.S. territories and tribal lands. No other sources of information were identified for this parameter.

3.3 Number of Closed LUST Site Releases (Parameter E)

The "number of closed LUST site releases" parameter is the number of sites where remediation has been completed. According to EPA (EPA OUST, 2004), this value represents the number of confirmed LUST site releases where remediation has been initiated and a regulatory agency has determined that no further actions are necessary to protect human health and the environment. Sites with post-closure monitoring are included in this category only if site-specific cleanup goals have been achieved. This parameter is important to ensure that closed sites are not factored into the future cost projection.

3.3.1 EPA OUST (2004)

Attachment 1 of this publication provides a table of state-by-state total of the number of "cleanups completed" as of September 30, 2004. The value used for this parameter (316,259) includes the total from all 50 U.S. states, excluding U.S. territories and tribal lands. As a point of clarification, because the number of sites with remediation "initiated" includes sites that have been closed, the total number of sites with ongoing remediation can be calculated by subtracting this parameter (316,259) from Parameter D (410,689), yielding a value of 94,430 sites.

3.3.2 GAO (2002)

The 2002 GAO testimony to Congress includes the following statement: "States reported to EPA that as of the end of 2001, they had completed cleanups at 64 percent (267,969) of the 416,702 known releases at tank sites and had begun some type of cleanup action for another 26 percent (109,486), as Figure 4 illustrates." Based on this report, a value of 267,969 was selected for this parameter.

3.3.3 ENSR Trust Fund Records (2005)

The ENSR questionnaire submitted to state agency trust fund programs in 2004 resulted in state-by-state values for the number of closed sites. Compiling the reported state data yielded a total value of 251,362 closed sites for this parameter.

3.4 Fraction of LUST Site Releases with MTBE (Parameter K)

MTBE is not detected at all LUST site releases. To determine which sites have MTBE impacts, we identified the fraction of site releases that contain MTBE in groundwater. This approach was used because of the high solubility and low adsorption properties of MTBE relative to other gasoline components, and its preference to dissolve in groundwater rather than adsorb to soil. This approach assumes that if MTBE is not present in groundwater, then that particular LUST site release does not have significant MTBE impacts requiring remediation and would not significantly alter the remediation costs. To eliminate bias and provide a more conservative (higher) value, there is no adjustment for the number of sites based on the concentration of MTBE detected. This approach simply accounts for whether MTBE was detected or not, regardless of concentration.

3.4.1 NEIWPCC (2000)

The New England Interstate Water Pollution Control Commission submitted a questionnaire to state regulatory agencies, with results provided in the following report: "Survey of State Experiences with MTBE Contamination at LUST Sites." Question 9a of the survey asked: "Approximately how often is MTBE detected in groundwater at gasoline contaminated LUST sites?" The responses were provided in ranges of 0-20%, 20-40%, 40-60%, 60-80%, and 80-100%. A total of 45 states responded. A single weighted-average percentage was calculated for this parameter, by multiplying the mid-point of each percentage range by the number of states reporting in that range, and then dividing by the total number of states reporting (45). This resulted in an overall percentage of 52%.

3.4.2 NEIWPCC (2003)

A NEIWPCC questionnaire was also available from 2003. The questions varied from the 2000 survey. To select a value for this parameter, responses to Question 19a were reviewed, which asked: "Out of the oxygenates that you sample and analyze in groundwater, what were the percent detections during 2002?" A total of 39 states provided responses, ranging from 3.5 to 100%. Although the question related to the fraction of samples containing MTBE, the responses were considered to be reflective of the fraction of LUST site releases that contain MTBE. A single weighted-average percentage was calculated for this parameter, by multiplying the mid-point of each percentage range by the number of states reporting in that range, and then dividing by the total number of states reporting (39). This resulted in an overall percentage of 54%, which is similar to the 52% value reported by NEIWPCC three years earlier (NEIWPCC, 2000).

3.4.3 ENSR US Data (2005)

The ENSR US Retail Petroleum Client Database was queried for the period from May 1995 to May 2005. The query included the number of LUST site releases with and without MTBE detected in groundwater. The fraction of LUST site releases with MTBE (75%) was calculated as number of sites with MTBE detected in groundwater, divided by the total number of sites.

3.5 Remediation Cost per LUST Site Release (Parameter O)

This parameter represents the average cost for remediation of an individual LUST site release, whether or not MTBE is present. The average cost is intended to include reported costs from investigation through remediation. This parameter does not differentiate costs for oxygenates or other contaminants, which may influence remediation costs. The cost basis for this parameter is a combination of data extracted from published data sources and ENSR internal data. The reported cost data from sources reviewed inherently incorporates a wide range of state-specific regulatory standards and remedial technologies. The costs reflect actual costs incurred to implement an appropriate technology and achieve a state-specific standard.

There are two types of values used to develop this parameter: single data points and state-by-state datasets. Several published data sources provide an estimate of the remediation cost per site, which (unless otherwise specified) are assumed to represent a nationwide average unit cost. The state-by-state datasets, however, consist of average unit cost data by state. To establish a nationwide average LUST site cost for the state-specific data sets, we developed a statistical process to weight the data reported for each state. The EPA OUST backlog (confirmed releases less closed sites) reported by state was used to proportion the relative contribution of the state cost data to the nationwide cost average. This method recognizes the significance of cost variations by state, and assigns a weighted value based on the LUST backlog of sites in each state. Because multiple sources of data may report information differently, it is possible that some cost sources are not as inclusive as others. This uncertainty is further explored in the sensitivity analysis provided in Section 6, where we explore the impact of eliminating selected source values for this parameter.

3.5.1 Wilson (2002)

An article entitled “Remedial Costs for MTBE in Soil and Groundwater,“ which was published by Wilson in the “Contaminated Soil Sediment and Water“ journal (Wilson, 2002) presents a table of costs for specific project types. Table 1 in the cited reference, presents the “Total Project Cost by Type of Site” for “service station/petroleum” type sites. According to Table 1, the “mean cost” for this type of site is $174,820, based on 276 sites.

3.5.2 GAO (2002)

The GAO testimony to Congress (GAO, 2002) presents the following statement relative to this parameter: “According to the EPA-sponsored survey, 16 states reported cost increases as a result of MTBE cleanup, most less than 20 percent; 5 states reported that their costs more than doubled. States spend, on average, about $88,000 addressing releases at each tank site in fiscal year 2001.” Based on this statement, a value of $88,000 was selected for this parameter. During our peer review process, a representative from ASTSWMO believed that this was initially an ASTSWMO-based value and thus, not as representative of the more recent ASTSWMO data (refer to ASTSWMO, 2004). The impact of this information was evaluated as part of our sensitivity analysis (Section 6), where we eliminate the GAO and other selected values for this parameter, and recalculated the result.

3.5.3 ASTSWMO (2004)

The Association of State and Territorial Solid Waste Management Officials presented results from a state financial assurance funds survey in June 2004. ASTSWMO records encompass a broader dataset than the other referenced sources for this parameter, because ASTSWMO includes non-gasoline LUST site data, such as releases from diesel fuel and heating oil LUST sites. As reported, information from 38 states with active trust fund programs was compiled, including the total number of LUST site releases, and the average cost per site release. The average cost was combined with the number of open sites in each state, by applying the LUST site database records (EPA OUST, 2004). Using these two factors, we calculated a weighted average cost per site of $100,217. During our peer review process, we recognized that trust fund data (such as ASTSWMO data) may not capture all remediation costs. Most state trust funds impose a one-time deductible that is not captured in the ASTSWMO data. There may also be remediation costs that have been determined to be ineligible based on program specific regulations. Potential ineligible costs include site-specific prorating based on compliance at the time of the release, initial response action costs, legal costs, and permit fees. An assessment of the impact of this potential underestimation of costs is included in the sensitivity analysis provided in this report.

3.5.4 Keller (1998)

Keller produced a paper entitled: "An Integral Cost-Benefit Analysis of Gasoline Formulations Meeting California Phase II Reformulated Gasoline Requirements." Table 7 in the paper, Total Groundwater Site Remediation, provides a range of costs, as well as "typical" costs, for site investigation, soil remediation, water treatment, and the total of each combined. The Keller data is based on sites with conventional gasoline, as well as gasoline with MTBE, and is summarized below in Table 4.

Table 4. Cost Data Provided by Keller (1998)

Reported Statistic	Gasoline with MTBE	Conventional Gasoline (without MTBE)
Range of Costs:	\$190,000 - \$750,000	\$97,000 - \$610,000
Typical Cost:	\$390,000	\$280,000

The paper defines "conventional gasoline" as not containing MTBE. The average of the "typical" cost reported for sites, with and without MTBE, was calculated to derive a value of \$335,000 for this parameter. This assumes that there were a similar number of sites in each category, and that the typical value of each is representative of the most probable cost.

3.5.5 ENSR Trust Fund Records (2005)

The ENSR questionnaire submitted to state LUST programs in 2004 resulted in state-by-state values for this parameter. The questionnaire asks for an average cost to clean-up sites in the particular state. Values were reported for 31 states, including low and high estimates of the average cost of remediation. Most responses provided the same value for the high and low estimate. Where these differed, the high value was used. These cost estimates were combined with the EPA's records of the number of LUST sites in each state (EPA OUST, 2004) to calculate a weighted average cost per site of \$136,069.

3.5.6 ENSR US Data (2005)

The ENSR US Retail Petroleum Client Database was queried for the period from May 1995 to May 2005. The query included remediation costs for 133 sites in 20 states. The average reported cost was calculated for each of the 20 states. These average costs were then combined with the number of sites in each state (EPA OUST, 2004) to calculate a weighted average cost per site of $251,182.

3.5.7 Martinson (2000)

A publication featured in "Underground Tank Technology Update," by the University of Wisconsin (Vol. 14, No. 6, 2000) provided estimated costs for remediation. The estimate was based on theoretically applying draft California guidelines, as well as historical costs incurred, for California leaking underground fuel tank (LUFT) sites. Bar charts of projected costs were provided for five classes of sites: BTEX onsite, BTEX on/offsite, MTBE Class A, MTBE Class B, and MTBE Class C. The three MTBE classes are based on potential vulnerability of nearby water supplies. Cost estimates for each class was separated into various phases of work, including site assessment and active remediation. To use this information in our study, we interpreted cost data from the bar charts, and then calculated the per-site remediation costs by averaging the values provided for each of the five classes. The result of these calculations yields a value of $280,000. This result assumes that there are an equal number of sites in each class.

3.5.8 Wilson (2004)

A recent article entitled "Costs and Issues Related to Remediation of Petroleum-Contaminated Sites" was presented at the National Groundwater Association (NGWA) Conference on Remediation: Site Closure and the Total Cost of Clean-up. The article provided statistical values (including minimum, maximum, mean, and median) for estimated site costs from a variety of sources, such as EPA's Cleanup Information (CLU-IN) database and state of Kansas records. The Wilson article provided average costs for each state by multiplying the site-specific cost data with the number of sites reported for each state. Wilson used the mean reported remediation cost (not median) for each of the state datasets, and the number of sites in each dataset. We did not need to derive our own weighted average cost for this data source, because Wilson provided state-based data. The value derived from Wilson (2004) for this parameter is $199,069.

3.6 Fraction of Remediation Cost Due to MTBE (Parameter Q)

This parameter represents the fraction of site remediation costs that are attributable to MTBE impacts. This fraction was calculated differently for the available data sources, based on the information provided in each relevant source. Calculation details are provided below for each of these sources. In general, this parameter reflects the cost of MTBE remediation divided by the total remediation cost, on a per-site basis. Our research relied upon published data sources and internal ENSR data for this parameter. For those sources that provided a total remediation cost, as well as a differential cost attributable to MTBE, a fraction of costs was easily obtainable to use for this parameter. Other sources provided a fraction, without the underlying cost data.

3.6.1 NEIWPCC (2003)

The NEIWPCC survey described previously for other parameters also included a question related to this parameter. Specifically, Question 39a/b asked: "Has MTBE had a noticeable impact on the cost of remediation in your state? If Yes, please indicate the percentage of the sites that fall into each category." The category options included: no increased costs; small increase in cost (<20%), significant increase in cost (20-50%), very significant increase in cost (50-100%), and cost more than doubled. A total of 43 states provided responses to this question. To derive a value for this parameter, an additional data source (EPA OUST, 2004) was necessary. The mid-point of each response range was multiplied by the number of LUST sites reported by EPA (EPA OUST 2004). Then a weighted average was calculated by adding the calculated per-state values together, and dividing by the total number of states reporting (43). This yielded an overall percent increase in remediation costs due to the presence of MTBE, weighted by state. To derive this particular parameter, the calculated percent increase (13%) was divided by the associated total (1.13%) to calculate a fractional MTBE cost of 11.5%.

3.6.2 Keller (1998)

As introduced for Parameter O, Table 7 of the Keller article provides cost estimates for sites with and without MTBE, as summarized on the following table for convenience (Table 5):

Table 5. Cost Data Provided by Keller (1998)

Reported Statistic	**Gasoline with MTBE**	**Conventional Gasoline (without MTBE)**
Range of Costs:	\$190,000 - \$750,000	\$97,000 - \$610,000
Typical Cost:	\$390,000	\$280,000

The fraction of costs attributable to the presence of MTBE was calculated by dividing the difference between the two typical cost values reported (\$110,000), by the average remediation cost of both categories (\$335,000), yielding a value of 33%.

3.6.3 ENSR US Data (2005)

The ENSR US Retail Petroleum Client Database query for the May 1995 to May 2005 period provided information pertaining to this parameter. The query included data for 130 sites in 20 states, with estimated remediation costs for sites with and without MTBE. For all 130 sites, the average remediation cost was \$174,574 per site. For sites where MTBE in groundwater was not detected, the average remediation cost was lower, at an estimated \$151,372 per site. For sites with MTBE, the average remediation cost was higher, at an estimated \$191,996 per site. The fraction of costs attributable to MTBE was calculated by dividing the difference between the two cost extremes (\$40,624), by the average remediation cost of both categories (\$174,574), yielding a value of 23%.

3.6.4 Martinson (2000)

The Martinson publication from the University of Wisconsin (Vol. 14, No. 6, 2000) provided estimated costs for remediation, which projected costs for sites with and without MTBE (refer to earlier Martinson discussion for Parameter O). To use this information for this particular parameter, we interpreted cost data from the bar charts provided, and then calculated the per-site remediation costs by averaging the values provided for each of the five classes presented (BTEX onsite, BTEX on/offsite, MTBE Class A, MTBE Class B, and MTBE Class C). Note that this assumes there are an equal number of sites in each class. To derive a value for this parameter, we subtracted the difference between average site costs with and without MTBE (\$123,200), and divided by the average value for all site categories (\$280,000), which yielded a value of 44% for the percentage of costs attributable to MTBE.

3.6.5 Wilson (2004)

The recent Wilson article provided statistical values (including minimum, maximum, mean, and median) for estimated site costs. As previously noted for this particular data source, because Wilson provided average costs per state, we did not need to derive our own state-weighted average costs. To derive a value for this parameter, we subtracted the difference between average site costs with and without MTBE ($43,795), and divided by the average value for all site categories ($199,069), to derive a value of 22% for the percentage of costs attributable to MTBE.

3.7 Fraction of Effort Not Yet Incurred for Ongoing LUST Remediation (Parameter AA)

The intent of this parameter is to recognize that a portion of remediation costs for open LUST site releases have already been incurred. This is an important concept when attempting to estimate the LUST site remediation costs "remaining" for existing LUST site releases. This was the most difficult parameter to quantify during our research, because very few published sources attempted to derive an estimate. Accordingly, several assumptions are necessary, which are described below for the two sources used. It is important to note that this parameter is used in the NCE to adjust the number of existing LUST site releases, not the cost data per LUST site.

3.7.1 ENSR US Data (2005)

The ENSR US Retail Petroleum Client Database query for the May 1995 to May 2005 period provided information pertaining to this parameter. Of the 130 sites used from the query, 10 projects were randomly selected to closely evaluate the distribution of remediation progress. We distributed the number of sites among four schedule milestones (0-25% complete, 26-50% complete, 51-75% complete, and 76-100% complete). Then an average cost per phase was calculated for the 10-site dataset. Subtracting the average unit cost incurred to date from the total estimated unit cost per project, and dividing by the total unit cost per project, yields a value of 44% for the fraction of project work not yet incurred.

3.7.2 Martinson (2000)

The Martinson publication from the University of Wisconsin (Vol. 14, No. 6, 2000) provided estimated costs for remediation, which included cost estimates for four phases of work (assessment, active remediation, passive remediation, and closure). To calculate a value for this parameter, we summed the reported values for similar project-phase cost data, across each of the five classes reported (refer to Martinson discussion provided for Parameter O). We then subtracted the unit cost incurred to date from the total estimated unit cost per project, and divided by the total unit cost per project, to estimate a value of 57% for the fraction of project work not yet incurred.

3.8 Summary of Input Variables

A summary of values used for the seven independent parameters in the NCE calculation is provided in Table 6. Two important points should be recognized when reviewing this information. First, the values shown are as-reported or calculated from the referenced published data sources or internal ENSR data. As introduced in Section 1, a critical aspect of our research involved assigning a reliability index to each of these values that accounts for inherent differences in reliability. Second, rather than calculating a weighted or representative value for each parameter, we compiled all values simultaneously to derive a distribution of potential results via a Monte-Carlo procedure. If we selected specific values or a mean value for each parameter, we would have introduced a level of bias. Alternatively, the Monte-Carlo approach we implemented for the NCE calculation reduces the potential for bias. Section 5 presents the theory and methodology used to derive an NCE distribution using all of the available values shown in Table 6, along with their associated reliability indices. Section 6 provides a sensitivity analysis to assess the impact of assumptions used in interpreting source data.

Table 6. Summary of Values for Input Variables

Data Source/ Parameter	**Number of Confirmed Releases**	**Number of LUST Site Releases with Remediation Initiated**	**Number of Closed LUST Site Releases**	**Fraction of LUST Site Releases Where MTBE is Detected**	**Remediation Cost Per LUST Site**	**Fraction of LUST Remediation Cost Due to MTBE**	**Fraction of Effort Not Yet Incurred for Ongoing Remediation**
NCE Parameter:	**C**	**D**	**E**	**K**	**O**	**Q**	**AA**
NEIWPCC (2000)				52%			
NEIWPCC				54%		11.5%	

Data Source/ Parameter	**Number of Confirmed Releases**	**Number of LUST Site Releases with Remediation Initiated**	**Number of Closed LUST Site Releases**	**Fraction of LUST Site Releases Where MTBE is Detected**	**Remediation Cost Per LUST Site**	**Fraction of LUST Remediation Cost Due to MTBE**	**Fraction of Effort Not Yet Incurred for Ongoing Remediation**
(2003)							
EPA OUST (2004)	445,002	410,689	316,259				
EDR (2005)	539,623						
Wilson (2002)					$174,820		
GAO (2002)	416,702		267,969		$88,000		
ASTSWMO (2004)					$100,217		
EPA (1998)[1]							
Keller UCSB (1998)					$335,000	33%	
ENSR Trust Fund (2005)	507,243		251,364		$136,069		
ENSR US Data (2005)				75%	$251,182	27%	44%
Martinson (2000)					$280,000	44%	57%
Wilson (2004)					$199,069	22%	

Notes:
NCE = Nationwide Cost Equation
Refer to reference list for full citations
Refer to parameter discussion for full descriptions
[1] Value of 39% provided for costs attributable to MTBE was based on insufficient data. Source: U.S. EPA, Office of Solid Waste and Emergency Response (OERR), January 1998, MTBE Fact Sheet #2. Remediation of MTBE Contaminated Soil and Groundwater

4. INTERNAL ENSR DATA

Our approach to estimating the NCE for LUST site releases with MTBE included supplementing published source data with internal ENSR data. We maintain two types of datasets that were used to complement the information obtained from published data sources: trust fund records and project-specific data. The methods used to compile and apply these datasets are described in the following subsections.

4.1 ENSR Trust Fund Records

ENSR's trust fund records are based on general trust fund information collected by our "Reimbursement Management Group," a dedicated team whose sole business is the compilation and submittal of LUST Trust Fund reimbursement claims. The trust fund information used in our evaluation was based on responses to a January 2005 questionnaire pertaining to the 3rd and 4th quarter of calendar year 2004. Trust fund information regarding the number of active and closed LUST site releases and the average cost to closure were compiled for use in the NCE. Table 7 summarizes this information from ENSR trust fund records.

Table 7. ENSR Trust Fund Records

Parameter	**Value**	**Comments**
Number of Active (Registered) USTs	968,812	Based on responses from 34 states. No response from AK, HI, IA, KY, MA, MI, MS, MT, NE, NH, NJ, NY, ND, OR, SD and WY.
Number of LUST Site Releases	255,879	Based on responses from 36 states. No response from AK, HI, IA, KY, MI, MS, MT, NE, NJ, NY, ND, OR, SD and WY.
Number of Remediated (Closed) LUST Site Releases	251,364	Based on responses from 32 states. No response from AK, CT, HI, IA, KY, MA, MI, MS, MT, NE, NH, NJ, NY, ND, OR, SD, TN and WY.
Estimated Remediation Cost per LUST Site Release	$136,069	Based on weighted responses from 31 states. No response from AK, CT, HI, ID, IA, KY, MI, MS, MT, NE, NJ, NY, ND, OR, RI, SD, TN, VA, WV and WY.

4.2 ENSR Project Data

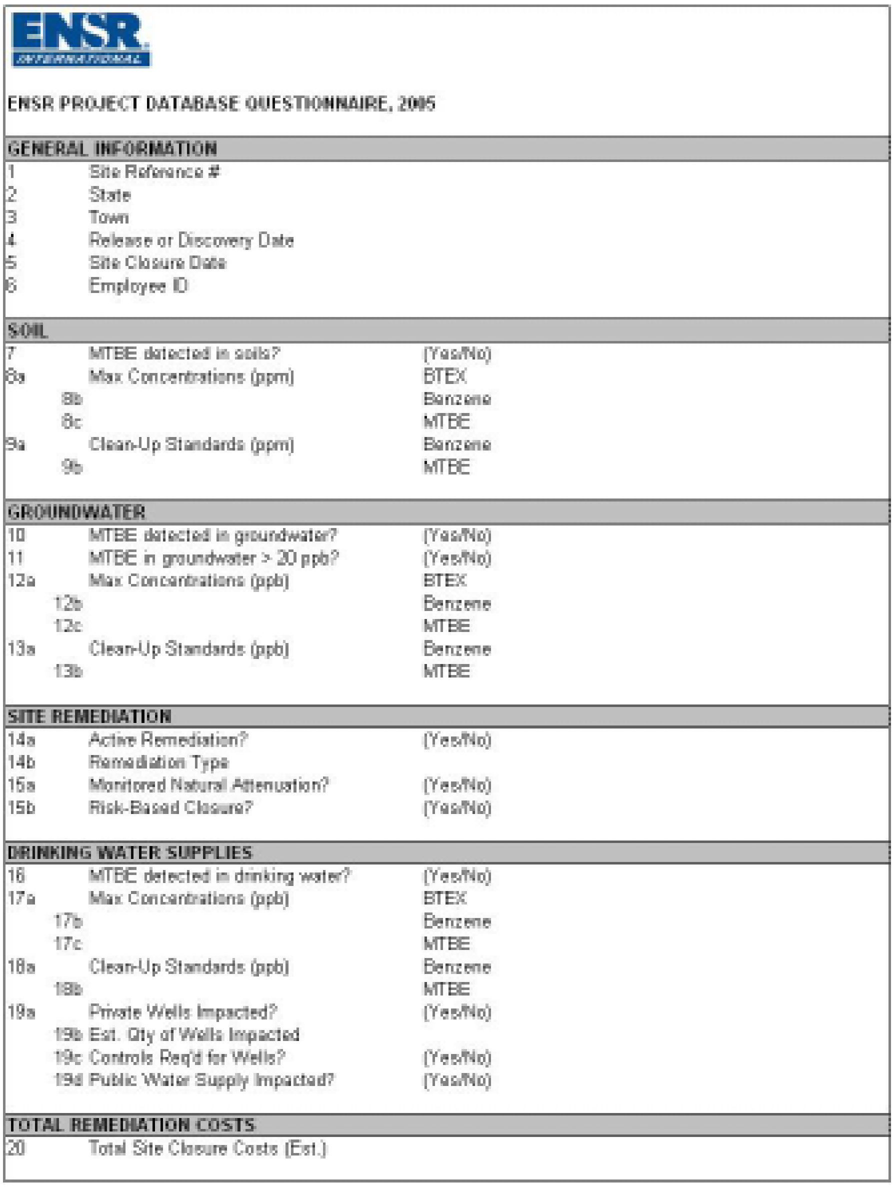
4.2.1 Site Information Query

To develop the ENSR project database for retail petroleum clients, a comprehensive list of closed LUST sites for our three largest retail petroleum clients was developed. The list included all current or former retail petroleum facilities, at which a gasoline release had been detected, and the site had been closed within the past 10 years. The query spanned a variety of gasoline-impacted LUST sites, states, and regulatory climates.

A preliminary screening was completed of the initial list to ensure that each project was associated with a LUST and that the release was attributable to gasoline. Projects eliminated during this preliminary screening included non-gasoline LUST sites, minor surface spills, dispenser collisions, and minor soil issues associated with piping upgrades. Once the final list was screened, a 25-question query was distributed to the ENSR Project Manager most familiar with each particular project. Project

Managers responded to the query, and the information was uploaded into a searchable project database. The information included data for MTBE and other gasoline constituents, including benzene, toluene, ethylbenzene, and xylenes (BTEX). The questionnaire also included specific questions regarding the effect of MTBE on site closure costs. A copy of the questionnaire is provided as Figure 3.

4.2.2 Evaluation of Compiled Results



ENSR PROJECT DATABASE QUESTIONNAIRE, 2005

GENERAL INFORMATION		
1	Site Reference #	
2	State	
3	Town	
4	Release or Discovery Date	
5	Site Closure Date	
6	Employee ID	
SOIL		
7	MTBE detected in soils?	(Yes/No)
8a	Max Concentrations (ppm)	BTEX
8b		Benzene
8c		MTBE
9a	Clean-Up Standards (ppm)	Benzene
9b		MTBE
GROUNDWATER		
10	MTBE detected in groundwater?	(Yes/No)
11	MTBE in groundwater > 20 ppb?	(Yes/No)
12a	Max Concentrations (ppb)	BTEX
12b		Benzene
12c		MTBE
13a	Clean-Up Standards (ppb)	Benzene
13b		MTBE
SITE REMEDIATION		
14a	Active Remediation?	(Yes/No)
14b	Remediation Type	
15a	Monitored Natural Attenuation?	(Yes/No)
15b	Risk-Based Closure?	(Yes/No)
DRINKING WATER SUPPLIES		
16	MTBE detected in drinking water?	(Yes/No)
17a	Max Concentrations (ppb)	BTEX
17b		Benzene
17c		MTBE
18a	Clean-Up Standards (ppb)	Benzene
18b		MTBE
19a	Private Wells Impacted?	(Yes/No)
19b	Est. Qty of Wells Impacted	
19c	Controls Req'd for Wells?	(Yes/No)
19d	Public Water Supply Impacted?	(Yes/No)
TOTAL REMEDIATION COSTS		
20	Total Site Closure Costs (Est.)	

Figure 3. ENSR Project Database Questionnaire

4.2.3 Development of Internal Cost Estimate

For each of the 133 sites solicited for the questionnaire, an estimated site closure cost was reported by the ENSR Project Manager. This estimate included costs associated with the investigation and remediation of the documented release. After compiling the cost data, our project statistician interpreted the information by applying a log-transformation to identify statistical outliers. In general, the reported costs were well described by a log-normal probability distribution. However, the three highest reported costs (each greater than $1 million) diverged from the log-normal probability straight line fit. After discussions with those Project Managers, we determined that the costs for those three sites were driven by a combination of BTEX contamination, litigation, and third-party involvement. Based on this information and the non-linear fit relative to the other data points, we considered these values to be outliers. The remaining 130 sites were used for internal cost estimation.

Although the ENSR internal dataset is limited relative to published data sources that span a greater number of sites across the U.S., several interesting observations of our internal dataset provide some insight on MTBE remediation costs. Observations from the ENSR internal dataset are listed below, and a full cost summary is provided in Table 8.

Table 8. Summary of Internal ENSR Remediation Cost Data

State[1]	**Minimum**	**Arithmetic Average**	**Median**	**Maximum**	**Number of Projects**
Arizona	$388,508	$497,764	$497,764	$607,019	2
California	$21,184	$144,658	$113,761	$418,635	16
Connecticut	$154,860	$154,860	$154,860	$154,860	1
Delaware	$538,581	$538,581	$538,581	$538,581	1
Illinois	$65,096	$196,216	$194,223	$392,835	6
Indiana	$45,063	$273,567	$183,312	$902,253	6
Massachusetts	$10,400	$149,450	$93,915	$841,195	31
Maryland	$21,982	$21,982	$21,982	$21,982	1
Maine	$3,787	$85,719	$5,245	$802,707	12
North Carolina	$259,972	$365,550	$365,550	$471,128	2
New Hampshire	$19,438	$43,450	$21,030	$133,958	5
New Jersey	$104,262	$208,914	$208,914	$313,565	2
Oregon	$17,634	$56,570	$56,570	$95,505	2
Pennsylvania	$766,743	$766,743	$766,743	$766,743	1
Rhode Island	$542,375	$542,375	$542,375	$542,375	1
Utah	$424,888	$424,888	$424,888	$424,888	1
Virginia	$4,639	$167,085	$54,739	$594,393	14
Washington	$57,078	$215,822	$138,859	$451,530	3
Wisconsin	$105,449	$237,270	$200,865	$469,270	15
West Virginia	$36,502	$118,727	$83,990	$366,912	8

State[1]	**Minimum**	**Arithmetic Average**	**Median**	**Maximum**	**Number of Projects**
Nationwide	$3,787	$178,574	$109,018	$902,253	130

Notes:
[1] This table includes U.S. states where ENSR has project sites for its retail petroleum work queried for this research; no states were specifically excluded.

- Closure costs for sites where MTBE was detected ($192K) were higher than costs at sites where MTBE was not detected ($151K). Average closure costs appear to increase with decreased MTBE concentrations (based on maximum MTBE concentrations).
- Drinking water impacts by MTBE appear to increase mean closure costs ($286K for impacted sites compared to $166K for sites with no drinking water impacts). This seems to be due to increased remediation costs since closure costs for active remediation sites with drinking water impacts ($336K) were significantly greater than for remediation sites without drinking water impacts ($201K).
- Active remediation sites had the highest closure costs, followed by risk-based closures. Closure costs for active remediation of sites with MTBE averaged $220K, compared to $203K for remediation of sites where MTBE was not detected in the groundwater. Similarly, costs for risk-based closure with MTBE averaged $119K, compared to $137K for risk-based closure where MTBE was not detected in the groundwater.

4.2.4 Quality Assurance Review

To evaluate the quality of the internal data compiled from ENSR Project Managers, we randomly selected a sample size of 25 projects from the database of 133 projects. For each of the 25 projects, our MTBE research team randomly confirmed the Project Manager responses to 11 of the 25 questions that were critical to the development of our internal cost estimate. Based on the quality assurance review, no errors warranting a re-evaluation of data were identified.

5. STATISTICAL ANALYSIS

Values for the input parameters in the Nationwide Cost Equation (NCE) presented in Section 2 show a variation within the group of data sources. In addition, there is a difference between the reliability of these data sources.

Both factors contribute to the uncertainty in the input parameters for the NCE. Through the additions and multiplications in the NCE, this uncertainty is propagated to the final estimate of the nationwide cost.

5.1 Uncertainty Propagation

If two random variables are added, the mean value of their sum is equal to the sum of their mean values. The standard deviation of the sum is equal to the square root of the sum of the squares of the standard deviations of the two random variables. If two random variables are multiplied, the mean value of their product is equal to the product of their means. The equation for the standard deviation of the product is more complex and is given by:

$$\sigma_C = \sqrt{(A^2 + \sigma_A{}^2)(B^2 + \sigma_B{}^2) - A^2 B^2} \qquad (5-1)$$

Where
A = mean of random variable “a”
B = mean of random variable “b”
σ_A = standard deviation of random variable “a”
σ_B = standard deviation of random variable “b”
σ_C = standard deviation of the product of random variables “a” and “b”

Just knowing the mean and standard deviation of the cost estimate does not allow one to specify a frequency distribution for this output variable. For example, one may want to know the probability that the cost estimate exceeds a certain value. The output variable frequency distribution will depend upon the input variable frequency distributions.

5.2 Monte-Carlo Analysis

To determine the cumulative frequency distribution of the cost estimate output variable, a Monte-Carlo analysis was performed. For each step of the Monte-Carlo procedure a set of input parameter values is chosen at random from the input parameter frequency distributions. With each set of input parameters, the cost output is calculated and saved. This procedure is repeated 100,000 times and the cost output values are sorted from lowest to highest to develop a cumulative frequency distribution of values. This Monte-Carlo analysis was performed using the @RISK software (Palisade Corporation, Version 4.5.4, Standard Edition). The software is an “add-in” to Microsoft Excel.

5.3 Data Source Reliability and Scoring

To quantify the reliability of available data sources, a scoring approach was developed that assigns a relative ranking of 1 to 5 (with 5 being the most reliable) using the following data source factors:

- Number of states included in this source (29% weighting)
- Number of sites included in this source (29% weighting)
- Publication year (29% weighting)
- Author affiliation; public or private (scale of 1 to 2; 13% weighting)

Figure 4 presents the relative reliability assigned to each of the 12 available data sources after applying this approach. A total score is computed for each data source. Additional detail for each source is provided in Table 9.

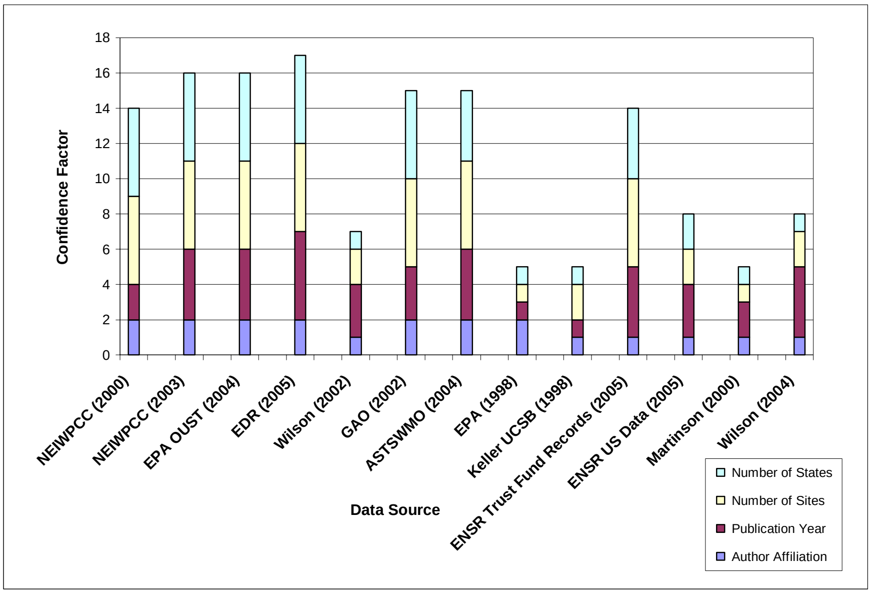


Figure 4. Source Data Reliability Indices

Table 9. Reliability Index Basis

Data Source/ Criterion	**Number of States Included in Dataset (1 to 5)**	**Number of Sties Included in Dataset (1 to 5)**	**Publication Year (Data Year if Available) (1 to 5)**	**Author Affiliation (1 or 2)**	**Total Score (4 to 17)**
NEIWPCC (2000)	5	5	2	2	14
NEIWPCC (2003)	5	5	4	2	16
EPA OUST (2004)	5	5	4	2	16
EDR (2005)	5	5	5	2	17
Wilson (2002)	1	2	3	1	7
GAO (2002)	5	5	3	2	15
ASTSWMO (2004)	4	5	4	2	15
EPA (1998)[1]	1	1	1	2	5
Keller UCSB (1998)	1	2	1	1	5
ENSR Trust Fund (2005)	4	5	4	1	14
ENSR US Data (2005)	2	2	3	1	8
Martinson (2000)	1	1	2	1	5
Wilson (2004)	1	2	4	1	8

Notes:

Number of States Included in Dataset: 0-10 (1); 11-20 (2); 21-30 (3); 31-40 (4); 41-50 (5)

Number of Sites Included in Dataset: 0-50 (1); 51-500 (2); 501-5,000 (3); 5,001-50,000 (4); >50,001 (5)

Publication/Data Year: 1997-1998 (1); 1999-2000 (2); 2001-2002 (3); 2003-2004 (4); 2005-present (5)

Author Affiliation: private (1); public (2)

5.4 Example Calculation

As previously described, the Monte-Carlo procedure minimizes potential bias by randomly combining input variables into the NCE calculation. Based on the number of parameters in the NCE, and the number of values for each parameter, there are 2,880 possible combinations for the final result. An example of one possible combination is provided below, which is useful to see how the NCE is applied. The reliability indices dictate the probability of particular values being selected in the 100,000-iteration Monte-Carlo run. If desired, individual states could use state-specific information for the input variables to estimate the cost for remediation of existing LUST sites in a particular state.

$$NCE = (H + G*AA) * K * S$$

$$H = C - D$$

= 445,002 – 410,689 (EPA OUST, 2004)
= 34,313

G = D – E
= 410,689 – 316,259 (EPA OUST, 2004)
= 94,430

AA = 57% (Martinson, 2000)

K = 54% (NEIWPCC, 2003)

S = O * Q
= $199,069 * 22% (Wilson, 2004)
= $44,230

NCE = (H + G*AA) * K * S
= [34,313 + (94,430 * 0.57)] * 0.54 * $44,230
= $2.08 billion

5.5 Input Parameter Distributions

For the Monte-Carlo analysis, a discrete probability distribution was selected for each of the input parameters. For each parameter a number of values are available from among the 12 data sources. The probability of choosing one of these values during an iteration of the Monte-Carlo procedure is proportional to the reliability score discussed earlier in this section. The probability of selecting each of the possible input values is illustrated in Figures 5 to 10. Note that a distribution figure is not presented for the "Remediation Initiated" input variable because only one value was available.

