CONTAMINATED SOILS, SEDIMENTS, WATER, AND ENERGY

Volume 15

Selected manuscripts from the 25th Annual International Conference on Soils, Sediments, Water and Energy

University of Massachusetts Amherst
October 19 – 22, 2009

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Bioremediation
Heavy Metals
Modeling
Pesticides
Phytoremediation
Radionuclides
Remediation
Risk Assessment
Sediments
Site Assessment

Edited by

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Edward Calabrese
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Foreword

In the Connecticut River Valley, autumn foliage and the sequence of passing cold fronts sweep away summer nostalgia and kick-start thoughts of winter and even that first unformed but undeniable anticipation of green shoots and warm weather waiting at the far side. And, for the past 25 years, autumn has also meant the annual International Conference on Soils, Sediments, Water and Energy in Amherst. It is not simple coincidence that the Conference is one of the most forward-thinking gatherings of scientists, engineers, and environmental practitioners. Our academic training means that autumn is a regular time of intellectual renewal and professional excitement. For many of us, our Circadian clocks peak in autumn—we do our best thinking while leaves are in high color and the air is fresh and dry.

It is not surprising that the Conference proceedings have demonstrated, year after year, that emerging ideas and new and productive concepts can be generated by participants in an institution like the Autumn Conference. And 2009 was no exception. As you peruse the Table of Contents, keep in mind how innovative our inquiries into emergent fields such as bioremediation, phytoremediation, and chemical remediation are, and how our deliberations keep mundane-sounding, but critically important topics such as heavy metals, modeling, pesticides, risk assessment, sediments, and site assessments fresh and in the forefront.

There were more than 140 presentations at the 2009 Conference. The best and the brightest are in your hands now, in the pages of this volume. As you leaf through these proceedings, we hope you resolve to join us next year, as the Conference enters its second quarter-century. Our collective efforts have made this conference an annual treasure. We'll see you in 2010!

Dave Ludwig
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About the Editors

Paul T. Kostecki's professional career has focused on research, education and trainingin environmental contamination with an emphasis on human and ecological risk assessment and risk management. His work includes soil ingestion estimates for children and adults; establishment of scientifically sound cleanup levels for soil; bioavailability of soil contaminants; fish as toxicological models for contamination assessment; and assessment and management of petroleum contaminated soils. Dr. Kostecki has developed and conducted over 45 conferences, workshops and courses both nationally and internationally, and hasmade presentations at over 100 national and international meetings. Since 1985, his conference at the University of Massachusetts Amherst on Contaminated Soils, Sediments and Water has attracted over 10,000 environmental professionals from over 40 countries. Dr. Kostecki has published over 100 articles and reports, co-edited/co-authored 25 Books and secured over $10M in research support.

Dr. Kostecki co-created the Association for Environmental Health and Sciences (AEHS) in 1989 and served as its Executive Director until 2009. In 2009, he established the AEHS Foundation. He help found Amherst Scientific Publishers and co-created seven peer-reviewed journals: Journal of Soil and Sediment Contamination (1990); Human andEcological Risk Assessment (1994); Journal of Phytoremediation (1998); Journal of Environmental Forensics (1999); Journal of Children's Health (2003); Non-Linearity Journal (2003); and Journal of Medical Risks (2004). In addition, Dr. Kostecki co-created the International Society for Environmental Forensics in 2002.

From September, 2003 to August, 2009, Dr. Kostecki served as Vice Provost for Research and Vice Chancellor for Research and Engagement at the University of Massachusetts Amherst. He presently serves as Special Advisor for the Clean Energy China Initiative, Office of the President, University of Massachusetts.

Edward J. Calabrese is a board certified toxicologist and professor of toxicology at the University of Massachusetts School of Public Health at Amherst. Dr. Calabrese has researched extensively in the area of host factors affecting susceptibility to pollutants and has authored more than 300 papers in scholarly journals, as well as 24 books, including: Principles of Animal Extrapolation; Nutrition and Environmental Health, Vols. 1 and 2; Ecogenetic: Safe Drinking Water Act: Amendments. Regulations, and Standards; Soils Contaminated by Petroleum: Environmental and Public Health Effects; Petroleum Contaminated Soils, Vols. 1, 2 and 3; Ozone Risk Communication and Management; Hydrocarbon Contaminated Soils, Vols. 1, 2, 3, 4 and 5; Hydrocarbon Contaminated Soils and Groundwater, Vols. 1, 2, 3, and 4; Multiple Chemical Interactions; Air Toxics and Risk Assessment; Alcohol Interactions with Drugs and Chemicals; Regulating Drinking Water Quality; Biological Effects of Low Level Exposures to Chemicals and Radiation; Contaminated Soils; Diesel Fuel Contamination; Risk Assessment and Environmental Fate Methodologies; Principles and Practices for Petroleum Contaminated Soils, Vols. 1, 2, 3, 4, and 5; Contaminated Soils, Vol. 1; and Performing Ecological Risk Assessments. He has been a member of the U.S. National Academy of Sciences and NATO Countries Safe Drinking Water Committees, and the Board of Scientific Counselors for the Agency for Toxic Substances and Disease Registry (ATSDR). Dr. Calabrese also serves as Director of the Northeast Regional Environmental Public Health Center at the University of Massachusetts, Chairman of the BELLE Advisory Committee and Director of the International Hormesis Society.

James Dragun, Ph.D., is a soil chemist with extensive experience dealing with soil remediation. He has addressed the extent, danger, and/or cleanup of chemicals at sites of national and international concern such as the oil lakes caused by the 1991 Persian Gulf War (Kuwait), VX chemical warfare agent for the U.N. Weapons Inspection Program (Iraq), malfunction of the Three Mile Island Nuclear Power Plant USA), and dioxin in Missouri (USA). Twenty-four nations including Japan, Canada, the United Kingdom, Australia, Germany, Switzerland, Italy, France, Spain, Scandinavia, and the Netherlands have utilized his expertise.

He founded and built an environmental engineering-science consulting company. For 18 years, he has led a team of specialists in chemical engineering,

civil engineering, environmental engineering, geotechnical engineering, mechanical engineering, physics, plant engineering, environmental science, geology, hydrogeology, chemistry, biochemistry, toxicology, and biology. Dr. Dragun and his associates have solved environmental issues for major companies and governments in six continents (Africa, Asia, Australia, Europe, North America, and South America).

Dr. Dragun is a full Professor at the University of Massachusetts and at Wayne State University, Detroit, MI. He has authored two college textbooks and co-authored/edited eight technical books. Also, Dr. Dragun has been the Editor-in-Chief of the International Journal of Soil and Sediment Contamination for over 15 years.

PART I: Bioremediation

Chapter 1

LIMITED-ACCESS BIOREMEDIATION IN A FACTORY SETTING

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ABSTRACT

A factory in New Hampshire had a volatile organic compound (VOC) release detected in a storm-water outfall pipe. Hydrogen Release Compound (HRC) injection was determined to be the best remedial solution. Tight soils, shallow water table, access limitations, and pending property sale complicated remediation. Groundwater was directly below the floor slab. The plume was centered on the storm-water drain which carries runoff from the upgradient parking lot under the building. The VOCs are believed to have entered the subsurface in the central area of the building through spillage; the storm drain system was a preferential pathway.

The groundwater contamination was addressed through bioremediation using HRC. Application required many injection points and applications, due to the low permeability of the soil. Due to interference with operations and property sale, repeated openings of the floor for injections using a drill rig were not feasible. Permanent injection points were installed, but would not be accessible for direct injection. Therefore, a trench was cut into the concrete floor slab between each point and the wall. Piping ran from the injection point to the wall, terminating at a standpipe with a quick-connect fitting. Each trench was then fillled with concrete to restore the floor slab.

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Since starting HRC treatment, VOC levels at the outfall have dropped to below the state regulatory standard. One well had levels of 1800 ug/L and 1200 ug/L of Cis-1,2 Dichloroethene and Vinyl Chloride in April, 2008. By January, 2009, both were below MCLs. Site closure is expected to be completed in a reasonable timeframe. The treatment has not interfered with Site activities or with sale of the Site.

Keywords: Remediation, HRC, chlorinated solvents, VOC, site assessment, property transaction

1. INTRODUCTION

A manufacturing facility in New Hampshire was the site of a chlorinated volatile organic compound (VOC) release first detected in a stormwater outfall pipe at the downgradient side of the facility. The compounds detected were Trichloroethene (TCE) and its daughter products. TCE was formerly used in degreasing during the manufacturing process, but had not been used for many years.

1.1 Conceptual Site Model

Groundwater at the site is shallow; in some locations it was encountered immediately below the floor slab. The groundwater contaminant plume was centered around a storm sewer which carries stormwater from the upgradient parking lot, under the building, to the downgradient side of the property, where it discharges to a small stream. The VOCs are believed to have entered the subsurface in the central area of the building through small spillages over many years; the storm drain system acted as a preferential pathway for contaminant migration. Site soils consisted mainly of silts and clays below foundation fill which consists of fine to coarse brown sand with some gravel. Groundwater contamination was present in both fill and native materials.

The source area for groundwater and surface water contamination appears to be in the area surrounding well MW-21, located in a former machine area near the drain line. Near this area, contaminated groundwater entered the drain line through cracks and joints in the sewer line, as indicated by manhole samples upgradient and downgradient of this area. Once in the drain line, the VOC contaminants flowed directly to the outfall area, where TCE was present in water at 16 ug/l. VOC levels in the stream continue to drop downgradient of the outfall at sampling location SS-1, with TCE at 10.6 ug/l.

Groundwater VOC levels trended downward along the path of the storm drain; the backfill surrounding it appears to have acted as a preferential pathway. From MW-21S, with the highest level of total VOCs at 314 ug/L, the nearest well

downgradient is MW-18S, which had a total VOC load of 226 ug/l; next is MW-15S, with total VOCs of 52.9 ug/l; MW-13D, with total VOCs of 24 ug/l; and finally T-01, with total VOCs of 7.9 ug/l. Only the monitoring wells located east of the drain line appeared to be affected; this is the natural downgradient groundwater flow direction.

Groundwater within the backfill immediately surrounding the drain line is assumed to generally follow the line south as a preferential pathway; other groundwater on the site flows towards an unnamed stream located east of the site.

The VOC contamination consists of trichloroethene and its daughter products. Natural attenuation appears to be occurring, based on the presence of daughter products such as cis(1,2)dichloroethene and vinyl chloride.

2. MATERIAL AND METHODS

Based on hydrogeological characterization of the site and the extent and magnitude of contamination, four remedial alternatives were identified that would reduce contaminant concentrations to levels at or below DES established limits. Those four alternatives were:

1. Natural Attenuation
2. Groundwater sparging with soil vapor extraction
3. Enhanced Natural Attenuation of groundwater hot-spot and In-Pipe Sparging of surface water in storm drain
4. Containment for water leaving the property

In addition, it was decided to repair the drain line to prevent groundwater infiltration, regardless of which alternative was selected.

The alternatives were compared for their effectiveness, feasibility or implementability, treatment time, and cost. Costs were based on capital expenditures (including pilot tests, construction, land, buildings, equipment, engineering, startup, and permits) and annual operating costs (including labor, materials, power, disposal of residues, monitoring, and equipment replacement). Costs had an accuracy of +/- 30 percent. A present worth analysis was used to evaluate the costs using a 5% interest rate.

The selected remedial technology was Alternative 3 in combination with the drain line repair. This alternative was selected based on the fact that Enhanced Natural Attenuation with HRC was found to be the most cost-efficient and effective solution, while repair of the drain line was a low-cost endeavor which would prevent future surface water contamination.

After conducting as much repair to the drain pipe as was possible, HRC was injected through a grid of both temporary and permanent points installed using direct-push technology. HRC application required a large number of injection points and repeated applications, particularly due to the low permeability of the majority of the soil. Repeated openings of the floor to conduct repeated injections using a drill rig were not desired by the client, due to potential interference with plant operations and with pending sale of the property. Therefore, permanent injection points were required. An HRC trench system was designed that would allow repeated injection of HRC yet not require access to the floor of the plant.

3. HRC INJECTION AND TRENCH SYSTEM

Initially, the permanent injection wells were installed using a direct-push rig and completed with roadboxes. When the trench system was installed, the wells had to be retrofitted. At each of the 22 permanent injection point locations, a trench of approximately 4" wide by 4" deep was cut into the floor slab using wet sawing techniques from the wellhead to the nearest wall. The concrete in each trench was broken out by the contractor. The trenches did not penetrate the total thickness of the concrete. MyKroWaters personnel then removed the roadbox and expansion plug from each well. A PVC 90 degree elbow was used to join the existing well to new PVC piping which ran horizontally from the well to the wall. Couplings were used in cases where more than 10' of pipe was needed. At the wall, a second elbow was used to connect the horizontal pipe to a vertical standpipe. In several cases, multiple elbows were needed to plumb the piping all the way to the standpipe, due to obstacles at the base of the wall. Each standpipe rose approximately 2' above floor grade, as close to the wall as was feasible, and was equipped with a ball valve to close the system when not in use, and a quick-connect fitting for future HRC injection. All PVC was 1" Schedule 80, and all fittings were glued using PVC primer and cement. Each finished standpipe, where feasible, was collared to the wall with metal strapping. Each point was further protected with a steel bollard.

Prior to pouring concrete, all dust and chips were removed from the trenches using brushes and industrial vacuums to allow a better seal of the new concrete to the sidewalls and floor of the trenches. Each trench was backfilled with concrete. The trenches were sealed with a clear-coat sealant.

After the installation of the trench system, the buyer was willing to move forward with purchase of the property, knowing that they would be able to place machinery where it was needed, without concern for allowing access to the injection points.

4. RESULTS

VOC levels have been reduced dramatically since the start of HRC treatment. Most importantly, VOC levels in the surface water at the outfall where TCE was originally detected have dropped to below the Ambient Groundwater Quality Standard (AGQS). One of the most contaminated wells had levels as high as 1800 ug/L cis-1,2 dichloroethene (cis-1,2 DCE) and 1200 ug/l vinyl chloride (VC), respectively, in April, 2008. By January, 2009, VC was below the laboratory detection limit, following a steady decline; and cis-1,2 DCE was at 1.4 ug/L, an order of magnitude below the AGQS.

Two wells, MW-73 and MW-21S, are examples of the results of the HRC injection program as discussed below.

MW-73 was sampled in January, 2008, prior to the first HRC injection in February. It contained levels of cis-1,2 DCE at 1500 ug/L; VC at 700 ug/L; 1,1-DCE at 14 ug/L; and trans-1,2 DCE at 120 ug/L, all of which were above AGQS. It was next sampled in April, 2008, two months after HRC injection. Cis-1,2 DCE had increased to 1800 ug/L, and VC had increased to 1200 ug/L, with 1,1-DCE and trans-1,2 DCE essentially unchanged. By May, 2008, three months after injection, cis-1,2 DCE had begun to drop, at 1400 ug/L. Since then, with monthly or bi-monthly sampling, the level of cis-1,2 DCE in MW-73 dropped steadily and has been below 5 ug/L since October, 2008 – a reduction by a factor of about 300 in less than one year. 1,1 DCE dropped below the AGQS in June, 2008, and has been non-detect since July 2008. Trans-1,2 DCE has been below AGQS since May, 2008 and non-detect since December 2008. VC continued to rise to its highest level in May 2008, at 1600 ug/l, more than double its original level, and then began to drop; by December 2008 it was below 5 ug/l and had been non-detect since April.

MW-21S contained levels of both cis-1,2 DCE and VC above AGQS in January 2008, at 244 ug/L and 69.7 ug/L, respectively. In April 2008, two months after injection, levels of both had doubled. Levels of cis-1,2 DCE steadily decreased after that, and were at 62.6 ug/L in December 2008, below AGQS. Since then, levels of cis-1,2 DCE in the well have rebounded slightly but remain at less than half of what they were in the corresponding month in 2008. VC increased to its highest level in May 2008, at 190 ug/L, and then began to decline steadily, also reaching its lowest level in December 2008. As with cis-1,2 DCE, the levels of VC have since increased. The increases in both cis-1,2 DCE and VC may be due to desorption of contamination from the aquifer solids as well as due to the increased bacterial activity forming the degradation of TCE, the principal contaminant.

In both cases, there is clear evidence of reductive dechlorination occurring. Both wells followed a similar timeline, with cis-1,2 DCE spiking two months after HRC injection, in April, 2008, and then reducing, and with VC spiking in May.

5. DISCUSSION AND CONCLUSION

Out of the 9 monitoring wells which started off above AGQS, three are well below AGQS for their primary contaminant; three have shown steadily reducing contaminant levels; and three have not shown improvement. The areas surrounding the three which have not improved were not thoroughly treated with HRC during the first injection events, and are now being treated more completely. Similar results are expected to the rest of the treatment areas.

Most importantly, the surface water contamination that was the original indicator of the release has been fully remediated. Some air sparging within the drainage pipe was conducted; however, the in-pipe sparging system has been inactive for several months. VOC levels at the outfall began to decline in November of 2008 and are now below detection limits. Surface water samples from downstream of the outfall began to decline in December of 2008 and are now also below detection limits.

Site closure is fully expected to be completed in a reasonable timeframe. The treatment method has not interfered with Site activities or with the sale of the Site.

Chapter 2

PERCHLORATE REDUCTION USING FINE MEDIA FLUIDIZED BED BIOREACTOR WITH OXIDATION-REDUCTION POTENTIAL-BASED FEED CONTROL

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ABSTRACT

Certain bacteria, prevalent in the environment, use perchlorate as an electron acceptor and reduce it to chloride under anaerobic conditions. To develop an ex-situ treatment system for perchlorate-contaminated groundwater, we performed bench-scale test using a fine media fluidized bed reactor (FMFBR; 0.5-ft diameter, 8-ft high) inoculated with a perchlorate-reducing culture. The system was operated under anaerobic conditions. A perchlorate-water solution was introduced into a recirculating stream in the FMFBR at an upward velocity of 16 cm/min. Acetate (acetic acid) was fed as an electron donor. The objective of this study was to establish a minimal acetate feed ratio for sufficient perchlorate reduction by monitoring oxidation-reduction potential (ORP) and, consequently, to prevent ORP from falling to a range of sulfate reduction, and to limit the biomass growth from excess acetate.

The FMFBR was able to degrade 3000 - 5000 μg/*l* perchlorate to less than 4 μg/*l* in a single pass (16 min empty bed contact time) without excessive hydrogen sulfide production, when effluent ORP (vs. Ag/AgCl) was -290 - -410 mV. Accurate feed control is essential since an imbalance in acetate feed ratio results in unreacted perchlorate or sulfide production. A base feed pump was used to provide 80 % of the acetate required and an ORP controller was used to trim and balance the feed rate using a second pump. The second feed pump was activated when effluent ORP rose to or above -315 mV and deactivated when it fell to or below -320 mV. Some oscillation of effluent ORP was observed, but perchlorate was not detected in the effluent when the oscillation was kept relatively small. Average acetate feed ratio was approximately 1.1-times stoichiometry. For more stable perchlorate degradation, we will examine an

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earlier ORP detection in the bioreactor column and a more flexible control method for acetate feed.

Keywords: perchlorate, groundwater, remediation, fine media fluidized bed bioreactor, oxidation-reduction potential (ORP)

1. INTRODUCTION

Perchlorate (ClO_4^-), an anion which forms perchlorate salts such as ammonium perchlorate (NH_4ClO_4), is a potential thyroid gland toxin and a widespread environmental contaminant. Perchlorate salts have been manufactured and used as an oxidizer component for explosives such as rocket/missile fuels, fireworks and safety flares (Motzer, 2001). Perchlorate is also known to occur naturally in some areas, especially arid and semi-arid region (Rajagopalan et al., 2006, Rao et al., 2007), and Chilean nitrate fertilizer (Urbansky et al., 2001). Perchlorate salts are generally highly soluble, and perchlorate anion is very mobile in aqueous phase (Motzer, 2001, Urbansky and Brown, 2003). Perchlorate has been found in water and soil throughout the United States (USEPA, 2005a); the chemical has been detected at nearly 270 sites, more than 45 of which are on the U.S. EPA's National Priority List (USEPA, 2009). Some states have set drinking water standards for perchlorate such as California (6 μg/*l*) (CalDPH, 2007) and Massachusetts (2 μg/*l*) (MassDEP, 2006), stricter than the recently issued interim health advisory level by the U.S. EPA (15 μg/*l*) (USEPA, 2008).

Despite its persistency in the environment, perchlorate can be used as an electron acceptor by certain bacteria under anaerobic conditions and reduced to innocuous chloride. Perchlorate-reducing bacteria have been isolated from various environments (Bruce et al., 1999, Coates et al., 1999, Herman and Frankenberger, 1999, Logan et al., 2001, Rikken et al., 1996, Wallace et al., 1996, Waller et al., 2004, Zhang et al., 2002). Oxidation of electron donors, such as acetate or hydrogen, is coupled to perchlorate reduction. When acetate was used as an electron donor, the following reaction takes place: $ClO_4^- + CH_3COO^- \rightarrow Cl^- + 2HCO_3^- + H^+$ (Rikken et al., 1996). Most perchlorate-reducing bacteria also utilize oxygen and nitrate, but not sulfate, as electron acceptors (Coates et al., 1999, Herman and Frankenberger, 1999, Logan et al., 2001, Rikken et al., 1996, Zhang et al., 2002). Microbes, including perchlorate-reducing bacteria, use oxygen, nitrate in that order of preference due to the energy gained from the reactions. The energy gained from perchlorate reduction is slightly higher than nitrate reduction/denitrification (Rikken et al., 1996), although previous studies demonstrated that nitrate reduction occurred either preferentially over or simultaneously with perchlorate reduction in batch systems (Bardiya and Bae, 2005, Chaudhuri et al., 2002, Gal et al., 2008, Herman and Frankenberger, 1999,

Nozawa-Inoue et al., 2005, Tan et al., 2004, Tipton et al., 2003). As anaerobic reactions progress, microbes, but not perchlorate-reducing bacteria, use sulfate as an electron acceptor.

Due to the microbial ability of perchlorate reduction, bioremediation technologies are promising for treating perchlorate contaminated water and soil. For ex-situ bioremediation of perchlorate-contaminated groundwater, biofilm reactors, such as packed bed, fluidized bed, and membrane reactors, have been developed and tested (Brown et al., 2005, Fuller et al., 2007, Hatzinger, 2005, Min et al., 2004, Nerenberg et al., 2003, USEPA, 2005b, Zhang et al., 2005). Of these types, fluidized bed reactors (FBR) have been applied for perchlorate treatment of groundwater in commercial scale at several sites (Hatzinger, 2005). In FBR, microbes are confined by adherence to particulate media, such as sand and granular activate carbon. The media are fluidized by upward flow of water. An organic electron donor such ethanol or acetate is typically provided to the FBR for reducing perchlorate. Overfeeding the electron donor, however, results in undesirable sulfate reduction, in which sulfide is produced, and overproduction of biomass solid.

In this study, we developed a fine media fluidized bed reactor (FMFBR) system for treating perchlorate-contaminated water. An FMFBR provides a large surface area for bacteria to adhere and can be operated in a plug flow mode hydraulically, which are important characteristics to carry out a high treatment efficiency with a low contaminant concentration (Weaver, 2006). The FMFBR, operated under aerobic conditions, has successfully been applied to treatment of MTBE/TBA-containing groundwater (O'Connell and Moyer, 2007). The reactor was modified for anaerobic treatment of perchlorate, in this study. A lab pilot-scale bioreactor was constructed to develop optimal operational conditions for perchlorate degradation. Effluent water was recirculated to provide a proper fluidization of the bed. A nitrogen purge was used to remove the CO_2 produced and to maintain anaerobic conditions. The oxidation-reduction potential (ORP) of the bioreactor influent/effluent was monitored to find an optimal range for perchlorate reduction. Use of ORP to balance the feed ratio of an electron donor (acetate) to perchlorate was tested to minimize sulfate reduction as well as solid production.

2. MATERIALS AND METHODS

2.1 Enrichment of Perchlorate-Reducing Culture

Perchlorate-reducing culture was developed from anaerobic digester sludge obtained from a wastewater treatment plant in South Orange County in California.

Two liters of a culture was prepared by mixing 400 m*l* of the anaerobic sludge in a growth culture medium containing perchlorate, acetate, and nutrients (NPK and trace minerals containing molybdenum (Bruce et al., 1999)) in a 2-*l* Erlenmeyer flask. Perchlorate concentration (in the 2-*l* culture) was 10 mg/*l* (0.1 mM). Acetate added to the culture was 120 mg/*l* (2.0 mM) initially, then decreased to 12 mg/*l* (0.2 mM), corresponding to 2-times stoichiometry of perchlorate reduction. When other electron acceptors, such as oxygen and nitrate, were present, acetate concentration was raised up to 30 mg/*l* (0.5 mM). Amounts of nutrients were changed in proportion to the acetate concentration: for 12 mg/*l* acetate, 4.3 mg/*l* NH_4Cl, 0.98 mg/*l* Na_2HPO_4, and 0.34 mg/*l* KH_2PO_4 were added. pH was adjusted to 7.0 - 7.2 using NaOH. The headspace was flushed with nitrogen (N_2) gas and the flask was closed with a rubber stopper. The culture was stirred slowly and incubated at 22 - 32 °C. When perchlorate was degraded < 1 mg/*l*, stock solutions of the chemicals were added again. From time to time a portion of the culture solution was discarded and replaced with fresh culture medium to remove accumulated salts.

2.2 Bioreactor Design and Operations

The FMFBR system consisted of a 12-gal (45-*l*) FMFBR column, a countercurrent gas-liquid packed column, and a 30-gal (113-*l*) equalization tank (Figure 1). The clear PVC FMFBR column was 6 inches in diameter and 98 inches high. Approximately 6 gallons (bulk volume, about 4 feet high in the FMFBR when settled) of fine silica sand was filled in the FMFBR column. Water was drawn from the equalization tank at a flow rate of 0.75 gpm (2.8 *l*/min) using a centrifugal pump and a flow control valve. The water was injected through a PVC pipe inserted in the center of FMFBR column and dispersed at the bottom through three holes, creating an upward flow for fluidization of the bed. The hydraulic loading rate was 3.8 gpm/ft^2 (upward velocity 16 cm/min), and the empty bed contact time was 16 min. The expanded bed height was 80 - 96 inches.

The water passed through the FMFBR and overflowed to the packed column which was 4 inches in diameter, 48 inches tall. The column was packed with a plastic filter medium and was purged with N_2 gas (1.5 - 2.0 *l*/min) to remove CO_2 produced by oxidation of acetate. The treated water was recycled to the equalization tank, where feed materials were added and spent solution was withdrawn.

Figure 1. Anaerobic fine media fluidized bed bioreactor system.

2.2.1 Start-Up and ORP Monitoring

As an inoculum for the FMFBR, 2 gallons of the batch culture was added to the stream so the microbes attach to the surface of the fine media while the liquid was recirculating. Perchlorate was added to the tank in batch mode for the first two months. The equalization tank was monitored for ORP, pH and perchlorate concentration. Acetic acid (10 - 100 mM (600 - 6000 mg/*l*)) was fed continuously to the bottom of the FMFBR at an average rate of 3 *l*/d using a metering pump. Nutrients were mixed with acetic acid (for 10 mM acetate, 215 mg/*l* NH_4Cl, 31 mg/*l* Na_2HPO_4, 34 mg/*l* KH_2PO_4, trace mineral solution) first, but due to biomass growth in the feeding stock even at the low pH (~3.6), they were added in batch mode later.

Bioreactor operation was then switched to continuous mode. Concentrated perchlorate (5000 - 10000 mg/*l* (50 - 100 mM)) was loaded to the equalization tank at a rate of 1.5 - 1.7 *l*/d by using a metering pump and mixed with the recycled liquid. Influent perchlorate concentration to the FMFBR was incrementally increased from 3 to 7 mg/*l*. Acetate feed rate was balanced with

perchlorate loading rate by manually adjusting the metering pump flow rate. NPK and trace minerals were also continuously provided with perchlorate and acetate, respectively. Bioreactor effluent ORP was monitored at the FMFBR outlet, before entering the gas-liquid packed column. Another ORP probe was later installed in the equalization tank to monitor influent ORP. Influent pH was also monitored in the tank.

2.2.2 Operation Using ORP-Based Feed Control

Two acetate feeders (75 - 100 mM each) were used to provide variable feed rates based on the change in effluent ORP. The first (base) acetate feeder provides nominal 80 % (actual 70 – 80 %) of perchlorate feed rate constantly. The second acetate feeder was controlled by an ORP controller (model 6311, Jenco Instruments, San Diego, CA) monitoring effluent ORP: the feed pump was activated when effluent ORP elevated to a high ORP set point and deactivated as the ORP lowered below the set point. The high set point used in this study was -300, -315, and -330 mV and the hysteresis value was 5 mV. Influent ORP (in the tank) was also monitored with an ORP probe and an ORP controller (model 3679N, Jenco Instruments). Influent perchlorate concentration was 2.3 - 3.6 mg/*l*.

Acetate injection point was changed to the pipe between the centrifugal water pump and the flow control valve to ensure mixing of acetate in the stream before entering the FMFBR column. This is because ORP changes and perchlorate degradation data suggested acetate was not mixed with the stream completely in the FMFBR when injected to the bottom, causing the delay in the response with the ORP-control mode. Influent pH was adjusted to 7.2 - 7.4 using NaOH to minimize effects of pH on ORP, though N_2 sparging at a flow rate of 1.8 - 2.0 *l*/min well maintained the pH in this range and the necessity of NaOH addition was minimal. Effluent pH before N_2 sparging was 0.15 - 0.17 lower than influent pH.

2.2.3 Measurement of Sulfide Production with Sulfate Loading

Sulfide production during the ORP oscillation was analyzed. Some sulfate was present in the tap water used but the amount was small and variable. Therefore, sodium sulfate (50,000 mg/*l* (= 520 mM) as SO_4^{2-}) was mixed with perchlorate solution and loaded to the equalization tank. Sulfate concentration added to the stream was approximately 20 mg/*l*. Estimated cumulative sulfate at the time of the samplings was 120 g, corresponding to 840 mg/*l* sulfate increase in the system (A semi-quantification showed a larger sulfate concentration probably due to sulfate carried over from tap water). N_2 sparging of effluent was stopped during the sampling not to purge H_2S out of the water. Influent pH decline during the sampling was small (-0.02). Influent perchlorate concentration was 2.6 - 3.4 mg/*l*.

Acetate feed rate was controlled based on effluent ORP measurement as described above, with the high ORP set point of -315 mV.

2.3 Analytical Methods

Perchlorate concentrations higher than 1 mg/*l* were measured using a perchlorate ion selective electrode (Cole-Parmer, Vernon Hills, IL) equipped with a multiparameter meter (5-Star benchtop meter, Thermo Scientific Orion, Beverly, MA). Perchlorate concentrations less than 1 mg/*l* were analyzed by ion chromatography (IC; analyses were performed by Calscience Environmental Laboratories, Inc., Garden Grove, CA), according to EPA method 314.0. The reporting limit was 2 μ g/*l*, though sample matrix interferences raised the limit to 4 - 20 μ g/*l*.

The ORP probe used in this study was a platinum-Ag/AgCl combination electrode (M-10-ORP, Endress+Hauser Conducta, Inc., Anaheim, CA). The values were indicated against Ag/AgCl, which are 200 mV smaller than against standard hydrogen electrode. pH 4 and 7 buffers saturated with quinhydrone (263 mV and 86 mV at 25°C, respectively) were used to check the calibration of ORP probes. pH was measured with a combination pH electrode (M-10, Endress+Hauser) equipped with the multiparameter meter. Dissolved oxygen (DO) was analyzed with a DO meter (model 55, YSI Inc. Yellow Springs, OH).

Sulfide concentrations in the liquid samples were measured using hydrogen sulfide test kit (model HS-C, Hach Company). Test strips were also used to measure concentrations of nitrate + nitrite (Hach Company) and sulfate (EMD chemicals) semi-quantitatively.

3. RESULTS

3.1 Perchlorate Degradation by Batch Enrichment Culture

With the anaerobic sludge as an inoculum, the batch culture degraded over 90 % of 10 mg/*l* perchlorate in less than 5 days. The culture soon became capable of degrading perchlorate from 10 mg/*l* to an undetectable level (< 2 μg/*l*) within 2 - 3 days. The culture also consumed nitrate and DO when they were present.

3.2 Perchlorate Degradation and ORP Changes in the Bioreactor

3.2.1 Perchlorate Degradation and ORP during the Startup of the Bioreactor

When starting up the FMFBR, about three days was needed to degrade more than 90% of 10 mg/*l* of perchlorate, probably due to the small density of perchlorate-reducing bacteria. As batch perchlorate degradation repeated, the degradation rate became much larger, suggesting the growth of perchlorate-reducers in the bioreactor. The ORP of the recirculating water was -200 - -270 mV when perchlorate concentrations were larger than 1 mg/*l*. As perchlorate was degraded to less than 1mg/*l*, the ORP dropped below -280 mV (down to -500 mV observed), and the bioreactor started generating sulfide and volatile fatty acid odors. The pH was 7.5 - 8.3 with no acid-base control.

3.2.2 Perchlorate Degradation and ORP Changes in Continuous Mode

In continuous mode, perchlorate (3 - 7 mg/*l*) was degraded to less than 1 mg/*l* in a single pass, provided that acetate feed rate was sufficient. IC analysis of the effluent samples confirmed the FMFBR was capable of degrading 4 - 5 mg/*l* of perchlorate to below 4 μ g/*l* in a single pass.

Small shifts in the feed ratio, however, often led to either overfeeding or underfeeding of acetate. The overfeeding caused a further decline in ORP toward sulfate reduction range, generating hydrogen sulfide; on the other hand, the underfeeding of acetate led to accumulation of perchlorate in the bioreactor. Our observations show that when the feed ratios produced effluent ORP in the -230 to -290 mV range, perchlorate was not completely degraded (Figure 2, right). To obtain effluent perchlorate values less than 1 mg/*l*, acetate feed rate had to be increased until the ORP dropped below -290 mV (Figure 2, middle). When acetate was overfed, effluent ORP dropped to less than -420 mV, acetate carried over into the surge tank initiating reactions there and a hydrogen sulfide smell was noted (Figure 2, left). The feed ratios producing effluent ORP of in the range of -290 to -410 mV resulted in over 90% of perchlorate reduction without considerable sulfide production. Influent ORP remained -220 to -250 mV, unless the reaction occurred in the tank by the excess acetate, causing influent ORP dropping lower than -370 mV (Figure 2, left). The average molar ratio of acetate to perchlorate was approximately 1.3, higher than the stoichiometry.

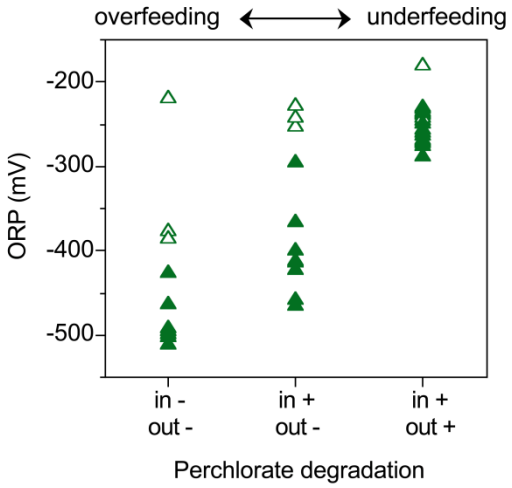

Figure 2. Relationship between perchlorate concentration changes and ORP of FMFBR influent (open triangle)/effluent (closed triangle). in + = measured influent perchlorate concentration was ≥ 50 % of the concentration estimated from the stock solution loading rate; in - = measured influent perchlorate concentration was < 50 % of the estimated concentration; out + = effluent perchlorate concentration was ≥ 1mg/*l*; out - = effluent perchlorate concentration was < 1 mg/*l*.

3.3 Perchlorate Degradation with ORP-Based Acetate Feed Control

3.3.1 Effect of Acetate Feed Rate on ORP Changes and Perchlorate Degradation

Based on the effluent ORP targets of -300 to -350 mV, a feed control system was set up with a base rate of acetate feed approximately equal to 80% of stoichiometry, and the balance being fed with a second pump (trim pump) adjusted based on the ORP detected at the exit from the fluidized bed. In the first set of experiments with the high ORP set point of -300, -315, and -330 mV, the flow rate of the trim pump, when activated, was approximately three times larger than that of the base acetate pump. Large oscillations of effluent ORP were observed in this set (Figure 3 a~c). After effluent ORP rose to the set point and the second acetate feed pump started running, the ORP elevated further for 12 ± 2 min, then declined below the set point. The ORP kept falling further for 13 ± 3 min even after the second pump stopped. Oscillation of influent ORP was much smaller than that of effluent ORP. The delay in the response of effluent ORP was likely caused by the travel time of the liquid from the acetate injection point to the bioreactor outlet, in particular, the bioreactor hydraulic retention time. Overall molar acetate feed ratio to perchlorate was approximately 1.2. Although the ratio indicated acetate was still fed in excess, the ratio was lower than the number observed without ORP control. Effluent perchlorate concentrations around the

second peak of effluent ORP curves were below 1 mg/*l*, but 400 and 180 μg/*l* of perchlorate was detected at the highest ORP by IC analysis with the set points of -300 and -330 mV, respectively (Figure 3 a and c). Perchlorate was not detected (< 4 μg/*l*) at the peak of ORP with the set point of -315 mV (Figure 3 b).

By lowering the flow rate of the second pump when activated and, consequently, decreasing the amount of acetate used for trim, the oscillations were damped considerably, especially with the high ORP set point of -315 mV (Figure 3 d and e). The molar acetate feed ratio to perchlorate decreased to 1.1. Perchlorate was not detected (< 4 μg/*l*) in the effluent with the high ORP set point of -315 mV (Figure 3 d). With the set point of -330 mV, 240 μg/*l* of perchlorate was detectable in the effluent at the second peak of effluent ORP (Figure 3 e). Although effluent perchlorate concentrations were undetectable (< 4 μg/*l*) at the peaks of effluent ORP curves in both experiments with the set point of -315 mV (Figure 3 b and e), repeated experiments revealed perchlorate was often detectable in effluent when the ORP oscillating more than observed in Figure 3d. Suppressing the oscillation appeared to be important to achieve sufficient perchlorate reduction.