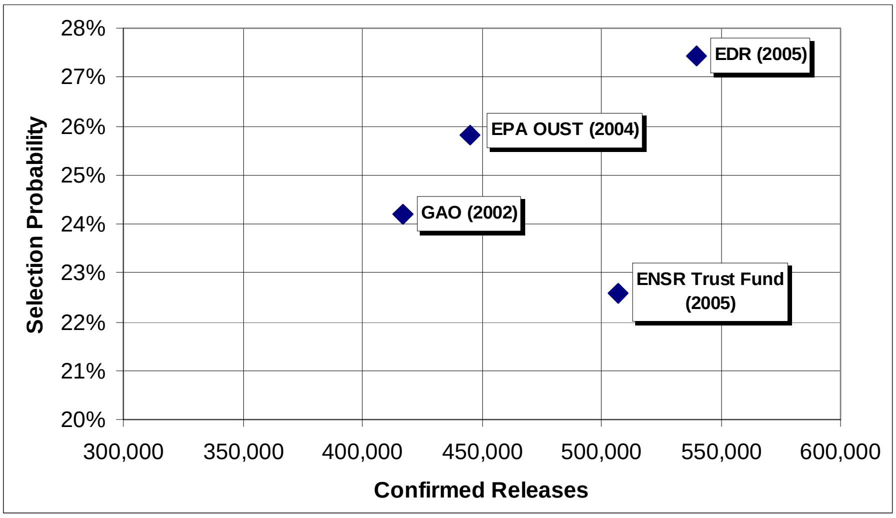


Figure 5. Number of Confirmed LUST Site Releases (Parameter C)

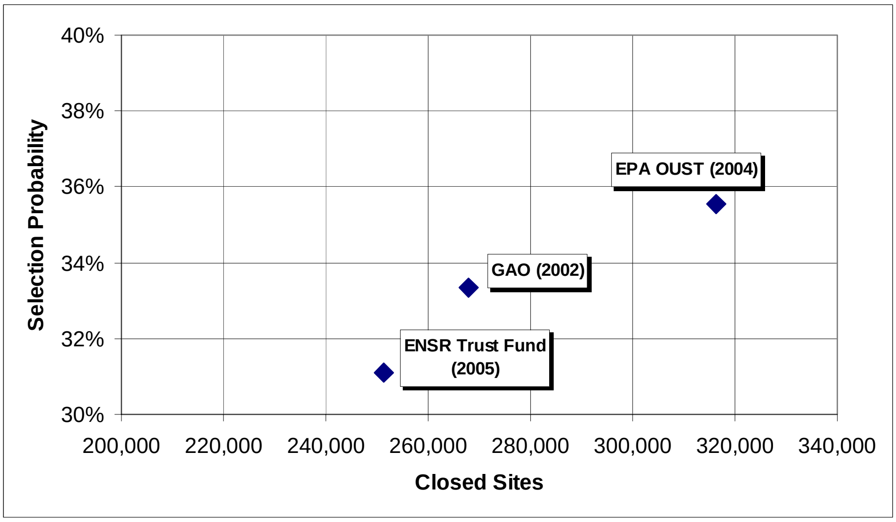


Figure 6. Number of Closed LUST Site Releases (Parameter E)

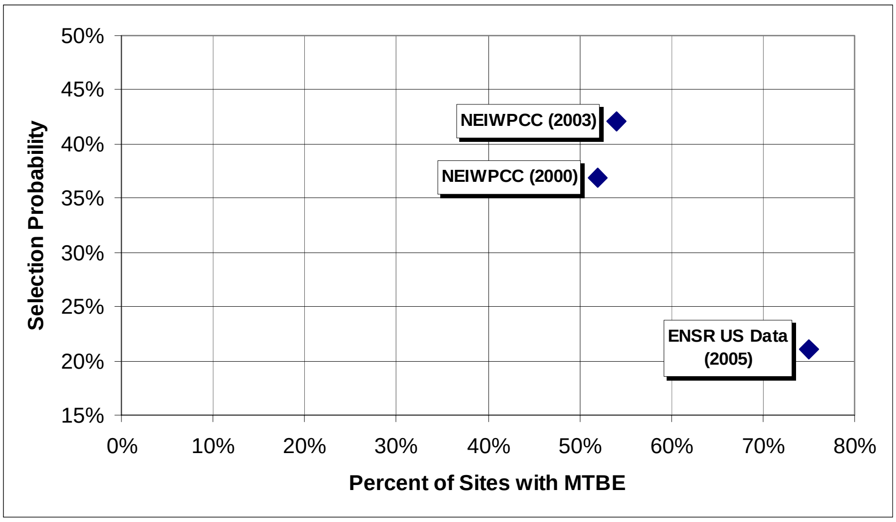


Figure 7. Fraction of LUST Site Releases with MTBE (Parameter K)

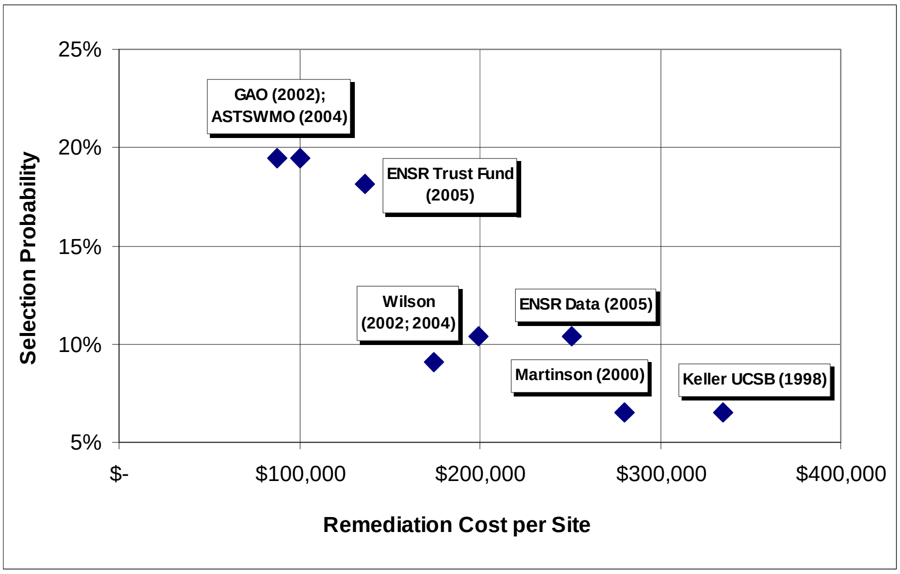


Figure 8. Remediation Cost per LUST Site Release (Parameter O)

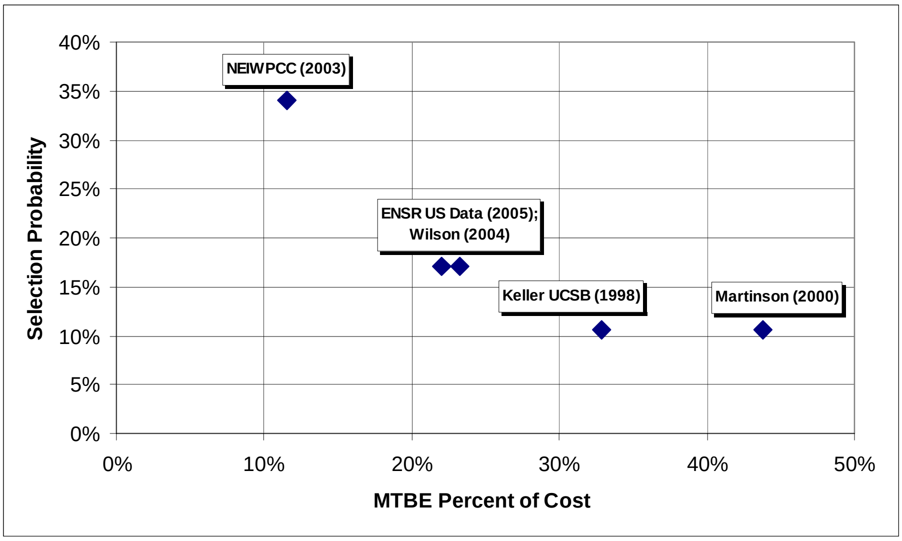


Figure 9. Fraction of Remediation Costs Due to MTBE (Parameter Q)

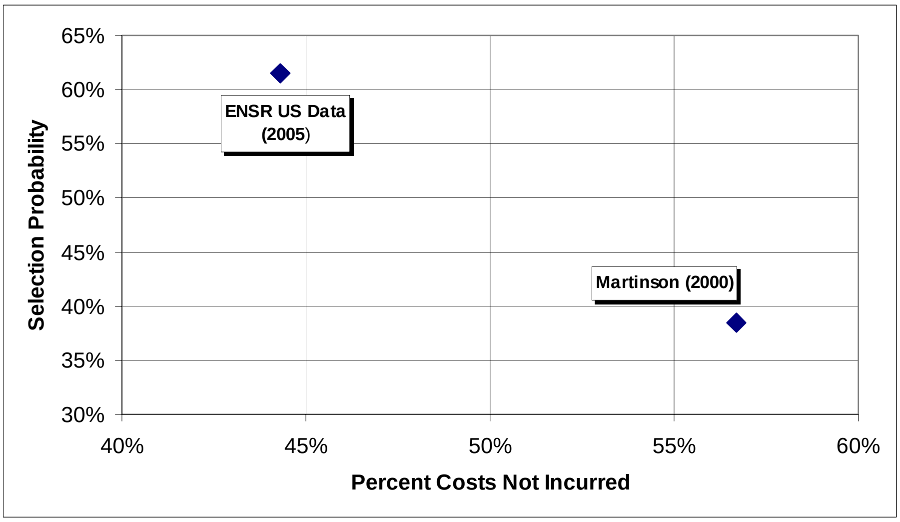


Figure 10. Fraction of Effort Not Yet Incurred For Ongoing Remediation (Parameter AA)

5.6 Output Parameter Distribution

From 100,000 iterations of the Monte-Carlo procedure, a distribution of the cost was determined. Prior to running the procedure, it was determined that no significant correlation existed between the input parameters.

Selected statistics of the generated (mid-range) cost distribution are given in Table 10, and a distribution graphic is provided in Figure 11.

As presented, the distribution generated by the Monte-Carlo procedure represents the distribution of the mid-range values for each of the input variables. A full distribution of all source data was not possible, given that none of the published data sources provided a full data range. The published data sources provided only average, mean, minimum, or maximum values, which enabled the calculation of a mid-range value, but not the calculation of a full source-data distribution.

Table 10. National Cost Summary Statistics Derived from Mid-range of Input Values

Statistic	**Value (billion)**
5th Percentile	\$0.48
Median	\$2.00
Mean	\$2.76
95th Percentile	\$7.70

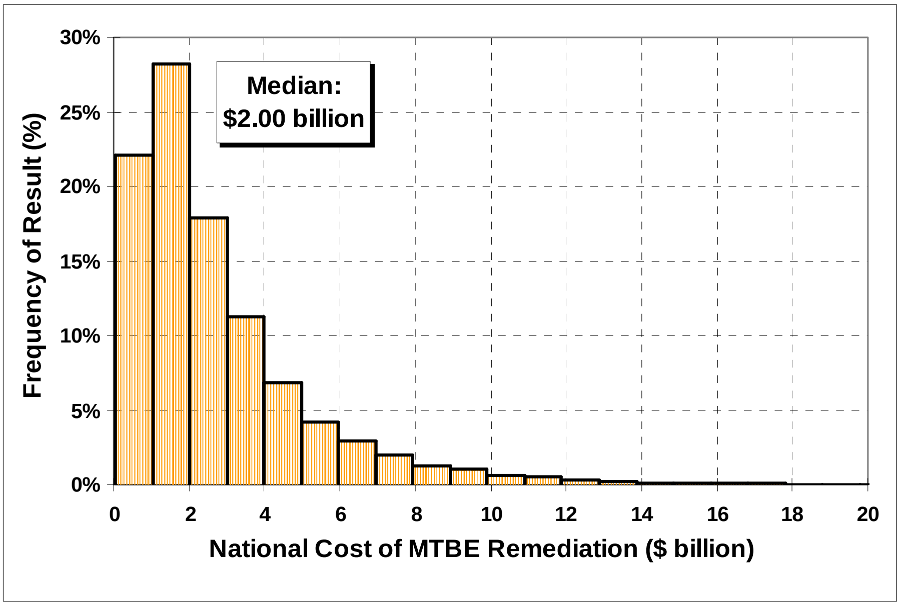


Figure 11. National Cost Distribution Derived from Mid-range of Input Values

6. SENSITIVITY ANALYSIS

When attempting to estimate a cost of this magnitude at a national scale, there are many assumptions and interpretations required. To maximize the precision of a cost estimate, it is necessary to incorporate as much publicly available information as possible. However, with the exception of our internal ENSR data, none of the available sources provide underlying datasets, or a statistical distribution of their results. With this level of uncertainty, much of the published data is subject to interpretation. For example, the basis of average remediation costs reported by different sources varied. The $88,000 unit cost reported by GAO (2002) could be dominated by LUST site releases without MTBE, whereas the Martinson (2004) unit cost of $280,000 is referenced as being inclusive of sites with MTBE. The selection of that parameter alone has an impact on the final cost result.

In addition to the variety of data sources, and clarity of the basis for the reported values, other facets of our calculations can lead to varied interpretations and results. During the peer review process, we received suggestions of items to evaluate in a sensitivity analysis. We combined these suggestions with our own observations, and selected three different scenarios to further assess. The following paragraphs present our analysis of these scenarios, and the results are summarized in Table 12.

6.1 Eliminate Reliability Indices

The reliability factors were selected after compilation of the available data sources. The intent of the cumulative reliability scores was to eliminate potential bias in selecting one particular source over another. This approach appeared to assign greater weight to lower values. For example, the unit costs shown in Figure 8 reveal lower values for GAO (2002) and ASTSWMO (2004) data, both of which received high reliability scores (15 out of a possible 17). To assess the impact of the reliability indices, we reapplied the NCE without the indices, using the same 100,000 iterations of the Monte-Carlo procedure. The result was a median value of $3.19 billion, which is higher than the result presented in this paper.

6.2 Eliminate Author Affiliation Factor

In the interest of minimizing potential bias, we gave preference to public sources over private sources. However, several comments were received during the peer review process, indicating that some of the private data sources could be equally, if not more, accurate than public data sources. The theory being that the author is more familiar with the reported data and underlying datasets. To assess the impact of the author affiliation factor, we recalculated the national cost without this factor, while still retaining the other reliability factors. We again used the same 100,000 Monte-Carlo simulations. The result was a median value of $1.98 billion, which is lower than our baseline result.

6.3 Eliminate Randomness of Differential Cost

An earlier version of the NCE developed in this paper used an “S” parameter, rather than individual “O” and “Q” parameters. The value for S was intended to represent the differential cost of MTBE remediation. A small number of published sources provided a value for S, but many sources provided values for either O (total site cost) or Q (fraction attributable to MTBE). By separating the S parameter into O and Q (i.e., S = O*Q), we were able to increase the number of available values for NCE calculation. During the peer review process, we recognized that this approach may randomly pair mismatching O and Q values during the iterative Monte-Carlo runs. That is, some reported O values may include only non-MTBE sites; if those particular values are combined with Q values intended for those sites with MTBE, the resulting product (O*Q) could present an underestimation of MTBE costs. To remedy this potential underestimation, we eliminated individual O and Q values, and recalculated the national cost using only matching pairs of values (i.e., S values). Table 11 presents the S values used to replace parameters O and Q. The S values are directly from the sources listed in the table.

By eliminating Parameter O, this sensitivity scenario also eliminates those values that were less supported during our peer review process. Specifically, the $88,000 value (GAO, 2002) may be less current than the $100,217 value (ASTSWMO, 2004), based on a representative from ASTSWMO who believes that the GAO value was based on an earlier ASTSWMO estimate. Further, the ASTSWMO (2004) and Wilson (2002) values may not include MTBE-impacted sites and thus, could be biased low for our NCE calculation. Similarly, the value of $136,069 (ENSR Trust Fund, 2005) may also have a heavy weighting of non MTBE-impacted sites, and thus could be biased low.

By focusing exclusively on the S values shown in Table 11, and incorporating no other changes to the NCE calculation, the resulting Monte-Carlo analysis yields a median value of $4.79 billion for the national cost, which is higher than our baseline result. Because this scenario eliminates the four lowest values for this parameter, and retains the four highest values, the increase in the final result is expected. Based on our review of the published source data, it may be inappropriate to rely solely on the sources that report the highest costs. The underlying datasets of those sources appear to be less robust and generally limited to fewer states and sites.

Table 11. Differential Cost of MTBE Remediation (Parameter S)

Source	**Remediation Cost per LUST Site Release (Parameter O)**	**Fraction of LUST Remediation Cost Due to MTBE (Parameter Q)**	**Differential Cost of MTBE Remediation (Parameter S)**
Keller UCSB (1998)	$335,000	33%	$110,550
ENSR US Data (2005)	$251,182	23%	$57,772
Martinson (2000)	$280,000	44%	$123,200
Wilson (2004)	$199,069	22%	$43,795

Table 12. Summary of Sensitivity Analysis

Sensitivity Factor	**Median Result (billion)**
None (No Change)	$2.00
Eliminate Reliability Indices	$3.19
Eliminate Author Affiliation Factor	$1.98
Eliminate Randomness in Differential Cost	$4.79

7. RESULTS AND DISCUSSION

This research yields an estimated value of $2.0 billion for the remediation of MTBE releases from existing LUST sites across the nation. The NCE developed through this research was used to estimate this national cost. The NCE was populated with a series of input parameters obtained from a thorough review of available published data sources, supplemented by internal ENSR data. Each data source was assigned a reliability index based on the comprehensiveness of the underlying dataset. A distribution of possible results was generated using 100,000 iterations of a Monte-Carlo procedure, which consisted of the mid-range values for each data source, matched with the associated source reliability index. The statistical distribution of the mid-range values yields a median value of $2.0 billion.

As clarified throughout this paper, our cost estimate is focused on remediation of MTBE releases associated with LUST sites. As recorded by EPA (EPA OUST, 2004), the types of releases include releases from tank overflows and leaks from pressure-relief valves, dispensers, piping networks, and other equipment typically associated with LUST systems. The release areas include the immediate vicinity of the release, such as soil and groundwater in the source area, as well contaminant plumes emanating from the release, which may include plumes that impact nearby water supplies, such as domestic wells or source-water aquifers. The remediation cost associated with these releases and areas encompasses costs ranging from initial site assessment to remediation and closure.

Assumptions contributing to this derived value are explored in the sensitivity analysis provided in Section 6. As shown, by changing selected inputs into the NCE calculation, one can generate an array of associated results. We consider our baseline assumptions (resulting in the $2.0 billion median value) to be the most balanced and representative set of assumptions, based on our review of the source data. The variations shown in Section 6 are exploratory in nature, to provide practitioners with a sense of how the median value may change if key assumptions are altered.

The range of the distribution presented in Section 5 can potentially be reduced by obtaining additional published source data to expand the available dataset, and by obtaining the full range of each data source to better quantify the underlying data distribution. Despite the variability and limitations of this research topic, the methodology applied is appropriate for the wide range of reported data, and very limited datasets. This work can be expanded upon as desired, to further reduce uncertainties, incorporate limitations discussed in Section 1, and continue to improve the precision of a national remediation cost estimate for LUST site releases where soil and/or groundwater has been impacted by the presence of MTBE.

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PART IV: Radionuclides

Chapter 12

SUMMER INDOOR RADON EXCEEDS WINTER INDOOR RADON

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Abstract: It has been considered true for many years, probably because of commentary in US-EPA publications for the general public, that winter concentrations of indoor radon are greater than summer concentrations. The higher amount in the winter is attributed to the observation that people normally keep their windows closed during the winter, allowing indoor radon concentrations to rise. The lower radon concentrations in the summer might occur because often open their windows, allowing low-radon outside air to enter the home. It now appears that seasonal rainfall can cause unexpected indoor radon concentrations. In our study of over 1000 homes, where indoor radon was measured seasonally over an entire year, a summer season that had above normal rainfall had higher indoor radon than the prior winter, which had below normal precipitation.

Key words: precipitation, radon monitors, radon, aeroradioactivity

1. INTRODUCTION

Soil and rock are the sources of most radon to which people are exposed. Homes with high concentrations of indoor radon have been discovered in many parts of the Appalachian Mountain system. In the following study regional levels of indoor radon are compared to precipitation, geological unit, home construction factors and soil radioactivity, as measured from an airplane (aeroradioactivity survey). Our investigation has concentrated on a set of over 1000 homes, about 70% of which are in Fairfax County in northern Virginia, and about 30% or which are in the surrounding counties in Virginia and Maryland. The following discussion will discuss primarily the indoor radon measurements within Fairfax County.

2. METHODOLOGY

The indoor radon monitors used in this study are from the Tech/Ops Landauer Corporation in Illinois. They are called "alpha-track monitors" and are of a type long used for geological investigations. The indoor radon monitor has a dust filter through which the radon can pass. A fraction of the radon produces alpha particles that penetrate the small square of plastic film inside the monitors, and produce alpha-tracks that are enhanced by chemical etching.

Participation in the test program required that the homeowner participate in a four-season testing period. The homeowner provided an exact location on a county map which, when compared to a geological map, made it possible to identify the geologic rock unit underlying the home. A questionnaire completed by the homeowner at the start of the test series served to quantify home construction factors (type of basement, age of home, etc.). Another questionnaire was completed at the end of each seasonal measurement interval to describe home use (number of heating days, number of days with opened windows, location of monitor, etc.). The first alpha-track radon monitor in each home was opened near the start of a season so as to facilitate a study of seasonal variations (winter was November, December and January, spring was February, March and April, summer was May, June and July, and fall was August, September and October). At the end of each seasonal interval, the homeowner was sent a quarterly report concerning the radon "picture" in Virginia and Maryland during the previous quarter.

3. EFFECT OF PRECIPITATION

In northern Virginia and southern Maryland, the local weather is monitored by about 300 volunteer weather stations. The weather reports are compiled by the National Oceanic and Atmospheric Administration, and distributed as monthly summaries. According to the weather summaries for the summer intervals, the two subsequent study summers had essentially the same maximum temperatures, but the second summer had about 20% more precipitation than the first summer and about 10% more precipitation than the previous winter, Table 1.

Table 1. Summer weather conditions

SEASON YEAR	TOTAL PRECIPITATION	AVERAGE TEMPERATURE
Summer 1	9.9 inches	84.4 °F
Winter	10.1	48.4
Summer 2	12.0	83.9

Note: This chart was generated from monthly weather summaries titled "Metropolitan Washington Climate Review" that cover Fairfax County, Montgomery County and adjacent areas. The compilations in this table are averages, obtained using measurements from the Washington-National Airport, Baltimore-Washington Airport, and Washington-Dulles Airports.

Although there is some disagreement on the effect of rainfall, we think that when the land surface is capped with intergranular water, soil radon cannot move vertically and escape directly from the soil to the atmosphere. When radon accumulates below this near-surface layer saturated with water in the soil around a home, one would expect that indoor radon would increase.

An overview of the seasonal indoor radon variations can be seen by compiling basement radon measurements in Fairfax County (see Table 2). Although it is commonly thought that indoor radon is always at its greatest concentration during the winter, this is clearly not always the case. The data show that the second summer had more precipitation than the previous winter and the previous summer, and the second summer had a higher regional radon average than the previous winter and the previous summer.

Table 2. Seasonal indoor radon measurements in Fairfax County, Virginia

SEASON AND YEAR	AVERAGE RADON	MEDIAN RADON	% OVER 4 pCi/l	% OVER 10 pCi/l	NUMBER OF HOMES
Basement Indoor Radon Measurements					
Winter 1	5.1pCi/l	3.9pCi/l	49%	9%	286
Spring 1	4.1	2.9	33	5	487
Summer 1	3.0	2.4	23	2	735
Fall 1	3.8	3.0	34	3	772
Winter 2	4.0	2.8	33	5	525
Spring 2	3.9	3.0	33	5	334
Summer 2	4.2	3.5	41	5	126
Fall 2	6.2	4.2	53	9	108

SEASON AND YEAR	AVERAGE RADON	MEDIAN RADON	% OVER 4 pCi/l	% OVER 10 pCi/l	NUMBER OF HOMES
First Floor Indoor Radon Measurements					
Winter 1	3.4pCi/l	2.4pCi/l	23%	5%	39
Spring 1	2.6	1.6	16	4	76
Summer 1	2.1	1.6	11	0	125
Fall 1	2.7	2.2	21	0	115
Winter 2	2.9	2.1	23	2	100
Spring 2	3.1	2.0	24	2	59
Summer 2	3.0	1.8	32	0	22
Fall 2	4.5	3.9	50	5	20

Note: summer 2 higher precipitation than summer 1.

4. OTHER COMPARISONS

From a geologist's point of view, the study area is very useful, comprising of a large diversity of rock units which includes poorly consolidated sediments, sedimentary rocks, igneous rocks and metamorphic rocks. Although the average indoor radon varies considerably from unit-to-unit, the summer-to-summer radon increase caused by precipitation is quite uniform as shown below in Table 3.

Table 3. Summer indoor radon compilations for geological units in Fairfax County, Virginia

GEOLOGICAL ROCK UNIT	NUMBER OF HOMES	AVERAGE RADON	MEDIAN RADON	% OVER 4 pCi/l
Indoor Radon Summer 1				
Coastal Plain Province				
Sedimentary Strata	92	1.9pCi/l	1.7pCi/l	7%
Culpeper Basin				
Diabase	22	1.9	1.7	0
Sandstone/ Conglomerate	40	2.6	1.9	13
Siltstone/Shale	8	5.4	2.7	38
Piedmont Province				
Meta-Mafic Rock	12	2.2	1.4	25
Occoquan Granite	54	2.6	2.0	13
Falls Church Tonolite	21	2.2	2.3	10
Sykesville Formation	107	2.9	2.4	20
Indian Run Formation	36	2.6	1.8	14
Annandale Group	52	3.2	2.6	31
Popes Head Formation	86	3.5	2.8	24
Peters Creek Schist	193	3.8	3.3	36
Indoor Radon Summer 2				
Coastal Plain Province				
Sedimentary Strata	7	2.4pCi/l	2.0pCi/l	14%

GEOLOGICAL ROCK UNIT	NUMBER OF HOMES	AVERAGE RADON	MEDIAN RADON	% OVER 4 pCi/l
Culpeper Basin				
Diabase	4	4.8	2.2	25
Sandstone/Conglomerate	3	5.5	6.5	67
Siltstone/Shale	4	3.5	2.6	25
Piedmont Province				
Meta-Mafic Rock	1	2.9	2.9	0
Occoquan Granite	6	4.0	1.7	33
Falls Church Tonolite	3	2.1	2.5	0
Sykesville Formation	9	3.0	2.1	22
Indian Run Formation	6	4.5	4.0	67
Annandale Group	11	4.7	4.4	64
Popes Head Formation	17	3.7	3.5	41
Peters Creek Schist	42	5.0	3.9	45

Note: summer 2 higher precipitation than summer 1

Other comparisons can be made using home construction factors. Most of the area homes have basements with walls composed of concrete blocks or poured concrete. Earlier studies have shown that basements with concrete block walls tend to have higher indoor radon concentrations during the winter. This is presumably because the blocks are joined by mortar which tends to crack, allowing soil gas enriched in radon to enter. During the study summers, this difference was noted, Table 4. Apparently the effect of basement wall construction persists during the summer, even though the summer is the interval when windows are most frequently left open to admit cooling (and low-radon) outside air.

Table 4. Comparison of basement wall construction with summer indoor radon

SEASON	TYPE OF BASEMENT WALL	AVERAGE RADON	MEDIAN RADON	% OVER 4 pCi/l	NUMBER OF HOMES
Summer 1	Concrete Block	3.0pCi/l	2.5pCi/l	24%	469
	Poured Concrete	3.0	2.3	19	237
Summer 2	Concrete Block	3.8	3.4	41	81
	Poured Concrete	4.6	3.5	40	40

Note: summer 2 higher precipitation than summer 1

Most homes have either a gas or oil furnace or use electrical heat, normally in the form of a heat pump. During the winter, homes with electrical heat tend to have higher than average radon concentrations, presumably because homes with a furnace develop a partial vacuum within the home when the furnace operates, and this partial vacuum draws into the home more radon-poor outside air than radon-enriched soil air. It is also interesting to note that while homes are not heated during the summer, homes with electrical heating systems had higher indoor radon, Table 5. The higher summer indoor radon in the group with electrical heating systems probably occurs because heat pumps are commonly used for whole-home cooling during the summer.

Table 5. Comparison of home heating system with summer indoor radon

SEASON	HEATING SYSTEM	AVERAGE RADON	MEDIAN RADON	% OVER 4 pCi/l	NUMBER OF HOMES
Summer 1	Oil or Gas	2.7pCi/l	2.3pCi/l	18	381
	Electrical	3.7	2.8	31	215
Summer 2	Oil or Gas	3.1	2.5	32	59
	Electrical	5.0	3.9	48	61

Note: summer 2 higher precipitation than summer 1. In the study area, the electrical heating system is usually a heat pump. Homes with a heat pump normally use the device for whole home cooling in the summer. A small percentage of the homes with both a heat pump (used mainly for temperatures above 40 degrees Fahrenheit) also had an oil or gas combustion system. These homes were listed under "Oil and Gas Heating System" since the oil or gas heater is more frequently used during the heating season.

We have found that a good and inexpensive radon potential map can be derived by a survey of surface radioactivity, measured from the air. An aeroradioactivity map is available for Fairfax County. As shown in Table 6, an increase in aeroradioactivity compares well with an increase in indoor radon. Relatively few characterizations of soil over a large area can actually be made during a single season. The only characterization of which the authors are aware is aeroradioactivity, in that several hundred square kilometers can be measured in a week, and several thousand square kilometers can be measured in a single season.

Table 6. Comparison between total gamma aeroradioactivity and summer basement indoor radon in Fairfax County, Virginia

AERORADIO-ACTIVITY	NUMBER OF HOMES	AVERAGE RADON	MEDIAN RADON	% OVER 4 pCi/l
Indoor radon measurements summer 1				
100-200 cps	51	2.7pCi/l	2.1pCi/l	18%
200-300 cps	142	3.0	2.1	23
300-400 cps	262	3.1	2.6	24
400-500 cps	94	4.0	3.1	35
500-600 cps	8	4.8	4.5	63
Indoor radon measurements summer 2				
100-200 cps	5	2.2pCi/l	2.2pCi/l	0%
200-300 cps	16	3.0	2.3	13
300-400 cps	45	4.3	3.7	47
400-500 cps	14	5.5	4.7	57

AERORADIO-ACTIVITY	NUMBER OF HOMES	AVERAGE RADON	MEDIAN RADON	% OVER 4 pCi/l
500-600 cps	1	-	-	-

Note: summer 2 higher precipitation than summer 1

5. DISCUSSION

The indoor radon concentrations in several hundred homes in northern Virginia show a strong dependence on weather conditions. A comparison between the indoor radon signature of the study area during adjacent summers shows generally higher levels of radon during the second summer, based on comparisons using geological units, basement wall construction and home heating system. The higher levels of indoor radon apparently occurred because the second summer had more rainfall, which prevented a significant amount of soil radon from escaping directly to the atmosphere. It now appears that the concentration of indoor radon is related to the amount of rainwater (or snow), which "caps" the ground and prevents soil radon from escaping out of the soil surrounding the home.

One implication of seasonal variations involves the estimation of annual radiation dose related to radon. It now appears that during some intervals, when rainfall is unusually low, indoor radon is reduced. Intervals with more precipitation would be characterized by a higher indoor radon signature. However, as shown in our study, one might find that dry winter conditions and wet summer conditions could result in similar radiation dose. To realistically estimate variations in the annual radiation dose for a large area like a county or state, it would be necessary to create a series of maps which present the radon situation for several combinations of temperature and precipitation.

6. CONCLUSIONS

Indoor radon concentrations show a strong dependence on precipitation, geological unit, home construction and soil radioactivity. Intervals of greater precipitation tend to have higher indoor radon. In a geologically complex terrain where geological units are numerous and genetically different, some units can be associated with significantly higher indoor radon. Homes with concrete block basement walls and electrical heating systems tend to have higher indoor radon. Soils with greater aeroradioactivity tend to have homes with higher indoor radon. With some care, prediction of indoor radon appears possible if the more important parameters are carefully measured.

The discovery of significant summer-to-summer variations, and the observation that sometimes the winter can closely simulate a summer in terms of indoor radon, indicates that single season measurements may not be very useful. This is apparent, even if the season of measurement is the winter. This reinforces the idea that "closed-home" conditions which are thought to simulate winter conditions can sometimes incorrectly estimate the annual dose, and that single short-term measurements under this condition should be interpreted with caution.

Chapter 13

MEASUREMENT UNCERTAINTY OF ACTIVATED CHARCOAL AND ALPHA-TRACK INDOOR RADON DETECTORS

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Abstract: According the US-EPA protocol, when a home is purchased it should be tested for indoor radon using a short-term (2-7 day) device like a container of activated charcoal, and the indoor radon concentration should be less than 4 pCi/L. When a home is tested because long-term occupancy is likely (e.g. many years), the test is commonly done using a long-term (e.g. 3-month) device like a container of film that can record the tracks produced by alpha tracks generated by radon and its immediate radioactive decay products. For long-term occupancy, the US-EPA recommends that the indoor radon concentration be less than 2 pCi/L. In our study of over 1000 homes, using both short-term activated charcoal detectors and long-term alpha-track detectors, we found that at the 70% confidence level, when trying to estimate the average indoor radon concentration over an entire year, an uncertainty of +/- 90% had to be applied to single activated charcoal detectors and +/- 30% to single alpha-track detectors.

Key words: indoor radon, radon monitors, home inspections

1. INTRODUCTION

By the early 1990's, homeowners across the world were alerted by a series of news media reports noting the recent discoveries of homes with dangerously high concentrations of indoor radon. More reports followed soon after concerning the radon testing activities of federal, state and county agencies concerned with public health. News media and civic association attention were directed toward radon testing companies, and toward investigators at George Mason University who had been studying airborne and waterborne radon as geological indicators of soil chemistry. Together with community activists, the investigators had developed a program designed to better understand the health risk related to radon in Virginia and Maryland. Through this arrangement, indoor radon concentrations were measured at weekly and monthly intervals in approximately 1800 homes. Over the study interval, to maintain community interest, homeowners were sent approximately 100 pages of material, including quarterly reports, informative literature about radon, and questionnaires.

The study concentrated on seasonal measurements of indoor radon, where winter is November, December and January, spring is February, March and April, summer is May, June and July, and fall is August, September and October. A questionnaire completed by the homeowner at the start of their test series served to quantify home construction factors (type of basement, age of home, etc.). Another questionnaire completed at the end of each seasonal measurement interval was used to describe home use (number of heating days, number of days with opened windows, etc.). Monitors were placed in a basement where possible. About 90% of the homes had basements, and of those, about 90% had the monitors in the basement. An activated charcoal monitor was placed in approximately 500 homes. Enough data were collected to facilitate a comparison between single activated charcoal measurements and single alpha-track measurements with the annual (year-long average) radon concentrations in many homes. The comparison is the purpose of this paper.

2. PRECISION AND ACCURACY

The most important problem faced by homeowners in determining if their homes have a radon problem is that radon is known to fluctuate rapidly, with low point to high point changes – due to weather and home use – commonly more than 100%. The question that this paper will address concerns the length of time required to obtain a meaningful estimate of the annual radon concentration.

When home owners test their own home, we found that radon monitors are usually placed in the home for less than one year, and subsequent testing is often not done even if the first measurement is of some consequence. The best estimate of indoor radon would obviously be obtained by monitors placed in homes at regular intervals over many years, or by indoor radon monitors carried by people over a significant portion of their lifetime. Neither method is likely to be used by even a small portion of the population. Since homeowners usually test their home once, with one detector, and since radon fluctuations do occur, the question becomes one of adequacy. Although there is some debate on this point, it is generally recognized that since both types of monitors have been approved by the US-EPA, they carry a measurement uncertainty of about +/- 25% at the 90% confidence level for their measurement intervals. The U.S. Environmental Protection Agency requires that the uncertainty be less than +/- 25% at 4 pCi/l (1 pCi/l = 37 Bq m $^{-3}$). But the real question is, how accurately does one want to estimate the annual radon concentration? How well can charcoal detectors and alpha-track detectors estimate the year-long average?

In the following discussions, it is assumed that neither the charcoal monitor nor the alpha-track monitor yield results that are biased toward too high or too low measurements. It is also assumed that the pattern of deviation of a single charcoal or alpha-track measurement from annual average is considered to be related to natural variations in indoor radon concentrations. The last assumption is that the annual radon concentration can be adequately estimated by averaging radon concentrations from a series of four alpha-track measurements, each over three months. With these assumptions, single charcoal and single alpha-track measurements can be compared to annual radon concentrations.

3. RADON MONITORS

The charcoal monitors used in this study (Air Chek, Inc) have a vapor barrier because the adsorption characteristics of charcoal monitors change measurably under "uncomfortable" humidity. Generally, a measurement interval of three to four days was used. In the following discussions, we report on homes having one charcoal measurement and an estimate of annual radon concentration, and on additional homes with a single charcoal measurement and an alpha-track measurement over the season of charcoal measurement.

The alpha-track monitors used in this study (Tech/Ops Landauer, Inc) have a dust filter through which the radon can pass. The nuclear tracks record on the small square of plastic film inside these monitors and are not affected by normal variation in home humidity and temperature. The dislocation sites (more commonly called alpha-tracks) are permanently recorded on film. Estimates of analytical uncertainly for the alpha-track monitors are dependent on the measurement interval, so an interval of three months was utilized.

4. ANNUAL RADON AND CHARCOAL MONITORS

Table 1 presents a comparison between activated charcoal measurements with annual radon concentrations. Charcoal-to-annual ratios of less than 1.0 represent cases where the charcoal measurement was less than the annual measurement: ratios of more than 1.0 represent cases where the charcoal was greater than the annual measurement.

Table 1. Ratios between the annual indoor radon measurements and indoor radon measurements obtained using containers of activated charcoal exposed for 3-6 days.

Charcoal/Annual	Measurements	Charcoal/Annual	Measurements
0.0 to 0.9	2 homes	1.01 to 1.1	14 homes
0.1 to 0.19	4	1.1 to 1.2	17
0.2 to 0.29	9	1.21 to 1.3	10
0.3 to 0.39	3	1.31 to 1.4	4
0.4 to 0.49	8	1.41 to 1.5	1
0.5 to 0.59	10	1.51 to 1.6	1
0.6 to 0.69	11	1.61 to 1.7	3
0.7 to 0.79	14	1.71 to 1.8	1
0.8 to 0.89	15	1.81 to 1.9	1
0.9 to 0.99	9	1.91 to 2.0	3
1.0	1	Over 2.0	11

56% of the charcoal measurements were less than the corresponding annual radon measurement and 44% were greater than the annual measurement.

Table 2 provides an estimate of the uncertainly that should be applied to a single charcoal measurement in order to estimate the possible annual radon concentration. For example, the data show that 67% of the homes yield a charcoal-to-annual deviation of up to +/- 40%. This could be rephrased to say that at the 67% confidence level, the uncertainty that would be applied to a single charcoal measurement is +/-40% of the charcoal measurement. Similarly, one would apply +/- 90% uncertainty to the charcoal measurement if one wanted to be very sure (e.g., 90% confidence level) of the possible annual radon concentration. Obviously, these uncertainties are considerably larger than the +/- 25% uncertainty noted earlier that is applied to a single measurement but only over the measurement interval. The much larger uncertainty is a consequence of the need to estimate the annual radon concentration as compared to the much less useful radon concentration during the measurement interval.