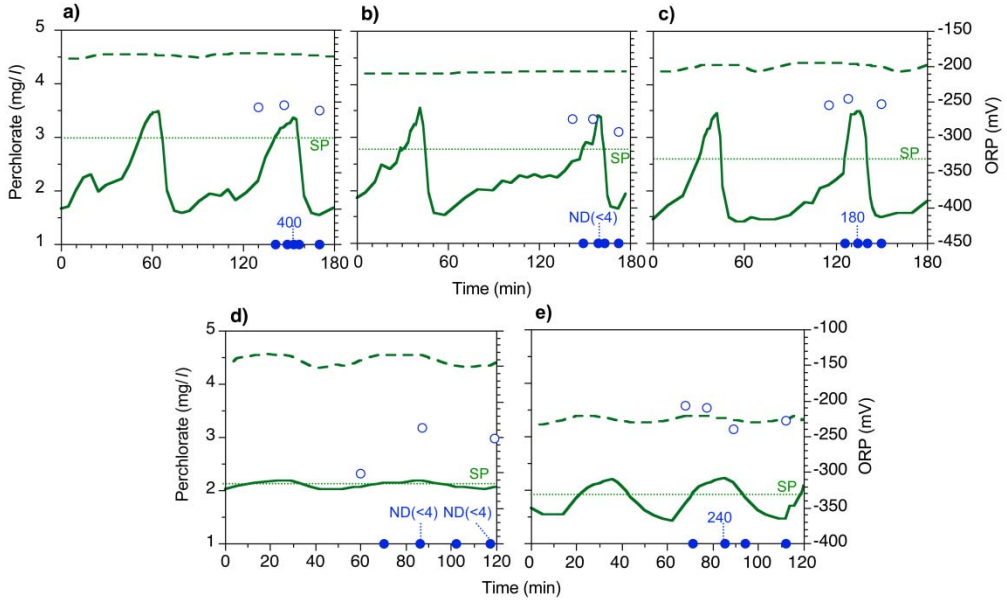

Figure 3. Changes in influent (broken line)/ effluent (solid line) ORP and influent (open circle)/effluent (closed circle) perchlorate concentrations. Perchlorate concentrations with values were analyzed by ion chromatography (unit: μg/*l*, ND = not detected). High ORP set points (indicated as "SP" and dotted line) used for the second acetate feeder activation were -300 mV (a), -315 mV (b and d), and -330 mV (c and e). The second acetate feed pump flow rate when activated was approximately 3x (a~c) or 1x (d and e) the base feed pump flow rate.

3.3.2 Sulfide production during ORP oscillation

Despite the continuous sulfate loading, hydrogen sulfide was not detected (< 0.1 mg/*l*) in the effluent samples around the second peak and bottom of the ORP curve, even at the lowest ORP (-325 mV) (Figure 4). Effluent ORP oscillation was very small in this experiment. Perchlorate was degraded to an undetectable level (< 20 μ g/*l*; a higher reporting limit due to the sample matrix interference).

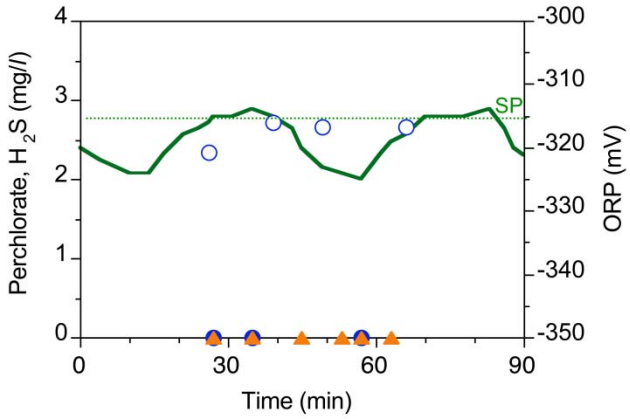

Figure 4. Changes in effluent hydrogen sulfide concentrations (closed triangle) and influent (open circle)/effluent (closed circle) perchlorate concentrations during a cycle of the second acetate feeder activation and deactivation. The solid line shows effluent ORP. The high ORP set point (shown as SP and dotted line) was -315 mV.

4. DISCUSSION

The bioreactor system has successfully degraded perchlorate to less than 4 μ g/*l* in a single pass. The anaerobic sludge used for the batch culture quickly gained the ability to degrade perchlorate, as expected from a previous study (Attaway and Smith, 1993). The inoculum (batch culture) was also capable of utilizing nitrate and oxygen. We did not monitor DO and nitrate in the FMFBR except the start-up period because the amounts provided to the stream were very small, although those electron acceptors would be consumed if present. Removal of oxygen can be done by purging or vacuum extraction, whereas nitrate may need to be treated together with perchlorate by providing sufficient electron donors. Care must be exercised, however, to limit the feed rate of electron donors to that required for perchlorate (and nitrate) reduction, in order to stop the anaerobic process before the reduction of sulfate to hydrogen sulfide.

Although perchlorate reduction appeared to occur over a range of redox potential or ORP which includes nitrate reduction/denitrification, the detailed

ORP data associated with perchlorate reduction activity are limited. Shrout and Parkin (2006) found perchlorate was completely degraded at -420 mV (vs. Ag/AgCl) but only partially degraded at or above -250 mV in their batch experiment. Our results in the continuous operation (without ORP control) were consistent with their results: although a partial degradation was observed at a higher ORP, complete perchlorate degradation was only observed when effluent ORP lower than -290 mV. The threshold value for complete perchlorate reduction was also well above the starting point of major sulfide production (by sulfate reduction), -350 mV (Connell and Patrick, 1968).

Our experiments confirmed that overfeeding the electron donor in a perchlorate treatment process produces sulfide. As effluent ORP dropped below -420 mV by continuous acetate overfeeding, a strong hydrogen sulfide odor was generated from the reactor and the color of the liquid turned black. Metal sulfides also appeared to be accumulated, causing the bed volume increase. When the reactor was operated under ORP control and acetate feed was limited, only a faint smell of hydrogen sulfide was detectable from the packed column gas outlet as effluent ORP declined below the set point. This level was not detectable by the hydrogen sulfide test kit, suggesting only ppb level of hydrogen sulfide was generated during the ORP decline.

Solid production increased dramatically when the acetate was overfed. Ideally, electron donor/carbon feeding should be limited to achieve near zero net growth of biomass to reduce the cost of chemicals and maintenance. The ORP-based feed control was successful in reducing the feed ratio close to stoichiometry in this study. Solids in the FMFBR were produced relatively slowly: settled bed height often remained in a similar range for a few months, although expanded bed height gradually increased. However, rapid increase in the bed height was observed when ORP was very low as described above or water was exposed to air due to maintenance. Oxygen not only competes with perchlorate reduction but also effectively increases biomass in the reactor. Removal of dissolved oxygen in the incoming stream should be performed if possible.

Although perchlorate could be degraded to an undetectable level ($< 4\ \mu g/l$) in this system with ORP-feed control, effluent ORP was still oscillated and a fine adjustment of acetate flow rate was needed to perform sufficient perchlorate degradation. A typical on/off-type process control causes oscillations of the controlled variable. Using the two feeders, one of which constantly provided a major portion of acetate required, alleviated the oscillation problem. Yet, monitoring ORP at the bioreactor outlet caused a delay in detecting the ORP change. For a more stable ORP control and a better perchlorate degradation performance, the following improvements are being considered: 1) detecting ORP change earlier; 2) changing feed rate continuously depending on ORP change

using a proportional-integral-derivative (PID) control system, rather than two feed rates by turning on/off the second feeder. The earlier detection may be done by installing an ORP probe in the bioreactor column. Near the mid-point of the reactor, about 4 feet from the bottom, the peaks and the bottoms of the ORP curve came about 8 minutes earlier (data not shown). Although the ORP values were slightly lower than those measured at the outlet, the slope change in ORP curve monitored near the mid-point of the bioreactor may be used for feed speed control. PID control can be used for responding the slope change as well as a more continuous change of feed rate. We will perform these improvements and investigate if ORP oscillations are minimized; hence, perchlorate degradation performance of the bioreactor is more stabilized.

5. CONCLUSION

The FMFBR has ability to degrade 3000 - 5000 μg/*l* perchlorate to an undetectable level (< 4 μg/*l*) in a single pass of EBCT 16 min. ORP-based acetate feed control reduced the feed ratio and is promising to solve the problems derived from overfeeding such as excess solid production of the bed and sulfide production. For a stable performance of the FMFBR, a more sensitive ORP control is needed. An earlier detection of ORP in the bioreactor column and a more flexible control method of acetate feed rate such as PID control may improve the control sensitivity.

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Chapter 3

APPLICATION OF MICROEMULSION TO REMEDIATE ORGANOCHLORINE PESTICIDES CONTAMINATED SOILS

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ABSTRACT

Microemulsion, a system containing water, surfactant, cosurfactant and oil phase, has the potential to enhance the solubility and bioavailability of hydrophobic organic compounds (HOCs). The aim of this study is to develop microemulsion which could enhance the bioremediation of organochlorine pesticides (OCPs) contaminated soils. After screening four surfactants and two plant oils, Triton X-100 and linseed oil were selected for microemulsion formation because of their respective instinctive higher solubilizing capacity over other candidates. Microemulsions formed with Triton X-100 and linseed oil could effectively enhance the aqueous solubility of 1,1,1,-trichloro-2,2-bis(p-chlorophenyl) ethane (DDT), and the enhancement was much higher than that achieved by Triton X-100 solution alone. Besides, the solubilization capacity of Triton X-100-linseed oil system was positively influenced by both cosurfactant (C/S ratios) and oil (O/S ratios) contents of the microemulsions. Desorption tests reveal that this microemulsion system is more effective than its counterpart Triton X-100 solution to desorb DDT from contaminated soil.

Keywords: remediation, microemulsion, organochlorine pesticides (OCPs), surfactant

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1. INTRODUCTION

Organochlorine pesticides (OCPs) have been used worldwide since 1940s due to their low cost and high effectiveness. However, most OCPs, e.g., lindane (γ-HCH) and 1,1,1,-trichloro-2,2-bis(p-chlorophenyl) ethane (DDT), are persistent, bioaccumulated, semivolatile, and highly toxic, which led to growing concerns on their potential contamination on the environment, and associated adverse effects on human health and wildlife (Kannan et al., 1992, Kucklick and Baker, 1998; Walker et al., 1999; Meijer et al., 2001). Both DDTr and HCHs are still detectable in sediments and soils throughout the world due to their heavy utilization and high environmental persistence (Meijer et al., 2001, Nakata et al., 2002). Owing to the serious health risks associated with even extremely low levels of such pollutants, increasing attention has been paid recently for developing innovative technology to prevent accumulation of organochlorine pesticides from soil to food. To date, the remediation options for soil contaminated by organochlorine pesticides include low temperature thermal desorption (Percin, 1995), incineration, bioremediation (Dua et al., 2002), photodegradation (Chu, 1999) and phytoremediation (Lunney et al., 2004; White et al., 2007). Among the various technologies, bioremediation is known to be advantageous for the environmental and economic reasons (Guerin, 1999).

Generally, soil pollutants are mainly degraded in solution as they are more available for microbial action (Harms and Bosma, 1997). However, most organochlorine pesticides are poorly soluble in water, and adhere tightly with soil particles through adsorption, electrostatic interaction and covalent bonding (Bollag et al, 1992). Therefore, the degradation of organochlorine pesticides in soils is usually slow and frequently unsatisfactory. To facilitate the degradation of organochlorine pesticides by microorganisms in soils, some surface-active agents (Quintero et al., 2005; Walters and Aitken, 2001; Kommalapati et al., 1997; Mulligan, 2005; Kantachote et al., 2004) have been employed to enhance the solubility and bioavailability of hydrophobic organic pollutants in soils. Nevertheless their effects on the degradation of pollutants still remain controversial since some of them may exert inhibitory effects on the degradative microorganisms. Microemulsion, consisting of surfactants, co-surfactants and oil, might be another potential candidate for remediation of soils due to its high solubilization capacity relative to the surfactant micellar solutions (Rosen, 1989).

Different from surfactant solutions, microemulsion are thermodynamically stable, isotropic, and macroscopically homogeneous dispersions of two immiscible fluids, generally oil and water, stabilized by surfactant molecules either alone or mixed with a cosurfactant, and the droplets of microemulsions are nanometer-sized (Kahlweit, 1988). Due to their special structure, microemulsions

exhibit good wetting ability, moderate viscosity, low interfacial tensions and high solubilization for both hydrophilic and hydrophobic compounds. As a novel emulsifying agent, microemulsions have been successfully used in soil washing and exhibit high efficiency in enhancing the solubility of some hydrophobic organic pollutants (Dierkes et al., 1998; Ying et al., 2002; Bragato et al., 2004). However, there is no application of microemulsions for remediating organochlorine pesticides contaminated soil.

Therefore, the objectives of the present study are to: (1) explore the feasibility of forming microemulsion using non-ionic surfactants and plant oils with the help of 1-pentonal as a cosurfactant; (2) investigate the effect of cosurfactant or oil content on the solubilizing capacity of a specific microemulsion system; and (3) preliminarily elucidate the effect of microemulsion system on the transfer of DDT from soil phase to aqueous phase.

2. MATERIALS AND METHODS

2.1 Materials

Triton X-100, Tween 80 and Brij 35 were the non-ionic surfactants tested in the present study because of their prevailing use in soil washing, and one biosurfactant, bile salt, is also tested in the present study. The three non-ionic surfactants and bile salt were purchased form Sigma Chemical Co., and all surfactants (purity >98%) were used as received from supplier without purification. The formula and properties of the surfactants are listed in Table 1. Two plant oils, soybean oil and linseed oil, were tested to check their suitability as the oil phase in this study because soybean oil is the most commonly produced vegetable oil worldwide and linseed oil is the most widely used vegetable oil in industry. These two plant oils (Sigma Chemical Co.) and 1-pentanol (purity >98%, Fluka Chemical Co.) were used without any further purification. n-hexane and acetone used were of analytical grade, while double deionized water was used for all tests.

Table 1 Characteristics of selected surfactants

Surfactant	Structure[a]	CMC (mg L^{-1})	MW	HLB[b]
Tween 80	$C_{18}S_6E_{20}$	11	1310	15.0
Brij 35	$C_{12}E_{23}$	76	1198	16.9
Triton X-100	C_8PE_{10}	131	625	13.5
Bile salts				

[a] C represents alkyl chain length (CH_2), P represents a phenol ring (C_6H_6), E represents an etgoxylate group (C_2H_4O), and S_6 represents a sorbitan ring.
[b] Hydrophile-lipophile balance

DDT used in this study was purchased from Sigma Chemical Co., and was 99% pure. It was used without any further purification.

2.2 Screening the suitability of surfactants for the formation of microemulsions with plant oils

Surfactants solutions at 10, 25, 50, 100 and 200 CMC (critical micelle concentration) were prepared individually with distilled water. 1-pentonal was added to each surfactant solution as a co-surfactant with a cosurfactant to surfactant ratio (C/S ratio) of 0.5:1, 1:1 or 1.5:1. For each solution, 2 g/L soybean oil or linseed oil was added, gently mixed and aged for 12-15 h at ~ 25 ^{o}C before subjected to stability evaluation.

In this study, the stability of micoremulsions was checked by both visual transparency check and centrifugation. The homogeneity and optical isotropy of microemulsions were examined by visual examination at room temperature. Then the stabilities of all samples were tested by carrying out centrifugation at 100 x g for 5 min (Prince, 1977). Samples without any phase separation were subjected to visual inspection and centrifugation again after 7 days. Three microemulsion systems without phase separation were identified as stable microemulsions.

2.3 Solubilization Study

Preparation of microemulsion: To determine the effect of C/S ratios on the solubilization of DDT by microemulsions, 1-pentanol, as cosurfactant was mixed with the Triton X-100 at the ratios of 1:3 and 1:6, to form the surfactant/cosurfactant phases. Then, the surfactant/cosurfactant phases were mixed with linseed oil according to the oil to surfactant ratio (O/S ratio) of 1:20 to obtain microemulsion precursors containing surfactant, cosurfactant and oil. The precursors were subsequently diluted with water to obtain microemulisons formed with various concentrations of surfactants and different C/S ratios. To study the effect of O/S ratio on the solubilizations of DDT by microemulsions, microemulsion precursors formed with a constant C/S ratio of 1:3 and three different O/S ratios, 1:20, 1.5:20 and 2:20, were prepared according to the procedures described above. Then, the precursors were diluted with water to obtain micromeulisons formed with various concentrations of surfactants and different O/S ratios.

Appropriate amount of DDT dissolved in acetone was carefully added to the bottom of 20 mL glass vials, and the amount of added DDT was well in excess of its aqueous saturation. After the acetone was evaporated, 10 mL microemulsions or surfactant solution prepared as described before were added into each vial. Duplicate tests were prepared for each microemulsion or surfactant solution.

These vials were capped with aluminium-lined cap and then shaken on a rotary shaker at 250 rpm at 25 ^{o}C for an equilibrium period of 72 h as determined from our preliminary study. After equilibrium was reached, the samples were filtered through a glass column packed with glass wool to remove any undissolved DDT particles. A 1-mL aliquot of the filtered solution was then carefully withdrawn with a volumetric pipette and extracted in n-hexane; dilutions were done in n-hexane as needed to bring the solute to a detectable concentration range. Analysis of DDT was carried out in an Agilent Gas Chromatography 7890 equipped with a Nickel 63 election capture detector (μECD) and a HP-5 column (30 m×0.32 mm ID, 0.25 μm film thickness). An injection volume of 1 μL was used (splitless injection) and the injector temperature was maintained at 220 ^{o}C. The oven temperature programmed to increase from 100 ^{o}C to 180 ^{o}C at 15 ^{o}C /min, held for 1 min, increased to 270 ^{o}C at 10 ^{o}C /min, and then held for 5 min. The ECD was maintained at 300 ^{o}C, and nitrogen was used as makeup gas at 60 mL/min.

Dilution effect on the solubilizing capacity of microemulsion system was also studied. Firstly, microemulsion precursor containing Triton X-100, 1-pentanol (with C/S=1:3) and linseed oil (with O/S=2:20) were prepared as described above. Then, the precursor was diluted carefully with water to obtain micromeulisons formed with a wide range of Triton X-100 concentration from 10 mg/L to 5000 mg/L. And the solubilization of DDT in these diluted microemulsions was investigated according to methods described above.

2.4 Batch Desorption Study

0.5 g DDT spiked soil was added to 20 mL glass vials for studying desorption of DDT in soil-water system under the influence of microemulsions and surfactant soultions. 10 mL of surfactant solutions or microemulsion covering a wide range of surfactant concentrations from 40 mg/L to 5000 mg/L were added to the vials. 0.02% NaN_3 was added to the mixture as microbial growth inhibitor (Wong et al., 2004). The samples were shaken on a rotary shaker at 250 rpm under dark at ambient temperature (25-28ºC). After an equilibrium period of 96 h as determined from preliminary study, duplicate samples were sacrificially collected and were centrifuged for 5 min at 3000×g to separate the aqueous phase from the soil particles. DDT concentration of the aqueous phase was quantified by GC/ECD as described above.

3. RESULTS AND DISCUSSION

3.1 Formation of stable microemulsions

As shown in Figure 1, 21 stable microemulsions were obtained from combinations of four surfactants and two plant oils. Among these 21 microemulsions, 10 were formed with Tween 80, 6 were formed with Brij 35 and 5 were formed with Triton X-100. However, no stable microemulsion was formed with bile salts. Both soybean oil and linseed oil could be used as the oil phase to achieve stable microemulsions with Tween 80, Triton X-100 and Brij 35. In fact, Zhao et al., (2006) has suggested that the tail length of the nonionic surfactant should be close to the carbon chain length of the fatty acid compositions in oil, and the size of head group in nonionic surfactant should not be too small (less than 5) or too large (larger than 40) in order to obtain stable microemulsions. In this study, Tween 80 could form more stable microemulsions than both Brij 35 and Triton X-100 that may be attributed to its special chemical structure containing 18 CH_2, close to the carbon chain length of the fatty acid compositions in both soybean oil and linseed oil having 23 ethoxylate groups (Warisnoicharoen et al., 2000). On the other hand, the HLB values of Tween-80, Brij 35 and Triton X-100 indicate that all micoremulsions formed are oil-in-water microemulsions (Ying et al., 2002), in which vegetable oils are emulsified by surfactants and cosurfactant.

While studying the microemulsion formation, the solubility of DDT in the proposed surfactants and oils were also investigated as the second parameter to select suitable surfactant and plant oil. As shown in Table 2, among the three surfactants which could form stable microemulsions with the two plant oils, Triton X-100 exhibited the highest solubilization capacity. Between the two plant oils, linseed oil exhibit 36.4% more solubilization than soybean soil, indicating that Triton X-100 and linseed oil would be a better candidate for the solubilization of DDT over other candidates.

Table 2. Solubility of DDT in surfactants or plant oils

Solution (wt %)	DDT solubilized (mg/L)
1% Triton X-100	134.7
1% Tween 80	112.3
1% Brij 35	42.6
Linseed oil	1.2×10^5
Soybean oil	8.8×10^4

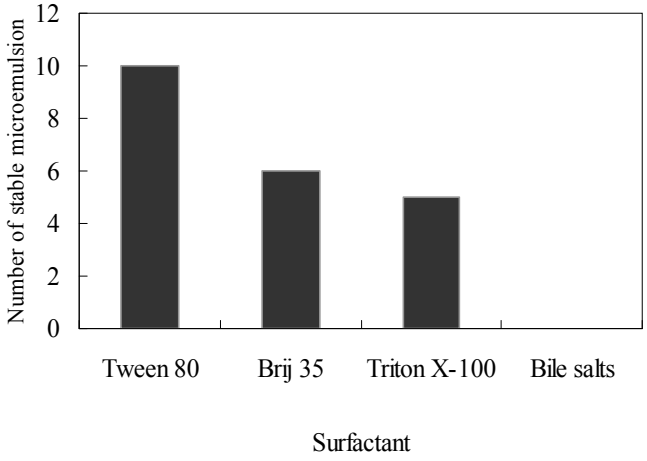

Figure 1. Number of stable microemulsion formations obtained with the three non-ionic surfactants and one biosurfactant

3.2 Factors influencing the solubilizing capacity of microemulsion formed with Triton X-100 and Linseed oil

In microemulsions, oil and water microdomains are separated by surfactant/cosurfactant interface (Kahlweit, 1988). When a hydrophobic solute is solubilized in a microemulsion, it may exist either in the oil volume fraction or in the volume fraction corresponding to the interfacial layer (Testard and Zemb, 1998). Thus, in addition to the surfactant content, both cosurfactant and oil fractions will also influence the solubilizing capacity of a microemulsion system. In this study, to elucidate the effect of cosurfactant content on the solubilizing capacity of microemulsions, the aqueous solubility of DDT in microemulsions formed with Triton X-100 and linseed oil, at different C/S ratios (1:3 and 1:6), and a constant oil to surfactant ratio of 1:20, was examined. Plots of the aqueous solubility of DDT as a function of surfactant concentrations used in micromeulsions are shown in Figure 2A. As presented, all the microemulsions formed could markedly increase the aqueous solubility of DDT within the concentration range of 1% (w/w) to 30% (w/w). At the same C/S ratio, DDT solubility increased linearly with an increase in surfactant concentrations of the microemulsions. Compared to treatment with Triton X-100 only, the microemulsions were more effective. As shown in Figure 2B, increasing the O/S ratios from 1:20 to 2:20 at a constant C/S ratio of 1:3 also resulted in an increase in the solubilization of DDT, indicating the positive effect of oil in the solubilization of DDT by microemulsions.

Solubilization capacity of a surfactant could be commonly quantified by the weight solubilization ratio (WSR) (Li and Chen, 2002), which is defined as the mass of HOCs solubilized by unit weight of surfactants above its CMC and can be calculated as follows:

$$WSR_{surf} = (S_{Surf*}\text{-}S_{CMC})/(C_{surf} - CMC)$$

where S_{Surf*} is the apparent solubility of solute at surfactant concentration of C_{surf} and S_{CMC} is the apparent solubility of certain compounds at CMC. Therefore, WSR can be obtained from the slope of solubilization curve in the range of surfactant concentrations above the CMC. In contrast to the surfactants solution, the WSR of solutes in microemulsion systems was proposed to be expressed as (Zhao et al., 2005):

$$WSR_{\mu E} = (S_{\mu E*}\text{-}S_{int})/C_{\mu E}$$

where, $C_{\mu E}$ is the microemulsion concentration at which $S_{\mu E*}$ is evaluated; S_{int} is the intrinsic water solubility of the solutes; and $S_{\mu E*}$ is the apparent solubility of solute in microemulsions. In the present study, the concentration of microemulsion is termed as total weight of surfactant, cosurfactant and oil present. Similar to that of surfactant solution, $WSR_{\mu E}$ could be calculated from the slope of the solubilization curve.

The calculated values of WSR_{surf}, $WSR_{\mu E}$ of DDT Triton X-100 souliton or in microemulsion systems are listed in Table 3. WSR of DDT in Triton X-100 solution was only 0.0131. However when Triton X-100 was employed to emulsify linseed oil and form microemulsions, the WSR of DDT has increased to 0.0214-0.0283, which was about 63.3-116.0% higher compared with Triton X-100 only. Besides, it could also be observed that increasing C/S ratios from 1:6 to 1:3 has led to 10.7% increase of WSR, and increasing O/S ratios from 1:20 to 2:20 resulted in 19.4% increase of WSR, indicating that both cosurfactant and oil content can positively influence the solubilizing capacity of microemulsion systems. Such a high enhancement of solubilizing capacity of Triton X-100 obtained through emulsifying alcohol and plant oil is reported for the first time. For instance, previous study on the solubilization of PAHs in microemulsion system based on sodium castor oil sulfate showed that the solubilizing capacity of microemulsion was only 14.6% higher than Triton X-100, and 40.2% higher than Tween 80 (Zhao et al., 2005).

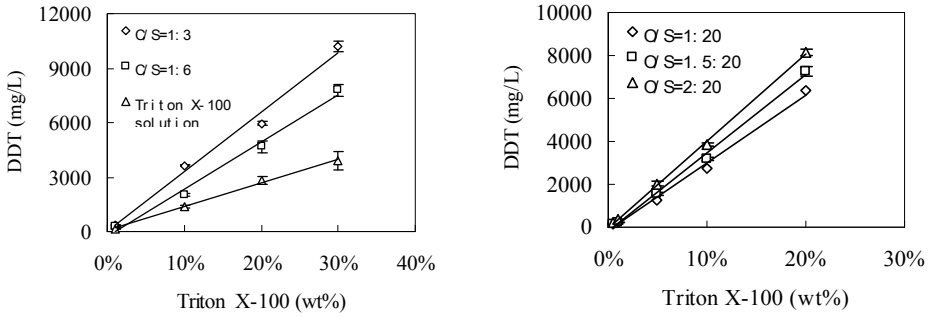

Figure 2. Effect of cosurfactant (C/S ratios) and oil (O/S ratios) content on the solubilizing capacity of microemulsion system based on Triton X-100 and linseed oil

Table 3 Weight solubilization ratios (WSR) of DDT in Triton X-100 solution and microemulsion systems formed with different C/S ratios and O/S ratios

	Triton X-100	Microemulsion (with fixed O/S=1:20)		Microemulsion (with fixed C/S=1:3)		
		C/S=1:6	C/S=1:3	O/S=1:20	O/S=1.5:20	O/S=2:20
WSR	0.0131	0.0214	0.0237	0.0237	0.0258	0.0283
R^2	0.997	0.991	0.988	0.994	0.996	0.999

3.3 Dilution effect on the solubilization capacity of microemulsion system formed with Triton X-100 and Linseed oil

It is well known that particle sizes or microdomain structures of microemulsions can be changed when diluted by water (Lawrence and Rees, 2000), and transfer of W/O microemulsion to O/W microemulsion can also be induced by dilution process (Constantinides and Yiv, 1995). Therefore, the best microemulsion (with C/S=1:3 and O/S=2:20) obtained in previous experiment was diluted to study whether the dilution of microemulsion could influence the solubilization of DDT. As shown in Figure 3, the solubilizing capacity of microemulsion system (with C/S=1:3 and O/S=2:20) decreased linearly with the decreasing concentration of Triton X-100 during dilution. However, at the same concentration of Triton X-100, microemulsion system always exhibited higher solubilizing capacity for DDT than Triton X-100 solution alone. When the Triton X-100 concentration was <1 CMC, both surfactant solution and microemulsion system did not solubilize the DDT due to the lack of micelle formation (Kile and Chiou, 1989). For example, about 39.7 mg/L DDT could be solubilized by microemulsion comprising 1000 mg/L of Triton X-100, while only 12.9 mg/L DDT was

solubilized by the same concentration of Triton X-100. This stable and higher solubilizing capacity of microemulsion over its counterpart surfactant solution above the CMC of surfactant imply that microemulsion can be a potential candidate to desorb HOCs from contaminated soils.

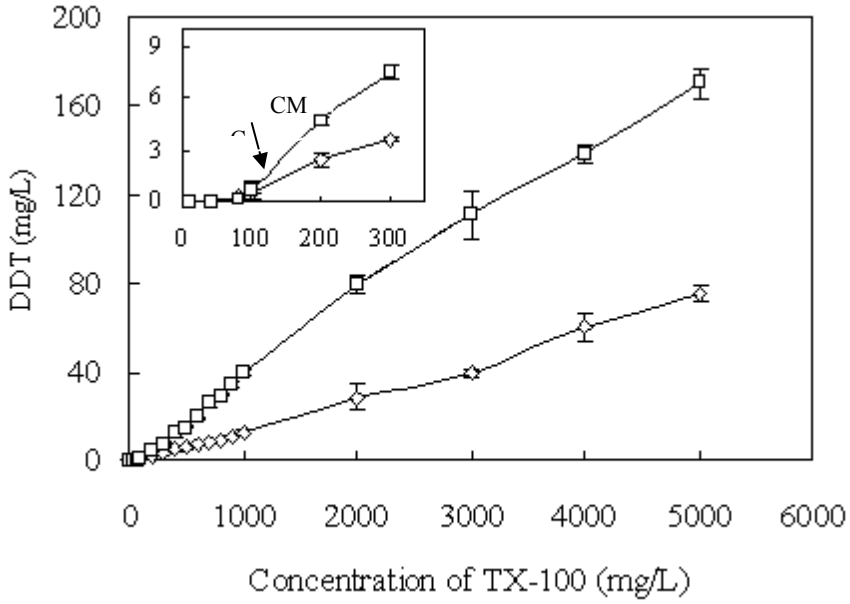

Figure 3. Dilution effect on the solubilizing capacity of both surfactant solution (◦) and microemulsion based on Triton X-100 and Linseed oil (▫)

3.4 Desorption efficacy of DDT from sandy loamy soil by Triton X-100 solution and microemulsions formed with Triton X-100

Desorption rate of DDT in soil-water systems by surfactant solution or microemulsions at a wide concentration range from 0 to 5000 mg/L Triton X-100 are shown in Figure 4. The desorption rates of DDT were about 0.052% by water without surfactant or microemulsion due to the higher octanol-water partition coefficient, Log K*ow*, of DDT. With an increase in surfactant concentration in surfactant solution and microemulsions, no significant increase of desorption of DDT was observed until the Triton X-100 concentrations exceeded about 200 mg/L (Figure 4, subset). This was probably ascribed to the fact that a portion of surfactant monomers were being lost from aqueous phase as the result of surfactant sorption on soil particles (Zhu et al., 2003, Cheng and Wong, 2005; Wang and Keller, 2008). Also, most studies indicated that the amount of surfactants required to desorb HOCs in soil- and sediment-water systems is considerably greater than the CMC in water (Zheng and Obbard, 2002; Cheng and

Wong, 2006). In some studies, this concentration was described as critical desorption concentrations (CDC), above which desorption process was sharply accelerated with increasing surfactant concentration (Yang et al., 2006, Zhou and Zhu, 2007). In the present study, the desorption rate of DDT from soil increased drastically when the concentrations of Triton X-100 exceeded 200 mg/L; and no differences of CDC were observed between surfactant solution and microemulsion up to 400 mg/L of Triton X-100. Above this concentration, the microemulsions achieved higher desorption than their corresponding surfactant solution. For example, with 1000 mg/L of Triton X-100, the desorption rates of DDT achieved by microemulsion and surfactant solution were 66% and 55%, respectively. However, the desorption enhancement achieved by microemulsion in water/soil system was much lower than the sloubilization enhancement achieved in aqueous solutions, implying the potential sorption of different components of microemulsions on soil particles.

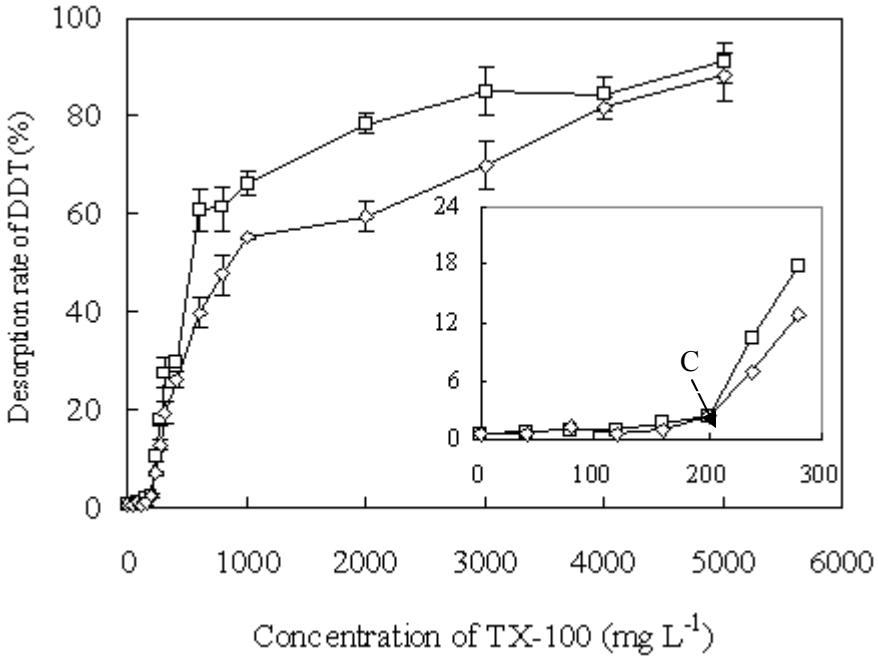

Figure 4. Desorption of DDT from loamy sandy soil by surfactant solution (◇) and microemulsion based on Triton X-100 and Linseed oil (□)

4. CONCLUSION

Four surfactants and two plant oils were tested for the possibility of forming stable microemulsions. Except the bile salt, other non-ionic surfactants formed

stable microemulsions. Among these, Triton X-100 and linseed oil were selected for further studies because of their respective higher DDT solubilizing capacity over other candidates. Microemulsions formed with Triton X-100 and linseed oil could effectively enhance the aqueous solubility of DDT, and the enhancement was 63.3-116.0% more than that achieved by Triton X-100 solution only. Besides, the solubilization capacity of Triton X-100-linseed oil system was positively influenced by both co-surfactant (C/S ratios) and oil (O/S ratios) contents of microemulsions. Similar to the aqueous system, desorption capacity of microemulsions was higher than the surfactant alone in water/soil system. Therefore, the microemulsion system is a potential candidate for the remediation of OCPs contaminated soil due to its higher solubilizing and desorbing capacity, though further studies are needed to investigate the detailed behavior of microemulsion in soil matrix and their effect on the biodegradation of OCPs by microorganisms.

6. ACKNOWLEDGMENT

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Chapter 4

BIOSURFACTANTS FROM *ACINETOBACTER CALCOACETICUS* BU03 ENHANCE THE BIOAVAILABILITY AND BIODEGRADATION OF POLYCYCLIC AROMATIC HYDROCARBONS

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ABSTRACT

Biosurfactants produced by an isolated thermophilic strain *Acinetobacter calcoaceticus* BU03 were demonstrated to be effective in enhancing the solubility of polycyclic aromatic hydrocarbons (PAHs) and the present study aimed at investigating its effectiveness in increasing bioavailability of PAHs in soil for biodegradation under thermophilic composting condition. At 25 times of its critical micelle concentration (CMC), biosurfactants by BU03 significantly increased the apparent aqueous solubility of phenanthrene (PHE) and benzo[a]pyrene (B[a]P) to 54.3 and 2.08 mg L^{-1}, respectively. After confirmation of its ability in enhancing the solubility of PAHs, the isolated biosurfactants were applied to a thermophilic soil composting system. Within 42 days of composting period, the degradation of PHE and B[a]P in the absence of the biosurfactants was 71.2 and 16.4%, respectively. Inoculation of *A. calcoaceticus* BU03 or biosurfactants produced by this strain significantly increased the emulsifying capacity of soil, and therefore enhanced the desorption of PAHs from soil to aqueous phase in which they can be degraded by an inoculated degradative strain *Bacillus subtilis* B-UM. Therefore inoculation of *A. calcoaceticus* BU03 or biosurfactants from BU03 together with inoculation of *B. subtilis* B-UM increased the degradation of B[a]P to 83.8 and 65.1%, respectively, while PHE was almost completely removed with these two treatments. The results indicate that the application of biosurfactants produced by *A. calcoaceticus* is an effective means to enhance the biodegradation of PAHs in thermophilic composting, while inoculation of biosurfactants producing strains in PAHs contaminated soil is a more practical and cost-effective approach than direct addition of biosurfactants.

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Keywords: biosurfactant, polycyclic aromatic hydrocarbons, *Acinetobacter calcoaceticus* BU03, biodegradation, phenanthrene, benzo[a]pyrene

1. INTRODUCTION

The remediation of soil contaminated by polycyclic aromatic hydrocarbons (PAHs) is of major importance because most PAH compounds are known as carcinogens and mutagens (Wilson and Jones, 1993). Owing to the serious health risks associated with even extremely low levels of PAHs, increasing effort has been devoted recently to develop innovative technology to remove PAHs from soil. Since PAHs are biodegradable in the presence of suitable microorganisms (Guerin, 1999; Sepic et al., 2003), thermophilic composting provides a cost-effective technology for the clean up of PAHs (Wong et al., 2002; Wan et al., 2003; Atagana, 2004). It exploits the degradative potential of indigenous or inoculated microorganisms or their extracts, to dissolve and biologically convert contaminants into less toxic compounds. Adenuga et al. (1992) showed that pyrene could be degraded during the composting of soil/sludge mixtures but the rate and extent were not mentioned in that study. PAHs with 2 or 3 rings, i.e., naphthalene, anthracene and phenanthrene (PHE) were removed to the remediation target of 1 mg kg^{-1} in three to four months of composting. However, one major constraint of this approach is the low bioavailability of PAHs especially those with high molecular weight. The fate of benzo[a]pyrene (B[a]P) during composting was investigated in a number of studies and the results showed that 29.9% and 65.6% of B[a]P was removed after 54 and 95 days, respectively and still quite substantial amounts remained in soil (Sasek et al., 2003; McFarland and Qiu, 1995). The low biodegradability of high molecular weight PAHs during composting is due to their low aqueous solubility and high sorption to soil particles (Kim and Weber, 2005; Doong and Lei, 2003). A promising means to enhance the bioavailability of PAHs is the application of surfactants. Addition of surfactant increased the solubilization and biodegradation of PAHs (Boonchan et al., 1998; Kim and Weber, 2005). Addition of nonionic surfactants has been shown to enhance the solubility, desorption and bioavailability of PAHs (Bernal-Martinez et al., 2005). However, in our pervious studies the addition of Tween 80 or Triton X100 caused inhibition on the biodegradation of PAHs due to the toxic effects of surfactants on a PAHs degrading bacterium *Bacillus subtilis* B-UM (Wong et al., 2004). Similar to synthetic surfactants, biosurfactants produced by microorganisms can enhance the solubilization and desorption of PAHs. Two kinds of rhamnolipids, i.e. dirhamnolipid and monorhamnolipid enhanced the biodegradation of PAHs in aqueous systems (Zhang et al., 1997). Biosurfactants from *Acinetobacter* sp. increased the apparent solubility and biodegradation of PAHs (Barkay et al., 1999), and they are more biodegradable and less toxic and

expensive as compared to chemical surfactants (Rosenberg and Ron, 1997; Zhao and Wong, 2009).

Although the use of biosurfactants for bioremediation of PAHs looks promising, the cost of biosurfactant production is about 3 to 10 times higher than that of the synthetic surfactants (Mulligan and Gibbs, 1993). To date, all of the studies of surfactant-aid bioremediation of soil were conducted under mesophilic conditions. Thermophilic condition may be more effective for the biodegradation of PAHs since elevated temperature is expected to increase solubility, and mass transfer rates of PAHs (Cheng et al., 2004). Under thermophilic condition, a high removal rate of PAH compounds from contaminated soil may be achieved and substrate utilization rates of thermophilic bacteria have been reported to be 3-10 times greater than that of mesophilic bacteria (Goswami et al., 1983).

In our pervious study a thermophilic bacterium, *Acinetobacter calcoaceticus* BU03, was isolated from petroleum contaminated soil collected from Dagang Oil Field, China (Zhao and Wong, 2009). Therefore in the present study, the potential of the biosurfactants produced by *A. calcoaceticus* BU03 in enhancing the solubilization and biodegradation of PAHs was investigated under thermophilic condition. Bench-scale thermophilic composting was performed to investigate the effects of addition of the biosurfactants and inoculation of *A. calcoaceticus* BU03 on the bioremediation of PAHs contaminated soil.

2. MATERIALS AND METHODS

2.1. PAHs

B[a]P and PHE (analytical grade of 96% in purity, Sigma Chemical Co. St Louis, MO, USA) were used in this study as model compounds of PAHs.

2.2. PAHs degradative bacterium

A PAHs degradative bacterium *Bacillus subtilis* B-UM, which was enriched and isolated from PAH-contaminated soil and compost in our research group (Wong et al., 2002), was used in the present study.

2.3. Preparation of biosurfactants

Cells of *A. calcoaceticus* BU03 were cultured in medium containing 10 g glucose, 10 g peptone, 4 g NaH_2PO_4, 0.01 g $FeCl_3$ and 0.025 g $MgCl_2$ per liter, pH 6.5 on a gyratory shaker (150 rpm) at 55°C. After 36 h, bacterial cells were removed by centrifugation at 6000 × g for 20 min. The supernatant was subjected to extraction

by adding 100 mL n-hexane to 300 mL supernatant and the extraction was repeated two more times. The emulsified phase was collected, washed twice with double distilled water (DDW) and rotary evaporated at 55°C. Residues were subjected to freeze-drying and dissolved in DDW. Undissolved material was removed by filtration through 0.45-μm cellulose acetate membrane.

Biosurfactants produced by *Pseudomonas aeruginosa* ATCC9027 were used in this study for comparison. *Pseudomonas aeruginosa* ATCC9027 was cultured in PPGAS medium (1.07 g NH_4Cl, 1.49 g KCl, 18.90 g Tris-HCl, 10.0 g glucose, 10.0 g peptone and 0.19 g $MgSO_4$ per liter) in a shaker set at 150 rpm and 37°C. After 72 h of incubation, bacterial cells were removed, by centrifugation and the supernatant was subjected to acid precipitation by adjusting the pH to 2.0 with 5N HCl. The precipitate was centrifuged at 8000 × g for 20 min and freeze-dried. The dried biosurfactants were extracted with n-hexane three times at room temperature. After evaporating the organic solvent on a rotary evaporator at 55°C, the biosurfactants were dissolved in DDW and filtered through 0.45-μm cellulose acetate membrane. The concentration of biosurfactants at 55°C was determined following the method of critical micelle dilution (CMD) method (Philp et al., 2002).

2.4. Effect of biosurfactants produced by BU03 on the solubility of PAHs

Five milligrams of PHE or B[a]P dissolved in dichloromethane (DCM) was carefully added to the bottom of a 20 mL glass vial. The amount of added PHE or B[a]P was well in excess of its aqueous saturation. After the DCM was evaporated, 10 mL Bushnell-Haas medium containing various concentrations of surfactants, i.e., 0, 0.5, 1, 3, 10 and 25 × CMC was added to the tubes. The vials were covered with aluminum foil and capped, and then shaken in a rotary shaker at 150 rpm and 55°C for an equilibrium period of 48 h determined in a previous study (Cheng et al., 2004). After reaching equilibrium, 2 mL sample was removed from each vial and filtered through a 10 mL glass syringe packed with glass wool to remove any undissolved PAHs particles. The solubilized PAH in aqueous phase was extracted three times with n-hexane. The extracts were combined and concentrated to appropriate volume for quantification of PAHs concentrations using a high-performance liquid chromatography (HPLC) equipped with a fluorescence detector (FLD). A sample volume of 15-μL was separated on a Reverse Phase C18 column (5 μm, 3.6 × 25 cm, Ultrasphere, Beckman) with 100% acetonitrile as mobile phase with a flow rate of 1.5 mL min^{-1}.

2.5. Effect of BU03 produced biosurfactants on the biodegradation of PAHs during thermophilic composting

Soil collected from abandoned shipyards at North Tsing Yi, Hong Kong SAR, China was air-dried at room temperature, sieved to < 2 mm and spiked with PHE and B[a]P dissolved in DCM to a final concentration of 250 mg kg^{-1} each The DCM in soil was allowed to evaporate in a fume hood for one day and the spiked soil was stored at room temperature for an aging process of 6 months before use.

Table 1 shows the 10 treatments of the composting study with a combination of contaminated soil, pig manure, chemical surfactant or biosurfactants produced by BU03, degradative microorganisms, as well as biosurfactants producing microorganisms. The bench-scale composting experiment was carried out in 1 L composting tanks and each treatment was performed in triplicate. Pig manure was mixed with soil at a ratio of 3:1 (w/w dry weight) as co-composting material to provide nutrient for microbial growth. About 600 g of soil-pig manure mixture were added to the composting tank. The moisture content of the composting material was adjusted to about 70% of its water-holding capacity with DDW. For the control treatment (Control), no pig manure was added to soil. The flasks were aerated by negative air pump conditioned at 350 mL min^{-1}, which should provide sufficient oxygen for the decomposition of organic matter. A condenser was connected to the outlet of each flash to reduce moisture loss from the system. All composting flasks were incubated at 55^{o}C for 42 days in order to achieve a thermophilic condition. Periodically, samples of composting material were collected from the composting flasks for the analysis of carbon dioxide (CO_2) evolution, total organic carbon (TOC) and total Kjeldahl nitrogen (TKN) using the methods of TMECC (2002). PAHs degradative and total heterotrophic populations, as well as PAHs in composting mass were determined as described elsewhere (Wong et al., 2002), while soil emulsifying activity followed that described by Zhao and Wong (2009).

2.6. Statistical analyses

Analyses were performed in triplicate samples and the mean values with standard error were presented. The data were subjected to one way analysis of variance (ANOVA) and Duncan's multiple range test using SPSS ver.11.5 software.

Table 1. Description of treatments employed in the thermophilic composting

Treatment	Degradative cells B-UM (CFU g^{-1})	Surfactants concentrations (× CMC)	Biosurfactants producing cells BU03 (CFU g^{-1})
Control	×	×	×
PM [a]	×	×	×
I [b]	10^7	×	×
I T[c]	10^7	10 (Tween 80)	×
B10[d]	×	10 (Biosurfactant)	×
I B1	10^7	1 (Biosurfactant)	×
I B10	10^7	10 (Biosurfactant)	×
I C [e]	10^7	×	10^7

a: PM indicates soil amended with pig manure only; b: I indicates the inoculation of degradative cells of B-UM; c: T indicates the addition of Tween 80; d: B indicates the addition of BU03 produced biosurfactants followed by a number which indicates the concentration (CMC); and
e: C indicates the addition of biosurfactant producing cells of BU03.

3. RESULTS AND DISCUSSION

3.1. Effect of synthetic surfactants and biosurfactants on solubility of PAHs

PAHs solubility was plotted as a function of aqueous surfactant concentrations in the range of 0 to 25 × CMC (Figure 1). Aqueous equilibrium concentration of PHE without surfactants was measured to be 1.82 mg L^{-1} at 55^{o}C in DDW, while that of B[a]P was undetectable. PAHs solubility was significantly enhanced at surfactant concentrations above their respective CMCs because of the formation of micelles. Among the tested surfactants, biosurfactants produced by BU03 were the most effective in enhancing the solubility of PHE and B[a]P. In the presence of biosurfactants from BU03 at 25 CMC, the aqueous solubility of PHE and B[a]P was increased to 54.3 and 2.08 mg L^{-1}, respectively.

3.2. Effect of biosurfactants produced by *A. calcoaceticus* BU03 on bioremediation of PAHs contaminated soil with thermophilic composting

3.2.1. Changes in nutrient contents

In general, there was a sharp drop in TOC in the first 7 days for the treatments amended with pig manure (Figure 2). During the initial period of composting, the rapid growth of microorganisms quickly reduced the TOC contents from 13.6 to

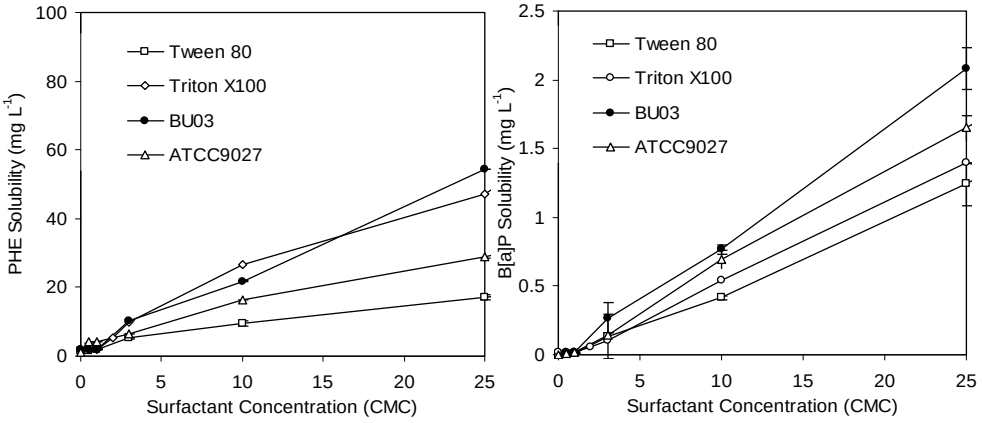

Figure 1. Effects of surfactants on the solubility of PHE and B[a]P.

about 6% and after 42 days, the TOC contents for all treatments were lower than 2%. Either addition of surfactants or inoculation of selected microorganisms did not affect the TOC contents significantly. In the Control without pig manure addition, the TOC content decreased from 3.4 to 0.44% within 42 days. The slow reduction in TOC content in the Control may be due to the low microbial activity and lack of readily metabolizable carbon sources in soil (Viel et al., 1987).

The concentrations of TKN decreased from 0.67 and 0.10 % to about 0.3 and 0.06 % over the composting period, for those treatments amended with pig manure and the Control, respectively (Figure 4). Similar to TOC content, the initial concentrations of TKN increased following the addition of pig manure while the addition of surfactants or inoculation of microorganisms did not cause any significant additional change.

Although nitrogen is a critical nutrient which usually limits PAHs biodegradation in soil (Ritter and Scarborough, 1995), addition of a single limiting nutrient may not benefit the growth of heterogeneous microorganisms (Breedveld and Sparrevik, 2000). In the bioremediation process, different microbial species may be required to degrade PAHs sequentially, and each species has its own nutrient requirements. Therefore, pig manure used in the present experiment served not only as a source of microbial population, but also as an organic material to provide nutrients for the growth of PAHs degradative microorganisms.

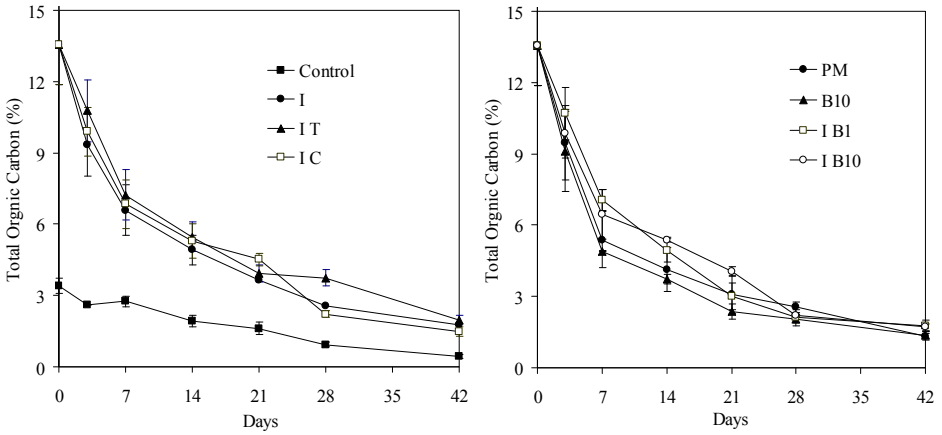

Figure 2. Changes in TOC during the thermophilic composting of PAHs contaminated soil.(Control = control soil only; PM= addition of pig manure only; I = inoculation of B-UM; T= addition of Tween 80; B = addition of biosurfactants produced by BU03; 1 = 1 × CMC; 10 = 10 × CMC; and C = inoculation of BU03)

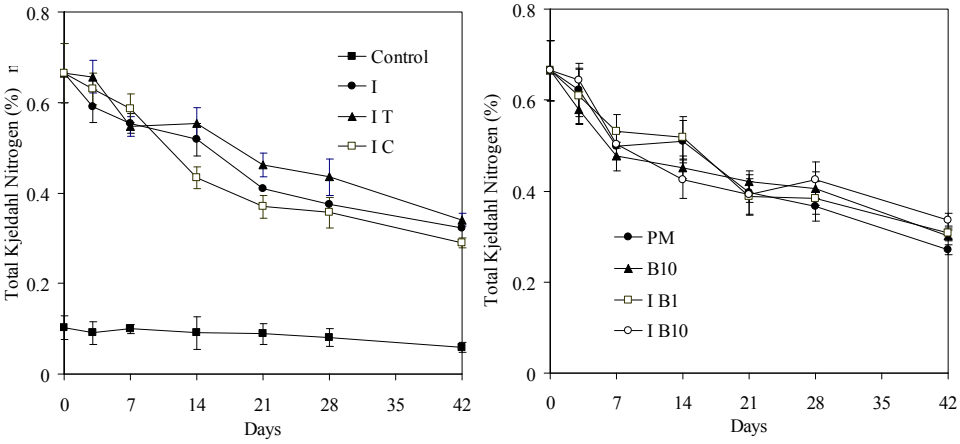

Figure 3. Changes in TKN during thermophilic composting of PAHs contaminated soil. Refer to Figure 2 for the legends explanation.

3.1.2. Carbon dioxide (CO_2) evolution

As an indicator to the microbial activities, the generation of CO_2 during the composting period is presented in Figure 4. The addition of pig manure significantly enhanced the CO_2 generation due to the increase in organic matter and also the high microbial activity in pig manure. In the first three days, the evolution of CO_2 for the treatments amended with pig manure increased to about 1.5 mM day^{-1} g^{-1}, and then decreased from day 3 to day 21 gradually followed by a levelling-off phase from day 21 to day 42. There was no significant difference in the generation of CO_2 caused by the inoculation of microorganisms and addition of surfactants. This might be possibly due to the large amount of CO_2 generated from the utilization of organic matter in pig manure that masked the effects of inoculated microorganisms and surfactants.

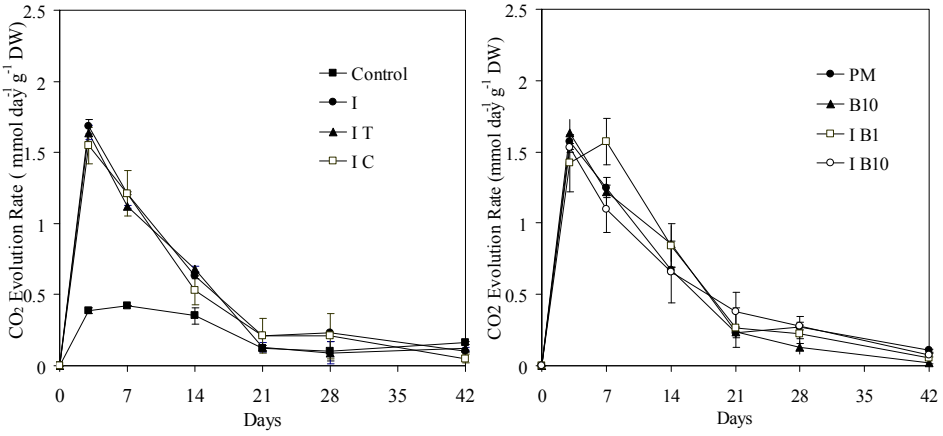

Figure 4. Carbon dioxide (CO_2) evolution during the thermophilic composting of PAHs contaminated soil. Refer to Figure 2 for the legends explanation

A close relationship between the generation of CO_2 and the utilization of TOC was observed in the present study since the CO_2 was the metabolic by-products of organic carbon produced by heterotrophic microorganisms during their respiration. Higher organic carbon contents would produce more CO_2 and thus the generation of CO_2 was proportional to the decrease in the organic carbon contents.

3.2.3. Heterotrophic and PAHs degradative bacterial population during thermophilic composting

The population of total heterotrophic microorganisms is shown in Figure 5. In the Control, the population of total heterotrophic microorganisms in the composting mass was significantly lower than other treatments with pig manure and microbial

inoculation during the composting period. The addition of organic amendment, i.e. pig manure, not only obviously increased the initial total heterotrophic bacterial population but also promoted the microbial growth, which indicates that the organic amendment might serve as both the source of and nutrients for microorganisms. In the treatments amended with pig manure, the heterotrophic microorganisms reached their maximum concentrations at day 7 and ranged from 3.49 to 4.52 $\times$ 10^8 CFU g^{-1}. No significant effect of the inoculation of microorganisms and addition of biosurfactants was observed on the total population of heterotrophic microorganisms, while Tween 80 slightly inhibited the growth of microorganisms.

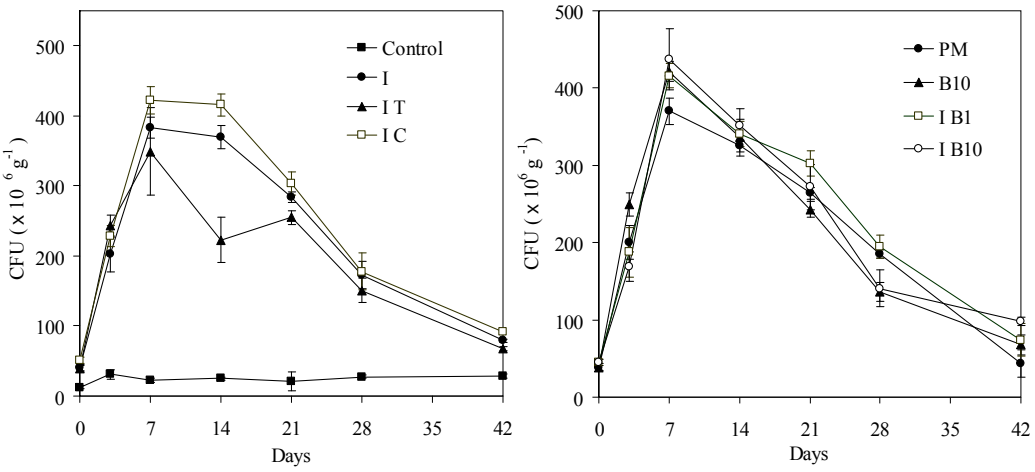

Figure 5. Changes in total heterotrophic bacterial population during the thermophilic composting of PAHs contaminated soil. Refer to Figure 2 for the legends explanation.

The growth of PAHs degradative microorganisms is shown in Figure 6. In the Control, the PAHs degradative populations in soil were quite small, and only increased slightly to 4.68 $\times 10^6$ CFU g^{-1} at the end of the composting period. The addition of organic amendment, i.e. pig manure, obviously promoted the growth of PAHs degradative populations, which indicates that the organic amendment may serve as nutrients for PAHs degradative microorganisms. The inoculation of B-UM further increased the degradative populations to 1.13 $\times 10^8$ g^{-1}. However, the addition of chemical surfactant, i.e., Tween 80 slightly inhibited the growth of degradative populations. The addition of biosurfactants produced by BU03 or inoculation of BU03 slightly increased the degradative populations but the difference was not significant.

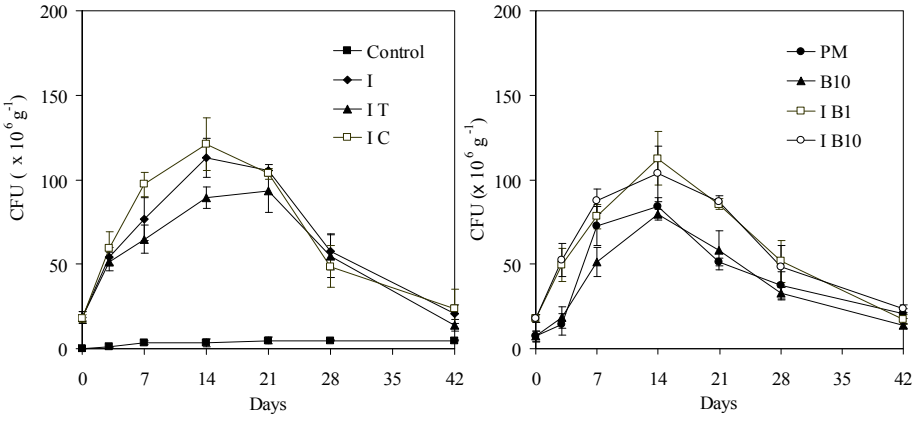

Figure 6. Changes in PAHs degradative bacterial population during the thermophilic composting of PAHs contaminated soil. Refer to Figure 2 for the legends explanation.

3.2.4. PAHs degradation during thermophilic composting

The removal of PHE and B[a]P during thermophilic composting is plotted with time in Figures 7 and 8, respectively. Within the experimental period of 42 days, the removal of PHE and B[a]P in the Control were 71.2% and 16.4%, respectively. More than 98% of PHE was removed from treatments with pig manure amendment and no significant difference was noted among these treatments. However, the removal of B[a]P differed significantly among the various treatments. In the treatment amended with pig manure alone, about 33.7% of B[a]P was removed. Addition of biosurfactants produced by *A. calcoaceticus* BU03 or inoculation of PAHs degradative strain B-UM increased the removal of B[a]P to 41.5 and 56.8%, respectively . The combined addition of B-UM together with *A. calcoaceticus* BU03 or biosurfactants produced by BU03 significantly increased the degradation of B[a]P to 83.8% and 65.1%, and the average removal rate of B[a]P was calculated as 4.95 and 3.85 mg kg^{-1} day^{-1}, respectively.

Few reports that documented the biodegradation of B[a]P reported that the resting cells of *Sphingomonas paucimobilis* EPA505 could degrade 33% of 10 mg L^{-1} B[a]P in aqueous systems (Ye et al., 1996). A bacterial consortium including members of the genera *Mycobacterium* and *Sphingobacterium* rapidly mineralized B[a]P in the presence of diesel fuel and the degradation rate was 1.08 mg L^{-1} d^{-1} (Kanaly et al., 2000). Besides, a litter-decomposing basidiomycete *Stropharia rugosoannulata* almost completely removed or transformed 10 mg L^{-1} B[a]P

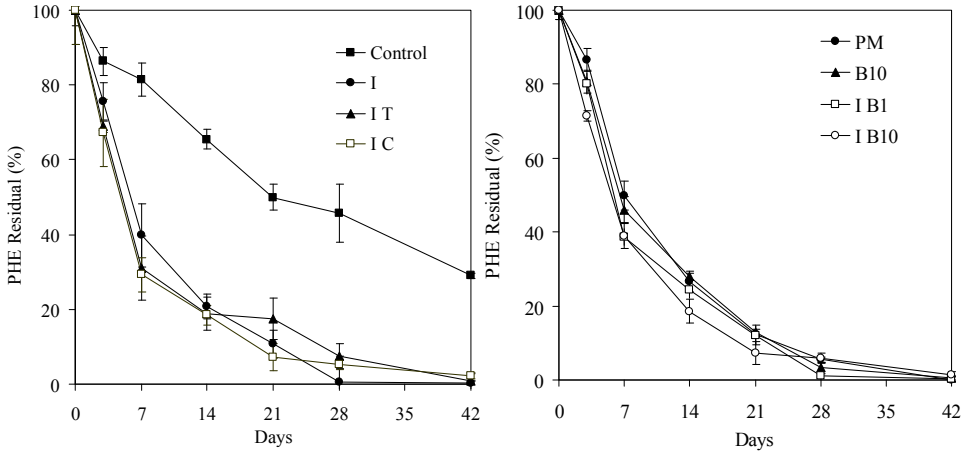

Figure 7. Removal of PHE during the thermophilic composting of PAHs contaminated soil. Refer to Figure 2 for the legends explanation.

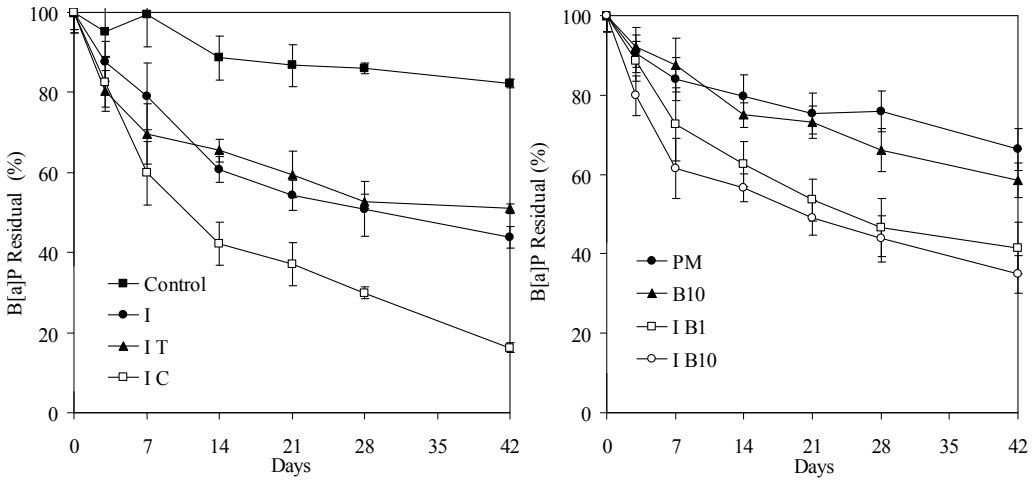

Figure 8. Removal of B[a]P during the thermophilic composting of PAHs contaminated soil. Refer to Figure 2 for the legends explanation.

within 6 weeks (Steffen et al., 2002). Another fungus, *Stropharia coronilla* degraded B[a]P in Mn^{2+}-supplemented cultures and the degradation rate was about 1.43 mg L^{-1} d^{-1} (Steffen et al., 2003). However, degradation of B[a]P in aged soil is thought to be slow due to the strong sorption of the substrate on soilparticulates (Hughes et al., 1997). The potential of *Phanerochaete sordida* to degrade PAHs in a creosote-contaminated soil was investigated under field conditions and none of those PAHs with five rings or more, was removed (Davis

et al., 1993), while a combination of bioaugmentation and biostimulation in landfarming increased the removal of B[a]P to 87% in 16 months. In the present study, 83.8% of B[a]P was rapidly removed from the contaminated soil in 42 days under thermophilic condition, owing to the application of biosurfactants and biosurfactants producing bacteria, indicating a potential for field application.

3.2.5. Emulsifying activity in composting material

To elucidate the mechanism responsible for the enhanced biodegradation of PAHs by biosurfactants or biosurfactants producing cells, emulsifying activity of composting mass was analyzed and presented in Figure 9. The emulsifying activity of soil was about 30 EU. The addition of pig manure initially increased the emulsifying activity to about 120 EU since the pig manure contained large amount of organic matters which may act as emulsifying agents. However, the emulsifying activity decreased sharply to the same level as the Control at the end of the composting period, due to the degradation of the emulsifying agents. Both the addition of the biosurfactants or inoculation of BU03 significantly increased the emulsifying activity. The emulsifying activity of the treatment with inoculation of BU03 was higher and lasted longer than those with the addition of the biosurfactants. Therefore the possible mechanism responsible for the effects of BU03 on biodegradation of PAHs might be due to the production of biosurfactants following the inoculation of BU03, as supported by the increase in emulsifying activity. Biosurfactants might increase the solubility and desorption of PAHs as indicated in the batch experiments. As a result, the bioavailability PAHs was increased and the biodegradation of PAHs was consequently promoted.

The direct application of biosurfactants may not be a practical approach for large scale application, since the production and recovery of biosurfactants is expensive. On the other hand, the inoculation of biosurfactants producing microorganisms into the composting mass resulted in a higher removal of B[a]P, which is likely a more practical and cheaper alternative for remediation of PAHs contaminated soils.

4. CONCLUSIONS

Biosurfactants produced by an isolated strain, *A. calcoaceticus* BU03 were more effective in enhancing the solubility of PHE and B[a]P than synthetic surfactants Tween 80 and Triton X100, as well as biosurfactants produced by *P. aeruginosa* ATCC 9027. In a bench scale thermophilic composting system for remediation of

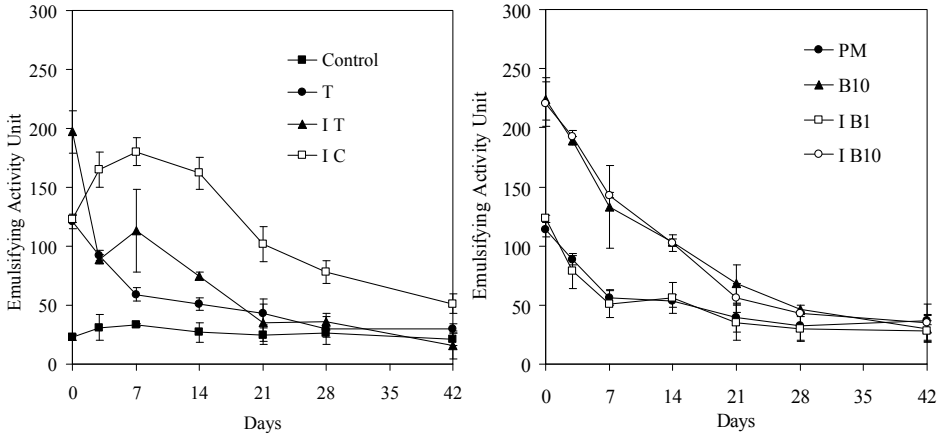

Figure 9. Changes in emulsifying activity of composing mass during the thermophilic composting of PAHs contaminated soil. Refer to Figure 2 for the legends explanation.

PAHs contaminated soil, addition of the biosurfactants and the inoculation of BU03 significantly enhanced the degradation rate of B[a]P to 3.85 and 4.95 mg kg^{-1} day^{-1}, respectively, which are higher than most of the studies to date. Results from the present study gave sufficient evidence to affirm that addition of the biosurfactants or inoculation of biosurfactants producing microorganism i.e., *A. calcoaceticus* is an effective method to enhance the bioremediation of soil contaminated by PAHs.

5. ACKNOWLEDGMENT

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PART II: Heavy Metals

Chapter 5

WIPE SAMPLING METHODOLOGIES TO ASSESS EXPOSURES TO LEAD AND CADMIUM IN URBAN CANADIAN HOMES

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ABSTRACT

Wipe sampling methods are widely used to quantify lead (Pb) loadings inside homes. In the present study we expand the wipe sampling method to investigate other elements in addition to Pb, namely cadmium (Cd) and the soil tracer yttrium (Y).

Following the ASTM 1728 sampling protocol, 1372 wipe samples (including field blanks and duplicates) were collected from 222 homes using Ghost Wipes™. All wipe samples were digested according to a modified version of the ASTM 1644 digestion protocol in which hydrofluoric acid was added to enhance extraction efficiency, and analyzed using ICP-MS. Recoveries assessed using NIST certified reference materials were 93±6% for Pb and 88±14% for Cd (n=66).

Results indicated that 43% of Pb and 23% of Cd samples were below LOD (932 ng m^{-2} and 125 ng m^{-2} respectively). Threshold values of 125 µg m^{-2} for Pb and 4.4 µg m^{-2} for Cd, identified using Q-Q plots, were used to distinguish "elevated" loading values from "background" loading values. Indoor sources and tracked-in soil were identified as potential contributors to elevated loading values. Spearman ranking indicated strong spatial associations amongst the metals. The study shows that wipe sampling provides useful information on room-to-room

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variability of metals, shedding light on possible sources of metals in residential environments.

Keywords: exposure assessment, housedust, metals, built environment

1. INTRODUCTION

The average Canadian spends 90% of their time indoors (Health Canada, 2009), and thus there is a growing demand for information on contaminant levels and sources in the indoor environment. In particular, information about sources of metals in the home is necessary to assess childhood exposures caused by ingestion of dust. Industrial land use, traffic emissions, and geological weathering results in the dispersal and settling of metals in soil and street dust which are tracked indoors by residents and their pets. Soil and street dust is thought to contribute anywhere from 20% to 95% of house dust (Rasmussen et al., 2001 and references cited therein). Metals can also originate from interior sources such as paint, household products, crafts and hobbies, and tobacco use, and tend to accumulate in house dust (Rasmussen, 2004).

Cadmium's (Cd) non-corrosive properties allow its application in batteries, pigments, metal coatings, and plastics (Schoeters et al., 2006). At elevated levels of exposure, Cd acts as a nephrotoxicant (Rasmussen and Gardner, 2008 and references cited therein) and as a carcinogen (Bussières et al., 2004). The principle non-occupational exposures to Cd occur through diet (Gamberg and Scheuhammer, 1994; Kormaniki, 2005) and tobacco use (Yapici et al., 2006). A recent risk assessment of Cd in house dust in the Netherlands (Oomen et al., 2008) estimated that the above pathways represent 90% of the total daily intake of Cd, and therefore ingestion of house dust containing Cd could potentially play a significant role in an individual's overall exposure. Cadmium and lead (Pb) differ from essential metals such as copper and zinc which are required by the body in trace quantities for optimal health.

The Canadian government has significantly reduced the Pb content of paint and gasoline over the past few decades (Canada Mortgage and Housing Corporation (CMHC), 2009). Relics of Pb's past abundant use appear during renovations of older homes, potentially increasing Pb exposure (Reissman et al., 2002). The extensive literature on childhood exposures to Pb, pointing to the severe consequences of overexposure on early brain development resulting in learning and behavioral problems, has led to a re-evaluation of the 10 micrograms per deciLitre blood Pb regulatory action value (Lanphear et al., 2000; Canfield et al., 2003; Lanphear et al., 2005). Hornung et al. (2009) identified the need to maintain low Pb exposure throughout childhood as blood Pb at 6 years of age was

found to be more highly correlated with neurological health effects than at 2 years of age.

Presently, there are no Canadian guidelines for metal loadings in indoor residential dust. The United States Environmental Protection Agency (USEPA) has set a regulation for Pb in house dust at 40 μg ft^{-2} on floors, based on the collection of house dust using the wipe method (USEPA, 2000). For the purpose of determining individual exposures to residential sources of Pb, many researchers view wipe sampling as superior to vacuum sampling. Wipe sampling mimics a child's hand contact with hard surfaces and it is thus argued that a child has greater potential to be exposed to metals in dust settled on smooth surfaces versus carpeted surfaces (Yiin et al., 2002). Additionally, Rodes et al. (2001) found that only one third of a child's hand actually touches a surface, therefore vacuum sampling may not represent tangible exposure. The question of where to sample was addressed by Wilson et al. (2006) as USEPA (2000) does not specify the optimal location or number of samples to be taken within the home. Wilson et al. (2006) identified the best predictor of elevated blood Pb in a child to be non-carpeted floor wipe samples collected in the home's entry area, living room, kitchen, and bedrooms.

The purpose of the present study is to quantify metal loadings in urban homes with the aim of establishing background levels for residential exposure in Canada. As such it represents the first published dataset of its kind for Canada. The only other published Canadian study to use wipes as the sampling medium was conducted by CMHC (1995) to test cleaning methods for Pb in paint dust. The present study also aims to identify differences in Pb and Cd loadings between rooms, thereby providing insight on possible sources. The entry of the home is a prime location to study metals that infiltrate the home from outdoor sources. Similarly, interior rooms such as kitchens, living rooms, and bedrooms are more likely to be influenced by indoor sources of metals. Ultimately, the information presented here will assist in quantifying typical Canadian exposures to Pb and Cd, and reveal ways to reduce exposures.

2. MATERIALS AND METHODS

2.1 Selection of Wipe Brand

Out of the many brands of wipes available on the market, the Ghost Wipes™ brand was selected for use in this study. Based on preliminary testing at Health Canada (Rasmussen, 2007a unpublished data) Ghost Wipes™ were determined to be optimal because they meet all criteria in the American Society for Testing and Materials (ASTM) method E 1792 (2002a); they completely digest in acid

(consistent with previous findings by Harper et al., 2002); and they contain very low background concentrations of the elements in this study. Ghost Wipes™ also meet criteria outlined by Millson et al. (1994) in their evaluation of market available wipes including robustness, high precision, and ease of use.

2.2 Sampling and Analysis

A total of 1372 wipe samples were collected from 222 homes between January and March 2008 in three Ontario cities: Barrie (57 homes), Greater Sudbury (86 homes), and Thunder Bay (79 homes). Homes were randomly selected as part of a sampling strategy designed for a larger nation-wide study (Rasmussen et al., 2007b), and therefore the sampling was not intended to be representative of individual cities. The present study incorporates all samples collected in the 2007-2008 sampling season. The collection of information by sampling technicians using questionnaires and interviews, and the communication of results and guidance to the participants, is described elsewhere (Rasmussen, et al. 2007b).

Up to ten wipe samples were collected from each home, from smooth surfaces in the middle of each room. Rooms that were sampled included: main entry, kitchen, living room, family room, adult's bedroom, child's bedroom, and child's primary play area, based on guidance provided by Wilson et al. (2006). Other rooms were occasionally included on an *ad hoc* basis. A total of 932 different rooms were sampled using wipes, yielding 932 individual wipe measurements plus 440 quality assurance measurements (total = 1372 wipes).

Wipe samples were collected according to ASTM E 1728 protocol (2002b), which prescribes a vertical and horizontal overlapping S-shaped movement applying even pressure to the floor surface. The collected wipe was folded inward to preserve the sample and placed directly into a labeled plastic digiPREP™ digestion tube which was sealed inside Ziploc™ bags for transport to the lab. The wipes were shipped to Health Canada, Environmental Health Centre, Ottawa Ontario, Canada, and stored frozen until time of analysis.