Table 2. Summary of radon measurements, in terms of the deviation between 3-5 day activated charcoal measurements and the annual measurement.

Deviation Above and Below Annual	Homes Within Each Deviation Level
Charcoal is +/- 10% of Annual	Found in 16% of the Homes
+/- 20%	35%
+/- 30%	53%
+/- 40%	67%*
+/- 50%	75%
+/- 60%	77%
+/- 70%	83%
+/- 80%	88%
+/- 90%	90%

5. ANNUAL RADON AND ALPHA-TRACK MONITORS

Table 3 shows that winter alpha-track measurements tend to be greater than the annual radon concentration, and summer measurement tend to be less than the annual concentration. Spring and fall measurements are less biased toward higher of lower measurements. This situation is obviously related to natural seasonal variations. One could apply a correction factor to adjust a measurement (Table 4), and one could then apply an uncertainty to the measurement to estimate the annual radon concentration.

Table 3. Ratios between the annual (year-long average) indoor radon measurements and the indoor radon measurements obtained using alpha-track monitors exposed for 3 months. Ratios are from 4 comparison experiments, plus the totals of the 4 experiments.

Alpha/Annual	**Number of Homes in Each Seasonal Interval**				
Measurements	Winter Homes	Spring Homes	Summer Homes	Fall Homes	Total Homes
0.0 to 0.19	2	3	2	5	13
0.2 to 0.39	9	21	34	13	77
0.4 to 0.59	20	44	128	34	226
0.6 to 0.79	76	138	227	85	526
0.8 to 0.99	154	234	172	203	763
1.0 to 1.10	126	146	60	140	472
1.11 to 1.3	110	136	76	112	434
1.31 to 1.5	109	71	14	87	281
1.51 to 1.7	78	20	9	24	131
1.71 to 1.9	22	6	3	11	42
Over 1.91	22	10	3	6	41
% with 3-Month <Annual	32%	53%	80%	41%	
% with 3-Month >Annual	67%	45%	19%	57%	

Alpha/Annual	**Number of Homes in Each Seasonal Interval**			
Median 3-Month/ Annual Ratio				
	1.12	0.98	0.83	1.04
*Average Seasonal Bias				
	+12%	-2%	-17%	+4%

* Seasonal Bias can be used to adjust a seasonal measurement so as to more closely estimate an annual measurement. For example, using the Summer column, increasing a summer measurement by 17% is close to the annual measurement.

Table 4. Summary of radon measurements, in terms of the deviation between a 3-month alpha-track measurement (season not designated) and the annual (year-long average) measurement

Deviation Above and Below Annual	**Homes Within Each Deviation Level**
3 month is +/- 10% of Annual	Found in 30% of the Homes
+/- 20%	60%
+/- 30%	75%*
+/- 40%	83%
+/- 50%	90%

6. DISCUSSION

A comparison between Table 2 and 4 shows the dramatic difference in the uncertainty estimate between the charcoal and the alpha-track detector. For example, one could say that at the 67% confidence level, one would apply a +/- 40% uncertainty to the charcoal measurement (see Table 2) and a +/- 25% uncertainty to the alpha-track measurement (see Table 4). To be very sure (90% sure) of the possible annual radon concentration, one would apply a +/- 90% uncertainty to the charcoal measurement and a +/- 50% uncertainty to the alpha-track measurement.

As was noted for the charcoal monitors the deviation of single alpha-track measurements from annual radon concentrations does not appear to be a function of indoor radon concentration. Deviations of about the same magnitude occur for both low and high radon concentrations for all seasonal intervals. The deviations are therefore concluded to be the result of natural variations in radon, and not measurement inaccuracies.

7. CONCLUSIONS

Almost all indoor radon measurements in Virginia and Maryland are obtained by homeowners using activated charcoal radon monitors or alpha-track monitors. Manufacturer estimates for the measurement interval (a few days for the charcoal and a few months for the alpha-track monitors) uncertainties are about +/- 25% at the 90% confidence level. However, much larger uncertainties must be applied to estimate the annual radon concentration. This uncertainty in estimating the annual radon concentration was about +/- 90% for the charcoal monitors and about +/- 50% for the alpha-track monitors.

One implication of these uncertainty estimates is that charcoal monitors should best be considered a "sampler" of indoor radon that is useful only for the measurement interval. Homeowners who wish to obtain a better estimate of annual radon should be advised to use a series of charcoal monitors (at least 5 over 10 weeks), or a single alpha-track monitor exposed for perhaps three months. It may also be important to reconsider the validity of using 4 pCi/l as an "action level" to be applied to a single charcoal measurement. A single charcoal measurement of 3.9 pCi/l could in fact come from a home that has an annual radon concentration of between twice and half of the single charcoal measurement.

Another important observation concerns the concept of "closed-home" measurements. The available data show that the closed-home condition often yields measurements that are less than the annual radon concentrations, and very often less than the "worst-case" conditions thought to prevail in the winter. Also, variables such as soil radon and soil permeability, as well as weather and home construction may interact in ways that often prevent a closed-home condition from facilitating a short-term (charcoal monitor) worst-case measurement. The obvious implication is that homeowners, realtors and scientists should be cautious when using charcoal measurements to estimate annual radon concentrations. This caution, plus a realistic estimate of the measurement uncertainties, can generate radon estimates that have significance.

PART V: Remediation

Chapter 14

THE VALUE OF ORGANOCLAYS IN PERMEABLE BARRIERS

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Abstract: The function of permeable barriers is to first, allow the groundwater to flow freely through them, and second, to entrap or destroy chemical contaminants such as metals and organic hydrocarbons. Certain organically modified clays have the ability to act as anion and cation adsorbents, allowing them to remove heavy metals such as Pb and Zn.

A Polar Organoclay removes anions such as hexavalent chrome, arsenate, phosphates, sulfates and nitrates from water. It can also remove humic acids, perchlorate and other negatively charged organic compounds.

A neutral type of Organolcay removes creosote, PNAH's, PCB, dioxene, BTEX and other non-polar organic hydrocarbons of low solubility very effectively.

For good measure, powdered activated carbon can also be included in the barrier mix. Such a design allows for a barrier that retards the movement of organic compounds and metals into the surrounding environment, be that a river or a lake.

This article presents new data on the organoclays capacity for contaminant removal which where obtained in column studies in the laboratory of the University of Virginia.

Key words: Organoclay; sulfate; phosphate; nitrate; perchlorate; chromium

1. INTRODUCTION

Organoclays have been a main staple in the groundwater remediation industry and industrial wastewater cleanup for some 20 years. They are usually incorporated as part of an activated carbon treatment train, such as in “pump and treat systems”. Activated carbon becomes fouled quickly in the presence of oil, grease, natural organic matter, PNA’s, PCB, BTEX, chlorophenols and other large organic hydrocarbons of low solubility. The end user improves the economics of the system drastically by including organoclay, because this media removes seven times as much oil from water as does activated carbon, thus cutting operations costs in half. The “roll off” problem, which takes place in the pores of activated carbon when adsorbed benzene is kicked back off by toluene and xylene due to their lower solubility, is eliminated (Alther, 2004). In those applications, a blend of organoclay with anthracite is usually provided. The organoclay tends to swell somewhat due to the presence of oil (which also reduces channeling), and reduces the filling of interstitial pore spaces by oil, which also results in fouling. Anthracite’s bulk density is almost the same as that of organoclay; therefore separation of the two media after the first backwash is minimized.

When used as a sediment barrier, the organoclay is present as a granule of about 20 x 50 mesh size. The purpose of that size is so that the granules blend in with the sediments, which are usually sand or sandy silt. The organoclay functions as a cap to retard the upward movement of contaminants into the surface water. Groundwater discharges into rivers and lakes. The plume is then either intercepted in this manner, by capping the river sediments with organoclay, or a slurry wall intercepts it where organoclay is blended in with the back fill. Slurry walls are used either as a permeable barrier for new landfills or superfund-type sites, or they are placed as secondary barriers around old, existing walls, which are leaking. In that case, the vibrating-beam type slurry wall is used because it is only 10 inches wide, vs. the three feet of conventional types, and they are much easier and quicker to construct. The backfill of the vibrating-beam slurry wall consists of powdered cement, bentonite, and organoclay, with the emphasis of the design being on the creation of a permeable barrier (Alther et al, 2003). Landfill liners can be constructed with granular or powdered organoclay, depending on the existing soil type (Alther, et al, 1988).

Soil stabilization is conducted by admixing with the soil a blend of Portland cement, fly ash, powdered organoclay and powdered activated carbon. Such a system, which has to pass the TCLP test, fixates organic hydrocarbons and heavy metals. There are two mechanisms by which organoclay and the contaminants are fixated:

In micro-encapsulation, the microscopic level, the organoclay and the entrapped organic contaminants are entrapped within the crystalline matrix of the solidified mass. This prevents degradation of the organoclay into ultra fine particles, which migrate and, potentially, release organic contaminants. Without the organoclay, the organic contaminants are not bound to the crystalline structure created by the cement and are easily released back into the environment.

In macro-encapsulation, at a larger scale, the organoclay with the sorbed organic contaminants is physically entrapped within the voids of the cementitious matrix inside the discontinuous pores. Only extreme freezing or thawing could break down this structure (Alther, et al, 1991).

2. DESCRIPTION OF ORGANOCLAY

Organically modified clays consist of bentonite, which is modified with quaternary amines (Theng, 1974). The major constituent of bentonite, which is a chemically altered volcanic ash, is the clay mineral montmorillonite. It has a cation-exchange capacity of 70-95 meq/g. The quaternary amines, which are used for this purpose, are of the cationic ammonium chloride type, which have a positive charge on one end of the chain. This charge, derived from the nitrogen ion at the carboxylic head, ion exchanges with sodium, calcium and magnesium ions on the surface of the montmorillonite. In this fashion, the hydrophilic clay becomes hydrophobic or organophilic and the entire structure becomes a non-ionic surfactant with a solid base. Upon introduction of some moisture, the amine chain, which hitherto lies on the clay platelet surface like the hair of an animals fur lies on its body, extends now vertically into the water. As organic hydrocarbons of low solubility pass by the particle, they dissolve into the organic phase where they are more soluble. This process is called "partitioning"(Smith & Jaffe, 1994). When an immiscible organic solvent such as octanol is added to water, which includes contaminants of low solubility, such as PCB, a portion of this compound will move out of the water and into the octanol, where it is more soluble. The relative solubility determines the amount retained in each phase. The concentration ratio of this compound in the two phases is constant over a wide range. This is known as the "partition coefficient, k", in this case the "Kow" octanol-water coefficient (Mortland et al, 1986).

This terminology can now be extended to contaminants partitioning from the water phase onto a solid phase, such as organic cations sorbed onto clay surfaces. The higher the solution concentration of a compound and the lower its solubility, the larger the quantity removed by the organoclay through partition. For example, the removal efficiency of organoclay for phenolic compounds is inversely related to the water solubility and amount of chlorination of the compound. Therefore, Pentachlorophenol (PCP, 14 mg/kg solubility in water) is removed in much larger amounts than straight phenol (77,500 mg/kg solubility). By plotting the solubility vs. the n-octanol water partition coefficient onto a graph, the relative ease of removal of organic hydrocarbons by organoclays can be estimated.

Since there are always more amine chains available than can be stoichiometrically affixed to the montmorillonite, the remainder tends to adhere to the fixated surfactant chains by a “tail-tail interaction”. That means that a non-ionic organoclay does have a small positive charge, which allows it to remove some anions, such as hexavalent chrome. Therefore, the organoclay has a slight anion removal capacity. It has become polar.

Since the bentonite, which makes up the bulk of the organoclay, is a natural cation-exchange resin, it retains some cation-exchange capacity, which helps in reducing the heavy metal content of the groundwater, which passes through the barrier (Alther, 2004).

3. LABORATORY TESTING METODS

3.1 The “Mini-Column” Technique

One gram of powdered organoclay is packed into a small vial or mini-column. A spiked solution of water is pumped through this column until the influent concentration of the contaminants equals that in the effluent. In this manner, the effectiveness of the organoclay for removing a certain organic hydrocarbon from water can be quickly determined. The advantage of this method is that the equilibrium concentration is the same as the influent concentration, and therefore under ready control (Alther, 2002).

3.2 The Jar Test

This test describes a single point isotherm, which is created by contacting a known weight of sorbent with the contaminated water. A known weight of sorbent, for example 1 gram, is slowly added into a 1000 ml jar filled with the contaminated water. The sorbent is then dispersed in the water by a shaking mechanism, a magnetic stirrer, or a paddle. After a predetermined time, usually 10 minutes, the solids are allowed to settle, followed by centrifugation. The amount of the remaining contaminant in the water is then determined. This test provides a quick performance evaluation, without having to perform the 10-point ASTM Isotherm test.

3.3 Column Test

The capacity of granular (8x30 U.S. mesh size) organoclay to remove heavy metals was also tested by means of a column test. A 30-inch long and 3-inch diameter column was constructed from poly-vinyl-chloride (PVC) and filled with the organoclay. A large amount of water was pored into a container and spiked with six metals, in this case Cu, Cd, CrIII, Ni, Zn, and Pb, and the solution forced through the column with a peristaltic pump. The column was first backwashed for several hours to displace air in pores and remove any fines. Once in operation, samples of the water where periodically collected and analyzed by means of Acetylene-Air Flame/ Atomic Adsorption (at the laboratory of the Dept. of Environmental Engineering, University of Virginia). Anions were also passed through columns in a separate set of tests.

4. RESULTS OF LABORATORY TESTS

4.1 Mini-Column Tests

In this test, powdered organoclay (1 gram), powdered activated carbon (1 gram) and a combination of powdered organoclay (0.5 gram) followed by powdered activated carbon (0.5 gram, in the same vessel), where tested by passing distilled water spiked with benzene, toluene and naphthalene through the vessel (Alther, 2002). The results are shown in Figure 1.

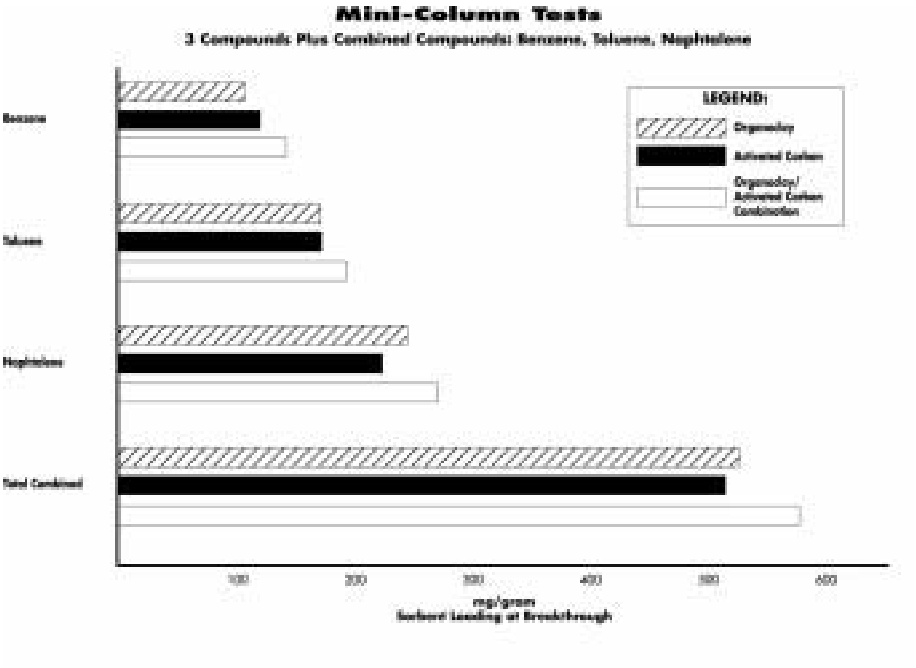

Figure 1. Mini-column tests showing the efficiency of organoclay for removing metals from water, followed by activated carbon, followed by the two sorbents in sequence in the same vial, in the removal of petroleum hydrocarbons from water.

Benzene breaks through first, followed by toluene and then naphthalene. This sequence is expected based on the solubility of these compounds.

Soil Stabilization. Table 1 below shows the results of tests conducted by mixing a sample of the solidification ingredients in a Hobart mixer with the contaminated soil.

An interesting observation is that the organoclay totally fixated highly soluble compounds such as vinyl and methylene chloride, acetone and chloro-ethylene compounds.

Table 1. Results of Laboratory Tests on Soil Stabilization. Jar tests for removal of heavy metals by organoclay.

Reagent: **90% silicates including cement** **10% organoclay**		**Mix Ratio:** **80% soil sludge** **20% reagent** **(i.e. 2% organoclay)**	
Test Number	**Contaminant**	**Contaminant Concentration**	
		Before Treatment	**After Treatment**
1	Vinyl Chloride Methylene Chloride Acetone	24 ppm 38 ppm 2,600 ppm	ND 7 ppb 151 ppb

Reagent: **90% silicates including cement** **10% organoclay**		**Mix Ratio:** **80% soil sludge** **20% reagent** **(i.e. 2% organoclay)**	
2	PCB (Alchor 1260)	320 ppm	ND
3	Total Grease & Oil	15,000 ppm	5 ppm
4	Creosol	7.5 ppm	0.4 ppm
5	Dichloroethylene	26-110 ppm	0.8 ppm
	Trichloroethylene	17-95 ppm	ppm
	Toluene	110-320 ppm	1.2 ppm
	Xylene	20-55 ppm	0.2 ppm
	Napthalene	22-43 ppm	0.02 ppm
	PCB	5-20 ppm	ND

Two organoclays where evaluated for their removal capacity of Pb from water, using EPA 6010 method. The organoclay included 23% of quaternary amine. Testing it with water, which contained 5 ppm and 10 ppm of Pb, respectively, showed that the organoclay removed Pb to less than 0.05 ppm in either case.

Another organoclay that contained 28% quaternary amine, was tested for its capability to remove Zn and Cd from water (EPA 6010 method), using 2 grams of clay, 100 ml water, pH 3-5; mixed in jar for 20 minutes.

The results are:

Input: 1 ppm Zn	Ret. less than 0.05 ppm;	Input: 2 ppm Cd	Ret. 0.11 ppm
5	0.71	5	1.5
10	7.2	10	7.1
1 ppm Cu:	0.03	2 ppm Ni	0.2
5	0.09	5	1.8 ppm
10 ppm	4.4 ppm		

These data show that 2 gram (sample size) of the organoclay can remove about 1.5 ppm of the metal.

Mercury was removed from water with an organoclay containing 29% of quaternary amine, using EPA 7470 testing method:

Inflow: 1 mg/l mercury;	outflow: 0.04 mg/l
0.5 mg/l	0.026 mg/l
0.1 mg/l	0.004 mg/l
0.2 mg/l	

4.2 Column Tests, Heavy Metals Removal

Tables 2-11 show the results of a column test conducted with granular organoclay, on a composite sample of six different metals. The U.S. mesh size of these granules is +8x-30 mesh, with a porosity of 36% (0.36). Calculations show that some 17% of the surface area of the bentonite is still available for ion exchange after conversion to an organoclay. Therefore the ion exchange capacity of the granular organoclay is about 0.16 meq/100 grams.

Table 2. Sorbent mass, porosity, flowrate and residence time information for each column experiment.

		Mass	**Porosity**	**Flow Rate**		**Residence Time**	
Metal	**Sorbent**	**(kg)**	**(lbs)**		**(mL/min)**	**(gal/hr)**	**(min)**
Pb	Organoclay	2.8	6.2	0.32	135	216	8.40
Cd	Organoclay	2.3	5.17	0.42	125.5	199	11.2
Cu	Organoclay	2.9	6.4	0.27	114	182	8.05
Zn	Organoclay	2.9	6.4	0.31	133	213	8.10
Cr	Organoclay	2.54	5.6	0.37	164.4	263	8
Ni	Organoclay	2.41	5.3	0.38	147.3	236	9.09

Table 3. 95% Breakthrough of each metal for the sorbent material given in pore volumes and minutes with estimated mass of metal sorbed per mass of sorbent in mg/kg, lb/lb and percent basis.

		Breakthrough		**Mass Sorbed**		**Mass Sorbed/Mass or Sorbent**		
Metal	**Sorbent**	**(pore vol.)**	**(min)**	**(mg)**	**(lb)**	**(mg/ kg)**	**(ln/lb)**	**% by weight**
Pb	Organo-clay	31.56	264	12,164	0.02682	4,321	0.004321	0.432%
Cd	Organo-clay	13.9	162.9	4,319	0.0095	1,841	0.0018	0.18%
Cu	Organo-clay	48*	386*	3,580	0.00789	1,233	0.001233	0.12%
Zn	Organo-clay	15.8	128	2,771	0.00611	950	0.000950	0.095%
Cr	Organo-clay	6.2	67.77	820	0.00180	323	0.000323	0.032%
Ni	Organo-clay	8.1	73.68	1,382	0.0029	572	0.000572	0.0572 %

Table 4. Column tests with sulfate (same description as Table 2). TC-75=Polar Organoclay

Sorbent	**Mass Sorbent**		**Porosity**	**Flow Rate**		**Residence**
	(kg)	(lb)		(mL/min)	(gal/hr)	(min)
TC-75	2.3	4.9	0.30	60	0.96	20

Table 5. Column tests with sulfate (same description as Table 3).

Sorbent	**Breakthrough**		**Mass Sorbed**		**Mass Sorbed/Mass Sorbent**		
	PV	**Min**	**(mg)**	**(lb)**	**(mg/kg)**	**(lb/lb)**	**(% by sorbent)**
First 95%	47	940	27,745	0.062	12,644	0.0126	1.26%

Sorbent	**Breakthrough**		**Mass Sorbed**		**Mass Sorbed/Mass Sorbent**		
breakthrough							
Second 95% breakthrough	12	240	2,697	0.006	1,226	0.0012	0.12%
Total	59	1,180	30,442	0.068	13,870	0.0138	1.38

Table 6. Column tests with phosphate (same description as Table 2).

Sorbent	**Mass Sorbent**		**Porosity**	**Flow Rate**		**Residence**
	(kg)	**(lb)**		**(mL/min)**	**(gal/hr)**	**(min)**
TC-75	2.2	4.9	0.30	60	0.96	20

Table 7. Column tests with phosphate (same description as Table 3).

Sorbent	**Breakthrough**		**Mass Sorbed**		**Mass Sorbed/Mass Sorbent**		
	PV	**Min**	**(mg)**	**(lb)**	**(mg/kg)**	**(lb/lb)**	**(% by sorbent)**
First 95% breakthrough	60	1,200	9,648	0.021	4,385	0.0043	0.43%
Second 95% breakthrough	17	340	2,033	0.004	924	0.0009	0.09%
Total	77	1,540	11,681	0.025	5,309	0.0052	0.52%

Table 8. Column tests with nitrate (same description as Table 2). EC-199=Non-polar Organoclay.

Sorbent	**Mass Sorbent**		**Porosity**	**Flow Rate**		**Residence**
	(kg)	**(lb)**		**(mL/min)**	**(gal/hr)**	**(min)**
TC-75	2.3	5.0	0.30	156	2.5	6.4
EC-199	2.2	5.0	0.31	160	2.5	6.3

Table 9. Column tests with nitrate (same description as Table 3).

Sorbent	**Breakthrough**		**Mass Sorbed**		**Mass Sorbed/Mass Sorbent**		
	PV	**Min**	**(mg)**	**(lb)**	**(mg/kg)**	**(lb/lb)**	**(% by sorbent)**
TC-75	142	928	52,485	0.117	23,850	0.023	2.385
EC-199	85	580	27,624	0.062	12,556	0.012	1.255

Table 10. Column tests with arsenate, perchlorate and chromium (VI) (same description as Table 2).

Sorbent	**Mass Sorbent**		**Porosity**	**Flow Rate**		**Residence**
	(kg)	**(lb)**		**(mL /min)**	**(gal/hr)**	**(min)**
TC-75 arsenate	0.396	0.88	0.33	8.3	.0133	20
TC-75 perchlorate	0.389	0.87	0.32	8.3	0.133	20
TC-75 chromium (VI)	0.391	0.87	0.33	8.3	0.133	20

Table 11. Column tests with arsenate, perchlorate and chromium (VI) (same description as Table 3).

Sorbent	**Breakthrough**		**Mass Sorbed**		**Mass Sorbed/Mass Sorbent**		
	PV	**Min**	**(mg)**	**(lb)**	**(mg/ kg)**	**(lb/lb)**	**(% by sorbent)**
TC-75 arsenate	27	540	715	0.0017	1,896	0.0017	0.18%
TC-75 perchlorate	10	200	259	0.0006	655	0.0007	0.07%
TC-75 chromium (VI)	25	500	2,319	0.005	5,858	0.0058	0.58

5. CASE HISTORIES

5.1 Soil Stabilization

A rolling mill sludge, which contained 10% oil and grease, was stabilized with a mixture of cement, silica additives and organoclay. This resulted in a mixture of 80% sludge, 17.7% cement blend, and 2.3% organoclay. Treated with these compounds, the sludge had unconfined compression strength of greater than 50 psi (after 28 days of curing per TCLP), and the TCLP yielded less than 5-ppm oil and grease. Powdered organoclay has the capability of removing 80% or more of oil and grease, from water.

A large Midwestern utility company, which owned property that included a former manufactured gas plant (MGP) site next to a river, had a soil on its site stabilized. This soil was contaminated with coal tar, which includes heavy oils (Bunker C) and pitch. This mixture included benzene, toluene, naphthalene, phentathrine, pyrene and phenolic compounds. The coal tar contaminated the soil below the groundwater table to a debt between 12 to 25 feet. Sediments in the river where contaminated at the sediment/water interface, to a debt of 3 feet

The mixture that was blended with the soil and sediments consisted of fly ash, Portland cement, powdered organoclay and powdered activated carbon. 22 truckloads of organoclay and activated carbon, each, were used.

The mixing mechanism consisted of an *in-situ* drilling system whereby the mixture was injected into the soil, and soil/mixture columns where constructed. The mixing of the additives was performed with a pug mill (asphalt type) mixer. At the bottom of each column sodium silicate was added to ensure maximum strength. The columns showed consistently more than 50 psi unconfined compression strength and passed the TCLP test.

5.2 Barrier Construction Next to a Refinery

A refinery next to the terminal of the Port of Portland in Oregon was responsible for an oil-contaminated Superfund site, from which oils oozed into the estuarine and coastal waters. A 15-feet wide wall was constructed; the contaminated soil was excavated and disposed of in a Subtitle D disposal site. A backfill, blended with 1% of powdered organoclay, was installed to function as a permeable sorption barrier. Laboratory tests had established that such a system would prevent oil from passing through the barrier, without creating a “bath tub” filled with water. Other authors have since conducted scientific studies, corroborating the feasibility of this method (Lo et al, 1997).

5.3 Landfill Liner Design

Such liners, which include organoclay, where first discussed by Alther et al (1989), and later by Smith et al, 2000. The short of it is, that a permeable barrier is created which allows clean water to pass, but retards and prevents inorganic and organic contaminants from ever leaving the site (Young Yoo et al, 2004). If such a barrier ever starts leaking, a thin slurry wall using the vibrating beam technology can be constructed around the landfill at economical costs.

6. CONCLUSIONS

This brief description of methods to establish permeable barriers around contaminated sites establishes the feasibility of the concept. This technology is a system, which has been long in coming, but should now be accepted as “state of the art” technology.

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Chapter 15

SORPTION/DESORPTION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZO FURANS (PCDDs/PCDFs) IN THE PRESENCE OF CYCLODEXTRINS

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Abstract: The goal of this study was to investigate the usefulness of cyclodextrins (CDs) for the removal of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo furans (PCDDs/PCDFs) in soil and water. Five CDs having different molecular cavities and active functional groups were selected and evaluated for their ability to include (trap) PCDDs/PCDFs in soil and water. For the soil experiments, CDs were added to the soil on day one and the concentrations of unbound PCDDs/PCDFs were monitored over a 28-day period. Parallel control experiments were conducted to assist in the process performance evaluation. The ability of CDs to remove PCDDs/PCDFs from the contaminated soil was dependent upon the type of CD used and constituents of PCDDs/PCDFs. Among the five CDs investigated, hydroxypropyl-β-cyclodextrin (HPBCD) gave the highest removal efficiency for all components of PCDDs/PCDFs. The removal efficiency of total PCDDs/PCDFs was 81% one day after application of CDs and then increased to 96% after 28 days. The α-cyclodextrin (ACD) and β-cyclodextrin (BCD) removed only 45% and 50% of the total PCDDs/PCDFs after 28 days, respectively, whereas hydroxypropyl-γ-cyclodextrin (HPGCD) removed 80% of the total PCDDs/PCDFs.

Key words: PCDDs/PCDFs; Cyclodextrins; Inclusion; Removal; GC-ECD; Soil

1. INTRODUCTION

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo furans (PCDDs/PCDFs) are persistent organic pollutants and have been determined to be toxic by many government agencies. PCDDs and PCDFs are formed as by-products from various combustion and chemical processes. They are produced during incomplete combustion of chlorine containing wastes like municipal solid waste, sewage sludge, and hospital and hazardous wastes and can become soil and water pollutants.

There are methods to remediate PCDDs/PCDFs including phytoremediation and thermal treatment (Kasai et al., 2000; Campanella et al., 2002; Kluyev et al., 2002). One of the technical challenges faced when remediating soil and sediments is the difficulty of leaching the sorbed (i.e. bound) PCDDs/PCDFs from the soil particles into the flushing medium. PCDDs/PCDFs, like other organic contaminants, tend to partition (sorb) onto suspended solid particles through various physico-chemical forces. Yoshii et al (2001) reported the high affinity of PCDDs/PCDFs with soil and the difficulty of the effective removal of the pollutants from the soil matrix. They used biphenyls to demonstrate the usefulness of cyclodextrins (CDs) to enhance the solubility of hydrophobic chemicals in the environment. Narita et al (2000) studied fluorescent molecular sensing for endocrine-disrupting chemicals (including PCDDs/PCDFs) and their analogs using regio-selective dansyl-tosyl-modified β-cyclodextrin (BCD) and γ-cyclodextrin (GCD) and found that these host compounds showed pure monomer fluorescence at 526 nm; the intensities of the guest-induced fluorescence either increased or decreased depending on PCDD/PCDF analogs. Otsuka et al (1999) carried out an on-line concentration of neutral analytes for CD assisted micellar electrokinetic chromatography (MEKC) in environmental analysis to enhance the UV detection sensitivity using several PCDD/PCDF compounds and found that the detection sensitivity increased 200 times.

PCDDs/PCDFs are hydrophobic and trapping them in the cavities of water soluble CDs may assist thedesorption of these compounds from within the structure of the solid particle into the surrounding medium. The overall objective of this project was to investigate the efficacy of different CDs as enhancers for the outward diffusion of PCDDs/PCDFs from contaminated soil and sediments. Five CDs were selected for this study: (1) α-cyclodextrin (ACD), (2) β-cyclodextrin (BCD), (3) hydroxypropyl-α-cyclodextrin (HPACD), (4) hydroxypropyl-β-cyclodextrin (HPBCD), and (5) hydroxypropyl-γ-cyclodextrin (HPGCD). The diameter of the molecular cavity and presence of active functional groups were taken into account in the selection of these CDs. The PCDDs/PCDFs were brought into contact with CDs in soil and water and the free (unbound) PCDDs/PCDFs were determined over time using gas chromatography – electron capture detector (GC-ECD).

2. APPROACH

The approach used in this study involved contacting CDs with PCDDs/PCDFs in aqueous medium and analysis of the unbound PCDDs/PCDFs using GC-ECD. Four essential steps were performed for the assessment of the process: a) mixing the PCDD/PCDF-contaminated soil with CDs, b) centrifuging the supernatant of the CD treated soil slurry to separate the liquid phase for analysis, c) extracting the sample with the organic solvent, and d) injecting the sample extract into the GC-ECD.

The GC-ECD measurements are used for investigation of the CDs capability to enhance desorption of PCDDs/PCDFs from the soil as well as for determination of the inclusion efficiency. The mixing step ensures that these pollutants are given enough contact time with CDs, whereas, the centrifugation is required to separate the liquid phase from the suspended solid particles and both of mixing and centrifugation should have no effect on the GC-ECD response. The extraction step provides important information on the inclusion as well as surface sorption since the included PCDDs/PCDFs may differ appreciably from that of the free PCDDs/PCDFs in terms of partitioning or diffusion from the water to the organic solvent.

The introduction of PCDDs/PCDFs in the hot injection chamber of the GC-ECD is interesting because the physico-chemical processes involved play a significant role in producing the signal profile. The fundamental processes that occur when the sample is injected include: (1) vaporization at 280°C inside the injector chamber, (2) purging the analyte vapour by the carrier gas to the GC column for separation, (3) detection with ECD, and (4) recording the signal.

The production of the GC-ECD signal of the free PCDDs/PCDFs is straightforward. The elevated temperature of the injection port causes the sample extract to vaporize (at least some of it). The vapour of the free PCDDs/PCDFs is carried out to the GC column where they are separated according to their physico-chemical properties and detected as they enter the ECD module. Regarding the bound PCDD/PCDF compounds, there are three scenarios as to what will happen when these compounds are deposited inside the hot injection port. These scenarios can be used as guidance for interpretation of the GC-ECD response to PCDD/PCDF-CD compounds, as follows:

Case I. The PCDDs/PCDFs-CD compounds vaporize and the vapor is carried out to the GC column. In this case, the included compounds may separate into peaks or overlap with the free PCDD/PCDF compounds. The overlap of the included PCDDs/PCDFS with the free PCDDs/PCDFs may result in enhancement or depression of the ECD signal.

Case II. The PCDD/PCDF-CD compounds dissociate into PCDDs/PCDFs and CDs causing no discrimination between the free PCDDs/PCDFs and the included compounds. The decomposition of the included compounds into free PCDDs/PCDFs results in no distinction between the bound and free PCCD/PCDF compounds. The signal of the CD treated sample, as well as, the untreated sample will be identical providing no further information about the inclusion even if it happens. In this case, another chemical identification technique would be necessary.

Case III. The PCDD/PCDF-CD compounds deposit onto the inner surface of the injector liner, hence escape detection by the ECD module. This case entails that these compounds are thermally stable and non-volatile inside the injection port. The sample residue is not evaporated and the included compounds simply deposit on the inner surface of the injection port. This may result in loss of the ECD's response to PCDDs/PCDFs, which can be interpreted as a sign of inclusion with CDs.

3. MATERIALS AND METHODS

Three sets of experiments were designed to investigate the usefulness of CDs as enhancers for desorption of PCDDs/PCDFs from contaminated soil. First, CDs were added to the PCDD/PCDF-contaminated soil to bring the sorbed PCDDs/PCDFs from the soil matrix to the surrounding medium. Second, the PCDDs/PCDFs and CDs were added simultaneously to the clean soil of the same matrix to investigate the surface deposition onto soil particles in the presence of CDs. Third, inclusion of PCDDs/PCDFs was performed in water without the soil. Control experiments were run parallel to the test experiments for comparison.

3.1 Chemicals and Solvents

The CDs (ACD, BCD, HPACD, HPBCD and HPGCD) were obtained from Sigma-Aldrich Canada. The isooctane and dichloromethane were distilled in glass, purchased from Caledon Laboratories. Some of the PCDDS/PCDFs (OCDD, OCDF and 1,2,3,4-TCDD) were obtained from the Analysis and Air Quality Division of Environment Canada's Environmental Technology Centre. Reference standard solutions of PCDDs/PCDFs were acquired from Wellington Laboratories.

3.2 Stock Solution of PCDDs/PCDFs for Spiking the Soil

The stock solution of PCDDs/PCDFs was prepared in a 500 mL round bottom flask. The residue of solvents was evaporated to dryness using a rotary evaporator at 60 °C. Then, 100 mL of water was added to the flask and heated in a water bath at 60°C for 1 hour until most of the PCDDs/PCDFs dissolved. The hot solution was transferred to a 1 L volumetric flask and the volume was completed to the mark with water. The solution was left in the fumehood overnight prior to testing. Table 1 shows PCDD/PCDF components and concentrations of the stock solution used for spiking the soil.

Table 1. PCDD/PCDF solution used for spiking the soil

Component	Concentration (ppm)
1,2,3-TCDD	1.80×10^{-1}
1,2,3,4-TCDD	2.96×10^{-2}
2,3,7,8-TCDD	2.58×10^{-4}
1,2,3,6,7,8-HxCDD	5.44×10^{-4}
1,2,3,7,8,9-HxCDD	1.76×10^{-5}
OCDD	3.12×10^{-2}
OCDD	5.26×10^{-2}

3.3 Preparation of the PCDD/PCDF-Contaminated Soil

The soil used was from a heavy-metal contaminated site in Eastern Canada. It was homogenized and air-dried in the fumehood, then sieved to remove particles greater than 2 mm. About 250 g of the soil was slurried with PCDD/PCDF solution using a mechanical mixer (Kitchen Aid model 4K45SSWH) and placed in the fumehood for two weeks where it was air-dried to be used for the desorption testing, with and without CDs. The other part of the soil, which contained no PCDDs/PCDFs, was set aside for the sorption experiments, also with and without CDs.

3.4 Desorption of PCDDs/PCDFs from the Spiked Soil

Five CDs (ABD, BCD, HPACD, HPBCD and HPGCD) were used as enhancers for desorption of PCDDs/PCDFs from the soil to the surrounding aqueous medium. Table 2 details reagents and amounts of soil used. Three sets of reaction vessels were prepared: Set one involved the inclusion of PCDDs/PCDFs with CDs in water, without the soil; Set two was designed for deposition of PCDDs/PCDFs onto the clean soil in presence of CDs, i.e., both CDs and PCDDs/PCDFs were in water added to the non-contaminated soil matrix; and Set three was conducted to leach PCDDs/PCDFs from the spiked soil, which was aged for two weeks. Samples were taken on days 1, 5, 8 and 28 for analysis using GC-ECD.

Table 2. Reagents and amounts of soil used

No	Sample ID	Water mL	Soil g	Stk, mL	ACD, g	BCD, g	HPACD, g	HPBCD, g	HPGCD, g
Inclusion testing in water									
1	WI-1	-	-	50	-	-	-	-	-
2	WI-2	-	-	50	1	-	-	-	-
3	WI-3	-	-	50	-	1	-	-	-
4	WI-4	-	-	50	-	-	1	-	-
5	WI-5	-	-	50	-	-	-	1	-
6	WI-6	-	-	50	-	-	-	-	1
Sorption testing (clean soil)									
1	ST-1	-	10	50	-	-	-	-	-
2	ST-2	-	10	50	1	-	-	-	-
3	ST-3	-	10	50	-	1	-	-	-
4	ST-4	-	10	50	-	-	1	-	-
5	ST-5	-	10	50	-	-	-	1	-
6	ST-6	-	10	50	-	-	-	-	1
Desorption testing (spiked and aged soil)									
1	DT-1	50	10	-	-	-	-	-	-
2	DT-2	50	10	-	1	-	-	-	-
3	DT-3	50	10	-	-	1	-	-	-
4	DT-4	50	10	-	-	-	1	-	-
5	DT-5	50	10	-	-	-	-	1	-
6	DT-6	50	10	-	-	-	-	-	1

Stk = stock solution of PCDDs/PCDFs

For each set of experiments, a control experiment was used. The control experiments contained all test reagents, but had no CDs. The response of GC-ECD to PCDDs/PCDFs in each vessel was documented over time.