The analytical method employed in this study was based on a modification of ASTM method E 1644 (2004), a nitric acid digestion. The modifications consisted of (1) adding hydrofluoric acid during digestion to increase digestion efficiency, (2) multi-element determination by ICP-MS, and (3) incorporating the use of a digiPREP™ heating block. The goal of adding hydrofluoric acid was to quantify total metals in the dust (i.e. maximize recovery). It is noted that the human gastrointestinal tract is estimated to be capable of absorbing less than 30% of the total Pb in house dust (Turner and Ip, 2007).

2.3 Quality Assurance and Quality Control

A 12 square inch plastic template was used to constrain the wipe sampling area, as prescribed by the ASTM E 1728 protocol (2002b). The template was cleaned with an alcohol wipe between rooms and a new template was used for each home. In each home sampled, one field blank wipe and one field duplicate wipe were collected. The field blank wipe was exposed to all handling procedures used for the samples with the exception that no surface was wiped (ASTM, 2002b). The room from which the duplicate was collected rotated amongst homes. The sampling strategy yielded a quantity of blanks (n=220) and duplicates (n=220) in excess of the minimum frequency of 5% as outlined in the ASTM E 1728 protocol (2002b), incorporating a high proportion of quality assurance data into the study design.

Throughout sample digestion, three procedural reagent blanks and three procedural wipe blanks were included per batch (n = 37 batches). Three certified reference materials for Pb and Cd were included: NIST 2583 indoor dust, NIST 2584 indoor dust, and NIST 2711 Montana soil (certificates do not include yttrium). The mean recovery and standard deviation of these certified reference materials was 93 ± 6% (n=66) for Pb and 88 ±14% for Cd (n=66).

The limits of detection (LOD) and quantification (LOQ) for each element were calculated based on three times and ten times the standard deviation of the lab procedural wipe blanks respectively (n=110). For sample results less than the LOD, half the LOD was substituted where required. The detection limits for Pb, Cd, and yttrium (Y) were calculated to be 932 ng m^{-2}, 125 ng m^{-2}, and 9.09 ng m^{-2} respectively.

2.4 Data Analysis and Units

SPSS® Statistics (version 17.0) and Microsoft Excel® (2007) with the Analyse-it add-in (version 2.20) were used for statistical analyses. Shapiro-Wilk tests of the datasets resulting from this study revealed non-normal distributions, and therefore non-parametric statistical methods were employed. Spatial relations were investigated using Spearman rank correlation coefficients, and 50^{th} and 95^{th} percentiles were used to summarize Cd and Pb loadings within rooms and within homes.

To convert from SI units (µg m^{-2}) used in the present study, to units of µg ft^{-2} (microgram per sq ft) used in the USA, multiply loading values expressed in µg m^{-2} by a factor of 0.0929.

3. RESULTS AND DISCUSSION

3.1 Wipe Data Quality

Field blank and collocated duplicates were collected from all but two homes in this study (n=220). The LODs, LOQs, and medians of the field blanks are reported for each element in Table 1.

Table 1. Limits of detection (LOD) and limits of quantification (LOQ) for Cd, Pb, and Y are based on 37 analytical batches (three procedural wipe blanks per batch). Results for field wipe values (median) include all field wipe blanks collected in this study (n=220).

	LOD (ng m^{-2})	**LOQ (ng m^{-2})**	**Field Wipe Blank (ng m^{-2})**
Cd	125	416	< LOD
Pb	932	3110	< LOD
Y	9.09	30.3	< LOD

The relative percent difference (RPD) between collocated duplicate samples was calculated using the equation RPD = $((dup_2-dup_1)/((dup_2+dup_1)/2)*100)$. Note that the mean RPD in the range between LOD and LOQ is greater than the mean RPD above LOQ (Table 2). The greater variability in the lower range (between LOD and LOQ) reflects a combination of field and analytical sources of uncertainty, and points to the need to consider the more rigorous LOQ as the appropriate criterion for quality assurance.

Table 2. Mean Relative Percent Difference (RPD) of collocated duplicates categorized by limits of detection (LOD) and quantification (LOQ). Total number of pairs = 220. See Table 1 for LOD and LOQ values.

	Duplicates < LOD	**Between LOD and LOQ**		**Duplicates > LOQ**	
	No. of pairs	**No. of pairs**	**Mean RPD**	**No. of pairs**	**Mean RPD**
Cd	53	103	51.3	64	39.4
Pb	100	40	71.8	80	41.2

Results for Pb showed that 382 samples were below LOD, which equals 43% of the total of 932 wipe measurements. For Cd, 196 samples were below LOD, or

23% of the wipe measurements. In the case of Y, 34 samples were below LOD (or 3.6% of the measurements). With respect to the LOQ, 511 samples (55%) were below the LOQ for Pb, 672 (72%) were below LOQ for Cd, and 106 (11%) were below LOQ for Y (n=932).

There were a total of 36 homes in which all Pb loading values, in all rooms, were below LOD. In the case of Cd, there were 11 homes in which all samples were below LOD. This yielded a subset of 186 homes for Pb, and 211 homes for Cd, in which at least one wipe sample exceeded LOD. It is this subset of homes which is subjected to further analysis and interpretation in the discussion below.

3.2 Lead Loadings

Figure 1 is a normality (Q-Q) plot of the maximum Pb loading observed in each of the subset of 186 homes having at least one wipe greater than the LOD. Note that the majority of the data fall on the line representing a lognormal distribution, with exceptions occurring at the extreme high and low ends. That portion of the dataset which falls on the lognormal line is considered the "background" subpopulation, for the purpose of this paper. Eight points occur above the breakpoint in the high end of the dataset, where the values start to trend away from the lognormal line (Figure 1). This breakpoint occurs at about 125 μg m^{-2} (or 12 μg ft^{-2}). Three homes within the elevated subpopulation had wipe samples exceeding the USEPA (2000) regulation for Pb in floor dust, i.e. 40 μg ft^{-2} or 431 μg m^{-2}.

The upper breakpoint in the Q-Q plot at 125 μg m^{-2} (or 12 μg ft^{-2}). is used herein as an empirical threshold to distinguish between "background" and "elevated" Pb loading subpopulations. This selection of a threshold at about 12 μg ft^{-2} is coincident with a recent US residential study which concluded that Pb loadings less than 12 μg ft^{-2} should be protective for the majority of children (Dixon et al., 2009).

Out of the eight above-threshold homes in Figure 1, three homes displayed the highest Pb loading in the entry way. In two homes the highest Pb loading occurred in an adult bedroom; in two homes the highest Pb loading occurred in children's bedrooms; and in one home, the highest loading occurred in a child's play room.

3.2.1 Sources of Lead

A room by room analysis was conducted with the aim of exploring potential sources of Pb (Table 3). Overall, the entry way displayed the highest median value however other noteworthy rooms include adult bedrooms and children play

rooms. Notably, the highest individual value was located in a child's bedroom. Lead loadings in the home's entry suggest outdoor sources such as track–in of dirt, whereas elevated loadings in bedrooms and play rooms suggest interior sources of Pb. It is concluded from the results shown in Table 3 that both indoor and outdoor sources of Pb contribute to Pb loadings in house dust.

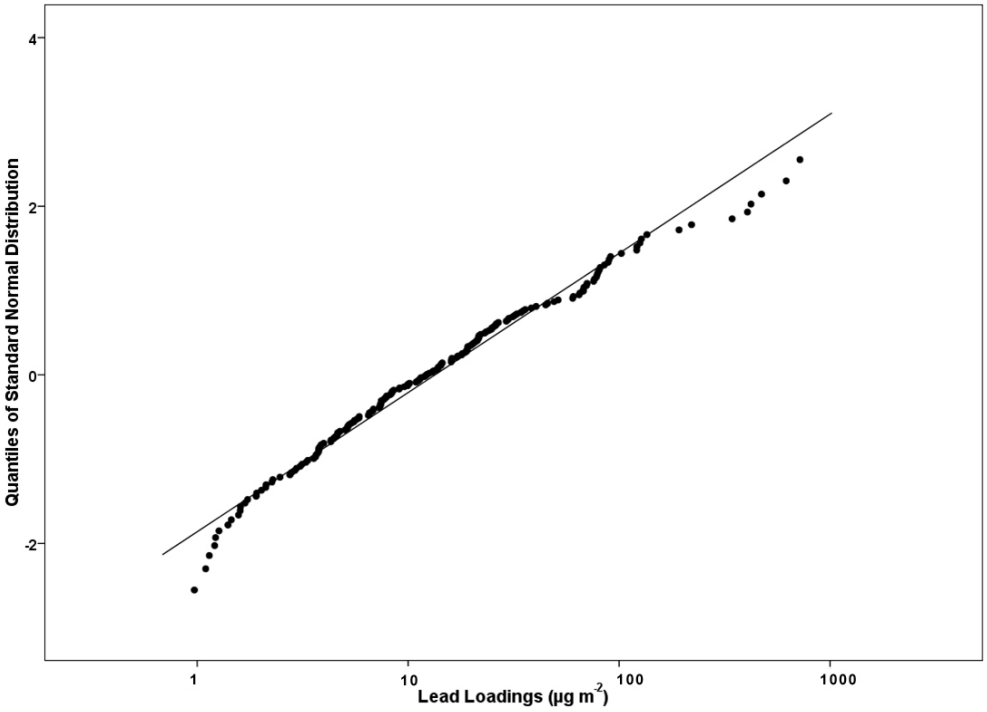

Figure 1. Normality Plot (Q-Q plot) for log transformed Pb loadings occurring in a subset of homes having at least one wipe above the limit of detection (n=186). Homes are represented by the wipe with the highest Pb loading, regardless of the room from which it was taken. The line through the data represents a lognormal distribution. Eight homes are above the breakpoint in the dataset which occurs at 125 µg m^{-2}.

Table 3. Summary of Pb loadings (μg m^{-2}) by room for all 222 homes sampled. (LOD = 0.932 μg m^{-2}).

Room	n	Percent Below LOD	50th Percentile	95th Percentile	Maximum value
Entry	208	22	5.64	87.5	619
Kitchen	218	49	1.02	21.2	165
Living / Family room	114	49	< LOD	40.9	485
Adult Bedroom	93	43	3.26	75.9	422
Child Bedroom	50	60	< LOD	133	720
Play room	23	26	3.50	66.9	220

Age of the home appears to be an important factor, as six out of the eight homes above threshold were built before 1960. The mean age of the eight above-threshold homes is 1954 ± 29 years, which is (on average) nineteen years older than homes in which all wipe samples were below LOD (1973 ± 22 years; n=36). A review of the literature indicates that Pb-based paint is most commonly cited as the primary cause of elevated Pb in older homes (Rasmussen, 2004).

Potential sources of metals in the above-threshold homes may be hypothesized based on questionnaire responses. Residents of two of the above-threshold homes were employed in jobs where Pb may be encountered (mining and shipyards). In one home, Pb is stored in the house for craft and hobby use. A resident of another home habitually conducts bodywork on vehicles in the driveway: the entry wipe for this home displayed both elevated Pb and Cd loadings. Recent renovations involving painting (four homes) and plumbing (one home) were reported to have occurred in some homes with elevated Pb loadings. This may be relevant as renovation activity in older homes can increase Pb availability where high Pb content paint has been used in the past (CMHC, 2009). Sampling technicians noted that old paint was chipping off the wall in one home with elevated Pb loading built before 1960. Two homes with high Pb loadings reported that occupant(s) smoke indoors, which may be relevant as Pb from tobacco use has been indicated as a source of Pb on interior surfaces (Gaitens et al., 2009).

3.3 Cadmium Loadings

A normality (Q-Q) plot for Cd loadings (Figure 2) indicated a breakpoint in the dataset at about 4.4 μg m^{-2} (0.4 μg ft^{-2}). There were nine homes in this study with Cd loadings above this threshold value: three of these were kitchen wipes, three were entry wipes, two were office wipes, and one was from an adult bedroom.

3.3.1 Sources of Cadmium

As in the case of Pb, there are both indoor and outdoor sources of Cd. Cadmium loadings are relatively high in home entry ways and adult bedrooms compared to other areas of the home (Table 4). As exterior sources of Cd are associated with both industrial land use and geological sources, track-in of dirt by residents and their pets is a plausible explanation for the observation of relatively high loadings in entry ways. Higher Cd loadings in adult bedrooms versus child occupied rooms suggest tobacco use as a possible source. Questionnaire data indicated that 14% of homes in the study were occupied by at least one person who smoked inside the home. House age may also be a factor: but the dataset is too small to determine significance: the average age of homes with Cd loadings above threshold was 1962 ± 29 years (n=9), compared to homes where all wipe samples were below LOD (1975 ± 23 years; n=11).

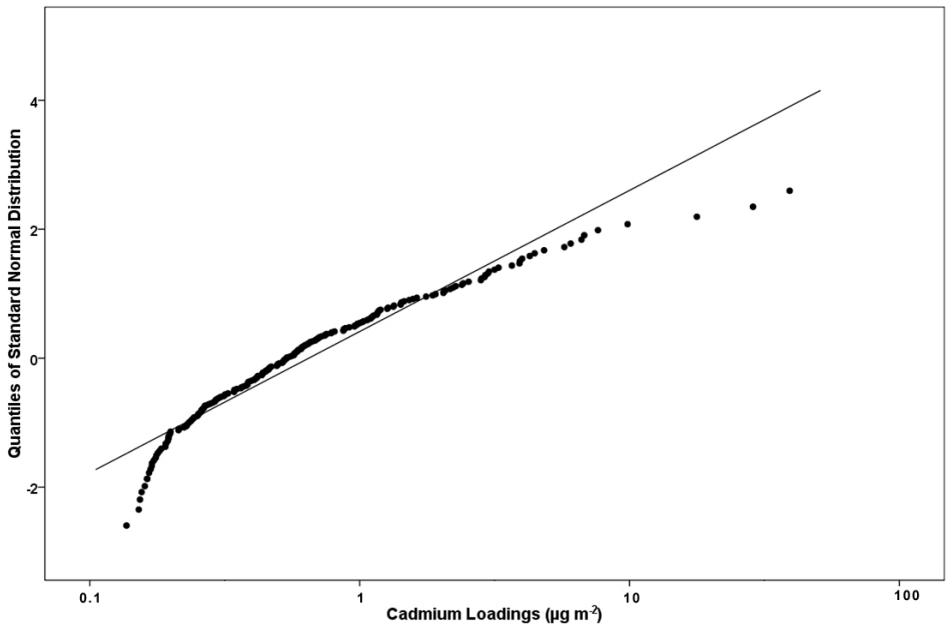

Figure 2. Normality Plot (Q-Q plot) for log transformed Cd loadings occurring in homes having at least one wipe above the limit of detection (n=211). Homes are represented by the wipe with the highest Cd loading, regardless of which room it was collected from. The line through the data represents a lognormal distribution. Nine homes occur above the breakpoint in the dataset which occurs at 4.4 µg m^{-2}.

Information gathered from the questionnaire results revealed clues about possible sources in the nine homes with above-threshold Cd loadings. In three homes where painting was listed as a hobby, elevated Cd loadings were observed

in the room where this hobby was conducted. Crafts and hobbies are known to have the potential to influence metal loadings in the home (Rasmussen, 2004), as Cd is a common component of certain paint pigments (Harte et al., 1991). In four other homes activities were reported that involve metal work such as welding, soldering, and body-work on vehicles. These activities are potential sources, as Cd is a common component of solders and fluxes (Harte et al., 1991). Of the two remaining elevated homes, one contained a resident who smokes and one had recent plumbing and painting renovations. Five of these nine homes above threshold were built before 1960.

Table 4. Summary of Cd loadings (μg m^{-2}) by room for all 222 homes sampled (LOD= 0.125 μg m^{-2}).

Room	n	Percent Below LOD	50th Percentile	95th Percentile	Maximum value
Entry	208	16	0.314	3.11	8.14
Kitchen	218	28	0.207	1.24	9.84
Living / Family room	114	20	0.239	1.20	5.66
Adult Bedroom	93	22	0.276	2.74	19.0
Child Bedroom	50	28	0.199	1.68	3.27
Play room	23	17	0.320	1.06	1.63

3.4 Metal Correlations

Spearman correlation coefficients (r_s) were calculated to compare Cd, Pb, and Y loadings for various rooms within the home. With regard to the entry wipe samples (n=208; Table 5) correlations between Pb and other metals were greater than $r_s = 0.5$, which are strong relationships according to definitions by Reimann et al. (2008). No significant differences were observed for analyses of individual locales compared to analyses of the entire dataset. Correlations were similarly strong for bedroom and other interior wipe samples (i.e. kitchens, living rooms, bedrooms, and playrooms; Table 5). Since all correlations were strong, information about precise sources of these metals could not be determined from this type of analysis.

Calabrese and Stanek (1995) recommended Y as a soil tracer for use in the estimation of soil ingestion rates. Yttrium is a rare earth element with an average concentration of 30 ppm in the earth's crust (Bottrill, 2001). The comparison of Y

against Cd, and Pb in wipe samples was included in Table 5 in an effort to identify the relative contribution of outdoor and indoor sources of these metals in different areas of the home (Table 5). The highest proportion of soil is likely to be found in dust samples collected in the home's entry areas, due to track – in of outdoor dirt by residents and their pets.

The results in Table 5 are inconclusive as to whether indoor or outdoor sources dominate. Strong Pb – Y correlations (r_s = 0.7) and strong Cd – Y correlations (r_s = 0.6) are found for wipes collected in entry ways (Table 5). However, correlations are equally strong for wipes collected in bedrooms and other interior rooms (Pb-Y r_s = 0.6, Cd-Y r_s = 0.6). These results suggest that both indoor and outdoor sources exist for all three elements.

Yttrium has limited use in household products: it is generally alloyed in small amounts with other metals, and is most commonly found as the oxide yttria (Y_2O_3), used for making red phosphors in colour television picture tubes (Chemistry Encyclopedia 2007; Bottrill 2001). In summary it appears that Pb, Cd, and Y are contributed to house dust from both indoor and outdoor sources, based on the correlations in Table 5 observed in all entry and interior subsets.

Table 5. Spearman rank correlation coefficients for Cd, Pb, and Y sub-divided by room. "Interior room wipes" include living rooms, kitchens, bedrooms, and play rooms.

Location	n	Cd-Y	Pb-Cd	Pb-Y
Entry wipes	208	0.6	0.7	0.7
Bedroom wipes	189	0.6	0.7	0.6
Interior room wipes	575	0.6	0.6	0.6

4. CONCLUSIONS

This research has generated the first multi-element wipe sampling database for background or baseline urban residential environments in Canada. The information obtained by applying the wipe methodology to Canadian residential environments assists in quantifying typical urban residential exposures to Pb and Cd, and reveals valuable information about variations in metal loadings amongst individual rooms within homes.

The results indicate that activities conducted in each room and the products used within them contribute to the metal level of that room. Similarly, outdoor sources contribute to differences in metal loadings of homes due to track-in of outdoor dirt by residents and their pets. The finding of strong correlations for Y against both Pb and Cd in entry areas as well as interior areas confirms that both indoor and outdoor sources are important for these three elements.

Ninety-nine percent of homes in this study fell below the USEPA regulation of 40 μg ft^{-2} (431 μg m^{-2}) for Pb in floor dust (USEPA, 2000). The finding that only a small percentage of homes had a wipe sample that exceeded the USEPA regulation (3 out of 222 in total) is consistent with US residential studies such as NHANES (National Health and Nutrition Examination Survey) which reported that the geometric mean of Pb in floor dust was 1.1 μg ft^{-2} (12 μg m^{-2}; Dixon et al., 2009). In the present study, analysis of the maximum wipe loading per home using Q-Q plots suggested thresholds of 125 μg m^{-2} for Pb and 4.4 μg m^{-2} for Cd, which are used to distinguish between background and elevated subpopulations. This dataset will contribute to the development of guidance for reducing exposures to residential Pb and Cd that is specific to the Canadian urban environment.

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Chapter 6

REMEDIATION OF A HEXAVALENT CHROMIUM RELEASE TO GROUNDWATER USING ION-SPECIFIC RESINS

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ABSTRACT

In March 1986, during installation of a monitoring well at an industrial electroplating facility a chrome rinse line was pierced by an auger. A six-inch recovery well was installed in the borehole at the release point and the recovered groundwater was pumped directly into the facility's wastewater treatment plant. In 1998, a site assessment identified elevated hexavalent chromium concentrations in groundwater in this area of the site. The assessment included the installation of monitoring wells which were sampled over several years. The data indicated that the concentrations in this area of the site were increasing. Additional investigations, conducted upgradient of the process line release, identified another source of hexavalent chromium – one of the platers inside the building.

A remediation system was designed to remediate the hexavalent chromium release which included the installation of five recovery wells and associated piping. In Fall 2006, step tests were conducted to determine the approximate pumping rate for the recovery wells. Based on the results of the test, pumping rates of up to four gallons per minute were included in the design.

A pilot test was subsequently conducted to confirm that the proposed treatment process, utilizing ion-specific exchange filters, was appropriate for the removal of hexavalent chromium and nickel. In addition, the data from the pilot test was used to determine the anticipated frequency of greensand filter backwash and change-out frequency for the resin containing hexavalent chromium.

The system was installed during Spring-Summer 2008 and includes three hexavalent chromium-specific resins and two nickel-specific resins in a remediation building at the site. The majority of the treated effluent is recharged upgradient of the system into a recharge pit to enhance flushing of the aquifer. The remainder of the treated effluent is discharged to the municipal sewerage system under an Industrial Pretreatment Permit.

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Keywords: groundwater, pollution, remediation, resins, hexavalent chromium

1. BACKGROUND

On March 11, 1986, during installation of a monitoring well between an industrial plating facility and a wastewater treatment plant, a chrome rinse line was pierced by a hollow stem auger at a depth of approximately 4.5 feet below grade. The rinse stream was turned off and the area was excavated to repair the line. It was determined that the rinse line, at the time of the release, had an average flow rate of five gallons per minute (gpm) with a concentration of 9.0 milligrams per liter (mg/l) of hexavalent chromium. Based on this rate, a maximum of 540 gallons of rinsewater was estimated to have been released during the incident.

The material surrounding the borehole was reportedly damp. However, the overburden soils surrounding the remainder of the rinsewater pipeline were dry upon excavation, indicating that the release did not migrate laterally along the pipe. Based on this observation, a six-inch recovery well was installed in the borehole at the release point and the recovered groundwater was pumped directly into the adjacent wastewater treatment plant. No additional assessment was conducted at that time.

On August 5, 1998, a monitoring well (MW-19-4SR) was installed immediately downgradient of the 1986 release area, adjacent to the wastewater treatment plant to determine whether hexavalent chromium concentrations continued to be present in groundwater in this area of the site. Numerous attempts were made to install the well as close to the release point as possible. However, due to the presence of numerous utilities, including high voltage electric, process lines, storm drains, sanitary sewer, and water lines, the only location available for boring installation was selected for the location of well MW-19-4SR. A groundwater sample was collected from well MW-19-4SR on August 17, 1998 and hexavalent chromium was detected at a concentration of 3.7 mg/l. The state standard applicable to the site was 0.3 mg/l.

On October 26, 1998, a second monitoring well (MW-19-5S) was installed approximately 120 feet downgradient of well MW-19-4SR. Both monitoring wells were sampled on November 3, 1998. Hexavalent chromium was identified at a concentration of 9.1 mg/l in well MW-19-4SR and 0.15 mg/l in well MW-19-5S. The laboratory analytical results are included in Table 1.

Based on the results of the 1998 assessment, a Class C Response Action Outcome - Partial (RAO-C) was submitted to the Massachusetts DEP indicating that the extent of the release had been delineated, but that a permanent solution as defined in the Massachusetts Contingency Plan (MCP – the Massachusetts Hazardous Waste regulations) had not been achieved. In accordance with the RAO-

C, groundwater samples were collected on an annual basis and submitted for laboratory analysis of hexavalent chromium. The results of the annual sampling of the two monitoring wells are presented in Table 1.

1.1 Additional Investigation

In September 2005, six additional soil borings (MW-1-05 through MW-6-05) were advanced at the site. The locations of the soil borings are depicted on Figure 1. Each of the borings was advanced to depths of between 22 and 25 feet below grade and completed as two-inch PVC monitoring wells. In general, the stratigraphy encountered in the soil borings was a sand underlain by a clay or silt.

No olfactory or visual evidence of contamination was identified during boring advancement. Consequently, one soil sample from each boring collected immediately above or at the observed water table was submitted for analysis of hexavalent chromium, trivalent chromium, and total chromium.

No exceedances of the applicable Method 1 Cleanup Standards were identified in any of the soil samples submitted for laboratory analysis. Total chromium was detected at a concentration above the most stringent standard, but both speciated concentrations were below their applicable soil standards indicating that neither of the applicable speciated standards were exceeded.

On October 6, 2005, the six newly installed monitoring wells and two existing wells (MW-19-4SR and MW-19-5S) were gauged and sampled. The groundwater samples were submitted for laboratory analysis of hexavalent chromium, trivalent chromium, and total chromium. Exceedances of the applicable Method 1 standards (GW-3) continued to be identified in wells MW-19-4SR and MW-19-5S. In addition, hexavalent and total chromium were detected above the Method 1 Cleanup Standards, in place at that time, in well MW-4-05, located downgradient of well MW-19-5S. In December 2007, the state cleanup standard changed and based on these "new" standards no exceedances were detected downgradient of well MW-19-5S during the October 2005 sampling event.

Based on the data collected at the site and the physical attributes of the subsurface environment the conclusions of the 2005 investigation indicated that it was unlikely that the elevated hexavalent chromium concentrations were attributable to the 1986 release. This conclusion was based on the theoretical hydraulic conductivity determined from the overburden materials observed during boring installation and the increasing concentrations identified at the site. The report also concluded that additional comprehensive response actions were required including the installation of additional wells to delineate the horizontal extent of the release beyond existing well MW-4-05 and soil borings inside the Plant #4 facility. The plant had recently been closed and the machinery had been

Table 1. Initial Groundwater Analytical Results

Well ID	MCP Standards		MW-19-4SR						
Date Sampled	**GW-3**	**UCLs**	**08/17/98**	**11/03/98**	**11/22/99**	**01/13/00**	**11/20/00**	**11/06/01**	**11/27/02**
Metals (mg/L)									
Hexavalent chromium	0.3	3	3.7	9.1	10	5	9.5	36	24.5
Trivalent chromium	0.6	10	NA	NA	NA	NA	NA	NA	NA
Total chromium	0.3	3	NA	NA	NA	NA	NA	NA	NA
Total nickel	0.2	2	NA	NA	NA	NA	NA	NA	NA

Well ID	MW-19-4SR (cont.)			
Date Sampled	**11/26/03**	**11/23/04**	**10/06/05**	**2/1/2006**
Metals (mg/L)				
Hexavalent chromium	37.4	21	16	2.7
Trivalent chromium	NA	NA	<5	NA
Total chromium	NA	NA	15	2.9
Total nickel	NA	NA	NA	NA

Well ID	MCP Standards		MW-19-5S						
Date Sampled	**GW-3**	**UCLs**	**11/03/98**	**11/22/99**	**01/13/00**	**11/20/00**	**11/06/01**	**11/27/02**	**11/26/03**
Metals (mg/L)									
Hexavalent chromium	0.3	3	0.15	0.74	0.62	0.1	2.3	3.06	5.52
Trivalent chromium	0.6	10	NA	NA	NA	NA	NA	NA	NA
Total chromium	0.3	3	NA	NA	NA	NA	NA	NA	NA
Total nickel	0.2	2	NA	NA	NA	NA	NA	NA	NA

Well ID	MW-19-5S (cont.)			
Date Sampled	**11/23/04**	**10/06/05**	**02/01/06**	**04/23/08**
Metals (mg/L)				
Hexavalent chromium	11	13	11	0.6
Trivalent chromium	NA	<5	NA	NA
Total chromium	NA	11	12	0.59
Total nickel	NA	NA	NA	0.12

UCL – Upper Concentration Limits

NA - Not analyzed

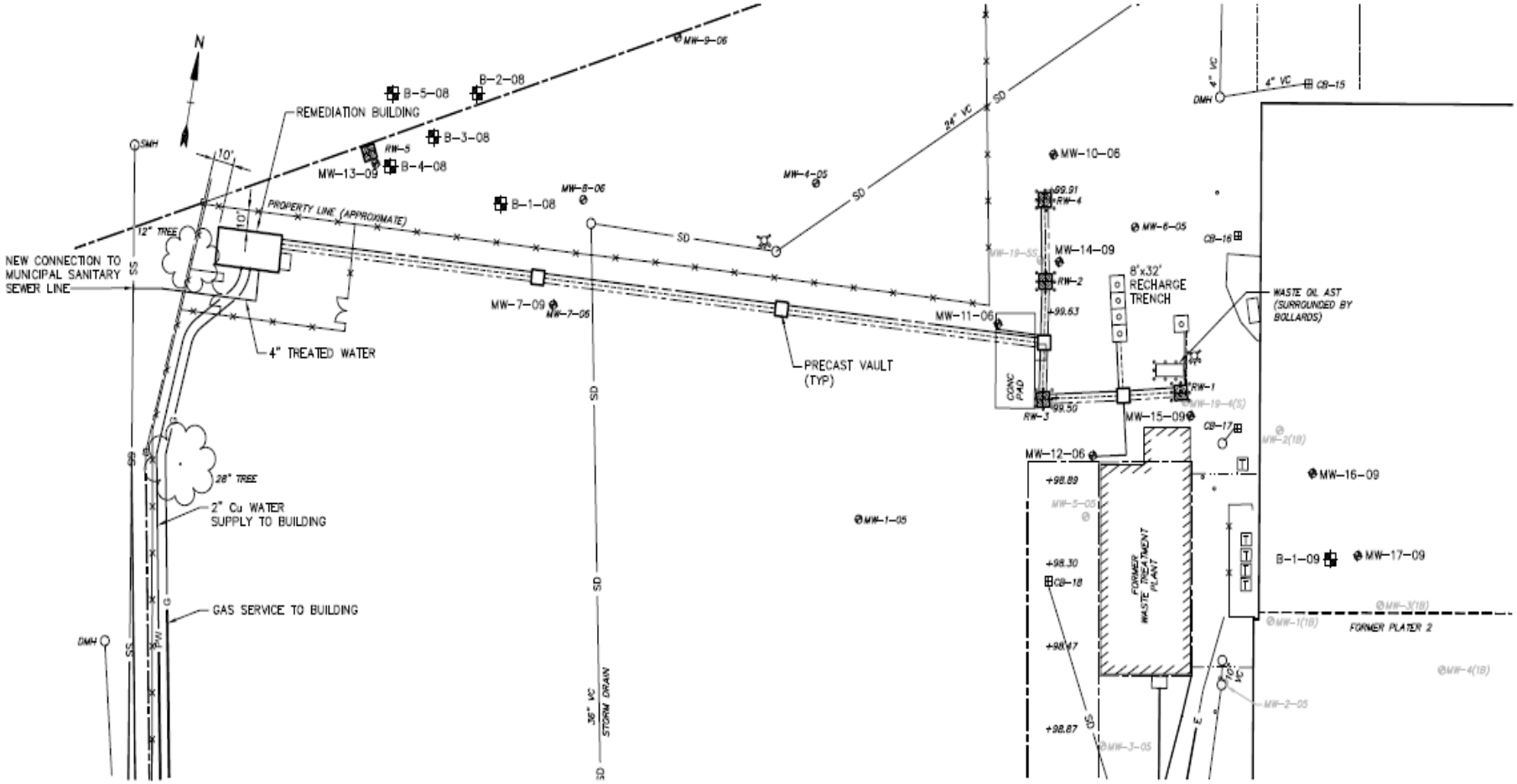

Figure 1. Site Plan

removed as part of the plant decommissioning process. The installation of interior soil borings/monitoring wells was recommended to determine the source of the hexavalent chromium release.

1.1.1 Source Investigation

On December 9, 2005, seven borings were completed inside Plant #4. Four of the borings were completed as monitoring wells, MW-1(IB) through MW-4(IB). The borings were advanced with a truck-mounted Geoprobe direct push rig. Following concrete removal, the borings were installed through the floor of the plant to evaluate soil conditions beneath the slab. Continuous soil samples were collected from the borings. The locations of the wells are included on Figure 1.

One sample from each boring was submitted for laboratory analysis of total RCRA 8 metals plus hexavalent chromium. The highest concentration of hexavalent and total chromium in soil were identified in the boring for well MW-3(IB). Total chromium in boring MW-3(IB) was detected at a concentration above the S-1/GW-3 standard, but both of the speciated concentrations were below their applicable soil standards indicating that neither of the applicable speciated standards were exceeded. However, the concentrations detected in boring MW-3(IB) were an order of magnitude higher than any concentration detected in soil at the site to date. Well MW-3(IB) was installed adjacent to one of the former platers inside the site building.

On January 11, 2006, monitoring wells MW-7-06, MW-8-06 and MW-9-06 were installed at the site downgradient of well MW-4-05 where elevated concentrations of hexavalent chromium had been detected in groundwater during a previous sampling event.

On February 1, 2006, monitoring wells MW-7-06, MW-8-06, MW-9-06, MW-1(IB), MW-2(IB), MW-3(IB), MW-4(IB), MW-19-4SR, and MW-19-5S were gauged and sampled using low-flow procedures. Elevated concentrations of hexavalent chromium were identified in wells MW-2(IB), MW-19-4SR, and MW-19-5S.

1.1.2 Building Demolition

On August 3, 2007, monitoring wells MW-1(IB), MW-2(IB), MW-3(IB), and MW-4(IB) inside the building, as well as wells installed adjacent to the wastewater treatment plant were abandoned in accordance with the *Standard Reference for Monitoring Wells* (DEP Publication #WSC-310-91) prior to the demolition of the site buildings. The wells that had been abandoned are identified using a gray notation on Figure 1. The demolition of the plant building was conducted during the summer and early fall of 2007 by the current site owner.

1.1.3 Pilot Test

On September 7, 2006, a six-inch recovery well (RW-1) was installed using hollow stem augers (HSA) adjacent to monitoring well MW-19-4SR. On September 27, 2006, a step test was conducted to determine the approximate pumping rate for the well. The groundwater pumped from the well was pumped into a fractionization tank. Based on the results of the test, the well maintained a steady groundwater elevation at 1.0 gpm.

Due to the low pumping rate, on October 18, 2006, a second six-inch well (RW-2) was installed adjacent to well MW-19-5S. Previous borings advanced in this area of the site indicated that a thicker area of fine sand was present in this area of the site and that this well may be able to maintain a higher pumping rate. Based on a second step test, well RW-2 was able to sustain a pumping rate of 4 gpm.

A pilot test was conducted to confirm that the remedial approach using a specific ion exchange filter was suitable for the site. In addition, the data from the pilot test was used to determine the anticipated frequency of greensand filter backwash and change-out frequency for the resin containing hexavalent chromium. The pilot study was initiated on October 20, 2006 on well RW-2.

The treatment unit utilized for the pilot included: a 10 micron (μ) cartridge filter, a potassium permanganate pretreated greensand filter (vessel size of 1.3 cubic feet (ft^3)), and a hexavalent chromium ion exchange resin (vessel size of 1.2 ft^3). Based on the results of the assessment and pilot test conducted at the site the installation of a pump and treat system using Siemens resins was proposed.

Based on the elevated detections in groundwater, a Release Abatement Measure (RAM) Plan for the remediation of the hexavalent chromium release, based on the results of the pilot test, was submitted to DEP on November 20, 2006. On November 30, 2006, six-inch recovery wells RW-3 and RW-4 were installed with a hollow stem auger drill rig. The locations of the wells are indicated on Figure 1.

1.1.4 Installation of Additional Monitoring Points

Between June 2008 and April 2009, additional monitoring wells were installed to provide site coverage and replace wells that had been destroyed or abandoned during demolition of the site buildings. The locations of the wells are included on Figure 1.

On April 13, 2009, soil samples were collected from just above the clay layer in wells MW-16-09 and MW-17-09 and boring B-1-09 (installed adjacent to well MW-17-09) and submitted for laboratory analysis of hexavalent chromium, total

chromium, and total nickel to determine whether high concentrations of chromium and/or nickel are present below the former platers, but above the underlying clay layer, and contributing to the groundwater impacts present at the site. The chromium concentrations were well below the applicable Method 1 standards. The concentration of nickel ranged between 21 and 42 mg/kg which exceeds the applicable Method 1 standard of 20 mg/kg. However, these concentrations are similar to those detected in soils previously identified throughout the footprint of the Former Plant #4 and consequently do not appear to represent an ongoing source to groundwater.

On June 20, 2008, five temporary monitoring points (B-1-08 through B-5-08) were installed with a Geoprobe direct push rig downgradient of well MW-8-06 to delineate the extent of the groundwater plume. Following installation of the wells, groundwater samples were collected via low flow methodology, from each of the temporary well points for analysis of hexavalent and total chromium. The locations of the points are included on Figure 1. Based on the elevated concentrations of hexavalent chromium in well points B-1-08, B-3-08, B-4-08 and B-5-08 DEP was notified of an Immediate Response Action (IRA) condition on July 9, 2008.

1.1.5 Immediate Response Action (IRA)

As previously discussed a pump and treat remediation system is currently operating at the site under a RAM for the remediation of hexavalent chromium-impacted groundwater. Following the detection of elevated hexavalent chromium in groundwater downgradient of the existing recovery wells in June 2008, DEP approved the installation of an additional recovery well (RW-5) that was piped to the remediation system under an IRA.

On October 16, 2008, recovery well RW-5 was installed in the approximate location of B-4-08 using a hollow stem auger drill rig. The location of the recovery well is included on Figure 1.

1.1.5.1 Sediment and Surface Water Sample Collection

As part of the IRA, semiannual sediment and surface water samples are collected from the Connecticut River at three locations (upstream, crossgradient, and downstream of the site) to confirm that the release is not impacting the river. The sampling was initiated in May 2008 and to date no detections of contaminants attributable to the release have been identified in the river.

2. SYSTEM DESIGN

The remediation design was based on a pump and treat system with recharge. The groundwater from five recovery wells (RW-1 through RW-5) is pumped through a two-inch high-density polyethylene (HDPE) pipe to a remediation building. The recovered groundwater flow goes through bag and cartridge filters for the removal of suspended solids. After these filters, the groundwater flows through a series of Siemens ion exchange resins for the removal of hexavalent chromium and nickel. The treated effluent from the ion exchange resins is stored in a tank, from which the majority of the water is pumped to the recharge pit and the remainder is discharged to the municipal sanitary sewer. The resins are transported off-site intact for regeneration and eventual re-use.

Conventional off-the-shelf treatment units were purchased for the removal of particulates, iron, hexavalent chromium and nickel from the recovered groundwater. The majority (approximately 80%) of the treated effluent is recharged upgradient of the recovery wells to expedite aquifer flushing through an underground pit and trench (Figure 1). The remainder of the treated effluent is discharged to the municipal sewerage system under a municipal Industrial Pretreatment Permit. System monitoring, including groundwater recharge elevations, is available within the treatment building and remotely via Supervisory Control and Data Acquisition (SCADA) systems.

3. OPERATION OF REMEDIAL SYSTEM

On a monthly schedule, samples from each of the recovery wells, system influent and effluent are screened with a Hach kit for total nickel and hexavalent chromium. Select samples may also be submitted for laboratory analysis to confirm the screening results. The data are used to determine if breakthrough is occurring from any of the resins. Based on the analytical data, the first resin cylinder was removed from the site on October 22, 2008 by Siemens for recycling and the remaining resins were moved up in line. A new resin cylinder was replaced at the end of the treatment. A second resin change-out was conducted in mid-February 2009.

The recovery well Hach results for nickel and hexavalent chromium, respectively, from each of the recovery wells are presented in Figures 2 and 3.

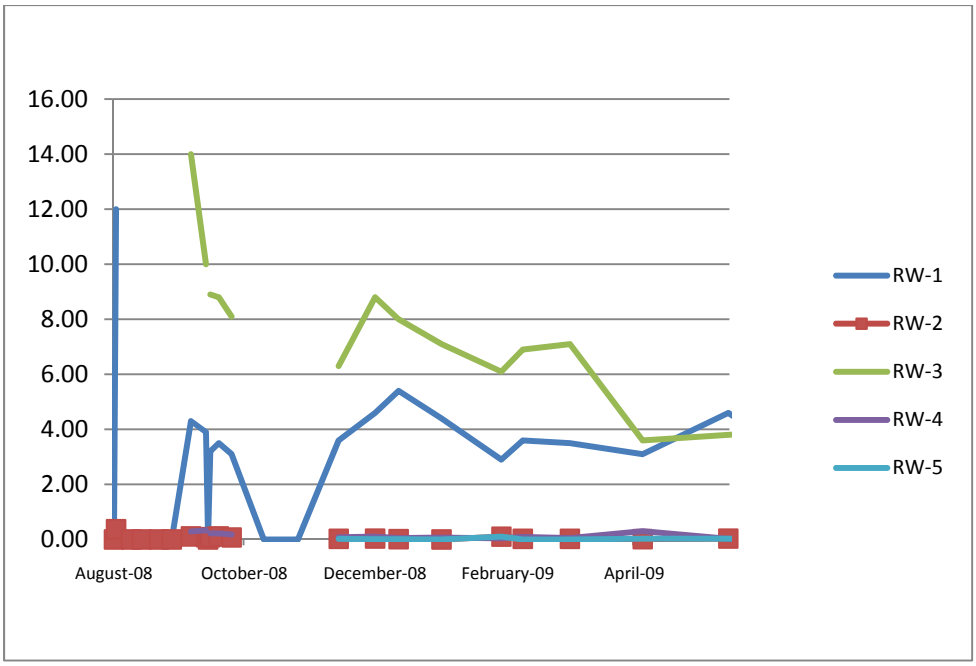

Figure 2. Graph of nickel concentrations between August 2008 and August 2009 in mg/l.

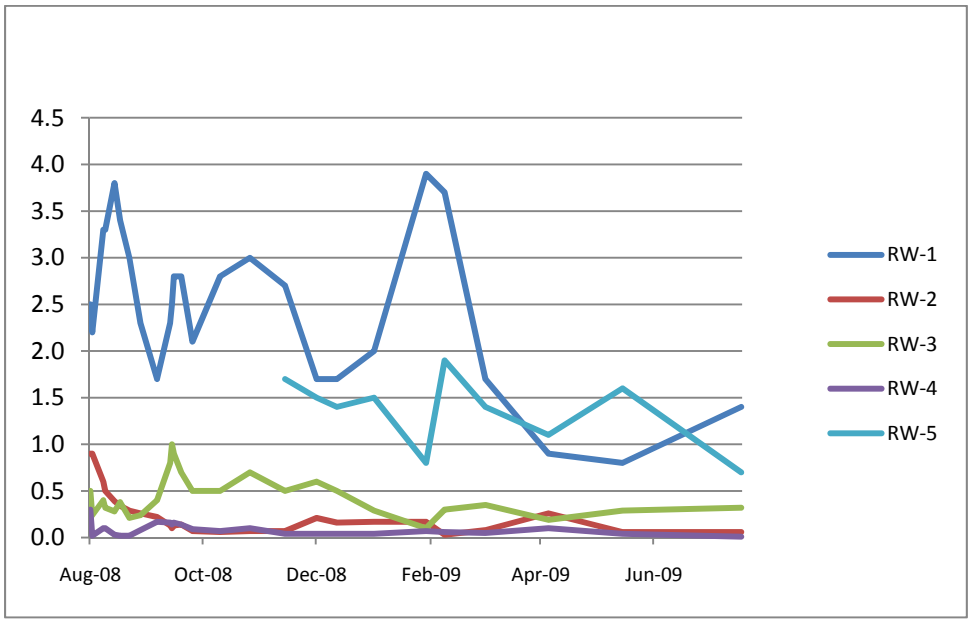

Figure 3. Graph of hexavalent chromium concentrations between August 2008 and August 2009 in mg/l.

4. CONCLUSION

Following demolition of the former industrial buildings and installation of the remediation system the site has been undergoing redevelopment. Two medical office buildings are currently being constructed on the site and a portion of the property is used as a parking lot for a nearby construction project. The remediation system layout was designed to maximize the developable portion of the site while still achieving the objectives of the cleanup.

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Chapter 7

MERCURY DEPOSITION FROM RAIN AND SNOW IN VIRGINIA

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ABSTRACT

Automated stations to collect rain and snow have been used for several years to quantify the weekly amount of mercury in rain and snow, and the weekly amount of precipitation, over much of the United States. Data from the Virginia collection sites in central and west-central Virginia are compiled and may be compared constantly to the on-line data reported from all the collection sites. While the sources for mercury in the atmosphere are numerous, most comes from coal-burning electrical power plants. Other locally significant sources of mercury exist, but none are known in central Virginia. Data show that the atmospheric content of mercury increases during prolonged intervals without precipitation (for example, several weeks without any rain or snow), and that the atmospheric content of mercury is exceptionally low following unusually prolonged precipitation events (several days or rain or snow). The regional variations of atmospheric mercury precipitation do not serve to identify any particular source of mercury (i.e., any particular coal-burning power plant), but instead indicate significant mixing of atmospheric mercury.

Keywords: mercury, pollution, precipitation

1. INTRODUCTION

The National Atmospheric Deposition Program (http: // nadp.sws.uiuc.edu/mdn/) of the U.S. Geological Survey and the U.S. Environmental Protection Agency established the Mercury Deposition Network (MDN) in 1995. The MDN consists

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of several hundred stations (ours is in Culpeper, VA) to accurately measure the concentration of mercury in precipitation in the United States and Canada. Data from the early years (through the present) of MDN activity showed that the greatest total amount of mercury precipitation was in the southeastern United States, around the Gulf of Mexico, probably because the area has relatively high total precipitation. The greatest amount of mercury precipitation during individual precipitation events is in the southwestern United States, which has low and infrequent precipitation events.

Atmospheric mercury is not considered dangerous to humans, but it becomes harmful following deposition, due to bioaccumulation and the formation of toxic mercury compounds in fish. High levels of mercury in fish is known to be dangerous if consumed by pregnant women and young children, because it causes birth defects and tissue damage (Gobeille et al, 2005). The toxic organic compound of mercury, methylmercury, moves through protective tissues and barriers in humans, including the blood-brain barrier and the placenta. More than 75% of the fish consumption advisories in the United States are due to high levels of mercury.

The national MDN database has been gathered to evaluate potential correlations between sources of mercury emissions to the atmosphere and mercury concentrations. It was anticipated that these measurements, plus an understanding of air movement in the atmosphere, could reveal areas where excess amounts of mercury emission and deposition occur. The central Virginia MDN site is operated in the Center of Basic and Applied Science in Culpeper, Virginia by faculty and students at George Mason University in Fairfax, Virginia. This MDN site, number VA-08, began providing weekly rainfall measurements and mercury collections in the fall of 2002. It is located about 30 kilometers east of site VA-28 located in western Virginia. This site is in the Shenandoah National Park. Site VA-28, and is operated by the United States National Park Service. These two sites are in comparatively close proximity to one another, but at different elevations (160 meters above sea level for the central Virginia site and 1075 meters for the western Virginia site). It was thought that knowledge would be gained by comparing the results from these two sites over 3 years, 2002 through 2005.

More than 30% of the mercury in the atmosphere is estimated to come from the factory production of metal, and almost 10% from the factory production of paper (Table 1). For this study, the most likely source for the mercury found in precipitation in the study area were assumed to be the coal-burning electric power plants located within 200 kilometers of these Virginia MDN sites. Data from the EPA Toxic Release Inventory (www . epa.gov/triexplorer) show that almost 60% of the atmospheric mercury in Virginia comes from such power plants.

Determining if there is a significant correlation between mercury deposition by precipitation and proximity to coal-burning power plants has been a continuing effort among concerned scientists. Increased regulation of coal combustion products has reduced mercury emissions, but mercury emission levels vary depending on the source and type of coal used, and the operating conditions at the plant. Currently no combustion regulation system is designed specifically designed for mercury removal, but particulate matter cleansing mechanisms control mercury emissions sufficiently to meet most standards.

Table 1. Estimates of mercury emissions in the Virginia EPA Toxic Release Inventory

Source of Mercury in the Atmosphere	**Emission in Kilograms**	**Percent of Total**
Coal-Burning Electric Utilities	575	58 %
Metal Production	320	33 %
Paper Production	70	7 %
Petroleum and Tobacco Production	11	1 %
Stone, Clay and Glass Production	7	1 %
Chemical and Other Production	< 1	trace

The processes by which trace elements like mercury are caught during the formation of cloud droplets, and then rain, sleet, hail or snow, or caught up by the impaction of precipitation drops, is well known (Walcek, 2003). What makes mercury more interesting is that most trace elements do not a typically occur in the gaseous state. At least in theory, atmospheric mercury should be deposited quickly, locally in proximity to, for example, the Virginia coal-burning electrical power plants.

2. METHODS

At all the MDN sites, precipitation is collected over 7 days in ultra-clean glass bottles, using a motorized collector that opens during the intervals of precipitation (Olson and DeWild, 1999). The cumulative weekly total precipitation is recorded, and with the water sample is sent to an EPA-approved laboratory to determine the mercury concentrations. From these data, total mercury and mercury concentrations are calculated, and these are shared among the MDN site operators. Mercury deposition data has recently been tabulated and made available on the Internet for the entire United States (NADP, 2007).

3. RESULTS

The annual mercury concentration in precipitation was about 7.5 ng/L (Table 2), which is similar to mercury deposition at the other MDN sites in Virginia and

adjacent states (Gay et al, 2006). The mercury concentrations tended to be higher in the summer and fall, which was also during these the time of highest precipitation, so the total amount of precipitated mercury is highest during these seasons. It has been speculated that higher atmospheric temperatures, which occurred during these seasons, facilitate greater dispersion of mercury (Banic et al, 2005).

It also appears that very large precipitation events can measurably reduce the atmospheric concentration of mercury. In the third week of 2003, Hurricane Isabel caused unusually steady and voluminous precipitation (plus high winds) over several days. The concentration of mercury in the precipitation was relatively low, probably because the early-storm precipitation washed most of the mercury out of the atmosphere in central Virginia (Kolker et al, 2004).

Table 2. Record of Mercury Deposition at VA-08 in central Virginia

Interval	**Concentration (ng/L)**	**Precipitation (**cm)	**Total Deposition (micrograms/square meter)**
Winter 02-03	5.7	9.2	0.5
Spring 2003	4.6	31.2	1.5
Summer 2003	10.3	42.3	4.3
Fall 2003	10	45.6	5.0
Winter 03-04	6.2	31.8	1.9
Spring 2004	8.8	12.0	1.0
Summer 2004	7.9	35.0	2.8
Fall 2004	7.0	37.0	2.6
Winter 04-05	4.3	31.2	1.4
Spring 2005	5.3	21.0	1.2
Summer 2005	7.9	21.9	1.8
Fall 2005	10.2	44.1	4.5
Winter 05-06	3.9	33.3	1.4

Mercury depositional network site VA-28, in the Shenandoah National Park in western Virginia, showed a generally similar pattern of mercury deposition to our central Virginia site. However, in the spring and summer, total mercury deposition at the higher-in-elevation western Virginia site was greater than at the lower central Virginia site, but the mercury was lower in concentration (Table 3). It seems likely that the greater total amount of precipitation at the western Virginia site brought down more mercury out the atmosphere, but diluted the mercury, compared to the central Virginia site.

Table 3. Record of Mercury Deposition at VA-28 in western Virginia

Interval	**Concentration (ng/L)**	**Precipitation (cm)**	**Total Deposition (micrograms/square meter)**
Winter 02-03	3.6	27.8	1.0
Spring 2003	4.4	47.1	2.0
Summer 2003	16.5	49.2	6.8
Fall 2003	9.9	64.4	4.2
Winter 03-04	4.8	39.0	1.8
Spring 2004	4.9	19.3	0.9
Summer 2004	8.4	37.9	3.2
Fall 2004	5.5	77.9	4.2
Winter 04-05	3.8	31.4	1.2
Spring 2005	4.1	24.3	1.0
Summer 2005	6.9	21.5	1.5
Fall 2005	6.9	41.7	3.1
Winter 05-06	3.4	51.5	1.1

4. CONCLUSION

Using the mercury data from MDN sites VA-08 in central Virginia and VA-28 in western Virginia, plus measurements from other MDN stations in the eastern United States, no correlations between mercury deposition and the location of mercury emissions into the atmosphere could be discovered. This is contrary to the anticipated results, but may have happened because: (1) The coal-burning plants do not, as is thought, generate most of the mercury in the atmosphere, (2) The majority of the mercury put into the atmosphere by the coal-burning precipitates well before it reaches sites in the MDN system, (3) The majority of the mercury, because of some not-understood process, is carried in the atmosphere well beyond the MDN sites in Virginia and adjacent states, and/or (4) more data from MDN sites are required to discover the depositional pathway for atmospheric mercury.

In the absence of measurements proving otherwise, it appears that the mercury deposition by precipitation in Virginia cannot be assigned or related to any of the mercury producing facilities in Virginia or elsewhere. The very similar mercury deposition record of the western and central Virginia sites suggests that mercury sources, including more nearby local sources, do not impact one MDN site more than another. At the present time, it appears that the pattern of mercury deposition is related to a large-scale source of atmospheric mercury. We suspect that the source from which the mercury deposited in central Virginia may, in the extreme,

involve most of the planetary atmosphere. In this model, the world's atmosphere contains a "pool" of disseminated mercury that continues to fall in the precipitation of Virginia and the rest of the planet's surface.

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Chapter 8

AN INVESTIGATION OF THE NATURAL AND ANTHROPOGENIC CONTRIBUTIONS OF ARSENIC TO URBAN FILL SOIL

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ABSTRACT

Arsenic in urban/historic fill soil, originating from both natural and anthropogenic sources, is a continuing concern from a human health risk point of view. This concern is heightened in urban gardens where the soil is to be used for growing vegetables for consumption.

The presentation explores the origin of arsenic present in New England urban/historic fill soil and will derive an understanding of the relative contribution of the natural and anthropogenic components using available data sets. These data sets include more than 5,000 urban soil samples from the Central Artery/Tunnel Project in Boston statistically analyzed using ProUCL 4.0. Data also includes more than 2,700 samples of a natural/rural background data set from a comprehensive study of rock and stream sediment arsenic in New England analyzed by the U.S. Geological Survey (USGS) (Ayotte and Robinson, 2007), supported by other available data sets resulting in a broad base of up to approximately 10,000 individual sample results. These multiple data sets will be reviewed and summarized such that there are a mean/median and upper values presented for natural soils and rocks and a mean/median and upper values presented for anthropogenic impacted soils, with and without outliers. From this compilation will be derived an understanding of the numerical differential between them. Finally, we will apply standard human health risk calculations, provided by the Massachusetts Department of Environmental Protection (MassDEP) (Office of Research and Standards, 2007), to illustrate the magnitude of potential effects of the natural soil and the anthropogenic–containing soil. The derived mean, median, and upper percentage values will be considered in the context of the human health risk assessment calculations. In conclusion, the

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exercise will identify the risk significance of the anthropogenic contribution relative to the natural soil and provide an understanding of the overall affect associated with background in the urban environment.

Keywords: Arsenic, anthropogenic

1. INTRODUCTION

The purpose of this investigation is to identify naturally and anthropogenic occurring concentrations of arsenic in soils in the Boston metropolitan area. Lead was included as a companion contaminant of concern. The investigation was undertaken by reviewing, summarizing, and working with readily available and relatively robust existing soil data sets. The identification of soil metal background concentrations is necessary in understanding what portion of the metals in a sample of urban/historic fill may be naturally occurring and defined as natural "background" concentrations. This understanding then provides the information needed to identify the anthropogenic component of the metals concentrations found in historic fill soil and also to understand relative risk-related impacts. From a regulatory perspective, natural conditions are not considered to pose an unacceptable risk in and of themselves regardless of the contaminant concentrations present.

Due to possible non-documentable anthropogenic influences, the data sets used cannot be claimed to represent purely natural soil results, with the exception of deep, uncontaminated clays and the referenced results of natural mineral/rock formations. However, we represent that this data assessment has resulted in moving relatively close to understanding the natural component for a number of metals, particularly in regard to the mean values for arsenic coupled with lead. Furthermore, the focus of a natural soil and urban fill metals assessment is logically directed to arsenic coupled with lead. These metals, in general, appear to exhibit the greatest human health risk significance based on our experience with risk characterizations at a multitude of urban/ historic fill sites.

2. MATERIALS AND METHODS

The following three data sets were readily available and utilized in this analysis:

Data for Natural Soil Located Immediately below Historic Fill: This data set was gathered from soil sampling and analysis results at a number of construction sites located in Boston and Cambridge. Data in this set is for soil that, by its location, visual assessment, and pre-characterization sampling and analysis site information, was identified as natural and was sampled and analyzed for reuse

following the removal of overlying historic/urban fill. The data is from soil expected to be relatively proximate to the original ground surface and under any organic layer, and tended to be relatively granular in nature. This data was believed to be the most representative of natural material of the several data sets considered with the exception of the marine clay (the third data set discussed below). The total number of samples with arsenic and lead results in this data set was 375. The exact locations are confidential per client request to allow use of the data.

Data for Central Artery/ Tunnel (CA/T) Soils: Data from the Central Artery/Tunnel Project, consisting of more than 6,000 soil samples, were sorted into two subsets of data and carefully adjusted to approximate the natural soil component. The two subsets, representing the 0-to17-foot-zone below grade and the >30-foot zone, were carefully reviewed. Some of the results were purged from the sets (as described below) to arrive at two data sets considered to represent the natural component of the metals. After reviewing the samples in the master data set, the total number of arsenic results was 3,523 while the number of lead results was 4,956. Following adjustment, more than 1,300 samples remained in the two sets and are considered as representative of natural soil. The >30-foot zone was appropriately believed to be largely representative of natural soil, while the shallower zone, even after adjustment, likely included results affected by an assortment of anthropogenic influences. Nevertheless, it was carried forward in the analysis since it was a considerable number of data points and could be advantageously contrasted with the other data. The 0-to-17-foot-zone was used rather than a 0-to-15-foot zone (MassDEP soil criteria: soil categories S-1, S-2, S-3 of the Massachusetts Contingency Plan) (Deparment of Environmental Protection, 2007) in order to capture a large number of split spoon soil boring samples programmatically collected in the 15-to-17-foot interval. Samples from >30 feet were generally assumed to be natural and were also presumed to include marine clay or a fine grained soil component. The data was used with permission of the project, with no identification herein of the exact locations upon client request.

Data for Marine Clay: This data set is from marine clay presumed to be entirely natural material deposited over a considerable period of time. This material was overlain by granular soil, a thin organic layer, and historic fill. The total number of marine clay samples was 240. The exact locations are confidential per client request to allow use of the data.

These three data sets were then tabulated along with two of the data sets from the MassDEP document (Office of Research and Standards, 2002), which were considered by MassDEP when selecting natural soil background maximums concentrations. The tabulation added weight to the overall analysis results and

allowed closer comparison with the MassDEP's previously selected numbers. The CA/T data set of the MassDEP document is an initial portion of the more than 6,000 results mentioned above.

The remaining available samples from the first three data sets, with outliers removed and summing in the two data sets from prior MassDEP work, totals more than 2,600 individual arsenic analyses and more than 3,000 individual lead analyses. More exact counts are provided in the tables below under the results and discussion section.

In regard to data management, the sample sets were reviewed and adjusted as follows:

Any metals data set with greater than 50% non-detects was not viewed as viable for our analysis and was not carried forward. This decision did not affect any arsenic or lead data sets. This approach eliminated antimony, selenium, silver, and thallium from the natural and CA/T soil data sets. These evaluations were focused on Resource Conservation and Recovery Act RCRA 8 or priority pollutant 13 lists of metals.

For management of the natural soils data set, the presence of volatile organics or polycyclic aromatic hydrocarbons was used to discriminate potentially affected soils and remove these from the data set. While the presence of organics does not necessarily mean the metals are anthropogenic, it was believed this approach would result in a more representative data set.

In managing the CA/T data set, most samples with lead in excess of 20 milligrams per kilogram mg/kg were rejected, as we surmised that 20 mg/kg is a natural background limit for lead. A review was conducted for the presence of other contaminants, particularly semivolatile organic compounds (SVOCs), and of lead at concentrations well above 100 mg/kg. This review was used to remove samples that appeared to be historically influenced or were likely part of sites of a release. These findings were also applied across the other metals tabulations to adjust the other metals data sets. As the MassDEP natural background concentration for lead is set at 100 mg/kg, this was initially used as a discriminator, with 20 mg/kg appearing to offer a more conservative threshold value based on the patterns in the results suggesting releases. We reviewed the data for surrounding samples initially removed as outliers/ anthropogenic influenced samples or sites of release, and surmised the high results, including lead concentrations, behaved more akin to a release than natural phenomenon. While this approach is questionable in certain respects, the results suggest a reasonably good fit with the other data sets and that the approach resulted in useful information.

Finally, the selected method of removing "outliers" (Department of Toxic Substances Control, 2007) was applied to further adjust the data assuming natural soil would exhibit a normal distribution. This method was selected from the literature and had been extensively applied to school sites in California with arsenic issues. The method removed outliers in a consistent mathematical manner. Data sets with and without these outliers are presented as the mathematical approach does not guarantee of definition of an outlier. The method uses quartiles. The data set is divided by the median number and then each sector is divided again giving a median number for the group above and the group below the overall median. Any number 1.5 times the range between the secondary (25% and 75%) medians is considered to be an outlier in either the high or low direction.

3. RESULTS AND DISCUSSION

Tables 1, 2, and 3 illustrate the treatment of the data sets for arsenic and lead, with and without outliers. This presentation is following the removal of those samples believed to be contaminated based on concentration patterns of other contaminants as described above and high lead levels. Note that the 0-to-17-foot CA/T data set had the largest number of outliers, a probable reflection of the residual anthropogenic influence not captured by the other adjustments. Since the computed number of outliers was consistently lower in the other data sets, and may have even included some natural soil results, less credence can be placed on the 0-to-17-foot set. It is suggested that the removal of outliers from that set may have made it reasonably comparable to the other sets. Hence, it was included in the analysis and the relative values portray a reasonably good fit.

The lowest metal concentrations were evident in the shallow and more granular soil, which was presumed to be natural, followed by the purged urban fill, mainly natural deeper soil, and natural marine clay. The mainly natural deep soil would have included a marine clay component and the purged urban fill was from a zone similar to the natural and just below it. This progression of increasing concentration suggests a consistent pattern of increased metals concentration with depth as the clay/fine grained component increases.

For contrast and verification of results, we provide a comparison against the MassDEP 2002 background document data sets for natural soils (Table 4). For metals, it is noted that the data from Haley & Aldrich (H&A) and the MassDEP (Office of Research and Standards, 2002) was introduced for a comparative review, carrying over the median/geometric mean, which differs from the median and the arithmetic mean of the other sets. That is the reason for bolding the values in the table. Also, we did not investigate the outlier issue in the two "borrowed" data sets in this comparison. Although the two data sets from the 2002 document

are not entirely comparable, we believe they are in fact mathematically proximate and may reasonably be displayed together. The geometric mean/median placement of the results in our mean column is noted in bold to be cautioned as not directly comparable. Generally, metals results are higher in the deeper finer grained soil.

In considering the results for arsenic, it can be surmised the MassDEP set most likely reflects more samples in the "arsenic belt" west of the Boston Metro area, while the data provided by the H & A data set is comparable by location to the natural and two purged CA/T sets (Table 4). The lead results in the MassDEP

Table 1. Natural Soil Collected Below Urban Fill by CDM (Concentrations in mg/kg)

Parameters	**Arsenic**	**Lead**
Detects	334	292
Non-Detects	3	51
Total	337	343
Number of Outliers	6	1
Deduct Outliers	331	342

Original Set	**Arsenic**	**Lead**
Mean	4.9	7.3
Median	4.4	7.6
80%	7.0	11.0
90%	9.2	13.0
95%	10.0	15.0

Outliers Removed	**Arsenic**	**Lead**
Mean	4.8	7.3
Median	4.3	7.6
80%	6.8	11.0
90%	8.8	12.0
95%	10.0	15.0

and H & A data set tend to be higher. This finding suggests there may be a quantity of anthropogenic material in these sample sets, or an outlier effect, and these sets did not appear to have outliers removed in any described manner. The MassDEP natural maximum values appear in the last column and results equal to or greater than these are illustrated for all the metals.

The remaining metal sets are relatively consistent for each parameter as well, with the following variations noted:

- Barium: H & A and CDM consistent, marine clay higher, MassDEP set lower
- Chromium: Relatively consistent, MassDEP set lower
- Copper: H & A and MassDEP higher in 90% and 95% categories, possible anthropogenic/outlier influence
- Nickel: MassDEP lower and H & A higher than our three sets
- Vanadium: MassDEP lower than CDM natural set
- Zinc: H & A and MassDEP higher in 90% and 95% categories, possible anthropogenic/outlier influence

Table 2. CA/T Soil Data Sets (0-to-17 feet) (Concentration in mg/kg)

Parameters	**Arsenic**	**Lead**
Detects	1018	831
Non-Detects	52	542
Total	1070	1373
Number of Outliers	46	3
Deduct Outliers	1024	1370

Original Set	**Arsenic**	**Lead**
Mean	6.1	8.0
Median	4.6	7.0
80%	9.0	13.0
90%	12.0	16.0
95%	15.0	18.0

Outliers Removed	**Arsenic**	**Lead**
Mean	5.2	7.9
Median	4.4	6.9
80%	8.0	13.0
90%	10.0	16.0
95%	12.0	18.0

As a further consideration and comparison, the USGS collected a large data set consisting of 1,597 stream sediment and 1,279 rock samples (2,876 total samples) in their quest for better identification of arsenic sources in the New England area. This was in response to problematic concentrations of arsenic in potable water wells (Ayotte and Robinson, 2007). In summary, the natural rock average was 7 mg/kg and the stream sediment average was 5.5 mg/kg. They note

that the stream sediment might be expected to contain some anthropogenic influence, particularly from the agricultural sector. The 5.5 mg/kg total arsenic value is close to the result extracted from the 0-to-17 foot value from the CA/T data set at 5.2 mg/kg. There is, moreover, consistency with these average results and all the soil results described above as they range from 4.7 mg/kg to 12 mg/kg total arsenic.

Table 3. CA/T Soil Data Sets (> 30 feet) (Concentration in mg/kg)

Parameters	**Arsenic**	**Lead**
Detects	326	215
Non-Detects	17	142
Total	343	357
Number of Outliers	9	0
Deduct Outliers	334	357

Original Set	**Arsenic**	**Lead**
Mean	8.1	7.1
Median	4.6	5.2
80%	9.0	12.0
90%	14.0	15.0
95%	16.0	17.0

Outliers Removed	**Arsenic**	**Lead**
Mean	7.5	7.1
Median	6.6	5.2
80%	11.6	12.0
90%	14.0	15.0
95%	15.0	17.0

4. CONCLUSIONS

The MassDEP maximum background soil detection for arsenic of 20 mg/kg for natural and urban fill soil is well supported by the above findings. While the derived natural soil numbers only bring one into a range of values due to limitations in identification and management of outliers, the results do provide valuable information. The data helps us understand background detection concentrations in the Boston Metro Area, as well as lend considerable overall support to the MassDEP selections in the 2002 document. While we believe natural lead in soil is generally less than 20 mg/kg, we suggest that the 100 mg/kg MassDEP number appears to be a reasonable maximum.

Table 4. Comparison of Data Sets Inclusive of MassDEP (2002) Sets

PARAMETERS (Total Samples in Group)	Sample Sources	Samples by Source	RESULTS				MassDEP (2002) Natural Background Number
			Mean	Median	90%	95%	
ARSENIC (2,653)	Natural	331	4.8	4.3	8.8	10	20
	CA/T 1	1024	5.2	4.4	10	12	
	CA/T 2	334	7.5	6.6	14	15	
	Marine Clay	236	12	12	14	16	
	DEP (1995)	139	*4.7*	4.8	17	24.5	
	H&A 2001	589	*5.5*	5.6	11	13	
BARIUM (1,125)	Natural	334	31	27	62	74	50
	CA/T 1	-	-	-	-	-	
	CA/T 2	-	-	-	-	-	
	Marine Clay	237	86	88	100	100	
	DEP (1995)	64	*15*	16	45	52.8	
	H&A 2001	490	*35*	36	80.9	89.3	
CHROMIUM (2,700)	Natural	333	19	16	37	42	30 (total)
	CA/T 1	1052	19	16	40	45	
	CA/T 2	342	37	37	60	63	
	Marine Clay	237	45	46	50	52	
	DEP (1995)	147	*10*	11	29	39	
	H&A 2001	589	*22*	22	44	50	
COPPER (1,647)	Natural	172	15	16	27	29	40
	CA/T 1	1010	16	14	28	32	
	CA/T 2	340	23	24	34	37	
	Marine Clay	-	-	-	-	-	
	DEP (1995)	103	*7.7*	7.3	38	56	
	H&A 2001	22	*26*	27	48	65	
LEAD (3,029)	Natural	342	7.3	7.6	12	15	100
	CA/T 1	1370	7.9	6.9	16	18	
	CA/T 2	357	7.1	5.2	15	17	
	Marine Clay	236	11	11	12	13	
	DEP (1995)	141	*20*	19	99	158	
	H&A 2001	583	*15*	24	79	112	
NICKEL (1,750)	Natural	280	15	14	25	30	20
	CA/T 1	1002	16	14	31	37	
	CA/T 2	343	28	29	43	45	
	Marine Clay	-	-	-	-	-	
	DEP (1995)	103	*4.6*	5.1	17	23	
	H&A 2001	22	35	35	68	70	
VANADIUM (73)	Natural	43	33	26	56	61	30
	CA/T 1	-	-	-	-	-	
	CA/T 2	-	-	-	-	-	
	Marine Clay	-	-	-	-	-	
	DEP (1995)	30	*7.6*	10	29	39	
	H&A 2001	-	-	-	-	-	
ZINC (1,772)	Natural	281	38	37	63	71	100
	CA/T 1	1017	46	42	81	93	
	CA/T 2	340	69	71	99	104	
	Marine Clay	-	-	-	-	-	
	DEP (1995)	112	*29*	28	116	131	
	H&A 2001	22	*67*	59	103	106	

NOTES: DEP (1995) and H&A (2002) from (Office of Research Standards, 2002). Italic mean values are "geometric mean or median" which differ from the mean. Shaded at or in excess of MassDEP (2002) selected number.

For further reference and information, the mean of the 0-to-17-foot CA/T samples for arsenic and lead, inclusive of all samples, was computed to be 8.9 mg/kg and 310 mg/kg respectively. This most closely fits in comparison to the ranges for natural soil derived above as shown in the Tables, per the adjusted 0-to-17-foot data set. These urban fill averages were derived using all values and ProUCL 4.0 as provided by U.S. Environmental Protection Agency. Our comparison with the derived natural component 0 to 17 feet suggests that anthropogenic arsenic and lead contribute approximately 8.9-5.2/8.9 =42 % and 310-7.9/310=97% to the urban/historic fill average respectively. This relationship also represents that portion of the potential human health risk impact of each. Furthermore, for arsenic, the 5.2 mg/kg and 8.9 mg/kg results, were applied to MassDEP Method 3 risk calculations per their short form. This application results in an excess lifetime cancer risk (ELCR) of 4E-06 and 7E-06 respectively, exclusive of the vegetable growing scenario. The 90% level of 10 mg/kg is close to the allowable no significant risk threshold of 1E-05 (ELCR).

As a final note, no data set can be viewed as purely natural other than the marine clay. Use of large data sets brings a certain perspective to the natural and historic fill environment and assists in understanding the magnitude of the source of metals present in natural soil and urban/historic fill. The data sets presented above are complementary and provide a range of natural soil metals concentrations in the Boston metro setting.

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Chapter 9

ARSENIC CLEANUP CRITERIA FOR SOILS IN THE US AND ABROAD: COMPARING GUIDELINES AND UNDERSTANDING INCONSISTENCIES

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ABSTRACT

Widely divergent cleanup targets, guidelines and standards for arsenic in soils have been established by many regulatory, scientific and advisory organizations in the past 25 years, both in the United States and in other countries. In contrast to many other substances, for which guidelines and standards are similar or identical among agencies, arsenic has provided a powerful study in just how many different ways a single issue can be viewed. This paper provides a detailed survey concerning the breadth of arsenic soil criteria that have been proposed and applied, and explores the basic differences in their derivation, which can be based upon toxicological properties, geological background levels, anthropogenic background contributions, and practical site-specific considerations. A broad comparison of extant values in common use for USEPA, individual states, and non-US entities will be presented, coupled with a discussion regarding common examples of the technical bases for arsenic soil cleanup guideline development. Arsenic target levels in many cases can dominate remedial considerations at sites where the applicable criteria are very stringent. Several case studies will be presented to illustrate the problems that are inherent in such variable criteria for this ubiquitous and extraordinarily common substance.

Keywords: Arsenic, soil, cleanup guidelines, criteria, risk, variability

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1. INTRODUCTION

Over the past few decades, arsenic has been increasingly examined and analyzed due to its toxicological properties, broad aspects of exposure potential, and historically inconsistent cleanup targets and guidelines. Arsenic is a metalloid found naturally at high concentrations in some soils that can not be destroyed by the environment; however, it can change form (e.g., organic to inorganic, altered valence states) or become attached to or separated from particles. Arsenic is a known human carcinogen at sufficient levels in water and air, but credible reports of soil-based health effects are quite limited. There are a variety of soil cleanup guidelines from the U.S. Environmental Protection Agency (USEPA), state agencies, and international agencies. The guidelines vary across about a 1000-fold range (0.039 to 40 mg/kg) in the U.S. alone. In this summary report, we present many of these guidelines, and explore the various foundations and supporting information on which the guidelines are predicated.

2. REVIEW OF ARSENIC SOIL CRITERIA IN THE U.S. AND ABROAD

2.1 United States

The USEPA Regional Screening Level (RSL) for soil arsenic under unrestricted use (e.g., residential) assumptions is 0.39 mg/kg (USEPA, 2009). This level is based on a target cancer risk of 1E-06, toxicological guidance values from the Integrated Risk Information System (IRIS), and standard assumptions for exposure assessment and risk assessment. As shown on Table 1, many of the individual state guidelines for residential soil are taken directly from, or calculated very similarly to, the USEPA RSL. However, some states use an alternative cancer risk level and/or different exposure assumptions, and many states take into consideration the presence of arsenic at significant concentrations in naturally occurring background soils. Section 3 presents details on the various derivations of selected guidelines that are presented in Table 1.

2.2 International

The international guidelines that were reviewed provide considerable grounds for additional in-depth research. As with the US guidelines, the international levels have diverse, and often unexplained, foundations, which result in widely varying concentrations. In general, however, the international guidelines are consistently

higher than the US numbers (5 mg/kg to 150 mg/kg for the selected countries that were reviewed; see Table 2).

3. ARSENIC SOIL CRITERIA: BASES & ASSUMPTIONS

3.1 Health Basis

The USEPA (2009) Regional Screening Levels (RSLs), as well as many state guidelines, are based on typical human exposure assessment assumptions (350 days/yr, 30 yr residence during a 70-yr lifetime, 100% relative bioavailability) and standard toxicological guidance values. The cancer target risk ranges from 1E-07 to 1E-04. At least 14 states (see Table 1) employ the USEPA RSL methodology and a 1E-06 cancer risk level, resulting in default guidelines that fall tightly between 0.38 mg/kg and 0.41 mg/kg. As noted later, that range is less than commonly encountered background soil arsenic levels in much of the country.

Whereas a systemic, or noncarcinogenic effects guideline typically is calculated as part of the process, it almost always is deferred based on using the lower of noncarcinogenic versus carcinogenic values. The exception is Texas, which uses a cancer risk level of 1E-04, resulting in a guideline of 34 mg/kg. The calculated noncancer guideline is 24 mg/kg, which thus becomes the state default Tier 1 Protective Concentration Level for residential exposure circumstances (TCEQ, 2009).

Recent information suggests that ongoing reassessment efforts by USEPA may further restrict the oral Cancer Slope Factor by as much as 15-20x, based on bladder and lung cancer studies. It should be noted that internal and external technical reviewers have rightly questioned such a dramatic reduction, noting that if those assumptions were correct we should be seeing an epidemic of bladder and lung cancer in the U.S., given that current drinking water guidelines are, and have been for decades, well above the new proposals in terms of ingested dose. The same can be said for the many countries outside the U.S. that have arsenic guidelines in drinking water and in soil that permit intakes that are considerably higher than the calculated health-based soil levels.

3.2 Ambient Background Basis

Many states use naturally occurring background soil arsenic levels as their default screening guidance. While these typically rely on geologic conditions, some jurisdictions also consider the possibility of historical anthropogenic contributions. The background concentrations found and reported herein range from 7 to 40 mg/kg. For Rhode Island, 7 mg/kg is the default guideline, based on

Table 1. Selected state cleanup guidelines for arsenic in soil for residential/unrestricted use.