3.5 GC-ECD Analysis

3.5.1 Calibration of GC-ECD

The calibration standard solution of PCDDs/PCDFs was prepared from reference solutions provided by Wellington Laboratories, shown in Table 3. The Gas Chromatograph used was HP 5800, Series II, equipped with electron capture detector (ECD) and HP Chemstation, both manufactured by Hewlett Packard Canada. The analytical setup of the system was as follows: The column was DB5-MS, 0.25 mm ID × 0.25 µm × 30 m. The temperature program: initial column temperature was 90°C held for 2 minutes, ramped to

200°C at 3.5°C /minute, then to 280°C at 2.5°C/minute; and then to 300°C at 20°C/minute, held for 5 minutes. The injection volume was 5 µL.

Table 3. Reference standard solution of PCDDs/PCDFs used to calibrate the GC-ECD

Compound	ppm
1,2,3-TCDD	0.0015
1,2,3,4-TCDD	0.1
2,3,7,8-TCDD	0.5
1,2,3,6,7,8-HxCDD	1.1
1,2,3,7,8,9-HxCDD	0.1
OCDD	2.2
OCDD	2.0

3.5.2 Analysis of the Sample

The water sample was withdrawn of the supernatant of the test vessel using a syringe and transferred into a test tube. It was centrifuged for 1 hour and the supernatant was extracted with isooctane and injected to the GC-ECD. Samples were taken immediately after contacting CDs with PCDDs/PCDFs in the reaction vessel. The steps are summarized as follows: Using a syringe, a 7 mL water sample was withdrawn from the supernatant of the sample of the reaction vessel into a test tube and was centrifuged for 1 hour to ensure that fine soil particles were separated from the water sample. Then, 5 mL of the water was withdrawn from the centrifuged sample with an Eppendorff pipette into another test tube. The sample was extracted with 1 mL of isooctane by vortex for 10 seconds and then was left for 10 minutes to allow phase separation. The sample extract was taken out of the test tube using a Pasteur pipette, placed into a GC vial and injected into the GC-ECD.

4. RESULTS AND DISCUSSION

4.1 Desorption of PCDDs/PCDFs from the Spiked Soil

Table 4 summarizes the efficiency of desorption of PCDDs/PCDFs from the soil into the surrounding medium calculated over a period of 28 days from the time of inoculation with CDs. Eq.1 was used to calculate the percentage removal efficiency using CDs relative to that of the control experiment, without CDs.

$$\% D_{Soil} = \frac{C_{CD} - C_{RS}}{C_{CD}} \times 100 \qquad (1)$$

Where,

$\%D_{Soil}$ = percentage of PCDDs/PCDFs removed from the contaminated soil using CDs relative to the control experiment without CDs.

C_{CD} = concentration of PCDDs/PCDFs in aqueous phase surrounding the CD-treated soil

C_{RS} = concentration of PCDDs/PCDFs in aqueous phase surrounding the control experiment

Initially, the desorption efficiencies of total PCDDs/PCDFs were almost nil for ACD and BCD, 16% for HPACD, 81% for HPBCD and 57% with HPGCD. On day 28 (end of testing), the removal efficiencies improved appreciably reaching 45%, 50%, 73%, 96% and 80% using ACD, BCD, HPACD, HPBCD and HPGCD, respectively. The effect of size of molecular cavity of the host molecule is evident in the inclusion efficiency obtained by these GC-ECD measurements. For the case of ACD and BCD the inclusion of total PCDDs/PCDFs increased only slightly (from 45% to 50%). The difference in the capability of CDs is noticeable using HPACD, HPBCD and HPGCD. The removal efficiency increased from 73% for HPACD to 96% for HPBCD and then decreased to 80% using HPGCD. Note that the existence of an active functional group to dissolute PCDDs/PCDFs into the surrounding medium is not enough for leaching these pollutants from the soil. In fact, it appears that the size of the cavity plays an important role in the desorption processes as demonstrated by the substantial difference in the removal efficiencies of HPACD, HPBCD and HPGCD, which have the same functional group (-CHCH$_2$OH), but different cavity sizes.

Not only the size of the molecular cavity of the host plays a role in the inclusion but that of the guest molecule is important as well. The contact time between the guest and host was found to be vital for the inclusion. A close look at the data in Table 4 it can be discerned that the PCDD/PCDF congeners had different affinities toward the same host. The inclusion improved over time suggesting that the inclusion process was not fast under experimental conditions. It was observed that at over a longer period of time some of the congeners had disappeared from the aqueous medium possibly because of surface deposition on the inner surface of the reaction vessel.

Table 4. Removal efficiencies of selected PCDDs/PCDFs from soil with different CDs over a period of 28 days

Day	Congener	$\%D_{Soil}$				
		ACD	BCD	HPACD	HPBCD	HPGCD
1	1,2,3-TCDD	-	-	17±3	82±9	58±13
	1,2,3,4-TCDD	-	-	-	66±6	55±8
	2,3,78-TCDD	-	-	-	-	-
	OCDD	-	51±5	83±9	10±4	31±7

	OCDF	-	-	44±3	37±7	45±5
	Total	-	-	16±	81±	57±
5	1,2,3 -TCDD	27±7	51±9	71±10	93±12	93±9
	1,2,3,4 -TCDD	-	50±6	82±8	91±9	92±7
	2,3,7,8 -TCDD	-	-	-	-	-
	OCDD	100±10	-	-	-	-
	OCDF	100±8	-	100±12	-	-
	Total	26±6	50±4	70±8	92±11	93±9
8	1,2,3 -TCDD	36±6	60±8	70±10	95±9	84±8
	1,2,3,4 -TCDD	49±8	59±4	65±5	94±6	90±9
	OCDD	-	-	-	-	-
	OCDF	-	-	-	100±9	100±13
	Total	25±5	53±4	64±7	94±8	81±6
28	1,2,3 -TCDD	45±8	51±5	73±8	96±12	80±9
	1,2,3,4 -TCDD	63±9	50±7	71±6	95±10	87±5
	2,3,7,8 -TCDD	-	-	-	69±6	-
	OCDD	-	-	-	-	-
	OCDF	-	-	-	-	-
	Total	45±5	50±3	73±8	96±12	80±10

“-“ indicates no removal

The behavior of the 2,3,7,8-TCDD was different. This congener did not show an appreciable affinity toward CDs investigated. Only at day 28, this congener demonstrated an inclusion efficiency of 69% with HPBCD. Other congeners did not show inclusion efficiencies and were excluded from data in Table 4. In some instances, these compounds caused either enhancement in the GC-ECD response or could not be detected at all. It is conceivable that these CD-included congeners were extracted into the organic solvent and interfered with that of the free congeners. This interference did not permit calculation of the inclusion efficiency but it could be used to indicate that a kind of interaction between the CDs and the PCDD/PCDF congener present.

Fig.1 depicts the GC-ECD response to the presence of total PCDDs/PCDFs leached from the contaminated soil to the surrounding water, normalized to the control test (i.e. all data points were divided by the highest value of the control). For illustration, the data were plotted in reverse order. The data of day 1 was obtained after one day of CD application; the other data were acquired on days 5, 8 and 28. As can be seen, HPBCD performed very well in leaching PCDDs/PCDFs from the contaminated soil relative to other CDs, reaching a maximum after 28 days. Note that in day 1, the GC-ECD response was higher compared to other sampled days, which is attributed to the presence of CDs causing signal enhancement. The HPGCD did not perform well in day 1 and then leveled off at day 8. This may be attributed to the stability of the PCDDs/PCDFs-HPGCD complex. The other three CDs showed some enhancement, but were not considered significant when compared to the HPBCD.

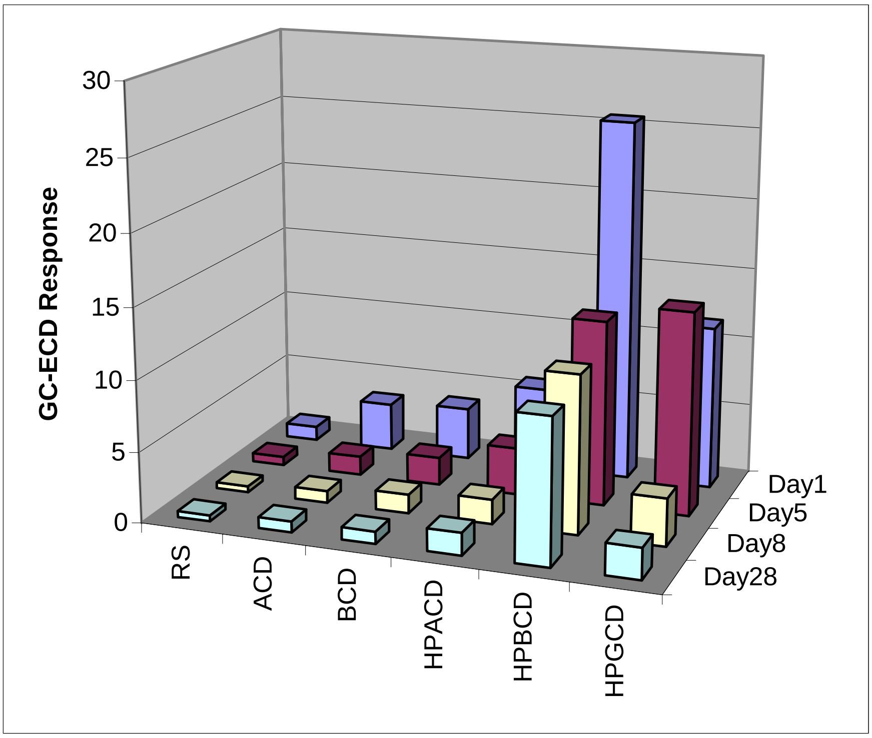

Figure 1. Desorption of total PCDDs/PCDFs from the contaminated soil with various CDs over a period of 28 days. The GC-ECD response is normalized to the control experiment "RS", which is contaminated soil slurried with water, without CDs.

It was observed that the GC-ECD response to 2,3,7,8-TCDD leached out from the soil using five different CDs, which is interesting because within HPBCD the behaviour of this congener was very different from the other congeners. It was detected initially in all tests except that of HPBCD, which did not show any appreciable removal until day 28 (end of testing). Other CDs did not show important leaching relative to the control experiment. This congener is the most toxic of the PCCD/PCDF compounds. So this result warrants further investigations. Fig.2 depicts chromatograms obtained using GC-ECD for the total PCDDs/PCDFs leached from the contaminated soil after 28 days, with and without HPBCD. As can be seen, HPBCD caused a significant enhancement in the removal of these pollutants from the soil matrix to the surrounding medium. Of the seven congeners of PCDDs/PCDFs investigated, 1,2,3-TCDD gave the highest GC-ECD response upon inoculation with HPBCD. Notice that OCDD and OCDF disappeared completely from the control and test experiments. This can be interpreted in terms of re-deposition onto soil and vessel surface because the tests were in batch experiment (i.e., the leachate was in contact with the matrix through the duration of testing).

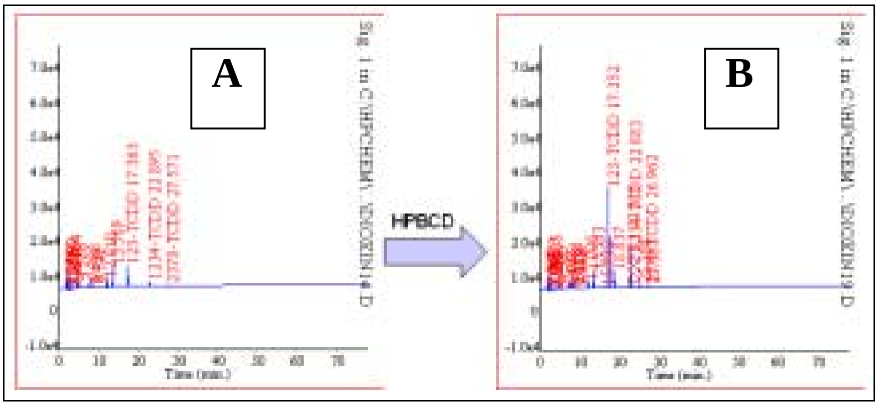

Figure 2. Typical GC-ECD chromatogram for desorption of PCDDs/PCDFs from HPBCD treated soil into the surrounding aqueous medium, after 28 days; 96% removal was obtained. A = control (contaminated soil + water, no HPBCD) and B = HPBCD-treated soil.

Fig.3 delineates the concentration of 1,2,3,4-TCDD desorbed from the contaminated soil to the surrounding water medium under the influence of five CDs. In these experiments, the PCDD/PCDF-contaminated soil was treated with different CDs and the monitoring of PCDDs/PCDFs leached from the soil into the aqueous medium commenced immediately. The control experiment was the same contaminated soil matrix without CDs. Initially, the rate of desorption was high and then levelled off after 5 days demonstrating a typical first order reaction. In all cases, the levels of the leached PCDDs/PCDFs were dependent on the type of CDs added to the soil. Among the five CDs investigated, HPBCD was the most effective in dislodging the contaminants from the soil matrix, as illustrated by the prominent level of HPBCD relative to others. The PCDDs/PCDFs detected at the start of testing were from the labile type of PCDDs/PCDFs loosely attached to the surfaces of the soil particles. The HPGCD was also effective in desorption of target contaminants from the soil. It should be mentioned that HPBCD and HPGCD are very similar with only one difference, the size of the cavity. HPGCD has an extra glucose molecule. One may interpret the difference between the desorption capacities of these two CDs in terms of fitting the PCDD/PCDF molecule inside the CD molecular cavity. The best fit will result in more PCDDs/PCDFs pulled out of the soil into the aqueous medium where the CD is present. The reason for choosing CDs with hydroxyl groups was to render these extremely insoluble PCDDs/PCDFs into water-soluble substances so that they could be leached out of the soil. The CDs with hydroxyl groups appeared to be those that could include

PCDDs/PCDFs and render them into water soluble compounds. This proved that the inclusion of PCDDs/PCDFs with CDs did indeed occur as demonstrated by detection of these contaminants in water.

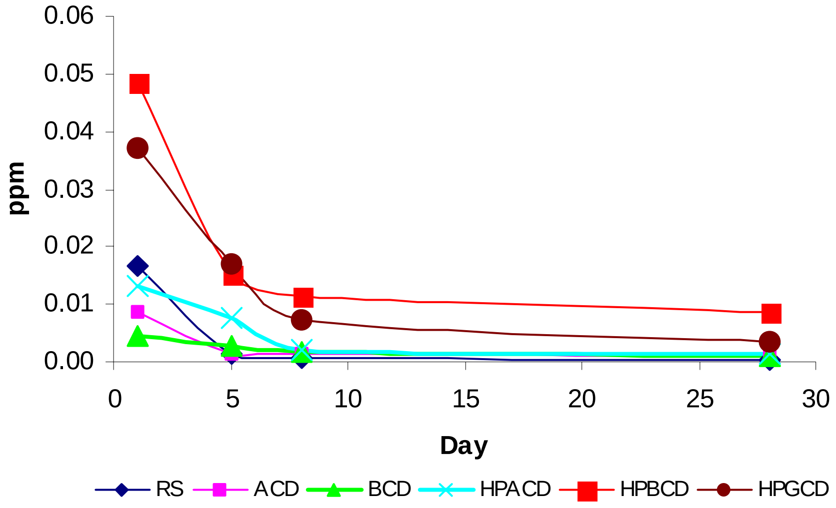

Figure 3. Concentration of 1,2,3,4-TCCD in water surrounding PCDD/PCDF-contaminated soil particles monitored using GC-ECD over a period of 28 days**.**

Fig.4 depicts the concentration of total PCDDs/PCDFs desorbed from the soil over a period of 28 days using different CDs. The rate of desorption decreased exponentially from the start of inoculation with the CDs to the end of testing (28 days) giving rise to different concentrations in the presence of CDs. As can be seen, again, the HPBCD performed very well with respect to other CDs in the removal of these contaminants from the soil over the entire period of testing. It was observed that HPGCD matched the efficacy of the HPBCD at day 5, but later, its capability decreased appreciably. One may advance a reason for this experimental observation in terms of stability of the HPGCD-PCDDs/PCDFs complex. It is conceivable that HPGCD formed a complex in a good yield at the time of sampling but that complex decomposed at later time thus releasing PCDDs/PCDFs and HPGCD. However, the performance of the HPBCD was far better than the HPGCD through the entire course of experiment (28 days). This performance may be explained in terms of the mechanism of inclusion with CDs. Although other CDs, like ACD, BCD and the HPACD were investigated, they could not match the capacity of HPBCD in terms of leaching capability of PCDDs/PCDFs from the soil. Notice that even though the HPACD has a solubilizing group (-OH), it did not do much in terms of removal of PCDDs/PCDFs. It is of interest to mention that at the end of the study, it was observed that a type of biological growth existed on some of the soil inoculated with CDs. One may wonder if that biological activity was active during the testing.

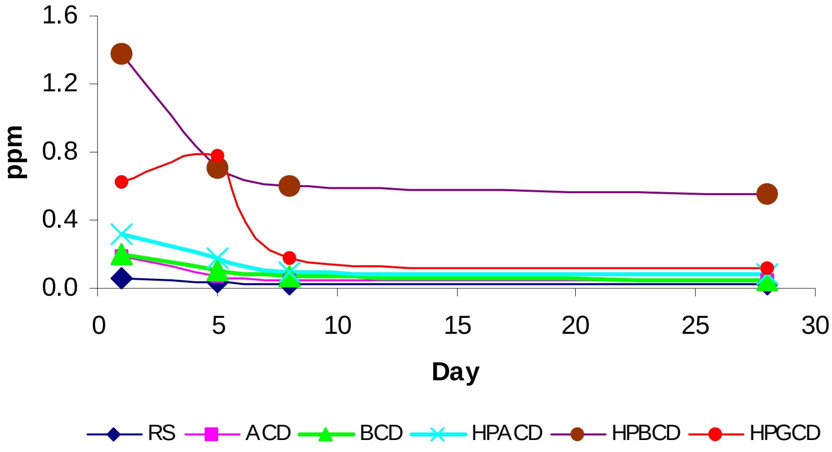

Figure 4. Concentration of total PCDDs/PCDFs desorbed from soil over a period of 28 days.

When a water solution containing HPBCD and PCDDs/PCDFs was introduced to clean soil it appeared that HPBCD prevented PCDDs/PCDFs from travelling from the aqueous medium to the soil particles. Fig.5 delineates the concentration of total PCDDs/PCDFs plotted as a function of types of CDs after 28 days of application. As can be seen, without CDs, specifically HPBCD, the soil sorbed PCDDs/PCDFs from the surrounding water, whereas, in the presence of CDs, the contaminants preferred to stay in the complex form in surrounding medium. Note that the BCD and the HPACD showed similar effect, but the HPGCD was the second most effective after the HPBCD at inhibiting PCDDs/PCDFs from moving toward the soil matrix. This is consistent with desorption experiments, where the HPBCD was found the most effective in pulling out the sorbed PCDDs/PCDFs into the surrounding aqueous medium.

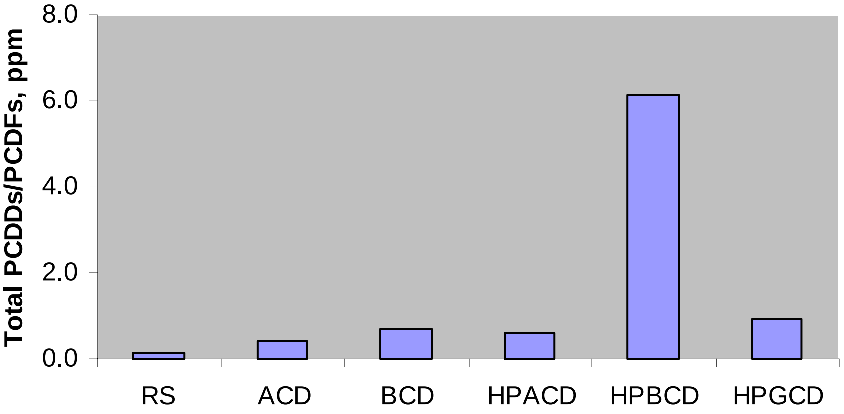

Figure 5. Prevention of PCDDs/PCDFs from sorption onto the soil matrix in presence of different CDs, after 28 days.

In water without soil, again different CDs had different effect on GC-ECD response. The ACD did not show any effect on the GC-ECD response, meaning no inclusion occurred. BCD and HPACD appeared to include PCDDs/PCDFs, whereas, HPBCD and HPGCD demonstrated an appreciable enhancement in the GC-ECD response (about 37 times). The difference in the GC-ECD response to the PCDDs/PCDFs in water, with and without CDs, can only be explained in terms of the physico-chemical properties of the included PCDDs/PCDFs. The PCDDs/PCDFs that bonded with the CDs behaved differently from those free of CDs, which was illustrated by the appreciable difference in the GC-ECD signals, specifically HPBCD. It is possible that during the GC-ECD analysis, the transformation inside the hot injection chamber and the detection with the ECD, the inclusion with CDs caused enhancement in the GC-ECD response. This is not a testing error because PCDDs/PCDFs are sparingly soluble in water and the phenomenon was observed repeatedly. It is also conceivable that the PCDDs/PCDFS may have deposited onto the inner surface of the test vessel and that the HPBCD dislodged them back into the water because the PCDDs/PCDFs are insoluble in water.

5. CONCLUSIONS

This work demonstrated the usefulness of CDs for the removal of PCDDs/PCDFs from the soil. Five CDs including ACD, BCD, HPACD, HPBCD and HPGCD were investigated for inclusion of PCDDs/PCDFs. HPBCD gave the highest removal efficiency for the majority of PCDDs/PCDFs components, ranging from 69% to 96% for 2,3,7,8-TCDD and 1,2,3-TCDD, respectively. The removal efficiency of total PCDDs/PCDFs was estimated to be 81% at the start (one day after CD application) and 96% after 28 days. The ACD and BCD removed only 45% and 50% of the total PCDDs/PCDFs after 28 days, whereas, HPACD and HPGCD removed 73% and 80% of the total PCDDs/PCDFs from the contaminated soil, respectively. The results showed that the existence of a solubilizing active group in the CD molecular structure alone is not enough to leach PCDDs/PCDFs from the soil. The size of the cavity plays a significant role as demonstrated by the different removal efficiencies of HPACD, HPBCD and HPGCD, 73%, 96% and 80%, respectively. It was observed at the end of the study that some type of growth developed in the CD-treated soil, indicating that biological activity had occurred. The nature of this growth has not been investigated further.

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Chapter 16

EMERGING SCIENCE SUPPORTING THE 2005 NATIONAL RESEARCH COUNCIL PERCHLORATE RISK ASSESSMENT

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Abstract: In sufficient amounts, perchlorate can inhibit iodine uptake by the thyroid, ultimately leading to diminished thyroid function. Recent studies in Europe and the United States have determined that maternal hypothyroidism during pregnancy, even when mild and considered subclinical, may be associated with impairment of normal brain development and intelligence in offspring. Concern about the possibility that iodine uptake inhibition from environmental perchlorate could result in impaired maternal thyroid function during pregnancy and adverse neurodevelopmental effects in the fetus, has led to proposed a proposed reference dose (RfD) as low as 0.00003 mg/kg-day. For 18 months during 2003 and 2004, a committee of the National Research Council (NRC) reviewed the science available in order to assess the risk of perchlorate ingestion. In the committee's January 2005 report, it concluded that the no-observed-adverse-effect level (NOAEL) is 0.4 mg/kg-day and that the no-observed-effect-level (NOEL) is 0.007 mg/kg-day. Based on the NOEL, the committee recommended an RfD of 0.0007 mg/kg-day. Subsequent to the NRC committee deliberations, five new scientific studies have been completed that strongly support the committee's NOAEL and NOEL and support that the recommended RfD is safe for even the most susceptible populations – fetuses of pregnant women with insufficient iodine consumption.

1. INTRODUCTION

Perchlorate is known to inhibit the thyroid's uptake of iodine, necessary for the production of thyroid hormones. Since medical doses of 4 to10 mg/kg-day were given in the 1950s and 60s, to treat overactive thyroid conditions, it is clear that these doses, perchlorate can inhibit iodine uptake by the thyroid sufficiently to lead to diminished thyroid function (hypothyroidism). Recent studies in Europe and the United States have determined that maternal hypothyroidism during pregnancy, even when mild and considered subclinical, may be associated with impairment of normal brain development and intelligence in offspring. The recent detection of perchlorate in drinking water and in foods has led to concern that iodine uptake inhibition from environmental exposure – typically thousands of times lower than doses given medically – could result in impaired maternal thyroid function during pregnancy and adverse neurodevelopmental effects in the fetus.

Because of these concerns, and because of controversies regarding previous risk estimates, the U.S. Environmental Protection Agency (EPA) requested in 2003 that the NRC review the available science regarding possible risks from ingestion of perchlorate from environmental sources. In January 2005, the NRC published its report on the *Health Implications of Perchlorate Ingestion*[1]. Relying primarily upon published, peer-reviewed studies in humans, the NRC committee identified three key risk assessment parameters for perchlorate:

- The **NOAEL** *[no-observed-adverse-effect-level - the highest dose at which no adverse health effects have been observed]*

- The **NOEL** *[no-observed-effect-level - the highest dose at which there are no statistically or biologically significant increases in the frequency or severity of any effect between the exposed population and its appropriate control]*

- The **RfD** *[reference dose - an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral dose delivered to the human population (including sensitive groups) that is likely to have no appreciable risk of harmful effects during a lifetime]*

In establishing a NOAEL from the literature, the committee observed that "it is highly likely that in people with a normal iodide intake the dose of perchlorate would have to reduce thyroid iodide uptake by at least 75% for a sustained period (several months or longer) for iodide uptake and thyroid hormone production to decline enough to cause adverse health effects … In adults, that is likely to require sustained exposure to more than 30 mg of perchlorate per day (0.4 mg/kg per day for a 70-kg person), on the basis of the clinical studies in healthy subjects and the studies of long-term treatment of hyperthyroidism."

Based on a 14-day clinical study of adults by *Greer et al*[2], the committee "identified a NOEL for inhibition of iodide uptake by the thyroid at 0.007 mg/kg per day". They further went on to assert that "…chronic exposure will have no greater effect than that resulting from short-term exposure. In fact, it may well have less effect because of the capacity of the pituitary-thyroid system to compensate for iodide deficiency by increasing iodide uptake."

The committee then departed from the traditional risk assessment approach of starting with a NOAEL in deriving the RfD. The committee applied the more conservative NOEL as the starting point and then applied an additional safety factor of 10 to protect the most sensitive population identified by the committee – fetuses of pregnant women who might have hypothyroidism or iodide deficiency. Thus, they adjusted the NOEL downward from 0.007 to 0.0007 mg/kg-day to derive the RfD. They went on to state that "using a nonadverse effect that is upstream of the adverse effects is a conservative, health-protective approach to the perchlorate risk assessment," and that this RfD "should protect the health of even the most sensitive populations."

Five additional human studies[3,4,5,6,7] relevant to perchlorate risk assessment were underway at the time the committee was deliberating, but were not yet peer reviewed. Those studies now have been completed and peer reviewed. The purpose of this paper is to examine whether the results of these five studies support the NOAEL, NOEL and RfD derived by the NRC panel.

2. REVIEW OF NEW STUDIES AND SIGNIFICANT FINDINGS

2.1 Tonacchera et al, 2004. Relative Potencies and Additivity of Perchlorate, Thiocyanate, Nitrate, and Iodide on the Inhibition of Radioactive Iodide Uptake by the Human Sodium Iodide Symporter.

It has been known for more than half a century that perchlorate is the most potent of several common substances such as nitrate and thiocyanate that also inhibit iodine uptake by the thyroid. Research in the 1950s and 60s indicated that perchlorate was about 10 to 20 times more potent than thiocyanate and about 100 to 200 times more potent than nitrate in blocking iodine uptake by the thyroid. Whether these relative potencies held throughout all concentrations or how the effects might combine was not known.

In 2001, Tonacchera and colleagues at the University of Pisa in Italy successfully inserted the gene that codes for the human NIS into a standard laboratory cell culture line. (The NIS, or sodium-iodide-symporter, is the receptor that actively transports iodine into the thyroid). They developed a new tool suitable to further explore how perchlorate, thiocyanate and nitrate interact and inhibit iodine uptake. In 2003-2004, the same researchers measured iodine uptake in the special cell culture with varying concentrations of perchlorate, thiocyanate and nitrate in the serum surrounding the cells. All in all, they conducted 776 separate measurements of iodine uptake and found that the relative potencies of perchlorate, thiocyanate and nitrate were constant over all concentrations and that the effects of combinations of these ions were simply additive. The dose-response curves as shown in Figure 1 are parallel over orders of magnitude of concentrations. Perchlorate is 9 and 150 times more potent than thiocyanate and nitrate respectively, in inhibiting iodine uptake by the thyroid.

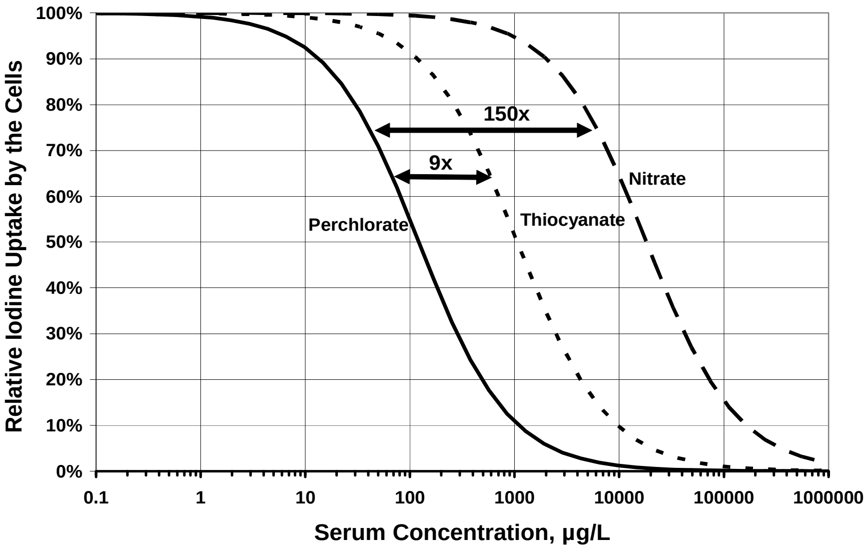

Figure 1. Dose – Response for iodine uptake and serum perchlorate, thiocyanate and nitrate concentrations (based on *Tonacchera et al, 2004)*

While the NRC committee NOEL and NOAEL are doses (mg/kg-day), the *Tonacchera et al* study relates serum concentrations (µg/L). Human data relating perchlorate dose (over four orders of magnitude) with serum perchlorate concentration have recently been published[7,8,9,10] and correlated[4]. The resulting correlation is presented as Figure 2. Using the correlation in Figure 2 and the *Tonacchera et al* relationship in Figure 1, the NRC-derived NOAEL of 0.4mg/kg-day would correspond to 72% inhibition of iodine uptake (compared with 75% in the committee report).

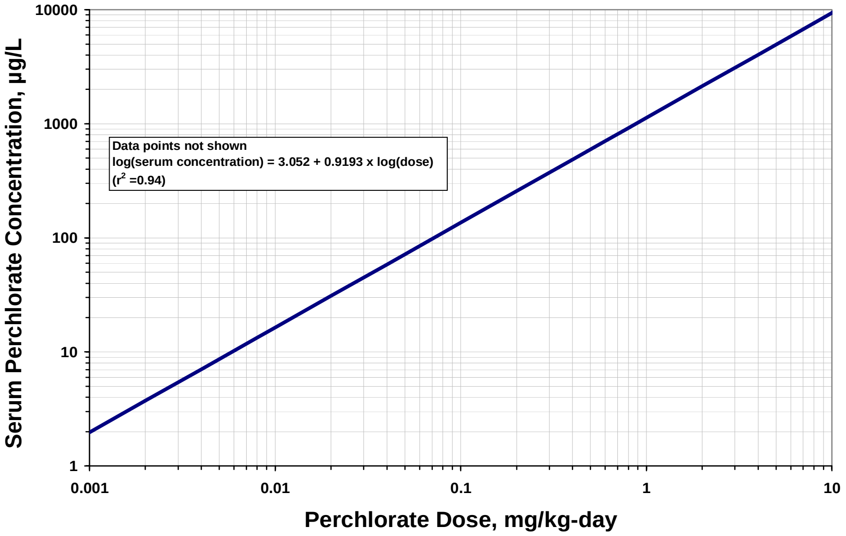

Figure 2. Relationship between perchlorate dose and serum perchlorate concentration from recently published studies, from Gibbs 2005[4]

Nitrate is common in green leafy vegetables as well as a common pollutant in drinking water. The maximum contaminant level (MCL) for nitrate is 10 mg/L as nitrate-nitrogen, which is equivalent to 45 mg/L as nitrate. Using standard assumptions, a 70 kg adult drinking 2 liters of water daily would ingest a nitrate dose of 1.3 mg/kg-day. This dose is equivalent to 0.0055 mg/kg-day of perchlorate in iodine uptake inhibition. Thus, although nitrate is common in our drinking water, the nitrate MCL is similar to the perchlorate NOEL. Thyroid effects from nitrate in drinking water are therefore unlikely, and none have been reported in the U.S.

2.2 Gibbs 2005. A Comparative Risk assessment of Perchlorate and Thiocyanate Based on Competitive Inhibition of Iodide Uptake as the Common Mode of Action

Sixteen published and peer-reviewed human studies relating serum thiocyanate concentrations and thyroid function were evaluated. These studies included chronic exposure among pregnant women and infants, exposure in regions with varying degrees of iodine deficiency, and exposure resulting in a wide range of serum thiocyanate concentrations. Sources of thiocyanate included medications, occupational exposures, milk preservatives, cassava and cigarette smoking. These studies, by proxy, fill many of the gaps in the perchlorate literature.

Table 1. Serum Thiocyanate Concentration Effect on Human Thyroid Function and Perchlorate Dose Required to Achieve an Equivalent Inhibition of Iodine Uptake

Observed Thyroid Effects from Thiocyanate in Published Studies	Serum Thiocyanate Concentration µg/L	Calculated Inhibition of Iodine uptake[1]	Equivalent Perchlorate Serum Concentration µg/L[1]	Equivalent Perchlorate Dose, mg/kg-day[2]
No thyroid effects, even in regions with mild to moderate iodine deficiency	2,500	70%	290	0.2
Adaptive thyroid effects (but not hypothyroid effects) in regions with iodine sufficiency or iodine deficiency	5,000	86%	580	0.5
Measurable hypothyroid effects regardless of iodine status	10,000	93%	1,150	1
Profound hypothyroid effects regardless of iodine status	50,000	99.9%	5,750	6

[1] Based on Figure 1
[2] Based on Figure 2

A summary of the key findings from the thiocyanate scientific literature is presented in Table 1. No adverse thyroid effects were observed at thiocyanate levels equivalent to 0.2 mg/kg-day or less of perchlorate (half the NRC NOAEL), even among pregnant women and neonates in regions with mild to moderate iodine deficiency. Adaptive but not hypothyroid effects were seen at perchlorate-equivalent doses slightly above the NRC NOAEL, and hypothyroid effects were clearly seen at perchlorate-equivalent doses 2½ times the NRC NOAEL. Profound hypothyroid effects were seen at perchlorate- equivalent doses that are in the range used pharmacologically to treat overactive thyroid conditions. Therefore, for the most sensitive subpopulation identified by the NRC panel, fetuses of pregnant women with insufficient iodine consumption, the thiocyanate literature shows that the NRC recommended RfD is many times lower than levels seen to be without any effects seen in these studies.

2.3 Braverman et al, 2005. The Effect of Perchlorate, Thiocyanate, and Nitrate on Thyroid Function in Workers Exposed to Perchlorate Long-Term

Twenty-nine perchlorate workers and 12 volunteer community controls in southern Utah were studied in 2004. This is the same perchlorate manufacturing facility in which the workers were studied by *Lamm et al*[11] in 1999, and the two study cohorts overlapped somewhat. The workers had all worked a minimum of two years at the facility and most had worked there much longer. Their work schedules are structured with three 12-hour shifts in a row followed by three days off. Important differences between the *Braverman et al*. study and *the Lamm et al.* study include:

- estimating work shift perchlorate doses from serum perchlorate concentrations,
- measuring concurrent serum nitrate and thiocyanate concentrations,
- measuring iodine uptake just before and just after the three 12-hour shifts,
- measuring thyroid volume by ultrasound, and
- including volunteer community controls for comparison.

About half of the workers had 12-hour shift perchlorate doses above the NRC NOAEL of 0.4 mg/kg-day and about half had doses below this level. All workers and community controls were healthy white adult males with iodine-sufficient diets. Although there was significant reduction in iodine uptake among the workers related to their perchlorate doses, there were no hypothyroid changes in the workers compared to the community controls or related to their individual perchlorate doses. Additionally, there was no increased thyroid volume among workers related to perchlorate dose or in comparison to community controls.

The significant findings in this study as it relates to the NRC committee report are:

- The perchlorate dose-response relationship for the workers for relative iodine uptake was nearly identical to that found in the two-week volunteer study by *Greer et al*[2], the study on which the NRC committee based the NOEL.
- The absolute iodine uptake of the perchlorate workers after three full days off was significantly higher than that of the community controls, and their absolute iodine uptake after three 12-hour shifts was about the same as the community controls.
- The workers' relative iodine uptake correlated very strongly with the relative iodine uptake predicted by *Tonacchera et al* (Figure 1).

Thus the *Braverman et al.* study demonstrated that with long-term perchlorate exposure, the thyroid adjusts by taking in iodine more efficiently. This observation substantiates the NRC committee assertion that with regard to inhibition of iodine uptake, "…chronic exposure will have no greater effect than that resulting from short-term exposure. In fact, it may well have less effect because of the capacity of the pituitary-thyroid system to compensate for iodide deficiency by increasing iodide uptake." This study also confirmed that the cell-culture-derived relative potencies for perchlorate, thiocyanate and nitrate from *Tonacchera et al.* are valid in living human subjects.

2.4 Crump and Gibbs 2005. Benchmark Calculations for Perchlorate from Three Human Cohorts

It is beyond the scope of this paper to fully discuss benchmark methodology, but in recent years, the statistical lower bound on a benchmark dose calculation (BMDL) has been accepted by the U.S. EPA as an equivalent to a NOAEL for risk assessment purposes. In *Crump and Gibbs 2005,* the authors performed benchmark calculations based on combined raw data from *Braverman et al 2005* and *Lamm et al, 1999.* Although both these studies are "negative" in the sense that no adverse effect was found and thus a NOAEL could not be established, BMDLs calculated from such negative results represent valid statistical lower bounds on the dose that accounts for a potential, but unobserved, adverse effect of perchlorate. Two standard indicators of hypothyroidism were selected for analysis: free thyroxine index

(FTI) and thyroid stimulating hormone (TSH). BMDLs ranged from 0.21 to 0.56 mg/kg-day based on FTI changes, and from 0.36 to 0.92 mg/kg-day based on TSH changes. Thus, these combined datasets are generally supportive of the 0.4 mg/kg-day NOAEL in the NRC committee report.

2.5 Tellez et al, 2005. Chronic Environmental Exposure to Perchlorate Through Drinking Water and Thyroid Function During Pregnancy and the Neonatal Period.

It has been known for many years that perchlorate is present naturally in nitrate fertilizer mined in the Atacama Desert in northern Chile. *Crump et al. 2000*[12] characterized the water supplies in the region and studied thyroid function among school children and infants in three cities with varying perchlorate in their municipal water supplies. There were no hypothyroid changes attributable to 110 to 115 ppb perchlorate in municipal drinking water relative to cities with non-detectable or much lower perchlorate concentrations. A follow-up study among pregnant women in the same region was then undertaken in 2002-2004.

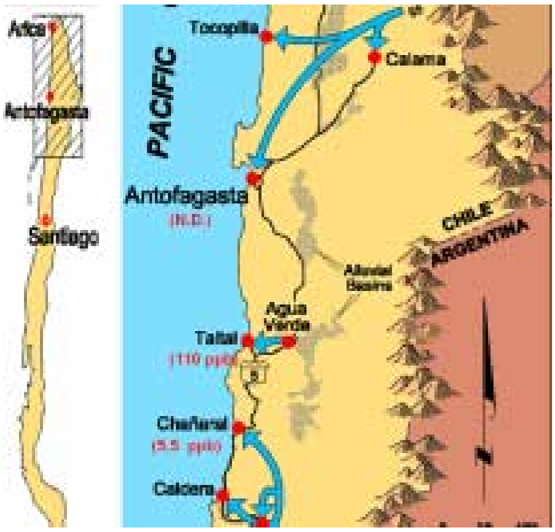

Figure 3. Study region in northern Chile. The primary study city, Taltal, obtains its municipal water from a well field in Agua Verde containing 110-115 ppb perchlorate. Antofagasta obtains its municipal water from snowmelt piped from the Andes. Chañaral obtains its municipal water from a well field in Copiapo to the south.

Tellez et al., of the Catholic University in Santiago, studied approximately 60 women during pregnancy and post partum in Taltal, a city in northern Chile where the entire municipal drinking water supply contains 110 to 115 ppb perchlorate. They compared these women's thyroid function during pregnancy and post partum with that of a similar number of pregnant women in each of two nearby cities: Antofagasta, with non-detectable perchlorate levels; and Chañaral, with 6 ppb perchlorate in the municipal drinking water. Neonatal thyroid function at birth was also evaluated via cord blood testing in each of the three cities. A map of the study region is shown as Figure 3.

Although iodine nutrition in this region has previously been excessive, changes in salt iodination were instituted in 2000, and the pregnant women studied in *Tellez et al.* had median urinary iodine levels of 269 μg/L, very similar to those in pregnant women in the U.S. surveyed by the Centers for Disease Control and Prevention (CDC) in the early 1970s and 1990s.

All maternal urine samples were analyzed for perchlorate by the CDC in 2004 using their latest technology (ion chromatography coupled with tandem mass spectrometry). A reliable estimate of the perchlorate excretion rate can made by expressing the urine perchlorate as a ratio with urine creatinine, and thus a reliable estimate of each woman's perchlorate dose over the preceding day or so also can be made. Cumulative distribution of perchlorate doses for women from the three cities was clearly different, as shown in Figure 4.

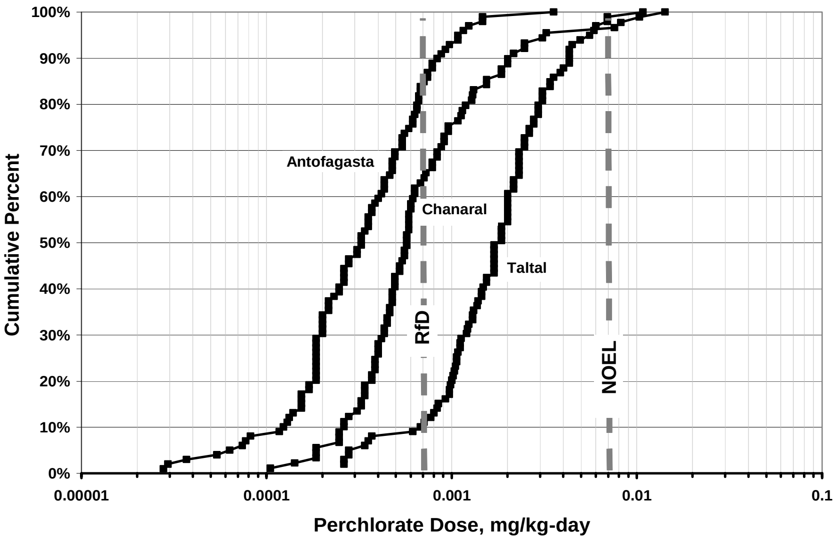

Figure 4. Cumulative distribution of maternal perchlorate doses as estimated from urinary perchlorate/creatinine ratios from three cities studied by *Tellez et al.* The NRC NOEL (.007 mg/kg-day) and RfD (0.0007 mg/kg-day) are shown superimposed.

It is apparent from Figure 4 that perchlorate dose is highly variable within each city. The women self-reported drinking a median of about one liter of tap water daily in addition to about 700 ml as sodas or bottled water. Using the median doses from Figure 4, it appears that in each city, the women were ingesting a median of about 20 to 30 μg perchlorate daily from sources other than tap water – most likely from food sources. No specific food sources of perchlorate were identified in this study. It also is apparent that only a few of the women were exceeding the NOEL as established by the NRC and none were exceeding the NOAEL. On the other hand, 15%, 35% and 90% of the women were exceeding the RfD in Antofagasta, Chañaral and Taltal respectively.

Tellez et al. evaluated maternal thyroid function in early (~16 weeks) and late (~33 weeks) pregnancy, and again post partum (~12 weeks). Newborn thyroid function was assessed from cord blood samples at birth. There were no maternal or neonatal hypothyroid effects attributable to perchlorate in Taltal relative to the two control cities, while typical thyroid changes associated with pregnancy were observed.

Perchlorate and iodine were assessed from breast milk samples obtained at the postpartum visit. Median breast milk perchlorate levels in each city were similar to the drinking water concentrations in the respective cities but the levels were highly variable. The levels ranged from < 4 μg/L in each city to a maximum of 1042, 61 and 204 in Antofagasta, Chañaral and Taltal respectively. The subject from Antofagasta with the highest breast milk perchlorate had non-detectable perchlorate in her home tap water but elevated urine perchlorate, suggesting a perchlorate source other than tap water. Mean breast milk iodine concentrations were 45, 33 and 38 µg/dL in Antofagasta, Chañaral and Taltal respectively. These levels were not statistically different and indicated acceptable iodine nutrition for the infants. No significant correlations could be established between breast milk perchlorate and either urine perchlorate or breast milk iodine concentrations.

3. DISCUSSION

Although they were not considered by the committee in their recommendation, taken together, the five new studies described herein are strongly supportive of the NRC committee report on the potential health effects of perchlorate. The new studies give more confidence to policy officials and the public by providing more evidence that environmental exposures to perchlorate are not likely to have any adverse effect, including to the most sensitive members of the population.

The subjects in the *Braverman et al.* occupational study had long-term perchlorate doses similar to the NOAEL, yet had no demonstrable hypothyroid findings. Benchmark dose analysis of the *Braverman et al.* and *Lamm et al.* study results yielded BMDLs that are generally in the range of the NOAEL and represent a valid statistical lower bound on a potential, but unobserved, effect of perchlorate. Comparative analysis of the thiocyanate literature, using relative potencies of perchlorate and thiocyanate from cell culture experiments, indicates that perchlorate doses of ½ the NOAEL do not cause any hypothyroid effects, even in sensitive subpopulations, while doses 2½ times the NOAEL cause hypothyroid effects in all populations. Thus, the NOAEL is very consistent with results of the newer studies.

The *Braverman et al.* occupational study demonstrated a long-term dose-response relationship between perchlorate ingestion and iodine uptake that is nearly identical with that from the two week study by *Greer et al.* Furthermore, *Braverman et al.* demonstrated that the workers had adjusted to the perchlorate and were actually more efficient at absorbing iodide than were community controls without exposure. Although only a few of the pregnant women studied by *Tellez et al.* had perchlorate doses exceeding the NOEL, many had doses approaching the NOEL, and there was no discernable tendency toward hypothyroid findings as perchlorate dose increased.

The RfD is intended to be a conservative concentration that protects even the most sensitive subpopulations for a lifetime. Among the pregnant women studied by *Tellez et al.*, 90% of the women from Taltal exceeded the RfD, yet there was no tendency toward hypothyroid findings in either mothers during pregnancy or the infants at birth. Thus the RfD, although conservative, is clearly protective of these most sensitive subpopulations.

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Chapter 17

OVERVIEW OF TWO LARGE-SCALE RESIDENTIAL SUB-SLAB DEPRESSURIZATION SYSTEM INSTALLATION PROGRAMS

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Abstract: Sub-slab depressurization (SSD) systems, commonly used to mitigate radon, create a vacuum beneath a building to prevent soil gas from entering the building as a result of pressure gradients that naturally exist between the building and the sub-slab region; the extracted soil gas is then vented directly to the atmosphere. This paper describes two large-scale residential SSD system installation case studies. The SSD systems were designed and installed to mitigate intrusion of soil gas, which contained low levels of volatile organic compounds, into (1) 100+ individual houses and (2) several buildings in a multi-structure condominium complex.

The SSD installation methodology consisted of the following components: stakeholder involvement, site assessment, feasibility study, pilot testing/design, installation, performance testing, and operations & maintenance. Public meetings were held and homeowner feedback was elicited to achieve an end product that not only mitigated vapor intrusion, but also was acceptable to the homeowner. The system design process incorporated the results of site-specific assessments and field pilot testing. These systems were installed in a design-build fashion using a variety of construction techniques. Following installation, the SSD systems were performance tested to ensure that the resulting suction field encompassed the entire sub-slab area.

Examples of the SSD system installations are presented. SSD system designs/components and construction techniques, issues, and challenges specific to the two case studies are discussed. System performance data and lessons learned from the SSD installations also are presented. In addition, a comparison of the operation of the engineered SSD systems to several radon mitigation systems previously installed using typical radon industry techniques is conducted to reveal some interesting results.

Key words: vapor intrusion; mitigation; sub-slab depressurization; SSD; volatile organic compounds

1. INTRODUCTION

During the past several years, the issue of vapor intrusion of gas-phase contaminants from soil gas systems into indoor air of buildings has gained much attention in the scientific community and environmental industry (Renner, July 2002). Recent advances in assessing the potential for contaminated vapor intrusion are resulting in more mitigation efforts to address vapor intrusion. A pollution issue in Denver, Colorado received national attention in 2001, when data revealed that indoor air in numerous homes was being impacted from a long-studied groundwater plume, previously thought to pose no risk (Obmascik, April 29, 2001). For most people, especially those with a public water supply, exposure to the indoor air is typically significantly higher than exposure to other environmental media. If this indoor air becomes contaminated with harmful constituents, there is a risk of potential consequences from this exposure. There exists a natural pressure gradient between buildings (lower) and soil gas beneath the buildings (higher). This pressure gradient facilitates the entry of soil gas and potentially any associated gas-phase contaminants such as radon and volatile organic contaminants (VOCs) into buildings, thus contaminating indoor air. Modern buildings are generally built to minimize natural exchange of indoor air with outdoor air, thereby exacerbating the impact of vapor intrusion.

The development and application of mitigation measures to address vapor intrusion have become integral components of this issue. Mitigation measures to minimize the levels of contaminants in indoor air include increasing the exchange (replacement) of indoor air with outdoor air using conventional air exchange systems. However, a more efficient technique of reducing contaminant concentrations in indoor air is to prevent the intrusion of the contaminants into indoor air (USEPA, 1991 & 1993). This can be achieved by: (1) sealing entry points for soil gas (e.g. crawlspaces, cracks, penetrations, and porous walls); and (2) installing a passive or active system to circumvent contaminated soil gas around the building by creating a vacuum below the building and venting soil gas directly to the atmosphere. An active system is referred to as a sub-slab depressurization (SSD) system (USEPA, 1991 & 1993). SSD systems are typically more cost effective than interior air exchange based systems (USEPA, 1993).

This paper presents two large-scale SSD system installation programs that were undertaken in Connecticut to address vapor intrusion issues affecting residential structures. To protect the confidentiality of homeowners, the locations of buildings where the SSD systems were installed are not provided in this paper. The first SSD system installation program involved the installation of systems in a residential neighborhood located downgradient (groundwater flow) of a former industrial complex. Environmental sampling conducted by the United States Environmental Protection Agency (USEPA) indicated the presence of low levels of VOCs in samples of soil gas and indoor air collected within the residential area. The VOCs trichloroethene (TCE) and 1,1-dichloroethene (1,1-DCE) were of primary concern based on risk assessment by the USEPA and the Connecticut Department of Public Health. In response to the detections of these VOCs, SSD systems were installed in 2001 and 2002 to mitigate vapor intrusion at nine buildings, consisting of seven single-family homes and two commercial buildings. Rather than proceeding with additional sampling and data evaluation within the residential neighborhood, a programmatic decision was made by USEPA to install SSD systems in up to 114 residential structures, commencing in Fall 2003. The systems were installed as a preventative measure against potential future vapor intrusion issues in the neighborhood. The USEPA enlisted the Connecticut Department of Environmental Protection (CTDEP) and its environmental engineering consultant, Metcalf & Eddy, Inc. (M&E), to implement the SSD system installation program to protect human health. M&E teamed with two environmental contractors to install the SSD systems.

The second installation program was implemented from February 2004 to May 2005 to address potential vapor intrusion issues at a condominium complex. As part of an area-wide investigation conducted by CTDEP, chlorinated VOCs were detected in groundwater samples that were collected in the vicinity of the condominium complex. CTDEP subsequently conducted sampling of groundwater and soil gas at the complex. Chlorinated VOCs were detected in groundwater and soil gas at concentrations above volatilization criteria specified in the State of Connecticut Remediation Standard Regulations (CTDEP, 1996) and Proposed Revisions, Connecticut's Remediation Standard Regulations, Volatilization Criteria (CTDEP, 2003) in the vicinity of five multi-unit residential buildings. As a result of TCE detections in soil gas in exceedance of CTDEP's proposed revised volatilization criteria, CTDEP contracted

M&E to design & install SSD systems at the five buildings to protect human health. M&E teamed with an environmental contractor to install the SSD systems.

2. SSD INSTALLATION METHODOLOGY

2.1 Overview of an SSD System

An SSD system intercepts the soil gas beneath a floor slab before it migrates into the living/working areas of a building. The system creates a zone of suction immediately beneath the floor slab to capture the soil gas and discharge it to the building exterior/outdoors. Each SSD system consists of the same general set of components as follows:

- Fan/Blower(s)
- Suction Piping
- Exhaust Piping
- Monitoring System and Alarm
- Electrical Service

Figure 1 presents a schematic of a typical SSD system installation. The SSD system fan has both an intake side and an exhaust side. Suction piping connects from the intake side of the fan to a suction hole through the (basement) floor slab. On the exhaust side of the fan, vent piping is connected from the fan to the final vent location. The exhaust piping terminates with a vent cap that prevents intrusion of rain and pests. Multiple fans and/or suction points may be used to create the necessary suction beneath all floor slabs and crawl spaces.

The SSD system also includes a monitoring system to ensure that the system is operating properly. The monitoring system consists of a differential pressure gauge which monitors for the presence of suction in the suction piping at all times. If the monitoring system does not detect any suction, a visual/audible alarm is activated.

2.2 Public Outreach

The USEPA, CTDEP, and M&E participated in public outreach efforts to ensure that the stakeholders understood the objectives and various facets of the SSD installation program. The public outreach consisted of:

- meeting with homeowners, building owners, the condominium association, and various representatives of these groups;
- holding public presentations and workshops; and
- distributing project-related information.

Based on these public outreach efforts, stakeholder concerns were incorporated into the SSD installation program. The public outreach effort facilitated an environment of cooperation and understanding between the residents, regulatory agencies, and environmental contractors.

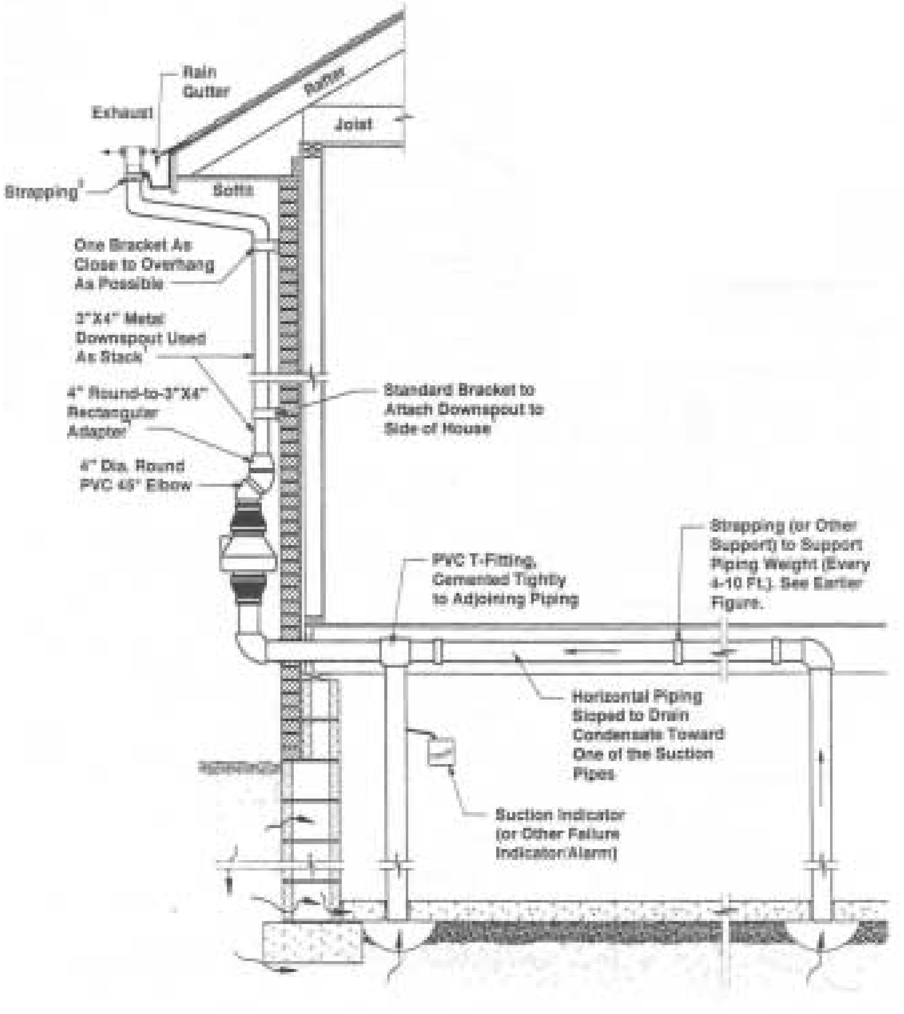


Figure 1. Schematic of Typical SSD System Installation (Source: USEPA, 1993)

2.3 SSD System Installation Program Approach

The approach for installing the SSD systems consisted of a number of steps. Prior to system installation, the property owner signed an access agreement allowing access for SSD system installation work. Once the access agreement was obtained, a site assessment was conducted of each building/property that included an inspection of the foundation walls, basement floors, crawl spaces, and other portions of the house in contact with the ground, and the development of a site plan & building layout. A field checklist was used to facilitate data collection.

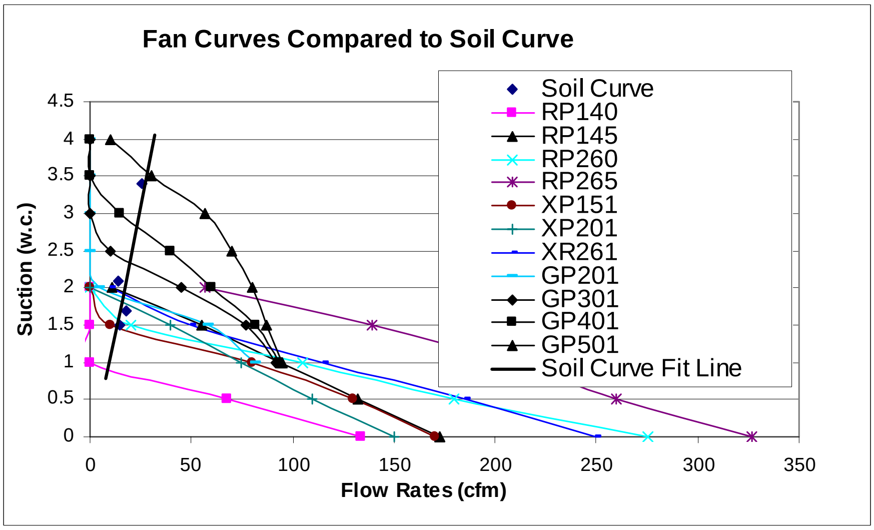
Upon the completion of the site assessment, a feasibility study was conducted. The feasibility study varied in complexity, depending on the conditions encountered during the site visit (e.g. size and layout of building). For the single-family residential homes, areas of the concrete slab had to be selected for pilot testing. The condominium buildings necessitated an evaluation of two significantly different approaches to mitigate vapor intrusion. One approach involved horizontal directional drilling in conjunction with traditional soil vapor extraction, while the second approach consisted of a complex SSD system. The second approach was selected as the preferred alternative based on technical feasibility, constructability given the site conditions, and cost.

Following the initial site assessment and feasibility study, field pilot testing was performed at each building in order to evaluate subslab soil flow characteristics under the application of suction. Flow characteristics included soil permeability, the presence of potential obstructions, and possible short-circuiting issues. The steps to the pilot test were as follows:

1. Core one or more temporary suction test holes through the slab being tested.
2. Drill several temporary test holes through the slab at varying distances from the suction test hole.
3. Apply varying levels of suction to the suction test hole using a portable blower / suction gauge unit vented to the outside.
4. Measure the corresponding levels of suction [inches water column (W.C.)] created at each test hole, using a digital micromanometer. The information recorded during the pilot test was recorded using a standard form.
5. The test holes were then temporarily plugged pending final installation.

Site-specific assessment information and pilot test data were used to design the SSD system. The system was designed to ensure that adequate suction is created beneath all floor slabs and crawlspaces (as appropriate). The objective was to achieve complete capture of the sub-slab region. For the design, the pilot test data was evaluated to determine the amount of suction required at each planned suction hole(s) to create adequate suction levels beneath the home. Pilot test data was then used to select the fan size necessary to generate the required suction level at the suction hole(s). Figure 2 presents a typical set of pilot test flow-suction data compared to performance data for several commercially available fans. From this analysis, the overall system layout was determined and the necessary system components were selected and sized. Design details and specifications for the system include:

- Number/location/layout of suction points;
- Number/location/layout of fans;
- Size and layout of fans and piping;
- Location of monitoring systems and alarms;
- Location of electrical service and on/off switch.



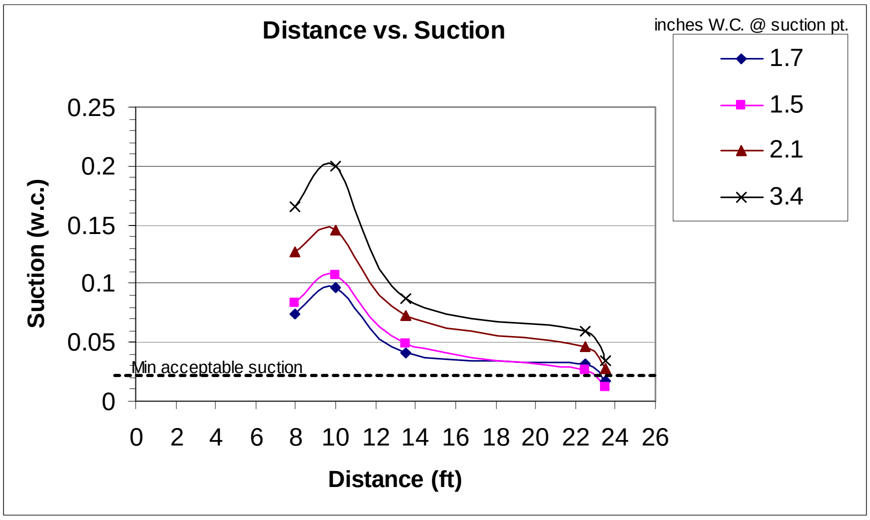


Figure 2. Example of Pilot Testing & Design Data.

Prior to installation, a plan of the proposed system was prepared and approved by the home/building owner. A critical component to the success of the installation programs was to ensure that the systems were acceptable to the home/building owner. In addition, required electrical and building permits were obtained from local governmental agencies.

Systems were installed in a design-build fashion using a variety of construction techniques. SSD system installation consisted of coring suction hole(s), installing fan(s), installing suction and exhaust piping, and installing other system components. Suction holes were cored through concrete slabs and/or foundation walls, depending on the building layout, results of the pilot testing, and input from the building owner. Piping was pitched back towards the suction holes. Fans were positioned on the exterior of buildings, while alarms were positioned in easily accessible locations in the vicinity of the suction hole(s). Traditional gutter material was used as exhaust piping in order to blend the system with the exterior of the home, and in one case, faux chimneys were constructed from enclosures built onto the building, which housed numerous fans, and terminated above the roofline. In addition, to eliminate soil gas intrusion pathways, concrete floors were repaired/replaced as necessary and all accessible cracks and openings in the foundation walls and floors were sealed with concrete, grout, caulk, and/or sealant. Electrical work was performed by a licensed electrician in accordance with the local, state, and national codes under a local permit.

Following system installation, a system performance test was conducted to confirm that the system is operating as intended. The performance test used several temporary test holes to measure and confirm that adequate suction is being created beneath the entire floor slab. The information collected during the performance test was recorded using a standard form. Following the performance test, all temporary test holes were filled and resealed with caulk or grout. Operations and maintenance issues are discussed as part of the case studies.

3. SSD INSTALLATION CASE STUDIES

3.1 Residential Neighborhood

In 2001-2002, seven homeowners and two building owners agreed to have SSD systems installed by EPA/CTDEP. During the 2003-2004 period, a total of 97 of 114 home/building owners granted access to CTDEP. This SSD installation program is summarized as follows:

- October – December 2001: 3 single-family homes & 2 commercial buildings
- October – November 2002: 4 single-family homes
- September 2003 – May 2004: 95 single-family homes & 2 apartment buildings

The residential neighborhood consisted of a variety of structures. The 102 single-family homes ranged from single- and multi-story buildings, with footprints ranging in area of ~600 to ~2,000 FT^2. These buildings were generally constructed between the early to mid 1800s to the mid to late 1900s, and varied in construction style (e.g. Colonial, Modern, Victorian). All of the homes had basements with either concrete slabs (of varying condition and configurations) or dirt floors. Foundation walls were constructed of concrete block, poured concrete, or stone masonry. A significant number of the homes had additions and/or crawlspaces. One commercial building was formerly a two-story Colonial/Cape-style residential structure.

Several homes had existing radon removal systems; these systems were evaluated and were found to provide incomplete coverage of the subslab area. This issue is discussed in the conclusions section of this paper.

The second commercial building and the two apartment buildings were constructed differently than the other buildings. The second commercial building was a ~3,500 FT^2 gymnasium of concrete block and floating slab-on-grade construction. The layout of the building consisted of a large open room and several smaller rooms. The two ~8,000 FT^2 multi-story apartment buildings were constructed of poured concrete walls and brick. Both buildings had basements with multiple floating concrete slabs.

While a number of smaller homes with simple layouts only required one suction hole and one fan to achieve complete capture of the subslab region, a significant fraction of the structures necessitated more complex approaches. The residential neighborhood presented a plethora of issues that were overcome during the installation program including: weather-related issues, deteriorated or non-existent concrete slabs, variability of subslab conditions, and a multitude of footprints and building layouts. Photographs of SSD installation features are presented as Figure 3.

Older residential structures featured masonry stone walls (some with deteriorated lime mortar), unsealed penetrations, concrete slabs in poor condition, and dirt floors. Masonry stone walls of poor condition were parge-coated with Portland cement to achieve a thorough seal. Although slabs of poor condition and dirt floors required the installation of a new concrete slab, in some cases this facilitated system installations. The absence of a concrete slab in good condition allowed for the placement of highly efficient subslab horizontal piping runs placed in stone-filled trenches. Figure 4 presents an example of one of the SSD installations that required sealing of stone walls, a new concrete slab, and horizontal piping runs. A minimal fan size was required to attain the required subslab suction field.

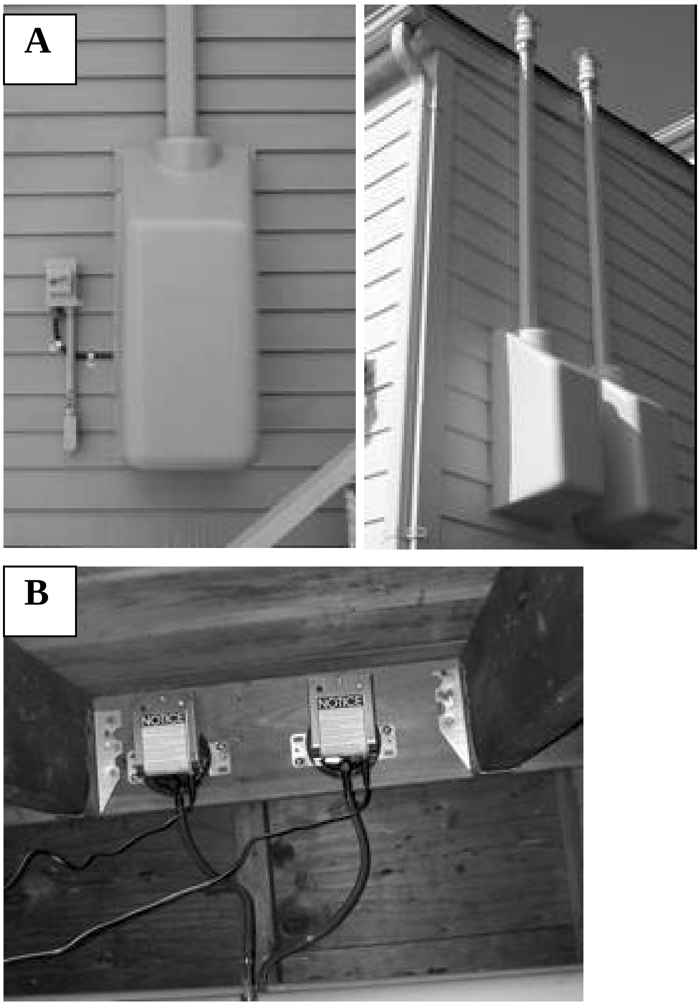


Figure 3. Photographs of Typical SSD System Installation Features. (A) Exterior SSD system components: covered fans, on/off switches, downspouts, and exhaust vent caps. (B) View of two SSD monitoring systems.

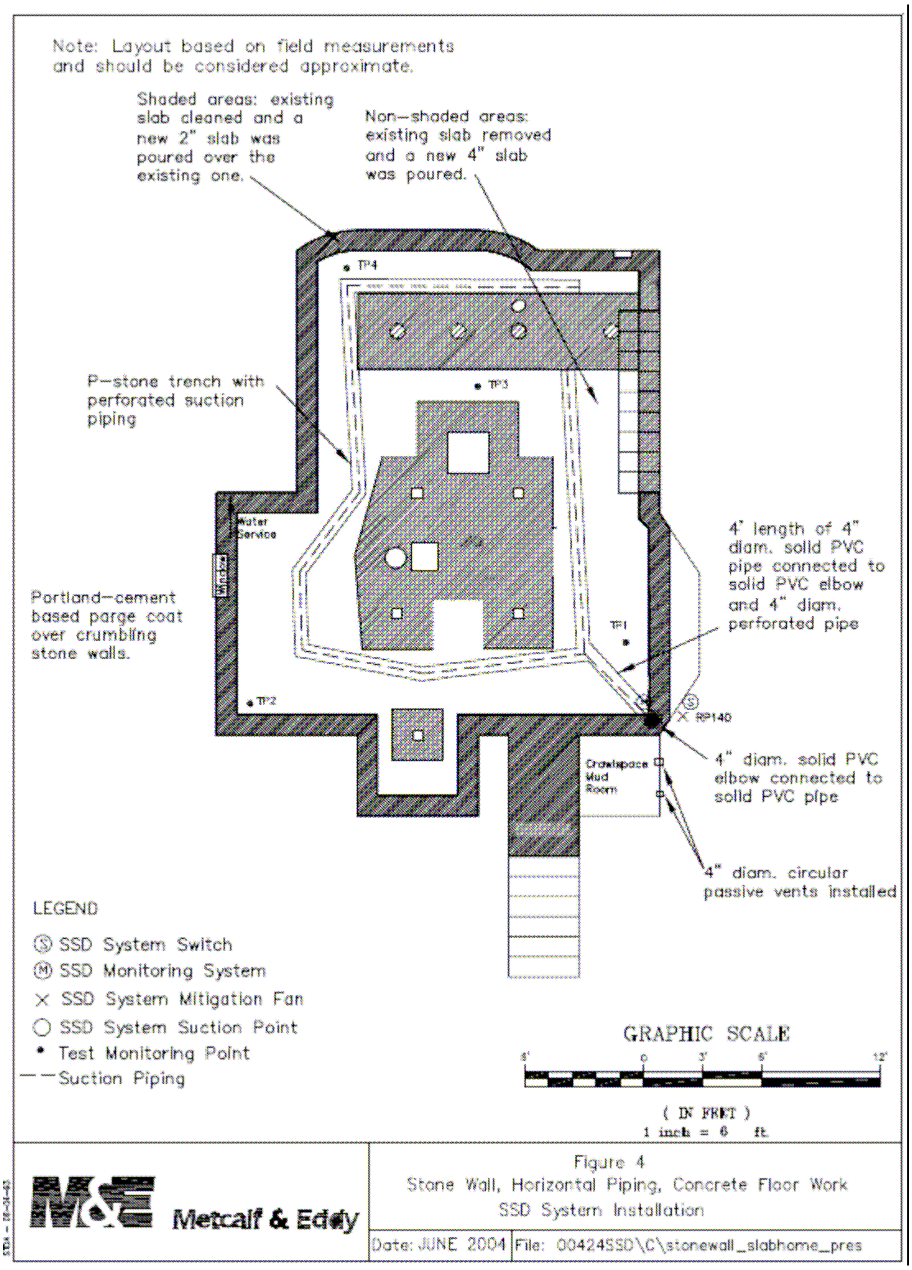


Figure 4. Single-Family Residential Structure Example 1: Sealing of Stone Walls, & Installation of Horizontal Piping Runs and a New Concrete Slab.

A significant characteristic of the neighborhood was the variability of subslab conditions and layout between the homes. A number of buildings had multiple slabs, separated by subsurface footings, with varying permeability. These cases were addressed using several suction holes, multiple pipes feeding single fans, differently sized fans, and flow control valves. An example of a multiple slab installation is provided as Figure 5. This installation required seven suction holes and two fans.

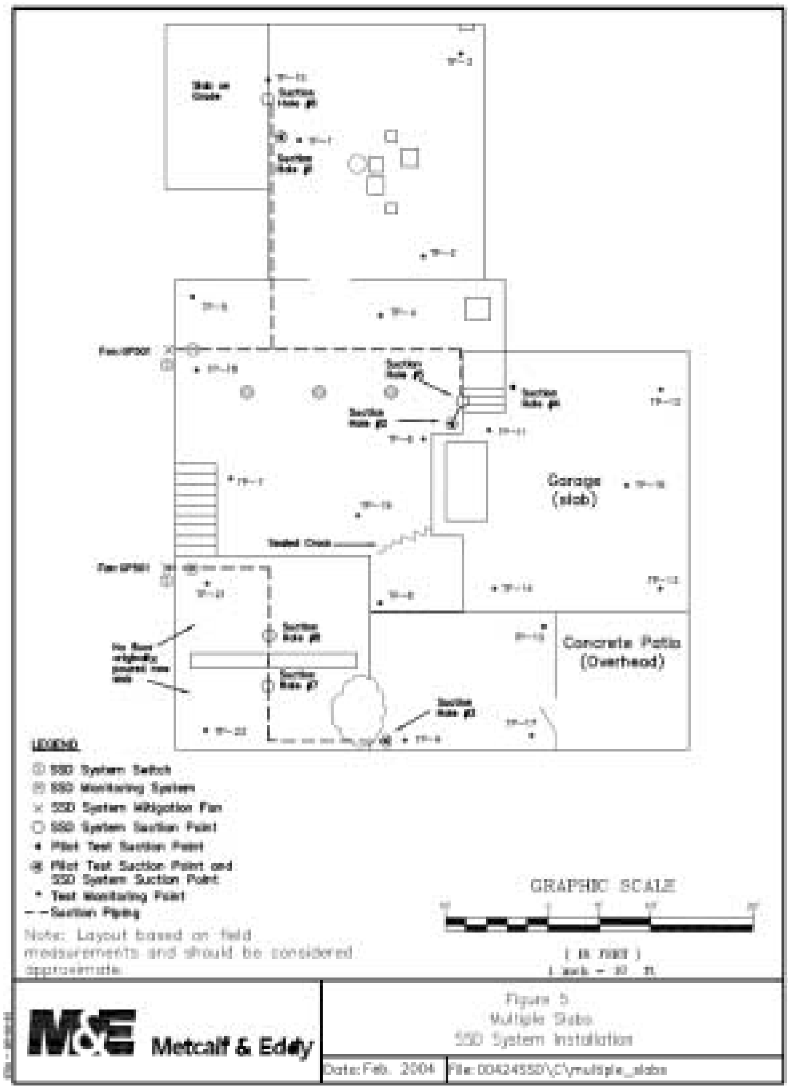


Figure 5. Single-Family Residential Structure Example 2: Multiple Slab Installation.

Additional challenges that were encountered during the installations were finished basements in some homes and crawlspaces. Finished basements required varying degrees of restoration, depending on the level of intrusion necessitated by the installation. In some cases, floors and walls were repaired and/or replaced. Crawlspaces presented another point of entry for vapor intrusion. Concrete slabs or vapor membrane barriers were installed in each crawlspace. The crawlspace was then vented separately or tied into the main SSD system with a smaller diameter suction line.

Many of the installations were conducted during winter months. Health & safety issues such as cold stress, slip/fall hazards, and working in unheated crawlspaces had to be addressed. Working styles were modified by dressing properly for the conditions, frequently cycling contractor technicians between indoor and outdoor work areas, and providing on-site heaters, if necessitated. Through these modifications, SSD system installations continued through the winter and the project schedule did not lag.