State	**Guideline (*mg/kg*)**	**Basis**
Wisconsin (WDNR, 2009)	0.039	Cancer (10^{-7} risk level), standard risk assessment assumptions and toxicological guidance values
California (CalEPA, 2005)	0.07	Cancer (10^{-6} risk level), 4% dermal absorption assumption, CalOEHHA Slope Factors
AL (ADEM, 2008), CO (CDPH, 2007), DE (DNREC, 2007), ID (IDEQ, 2004), LA (LDEQ, 2003), MD (MDE, 2008), MS (MSDEQ, 2002), NC (NCDENR, 2005), OK (OKDEQ, 2007), OR (ODEQ, 2005), VA (VDEQ, 2009), WV (WVDEP, 2009), WY (WDEQ, 2009)	0.38 to 0.41	Cancer (10^{-6} risk level), either direct cite to EPA, or state-specific calculation with standard risk assessment assumptions and toxicological guidance values
Maine (MDEP, 2009)	1.4	Cancer (10^{-5} risk level), CalOEHHA Slope Factors
Florida (FDEP, 2005)	2.1	Cancer (10^{-6} risk level), 33% oral bioavailability, state-specific exposure assumptions
New Mexico (NMED, 2009)	3.59	Cancer (10^{-5} risk level), standard risk assessment assumptions and toxicological guidance values
Indiana (IDEM, 2009)	3.9	Noncancer soil-plant-human uptake (based on USEPA soil screening guidance)
Ohio (OEPA, 2008)	6.7	Cancer (10^{-5} risk level), 3% dermal absorption assumption
AZ (ADEQ, 2002), IA (IDNR, 2004), KS (KDHE, 2007), KY (KEEC, 2004), MA (CMR, 2003), MN (MDEQ, 2005), MO (MRBCA, 2006), NH (NHDES, 2007), NJ (NJAC, 2008), NY (NYSDEC, 2006), PA (PDEP, 2001), RI (RIDEM, 1996), WA (WAC, 2007)	7 to 40	State-specific Natural Background
Texas (TCEQ, 2009)	24	Noncancer (lower than cancer endpoint at 10^{-4} risk; 34 mg/kg)

Table 2. Selected international cleanup guidelines for arsenic in soil for residential/unrestricted use.

Country	**Guideline** *(mg/kg)*	**Basis**
Finland (FME, 2007)	5	Threshold value based on background and groundwater protection; lower and upper guidance values for ecological endpoints are 50 and 100 mg/kg, respectively; human health-based values were less restrictive
Canada (CCME, 2007)	12	Soil Quality Guideline - lower of the human health SQG or eco SQG
UK (England, Northern Ireland, Wales; UKEA, 2009)	32	Derived from UK oral Index Dose for drinking water, based on oral and dermal exposure of a young child
Netherlands (NEAA, 2008)	76	Soil Intervention Value indicating severe contamination condition – based on 10^{-4} risk level
Australia (ANEPC, 1999)	100	Health-based Investigation Level based on protection of a 2.5 year old child exposed to 100 mg soil/day via oral, dermal and inhalation routes
Japan (JME, 2003)	150	General soil value; 15 mg/kg applies to rice fields

the upper limit of statewide natural background, and any detection above this level is initially assumed to be from a release of arsenic-containing material (RIDEM, 1996). Kentucky's guideline (9.4 mg/kg; KEEC, 2004) represents the 95% upper confidence limit of the mean ambient background, and Illinois (IEPA, 2007) employs the mean concentration of soil samples from non-metro counties (11.3 mg/kg). Additionally, based on ambient background, New Jersey (NJAC, 2008) uses a concentration of 19 mg/kg and Montana uses 40 mg/kg, based on the 95% UCL of 209 native soil samples (MDEQ, 2005). These guidelines are all derived from different aspects of the land including varied backgrounds and soil types, but clearly are independent of considerations regarding potential health effects. Again, given the widespread existence of elevated arsenic concentrations in soil, many of which are naturally occurring, the question has been raised regarding an apparent absence of arsenic-related adverse health effects in those states.

3.3 Alternative Basis

At least one state agency, Indiana (IDEM, 2009), bases their soil arsenic screening guideline on a soil-plant-human exposure pathway uptake estimation. The Residential Closure Level for direct exposure in Indiana is 3.9 mg/kg, and is calculated based on the USEPA (2006) Soil Screening Guidance for vegetable uptake.

3.4 Bioavailability Considerations

The Florida Department of Environmental Protection (FDEP) commissioned the University of Florida to conduct a primate feeding study to determine the relative oral bioavailability of arsenic in several Florida-specific soils. Based on the results of that study (Roberts et al., 2001), the FDEP soil cleanup target levels for arsenic employ an oral bioavailability adjustment factor of 3x. On that basis, combined with other route-specific considerations, the Florida default direct exposure Soil Cleanup Target Level (SCTL) was adjusted from 0.8 mg/kg to 2.1 mg/kg for the cancer endpoint (FDEP, 2005). No other state agencies were identified which explicitly incorporate bioavailability of less than 100% in calculating state soil arsenic guidelines.

4. REGULATORY APPLICATION AND CHALLENGES

Due to arsenic's prevalence and long history of use, academic study, and regulation, it would seem that more wide-ranging consensus concerning health protective guidelines would exist in the regulatory community. The rather obvious, somewhat rhetorical, questions raised earlier regarding the lack of arsenic-related health effects, when ostensibly health-protective levels are exceeded on a routine basis, demonstrates the challenges that arsenic presents, particularly in soil and other non-drinking water exposures.

4.1 Case Studies

A relatively similar list of site types can be compiled across states, based on known industrial, commercial and recreational land uses. The following are selected examples of the categories of sites commonly identified where arsenic in soils can be a significant consideration.

Golf Courses - frequently have elevated soil levels due to historical arsenical herbicide/pesticide use. Site-specific risk-based protective levels are rarely exceeded when realistic exposures are considered (e.g., reduced frequency of exposure, exposure unit concentrations). Recent increases in reconfiguration and residential development of some golf courses has caused a recent focus on the issue.

Former Agricultural Properties - notable impacts from proper, legal, historical application of fertilizers. Can be financially and technically difficult to convert to residential use with sitewide exceedances of health-based criteria.

Railroad Rights of Way - common to find elevated soil arsenic due to historical arsenical herbicide use. Rails-to-trails conversions and other beneficial

use projects typically must demonstrate that risks are limited based on planned use and engineering controls (e.g., paving, fencing, mulching, ground cover maintenance).

Coastal and Mountain Properties - may show elevated background soil arsenic as a result of marine environments or local geologic formations. Costly characterization often is needed to prove natural occurrence.

4.2 Historical Perception

In addition to the beneficial applications and natural occurrence which result in enhanced presence of soil arsenic relating to the land uses discussed above, arsenic has a historical media presence that often overshadows the apparent limited risk that it may pose from direct soil exposures. Arsenic is a classic, archetypal poison at high levels, yet it also is an historical and ongoing medicinal agent, currently approved for treatment of very specific cancer conditions (relapsed or refractory APL). Furthermore, recent media and regulatory attention pertaining to tanning beds being deemed "equally as deadly as arsenic and mustard gas" produced unfortunate comparisons. This leaves the impression that arsenic, no matter the exposure medium or conditions, is deadly. Even under the exposure condition that is closest to that which forms the basis for the toxicological guidance values, that of drinking water ingestion, the protective level is not health-based. Rather, the present arsenic MCL (10 ug/L) is based on considerations of technical and feasibility limitations of drinking water supply systems, and is promulgated at a level considerably higher than if it were strictly health-based. Further, the immediate former MCL was 50 ug/L for approximately 50 years. Yet, there evidently is no related cancer epidemic to report.

5. DISCUSSION

While an abundance of caution should always be the rule when assessing risk, the evaluation of potential risk from exposure to arsenic in soil suffers greatly from a lack of consensus from the regulating and scientific community. There recently has been proposed a downward change to toxicity guidance that, if implemented, will lower health-based soil guidelines 15-20x. In Florida alone, this will once again result in guidelines that are below 1 ppm, a level that is not significantly different than natural background throughout much of that state, and indeed the nation. In the classic toxicologist's quote from Paracelsus nearly 500 years ago, the dose makes the poison. In the case of arsenic in soil, it is evident that what that dose may be, and its health significance, is open to interpretation, and theoretically ranges from less than 0.05 parts per million to well over 100 parts

per million. The continued reliance on the jumble of guidelines that are either health-based, but inappropriate for most soil exposures, or that are based on natural background, with no acknowledgement of potential toxicity at all, does not serve the science of risk assessment or toxicology well.

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PART III: Modeling

Chapter 10

USING GENETIC ALGORITHMS ON GROUNDWATER MODELING PROBLEMS IN A CONSULTING SETTING

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ABSTRACT

This paper presents a practical application for writing and applying simple genetic algorithms (GAs) for the common groundwater flow model, MODFLOW. The method employed by GAs is derived from the driving forces of evolution in the natural world. They employ functions that mimic natural evolutionary processes including selection, mutation, and genetic crossover. A GA solves mathematical problems where a desired outcome to the problem is defined (for example, calibration targets or remediation goals), but the inputs needed to arrive at this outcome are unknown. Our paper includes an introduction to genetic algorithms, the pseudocode of our genetic algorithm for MODFLOW, and the results of an experiential application. Due to the lack of commercially available GAs for MODFLOW, we coded a simple algorithm in Visual Basic Script and applied it to an example model. In the example model, the GA was used to conduct parameter estimation on a MODFLOW model of a river basin in New England that we had previously developed and calibrated in our practice. The calibration target used was net groundwater flow into the river. Four model input parameters were selected as chromosomes for the GA to act on: recharge, river conductance, and two general head boundaries. An initial population of 100 models was developed by varying the value of the gene parameters. The GA ran a MODFLOW simulation for each member of the population, extracted each output file, and established the error of each model from the calibration target. It then evolved the entire population of models towards the calibration target. The GA converged on a single set of input parameter that established best-fit values for all of the

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chromosome parameters. Genetic algorithms provide a practical alternative to trial-and-error and automated statistical calibration procedures, and can also be used for optimization.

Keywords: groundwater modeling, MODFLOW, parameter estimation, optimization, genetic algorithm.

1. INTRODUCTION

This paper presents a practical application for writing and applying simple genetic algorithms for MODFLOW. Such algorithms can be used for optimization and/or parameter estimation in groundwater modeling problems. The method presented is intended for environmental consultants who may tend away from using evolutionary algorithms in their practice due to the associated complexities and costs. Below we have presented a brief introduction to genetic algorithms, the pseudocode of our genetic algorithm for MODFLOW, and the results of an experiential application of this code to a parameter estimation problem.

1.1 Uses and Structure of Genetic Algorithms

The purpose of genetic algorithms (GAs) is to solve complex mathematical problems. GAs can be applied to almost any real world problem that can be structured numerically, from manufacturing supply-chain management to host/parasite relationships. Economic, legal, or political optimization can also be solved, as long as the problem can be constructed numerically (Mitchell and Taylor, 1999).

GAs are derived based on the driving forces of evolution in the natural world and include functions that mimic natural evolutionary processes including selection, mutation, and genetic crossover. A GA solves mathematical problems where a desired outcome to the problem is defined (for example, calibration targets or remediation goals), but the inputs needed to arrive at this outcome are unknown (input parameter values, numbers and locations of pumping wells, etc).

Genetic algorithms have many advantages over derivative-based optimization techniques, such as linear programming (Rizel and Eheart, 1994). They do not require continuity or convexity of the objective function (Espinoza et al., 2005). They are also free of the numerical difficulties that are frequently associated with derivative based optimizers (Wang and Zheng, 1997), and they can incorporate changing conditions and noisy observational data (Fogel, 2008).

In GA terminology, the term *member* refers to a set of trial input parameters. *Chromosomes* refer to each input parameter. When the chromosomes of a

specific member are input into the problem and the problem is solved, the result will contain some degree of error when compared to the desired solution to the problem. Those members with less error are described as being *fitter* than those members with more error. *Population* refers to a collection a members. Populations are developed in a series of iterations, called *generations*. *Parent* population refers the ith iteration of populations and *child* population refers to the ith + 1 iteration (Mitchell and Taylor, 1999). Genetic algorithms allow the population to evolve over many generations until the population of resulting members converge on the desired solution. The evolutionary process includes these basic steps: 1.) an initial population is developed 2.) the fitter members of the population are selected as parents for the next generation 3.) mutation and genetic cross-over are conducted on the parent generation to create the child population, and 4.) steps 1-3 are repeated iteratively to move the entire population closer to the desired solution (Fogel, 2008).

An important step in any GA effort is the selection of GA operative parameters. These are differentiated from the chromosome parameters as follows: The chromosome parameters are inputs to the mathematical problem to be solved. The GA operative parameters are the parameters that control the GA mathematical algorithm. These include the population size, the number of generations, and the mechanism and frequency of cross-over, and mutation.

Since the 1970s researchers have been striving to identify a set of guiding principals that apply across all applications to establish equations for calculating operational parameters (Fogel, 2008). However, the work of D.H. Wolpert and W.B. Macready, *No Free Lunch Theorems for Optimization*, presented a proof showing that any possible guideline to setting operational parameter values is, by definition, problem-specific (Wolpert and Macready, 1997). That is, there are no universally applicable guidelines that can be used with all problems.

Although the No Free Lunch theorem indicates that absolute guidelines for setting parameter values cannot be established, it is certainly possible to set unsuccessful parameter values that will cause the GA to fail. For example, too large a mutation/crossover rate could cause the GA not to converge; too low a mutation/crossover rate could cause the GA to converge early; too small a population size could result in fewer solution sets being explored; etc. Another problematic phenomenon that has been identified is genetic drift, which occurs when mutation/crossover causes genes to fluctuate away from the best solution set and converge on non-optimal values. Reed et al. (2000) presented a method for setting certain GA operational parameters with the goal of avoiding genetic drift and poor solution set search for water resource problems. Such techniques may be helpful in establishing initial parameter values which can then be refined through trial and error.

Considering the still weak theoretic basis for GAs, perhaps the best method of determining that GA operative parameters have been set appropriately is that they result in convergence on a successful solution. As Back et. al. (1997) explained in their work *Evolutionary Computation: Comments on the History and Current State*, "We know that they work, but we don't know why." Thus the GA can be considered successful when it successfully locates input sets that satisfy the needs of the user.

In our application, trial and error were used to establish all GA parameters including the probability values for the rates of mutation and crossover. When a mutation occurred, its size was managed through a mutation scale factor, which represented the maximum percentage of the original value that could be added or subtracted. The coded equation for the mutated MODFLOW input parameter had the following structure:

$$P_n = P_o + P_o * R * F$$

P_n = new MODFLOW input parameter value
P_o = old MODFLOW input parameter value
R = random number between -1 and 1
F = the mutation scale factor (a constant)

Our work contains a noteworthy derivation from canonical GAs. We did not convert the gene parameters to binary strings. Historically, there has been a strong preference for mapping gene parameter values to binary strings prior to GA manipulation, the basis of which comes from GA schema theory. The schema theory, the roots of which go back to Holland, sought to characterize the underlying mathematical structure of GA search (Fogel, 2008). The theory stated that binary mapping would provide for more optimal sampling of the solution space (Back et al., 1997). More recent work has called schema theory into question, at least as it applies to many real world problems (Fogel, 2008). Binary coding may improve the performance of some models, but there are some known disadvantages to using binary strings. Primarily, that such coding may introduce additional multimodality, making the binary problem more complex than the original one (Back et al., 1997). For the purposes of this exercise, the disadvantage of mapping parameters to binary strings is more prosaic: it adds complexity to the writing, reviewing, and debugging of the code and, as our primary objectives are efficiency and cost effectiveness, this approach has not been employed. However, the method described in this paper could be easily modified to include mapping to binary strings.

Finally, an important step in GA development is placing appropriate constraints on the MODFLOW input parameters. In our application, when constraints were not controlled, the GA gravitated to unrealistic results, such as reversing the direction of flow in the river or converging on a water table 100 feet below sea level. In real world applications, parameters such as the elevation of the water table would probably be known within some narrow range. Placing tight constraints on MODFLOW input parameters, when appropriate, will limit the solution set such that only realistic values can be searched.

2. MATERIALS AND METHODS

Our impetus for this effort was the lack of commercially available GA codes for MODFLOW 2000. MODFLOW 2000 is one of the most popular groundwater modeling programs in existence, and thus is familiar to many consultants, their clients, and regulators (McDonald and Harbaugh, 1988; Winston, 1999). We chose to focus on MODFLOW 2000 because it is the program that we use most often in our own practice for large scale groundwater modeling problems.

We are not aware of any commercially available MODFLOW GUI software that includes a GA function. Because no commercial GA software is available, we also looked into open source GAs for MODFLOW. At the time of this writing, we are aware of one open source genetic algorithm for MODFLOW 1988, published by Chunmiao Zheng of the University of Alabama. This code is called MGO (Zheng and Wang, 2003). MODFLOW 1988 has been replaced in most consulting settings by MODFLOW 2000. A search was conducted for an open source GA for MODFLOW 2000, but a code was not found. Zheng and Patrick have written a genetic algorithm for MODFLOW 2000, called ModGA, which is owned by DuPont and is not commercially available (Zheng, 1997).

In the example presented in this paper, we developed a Visual Basic Script code to run a simple GA in conjunction with MODFLOW code to conduct parameter estimation. The presented code could be easily restructured for optimization problems. In order to apply the GA, the MODFLOW model must first be set up and roughly calibrated. Those input parameters designated as chromosomes must be identified and the range of reasonable values for these parameters must be established. A calibration target must be identified (for example, water table elevations could be used as the calibration target.)

The steps of our code are as follows:

1. The code is given the developed MODFLOW model and chromosome parameter values for the initial population.

2. The code reads the existing MODFLOW input files and duplicates those files for each population member while replacing the original chromosome parameters with unique chromosome parameter values for each member.

3. The code calls and runs MODFLOW for each population member.

4. The code reads the MODFLOW output files and calculates the error between each model's output and the user defined calibration target.

5. The code selects the fitter solutions using tournament selection; these fitter models become the parents of the next generation.

6. The code randomly conducts mutation and genetic crossover on some of parent models to create child models; other parent models advance into the next generation without mutation.

7. The entire process is repeated for the user-specified number of generations.

We used a simple naming convention for all MODFLOW files that included the generation number and the population member number in each name. This allowed for ease of coding, as the i and j integers from the do-loops were simply encoded in the file names. For ease of analyzing the results, each generation was saved in a unique folder.

The simple genetic algorithm for MODFLOW is presented in Figure 1 in Chapra and Canale's pseudocode (Chapra and Canale, 2002).

3. RESULTS AND DISCUSSION

3.1 GA Application

In our application, the GA was used to conduct parameter estimation on a MODFLOW model of a portion of a river basin in New England that had previously been developed in our practice and calibrated by trial-and-error methods. The model grid is shown in Figure 2. Four parameters were selected as the genes for the GA to act on: recharge, riverbed conductance, and two general head boundaries which define the upstream and downstream limits of the basin within the model. These were considered the parameters with the most uncertainty associated with them due to the inability to measure them in the field; other model parameters were kept constant. An initial population of 100 models was developed by varying the values of these chromosome parameters. The calibration target used in this application was net flow of groundwater into the river (calculated as the difference in streamflow between up and downstream USGS gauging stations). The GA code ran a MODFLOW simulation for each

```
DEFINE population size
DEFINE number of generation
DEFINE calibration target
DEFINE initial values of experimental parameters for first generation
DEFINE original MODFLOW model
DEFINE mutation and crossover factors
DOFOR i = 1 to number of generations
  DOFOR j = 1 to population size
'Create MODFLOW files for the population
    READ the original MODFLOW input files for non-chromosome parameters
    WRITE a copy of non-chromosome input files under the unique name of each
      member
    WRITE a copy of the MODFLOW NAM file for each member
    READ the original MODFLOW input files for chromosome parameters
    REPLACE the original chromosome parameter with the member specific
      chromosome value
    WRITE the member specific input files for chromosome parameters under the
      unique name of each member
'Run MODFLOW for each member of the population'
    CALL MODFLOW and run for each member
'Calculate each member's error'
    READ MODFLOW output file for each member
    IF member failed to converge THEN
      member error = non-convergence flag
    ELSEIF member converged
      member error = ABS(calibration target - member MODFLOW output)
    ENDIF
  ENDDO
'Conduct tournament selection to select fitter members'
  DOFOR k = 1 to half population size
    member a = RANDOM member of population
    member b = RANDOM member of population
    IF member a's error = non-convergence flag THEN
      IF member b's error = non-convergence flag THEN
        winner e = original model
      ELSE
        winner e = member b
    ELSE
      IF member b's error = non-convergence flag THEN
        winner e = member a
      ELSE
        IF member a's error <= member b's error THEN
          winner e = member a
        ELSE
          winner e = member b
        ENDIF
      ENDIF
    ENDIF
(Figure 1 continued on next page)
```

Figure 1. Pseudocode for the MODFLOW GA (continued on next page)

```
(Figure 1 continued from previous page)
(Repeat tournament selection for RANDOM members c and d and find winner f)
'Create child models from tournament winners through crossover and mutation.
'Conduct crossover on chromosome parameters when crossover factors apply.
'Crossover threshold and factor are set such that this is a rare occurrence.
    DOFOR m = 1 to number of chromosome parameters
      IF crossover factor * RANDOM < crossover threshold THEN
        experimental parameter m of child k = experimental parameter m of
          winner f
        experimental parameter m of child k + half population size =
          experimental parameter m of winner e
      ELSE
        experimental parameter m of new member k = experimental parameter m of
          winner e
        experimental parameter m of new member k + half population size =
          experimental parameter m of winner f
      ENDIF
    ENDDO
'Conduct mutation on chromosome parameters when mutation factors apply.
'Mutation factor 2 may be positive or negative.
    DOFOR n = 1 to number of experimental parameters
      IF mutation factor 1 * RANDOM < mutation threshold THEN
        experimental parameter n of new member k =
          experimental parameter n of new member k + RANDOM * mutation factor 2
      ENDIF
    ENDDO
(Repeat for mutation DO loop for new members k + half the population size)
  ENDDO
ENDDO
```

Figure 1. Pseudocode for the MODFLOW GA (continued from previous page)

member of the population, extracted each output file, calculated the groundwater discharge from each output file, and established the error of each model from the calibration target. Then, the GA selected the most fit solutions (closest to the calibration target) and developed the next generation. Repeating this process for several generations evolved the entire population towards the calibration target as described above until the all the members converged on a single set of input parameters.

Due to the simplicity of the experimental application described (i.e. only four genes were manipulated), the model rapidly converged until the error of the entire population was below an absolute percent error of 10%. After which, convergence continued more slowly. Figure 3 shows a graph of the absolute percent error versus the generation number. Each point on the graph is the error (different between model result and calibration target) for one member of the generation. Each generation includes 100 members. Thus at later generations, the error for all members of the population had converged on to a low level.

Running our GA application for a population size of 100 members for 50 generations took approximately 11 hours of computation time on a desktop PC. For the purposes of observing the evolutionary progress, all input and output files were saved. These files represented a memory burden of 260 MB. The GA could be programmed to delete files after use as needed based on memory constraints.

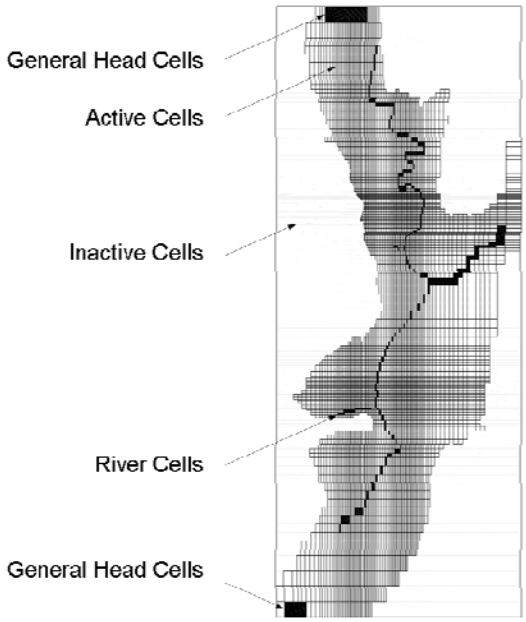

Figure 2. Model Grid

3.2 History and Present State of Genetic Algorithms in Water Resource Problems

This section briefly describes the history and current state of genetic algorithms as the relate to water resource problems. Genetic algorithms were first conceptualized in 1962 by J. H. Holland in his work *Outline for a Logical Theory of Adaptive Systems* (Holland, 1962). However, due to the expense and limited capacity of the computers at the time, GAs were not widely used until the 1970s. In the 1980s, improvements in computer technology allowed practitioners to apply GAs and other evolutionary algorithms to real world optimization problems. Their application became so common in the 1980s that by 1985, international conferences began being held on the subject (Back et. al., 1997).

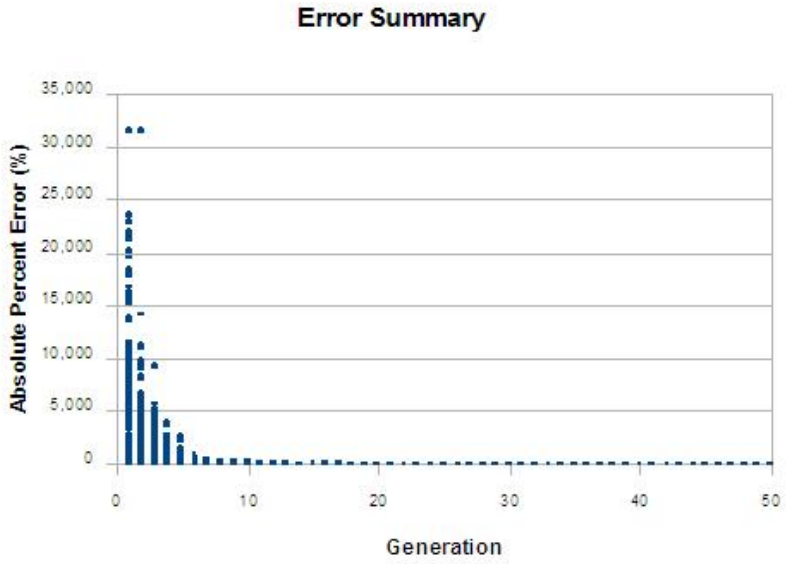

Figure 3. Error Summary – Absolute Percent Error versus Generation Number

For more than a decade, evolutionary algorithms have been applied to a wide variety of groundwater modeling problems. They are especially useful for the placement of wells in pump-and-treat well-field remediation systems, due to large possible solution set for these problems and the difficulty of testing all possible variations by hand (Chang and Hsiao, 2002). They have also been applied in parameter estimation in water resource problems (Kalwij and Peralta, 2006).

While research continues to advance on this subject, the practical application of these techniques is still hampered by resource limitations (Johnson and Rogers, 1995). These practical constraints are mainly associated with computational limitations, (Wang and Zheng, 1997) but they also include the human effort involved in properly setting up and coding the problem.

The uses of GAs are very broad in groundwater modeling applications, but they can generally be categorized as either parameter estimation or optimization problems (Babbar and Minsker, 2006; Tsai et. al., 2003).

A simple GA is best suited to finding a single set of input parameters that result in the desired solution to a problem, as the interaction between population members causes the chromosomes of the all members in a population to cluster around a single value. However, complex GA protocols have been developed which find multiple chromosome sets. Research continues to be conducted on so-called niche GAs. The theory of niche GAs is metaphorically parallel to

evolutionary niches that occur in nature, where populations are isolated from each other and evolve different mechanisms for solving the same problems. Some examples of work that has been conducted in this area include Vector Evaluated GAs (Schaffer, 1985) and Niched Pareto GAs (Horn et al., 1994).

In their work *Massive Multimodality, Deception, and Genetic Algorithms*, Goldberg et al. (1992) set up an experimental function with over five million local optima and 32 global optima. They showed that a simple GA could find one of the global optima if the correct GA operational parameters were used. They also developed a niched GA that successfully located all 32 global.

All of these trends indicate the advances and likely long-term utility of GAs in water resources applications in the future.

4. CONCLUSION

In conclusion, genetic algorithms provide a practical alternative to trial-and-error and automated statistical calibration procedures, and can also be used for optimization. Here we have presented a practical method for writing and applying simple genetic algorithms for MODFLOW to be used in optimization and/or parameter estimation in groundwater modeling problems. Genetic algorithms have advantages over other commonly-used parameter estimation and optimization methods. It is hoped that this example increases awareness of the availability of these methods, demonstrates the use of GAs in a non-academic setting, and encourages further such applications in the future.

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PART IV: Pesticides

Chapter 11

USE OF BIOMARKERS AND PREDICTED ENVIRONMENTAL CONCENTRATIONS (PEC) TO SELECT RELEVANT PESTICIDES APPLIED TO SOIL

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ABSTRACT

In our country, many different types of pesticides may be applied to cut flower crops in order to protect them. Two groups of these compounds, organophosphate (OP) and carbamate (CA) are used in high quantities. Both of them produce inhibition of cholinesterase activity in different organisms. This characteristic is used to identify the presence of these compounds with fast tube tests. On the other hand, some lixiviation models like PESTAN and others have been used in ecological risk assessment studies to get the Predicted Environmental Concentrations (PEC) of pesticides in soil. The aim of this research is to determine if PEC of several OP and CA compounds applied to a flower crop area, will show any correlation with inhibition of cholinesterase activity detected in soil extracts. Samples of surface soil (0 – 30 cm in depth) and subsurface soil (30 to 60 cm in depth) were taken from a flower crop area in which, during the last two years, OP pesticides (like acephate, dimetoate and methyl parathion), and CA pesticides (like carbendazim, carbofuran and metomil) were applied. Weekly loads of these pesticides were registered to estimate the annual load of each compound. Physicochemical analysis and relative inhibition of cholinesterasic

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activity were developed for each soil sampled. PEC values were estimated using PESTAN (US-EPA) lixiviation model for each pesticide considering the data of physicochemical analysis of each soil sampled. From all pesticides tested only acephate and metomilo showed a significant correlation ($p < 0.01$) between PEC values and inhibition cholinesterase activity of soil extracts. These results suggest that inhibition of cholinesterase activity observed in soil extracts is produced mainly by these two pesticides. Further studies could be oriented to measure concentrations of acephate and metomil to develop actions to reduce their environmental impact.

Keywords: Pesticides in soil, cholinesterase activity in soils, organophosphorous and carbamate pesticides in soil

1. INTRODUCTION

A problem observed in flower crop areas located in developing countries is the use and application of many kind of pesticide compounds in complex mixtures (Moncada, 2006). Some flower crops get almost ninety loads of pesticides during a six month time space. This represent a meaningful load of pesticides which can be reach the soil and travel through it.

The knowledge of pesticides mobility through soil is very important to identify exposure conditions of non target organisms and to prevent potential contamination of surface water and groundwater resources (Rao and Hornsby, 2001), and health and environmental risks (Ahlers and Martin, 2003; Finizio and Villa, 2002; Villa et al., 2003a).

When complex mixtures of pesticides are present in soils, the quantification of each compound requires a lot of time and it represent a high cost (Villa et al., 2003b), for this reason it is very useful to develop preliminary screening procedures in order to identify which of these compounds are of special interest and select the appropriate methods to identify and quantify them.

Organophosphorate and carbamate compounds are two major group of pesticides used in flower crops in Mexico. Both groups produce inhibitory effects on cholinesterase activity in different organisms, this characteristic has been used to identify the presence of these compounds in the water (Hamers et al., 2000), food (Schulze et al., 2002) or, like in this case, in soils with the use of biosensors and fast tests (Guerrieri et al., 2002; Andreou and Clonis, 2002) . On the other hand, different lixiviation models lixiviation have been applied to determine Predicted Environmental Concentrations (PECs) of these compounds. PECs are values used in ecological risk assessment studies (Villa et al., 2003b; Peterson, 2006).

The aim of this study was to determine if cholinesterase activity inhibition used as a marker of presence of organophosphorate, and carbamate pesticides and detected in soil extracts samples from a greenhouse flower crop area, combined with environmental concentrations estimated (PEC) by lixiviation models like PESTAN (Pesticide Analytical Model Version 4.0, US-EPA) developed by the Center for Subsurface Modeling Support (CSMoS) (Ravi and Johnson, 1986; Stacy et al., 2007), can be used as a useful primary method to identify and select relevant exposure concentrations of these pesticides. PESTAN model is based in an analytical solution of advective-dispersive-reactive transport equation for pollutant movement in soil developed by Enfield et al., 1982, which can be used with an user-friendly interface in the Windows operating system (Stacy et al., 2007).

2. MATERIALS AND METHODS

2.1 Soil Sampling

Georeferenced soil samples of 1 Kg were taken from a greenhouse flower crop area of Gerbera (*Gerbera jamesonii*). Twelve samples from a surface soil fraction (0 to 30 cm in depth) and twelve from a subsurface soil fraction (30 to 60 cm in depth) were sampled using a clay auger (Mason, 1992). Gerbera is an important type of flower crop for exportation with high sales in the international flower market. During 2004 and 2005 years all the loads of pesticides used in this area

Table 1. Annual load of pesticides used in Gerbera crop area which were selected to calculate data of Predictable Environment Concentrations (PECs) by PESTAN model

Pesticide	**Group**	**Load of Pesticide (Kg/ha/año)**	**Year**
Acefate	Organophosphorous	6.68	2004
Carbendazim	Carbamate	0.24	2005
		0.19	2004
Carbofuran	Carbamate	0.51	2004
Dimetoate	Organophosphorous	1.94	2005
		6.96	2004
Metomil	Carbamate	0.43	2005
		0.065	2004
Methyl Parathion	Organophosphorous	0.24	2004

to protect the crops were registered. This information was used to estimate annual load of each pesticide expressed as Kg/Ha/Year (Table 1). Each soil sample was placed in a plastic bag and it was transported to laboratory to develop the physicochemical soil test and the percent of cholinesterase activity inhibition test in a soil extract.

2.2 Soil Physicochemical and Cholinesterase Inhibition Tests

Physicochemical soil test included the measure of pH, texture, composition, conductivity, percent of organic matter and moisture, according to the methods of the Soil Survey Standard Test Methods of Department of Sustainable Natural Resources of Australia, also, according to the normalized Mexican test (NMX): NMX-AA-021-1985, NMX-AA-016-1984, NMX-AA-025-1984, NMX-AA-052-1985 y NMX-AA-015-1985.

To prepare soil extracts, each soil sample was homogenized, and a portion of 20 g of soil was added with 50 mL of acetone, the mixture was shaken during 10 minutes, at the end of this time mixture was filtered through Wattman Num. 1 filter paper, the filtrated solution was collected in a glass beaker, then acetone was evaporated in a water bath at 35°C until dry.

The field kit “In Quest OP/Carbamate Screen” ®, which is used as colorimetric assay for the qualitative detection of organophosphate and carbamate pesticides, was used in order to quantify the cholinesterase activity. In this study, we modified the procedure to enable the results to be read by a spectrophotometer "Thermolyne Spectronics model Genesys-6,"; the measurement of light absorbance affords a semiquantitative measure of enzymatic reaction.

In this case, dry residue was dissolved in a glass beaker with 2.5 mL of OP/Carbamate Screen wash solution A ®, from this solution was taken 1mL to add to buffer/chomogen reagent ® and vigorously shaken in a vortex. This solution was added to a tube with lyophilized acetylcholinesterase, this tube was incubated in a water bath during 20 minutes and then filtered and poured into a quartz cuvette to read the absorbance at 480 nm.

The basic principle underlying this test is the inhibition of the acetylcholinesterase enzyme produced by organophosphate and carbamate compounds. When these pesticides are absent in a soil extract, acetylcholinesterase hydrolyzes a chromogenic ester compound ®, which is used as a substrate and suffers oxidation to become deep blue in color. If these pesticides are present in the extract of soil sample, they produce a decrease of color proportional to pesticide concentration (In Quest OP/Carbamate Screen ® Data sheet of Kit).

The change of color was measured in absorbance units at 480 nm, absorbance of a blank sample without pesticides was considered as 100% of cholinesterase activity or 0% of relative inhibition, absorbance of each soil sample extract was referenced to this parameter as relative enzymatic activity expressed in %. The reduction of this relative activity was expressed as % relative inhibition of cholinesterase activity in a given soil sample. Positive controls were prepared using solutions with known concentrations of carbofuran and metamidophos, two pesticides used commonly in pest control for Gerbera crops.

2.3 Use of PESTAN Model to get PECs of Pesticides

Based on information data about physicochemical characteristics of each soil sample, the annual load (measured in Kg/Ha/Year) of each of the applied pesticides and their physicochemical data and also irrigation conditions as inputs for PESTAN model, data of PECs were calculated for each pesticide.

2.4 Statistical Analysis of Data

Association between physicochemical data and cholinesterase activity measured in different (surface and subsurface) soil samples from the Gerbera crop area were developed by a statistical correlation analysis using rho Spearman coefficient, previously knowing the normality characteristics of the different data. Significant values were taken when correlation was $p < 0.05$. All statistical tests were developed by SPSS v.11 software.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Characterization and Relative Inhibition of Cholinesterase Activity

Tables 2 and 3 show physicochemical data of different soil samples from the Gerbera crop area surface and subsurface fractions, and percent of relative inhibition of cholinesterase activity measured for each soil fraction.

Values of organic carbon and the percent of organic matter were higher in surface soil fractions than in subsurface soil fractions. Also lightly higher values of percent of sand were found in the subsurface soil fraction. Conductivity values were higher in the surface soil fraction than in the subsurface soil fraction.

In some cases, higher percent values of relative inhibition of cholinesterase activity were detected in subsurface soil fractions. The level of relative inhibition of cholinesterase activity measured in surface and subsurface fraction of soil

samples can be considered as a marker of organophosphorous and carbamate pesticides present in soil, which they are compounds that produce inhibition of this enzyme in live organisms.

Non-significant correlation was detected between inhibition levels of cholinesterase activity and physicochemical data from surface and subsurface soil fractions.

Table 4 shows physicochemical properties of some of organophosphourus and carbamate compounds used in the Gerbera crop area. Some of these compounds can be considered as low persistence compounds but their higher frecuency of application and acidic conditions present in soil could produce that some of them have longer life in soils, for example carbendazim, carbofurane and clorpyrifos.

With the pH values form the sampled soils (pH = 5.55 in surface soil samples and pH = 5.51 in subsurface soil samples) it is suggested they could be classified as light acidic soils (NOM-021-RECNAT-2000, 2002). Previous studies have shown that acidic soils can increase persistence of organophosphorous pesticides (Pantelelis et al., 2006), and decrease microbial activity required to breakdown these substances (Nannipieri et al., 2003; Singh and Walker,2006).

Structure of soil describes physical and structural characteristics from it, and these characteristics can determine the movements of water and pesticides solubilized in the soil and some interactions between soil and pesticides (Carter, 2000; Ciglasch et al., 2005).

According to the percent of sand, silt or clay presented in the diferent samples of soil, surface and subsurface soil fraction were clasified as clay-loam and loam soil texture respectively. A higher percent of sand could represent more filtering capability and some ionic and soluble pesticides like metamidophos and metomil could move to the subsurface soil fraction and explain the values of relative inhibition of cholinesterase activity measured in this level.

A significant correlation between % of clay in surface fraction with % of clay in subsurface fraction was observed ($R = 0.779$; $p < 0.05$), also significant correlation between % of moisture in the two fractions and % of sand ($R = 0.703$; $p < 0.05$), suggesting homogeneity of two layers of soil. The highest correlation was observed between values of relative inhibition in percent of cholinesterase activity measured in surface soil fraction with values of percent of relative inhibition of cholinesterase activity measured in subsurface soil fraction (rho = 0.881; $p < 0.001$).