3.2 Condominium Complex

The condominium association granted access to the CTDEP to install SSD systems in five multi-unit residential buildings that CTDEP identified as having potential soil vapor volatilization issues. Installations were performed in four buildings in February to April 2004, while the fifth building received a SSD installation during the period of Fall 2004 to Spring 2005.

The first four condominium buildings were multi-storied with four identically sized units on each floor. Each of these four buildings had a footprint of ~5,000 FT^2 and the foundation walls were of concrete block wall construction. The first four buildings were each built with four identically-sized crawlspaces under each floor. The crawlspaces had separate floating concrete slabs of poor quality (extensive cracking) and were ~1.5-3 FT high, making them confined spaces. The fifth building was multi-storied with eight units on each floor, and had a footprint of approximately ~15,000 FT^2. Unlike the first four buildings, the fifth building was concrete slab-on-grade construction with eight equally-sized separate slabs.

The condominium association requested that SSD suction holes, piping, and associated appurtenances be hidden from view to the extent possible. On the first four condominium buildings, this request was satisfied by pilot testing and installing suction holes and suction piping within the crawlspaces beneath the buildings. Prior to conducting the pilot studies, each crawlspace had to be cleaned of debris and wastewater that obstructed the work areas. Due to the nature of the crawlspaces, all pilot testing and system installation activities had to be performed by engineers and contractors trained in confined-space operations.

Due to the highly variable subslab nature observed for all five buildings; suction results varied greatly from slab to slab. Fan types were selected based on pilot testing data review; smaller fans were selected for slabs with fairly permeable subslab behavior, in order to save on long-term electrical costs.

A variety of construction techniques were utilized to install the systems. Suction holes (~4 inch diameter with a 12 inch sub-slab void space) were installed by using a hammer-drill and manual excavation. Piping consisted of 3 and 4 inch diameter schedule 40 PVC and was installed while maintaining pitch and allowing for future access throughout the crawlspace. Penetrations through foundation wall and sill plates were sealed according to fire code. In addition, deteriorated and cracked portions of the concrete slabs and floor/wall joints were caulked and/or covered with concrete to achieve a seal, thereby preventing short circuiting of the vacuum. Fans and alarms were mounted on the ends of the buildings.

Figure 6 presents a typical layout of the SSD system as it was constructed in one of the first four buildings. Note the network of pilot test/suction holes and piping that were required to achieve complete capture of the subslab region. A total of 16 suction holes, ~ 300 ft of piping, and 4 fans were utilized. Note that the number of suction holes varied per crawlspace, based on pilot and performance testing. The differential pressures (inches W.C.) measured during the performance testing performed following the installation are shown. Adequate suctions are achieved throughout the subslab area.

Due to the differences in building construction, the SSD system installation in the fifth condominium structure proceeded in a different manner compared to the first four. Although pilot testing was conducted using both vertical holes inside of homeowners' units and horizontal holes through the foundation walls, the final design required that suction holes only be installed horizontally through foundation walls. To help propagate suction, perforated suction piping was inserted into all the horizontal suction holes beneath the floor slab. To insert the perforated piping beneath the floor slab, an Air Spade™ and shop vacuum were used.

A network of trenches required excavation to allow for the placement of the subsurface piping runs. Excavation was performed using a mini-excavator or by hand when subsurface utilities were encountered. As much of this phase of work was conducted during the winter months, heat coiling and insulation blankets were used to prevent soil from freezing. Due to the topography and building layout, sloping of the piping back to the suction holes could not always be achieved. Therefore, a number of condensate drip legs were installed at strategic locations within the system to allow for the removal of water from the system. The drip legs were installed with access covers to allow for future operations and maintenance activities.

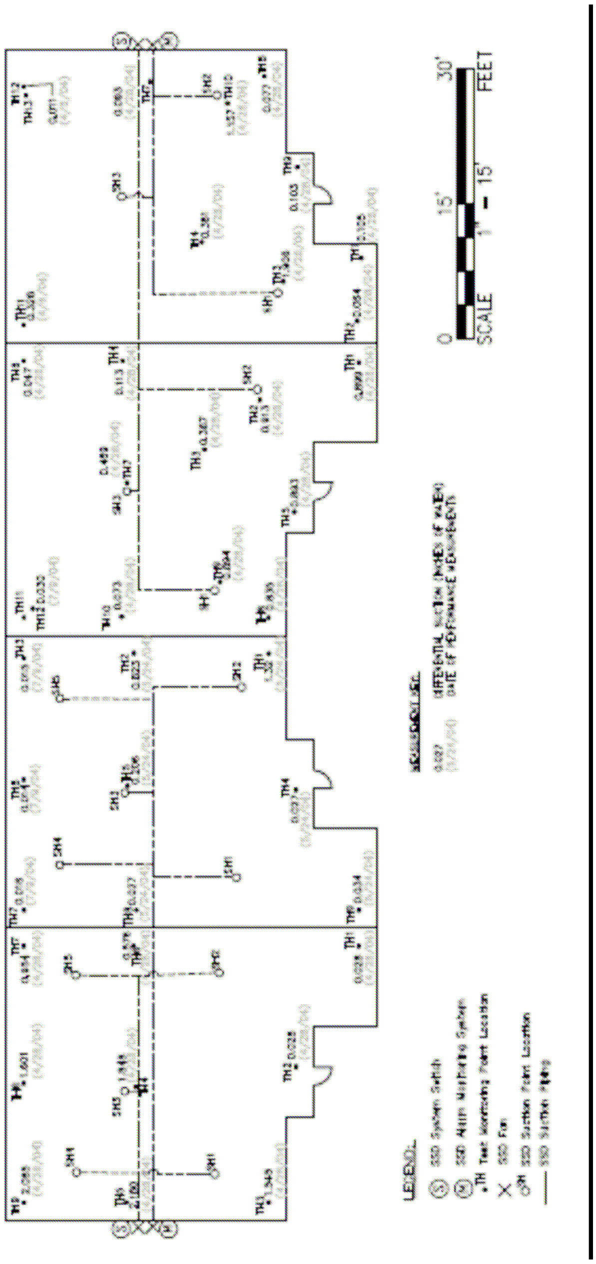


Figure 6. Condominium Building Example 1: Crawl Space Installation.

The fifth building's SSD system is presented as Figure 7. The extensive network of pilot test/suction holes and piping required to achieve complete capture of the subslab region is shown. A total of 39 suction holes, ~2,500 ft of 4 inch diameter schedule 40 PVC piping, 16 condensate drip legs, and 16 fans were utilized to construct the whole system. The fans and alarms were housed in two enclosures located on the ends of the building. The enclosures were constructed to match the exterior façade of the condominium building, and were also constructed with sound dampening materials. For each enclosure, a chimney structure was constructed to house the exhaust piping. The differential pressures (inches W.C.) measured during the performance testing performed following the installation is shown. Similar to the first four buildings, adequate suctions are achieved throughout the subslab area.

During all five installations, field changes were made to the original design. Based on the results of performance testing conducted while the installations were underway, several subslab areas requiring additional suction were identified. Additional suction holes and associated piping runs were installed to achieve required capture. Further, several instances of surface water runoff issues were encountered during the installation process. As part of the installations, these water runoff issues were corrected to alleviate future wet-crawlspace issues and to minimize the effect of water runoff on the SSD systems.

To complete the installations, site restoration activities were conducted. Site restoration consisted of the following tasks:

- Top soil placement, preparation, and establishment of grass seed
- Replacement and repair of landscape features
- Concrete sidewalk replacement and repair
- Surface drainage structure repair and replacement

3.3 System Maintenance

CTDEP has assumed responsibility for maintenance of the SSD system (including fan replacement) while there is an unacceptable risk caused by potential soil gas migration into the home. Maintenance agreements stipulating CTDEP's responsibility were signed by all parties receiving SSD system installations. The agreements were provided to each homeowner; they are signed by DEP.

Normal system operation does not require involvement from the homeowner / building owner except for routine inspection. If the audible/visual alarm signals a loss in suction within the system, the homeowner / building owner has been instructed to contact a specific person at the CTDEP. Contact information is also available on a label affixed to the system near the alarm should building ownership change, etc. Maintenance calls are then forwarded to an on-call environmental contractor. The fans that were employed for these installations have a 5 year manufacturer's warranty and are relatively simple to replace.

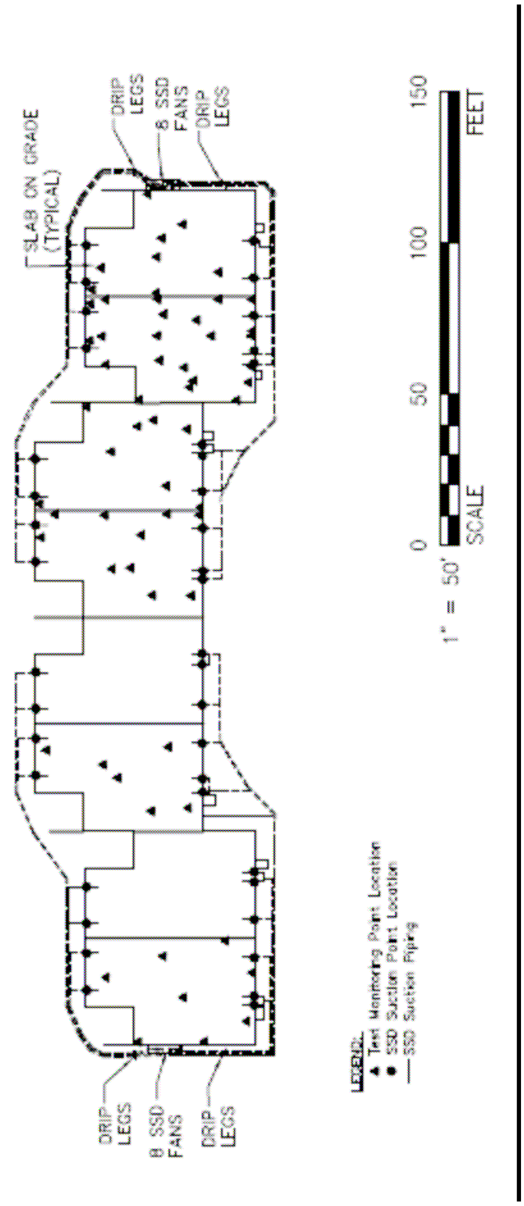


Figure 7. Condominium Building Example 2: Slab-On-Grade Installation.

Several other activities comprise the longer-term maintenance of the systems. These tasks include repairing system components damaged from extreme weather events. Particular to the installation performed at the fifth condominium building, any water that has accumulated within the drip legs requires removal. In addition, annual neighborhood inspections of the system components located on the exterior of the residential structures are performed.

4. CONCLUSIONS

4.1 System Performance

All of the systems are currently depressurizing subslab regions; several of the systems have been in operation for almost four years. A few of these systems have required minimal maintenance, including fan replacement, minor piping repairs, and removal of ice buildup during the winter. However, the majority of the SSD systems have not required attention except for the annual survey.

The post-installation performance test provides physical evidence that the system is achieving the goal of complete capture of the subslab area. However, some additional testing had been conducted. USEPA conducted some follow up testing for VOCs in indoor air of several of the homes within the residential community; the results of this testing indicated significant reductions in VOC levels. CTDEP conducted radon (as a surrogate for VOCs) testing of indoor air before and after installation in a select set of homes; these results also indicated that vapor intrusion had been mitigated. In the case of the condominium complex, CTDEP performed testing of soil gas in the close proximity of the first four buildings before and after the installation of the SSD systems. Levels of VOCs in soil gas were below the proposed revised volatilization criteria following the initiation of the SSD systems.

4.2 Critical Issues and Lessons Learned

The success of these large-scale SSD system installation programs was primarily due to the synergistic efforts of the regulatory agencies involved and the overall project approach. A critical component of the program was maintaining communication between the regulatory agencies and the stakeholders. Potential misunderstandings or mistakes were minimized, and any issues that arose were solved in a timely fashion.

The design-build approach included: pilot testing (sometimes iterative); designs that considered building owner concerns; installations with the flexibility of field changes; and performance testing. These facets allowed for expedited installations and a minimization of disturbance to residents.

The scale of the installation projects allowed for some economies of scale. Construction techniques between homes were similar and relatively simple to employ, allowing several installation crews to perfect these techniques and operate simultaneously on multiple structures. The system components were generally standardized, allowing for judicious replacement of compromised or incorrect pieces.

As indicated earlier, radon systems had been installed in several residences prior to the commencement of the residential neighborhood SSD installation program. These systems were assessed by measuring the differential pressures that existed in the well-established suction fields. The extents of adequate subslab suction field for the five systems ranged from 25 to 50 % of the slab area. This result suggests that engineered sub-slab depressurization systems provide more consistent results compared with traditional radon systems.

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Chapter 18

ACCUMULATION OF HEAVY METALS BY CUCUMBER AND *BRASSICA JUNCEA* UNDER DIFFERENT CULTIVATION CONDITIONS

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Abstract: Pollution by heavy metals from industries, the storage of polluted wastes, and agricultural fertilizer pose a serious threat to human health. These pollutants may pass into the soil where plant uptake or leaching to groundwater can contaminate the food chain. Phytoremediation is the technique for removing contaminants in the environment by plants, and is being currently researched world-wide. Evapotranspiration is also responsible for moving contamination into the plant shoots. Because contamination is translocated from the roots to the shoots, which are harvested, contamination is removed while leaving the original soil undisturbed. Some plants that are used in phytoextraction strategies are termed "hyperaccumulators", which are plants that achieve a shoot-to-root metal-concentration ratio greater than one. *Brassica juncea* is well-known as Pb hyperaccumulator. Cucumber is also requently used to study the transportation mechanism of heavy metals, because its sap is easy to collect. This study focused on whether or not the cultivation temperature of the plants relates to the transportation of heavy metal. Using Cucumber and *Brassica juncea*, plants were cultivated under hydroponics with Pb (60 to 600 ppm). The cultivation temperature was changed from 8 degrees to 30 degrees for 96hours. We measured Pb concentration and GSH concentration and protein concentration every 24 hours. Pb concentration was measured by AAS after being ashed with a microwave system. GSH and protein concentrations were measured after crushing with liquid nitrogen by HPLC. At 25 degrees, the amount of absorption of lead in the cucumber was at maximum. However for *Brassica juncea*, the amount of absorption of lead was at maximum at 12 degrees. This result shows that the heavy-metal accumulation time differs in each plant. It was shown also that GSH and protein concentration were related closely to the accumulation of heavy metal and to the cultivation temperature.

Key words: Phytoremediation; heavy metals; Cucumber; *Brassica juncea*; Pb; GSH; Amino acid; Hly

1. INTRODUCTION

Phytoremediation is the general term for the environmental purification technology that uses plants to remediate soils. Phytoextraction is a particular remediation method used to remove heavy metal from polluted soils. There are two methods of phytoextraction (accumulation of heavy metal by a plant). In the first method, a chelating agent is added to the soil when the biomass of the plant body has almost matured at which time the chelating agent can absorb the heavy metals rapidly. In the second method, the plant is allowed to continuously absorb heavy metals depending on the growth stage (Salt et al., 1998).

The first method using chelating agents is effective for heavy metals (lead or cadmium) which are insoluble in a conventional soil environment. Chelating agents used are citric acid of an organic acid as well as EDTA or EGTA. The addition of a chelating agent can increase the accumulation ability in plants where the natural accumulation rate is comparatively low. For example, the soil can absorb 0.01-0.06% lead in a dry weight without a chelating agent: with the addition of a chelating agent, it can suck up lead more than 1% lead in a dry weight (Huang et al., 1997, 1996; Blaylock et al., 1997). However, it is dangerous to add excessive amounts of chelating agents as they allow heavy metal immobilized by rain to invade ground water.

The second method of phytoextraction, which allows the plant to continuously absorb heavy metals, often uses a hyperaccumulator to accumulate heavy metal.

As has been shown, the accumulation stage of heavy metal in plants is important for phytoextraction. Both cultivation condition and temperature are thought to be important factors in the accumulation of vegetal heavy metal in particular. For example, a seasonal variation is suggested for *Artemisia princeps*, given the migration pattern of copper from subterranean root to above-ground shoot. (Takeda et al., 2004).

In this study, we investigated how cultivation conditions were related to the accumulation of heavy metals by using *Brassica juncea* and cucumber. From the early spring to the beginning of summer, *Brassica juncea* is a viable lead accumulation plant. In contrast, the cucumber is a non-accumulation plant, but the collection of sieve-tube fluid and excretory-duct fluid is unproblematic and the heavy metal displacement configuration from subterranean root to above-ground plant is easy to study.

2. MATERIAL AND METHODS

2.1 Plants

A cucumber (*Cucumis sativus*, Takii Seeds, Kyoto, Japan) was germinated with 0.5mM CaCl2 solution, and pre-incubated for one week at 25 degrees Celsius, in a dark period of 12 hours and a light period of 12 hours. *Brassica juncea* (obtained from the Kizu River) was germinated with vermiculite, and pre-incubated by using Hoagland solution (Hoagland et al., 1938) for one week at 25 degrees Celsius, in a dark period for 12 hours and a light period for 12 hours.

2.2 A variation of lead concentration with culture temperature

For four days, we cultivated one of each plant (Light 12 hours, Dark 12 hours), each in a lead solution (a cucumber, 60ppm $Pb(NO_3)_2$, *Brassica juncea* 600ppm $Pb(NO_3)_2$ component 1/2Hoagland aqueous solution) at 8 degrees Celsius; 12 degrees Celsius; 25 degrees Celsius; and 30 degrees Celsius. We measured lead concentration in each plant body every day. We then used nitric acid and H_2O_2 and did wet ashing in a microwave oven after drying the plants in dry oven at 80 degrees Celsius for 24 hours. The lead concentration was measured using atomic absorption spectrophotometry.

2.3 The measurement of GSH (reduced glutathione) concentration and amino acid concentration of a cucumber

We added 10 mM Tris-Buffer (pH8.5) and crushed root at 25 degrees Celsius and 30 degrees Celsius after freezing it in liquid nitrogen, then collected the supernatant by centrifugation (1. 1200g, 15 minutes, 4 degrees Celsius; 2. 1200g, 5 minutes, 4 degrees Celsius). The supernatant GSH and amino acids were measured using 100 μM 5,5'-dithiobis-(2-nitrobenzoic acid) solution for GSH, and an Ez faast Amino Acid Kit for the amino acid.

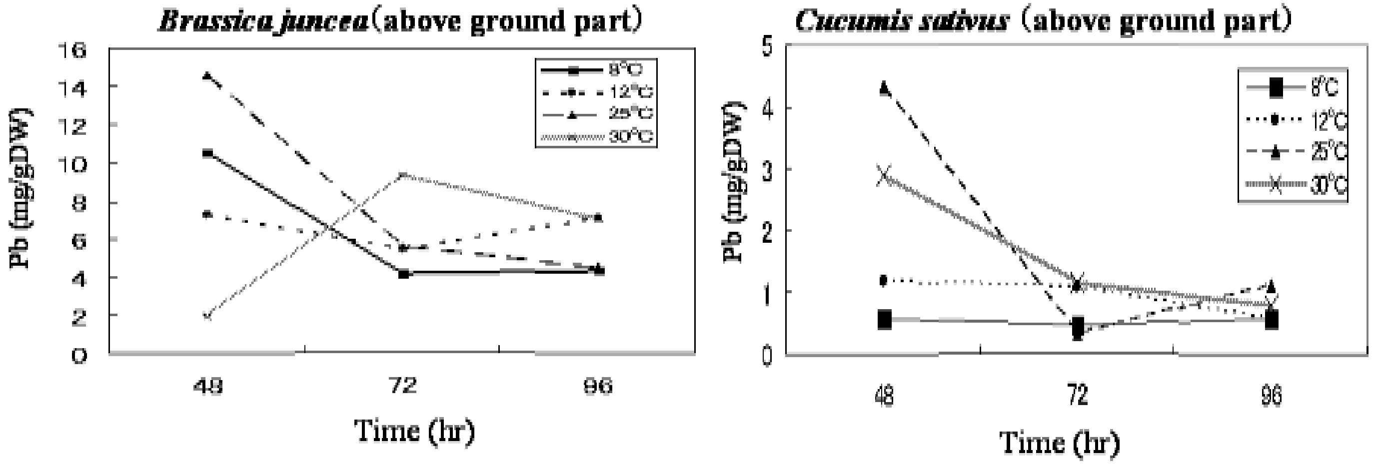

Figure1. **Variation of lead concentration with culture temperature lead concentration.**

Brassica juncea **600 ppm;** ***Cucumis sativus*** **60 ppm.**

3. RESULTS AND DISCUSSION

3.1 A variation of lead concentration with culture temperature

After 48 hours, at 25-degrees Celsius, both plants show a high accumulation of lead. At 30-degrees Celsius, the cucumber showed a higher accumulation. After 96 hours, the cucumber is the same temperature in all four plants. It is thought that the mechanism, which does not absorb lead intentionally by having shown approximately the same quantity of accumulation works. Unlike the cucumber, *Brassica juncea* showed a high accumulation at a temperature level of 8 degrees Celsius and at 12 degrees Celsius. By 72 hours at 30 degrees Celsius, accumualtion gradually increased in *Brassica juncea*. Both the cucumber and *brassica juncea* had a similar accumulation and in both plants the accumulation decreased over time. But *Brassica juncea* maintained some lead accumulation. Also, there was a variation in the quantity of lead accumulation at 12 degrees Celsius area through the experimental period. For foreign material such as lead, an accumulation plant, such as *Brassica juncea*, does detoxication positively to understand it from two kinds of vegetal differences, and the mechanism that can store some lead is present in the above ground part. In contrast, it is thought that only the discharge, or the non-absoption mechanism, works with a non-accumulation plant such as a cucumber. In addition, it is suggested that temperature can become an important factor in the detoxication mechanism of an accumulation plant. See Figure 1.

3.2 GSH (reduced glutathione) concentration and amino acid concentration of a cucumber

An increase of GSH in comparison with control in lead exposition area was revealed when quantity of GSH calculated increase rate according to an area for 1 in normal GSH (Figure 2). Table 1 showed the content of detected amino acid. The roots of control and experimental area of 25 degrees Celsius, and control and control of 30 degrees Celsius were measured. The glutamic acid and the cysteine which synthesized glutathione were not detected, but hydroxylysine (Hly) decreased in comparison with the control in the lead exposition experiment area. Hly is an amino acid constituting collagen. Hly was used with a part of defense action for lead, and it was suggested that it decreased.

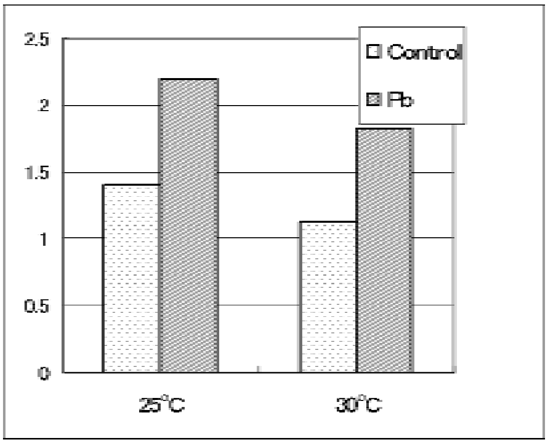

Figure 2. GSH concentration of a cucumber.

Table 1. Concentration of Amino acids in Cucumber roots incubating at 25 and 30 degrees Celsius for 72 hours

Amino acid nmol/g DW	**25°C**		**30°C**	
	control	**Pb**	**control**	**Pb**
THR	3150	916	8475	7261
SER	8961	3822	ND	4607
ASP	ND	ND	160051	ND
HIS	ND	ND	ND	4976
PRO	2708	2979	ND	2705
HLY	3717	2162	23016	9636
TLY	ND	ND	18054	ND

ND: Not detected
Control is incurvated with ½ Hoagland aqueous solution,
Pb is incuvated with 60 ppm $Pb(NO_3)_2$.

4. CONCLUSION

An absorption system of heavy metal works in the resistance mechanism of heavy metal and completely different pathway, and it is thought that hyperaccumulator and accumulator usually develop than a plant in detoxication mechanism of heavy metal. We suggested that cultivation temperature became an important factor by these investigational processes. Accumulation mechanism is not clarified, however, cannot absorb a plant easily because actually mobility of heavy metal in the soil is low. For example, *Thlaspi caerulescens* known as hyperaccumulator of Zn did not show a correlation between Zn content and plant accumulation Zn quantity in the soil (Knight et al., 1994). However, it is the dose which is important whether it let extracted quantity of Zn in soils and absorbed dose extract heavy metal how from the soil by being correlative (Romheld, 1991). We suggested that potential accumulation class was present in a herb plant (Takeda et al., 2005). The result can become a help to clarify an accumulation mechanism of heavy metal from such a point of view.

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PART VI: Sediments

Chapter 19

INNOVATIVE SYSTEMS FOR DREDGING, DEWATERING OR FOR *IN-SITU* CAPPING OF CONTAMINATED SEDIMENTS

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1. INTRODUCTION

Dredging has evolved into a highly sophisticated process drawing from some of the latest technology. The methods of navigational dredging range from clamshell buckets to sophisticated hydraulic dredges. More recently, these techniques have evolved into the processes used for environmental dredging applications.

High concentrations of certain contaminants in sediments pose human heath and ecological risks. Dredging of contaminated sediment provides a method of removal of these contaminants of concern (COC). One of the most obvious benefits of environmental dredging is the fact the contaminated sediments are permanently removed from the water body. These sediments are typically disposed of in an upland containment facility or landfill. In some cases disposal of contaminates may not be permitted or the costs to transport them to a permitted facility may be very high.

Alternate uses for the contaminated sediments may be considered and may help to reduce or eliminate risks. The cost of these alternate treatment and use methods must be evaluated against other permissible disposal options.

Of paramount concern when dredging is the ability of the process to remove the COCs to a level that is below the regulated concentration. Although dredging techniques have been demonstrated to reduce sediment contaminant concentrations, it appears that these techniques can result in residual contamination. This residual contamination may be the result of re-suspension of contaminates into the water column or sloughing of adjacent materials into the dredged areas. Concern over these residual concentrations may lead to subsequent passes or other means to minimize risk from the residuals.

The impacts of the cleanup activity to the surrounding area need to be evaluated regarding the impact of the operation or long-term disturbance of an area. A dredging operation will typically require some sort of sediment dewatering process. After removal of the solids, the associated water may have to be treated before it can be discharged back into the waterway. Because of these facts a dredging operation typically requires onshore support facilities. Construction of these facilities will likely impact the area surrounding the dredged area.

2. *IN-SITU* CAPPING

An alternate solution to dredging contaminated sediments is to cap them in place. *In-situ* sediment caps are typically designed, using computer modeling, to take into consideration stabilization and physical isolation of the sediments as well as contaminate transport mechanisms (Palermo et al. 1998). But there remains some uncertainty, due to the limited available information on many of the mechanical processes that can affect the long-term stability of the cap. Concerns exist over the effects of ice heaving, currents, tides, wave action, propeller and thruster wash on the cap. Caps may be limited to areas where concerns over these erosion forces do not exist. Alternatively, these concerns are typically addressed by increasing the cap thickness to the point that it exceeds the thickness of material that may be affected by such forces. Additional research in this area may provide a clearer understanding of these forces on a cap design. Another alternative is to include a component in the cap design that would act to minimize the effect of these erosion forces.

A proper cap design should take into account the indigenous benthic community. To do so means to properly address the potential for biointrusion into the contaminated sediment. This is typically done by increasing the overall cap thickness to the point that it exceeds the depth of penetration of the local benthos. Another approach is to block biointrusion with some other layer in the cap design.

Construction processes have evolved to allow an accurate placement of the cover materials in a traditional sand cap. Although these processes have advanced, an allowance in the cap design is typically made to account for the spatial variability of the cover material placement. Once again this allowance usually entails adding more material to account for the variability of placement. Methods of ensuring uniform placement of materials are needed.

With all of the variability in the conditions which a cap may be in service, comes a degree of uncertainty. This uncertainty is typically compensated for by adding more and more material to the cap design. For this reason cap designs may become impractical in water depths that do not even exceed the total cap thickness. Clearly, the impact to navigability must be assessed when evaluating whether a cap design is practical. From a practical point, if a thin cap can be designed that provides as good or better performance than a traditional sand cap, then the capping alternative may become a practical solution for a wider range of applications.

Despite the variability in cap designs based on the range of considerations herein, *in-situ* capping whether traditional or thin cap design does offer some inherent advantages over dredging. First, the cost to cap is typically only 30 percent of the cost to dredge and dispose (Evison et al. 2004). In addition to the cost advantage, typically a remediation of contaminated sediment can be completed faster by *in-situ* capping than by dredging. This may be of significance to a heavily navigated area or an area where recreational use needs to be restored rapidly. Finally, the impact on surrounding areas may be of importance. In an urban setting the shoreline may not be conducive to the operation of a dewatering facility. Or, the impact of having sustained dredging operations to the area may be financially significant. These impacts are generally less if capping is chosen as the remedial option.

3. REACTIVE MATERIALS

Various reactive materials (e.g., activated carbon, apatite, organoclay, zeolite, zero-valent iron) are used for water, wastewater and groundwater treatment and can be applied to *in-situ* capping. Activated carbon is a widely used adsorptive media for water treatment removal of phenol, halogenated compounds and pesticides. Activated carbon is made by the thermal decomposition of various carboneous materials followed by an activation process. Raw materials include woods, rice hulls and nutshells. The resulting activated carbon is amorphous and contains complex networks of interconnected micropores (Thomas and Crittenden, 1998). Apatite, $Ca_{10}(PO_4)_6(OH,F)_2$, is a commercially available mineral that has been shown to be effective at sequestration of lead. Apatite removes contaminants from water through three mechanisms: ion exchange, isomorphic substitution and precipitation (Gardner and Stern, 2004).

Organoclays are surface-modified clays that have been shown to be effective adsorbents for insoluble and partially insoluble compounds. The production of organoclays replaces the surface cation of bentonite or hectorite clay with an organic molecule. Quaternary amines based upon tallow are the most commonly used organic compound. The resulting organoclay is oleophilic, hydrophobic and permeable. A properly compounded organoclay will exhibit minimal swelling upon organic adsorption and maintain high permeability. Several manufacturing quality control tests have been developed using x-ray diffraction and thermo gravimetric analysis to assure proper compounding. In treatment of produced water from offshore crude oil production organoclays have removed polyaromatic hydrocarbons to non-detect levels (Darlington 2002).

Zeolites are porous crystalline aluminosilicates. Both natural and synthetic zeolites are used commercially for their adsorption, ion exchange, molecular sieve and catalytic properties. Zeolites are used in water treatment for removal of nitrates and metals such as lead, zinc, and copper (Thomas and Crittenden, 1998). Zero-valent iron, Fe(0), is a strong reductant and has been used successfully in permeable reactive barriers for the dechlorination of chlorinated hydrocarbons and the reductive precipitation of chromate (Cr^{+6} as CrO_4^{-2}) (Powell 2002). Reductive precipitation involves the transfer of electrons from Fe(0) to the hexavalent chromium and transforming the chromium to a less soluble form, $Cr(OH)_3$.

3.1 Bulk Deployment

A layer of reactive material can be placed in bulk using a clamshell, pouring from super sacks or pumped through a tremie pipe. At the Anacostia River Demonstration Project in Washington, D.C. apatite material was placed in bulk over sediments using a clamshell. The clamshell was opened just above the surface and the material settled over the sediments. The target thickness was 150 mm. Core samples indicated that the actual thickness was 130 mm ± 45 mm. A sand layer approximately 150 mm thick was placed over the apatite to allow for colonization by benthic organisms. Operator experience and a global positioning system on the crane were critical for controlling the thin lifts. In the Willamette River in Oregon, a

600 mm thick organoclay bulk layer was placed over hydrocarbon non-aqueous phase liquid (NAPL) seeps using 1800 kg super sacs. The super sacs were positioned over the area with a backhoe and then the bottom of the sacs was opened above the surface allowing the organoclay to pour out and settle over sediments (Fig. 1). An articulating concrete mat was placed over the organoclay cap for protection.

Figure 1. Deployment of Organoclay Cap at Willamette River

4. REACTIVE MATERIALS MAT

A system has been devised that encapsulates reactive materials within a geotextile composite that can be easily deployed as an *in-situ* capping material over sediments. Geotextiles are textiles that are manufactured into flexible, porous fabrics with synthetic fibers. Synthetic fibers are resistant to biodegradation. Geotextiles have varying properties based upon the type of polymer, the type of fiber and fabric style. The four main functions of geotextiles are separation, reinforcement, filtration and drainage. Geotextiles have used in civil engineering, and particularly coastal work, for decades. Some early uses of geotextile were seen in the late 1950s behind precast concrete seawalls and under large riprap (Koerner, 1998).

Reactive mats have been constructed by CETCO using two methods. The first method is needlepunching. This method has been used since the late 1980s to manufacture geosynthetic clay liners. In the needlepunching operation a layer of geotextile, either woven or nonwoven, is fed onto the line. A hopper disperses an even layer of the reactive material onto the geotextile. A top nonwoven geotextile is then unrolled on top of the reactive material. The material is then fed through a loom where nonwoven fibers are needlepunched through the reactive material and into the lower geotextile. Typical thickness of the needlepunched mat is 6 mm. The reactive mat is rolled onto a core tube and then wrapped in a polyethylene bag.

The second method is a laminating method (Fig. 2). This method allows a higher mass per unit area than needlepunching and the ability to use abrasive reactive materials that cannot be needlepunched. In the laminating method a nonwoven core is bonded either by needlepunching or adhesive to a geotextile. The bonded material is then fed core side up through the line. Reactive material is fed onto the core from a hopper. The core has an apparent opening size (AOS) that is larger than the maximum particle size of the reactive material. The reactive material is worked into the core openings by suction and/or vibration. A cap geotextile is then bonded to the top of the core by heat or adhesive. Typical thickness of the laminated mat is 11 mm. The reactive mat is rolled onto a core tube and then wrapped in a polyethylene bag.

Certain reactive materials, such as activated carbon, are buoyant. The reactive mat may be engineered with a geotextile with a high specific gravity and/or a fraction of sand mixed with the reactive material to counteract the buoyancy.

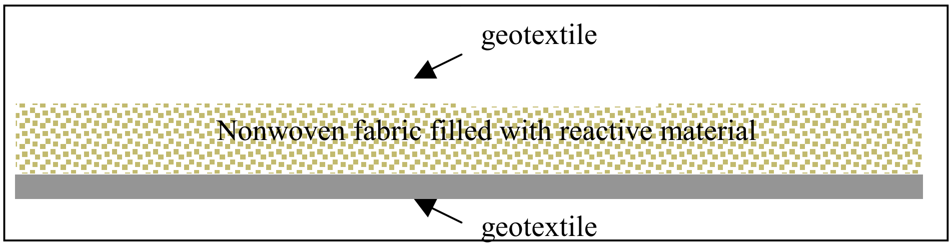

Figure 2. Cross section of laminated reactive core mat

4.1 Benefits

One advantage of a reactive cap over a sand cap is reduced cap thickness. Lab column testing and modeling illustrate that a thin layer of highly adsorptive material such as activated carbon can have over 100 times the adsorption capacity for PCBs as sand or organically-rich soil containing 3.8% carbon fraction (Murphy and Lowry, 2004). Project specific conditions and adsorptive material properties will affect results. However, a 10 mm thick reactive mat can theoretically replace 1 m of sand or soil. This can help maintain navigable depths and flow capacity of waterways.

One factor with using reactive materials is their cost. By constructing a mat encapsulating the reactive materials within geotextiles they can be used in a controlled and potentially cost-effective manner. The reactive mat also combines the benefits of reactive materials and geotextiles.

The U.S. EPA program on Assessment and Remediation of Contaminated Sediments (ARCS) has developed guidance on the design of *in-situ* caps that includes laboratory tests and models of the following key processes; advective/diffusive contaminant flux, bioturbation, consolidation and erosion. The potential functions of geotextiles in *in-situ* cap designs include: 1) providing a bioturbation barrier; 2) preventing mixing of cap materials with underlying sediments; 3) reducing contaminant flux; 4) promoting uniform consolidation; 5) stabilizing the cap; and 6) reducing erosion of the capping materials (Palermo, et al. 1998). Since the reactive mat is constructed with two geotextiles, the composite mat can be designed to perform multiple cap functions.

Hampton et al. (2002) showed that geotextiles can greatly reduce movement of benthic invertebrates in sediments. As previously stated, a geotextile with a proper AOS can contain the cap material and prevent mixing into the underlying sediments. The permittivity of the geotextiles can reduce contaminant flux and/or promote uniform flow during consolidation. The multiaxial tensile strength of the geotextiles can provide stabilization to the cap. At the Anacostia River Demonstration Project the reactive mat was installed over soft sediments with 0.6 kN/m^2 undisturbed shear strength (at 600 mm depth) per field vane shear ASTM D2573 test results. The geotextile, along with appropriate armoring, can also help reduce erosion of the capping material.

4.2 Mat Deployment

Reactive mats may be deployed in a number of ways. The Anacostia River demonstration project was a successful demonstration of a barge-based deployment technique (Fig. 3). In this demonstration, a barge-mounted crane was used to position the rolls and unroll the reactive mat underwater. The mats were first submerged to allow them to absorb water and displace entrained air. Then the rolls were positioned 450 mm above the river bottom and anchored with sand at one end. The crane was able to swing across and unroll the mat. The installation was assisted by a global positioning system and coordinated by a diver in radio communication with the crane operator. A sand layer approximately 150 mm thick was placed over the reactive mat for protection and to allow for colonization by benthic organisms.

Figure 3. Reactive material mat being prepared for deployment on the Anacostia River

Land based deployment techniques may also be used to deploy reactive mats. Rolls may be positioned on shore suspended by a spreader bar system with a clamp connected to the leading edge of the roll. The material is then pulled off the roll using a winch that is either mounted on a barge or on the opposite side of the waterway.

Deployment techniques may also take advantage of temporary buoyancy before the mat absorbs water and displaces air to allow the material to "float" into position and subsequently sink as it takes on water. This technique is planned for capping approximately 4 hectares of hydrocarbon contaminated sediment with an activated carbon reactive mat in a Minnesota bay in late 2005 or early 2006.

5. CONCLUSIONS

The environmental remediation community is seeking innovative methods to remediate contaminated sediments. Reactive materials and geotextiles have been used extensively in civil engineering for water treatment and coastal applications, respectively. The use of reactive materials for *in-situ* capping of contaminated sediments has many potential benefits. A reactive material mat combines the benefits of reactive materials and geotextiles in addressing concerns with *in-situ* capping. Several techniques have been used or planned for deployment of reactive material mats. It is likely that as the reactive material mat technology develops, the methods of deployment will also evolve.

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Chapter 20

EXCAVATION OF PCB-CONTAMINATED SEDIMENT ADJACENT TO THE INTAKE OF A 12-MGD DRINKING WATER PLANT

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Abstract: The Record of Decision (ROD) for the former Westinghouse plant in Sharon, Pennsylvania issued in February 2003 included the removal of approximately 4,000 CY of PCB-contaminated sediment from several locations along the Shenango River to a cleanup goal of 1.0 mg/kg. Delineation sampling indicated a maximum total PCB concentration of 385 mg/kg, although 97% of the sediment samples were less than 50 mg/kg, and 88% of the samples were less than 10 mg/kg. Remediation planning was complicated by the presence of a 12 MGD drinking water plant with a surface intake less than 150 feet from the remediation areas, along with an active 24-inch cast iron water line crossing the river underneath the riverbed. Given the water depth and composition of the riverbed, as well as potential flow velocities during high flow periods, it was determined that the best means of protecting the water plant intake during the remediation would be to isolate the excavation areas using sheet piling, with placement of silt screens around the intake as well as downstream of the pile installation areas. In addition, a mobile laboratory was brought on site to provide rapid analysis of surface water samples at quantitation limits of 0.05 ug/l, in order to provide reassurance to all interested parties that the water supply would not be impacted by the work.

Remediation commenced in late summer 2004, and to date, more than 1,600 surface water samples have been collected downstream of active work areas, including more than 680 samples collected directly from the water plant intake. PCBs have been detected in only one of the water samples collected from the intake (0.07 ug/l), and only 19 other samples collected downstream of work areas were found to contain PCBs (up to 0.54 ug/l). The sediment remediation, delayed by Hurricanes Frances and Ivan, is expected to be completed in October 2005.

Key words: PCBs; sediment; dredging; wet excavation; sheet piling; riparian soil; drinking water; river; mobile laboratory.

1. INTRODUCTION

The former Westinghouse plant in Sharon, Pennsylvania, approximately 60 miles north of Pittsburgh, had a 65-year history of use as an electrical transformer manufacturing facility, at one time employing more than 10,000 workers. Prior to and since the plant's closure in 1985 and subsequent listing on the National Priorities List, the site has undergone a substantial amount of environmental investigation, remediation, and industrial redevelopment. Pursuant to a 2000 Record of Decision (ROD) issued by USEPA, more than 20,000 tons of soil containing polychlorinated biphenyls (PCBs) was excavated from various portions of the site for off-site disposal.

A second ROD was issued in 2003 to address contaminated groundwater (long-term monitoring with a Technical Impracticability Waiver) and sediments in the Shenango River, approximately ¼ mile west of the site. Although the Human Health Risk Assessment concluded that PCB-contaminated sediments did not pose a direct risk to humans, the PA Fish and Boat Commission indicated that removal of contaminated sediments from the river may eventually lead to the reduction of the fish consumption advisory for a 3-mile stretch of the river from "Do Not Eat" (for muskie and carp) to the statewide advisory of no more than one meal per week. On this basis, the USEPA ROD mandated the removal of about 4,000 cubic yards of sediments containing greater than 1 mg/kg total PCBs to a maximum depth of 4 feet over a ¼-mile stretch of the river. (Note that the total quantity of sediment actually removed at the conclusion of the project will be about 9,000 cubic yards.)

The subject stretch of river runs from the Clark Street bridge to a low-head dam adjacent to the Aqua America water plant, and is about 150 feet wide with a typical mid-channel depth of 3 to 12 feet, as shown on Figure 1). Typical river low rates are 250 to 1,000 cfs, although flows during storm events can exceed 3,000 cfs. Based on the findings of pre-remediation delineation sampling, three distinct areas of PCB-contaminated sediments were found within the subject area (a fourth area was found during the course of the remediation effort). The maximum total PCB concentration detected was 385 mg/kg, although 97% of the sediment samples were less than 50 mg/kg, and 88% of the samples were less than 10 mg/kg.

Complicating factors in developing the design for this remediation included:

- The Aqua America drinking water plant, which draws 12 million gallons of water per day from the Shenango River and serves 80,000 people in a three-county area, located within 150 feet of the proposed remediation areas;
- The presence of a natural gas line and an active 24-inch cast iron water supply line crossing underneath the river;
- A 54-inch storm sewer outfall at the center of one of the excavation areas;
- The operation of a flood-control dam about 3 miles upriver, causing wide variations in river flow rates and the potential for river depths to vary by three feet or more; and
- Steep river banks and the relative lack of suitable undeveloped land with good river access for use as a staging and materials handling area.

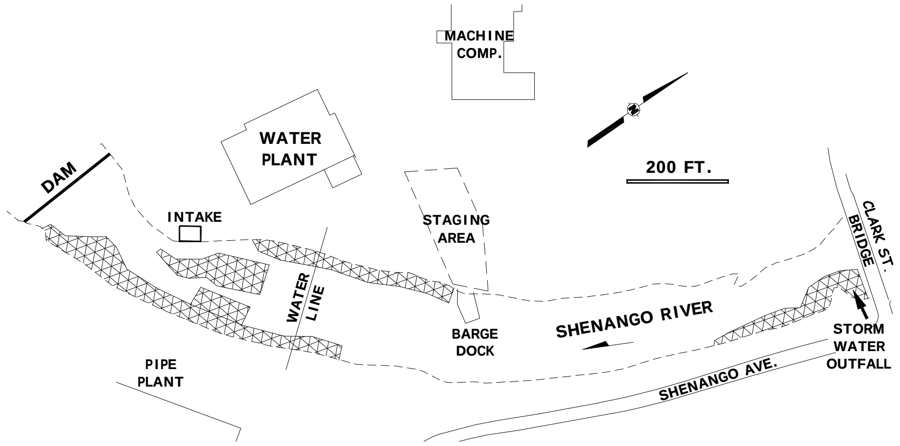

Figure 1. Project map with excavation areas highlighted.

Based on these considerations, it was determined that the primary objective in preparing the remedial design would be to develop a removal process which would cause the least potential for impacts to the drinking water supply, with an appropriate surface water monitoring program to verify that this objective was being met on a near real-time basis.

2. REMEDIAL DESIGN APPROACH

2.1 Remediation Method

Several options were evaluated for performing the mandated removal without impacting the drinking water intake, which was located within 200 feet of the proposed work areas. One option was to provide and alternate water source by pumping water from upstream of the work area ¼ mile to the drinking water intake; however, given the shallow nature of the river upstream of Clark Street and the quantity of water needed, this was determined to be not practicable. Thus, we focused on selecting a removal method which would minimize resuspension of sediment to the channel.

The first removal method evaluated was mechanical or hydraulic dredging using a series of silt curtains and screens to isolate the active work area from the rest of the river and the intake. Reviewing the available data from other remediation projects, it was apparent that while this method could be performed in a manner that minimizes resuspension at a distance downstream, it was not certain that resuspension would be negligible within a hundred feet of the work area, which would be necessary for this site, from both a protective sense and in terms of public perception. In addition, the physical characteristics of the riverbed (significant presence of cobbles and debris typical of an urban/industrial water body) and the relative lack of open space adjacent to the river for wet material processing were viewed as incompatible with this removal method.

Accordingly, we elected to perform the required removal by isolating the work areas from the river channel, with dewatering of the area and subsequent excavation using conventional excavating equipment. This would allow the work to be performed with a minimum of resuspension to the main river channel, and would also provide some protection from strong river currents during high flow events. Dewatering prior to excavation would also allow a more precise removal than could otherwise be accomplished with typical dredging approaches. This would also result in a much drier excavated material, thereby reducing the amount of processing prior to transportation for off-site disposal.

Isolation of each of the excavation areas was performed using interlocking steel sheet piles, typically driven 20-25 feet into the riverbed (see Figure 2). Portable water dams were also evaluated, but were determined to be inappropriate for this application, given the relatively deep water depths and potential variation in flows and water levels. Sheeting was installed on three sides of each area, with the riverbank providing the fourth side. Although the sheeting was generally installed beyond the areas of contaminated sediment, semi-permeable silt screens were installed immediately downstream of the sheeting installation location, as well as surrounding the water plant intake (Figure 3) to provide additional protectiveness. Flow from the storm sewer outfall at one of the areas was pumped around the excavation area using an inflatable plug and a six-inch pump.

Figure 2. Isolated/dewatered excavation area

Figure 3. Silt screens surrounding water plant intake.

Once an area was enclosed, four-inch and six-inch pumps were used to dewater the area, under discharge requirements specified by the PADEP (3 ug/l). Initially, water from each area was directly discharged downstream of the water plant. As the water level neared the bottom of the river and monitoring (as discussed below) indicated increasing levels of turbidity and/or PCBs in the water being pumped, the water was passed through an on-site treatment system (solids filtration and carbon adsorption) prior to discharge.

Excavation was typically accomplished using a long-stick excavator positioned on a barge just outside the work area. The excavator transferred material from the excavator to a rolloff positioned on a second barge for transit to the material handling area. When necessary, quick lime was mixed with the excavated material to dry it sufficiently for transport to the off-site disposal facility. Typical lime addition rates for the excavated material were between 5 and 10 percent by mass.

2.2 Monitoring Approach

Preliminary evaluations indicated that the likelihood of impacts to the drinking water supply was negligible. Nonetheless, special attention was given to developing a monitoring approach that would provide a high level of confidence that resuspension was minimized while enabling a quick response in the unlikely event that the water supply was endangered.

Resuspension standards were developed in order to meet these goals, based on total PCB concentrations in surface water samples. For samples collected immediately downstream of active work areas, the Evaluation Level and Control Level were established at 0.25 and 0.5 ug/l, respectively. At the water plant intake, the respective action levels were set at 0.05 and 0.1 ug/l. These action levels were set to provide a significant factor of safety without regard for the mixing and settling of resuspended particles between the work area and the intakes.

Surface water monitoring locations were established at four locations: upstream of the active work area, immediately downstream of the active work area, at the water plant intake, and downstream of the dam adjacent to the water plant. Water samples were collected at each of these locations at 90 to 120-minute intervals during intrusive work activities.

After briefly considering immunoassay test kits, we decided that procuring the services of an on-site laboratory would provide a more appropriate level of confidence in the analytical results with no significant loss in turnaround time and cost. Environmental Chemistry Consulting Services, Inc. of Madison, Wisconsin mobilized four GC/ECD units for PCB analysis, with one unit dedicated for soil/sediment samples, using lab space provided by the water plant (Figure 4). Samples were analyzed by USEPA Method 8082, with a reduced reporting limit of 0.05 ug/l, and a typical turnaround time of 90 minutes. With this setup, ECCS was able to analyze up to 30 samples per day.

Figure 4. On-site lab space with 4 GC/ECDs

2.3 Additional Challenges

In the course of implementing the design, several challenges were encountered. During sheet pile installation, the water company notified us that the location they previously provided for the water line crossing the river was off by approximately 150 feet. As the new location brought the line through the center of a proposed excavation, the design had to be modified and a new procedure developed for excavating material within 20 feet of the line. Since the area could no longer be enclosed with sheet piling, impermeable silt curtains were used to isolate the area, and "wet excavation" was performed.

Also during sheet pile installation, the remnants of Hurricanes Frances and Ivan dumped a combined 7.2 inches of rain within 11 days in September 2004. As a result, river flows exceeded 2,500 cfs for about 3 weeks. As barges could be safely moved on the river only at flows below ~1,500 cfs, work area sequencing had to be modified. 5.2 inches of rain over 12 days in January 2005 resulted in river flows over 3,000 cfs for 3 weeks, flooding most of the work areas (Figure 5) and causing a temporary shutdown of the project.

Figure 5. Flooded excavation area.

Lastly, sediment sampling performed during the remediation resulted in the discovery of an additional area requiring removal, located within 50 feet of the water plant intake. As this area was in the center of the river, sheeting was installed on the three sides nearest the intake, an impermeable silt curtain was used on the fourth side (supported by steel beams or piles every 20 feet), and the excavation was performed without dewatering. The silt screen surrounding the intake was also replaced prior to performing this work.

3. RESULTS/CONCLUSIONS

From the start of intrusive activities in August 2004 through mid-September 2005, over 1,600 surface water samples have been collected from downstream of active work areas, including 680 samples from the water plant intake.

Of the 680 samples collected at the water plant intake, only one sample exceeded the 0.05 ug/l Evaluation Level, with a PCB concentration of 0.07 ug/l. PCBs were not detected in any other sample collected from the intake.

Of the remaining 920+ surface water samples collected downstream of active work areas, only one result exceeded the 0.5 ug/l Control Level (0.54 ug/l, attributed to a barge scraping the riverbed), and only three additional samples exceeded the 0.25 ug/l Evaluation Level. PCBs were detected in 15 other surface water samples at concentrations below the Evaluation Level.

Thus, implementation of this remediation and monitoring program has to date effectively met the objective of performing the required removal without adversely impacting the public water supply. The installation of sheet piling, while time-consuming and costly, has effectively mitigated the threat posed by resuspension of excavated sediments.

Chapter 21

USE OF A BENCH-SCALE TREATABILITY STUDY TO DETERMINE COST-EFFECTIVE DISPOSAL METHODS FOR CONTAMINATED SEDIMENTS

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Abstract: Cost-effective disposal is a major concern for sediment remediation projects that require removal of sediments. To meet landfill criteria sediments must pass tests for hazardous waste content, hazardous waste leachability and residual moisture content. Knowledge of these parameters is essential before the cost of the remediation can be estimated. CRA has developed a laboratory treatability study procedure to obtain the required information rapidly. An example of the application of this procedure is a treatability study that was conducted on heavy metal contaminated dredged sediment from a site in Michigan

Three sediment samples were obtained and composited to form a sample that would be representative of site conditions. To be acceptable for disposal at a non-hazardous waste landfill the sediment samples must pass TCLP, stability criteria, and the paint filter test. Sediment leachate data showed that the sediment met only TCLP criteria, therefore stabilization was necessary. Ten polymers were evaluated for their effect on solids settling. A sediment slurry was settled with and without polymer treatment and the supernatant and settled solids were collected. A filter press was used to dewater the settled solids to produce a filter cake, which was tested for water content, TCLP metals, and the paint filter test. The effects of solidification agents on the settled solids were also evaluated. The agents tested were Portland cement, fly ash, and cement kiln dust. The results showed that untreated settled solids did not meet landfill stability requirements. The ability of polymer treatment, solidification and filter cake from dewatering using a filter press to meet the landfill stability requirements will be described. Based on the results of the treatability study a cost-effective technique for sediment treatment and disposal was determined.

Key words: Treatability study; sediments; heavy metals; disposal method; contamination

1. INTRODUCTION

In Michigan, lake sediment was contaminated with heavy metals such as arsenic, cadmium, chromium, lead and mercury. It was determined that the sediment would be dredged and safely disposed of in a landfill. A treatability study was conducted to determine a cost-effective disposal method for the dredged sediment.

2. MATERIALS AND METHODS

2.1 Task #1 Sample Characterization

One water sample and three sediment samples were obtained. In order to form a representative sample, a composite was formed from the three sediment samples. The tests performed on the composite include:

Target Analyte List (TAL) metals (SW-846 Method 6010B/747 IA);

- TCLP Metals;
- Water content (USEPA 160.3);
- Grain-size distribution (from Sieve Analysis, ASTM D422);
- Grain-size distribution for finer fraction (from Hydrometer Analysis, ASTM Dl 140);
- Paint Filter Test; and
- Visual observation during sample collection.

The water sample was analyzed for:

- Turbidity (USEPA 180.1);
- TOC;
- TAL metals (USEPA 200.7/245.1); and
- Visual observation during sample collection.

2.2 Task #2 Polymer addition

After sample characterization, polymers were added to observe the effect of polymer treatment on the settling of the solids. Ten polymers were evaluated at the recommended dose rates.

2.3 Task #3 Column Settling

A column settling test was conducted on the sediment slurry. Supernatant was collected at 2, 8, and 24 hours. The height of the sediment-water interface was recorded. Percent moisture of the settled solids and metal content were also analyzed.

2.4 Task #4 Filter press efficiency

The efficiency of using a filter press to dewater the solids was evaluated. Sediments that are hydraulically dredged require mechanical dewatering and polymer conditioning. A bench scale filter press apparatus was used for solid dewater. The sediment was pressed in a circular mold between two plates for 45 minutes, producing a filter cake.

The filter cake samples were tested for:

- Water content (USEPA 160.3);
- TCLP metals; and
- Paint Filter Test.

The dewatering filtrate was tested for:

- TSS (USEPA 160.2);
- Visual observation during sample collection; and
- Total Metals.

2.5 Task #5 Evaluation Solidification Agents on Raw Slurries and Filter Cake

Solidification and stabilization tests were conducted on the sediment slurries. The reagents used were Portland cement, fly ash and cement kiln dust.

The following treatments were tested:

i). 2.5% Portland Cement
ii). 5% Portland Cement
iii). 2.5% Portland Cement and 2.5% Fly Ash
iv). 2.5% Fly Ash and 2.5% Cement Kiln Dust
v). Control (no additions)

2.6 Task #6 Evaluation of Treatment Requirements for Water

Water discharged from settling tanks or filter press treatments must meet the NPDES permit limits. The total metal data from the initial water sample, supernatant, and filtrate will be examined and compared to the expected NPDES permit limits.

3. RESULTS

3.1 Task #1 Sample Characterization

Soil analysis indicated that the soil contained arsenic, cadmium, chromium, lead and mercury. The highest concentration was chromium present at 9700 mg/kg. Hexavalent chromium was not detected in the samples. Chromium was the only metal detected in the water sample at a concentration of 0.0057 mg/L. Hexavalent chromium was not detected. The water sample was clear with no measurable turbidity.

The analysis of grain size indicated that the sediment samples consisted of mainly sand and silt with very little gravel or clay. Tables 1 and 2 show the results of the sample characterizations.

Table 1. Initial Characterization of Sediment

	Composite Sediment	**Landfill Acceptance Levels**
Water Content (%)	79.2	
Total Metals (mg/kg)		
Arsenic	9.4	
Cadmium	6.4	
Chromium	9700	
Lead	115	
Mercury	0.86	
Hexavalent chromium	ND	
TCLP (mg/L)		

	Composite Sediment	**Landfill Acceptance Levels**
Arsenic	ND	5
Cadmium	0.011	1
Chromium	0.63	5
Lead	ND	5
Mercury	ND	0.2
Grain Size Distribution (%)		
Gravel	0.4	
Sand	54.4	
Silt	43.8	
Clay	1.4	
Paint filter test (pass/fail)	fail	

Table 2. Initial Characterization of Water

	Concentration
Total Metals (mg/L)	
Arsenic	ND
Cadmium	ND
Chromium	0.0057
Lead	ND
Mercury	ND
Hexavalent chromium	ND
Total Organic Carbon (mg/L)	3
Turbidity (NTU)	ND

3.2 Task #2 Polymer Addition

The settling test indicated that the addition of the polymers produced a clear supernatant, but did not enhance the settling of the sediment after the treatment therefore treatment with the polymer was discontinued.

3.3 Task #3 Column Settling

The sediment-water interface increased after two, eight, and twenty-four hours. After twenty-four hours, sediment settling was not observed.

Metals analysis results for the supernatant water and TCLP analysis results for the settled solids indicated that chromium was the only metal detected in the supernatant water at a level of 0.18 mg/L. Cadmium was the only metal detected in the leachate from the settled solids at a level of 0.011 mg/L. This value is below the allowable cadmium leachate value for landfill acceptance. The column settling results appear in Table3.

Table 3. Column Settling Test

Time Parameter	2 hours	8 hours	24 hours	Landfill acceptance levels
Distance of sediment-water interface from column top (mm)	8	22	48	
Turbidity of supernatant (NTU)	1080	720	122	
Metals in Supernatant (mg/L)				
Arsenic	---	---	ND	
Cadmium	---	---	ND	
Chromium	---	---	0.18	
Lead	---	---	ND	
Mercury	---	---	ND	
TCLP Metals for Settled Solids (mg/L)				
Arsenic	---	---	ND	5
Cadmium	---	---	0.011	1
Chromium	---	---	ND	5
Lead	---	---	ND	5
Mercury	---	---	ND	0.2

3.4 Task #4 Filter Press Efficiency

The pressing process produced a solid free-standing filter cake. The filter papers that had been used to press the cake released cleanly. The filter press results appear in Table 4.

Table 4. Filter Press Test

Parameter	Sample	Landfill Acceptance Levels
Filter cake water content (%)	53.1	
Paint filter test on cake	pass	
Unconfined compressive strength of cake (psi)	5	
Total suspended solids in filtrate (mg/L)	110	
Metals in filtrate (mg/L)		
Arsenic	ND	
Cadmium	0.00079	
Chromium	0.48	
Lead	ND	
Mercury	ND	
TCLP metals for filter cake (mg/L)		
Arsenic	ND	5
Cadmium	0.025	1
Chromium	ND	5
Lead	ND	5
Mercury	ND	0.2

The water content of the filter cake was 53.1%. The cake passed the paint filter test and had an unconfined compressive strength of 5 psi. TCLP results indicated that cadmium was the only metal detected in the leachate from the filter cake at a level of 0.025 mg/L, which is well below the level required for landfill acceptance.

The dewatering filtrate was a clear straw-colored liquid. TSS and total metals results indicated that cadmium and chromium were detected in the filtrate water.

3.5 Task #5 Evaluation of Solidification Agents on Raw Slurries and Filter cake

The effect of the solidification agent was conducted on the on the raw slurries only since the filter cakes passed the paint filter test. The treatments set up were 10% PC, 15%PC, 20%PC, 5%PC-5%CKD, 7.5%PC-7.5% CKD, and 10%PC-10% CKD. The samples cured for 28 days and were monitored using a pocket penetrometer.

After curing, the samples were tested for unconfined comprehensive strength, total metals, and TCLP metals. The results of the penetrometer readings appear in Table 5.

Table 5. Solidification Tests-pocket penetrometer readings

Parameter	**control**	**10% PC**	**15% PC**	**20% PC**	**5%PC 5% CKD**	**7.5%PC 7.5%CKD**	**10%PC 10% CKD**
Penetrometer reading (psi)	<0.22	0.43	0.87	2.4	0.43	2.3	3.9

3.6 Task #6 Evaluation of Treatment Requirements for Water

The original water sample and all water generated by the treatments in this study met the NPDES permit limits.

The samples contained chromium, but there is no permit level for chromium.

The pH of the supernatant and the filter press filtrate were above 7.0, which is acceptable.

4. DISCUSSION

Initial analysis indicated that the metal content of the sediment samples did not leach at levels that exceed the landfill acceptance criteria, so the stability requirement will determine whether the sediments can be accepted at a landfill. The stability requirement is 150 pounds per square foot (1.04psi). The addition of polymers did not assist in the stability of the sediments.

Settlings of the sediments removed some of the water, but since the sediment consisted mostly of silt, significant dewatering through settling alone was not attainable. Filter press treatment of the settled solids would achieve landfill stability acceptance criteria. The filter cakes had an unconfined stability of 5 psi, which is acceptable.

Based on results from the original water and the water generated from the treatments, the water does not need treatment to meet the NPDES permit limits.

Stabilization of the sediment using stabilizing agents is more cost effective than filter press treatments. The 7.5% Portland cement and 7.5.5 cement kiln dust allowed the sediment to meet landfill requirements.

5. CONCLUSIONS

- Leaching of metals from the sediment was not a concern;
- Polymer treatment was not effective;
- Untreated settled solids did not meet landfill stability requirements;
- Filter press treated yielded a filter cake that met landfill stability criteria;
- Solidification using Portland cement and cement kiln dust was more cost effective than filter press treatment; and
- All treated waters met expected NPDES requirements, therefore no further was required treatment.

PART VII: Site Assessment

Chapter 22

INL SUBSURFACE WIRELESS SENSOR PLATFORM

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Abstract: The Idaho National Laboratory is developing a versatile micro-power sensor interface platform for periodic subsurface sensing of environmental variables important to waste disposal sites such as volumetric moisture, water potential, and temperature. The key characteristics of the platform architecture are that the platform is passive until externally energized—no internal power source is required—and that it communicates with a "reader" via short-range telemetry—no wires penetrate the subsurface. Other significant attributes include the potential for a long service life and a compact size that makes it well suited for retrofitting existing landfill structures. Functionally, the sensor package is “read” by a short-range induction coil that activates and powers the sensor platform as well as detects the sensor output via a radio frequency signal generated by the onboard programmable interface controller microchip. As a result, the platform has a functional subsurface communication range of approximately 10 to 12 ft. and can only accept sensors that require low power to operate.

Key words: Wireless; sensor platform; subsurface sensing; moisture; water potential.

1. INTRODUCTION

For many of the soil waste sites within the Department of Energy complex, in-place containment with surface barriers (caps) is expected to be the primary means of remediation. As part of the capping process, there will be years of post-closure monitoring to assure/verify performance. Consequently, monitoring technologies are needed that are economical, reliable, require low-maintenance, and have the potential for a long service life. Implementation techniques will need to minimize the impact of the monitoring technology on cap integrity.

An example is found at DOE's Hanford Site. The 200 Areas of the Hanford Site are on the National Priorities List under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980. Operations in the 200 Areas were related to separation of nuclear materials from spent nuclear fuel. Significant quantities of chemical and radioactive waste, as well as chemicals associated with the separations processes, were disposed to the environment. The 200 Areas contain about 800 soil waste sites, including liquid-disposal structures, solid-waste burial sites, and spills. Types of waste received at these sites include radioactive, mixed radioactive, hazardous, sanitary, and demolition waste. The use of surface barriers (caps) is expected to be the preferred approach to containment as identified in the DOE-RL baseline (DOE-RL, 1999a). Barrier performance data are needed for remediation decisions and, if barriers are selected, to verify their performance.

A number of different methodologies are used to monitor the performance of barrier caps, including monitoring wells, bore hole sampling/sensing, lysimeters, and networks of embedded sensors wired to data loggers or telemetry units. The wires associated with embedded systems can present difficulties during construction and subsequent cap maintenance because the wires penetrate the cap, providing potential paths for water infiltration. Any maintenance of the sensors after extended service also means additional penetrations and disruption of barrier integrity. An approach to mitigate a number of these issues is to implement a sensor platform that is both wireless and passive with the potential for extended service. In most cases, platform service life will be limited to the useful service life of the integrated sensors interacting with the environment.

The Idaho National Laboratory (INL) is developing a sensor platform that is both wireless and passive. Passive is defined as not having an onboard power supply. The platform architecture has the following attributes: 1) all platform components are inactive until energized by an external power source, thus no internal power such as a battery is required; 2) a magnetic induction field generated by a "reader" is used to both power and communicate with the platform, eliminating the need for wires to penetrate to the subsurface; 3) sensor platforms are individually addressable, allowing a single reader to interrogate a number of different platforms; and 4) each platform can support multiple low-power sensors. Although well suited for the intended application, this approach does have inherent limitations and/or tradeoffs. These include a limited functional range, as defined by the extent of the interrogating induction field; and, a power budget as defined by the onboard energy storage capacitors that provide power to platform components as well as integrated sensors. Specific applications require tradeoffs between charge time (measurement cycle time), available power, and working depth. For example, an increase in required power to run sensors will result in either a reduced working depth and/or an increase in charge time. A working configuration as it relates to a landfill cap is illustrated in Figure 1.

2. MATERIAL AND METHODS

The platform is designed around a microcontroller produced by Microchip Technology.[1] In essence, it is a single-chip computer containing onboard nonvolatile memory, multiple analog-to-digital (A/D) channels, and digital communication ports. The microcontroller can be programmed and/or hardwired to handle all of the logic needed for power management, operation of one or more sensors; and communication with the reader. Associated with the microcontroller are circuits to communicate as well as collect and store energy from the aboveground reader. Telemetry and power transfer between the reader and sensor platform are accomplished through a low-frequency magnetic field (nominal 125 kHz working frequency). The reader is a conventional radio transceiver connected to a resonant antenna.

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[1] Microchip Technology Inc., Programmable Interface Controller PIC16F877A.

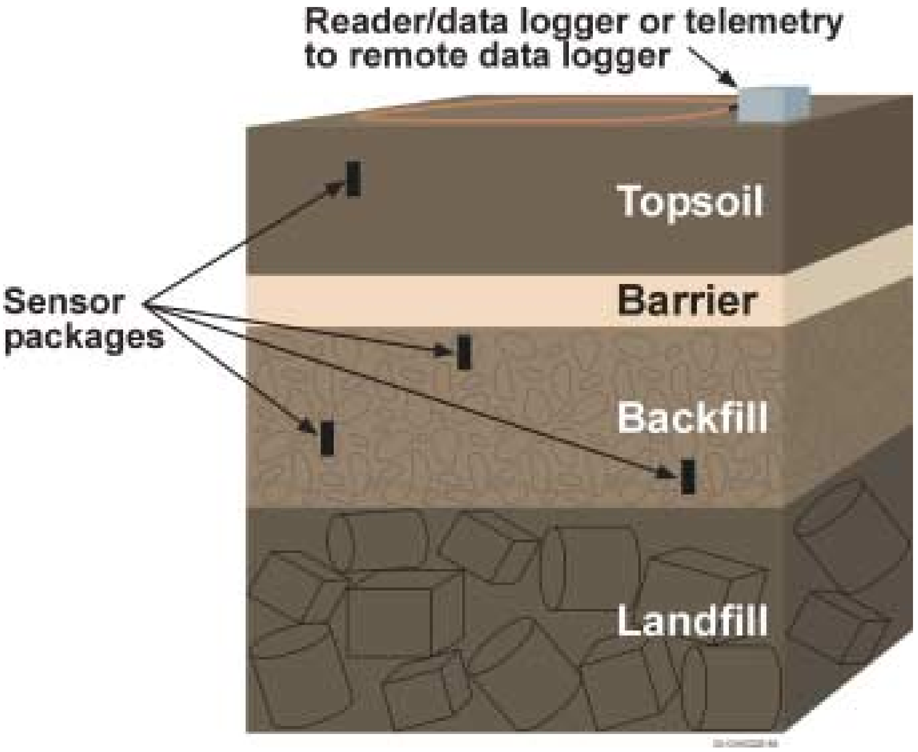

Figure 1. Functional configuration for INL sensor platform as it relates to a landfill barrier cap.

The basic sequence to acquire sensor readings is as follows: The reader sends out energy in the form of an alternating magnetic field, which is captured and stored in a capacitor within the platform/sensor package. When sufficient energy has been collected, the microcontroller will initiate a routine to have one or more sensors perform a measurement. The values collected (e.g. volumetric moisture, temperature, and/or pressure) are then digitized. At that point, the microcontroller powers the probe transmitter and also controls frequency-shift keying to impress the digital readings on the transmitted waveform, with subsequent decoding by the reader. The reader supplies instructions to the platform, as well as energy. For example, the platform might be instructed to report the value of a particular onboard sensor or to adjust the operating range of a sensor.

Figure 2 shows a simplified block diagram of the probe. The antenna, actually a resonant circuit, is used both for capturing energy from the reader and transmitting data back to the reader. As energy builds in the storage capacitor, the microcontroller begins to operate and polls the energy detector circuit to determine if the capacitor is fully charged, i.e. has a 5 Volt reserve available for use. When that condition is achieved, the RF detection circuit is polled to determine if the reader is still transmitting the energizing pulse. If not, the reader has stopped to listen. If so, the microcontroller interrogates the sensor(s), which requires applying power and digitizing its analog output. At this point, the measurement results are stored in the microcontroller's memory. Power is then applied to the transmitter, which in turn drives the antenna. Frequency-shift keying is accomplished by switching a small capacitance in and out of the resonant circuit of the antenna; the switching is controlled by the communications port on the microcontroller. The receiving process is straightforward. An FM receiver is tuned such that its passband is centered on one of the frequency components of the modulated wave. This produces analog output from the receiver that is level shifted to become a proper RS-232 signal. That signal is captured by the serial port of a computer, which serves as the data logger.

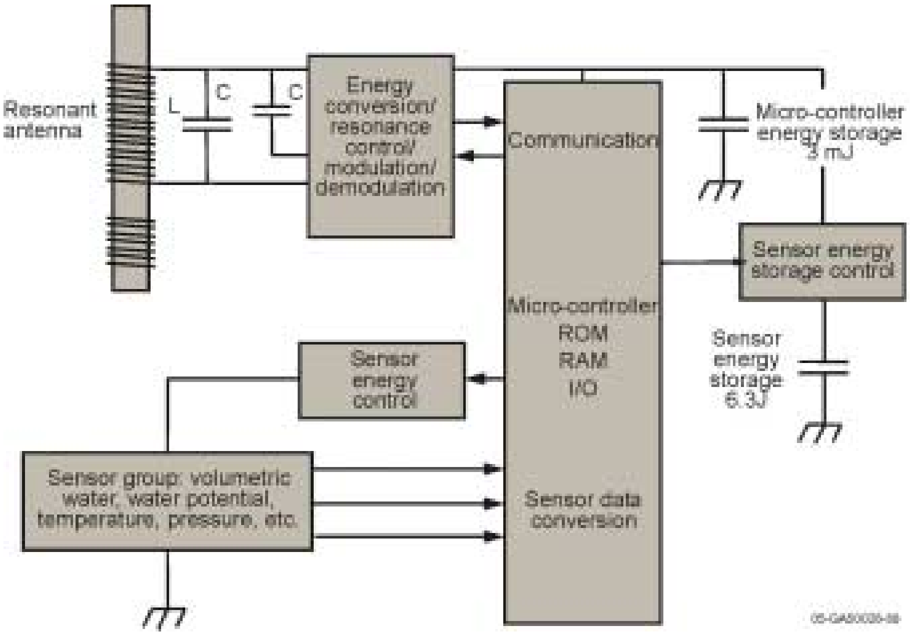

Figure 2. Simplified block diagram of the sensor platform and reader.

3. RESULTS

To date, the development of the INL sensor platform has progressed from a breadboard model demonstrating feasibility (Kunerth et al., 2001) to a number of prototype models that have been tested in the field.

Early prototype platforms with temperature, pressure, and volumetric water sensors were developed and tested at a moisture-sensor calibration facility at the Nevada Test Site (NTS) developed for the calibration of neutron moisture meters in different well-casing types. This facility consists of arrays of time domain reflectometry (TDR) probes buried at depths of 1, 2, and 3 feet in screened alluvium. TDR probes measure water content. The TDR probes were calibrated in the laboratory using NTS alluvium prior to installation in the field and provide accurate measurements of volumetric water content. Use of this facility permitted the direct comparison of the INEEL sensor technology to an accepted moisture measurement technology. Four prototype sensor packages were buried at various depths in the NTS facility within the sensing volume of the TDR arrays. Subsequent to burial, the area was flooded and the water infiltration recorded with time, see Figure 3. Figure 4 presents the volumetric water measurements recorded for INL sensor package #3 with time. Figure 5 shows the volumetric water measurements made by TDR sensors at the 1-ft level. Spaces in the data resulted from alternating measurements between the TDR probes and the INEEL sensors. Cross talk between the two sensor types, TDR and INL platform, prevented their simultaneous use. The platform's volumetric water sensor uses a calibration provided by the manufacturer that is not specific to each probe or the composition of the alluvium at the NTS. This resulted in absolute measurements that were different from those obtained from the TDR probes, but the INEEL sensor packages did duplicate the TDR's response to the wetting front moving through the soil.

Figure 3. INL wireless sensor platform field test. For this test, the buried sensor packages (marked by the blue flags) are located on the exterior of the antenna encircling the aluminum well casing.

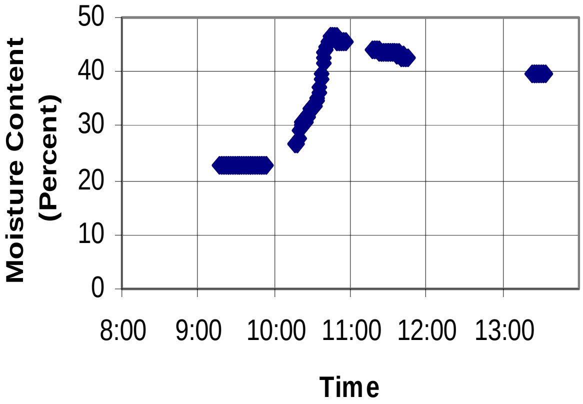

Figure 4. Volumetric water measurements recorded by INL Sensor Package #3 as water infiltrated into the soil. Sampling depth for this sensor package was 13 to 20 inches.

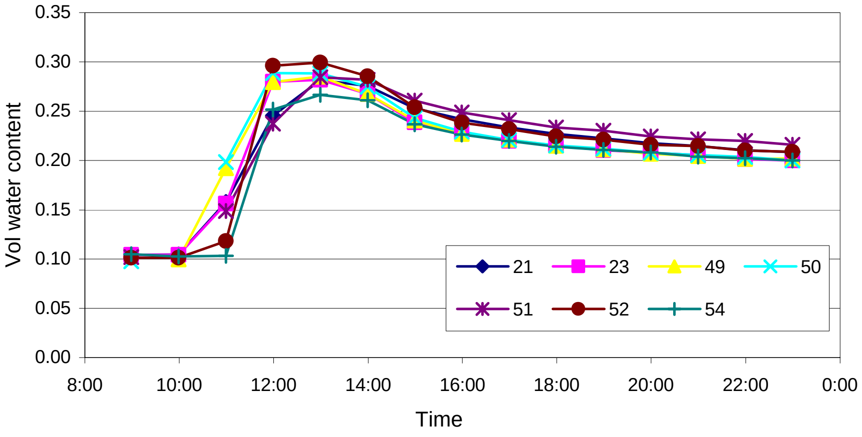

Figure 5. Volumetric water measurements recorded by NTS TDR sensors at a 1 ft. (TDR measurements provided by Charles Lohrstorfer and Alen Wittig, NTS.)

A second field test was performed with similar prototype sensor packages capable of monitoring volumetric water, temperature, and pressure. These packages were embedded in a barrier cap during construction at a superfund site in South Dakota. A year later, after construction was complete, the sensor packages were located and sensor data collected without any platform failures. Figure 6 shows a sensor package as it was being embedded and the barrier cap under construction.

After the field testing at NTS, a heat-dissipation-based matric water potential sensor was added to the sensor platform. To accomplish this task, the capabilities of the platform were extended to include two separate energy storage banks that could be individually charged and controlled. The primary storage bank is used to power the basic functionality of the platform and one or more low-power sensors such as temperature and volumetric water. The second storage bank is significantly larger (6.3 joules versus 0.003 joules) and is used to power the energy-intensive water potential measurement or other tasks that require extended power. This storage bank is software controlled and is only active when commanded. However, due to the size of the second bank, charge / measurement cycle times are significantly longer when activated, i.e. hours versus seconds for the primary bank alone. Figure 7 shows sensor packages with platforms having commercial volumetric water, water potential, and temperature sensors. To date, all sensors used with the platform have been commercial off-the-shelf technologies.[2,3,4]

[2] Decagon Devices Inc., Pullman, WA, ECH$_2$O volumetric water sensor.

[3] Campbell Scientific Inc., Logan, UT, 229-L matric water potential sensor.

Calibration of the water potential sensor using a modified pressure plate extractor system engineered and build by NTS personnel is underway. Figure 8 shows the calibration system along with sensor data periodically collected at different system pressure settings. Two sensor packages are set vertically in the green plastic pipes attached to the lid of the pressure plate extractor. A small hoop resonant antenna is mounted above the pressure system. It is connected to a reader and laptop computer that controls data acquisition. The plastic pipes are used to allow the alternating magnetic field generated by the reader to couple with the sensor platforms encased within the pressure system. The system is programmed to periodically collect data from the two sensor packages at set time intervals. Upon completion of the calibration process, the sensors packages will be field tested at NTS.