3.2 Modeling Lixiviation of Pesticides used in Gerbera Crop Area with PESTAN to get PECs Values

To get PECs values of each pesticide we consider a scenario with a recharge value of 0.0134 cm/h, based in pluvial precipitation recived during a year, according data registered from two meteorological stations nearest to greenhouse area. Tables 5 and 6 show results of PECs values calculated with PESTAN model considering a recharge of 0.0134 cm/h.

Correlation coefficients of Spearman (rho) between PECs and relative inhibition in percent of cholinesterase activity were determined using SPSS statistical program and are shown in Table 7. It was observed that only PECs of acefate estimated at 100 days show a significant correlation (rho = 0.734; $p < 0.01$) against values of relative inhibition in percent of cholinesterase activity measured in the subsurface soil fraction (30 to 60 cm in depth).

Also, PECs of metomil obtained at 60 days from the surface soil fraction showed significant correlation (rho = 0.734; $p < 0.05$), against of relative inhibition in percent of cholinesterase activity measured in the subsurface soil fraction (30 to 60 cm in depth). These values sugest that pesticides acefate and metomil contribute in first place, to produce the inhibitory effect of cholinesterase activity observed in subsurface soil fraction.

Transport of pesticides in soil involved complex fenomena and their movement is related with water migration through soil which is important to soluble pesticides (Wang et al., 2004), but chemical sorption and degradability could be important also to pesticides with low solubility (Zhang et al., 2000). In the first case the water flux can influence the translocation of pesticides like acefate and metomil located in surface soil fraction move to subsurface soil fraction (Ciglasch et al., 2005), this flux can be facilitaded when there is a major content of sand in soil fraction (Rao and Hornsby, 2001).

Bioassays developed with different organisms like cladocerans (Barata et al., 2007), earthworms (Caselli et al., 2006; Denoyelle et al., 2007) and others have been used in ecotoxicological studies to identify water and soil pollution produced by pesticides. The use of cholinesterase activity inhibition as biomarker of effects of organophosphorous an carbamate pesticides in these bioassays is well recognized. In some cases this characteristic is used to classify the risk of polluted areas (Hagger et al., 2008).

Table 2. Physicochemical test results from surface samples of soil (0 - 30 cm in depth) from crop area of *Gerbera jamesonii*.

Num sample	Moisture %	pH Water	pH Ca^{++}	Organic carbon %	Organic matter %	Sand %	Clay %	Silt %	Texture	Conductivity (µS/cm)	% Inhibition Cholinesterase
1	4.55	5.97	5.37	1.12	1.94	40.2	24	35.8	Loam	1082	24.79
2	4.00	5.88	5.48	0.83	1.43	30.4	37.8	31.8	Clay-loam	317	4.48
3	4.42	6.02	5.77	0.95	1.64	32.4	38	29.6	Clay-loam	1167	32.50
4	4.01	5.90	5.44	1.55	2.68	30.4	35.8	33.8	Clay-loam	651	42.19
5	3.57	5.39	4.91	1.32	2.27	38.4	29.8	31.8	Clay-loam	406	37.50
6	3.81	5.14	4.69	1.45	2.51	34.4	30	35.6	Clay-loam	552	20.94
7	3.86	5.90	5.44	1.88	3.25	40.2	24	35.8	Loam	1860	10.21
8	3.50	6.03	5.49	1.14	1.97	48.4	20	31.6	Loam	368	29.90
9	3.77	6.41	5.98	1.18	2.04	38.2	36	25.8	Clay-loam	1119	39.17
10	3.11	7.15	6.45	0.99	1.70	40.4	24	35.6	Loam	390	25.63
11	4.11	6.42	5.89	0.99	1.70	36.4	32	31.6	Clay-loam	479	67.71
12	3.57	6.55	5.72	1.24	2.14	40.4	32	27.6	Clay-loam	566	54.48
Mean	**3.86**	**6.06**	**5.55**	**1.22**	**2.11**	**37.5**	**30.2**	**32.2**	**Clay-loam**	**746**	**32.45**
S.D.	0.39	0.52	0.46	0.29	0.51	5.12	6.10	3.32		466.1	17.62

Table 3. Physicochemical test results from subsurface samples of soil (30-60 cm in depth) from crop area of *Gerbera jamesonii*.

Num sample	**Moisture %**	**pH Water**	**pH Ca^{++}**	**Organic carbon %**	**Organic matter %**	**Sand %**	**Clay %**	**Silt %**	**Texture**	**Conductivity** (μS/cm)	**% Inhibition Cholinesterase**
1	8.0142	6.19	5.68	0.4056	0.6993	60.4	8	31.6	Sandy-loam	564	30.00
2	3.7401	5.88	5.38	1.2441	2.1448	32.4	33.8	33.8	Clay-loam	402	0.00
3	4.9855	6.22	5.76	0.3276	0.5648	34.4	32	33.6	Clay-loam	1160	41.98
4	4.5040	5.78	5.29	0.9321	1.6069	34	28	38	Clay-loam	335	50.10
5	4.0218	5.7	5.07	0.7956	1.3716	36.2	26	37.8	Loam	211	44.06
6	4.9459	5.75	5.25	0.8736	1.5061	42.2	22	35.8	Loam	301	38.33
7	4.6738	5.3	5.02	0.9516	1.6406	38.2	26	35.8	Loam	778	24.79
8	4.0473	6.11	5.61	0.8151	1.4052	54.4	16	29.6	Sandy-loam	417	35.63
9	6.1571	6.52	5.75	0.5031	0.8673	42.4	30	27.6	Clay-loam	425	37.40
10	2.2900	6.34	5.58	0.1911	0.3295	40.4	20	39.6	Loam	230	28.54
11	4.9188	6.6	6.02	0.7566	1.3044	42.4	35.6	22	Clay-loam	681	63.33
12	4.4557	6.52	5.75	0.4056	0.6993	42.4	29.8	27.8	Clay-loam	291	48.65
Mean	**4.72**	**6.07**	**5.51**	**0.68**	**1.17**	**41.6**	**25.6**	**32.7**	**Loam**	**482.9**	**36.90**
S.D.	1.38	0.39	0.31	0.31	0.54	8.2	7.9	5.2		275.5	15.71

Table 4. Physicochemical properties* of organophosphate and carbamate pesticides inhibitors of cholinesterase activity used to control pests in crop area of *Gerbera jamesonii*.

Active Chemical	No. CAS	Chemical Group**	Use***	Clas.Tox. (WHO)	Molecular Weight	Water Solubility	Vapor Pressure	Partition Coefficient (Kow)	Adsorption Coefficient (Koc)	T ½ Soil
Acefate	30560-19-1	OP	I	III	183.17	79 g/100mL to 20 °C; 650 g/L to 20°C	2.3 x 10 E-6 mbar a 24°C; 1.7 x 10 E-6 mmHg to 24°C	-1.87	0.48	< 3 to 6 days in anaerobic and aerobic soils respectively
Carbendazim	10605-21-7	CA	F	III	191.2	0.0008 g/100 mL to 24°C; 8 mg/L to pH 7	< 100nPa A 20°C	1.49	1900	320 days (Colombia Ministery)
Carbofurane	1563-66-2	CA	I, N	Ia - Ib	221.25	320 mg/L@ 25°C	2.7 mPa @ 33°C	1.23 - 1.41	22	30 a 120 days
Chlorpiriphos	2921-88-2	OP	I	Ib	350.62	2 mg/L @ 25°C	2.5 mPa @ 25°C	4.699	6070	11 a 141 days
Diclorvos	62-73-7	OP	I	Ia	220.98	0.8 g/ 100 mL to 20 °C	290 mPa @ 20°C (1.6 Pa a 20 °C, ICSC)	1.47	30	7 days
Dimethoate	60-51-5	OP	I	Ib	229.28	25 g/L @ 21°C	1.1 mPa @ 25 °C	0.699	20	20 days
Metomil	16752-77-5	CA	I	Ia	162.21	57.9 g/L @25°C	6.65 mPa @ 25°C	0.6	72	14 days
Monocrotophos	2157-98-4	OP	I	Ia	223.2	Soluble in water (100 g/100 mL of water to 20°C)	2.9 x 10 E-1 mPa 20°C (0.0003 Pa a 20°C)	-0.22	ND	7 days in soil exposed to sun light
Oxamyl	23135-22-0	CA	I	Ib	219.25	Soluble in water	14.1 mm Hg a 20°C (31 mPa a 25°C Extoxnet)		0.15	10.7 days (5.73 days in anaerobic soil) 4 a 20 days (Extoxnet)
Methyl Parathion	298-00-0	OP	I	Ia	263.21	55-60 mg/L @25°C	1.3 mPa 20 °C	3.51 - 3.83	5100	1 a 30 days with a representative value of 5 days

(*) All data were obtained from specialized databases: PAN, EXTOXNET, ICSC, NIOSH, IRIS, and Security data sheet (MSDS)
(**) OP Organophosphate, CA Carbamate; (***) I, Insecticide; F, Fungicide; N Nematicid

In the same way, during the last twenty years, many devices of biosensors (Andreescu and Marty, 2006) and bioanalytical test (Luque de Castro and Herrera, 2003) based on cholinesterase inhibition enzyme have been used for environmental monitoring (Rodriguez-Mozaz et al., 2005) and developed to identify and quantify exposure to organophosphorous and carbamate compounds in food (Amine et al., 2006), water (Arduini et al., 2006) and soil (Velazco-García and Mottram, 2003).

In the present study, relative cholinesterase activity inhibition observed in soil extract samples can be considered as a preliminary test to identify inhibitory compounds of this enzyme. The relative inhibition of cholinesterase activity observed in the surface and subsurface soil fractions is a marker of inhibitory substances in this case organophosphorous and carbamate compounds present in the complex mixture of pesticides applied in the flower crop area.

When combine these results of cholinesterase inhibition with PEC values determined by PESTAN ® model for the different pesticides and only the PEC values of acefate and metomil presented a good correlation, this suggest a promissory application to identify witch of the different pesticides applied in crop areas are responsible of this effect and also to identify possible hot spots of these compounds present in a crop area.

In PESTAN model, vertical transport of solved pollutants through vadose zone of soil is simulated as polluted water block which migrates into an homogeneous soil. The polluted block starts its travel through soil when the first precipitation happens at a rate equal to water pore rate. Once the polluted block is into soil, transport of pollutant is influenced by sorption and dispersion process (Ravi and Johnson, 1986; Stacy et al., 2007).

The relative inhibition observed is not specific to any of the applied pesticides, however, by setting the correlation with the PEC acquired by the PESTAN simulation model, it was possible to see that only some of the applied pesticides (acetafe and metomil) showed a meaningful correlation ($p < 0.01$) against the values of relative inhibition of cholinesterase activity evaluated values.

This selectivity can be explained considering that organophosphorous and carbamate pesticides will be moving through soil at different rate depending on their own physicochemical characteristics, for example solubility, affinity to organic matter of soil (Koc) and others (Sun et al., 2008; Franco and Trapp, 2008) and physicochemical properties of soil, for example texture, porosity, organic matter content, clay, and others (Wang el al., 2004).

In this case acefate and metomil are water soluble pesticides. When we take account the preparation of soil extract with acetone, we consider that almost all

Table 5. Predictable Environment Concentrations (PECs) of pesticides used in Gerbera crop area, data estimated by PESTAN model
Inputs for scenario: surface soil fractions (0 to 30 cm in depth); recharge = 0.0134 cm/h

Pesticide (distance to soil surface = 30 cm)	**Time considered for lixiviation (days)**	**PECs (ppb) calculated for each sample point**											
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Metomil	60	17.54	32.69	18.06	1.6	1.66	1.66	0	3.33	4.95	13.26	14.79	3.31
	100	0	119.29	103.17	27.67	43.69	34.12	6.63	76.53	69.05	113.87	94.67	56.39
	500												
Carbofuran	60	22.92	14.63	12.95	15.93	15.89	15.99	25.27	28.26	15.18	23.79	13.65	15.60
	100	0.947	0.943	0.544	2.59	1.80	2.33	8.50	1.38	1.17	0.630	0.675	1.44
Dimetoate	60	0.660	35.15	40.51	55.28	53.36	54.95	101.21	89.82	49.41	72.13	43.09	51.50
	100	0.00018	0.806	1.272	6.496	4.390	5.794	21.54	2.964	2.814	1.306	1.588	3.491
Acefate	100	13.73	65.96	79.47	121.47	93.96	121.27	13.88	13.99	93.46	13.66	79.63	107.08
	500	0	0	0	0	0	0	0	0	0	0	0	0
Carbendazim	100	0	0	0	0	0	0	0	0	0	0	0	0
	500	0	0	0	0	0	0	0	0	0	0	0	0

Table 6. Predictable Environment Concentrations (PECs) of pesticides used in Gerbera crop area, data estimated by PESTAN model
Inputs for scenario: subsurface soil fractions (30 to 60 cm in depth), distance to soil surface = 60 cm; recharge = 0.0134 cm/h

Pesticide (Distance to soil surface in cm)	**Time considered for lixiviation (days)**	**PECs (ppb) calculated for each sample point**											
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Metomil (60)	100	51.40	1.55	74.12	1.55	1.58	3.16	1.60	1.61	15.26	193.47	1.56	39.13
Metomil (30)	100	84.11	59.56	77.08	102.32	147.96	135.64	123.25	152.50	120.62	10.22	125.67	102.35
Carbofuran (30)	60	5.17	15.53	4.10	13.08	16.81	20.18	32.31	22.65	6.79	1.30	10.63	5.28
	100	0.0054	1.394	0.0224	0.565	0.202	0.357	0.505	0.222	0.0769	0.00054	0.273	0.041
Carbofuran (60)	60	5.56	0.026	0.989	0.110	0.772	0.462	0.319	0.931	0.600	4.347	0.244	0.803
	100	0.596	0.772	0.245	0.827	1.998	2.324	2.477	3.424	0.460	0.0703	0.728	0.340
Dimetoate (60)	60	20.83	0.159	3.51	0.565	3.745	2.446	1.788	5.041	2.336	14.28	1.090	2.960
	100	1.356	2.698	0.666	2.573	5.520	6.737	7.431	9.378	1.269	0.176	2.127	0.925
Dimetoate (30)	60	13.64	51.13	12.32	40.97	48.73	59.67	66.94	64.14	20.37	3.74	32.47	15.83
	100	0.0105	3.358	0.0547	1.325	0.412	0.732	1.046	0.413	0.181	0.00123	0.634	0.098
Acefate (60)	100	78.83	1752.7	1361.4	1643.8	438.7	680.5	508.6	134.0	1448.9	219.8	1553.8	1404.6
	500	0	0	0	0	0	0	0	0	0	0	0	0
Acefate (30)	100	0	93.6	51.8	79.5	13.3	12.6	13.6	14.6	52.2	14.0	79.0	51.0
Acefate (90)	100	1984.1	1003.4	1555.8	1192.5	2741.1	2743.0	2739.0	2513.1	1422.8	2470.0	1290.5	1495.7
Carbendazim	100	0	0	0	0	0	0	0	0	0	0	0	0
	500	0	0	0	0	0	0	0	0	0	0	0	0

Table 7. Non parametric correlation values (rho) between PECs calculated by PESTAN model and percent of relative inhibition of cholinesterase activity measured in surface and subsurface soil fractions from Gerbera crop area. Recharge value = 0.0134 cm/h

Pesticide (Scenario)	**Correlation value (rho) with surface cholinesterase inhibition**	**p <**	**Correlation value (rho) with subsurface cholinesterase inhibition**	**p <**
Carbofuran (100 days, surface)	-0.070	NS	0.098	NS
Carbofuran (60 days, surface)	-0.420	NS	-0.441	NS
Carbofuran (30 cm, 100 days, subsurface)	-0.203	NS	-0.007	NS
Carbofuran (subsurface cm, 60 days, subsurface)	-0.315	NS	-0.133	NS
Carbofuran (60 cm, 100 days, subsurface)	-0.308	NS	-0.098	NS
Carbofuran (60 cm, 60 days, 1subsurface)	-0.014	NS	-0.140	NS
Acefate (30 cm, 100 days, surface)	**0.517**	**NS**	**0.734**	**0.01**
Acefate (60 cm, 100 days, subsurface)	0.301	NS	0.294	NS
Acefate (30 cm, 100 days, subsurface)	**0.517**	**NS**	**0.734**	**0.01**
Dimetoate (100 days, surface)	-0.140	NS	0.294	NS
Dimetoate (60 days, surface)	-0.077	NS	-0.084	NS
Dimetoate (60 cm, 100 days, subsurface)	-0.371	NS	-0.168	NS
Dimetoate (60 cm, 60 days, subsurface)	-0.077	NS	-0.154	NS
Dimetoate (30 cm, 100 days, subsurface)	-0.203	NS	-0.007	NS
Dimetoate (30 cm, 60 days, subsurface)	-0.364	NS	-0.189	NS
Metomil (100 days, surface)	0.301	NS	0.294	NS
Metomil (60 days, surface)	**0.517**	**NS**	**0.734**	**0.01**
Metomilo (30 cm, 100 days, subsurface)	0.056	NS	0.224	NS
Surface Cholinesterase	1.0	-	**0.881**	**0.01**
Subsurface Cholinesterase	**0.881**	**0.01**	1.0	-

organophosphorous and carbamate pesticides are more soluble in acetone than in water. This gently extraction was useful to through out some of the more soluble pesticides present in the complex mixture.

4. CONCLUSION

Measures of inhibition cholinesterase activity levels can be considered like an instant photographic picture taken in a specific time of an inhibitory substance or substances present in a soil fraction taken in a specific time. The same occurs when a chemical analysis of a pesticide is developed in a soil sample, in this case a selected pesticide is monitoring through concentrations in field.

Our results suggests that measure of the relative inhibition of cholinesterase activity measured in a soil extract, associated with the predicted environmental concentration (PEC) acquired by the PESTAN simulation could be used to identify pesticides organophosphorous or carbamate compounds presented in a complex mixture which are responsible of inhibition observed and prioritize which of them need to be analyzed by chemical methods in further studies.

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PART V: Phytoremediation

Chapter 12

PHYTOREMEDIATION AS GREEN INFRASTRUCTURE AND A LANDSCAPE OF EXPERIENCES

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ABSTRACT

The idea of reconciling landscapes through remediation is not new to the discipline of landscape architecture. However the potential of using transformative remediation to build urban form as a large-scale landscape network and that makes the process of remediation part of an urban landscape experience is still underdeveloped in theory and practice. This paper examines how a remediation process could be exhibited and become a staged design element, and how landscapes of cleaning can become part of the urban infrastructure to create new neighborhoods for research, education, working, and living. The example of two adjacent sites on the contaminated Elbe – Island in Hamburg, Wilhelmsburg Germany demonstrates how the purification process of water and soils can be showcased and experienced by the public and how the landscape framework becomes part of the urban infrastructure. The paper proposes a structural landscape framework for how remediation could become an artistic, aesthetically pleasing intervention with environmental value.

Keywords: connectivity, experience, green infrastructure, green urbanism, landscape architecture, landscape urbanism, phytoremediation

1. INTRODUCTION

Urban brownfields are a challenging and a common landscape especially in industrial and post-industrial cities. They inhibit economical growth and use of urban land. Their industrial heritage often isolates them from the urban fabric and

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creates physical barriers. However the sensual, aesthetic quality that goes along with derelict land has been discovered by implemented designs in landscape architecture (Kirkwood, 2001, Latz, 2001, Latz and Partner, 2008, Weilacher, 2008). Prominent examples for remediated new parks on former urban brownfields include: Landscape Park Duisburg-Nord (Latz, 2001 Latz and Partner, 2008, Weilacher, 2008), and the Gas Works Park in Seattle (Johnson, 1991) and the Westergasfabriek Park in Amsterdam (Spens 2007). While they are successful examples of urban park developments that are remediated landscapes they are still not well integrated into their larger urban context. A systematic and strategic approach to remediation landscapes that are connected from the regional to the local scale and that tie into the urban fabric as a continuous network and as a part of a green infrastructure framework is still underdeveloped.

Another objective of this research is the exploration to reveal phytoremediation as an aesthetic experience. Can plants be used as a visible design medium determining each stage of the cleaning process as a sensual experience and create a unique and meaningful landscape? The proposal is made to understand phytoremediation as a process-oriented tool for an evolving green infrastructure network that defines new landscapes. This paper begins with a description of phytoremediation and explains the key elements of green infrastructure. A recent case application conducted by Richard Weller (Weller, 2008) illustrates how green infrastructure can shape urban form. Finally two visionary design proposals by the UMASS Urban Design Laboratory 2007 and 2008 for contaminated sites on industrial brownfields on the Elbe – islands in Hamburg, Wilhelmsburg demonstrate how a landscape of remediation shapes the framework for new urban infrastructure, connects to the existing urban fabric, and becomes a rich aesthetic experience.

2. PRINCIPLES OF PHYTOREMEDIATION [1]

Phytoremediation has the capacity to assist in the remediation of polycyclic aromatic hydrocarbons, oils, greases, and heavy metals – which are among the common toxics found in urban brownfields. The simultaneous treatment of these multiple contaminants makes phytoremediation a cost effective and attractive option for urban brownfield areas (Raskin and Ensley, 2000) [2]. Plants typically used in phytoremediation include hybrid poplars, willows (Populus ssp., Salix ssp.), grasses, reeds, and cattails (Festuca ssp., Lolium ssp., Phragmites spp., Typha spp.), penny-cress and mustard (Brassica ssp., Thlaspi ssp.) (Marmiroli and McCutcheon, 2003). These plants' root systems help to rebuild soil structure in the rhizosphere, and through the deposition of organic material from leaves, branches and root cells. Another advantage is that remediation can take place

without minimal disturbance of the site and can be tailored as site-specific solutions. As a process-oriented tool phytoremediation takes a long time, often years or decades. The time dimension can be turned into an advantage if each stage of the cleaning process has a distinct character and sense of place while performing remediation and simultaneously creating green infrastructure.

3. GREEN INFRASTRUCTURE

Green infrastructure is an emerging planning and design concept that provides a framework for conservation and development. It acknowledges the need for providing places for people to live, work, shop, and enjoy nature. Green infrastructure helps communities to plan development in ways that optimize the use of land to meet the needs of people and nature. Green infrastructure can shape urban form, is principally structured by a hybrid hydrological drainage network, complementing and linking relict green areas with built infrastructure that provides ecological functions (Benedict and McMahon, 2006). It applies key principles of landscape ecology to urban environments as a multi-scale and multi-layered approach. The green infrastructure pattern derives from ecological and social process relationships with an emphasis on connectivity (Ahern, 2006). Following the principles of green infrastructure as a planning and design concept, phytoremediation can become one significant and complimentary element that creates the framework for future development.

4. CASE APPLICATION FOR GREEN INFRASTRUCTURE - PERTH, WESTERN AUSTRALIA

Weller (Weller, 2008) superimposed current landscape urbanism ideas (Waldheim, 2006) onto quotidian suburban master planning. In the Wungong Urban Water Landscape Structure Plan he joins planning and design, focuses on landscape as an infrastructural system and aims for structural influence. Existing vegetation and the Wungong River System are part of the landscape structure that ensures the protection and creation of landscape systems – habitat, drainage and open space. Park avenues become a system of linear elements for stormwater treatment and recreational corridors. They create the framework that organizes roads, schools, and developable land. Weller's approach is applied and reflected in the design proposals of the UMASS Urban Design Laboratory. The phytoremediation network is the basis for green infrastructure. It establishes the framework to (re-) connect a derelict site to an adjacent neighborhood.

5. REMEDIATED LANDSCAPES "RHIZOTOPIA" AND "VERINGKANAL WATER CYCLES" - [4]

Two recent studies by the UMass Urban Design Laboratory engage phytoremediation, green infrastructure and urban experience. Both study areas are located in the western territory of the International Building Exhibition Hamburg 2013 on the Elbe islands in Hamburg, Wilhelmsburg and are dominated by industrial brownfields close to residential areas. A former oil refinery is the core area of "Rhizotopia". Soils and ground water are contaminated with toxic organic materials and heavy metals. The second study area, the Veringkanal, is a once important industrial canal of the Elbe islands. The high contamination with heavy metals in the sediments prevents adaptive reuses of the canal.

5.1 Rhizotopia

The proposal for a "Remediation infrastructure as a green infrastructure framework" transforms the contaminated waste landscape into a healthy urban landscape that is well integrated with the city. The reed and grass planted remediation ditches and multi-lane alleys of fast-growing, deep rooting hybrid poplars and willows become part of the street and pedestrian circulation network that structures the urban form for the future and connects to the existing neighborhood (Figure 1). After the area is cleaned up, the water remediation network can be transformed into a surface stormwater treatment system and the multi-lane alleys can become street boulevards.

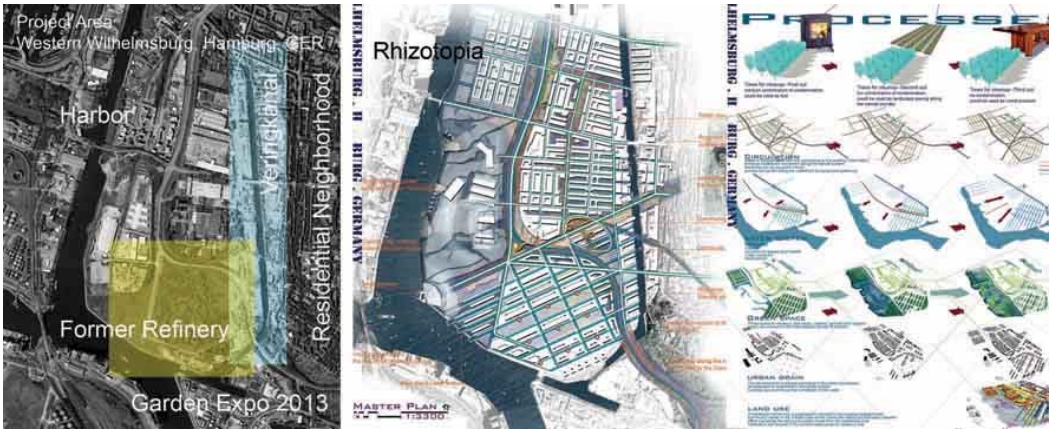

Figure 1. Project Areas - The remediation network provides the framework for a multi layered green infrastructure as design system. (Samimi, Wang, 2007)

The ditches are also a physical reference to the historical water layer infrastructure of the Elbe-islands with a hierarchy of inter-connected ditches and

swales that create a unique land-water topology. In addition, the remediation infrastructure is a habitat for wildlife, and the poplars and willows can be harvested and used as fuel or building material. Monitoring infrastructure complements the remediation grid system: An underground interpretive laboratory, the "Rhizotron", is designed for examining plant root growth. As public stations they contain enclosed columns of soil with transparent windows that permit viewing, measuring, and photographing the slow process of phytoremediation (Figure 2).

In conclusion, pedestrian movement within the remediation framework becomes an aesthetic experience that changes over time through the successional and adaptive media of plants and the water ditches as organizing elements for remediation and surface stormwater treatment in a later phase. This multi-layered green infrastructure is complemented by educational elements.

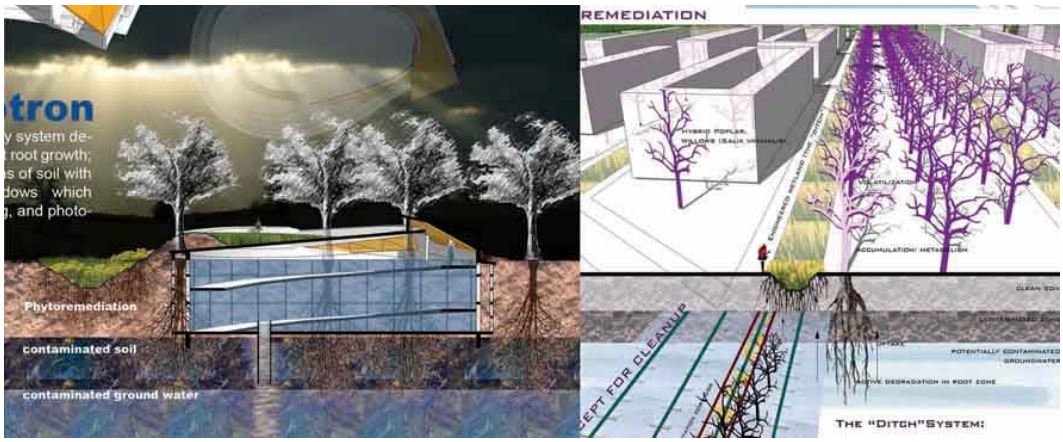

Figure 2: Rhizotron: An underground laboratory designed for examining and experiencing plant root growth complements the green infrastructure of ditches and tree boulevards. (Samimi and Wang, 2007)

5.2 Veringkanal Water Cycles

For the area around the Veringkanal the remediation strategy incorporates decentralized storm and waste water treatment proposals that are interlinked through the processes of water cycling. Indigenous wetland vegetation like Phragmities and Iris are planted in the drained canal. Periodic flooding establishes a dynamic water table that supports the development of a biologically-active wetland zone. Seasonal harvesting of biomass ensures that metals in the plant material are removed from the nutrient cycle, and safely incinerated as fuel for heating buildings. New development will follow strategies of decentralized storm

and waste water treatment that reduces burdens on existing urban infrastructure. Remediation and self-sustaining systems introduce new landscapes of sensual experiences. The Veringkanal becomes the central spine for arterial lateral branches. Stormwater is collected from the adjacent neighborhood and flows into the canal. These branches simultaneously create a new trail system for pedestrians and cyclists and make the Veringkanal an urban greenway (Figure 3).

Figure 3: Plants for remediation and waste treatment are green infrastructure as a changing landscape for sensual experience . (Lynch et al, 2008)

6. CONCLUSION

Principles from the emergent theories of Green Infrastructure can be understood and applied in a new way to form unique landscapes of remediation. Transformative remediation as a systematic design tool provides conceptual bridges between aesthetics and ecological design. F. L. Olmsted designed urban landscapes as experiences as well as environments. ”Antiquated conceptions of landscape beauty … persist and must be reconsidered through the lens of new paradigms of ecology” (Meyer, 2008). Stokman (2008) proposes urban constructed wetlands as part of the people’s experience of ecological processes in the landscape. Designing performance - oriented phytoremediation landscapes is a process of manipulating time because of their dynamic quality.

Thus phytoremediation as an experience and framework calls for:

1. Re-creation of systematic connectivity - from isolation to network in a flexible framework that structures a multi – layered urban infrastructure.

2. Visible transformation of toxics and contaminants as a sensual experience through the dynamic media of the landscape. Staging of phytoremediation as landscape typologies.
3. Landscapes to support environmental education and interpretation.
4. Remediation as a tool to build new districts and neighborhoods on former brownfields and a source for economic growth and revitalization.
5. Integration of micro scale with urban and regional scale as a multi-scale approach.
6. Decentralized, local, on-site strategies.
7. Interdisciplinary collaboration between scientists, designers, and planners.

The long-term time requirement for phytoremediation can also provide an opportunity: Changing and growing plant communities can be staged, each step of the cleaning process can transform into specific landscape typologies that build up the framework for urban form and green urban infrastructure and that is simultaneously a landscape of experiences. The design proposals of the Urban Design Laboratory explored the potential to make remediation landscapes useful and beautiful.

7. ACKNOWLEDGEMENTS

I thank the students of the UMASS Urban Design Laboratory 2007 – 2008 for their inspiring and thoughtful work and the IBA Hamburg, specially Hubert Lakenbrink and Jost Vitt, for their great support. I thank Professor Guy Lanza for helping in creating a bridge between design and sciences. I thank Prof. Jack Ahern, Yaser Abunnasr, and Prof. Niall Kirkwood for their critical feedback.

8. ENDNOTES

[1] Phytoremediation and Bioremediation designate different concepts and potential applications. Because this paper does not focus on the scientific use of remediation methodologies the term “phytoremediation” is used throughout. Phytoremediation is a plant-based approach and bioremediation is a microbial approach. Bioremediation uses micro-based technology for the degradation of organic compounds. Phytoremediation uses green or vascular plants to remove organic contaminants or heavy metals from the environment. Phytoextraction is the use of metal-accumulating plants that can transport and concentrate metals from the soil to the roots and aboveground shoots. Rhizofiltration is the use of plant roots to absorb, concentrate, and precipitate heavy metals from water (Ensley, B. 2000, pp. 4-5). In: Phytoremediation of Toxic Metals (Raskin, I. and Ensley, B. Eds.). New York, John Wiley and Sons.

[2] Ensley compares the economical benefit of phytoremediation to conventional remediation methods:: “The relatively low potential cost of phytoremediation allows the treatment of many sites that cannot be addressed with currently....available methods… The economic and

environmental advantages provide an excellent reason for the use of this approach in the treatment of contaminated sites. Plants can be grown and harvested economically; leaving only residual levels of pollutants (Ensley, B. 2000. Rationale for Use of Phytoremediation. pp. 3-11). Conventional cost double and more (Glass, D.J. 2000. Economic Potential of Phytoremediation. pp. 15-31. In: Phytoremediation of Toxic Metals (Raskin, I. and Ensley, B. Eds.). New York, John Wiley and Sons.

[3] Benedict and Mc Mahon describe principles of Green Infrastructure. Most relevant are: 1. Connectivity is key. 2. Context matters. 3. Green infrastructure should be grounded in sound science and land-use planning theory and practice. 4. Green infrastructure can and should function as the framework for conservation and development. 5. Green infrastructure should be planned and protected before development. …7. Green infrastructure affords benefits to nature and people. 9. Green infrastructure requires making connections to activities within and beyond the community. 10. Green infrastructure requires long-term commitment. (Benedict, M.A. and McMahon, E.T. 2006. 37)

[4] Strategies and visions were developed under my direction in the UMASS Urban Design Laboratory 2007and 2008. The scientific framework was established in collaboration with Prof. PHD Guy Lanza, Department of Environmental Sciences, UMASS. Rhizotopia design team: Jinglan Wang, Duanchai Samimi (2007)
Veringkanal design team: Todd Lynch, David Maynes, Chris Metz, Duanchai Samimi (2008)

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PART VI: Radionuclides

Chapter 13

RADON REMOVAL FROM POTABLE WATER SUPPLIED BY MUNICIPAL AND SINGLE HOME WATER WELLS

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ABSTRACT

Activated charcoal can remove contaminants such as radionuclides from potable water. In northern Virginia, a community water well normally producing about 17 million gallons of water per year plus many small homesite water wells were used to study the monthly and seasonal variation in waterborne radon concentration, These wells were also used to study the ability of activated charcoal to capture the dissolved radon before it reaches the home occupants. It was found that the percentage of radon removal was related to the volume of treated water, the type of activated charcoal, and the length of time that the charcoal was used. In brief, if sufficient activated charcoal was placed in the water treatment tank, the removal of waterborne radon could reach 90 percent. While the intensity of radiation that escaped through the walls of the capture tank was easily detected, estimates indicate that the health risk was minimal while the capture tanks were in operation, and during the replacement of the used and radioactive charcoal.

Keywords: radon, water, remediation

1. INTRODUCTION

Naturally occurring radionuclides are trace elements when found in rocks, soils, and water. There are 2,000 known radionuclides, which are species of atoms that

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emit radiation as they undergo radioactive decay through emission of alpha, beta, and gamma rays. The radioactive isotopes that carry the most health risk are alpha-particle emitters. Most of the radon in nature is Rn-222, which is an alpha-emitter, and is part of a decay series that includes other alpha-emitters including radium (Ra-226) and plutonium (Po-218, Po-214, and Po-210), which can cause cancer.

Radon is in groundwater that travels through cracks in bedrock. Water from wells normally has a much higher concentration of radon than the surface water in rivers, lakes and streams. The radon in groundwater as it is pumped out of a well remains in the water until the water escapes from a water outlet in the home.

Since it easily transfers from water to air, radon is rarely found in surface waters. Radon levels can vary greatly from one region to the next, because of differences in the local geology. Radon in well water also varies due to local, site specific factors such as well depth, distance from the radon source, pumpage patterns and the characteristics of the radon source.

The USEPA has concluded that the ingestion of radon and its decay products (mainly in well water) poses significant cancer risks other than lung cancer. The USEPA has noted that the cancer risks from radon in water (soft tissue cancer) are high. The cancer risk from radon in water is higher than the cancer risk nationally estimated to result from any other drinking water contaminant. Hess et al (1983, 1985) showed a correlation between radon in potable water and the incidence of cancer of many types. Under some circumstances, it seems likely that ingested radon could give a significant radiation dose to the stomach, which can lead to a significant risk of stomach cancer (Hursh et al., 1965). Radon decay products may also give a substantial dose to skin, since ingested radon escapes by in part through the skin (Harvey, 1971).

In 1992, Congress directed the USEPA to report on the risks from exposure to radon, the costs to control this exposure, and the risks from treating to remove radon. Drinking water that is contaminated with radon in excess of the USEPA's proposed MCL of 300 pCi/L is used by over 19 million people according to available USEPA data and poses significant, but avoidable health risks (USEPA, 1995). As required by the 1996 amendments to the Safe Drinking Water Act (SDWA), the USEPA should have established an enforceable standard for radon in tap water by the year 2000. Almost 2 of every 10,000 individuals exposed to 300 pCi/L of radon in water would develop a fatal case of cancer as a result of exposure to radon at this level.

In north-central Virginia and south-central Maryland, municipal water supplies obtained from reservoirs provide radon-free potable water. However, the average waterborne radon concentration in private and municipal water wells in

north-centralVirginia and south-central Maryland is much more than the USEPA's MCL for radon (Mose et al., 2001).

Most of the wells examined in most of the following study are in several different types of rock in northern Virginia and southern Maryland. The geological units in the northern Virginia and southern Maryland Appalachians are found over vast areas. Each unit can be traced over most of the terrain. The oldest unit in the study area is a quartzite, which was deposited as beach sand almost 600 million years ago. The deposition of this sand marks the beginning of a 200 million year interval, during which an increasing deep sea covered what is now the Piedmont Province of eastern Virginia and Maryland. Many additional layers of sedimentary and volcanic strata were deposited in this ancient pre-Atlantic ocean basin until about 400 million years ago. During the interval between approximately 400 and 300 million years ago, these ancient sedimentary and interlayered volcanic strata were deeply buried, to depths of about 5 miles. The sand was recrystallized into the metamorphic rock called quartzite. Clay rich strata formed mica-rich and feldspar-rich (felsic) metamorphic rocks. In some areas, high temperatures produced chambers of molten material which subsequently cooled to form the granites of the Appalachian Mountain system.

About 10% of the homes in northern Virginia use well water. The water from some of these wells exceed 4,000 pCi/L of radon, the average is about 2,000 pCi/L, and few homes have waterborne radon as low as 300 pCi/L . In the study area, water wells in the quartz rich sedimentary rocks yield well water that averages about 1,000 pCi/L. Wells in the felsic metamorphic rocks average about 2,000 pCi/L, and wells in the granite rocks average about 5,000 pCi/L.

Although it is known that radon and its decay products in well water can cause cancer, inexpensive methods of removing these radionuclides. The following report was based on measurements designed to determine the variability through time of radon concentrations in well water, well-to-home decreases in waterborne radon, and the effectiveness of radon removal from well water by using tanks of activated charcoal in large systems and small home systems.