Figure 6. INL wireless sensor platform field test at superfund site in South Dakota.

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[4] Microchip Technology Inc., Chandler, AZ, TC1047AVNB temperature sensor.

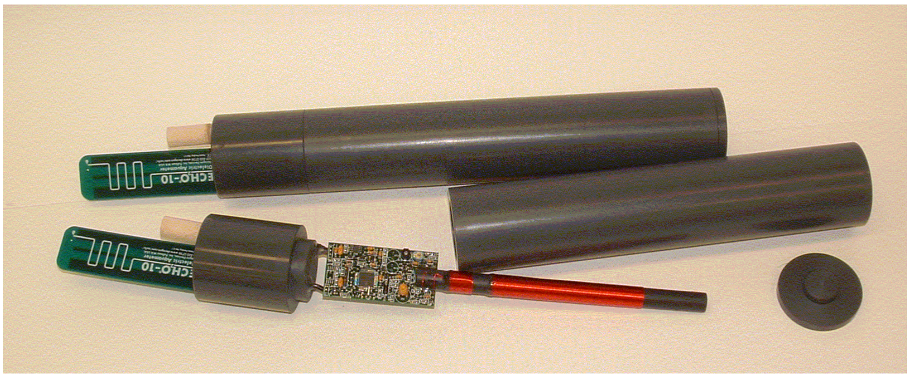

Figure 7. Sensor packages with INL platform and integrated volumetric water, water potential, and temperature sensors

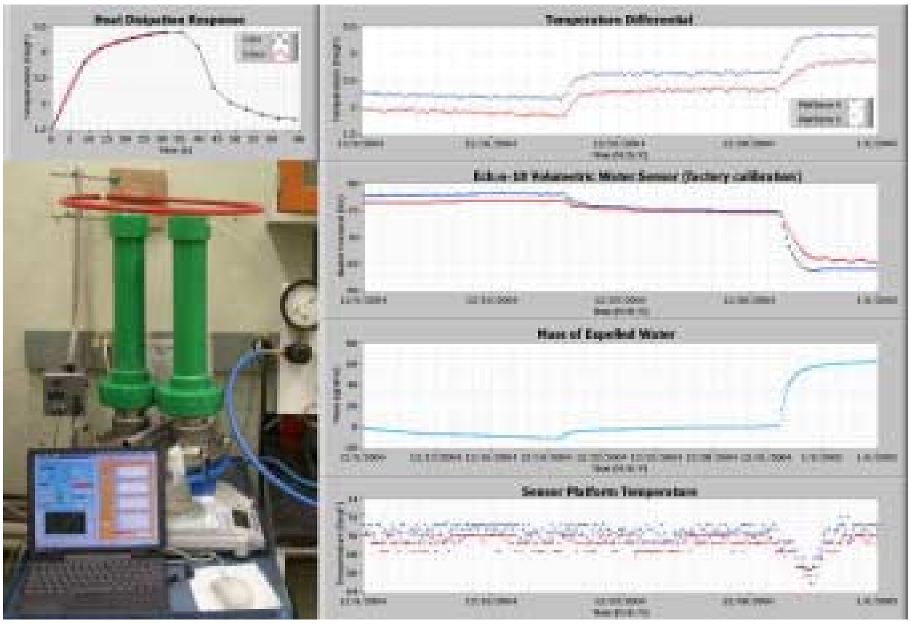

Figure 8. NTS-modified pressure plate extractor system used to calibrate the water potential sensors. The two green plastic tubes house two sensor packages during calibration as well as allow the alternating magnetic fields generated by the reader and sensor platform to pass through the pressure system boundary.

4. DISCUSSION/CONCLUSIONS

The INL sensor platform was developed to provide a method for long term subsurface sensing that does not require wires to penetrate the barriers. Due to the passive nature of the design, no maintenance needs to be performed and the low-duty cycle provides the potential for a long service life. Service life will, in most cases, be defined by the service life of the sensors that directly interact with the environment or their ability to maintain calibration. Although the platform has been demonstrated to be fully functional, there are operational limits that define how the platform can be implemented.

Those limitations are:

1. A reader is required to be temporarily or permanently located on the surface to provide power and communications when measurements are made. An exception to this is possible if the platform is configured and programmed to use the large secondary energy storage bank to run low-power sensors for an extended period of time after the reader has been shut off or removed.

2. Operational depths are defined by the extent to which the resonant antennas on the reader and sensor platform can couple to transfer power and communicate. Laboratory and field testing at the INL indicates that the present system is limited to approximately 12 ft. Also note that the physical alignment of the antennas contribute to the efficiency of energy transfer, i.e. maximum efficiency is achieved when they are coaxial. Soil types and water content may also influence operational depths, but all testing to date suggests that the effects are small.

3. There is a trade off between operational depth and measurement cycle time. Increased working depths result in weaker magnetic field strengths and thus less energy transfer. As a result, it takes longer to charge the energy storage banks. At maximum operational depths, a platform with low-power sensors can be energized and read in seconds while it will take hours to charge the secondary energy storage bank for use with a high-power sensor such as the heat dissipation water potential sensor.

In conclusion, the INL sensor platform does provide a viable means for subsurface sensing when it is desirable not to penetrate structures with wires.

ACKNOWLEDGEMENTS

The Advanced Monitoring Systems Initiative (AMSI) provided support to INL for the design, development and testing of the moisture sensors. AMSI is an integrated DT&E project that aggressively searches for, develops, tests, evaluates, and integrates promising new sensors and monitoring systems for end-user applications. AMSI is funded through the National Nuclear Security Administration's Nevada Site Office, and managed by Bechtel Nevada (BN).

AMSI also designed the required modification to the water content calibration system, funded the BN Engineering Department to complete design drawings and specifications, and the fabrication group to manufacture this innovative design. Work at INL was performed under DOE Idaho Operations Office Contract DE-AC07-05ID14517.

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Chapter 23

FIELD INVESTIGATION OF PAHS IN SOILS AROUND NARA CITY IN JAPAN

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Abstract: PAHs are the general term for compounds having two or more benzene rings. These are discharged from diesel motor gas, tanker accidents, oil emissions by cars, and so on. They float in the atmosphere, and it is considered that they are absorbed in soil as a result of rain. Generally, compounds that have two and three benzene rings show only toxicity, whereas those having four or more benzene rings show toxicity, carcinogenicity and mutagenicity. Benzo(a)pylene has been shown to be an endocrine disrupter. We investigated the action of 16 PAHs specified by the U.S. EPA in soil around Nara city in Japan. Soil was collected from different locations involving traffic and vegetation. Soils from three locations around our university were collected every month, to investigate seasonal movement. PAHs were extracted from soil by soxhlet extraction with dichloromethane. They were then analyzed quantitatively by HPLC/UV. We classed PAHs by number of rings, and examined the concentration and seasonal movements. All content of 16 PAHs in soils increased in proportion to traffic volume. At the same locations of traffic volume, the gravitation at a location with plant with all content of 16 PAHs in soils was, furthermore, found to have a low concentration. There were different seasonal movements of the 2, 3-ring and 4, 5, 6-ring PAHs. 4, 5, 6-ring PAHs have a strong correlation with each other ($r>0.79$), but there were no correlations between 2, 3-ring and 4, 5, 6-ring PAHs. As a result, the traffic volumes are exposition sources of 4, 5, 6-ring PAHs in soils.

Key words: PAHs; soils; field investigation; diesel motor gas; tanker accidents; oil emissions; benzo(a)pylene; Nara City; Japan; traffic; vegetation

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants found in air, sea, river water and soil. They occur as common constituents of gasoline, coal tar and shale oil, but are most frequently formed by incomplete combustion of fossil fuels (Pothuluri and Cerniglia, 1994; Maila and Cloete, 2002). Therefore, these substances are long-lasting, poorly degradable pollutants that accumulate in the environment. Furthermore, these substances present a great affinity for organic materials in soil such as humus. Some PAHs are known to be carcinogenic and mutagenic (Laflamme and Hite, 1978; Pahlman and Pelkonen, 1987). Benzo(a)pyrene especially is known as an endocrine disrupter (Liu and Korenaga, 2001). Sixteen PAHs have been selected by the US Environmental Protection Agency (EPA) as Constant Decree priority pollutants for regulatory purposes (Hodgeson, 1990). The potential for atmospheric concentrations of PAHs to accumulate in many geographical locations of the world has been determined and reported, e.g., Massachusetts, USA (Allen et al., 1996), Athens, Greece (Viras et al., 1987), Mumbai, India (Kulkarni and Venkataraman, 2000), Lahore, Pakistan (Smith et al., 1996), and Kuala Lumpur, Malaysia (Omar et al., 2002). However, there is still very little information on the concentration of these substances in soil.

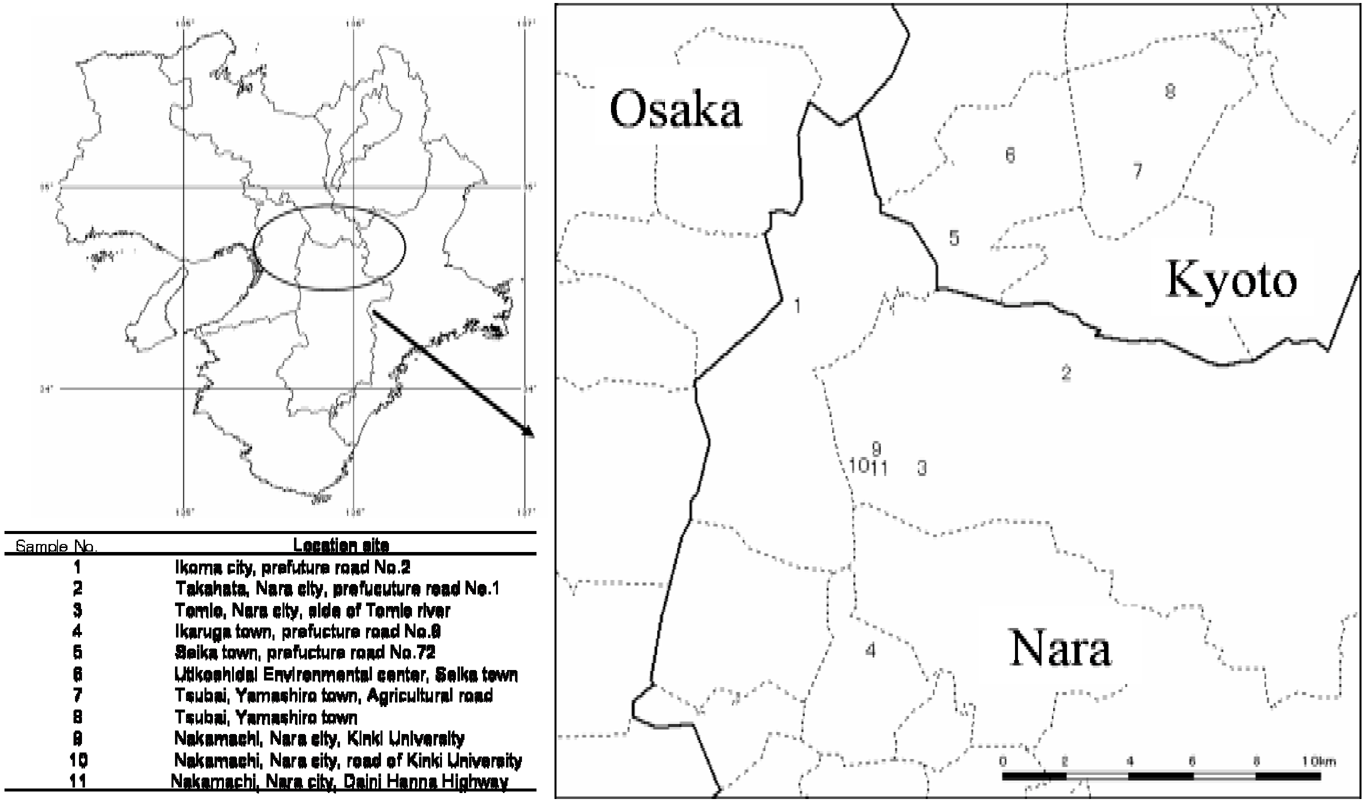
The remediation of organic pollutants uses physical and chemical techniques. The cost, however, is very expensive and the processes require significant labor. The solutions to this problem are bioremediation and phytoremediation. Bioremediation is a technique by which pollutants are biodegraded by bacteria. It has been reported that white rot fungi can extensively biodegrade PAH (Bumpus, 1989; Zheng and Obbard, 2002), because white rot fungi are capable of non-specifically oxidizing aromatic compounds through the abstraction of an electron or a hydrogen atom. (Barr and Aust, 1994; Hattaka, 1994). Phytoremediation is the process by which contaminants in the environment are removed by plants (Cunningham et al., 1996). The targets of phytoremediation are various pollutants, e.g. heavy metals, NOx, SOx, agricultural chemicals and PAHs. Enhancement of PAH degradation in soil rhizospheres has been shown in several studies (Aprill and Sims, 1990) (Qiu et al., 1994; Reilley et al., 1996) (Binet et al., 2000). Grasses are being used for microbial colonisation due to their fibrous root systems with extensive surface areas (Adam and Duncan, 2002). The studies and investigations have not provided sufficient information regarding the relationship between soil PAHs and vegetation.

In this study, we investigated the actions of 16 PAHs specified by the U.S. EPA in soil around Nara city in Japan.

2. MATERIALS AND METHODS

2.1 Soil Sampling

Soil was collected from various sites in highly trafficked and vegetated areas, as well as three sites around the university, in Figure 1.



Sample No.	Location site
1	Ikoma city, prefuture road No.2
2	Takahata, Nara city, prefucuture road No.1
3	Tomio, Nara city, side of Tomio river
4	Ikaruga town, prefucture road No.9
5	Seika town, prefucture road No.72
6	Utkoshidai Environmental center, Seika town
7	Tsubai, Yamashiro town, Agricultural road
8	Tsubai, Yamashiro town
9	Nakamachi, Nara city, Kinki University
10	Nakamachi, Nara city, road of Kinki University
11	Nakamachi, Nara city, Daini Hanna Highway

Figure 1. Sampling sites around Nara City and location site.

2.2 Concentrations of 16 US EPA-identified PAHs in soils

Collected soils were sieved with a 2.0 mm nylon mesh sieve. PAHs were extracted from 5.0 g of soil by soxhlet extraction with 120 ml of dichloromethane. These extractions processes were repeated three times. Extracted solutions were condensed to 1.0 mL by an evaporator using N_2. The concentrations of 16 PAHs were determined by HPLC analysis. HPLC determination was performed using a Shimadzu Co, Ltd. LC-10AT binary pump and SPD-10A UV/VIS detector. Column and analytical parameters were as follows

Column: 25 cm × 4.6mm i.d. stainless steel analytical column packed with 5 μm Supercosil LC-PAH (Superco).

Analytical parameters: 5 min after starting analysis, linear gradient elution from 40: 60 acetonitrile/water to 100:0 acetonitrile/water 35 min after starting analysis. The temperature of the column was 23 degrees, flow rate was 1.0ml/min and detection wavelength was 254nm. Injection volume was 5.0μL.

2.3 Classed PAHs

We classed PAHs by number of rings, and examined the concentration and seasonal movements. Table 1 indicates the ring numbers of 16 PAHs.

Table 1. Ring Numbers of 16 PAHs

name	**ring numbers**
naphthalene	2
acenaphthylene	3
acenaphthene	3
fluorene	3
phananthrene	3
anthracene	3
fluoranthene	4
pyrene	4
benzo[a]anthracene	4
chrysene	4
benzo[b]fluoranthene	5
benzo[k]fluoranthene	5
benzo[a]pyrene	5
dibenz[a,h]anthracene	5
benzo[glu]perylene	6
indeno[1,2,3,-cd]pyrene	6

3. RESULTS AND DISCUSSION

3.1 Quantity of distribution of PAHs in soils of different geographical condition

Table 2 summarizes the concentrations of 16 PAHs at different vegetated and trafficked sampling sites of Nara City in Japan. Heavy traffic caused higher concentrations of total PAHs. However, sites with extensive vegetation in the same trafficked area had lower concentrations of total PAHs. When classified by the number of benzene rings, vegetation greatly influenced the number of rings. Since 2- and 3-ring PAHs have higher volatility, these did not remain in soil, while 4- to 6-ring PAHs more easily remained in soil, and were degraded by plants and bacteria.

Table 2. Concentration of total and ring number of Pahs (mean ± S.D.) at different sites (Sample No. 1-8)

Sample No.	**Traffic***	**Vegetation****	**Concentration (mg/kg soil)**					
			Total PAHs	**2-ring**	**3-ring**	**4-ring**	**5-ring**	**6-ring**
1	++	-	4.25±1.18	0.29±0.07	1.06±0.29	0.53±0.17	1.21±0.27	1.16±0.39
2	++	-	3.86±1.31	0.29±0.05	1.13±0.32	0.66±0.44	0.90±0.15	0.90±0.36
3	++	+	2.59±1.53	0.38±0.22	0.82±0.69	0.50±0.29	0.54±0.30	0.35±0.25
4	+	+	0.51±0.13	0.11±0.02	0.26±0.04	0.10±0.03	0.03±0.04	0.01±0.01
5	+	+	0.37±0.12	0.03±0.01	0.07±0.02	0.08±0.01	0.15±0.05	0.05±0.01
6	-	++	0.25±0.12	0.06±0.05	0.08±0.02	0.04±0.04	0.05±0.09	0.02±0.03
7	-	ND	1.07±0.38	0.35±0.01	0.47±0.20	0.12±0.08	0.10±0.09	0.03±0.05
8	-	-	1.05±0.26	0.02±0.16	0.63±0.04	0.10±0.01	0.07±0.00	0.04±0.04

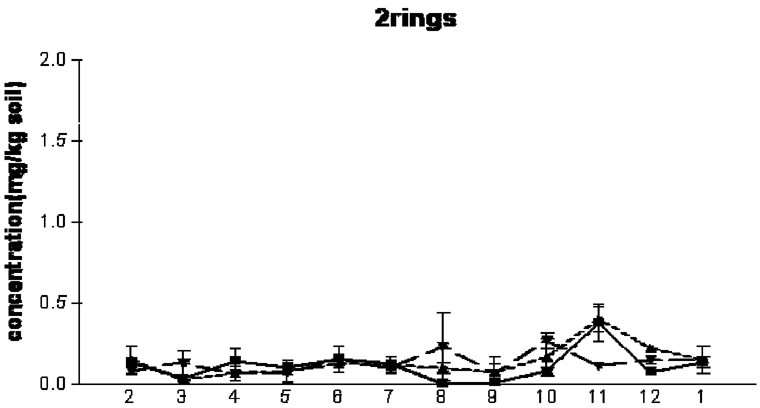
*++: >5,000 cars/day, +: 500-5,000 cars/day, -: <500 cars/day

**++: whole surface vegetation, +: 70% covered vegetation, -: less than 50% covered vegetation

ND: No vegetation

3.1 Seasonal variations

Figure 2 indicates the variation of total and ring number of PAHs concentration in soils at three sites (No. 9-11) around Kinki University between February 2003 and January, 2004. Although a significant variation was not recorded overall, in November all three sites showed decreased total PAHs. More so at site no. 11 (the Daini Hanna Highway) compared to the two other sites (No. 9 and 10). At site no.11, plant residue accumulation due to fallen leaves and the apoptosis of herb plants together with atmospheric fallout and road dust, decreases the total PAH concentration in the soil. PAH levels at site No.11 return to the same levels as sites Nos 9 and 10 in January as the accumulated layer begin to be removed by physical actions such as seasonal wind and degradation action by organisms such as microbes. As for 2- and 3-ring PAHs, there is not the difference that each of the three sites of others fluctuating greatly is large after October. In contrast, for 4 or more benzene rings in PAHs, fluctuation was observed in soils between April and July, and October to December. Based on the above observations, Table 3 and Figure 3 show a correlation coefficient for content by the number of benzene rings in PAHs from February, 2003 to January, 2004. 4-, 5-, and 6-ring PAHs have strong correlations with each other ($r>0.79$), but there are no correlations between 2-, 3-ring PAHs and 4-, 5-, 6-ring PAHs. This suggests a different origin for 4-, 5-, 6-ring PAHs, i.e., their source is different from that of 2-, 3-ring PAHs. By investigation under different environments and geographical conditions, PAHs having more than 4 rings were found in sites with high traffic volume, and the content was high. It is thus thought that exhaust gases from cars are the main exposition source of PAHs having more than 4 rings. Since 2- and 3-ring PAHs have higher volatility, they are of atmospheric origin. However, we found a positive correlation of around 0.6 between 3-ring PAHs and 4-, 5-ring PAHs. From this, it was thought that microbial degradation processes stay behind through various pathways in the soil as well as one exposition source.


2rings
concentration(mg/kg soil)
2.0
1.5
1.0
0.5
0.0
2
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5
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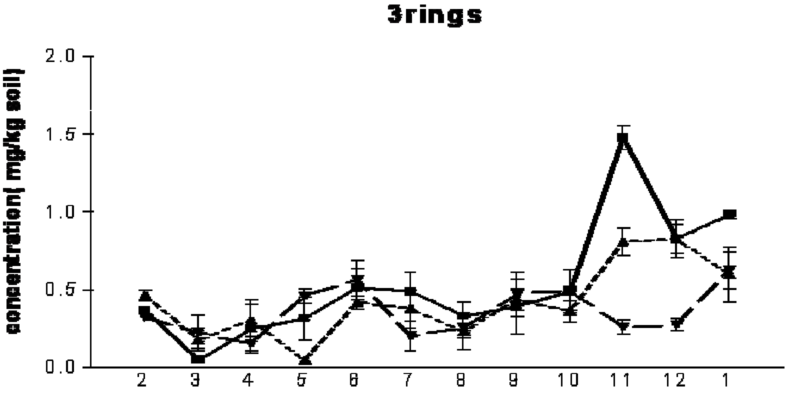
10
11
12
1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0.5
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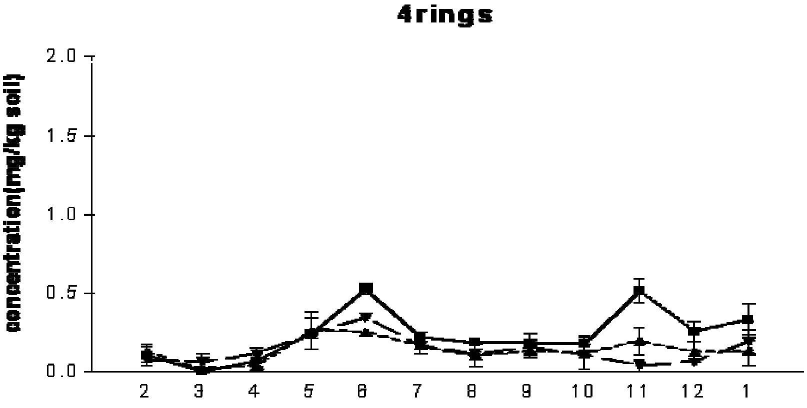
4rings
concentration(mg/kg soil)
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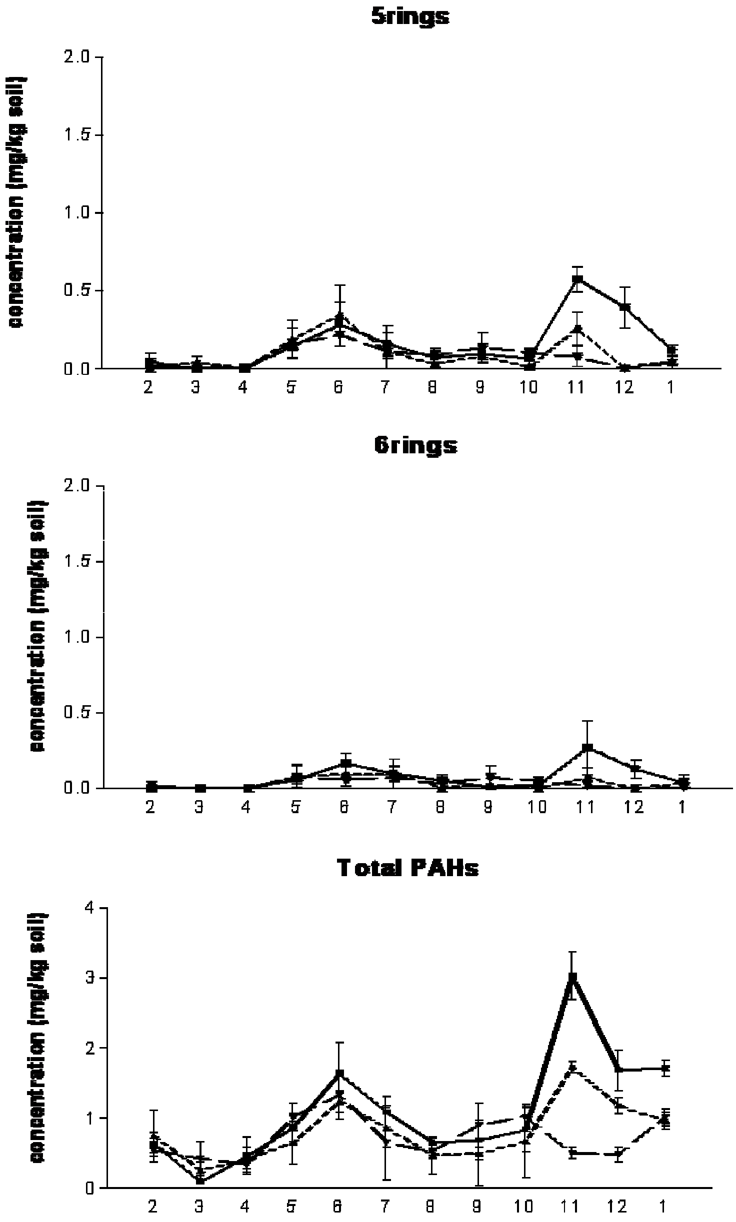

Figure 2. Variation of total and ring number of PAHs concentration in soils since Feb 2003 to Jan 2004.

■: Sample No. 9; ▲: Sample No. 10; ▼: Sample No. 11, Data represent mean±S.D.

Table 3. Correlation coefficient of different numbers of PAHs (No. 8-11)

	2-ring	**3-ring**	**4-ring**	**5-ring**	**6-ring**
2-ring	-	0.650**	0.348	0.431**	0.414
3-ring		-	0.618**	0.635**	0.592**
4-ring			-	0.796**	0.810**
5-ring				-	0.926

**: p<0.01

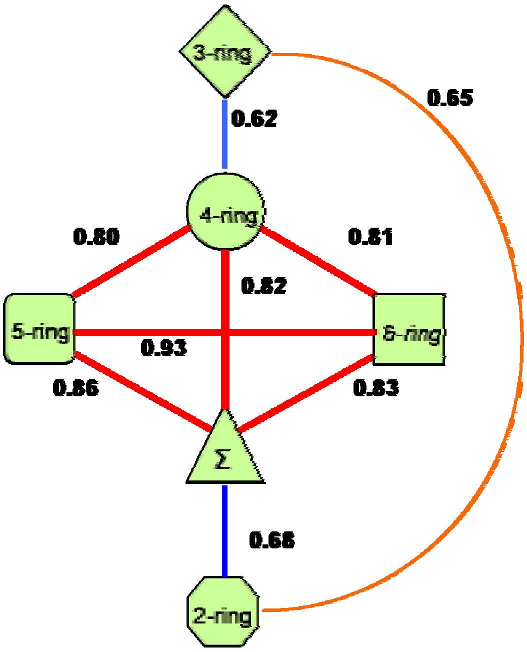

Figure 3. Correlation for content by the number of benzene rings in PAHs

4. CONCLUSION

We investigated the action of 16 PAHs specified by the U.S. EPA in soil around Nara city in Japan. We classed PAHs by number of rings, and examined their concentration and seasonal movements. The content of all 16 PAHs in the sampled soils increased in proportion to traffic volume. At the same locations of traffic volume, the gravitation at a location with plant with all content of 16 PAHs in soils was, furthermore, found to have a low concentration. There were different seasonal movements of the 2, 3-ring and 4, 5, 6-ring PAHs. 4, 5, 6-ring PAHs have a strong correlation with each other (r>0.79), but there were no correlations between 2, 3-ring and 4, 5, 6-

ring PAHs. As a result, the traffic volumes are exposition sources of 4, 5, 6-ring PAHs in soils.

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Chapter 24

BENEFICIAL USE OF C&D RECOVERED SCREEN MATERIAL IN RESIDENTIAL APPLICATIONS: A CASE STUDY

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Abstract: Florida has established guidelines to encourage recycling and use of recycled materials in a manner protecting public health and the environment. Recovered screened material (RSM) generated at a construction and demolition (C&D) debris recovery facility is a recycled material with reuse potential. In order to reuse RSM, it must be shown that the material poses no significant threat to public health or the environment. The Sun Recycling facilities in Broward and Palm Beach counties are C&D facilities, generating RSM (i.e., soil with wood, concrete, other C&D particles) through mechanical separation using screens. The process generates RSM meeting state requirements for industrial, commercial, and residential use. RSM was used on residential lots in Miramar to elevate low areas (excluding building pads). In accord with Broward County Environmental Protection Department (EPD) and Palm Beach County Department of Health (DOH) permits, Sun facilities perform regular testing of RSM. RSM tests showed arsenic (As) concentrations below state criteria. Quarterly testing did not detect volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), or pesticides. RSM was delivered to homesites and mixed with existing site soil. To address concerns raised by some residents, Miramar hired a consultant to collect samples for arsenic and total recoverable petroleum hydrocarbons (TRPH), resulting in reports of some As levels above residential criteria. Further sampling/analysis of RSM and local soils in the neighborhood were performed by Broward EPD and Sun. Results of As and speciated TRPH analysis performed by the Miramar, Broward EPD, and Sun will be discussed. A consensus conclusion of acceptable conditions was reached by all parties.

Key words: Recycling, RSM, arsenic, TRPH, C&D, public health, soil, residential

1. INTRODUCTION

Construction and Demolition (C&D) debris processing facilities generate, among other recyclable products, a soil-like material which is the result of multiple sorting and screening operations. This Recovered Screen Material (RSM) consists primarily of soil particles and other materials that can pass through a small screen (e.g., wood, rock, drywall, concrete). Florida Statutes articulate the clear intent of the legislature to encourage recycling and use of recycled materials, so long as that recycling process is conducted in a manner that protects public health and the environment. The Florida Department of Environmental Protection (FDEP) has established specific criteria and guidelines for the use and reuse of RSM under the auspices of the solid waste management rule and associated guidance documents (e.g., FDEP, 1998). The FDEP guidance defines requirements for the following: sampling and analytical testing of RSM, establishment of use restrictions (e.g., residential, commercial/industrial), and explicit criteria for RSM management.

This paper describes a successful case study involving the use of RSM in a residential application in Broward County, Florida, including important aspects of site characterization, regulatory oversight, citizen concerns, public dialogue, and ultimately a demonstration of safe and proper use of the RSM product.

2. CASE STUDY DETAILS

As a part of the initial permitting process with local and state regulatory agencies, RSM from a variety of batches at one C&D processing facility was sampled over a period of weeks and months to develop a profile regarding the chemical quality of the product, as well as its variability. Many samples were collected and analyzed for metals, volatile organic compounds (VOCs), semivolatile compounds (SVOCs), and pesticides. Throughout the initial characterization period, the RSM samples failed to show exceedances beyond state soil criteria in any of these categories. This demonstration of acceptable RSM for future use is related to the sequence of the processing elements at the facility and to the fact that it does not accept any materials that contain potentially hazardous substances (e.g., hazardous waste, batteries, tires, oil, drums, asbestos, or garbage).

In addition to the initial pre-permit RSM characterization, routine testing was conducted at the C&D processing facility on a weekly/quarterly basis for a variety of parameters to document ongoing permit compliance for unrestricted uses of the RSM (e.g., residential).

This case study focuses on a several month period in 2004 when, due to periodic flooding of low-lying properties, a number of homeowners in Miramar, a small Broward County municipality, elected to have RSM placed on their lots as fill material. Prior to placement of the RSM, sites were cleared of vegetation and "demucked" to remove the highly organic surface layer. Following RSM placement, the muck and soil were mixed with RSM, and the areas were regraded and seeded.

3. RESULTS

Following the application of RSM to approximately 60 properties in one subdivision neighborhood in Miramar, several property owners complained to the City, and the City staff collected unannounced samples of what were believed to be lots where soil and RSM had been mixed and graded. The RSM was used to raise the elevation of the lots to address historical flooding concerns.

Following analysis of those samples a number of statements were publicized in the news media with regard to the "elevated concentrations of arsenic and Total Recoverable Petroleum Hydrocarbons (TRPH)" in those samples. In the simplest interpretation, the maximum arsenic concentration (3.2 mg/kg) and maximum TRPH concentrations (680 mg/kg) in City samples were in excess of FDEP default residential Soil Cleanup target levels (SCTLs) of 2.1 mg/kg (arsenic) and 460 mg/kg (TRPH), respectively. Principal concerns were raised about the potential hazards posed by the observed concentrations. These complaints resulted in the City placing a moratorium on further use of RSM, which initiated a several-months-long process of resampling, assessment of background, naturally occurring soil concentrations of arsenic, as well as a series of risk assessment steps which sought to place the observed concentrations into appropriate perspective for the City and for the residents.

Table 1. Florida SCTLs for Individual TRPH Fractions

TRPH Fraction	SCTL (mg/kg)		
	Residential	Industrial	Leachability [a]
C_5-C_7 Aromatic	340	1800	34
>C_7-C_8 Aromatic	490	3700	59
>C_8-C_{10} Aromatic	460	2700	340
>C_{10}-C_{12} Aromatic	900	5900	520
>C_{12}-C_{16} Aromatic	1500	12000	1000
>C_{16}-C_{21} Aromatic	1300	11000	3200
>C_{21}-C_{35} Aromatic	2300	40000	25000
C_5-C_6 Aliphatic	6200	33000	470
>C_6-C_8 Aliphatic	8700	46000	1300
>C_8-C_{10} Aliphatic	850	4800	7000
>C_{10}-C_{12} Aliphatic	1700	10000	51000
>C_{12}-C_{16} Aliphatic	2900	21000	*
>C_{16}-C_{35} Aliphatic	42000	280000	*

[a] Based on the acceptable concentration of 5000 µg/L for groundwater and surface waters.
* Not a health concern for this exposure scenario.
SCTL = Soil Cleanup Target Level.

Followup sampling and analysis were conducted by Broward County Department of Planning & Environmental Protection (DPEP), which now is known as the Environmental Protection Department. Samples for assessing RSM concentrations were selected from lots where RSM was applied and mixed with soil. In addition, a number of unimpacted surface soil samples were collected by Broward DPEP staff, in order to establish surface soil background arsenic concentrations.

For arsenic, the three (3) City samples of RSM/soils showed 2.9 to 3.2 mg/kg, which is quite consistent with known background concentrations in many southeast Florida soils. In comparison, the six (6) samples collected by County staff showed arsenic at 2.31 to 2.95 mg/kg, values quite similar to the City samples. The FDEP default SCTL for arsenic in unrestricted circumstances is 2.1 mg/kg. In addition to the RSM/soil samples, County staff collected five (5) samples for assessment of background (i.e., naturally occurring) arsenic in soils. Those data showed a background range of 3.37 to 13 mg/kg (average 6.9 mg/kg), compared with U.S. Public Health Service estimates of 5 mg/kg as a U.S. average, while U.S. EPA estimates 3 mg/kg for Florida as a statewide average. A more recent University of Florida study conducted for FDEP concluded that the general background arsenic concentration was 6.6 mg/kg, and was on the order of 12 mg/kg for Broward County. Thus, it clearly was demonstrated that arsenic in the RSM/soil samples was not elevated as a result of the use of RSM. These determinations were reached during consultation between the toxicologist retained by the C&D facility, the toxicologist retained by the City of Miramar, County staff, and City staff.

For TRPH, the issue is much more complex, since there are both background considerations for TRPH, as well as differential toxicity of various hydrocarbon molecular weight fractions. The state, FDEP, has established 13 categories of petroleum hydrocarbon toxicity consistent with the classifications of the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG, 1997), as shown in Table 1. It frequently proves useful, as in this case, to conduct more sophisticated analyses on the TRPH group, in order to determine which fractions are most dominant. For example, weathered or high molecular weight hydrocarbons exhibit very limited toxicity (residential SCTL 42,000 mg/kg for 16 to 35 carbons), while lighter molecular weight, more volatile hydrocarbons exhibit greater toxicity (residential SCTL 340 mg/kg for 5 to 7 carbons). City samples showed TRPH in RSM/soil samples at 250 to 680 mg/kg, while County samples exhibited 486 to 2,810 mg/kg. Further, the County samples from background locations exhibited 449 to 727 mg/kg TRPH, leading to a conclusion that City results were due to naturally occurring background, rather than RSM "contamination". Nevertheless, fraction-specific TRPH analysis by the County demonstrated that essentially all of the TRPH was in the high molecular weight, very low toxicity category and, thus, did not represent a threat to public health.

Groundwater sampling did not show elevated concentrations of either arsenic or TRPH components. Thus, the investigations and regulatory decisions focused on potential soil impacts.

Following the collection and interpretation of the newer analytical data for the site, several meetings were held among County staff, City staff and scientific consultants to discuss appropriate responses. While there was a consensus that the comprehensive data set did not indicate a human health or ecological problem, a constructive decision was made to hold a public meeting to present the data in an open forum and to respond to citizen concerns and questions. At this meeting, brief presentations were made by County and City representatives both of a scientific nature and an administrative nature, given some questions about the need for permits to apply RSM as fill material. The meeting concluded amicably, and no restrictions remain on the use of RSM on residential lots in Broward County, with the exception of ongoing mandatory monitoring protocols to ensure the consistent composition of the RSM.

4. DISCUSSION AND CONCLUSIONS

Residual Screen Material (RSM) from Construction & Demolition (C&D) debris processing operations, when properly sampled, characterized, and installed, can be suitable in mixed or unmixed condition for use as soil under residential land uses without presented health risks. This case study successfully demonstrates an appropriate application of RSM product testing/analytical procedures, public involvement, and regulatory oversight concerning such uses involving a commercial C&D facility permittee, state and local governmental entities, and the general public. Both arsenic and Total Recoverable Petroleum Hydrocarbons (TRPH) initially were suggested to be health concerns associated with RSM. However, following further sampling of site and background locations and more sophisticated analysis for TRPH, a clear demonstration was made that arsenic and TRPH either were present at levels which did not exceed natural background values, or were present at levels that were not of concern from a human health perspective. At the end of the process, there was general consensus by all parties (City, County, permittee, public) that the RSM did not pose a threat to human health or to the environment. This case study represents a success in terms of innovative application of recycling technology, productive use of sophisticated analytical techniques, and constructive dialogue among agencies, the permittee and the general public.

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Index