2. DETERMINATION OF THE VARIABILITY THROUGH TIME OF RADON CONCENTRATIONS IN WATER WELLS, USING SHORT TIME INTERVALS (HOURS AND DAYS)

In most homes with wells, water is used repeatedly over short time intervals. Sometimes a much larger volume is used over a few days, as for example when watering a lawn or garden. More commonly, water is frequently used in smaller volumes, for operating showers, dishwashers and cloths washers. In all the cases,

most of the well water comes from the cracks in the local bedrock in the vicinity of the well.

As a pump runs, it lowers the level of water in the well and agitates water in the well. It was anticipated that waterborne radon would decrease during repeated and prolonged use of a water well, when some radon is lost by coming out of the water in the well and escaping out of the top of the well. However, no known experiments have been performed to test this possibility. It equally might be true that as water is removed from the well by the pump, water with more radon might enter the well. Data from several experiments are given in Table 1.

Table 1. Daily and Hourly Tests of Waterborne Radon

Experiment 1. Well in Fairfax, VA

Date	Time	Well Water Radon (pCi/)
4/02/06	1000	3820
4/18/07	900	2400
6/02/07	1100	2600
6/03/07	1100	2700
6/04/07	1000	2320
6/05/07	1200	2240
6/06/07	1300	2450
6/07/07	900	2250
6/10/07	1300	3650
6/10/07	1330	3020
6/10/07	1430	2620
6/10/07	1530	2380
6/10/07	1630	2160
6/10/07	1930	2100
6/10/07	2200	1820
6/10/07	900	3650
6/12/07	1100	2980

Experiment 2. Well number 1 in Culpeper, VA

Date	Time	Well Water Radon(pCi/)
2/20/06	1000	240
4/13/07	1230	520
4/13/07	1330	<100
4/13/07	1430	<100
4/20/07	1300	150
4/20/07	1330	100
4/20/07	1400	600
4/20/07	1430	210

Experiment 3. Well number 2 in Culpeper, VA

Date	Time	Well Water Radon(pCi/)
2/15/06	1800	570
2/20/07	1000	300
4/22/07	0800	700
4/22/07	0900	600
4/22/07	1100	540
4/22/07	1200	480
4/22/07	1300	470

2.1 Results

As shown in Table 1, waterborne radon did not show a steady increase or decrease when tested once a day, over several days. However, when waterborne radon was tested once an hour, over several hours, the waterborne radon concentration decreased. The pattern of change reveals the probable explanation.

The Experiment 1 well, VA well, when tested hourly on 6/10/07, showed a steady decrease in waterborne radon. The Experiment 2 well, when tested hourly on 4/22/07, also showed a steady decrease in waterborne radon. The Experiment 2 well is only about 300 meters from the Experiment 3 well, and because of similar geology, should have similar waterborne radon. However, the Experiment 2 well provides considerably less water, because there are fewer cracks in the bedrock in the vicinity at this well site compared to the Experiment 3 well. It was observed, as shown on Table 1, that the radon in the Experiment 1 well was initially similar (a few 100 pCi/L) to that in the Experiment 3 well. However, after about I hour the amount of water coming out of the Experiment 2 well decreased greatly, to about 1/10 of its original productivity. At the same time, the amount of waterborne radon decreased greatly.

It seems likely that when the level of water in the Experiment 2 well is lowered, the water pump is “churning” the water, which happens when the water level is so low that the top of the water pump is exposed. In this condition, radon dissolved in the water would be driven out of the water around the pump, and would escape up the nearly empty well pipe. The water that does get pushed out of the well by the pump should then have considerably less radon. As shown in Table 1, in all three experiments, the waterborne radon hour-to-hour decrease is a mechanical phenomenon relate to water agitation caused by the well water pump.

3. THE WELL-TO-HOME DECREASE IN WATERBORNE RADON

The concentration of radon in drinking water decreases in the distribution system when it travels from the treatment plant to customers. Measurements were made of potable water radon at Prince William well sites and at homes served by these wells. The water collections were made using the kitchen water faucet, after running the water for a few minutes until it seemed not to get any colder. Then the water faucet was turned to slow non-turbulent flow. The non-turbulent method of collection is the best, because it reduces loss of radon during the moment of sample collection.

Water was also collected as it flowed out of the wellhead collection tank, to determine the level of radioactivity that was being sent to the homes. Well number WO-6 was selected for the well-to-home study (Table 2).

3.1 Results

In this study of well-to-home loss of radioactivity, the well-to-home loss of radioactivity was about 30%. This seems large, because in this community as in most large systems, normally less than one day occurs between the times that well water is pumped from storage tanks to the time it reaches the surrounding homes (Mose, 2007). The half-life for radon-222 is 3.8 days, so one might expect that a loss of radioactivity of less than 30% (perhaps 20%) would occur between when water is taken out of the wells and when the water arrives at the homes.

Perhaps the well-to-home time interval is actually more than one day. Perhaps some radon gas escapes from the pipes and tanks (radon can escape through holes smaller than holes through which water can escape). In fact, another factor may play a role in affecting the well-to-home change. It is known that metals such as radium (which decays to radon) can accumulate on the interior walls of water pipes. Pipes that are older might be expected to have more accumulation of radium and other uranium-chain radionuclides on the interior of the pipes, which should serve to increase waterborne radon concentrations after the water leaves the water well, and thereby reduce the well-to-home decrease.

In any event, the well-to-home loss of radioactivity, at 30%, is still too small to make the water safe. That is, while water provided by the Prince William Service Authority (PWCSA) well WO-6 is always in excess of 2,000 pCi/L, the well-to-home decrease does not ever cause the waterborne radon in the home to fall below the USEPA's MCL of 300 pCi/L.

4. THE DETERMINATION OF THE EFFECTIVENESS OF RADON REMOVAL FROM WELL WATER BY USING TANKS OF ACTIVATED CHARCOAL.

There are two technologies most commonly used for removal of radon from well water. They are Aeration and Granulated Activated Charcoal (GAC). GAC in the United States has long been used for the control of synthetic organic chemicals and taste and odor problems. Since the detection of high levels of radon in drinking water supplies, a number of research studies have been undertaken to evaluate the effectiveness of GAC for controlling radon. As the water moves through a bed of activated carbon, the radon is adsorbed onto the carbon until all the available GAC surface area is taken up.

Table 2. Decrease of waterborne radon between the Algonquin Hills System Well Number WO 6 and a home on Running Dear Road in Prince William County, Virginia

Date	Well (pCi/)	Home(pCi/)	Decrease
02/05/91	2540	1750	31 %
02/11/91	N/A	1080	N/A
02/12/91	3510	2140	39
02/15/91	2010	940	53
03/28/91	2610	1990	24
04/02/91	2640	1830	31
06/06/91	2430	1780	27
06/07/91	2150	1780	17
06/24/91	2460	N/A	N/A
07/10/91	3260	2680	18
07/25/91	2630	1830	30
11/19/91	2230	1320	41
12/16/91	2130	1730	19
Avg = 30	Avg = 2558	Avg = 1797	

The adsorption process occurs when the radon molecules diffuse through the water to the surface of the GAC. Radon sorbs at the interface between the water and the carbon. Therefore, the higher the surface area of the GAC, the more effective is the adsorption process. The outer surface of the carbon provides some area for adsorption, but most of the surface area is in the pores within the carbon particles.

Contaminant removals are a function of the available interfacial area between water and GAC, and the rate at which the water flows through the GAC. The success of a GAC system also depends on competitive adsorption from natural organic matter in the water, which can compete with radon for adsorption sites. Also, adsorption can be greatly limited by suspended solids in the water, which coat the outer surface of the GAC. These solids are often oxides and carbonates of Fe, Mn and Pb. Consequently, GAC systems may require some kind of pretreatment to minimize the organic loading of the carbon, and eventually clogging of the carbon bed. Filtration ahead of the GAC system is the most common solution to prevent clogging of the GAC bed.

In theory, waterborne radon is retained in the GAC, and the water leaves the charcoal tank relatively free of radon and radon decay products. GAC systems have been shown to be effective at lowering waterborne radon levels, but more needs to be known about the length of the complete removal interval, and about the radioactivity that builds up in the filter bed.

Gamma radiation exposure from GAC tanks and waste disposal issues of used GAC related to the accumulation of radioactivity on the media are two concerns associated with using GAC for radon removal in homes. The decay of radon within the GAC bed results in the growth of radon progeny. Beta, gamma and alpha emissions come from the decay of Po-218, Pb-214, Bi-214 and Po-214, which have short half-lives. In addition to these radioactive decay products, there is also a buildup of radioactive Pb-210 on the GAC bed, and Pb-210 has a long half-life (22 years). In short, the accumulation of radon and other radionuclides on the activated charcoal poses a potential health risk to home occupants.

Fortunately, only gamma radiation can pass through the walls of a GAC tank. The level of gamma radiation surrounding the bed depends on the influent radon level, radon effluent level, the distance from the bed. The exposure rate is significantly lower a few feet from the GAC bed, compared to the maximum exposure rate found at the surface of the GAC vessel.

All types of GAC have a finite adsorption capacity that is determined by the characteristics of the targeted contaminant. When the contaminant begins to appear in the effluent, breakthrough is said to have occurred. In the radon adsorption process, an adsorbed radon atom decays, reducing the interfacial

concentrations of radon and restoring some adsorption capacity to allow new radon atoms to become adsorbed. Once the breakthrough concentration reaches an excessive level, the carbon must be regenerated or replaced.

4.1 Results

4.1.1. Measurements Using a Large Water Treatment System

One of the study wells in Prince William County (well WG-7) delivers about 17,000,000 gallons of VOC-free potable water each year to Prince William County residents. For many years GAC has been used to remove Volatile Organic Carbon (VOC) present in well WG-7. The water is rendered VOC-free by passing it through two 2,000 cubic foot tanks containing GAC. Well WG-7 was selected for a radon study, because in theory VOC removal and radon removal might be similar (Table 3).

At well WG-7, the GAC in each of the two tanks is changed in alternating years. That is, once a year the older charcoal in one of the tanks is replaced. The tank with the older charcoal is filled with new charcoal (the old charcoal goes to a landfill), and the water pathway is changed so as to have the water pass through the tank of one-year-old charcoal, and then through the tank of just-replaced charcoal.

Table 3. Radon from Prince William County well WG-7.

Tank Well Water	Month	Radon Concentration(pCi/L)	% Reduction
Well water	03	1800	-
After first tank		1880	0%
After second tank		730	59%
Well water	06	1640	-
After first tank		1290	0%
After second tank		800	38%
Well water	07	2330	-
After first tank		2040	12%
After second tank		750	68%
Well water	02	2190	-
After first tank		830	62%
After second tank		90	96%
Well water	02	No measurement	-
After first tank		1250	
After second tank		310	
Well water	03	1680	-
After first tank		1280	24%
After second tank		350	79%
Well water	03	1760	-
After first tank		1250	29%

Table 3. Continued

Tank Well Water	Month	Radon Concentration(pCi/L)	% Reduction
After second tank		430	76%
Well water	04	1990	-
After first tank		1080	46%
After second tank		460	77%
Well water	05	2150	-
After first tank		1720	20%
After second tank		570	73%
Well water	06	2160	-
After first tank		1650	24%
After second tank		560	74%
Well water	08	2090	-
After first tank		1540	26%
After second tank		620	70%
Well water	09	1650	-
After first tank		1440	13%
After second tank		690	58%
Well water	11	1950	-
After first tank		1260	35%
After second tank		580	70%
Well water	12	2160	-
After first tank		1780	18%
After second tank		740	66%
Well water	01	2110	-
After first tank		1690	20%
After second tank		240	89%
Well water	03	1830	-
After first tank		1820	0.5%
After second tank		810	56%

Currently there are no Federal regulations governing the disposal of radioactive waste generated by water treatment facilities. The US Nuclear Regulatory Commission's does not regulate naturally occurring radioactive material. The USEPA notes that most States deal with the disposal of radioactive water treatment residuals on a case-by-case basis. The States have no specific regulations or guidelines for these radioactive residuals, but instead apply existing solid waste or hazardous waste disposal requirements. Since a GAC system in a home creates such a small volume of radioactive charcoal, GAC from homes are normally disposed as normal trash.

Tests using a field radiation meter first were conducted on the outside of the two charcoal-containing tanks at well WG-7 to make sure that it was safe to work around the tanks. The measurements showed that while the charcoal does retain radionuclides, the intensity of gamma-radiation from radon decay product Bi-214

(a short-lived, but strong gamma emitter) outside the tanks is not a significant health risk, even assuming long-term exposure. That is, a person whose office is inside the building containing the tanks would not be exposed to a significant gamma-dose assuming 40 hours/week in the office. Other forms of radiation, such as beta and alpha radiation, cannot escape the metal tanks as long as the charcoal remains in the tanks.

The investigation conducted to determine the radon-removal effectiveness of GAC to remove waterborne radon at well WG-7 in Prince William County showed that well water from well WG-7 exceeds 2,000 pCi/L, but after the water passes through the two GAC tanks, the waterborne radon is less than 800 pCi/L.

After flowing through one large tank of GAC, the waterborne radon from well WG-7 decreased by an average of 22 % from the untreated well water. It decreased by 70% after a second large tank of GAC. Although the radon in the water leaving the charcoal treatment at well WG-7 is not reduced to less than the USEPA's MCL of 300 pCi/L, most of the radon was removed. This is important, considering that this is a high volume well, sending thousands of gallons each day to homes in Prince William County. The reduction in health risk is significant

4.1.2 Measurements Using Small Water Treatment Systems

The National Inorganics and Radionuclides Survey (NIRS) conducted by EPA indicated that the concentration of radon in United States groundwater supplies ranged up to about 25,000 pCi/L (Longtin, 1988). Levels of radon in groundwater supplies had range of 100 to 1000 pCi/L for 61.5% of the 978 sites sampled in the NIRS. The highest levels of radon observed in the NIRS were in small system supplies serving fewer than 500 people. About 83% of groundwater systems have a radon concentration of less than 500 pCi/L and that about 10% of ground water systems have a radon concentration between 500 and 1000 pCi/L.

Point of entry GAC units consist of a metal or a fiberglass pressure vessel containing one or more cubic feet of activated carbon. The two basic configurations for homesite operation is the down flow fixed bed and the up flow fixed bed. The system is operated by gravity or under pressure. Downward flow systems are also used when the unit is used to filter out suspended solids. Two or more fixed beds operated in parallel typically are used when a high flow rate would require a vessel diameter too large to be economical or feasible. Down flow fixed bed systems are the simplest configuration for radon removal of groundwater at the point where it enters a home.

In most homes, GAC systems operate in an up flow mode where the contaminated water is introduced under pressure at the bottom of the carbon bed,

and flows up through the bed to the top. The radon moves with the water up through the GAC bed until there is available area for adsorption to take place.

After some experimentation, it had been determined that GAC made from cocoanut provided the best radon removal among the many types of GAC available to water treatment companies. In Table 4, the results of using GAC made from coconut shells are reported for several homes in northern Virginia over the past 15 years.

Experiments conducted prior to the results presented here determined that GAC volumes less than 2 cubic feet were not effective for long-term (more than one year) removal of waterborne radon in significant amounts (Mose, 2007). The systems installed in the homes summarized in table 10 all were 2 to 2 1/4 cubic

Table 4. Reduction of Waterborne Radon in Northern Virginia Homes

Home	Pre-Remediation(pCi/)	Post-Remediation(pCi/)	% Decrease	Location
1	1990--------- 3070	NA	-	Great Falls, VA
	12/27/90----3690	12/27/90----150	96%	
	01/20/92----3130	01/20/92----580	81%	
	09/19/92----1990	09/19/92----740	63%	
2	02/11/91--- -3890	NA	-	
	10/09/91----3590	10/9/91-------850	76%	Annandale, VA
3	01/31/91----4490	NA	-	
	04/08/91----3890	04/08/91--------150	96%	
	05/14/91----4710	05/14/91--------350	93%	
	08/28/92----3890	08/28/92------2370	39%	
	09/16/92----4350	09/16/92-------2830	35%	
4	1990--------11,380	NA	-	Clifton, VA
	01/18/91-----9290	01/18/91------1590	83%	
	03/31/91---10,330	03/31/91------1780	83%	
	06/05/91-----6620	06/05/91------1110	83%	
	06/11/91---12,190	06/11/91------1610	87%	
	09/03/91-----8880	09/03/91------3910	56%	
	04/11/92-----6800	04/11/92--------450	93%	
	08/28/92-----9900	08/28/92------2770	72%	
	04/30/97----10750	04/30/97-------400	96%*	
	06/12/98-----8640	06/12/98--------800	91%	
5	01/19/91-----3180	NA	-	Great Falls, VA
	08/02/91-----2990	08/02/91-------450	84%	
	01/20/92-----3360	01/20/92-------970	71%	
	09/19/92-----3040	09/19/92------1080	64%	
	05/13/93-----2390	05/13/93------<100	96%	
6	03/12/91------4620	NA	-	
	09/03/91------2960	09/03/91------475	84%	Clifton, VA
7	01/15/91-------1630	NA	-	
	04/06/91-------2340	04/06/91------150	94%	Dale City, VA
	01/18/92------1780	01/18/92------180	90%	
	NA	04/26/97------400	-	

Table 4. Continued

Home	Pre-Remediation(pCi/)	Post-Remediation(pCi/)	% Decrease	Location
8	03/24/92------4550	NA	-	
	08/18/92------4890	08/18/92---------250	95%	Oakton, VA
	05/13/93------4840	05/13/93--------2460	49%	
9	08/18/92------8390	NA	-	
	04/08/97------7490	04/08/97-------1960	73%	Clifton, VA
10	1990---- -----5650	NA	-	McLean, VA
	11/10/90-- --6530	11/30/90-------1750	73%	
	10/30/90--- -4190	10/30/90--------650	85%	
11	10/05/92------3320	NA	-	Clifton, VA
12	03/25/93------4500	NA	-	
	04/30/97-----6270	04/30/97-----2120	66%	Clifton, VA
13	12/18/90-----7320	NA	-	Great Falls, VA
	04/24/93------7700	04/24/97------310	96%	
14	12/18/90-----7060	NA	-	Great Falls, VA
	04/6/91------7180	04/06/91-----460		
15	04/17/91----4340	04/17/91------560	87%	Clifton, VA
	06/21/91----4090	06/21/90------140	96%	
	08/22/92----5200	08/22/92----<100	98%	
16	04/28/92-----7190	NA	-	Clifton, VA
	12/18/99-----9740	12/18/99---<100	99%	
17	11/1/90-----5020	NA	0	McLean, VA
	11/10/90---4360	11/10/90-----1440	67%	
	01/18/91----5570	01/18/91------110	98%	
	02/18/92----4200	02/18/92------240	94%	
18	1990---------4360	NA	-	Clifton, VA
	03/30/91----4570	03/30/91-----250	94%	
	08/28/92----4370	08/28/92-----290	93%	
19	1990--------5000	NA	-	Oakton, VA
	03/30/91---4120	03/30/91------280		
20	04/02/06 3820	540	86%	Fairfax, VA
	04/18/07 2400	570	76%	
	06/02/07 2600	810	69%	
	06/03/07 2700	880	67%	
	06/04/07 2320	630	72%	
	06/05/07 2240	630	72%	
	06/06/07 2450	810	67%	
	06/07/07 2250	630	72%	
	06/10/07 3650	850	82%	
Time for 06/10/07 date				
	1300 3650	850	77%	
	1330 3020	830	73%	
	1430 2620	640	76%	
	1530 2380	630	73%	
	1630 2160	640	70%	
	1930 2100	600	71%	
	2200 1820	570	69%	
	06/12/07 2980	660	78%	

Table 4. Continued

Home	Pre-Remediation(pCi/)		Post-Remediation(pCi/)	% Decrease	Location
21	09/92	3130	580	81%	Great Falls, VA
22	10/14/05	1050	<100	90%	Woodbridge, VA
	01/13/06	1870	<50	90%	
23	10/01/89	5260	820	84%	Clifton, VA
	1990	NA	930	-	
	1990	4990	<50	90%	
24	01/13/06	2000	<100	90%	Woodbridge, VA
	01/13/06	3580	680	81%	
25	01/14/06	3400	NA	-	Great Falls, VA
	12/14/06	3500	320	91%	
26	07/25/05	2340	<100	90%	Woodbridge, VA
	01/13/06	NA	<100		
27	03/07	1700	NA	-	Aldie, VA
	07/09/07	1350	190	86%	

feet of coconut GAC in one tank, and used an upward flow of well water through beds of the charcoal.

The experiments reported here, with 2 to 2 ½ cubic feet of GAC made from cocoanut shells, removed between 70% and 90% the waterborne radon. The percent removal did not show a steady increase or decrease through time. Changes did occur through time, in that the % decrease rose or fell in an apparent random fashion.

In one experiment (see home 20, data for 6/10/07), pre-GAC and post-GAC were obtained hourly as water continuously flowed into a sink. The pre-GAC measurement of waterborne radon decreased, but the post-GAC measurement showed an almost constant % decrease of about 70%.

5. CONCLUSION

The month-to-month variations of water radioactivity cannot be related to the chemistry of the rocks holding the groundwater, because the uranium content of the rock reservoir from which ground water obtains radon does not change. It seems more likely that rainfall changes might cause seasonal radioactivity changes in well water. The monthly amount of new downward moving water derived from rainfall does change. During late spring to early summer, when more rainfall normally occurs, the radioactivity of groundwater increases.

Waterborne radon did not show a steady increase or decrease when tested once a day, over several days. However, when waterborne radon was tested once an hour, over several hours, the waterborne radon concentration decreased. It seems likely that when the level of water in a well lowers due to frequent

pumping, the water pump is "churning" the water. Dissolved radon in the water is driven out of the water around the pump, and escapes up the empty well pipe. Consequently, the water that does get pushed out of the well by the pump has less and less dissolved radon. In the study of well-to-home loss of radioactivity, the well-to-home loss of radioactivity was about 30%. This seems to be large, because in this community as in most large systems, normally less than one day passes between the times that well water is pumped from storage tanks to the time it reaches the surrounding homes. The half-life for radon-222 is 3.8 days, so one might expect that a loss of radioactivity of less than 30% between when water is taken out of a well and when the water arrives at a home. Perhaps the well-to-home time interval is actually more than one day. Perhaps some radon gas escapes from the pipes and tanks. In any event, the well-to-home loss of radioactivity, at 30%, is too small to make the water safe. For example, water provided by the Prince William Service Authority (PWCSA) well WO-6 is always in excess of 2,000 pCi/L, the well-to-home decrease does not ever cause the waterborne radon in the home to fall below the USEPA's MCL of 300 pCi/L.

An investigation conducted to determine the effectiveness of GAC to remove waterborne radon from large-productivity water systems showed that in a case where radioactivity exceeds 2,000 pCi/L, after the water passed through two GAC tanks, the waterborne radon was less than 800 pCi/L. Although the radon in the water leaving the charcoal treatment was not reduced to less than 300 pCi/L, most of the radon was removed. This is a high volume well, sending thousands of gallons each day to homes, so the reduction in health risk is significant.

In a study of approximately 25 homes with wells, two or more cubic feet of activated charcoal made from cocoanut shells removed, on average, about 70% of the waterborne radon. The effectiveness of the GAC systems in the homes sometimes showed considerable variation through time, but the data do not show a steady increase or decrease in radon removal.

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PART VII: Remediation

Chapter 14

IN SITU WASHING BY SEDIMENTATION METHOD FOR CONTAMINATED SANDY SOIL

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ABSTRACT

We propose a new method of in situ soil remediation called in situ washing by sedimentation (IWS), accomplished by injecting a high air-pressure into a mixture of saturated water-sandy soil at a certain depth (D) and hydraulically separating the soil particles based on their particle size and density. This physical segregation exploits the distribution of contaminant in the soil by physically separating a selected contaminant-rich fraction. For the in situ application, the physical segregation by sedimentation and on-site water wash treatment happen as an integrated process. The advantage of IWS that the washing and segregation processes take place simultaneously during the remediation process, quick, effective and cheap since there are no costs for excavation of contaminated soil from the site. The effect of soil-water ratio and diameter geometry of the column on the effectiveness of segregation by IWS was investigated. A series of laboratory test were conducted to optimize the soil water ratio for the best segregation process. Soil-water ratio 1:2 (v/v) was found to be optimum for particle segregation produced by IWS . The suitability of IWS for Polycyclic Aromatic Hydrocarbon (PAH) remediation, such as Napthalene, Phenantrene and Pyrene, were examined by batch sedimentation column experiment. The laboratory experiment was effective to produce a distinct size segregation of the contaminated soil into the coarse and fine fractions, as well as the wash water, indicating that a significant reduction in Napthalene, Phenantrene and Pyrene level (90%) may be achieved. The experimental results show that the removal

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efficiencies depend on the initial concentration of PAH in the soil sample, the duration of washing and the addition of biosurfactant in the washing solution.

Keywords: In-situ washing, sedimentation method, soil-water ratio, metal contamination

1. INTRODUCTION

Several technologies have been developed for the remediation of contaminated soil. Broadly speaking, they can be grouped in the following categories, *ex situ* technologies where the contaminated soil is removed and treated away from the site that has to be cleaned up and *in situ* technologies, where the contaminated soil is cleaned on site.

There are various options in each of these categories. *Ex situ* technologies include incineration, extraction, *ex situ* washing, and *in situ* technologies include soil vapor extraction, soil flushing, bioremediation and phytoremediation. The major advantage of *ex situ* technologies is that it takes relatively little time to remove the contaminated soil. The soil is excavated, treated or replaced and then filled in again. By comparison with *in situ* methods, however, method of *ex situ* soil remediation has many drawbacks. They are expensive, large quantities of soil have to be transported often in residential areas, there are risks to buildings and other structures especially with major excavations, contaminants can be emitted during excavation, and it causes major disruption of daily life in the area to be remediated.

Increasingly, *in situ* technologies are used for sustainable clean-up of contaminated sites (Otten, et al., 1997). Air and water extraction have in practice proved to be reliable methods for various types of soil remediation (Bass et al., 2000, Reddy et al., 1995, Hutzler et al., 1991). Although bioremediation and phytoremediation was also used, this technology works too slowly to be fully effective as a remediation technology (Cunningham et al. 1995, Milic, et al., 2007).

Soil washing was conventionally performed *ex situ* in treatment plants that employ extracting chemical to remove contaminant from soil into aqueous solution (Mann, 1999; Abumaizar and Smith 1996; Cline and Reed, 1995; Griffiths, 1995). Few studies of *in situ* soil washing have been conducted, even though *in situ* soil washing could be suitable for certain contaminated soil in the field (Nash and Traver, 1993; Niven and Khalili 1998; and Makino and Kamiya, 2006).

We propose a new method of *in situ* soil remediation called *in situ* washing by sedimentation (IWS), accomplished by injecting a high air-pressure into a mixture of water-sandy soil column at a certain depth (D) and hydraulically separating the soil

particles based on their particle size and density, as shown in Figure 1 (Budianta et al, 2005, 2006a, 2006b). This physical segregation exploits the distribution of contaminant in the soil by physically separating a selected contaminant-rich fraction. Several researches indicate that the finest parts of soil are particularly active in the sorption processes of organic as well as inorganic contaminant (Evans et al., 1990; Hwang and Cutright, 2002; Abollino et al., 2003; Echeverria et al., 2002). For the *in situ* application, the physical segregation by IWS and on-site wash water treatment happen as an integrated process and it is important to isolate the site to protect the leakage of the aqueous solution used (Figure 1). The advantage of IWS was that the washing and segregation processes take place simultaneously during the remediation process, quick, effective and cheap since there are no costs for excavation of contaminated soil from the site. The fine fraction is recovered for further treatment or disposal. The wash water is completely collected, treated and recycled.

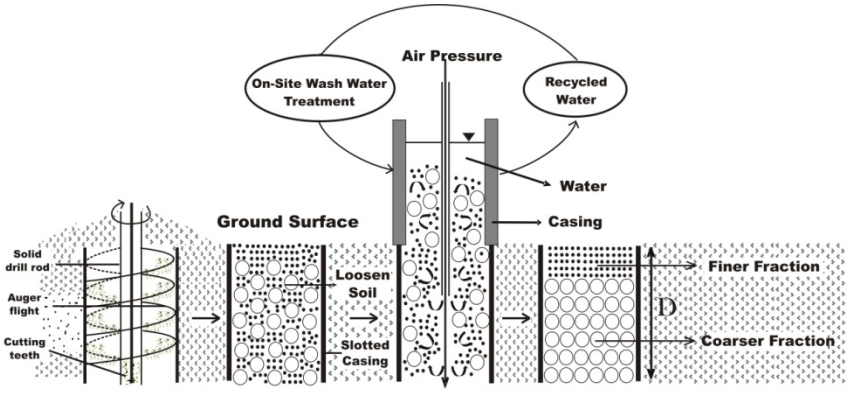

Figure 1. In situ Washing by Sedimentation Method (IWS)

The objective described in this paper, first was work on the simple-batch laboratory-column experiment of IWS by a systematic investigation on the evaluation of the effect of soil-water ratio and diameter geometry of column on the effectiveness of particle segregation by IWS in laboratory scale. Secondly, our second goal was to observe the removal of metal-contaminated sandy soil by IWS in batch laboratory experiment.

2. MATERIAL AND METHODS

Experiment were conducted on the uncontaminated soil were collected from Ota

District Tokyo in 1.5 m depths. The result of grain-size distribution indicated that the original soil sample contained approximately 10-20% clay-silt size particles and the remaining was sand (sandy soil).

2.1. The Effect of Soil-water Ratio on the Effectiveness of Particle Segregation by IWS

The objective of this experiment was to evaluate the effect of a soil-water ratio on the effectiveness of particle segregation by IWS. Environmental and economic concern required that the volume of water solution used on IWS in order to obtain sufficient particle segregation should be kept to a minimum. Generally, one of the main drawbacks of the washing method on soil remediation is the vast consumption of water required to make up the washing solution for the removal of the contaminants that have been retained in the contaminated soil. In IWS, we propose for washing solution which must be subsequently be on-site treated before it can be re-use. A series of laboratory experiment were carrying out to optimize the soil-water ratio for sufficient particle segregation.

Experiment was conducted in the cylinder tube of 2000 ml in volume with 90 mm inside diameter. For constant mass of 810 g dry soil, different volumes of water solution were used and were described in Table 1. The value of 300 ml volume of dry soil sample was divided by 2.710 g/cm^3 measured density.

After the soil sample and the water solution was prepared into the cylinder tube, the column then was stirred for one minute and let sedimentation occur for 30 minutes. Theoretically, the soil particle in the column will settle in a descending order of particle sizes with the top part of the soil layer consisting of smaller particle. The segregation of the soil particle into nominal size fraction in this experiment depends on the sedimentation process on hindered settling in the high sediment concentration.

Table 1. The water solution and the dry sample soil used

No. Tube	Soil sample gram (milliliter)	Volume of Water (ml)	Soil-Water Ratio (v/v)
1	810 (300)	300	1:1.00
2	810 (300)	400	1:1.33
3	810 (300)	500	1:1.67
4	810 (300)	600	1:2.00
5	810 (300)	700	1:2.33
6	810 (300)	800	1:2.67

The next step, all the cylinder tubes containing sedimentation soil column was kept in a refrigerator for -18^0 C temperature, in order to obtain an undisturbed frozen

soil column sample. After 24 hour, the frozen soil column samples then were taken out and marked. The purpose and the advantage of this freezing was to obtain a selected frozen column soil sample accurately by slicing the soil column without disturbing the sedimentation column. These undisturbed frozen soil column samples then were cut into several certain thicknesses and were analyzed for particle size distribution (Figure 2).

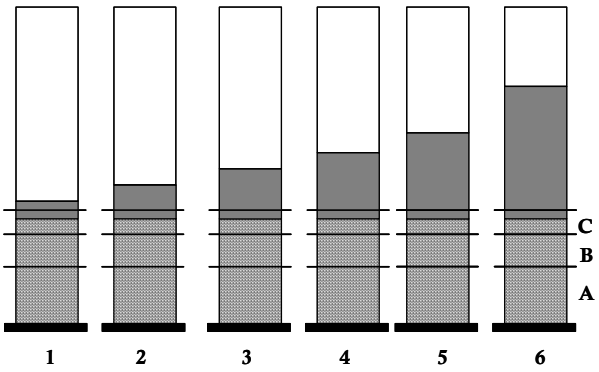

Figure 2. An illustration of undisturbed frozen soil column *(not to scale or actual size)*

The experiment was continued by observing more accurately the two soil fractions considered in this study. The terminology "fine" and "coarse" particles was used as the results of particle segregation by IWS. As previously stated, the top layer was assumed to be fine fraction and the bottom layer was assumed to be coarse fraction assumed reflects the high and low content contaminant in each fraction**.** Similar to previous experiment which conducted in the cylinder tube with 90 mm inside diameter, the optimized the soil-water ratio 1:2 (v/v) consist of 810 g dry soil and 600 ml volumes of water solution were used.

After sedimentation column was created, the top layer consisting of fine fraction was sampled very carefully by using small spoon, after the wash water was removed by suctioning. The fine fraction was then determined for particle size distribution analysis. Corresponding to the fine fraction, the remaining coarse fraction in the bottom part of the sedimentation column was also determined for particle size distribution analysis. The result of particle size distribution analysis was shown in Table 2. The fine fraction separated in the study was labeled as Clay and the coarse fraction was labeled as Fine Sand. These two fractions were then dried and weighed. The result can be seen in Table 2. The percentage of saturated volume was obtained by measured the height of each fraction in the sedimentation column.

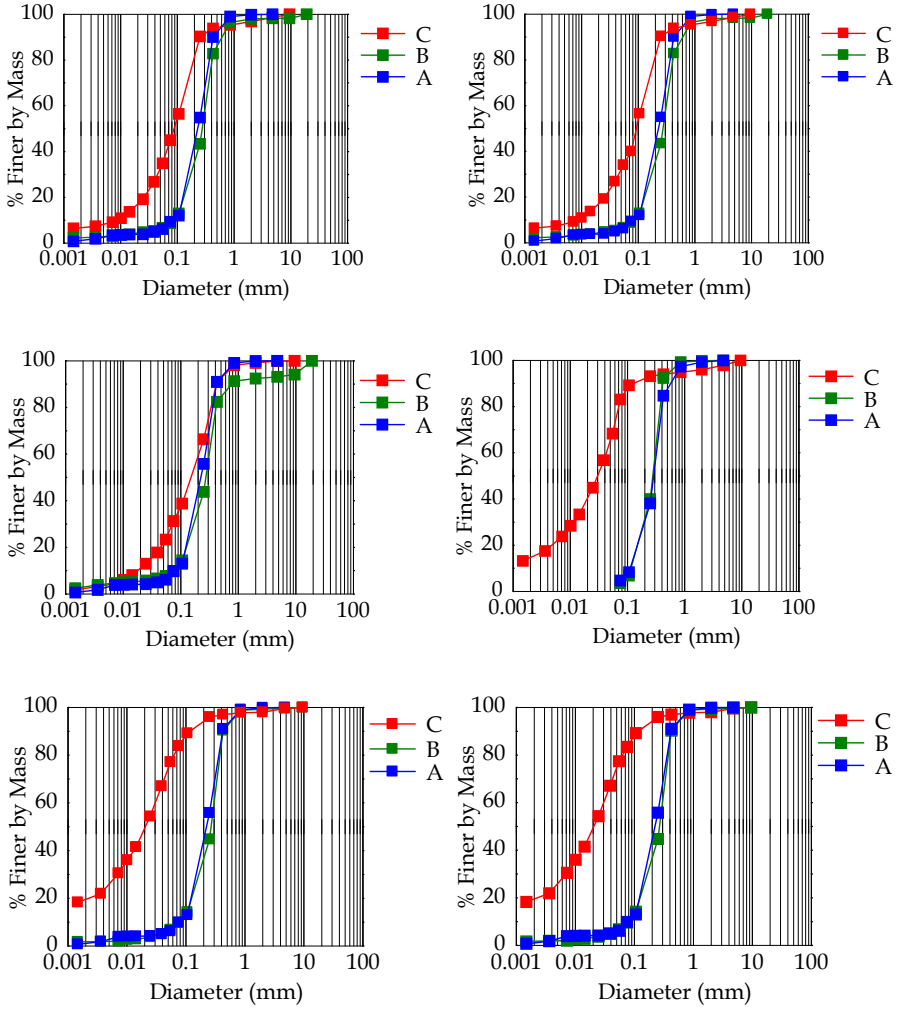

Figure 3. Particle size distribution analysis of selected frozen sedimentation column in each tube

In this stage, these two fractions separated (coarse and fine) was also determined for several parameter. It shows that the fine fractions have the high specific surface area, the high organic content, and containing of 1:2 clay minerals such as illite. It can be understood that the fine fraction separated by our sedimentation column particularly active in the sorption processes of contaminant.

Table 2. Particle size distribution analysis of fine and coarse fraction

Fraction observed (Size Diameter)	Fine	Coarse
Gravel 2-75 mm %	0.0	0.9
Sand 0.075-2 mm %	1.0	43.8
Fine Sand 0.075 mm %	6.9	48.5
Silt 0.005-0.075 mm %	37.0	5.1
Clay <0.005 mm %	55.1	1.6
Uniformity Diameter (mm)	-	2.59
	Clay	Fine Sand
Percentage Dry Weight	4.5	94.5
Percentage Saturated Volume	10	90

2.2. Removal of the organics contaminant on the sandy soil by IWS

2.2.1. Batch Sedimentation Column Experiment

Naphthalene (NAP), phenanthrene (PHE) and pyrene (PYR) were selected as example of PAHs representing organics contaminant. Two artificial contaminated soils were prepared by dissolving uncontaminated soil which collected from Ota District Tokyo (see Table 1 for detail) with an appropriate quantity of NAP, PHE and PYR solution as described by Sawada, et al., 2004. Briefly, uncontaminated soil sample was spiked with solution of NAP, PHE and PYR for three days to allow the dispersion and sorption of the contaminant in the soil matrix. (A) Soil with low concentration of PAH; (B) Soil with high concentration of PAH, by spiking uncontaminated soil sample with 500mg/kg of NAP, PHE and PYR solution for soil A and 1000 mg/kg for soil B. All samples then were determined for PAH concentration after ethanol digestion by using a Gas Chromatography Mass Spectrometry (GC-MS) under optimized operating condition. The resulting of the artificial contaminated soils had a final concentration of 30, 75 and 50 mg/kg of NAP, PHE and PYR on Soil A and 250, 490 and 350 mg/kg of NAP, PHE and PYR on Soils B.

Experiment was conducted by using air pressure created by air pump injected into the soil-water column on 90 mm internal diameter cylinder tube (Figure 4). A 0.5 kg dry PAH-contaminated soil sample was used and 370ml water was added based on the optimized soil-water ratio 1:2 (v/v) obtained from previous experiment. Seven similar tubes were constructed and the air pressure was introduced into each tube for 1, 2, 3, 4, 5, 10 and 15 minutes to observe the effect of washing duration.

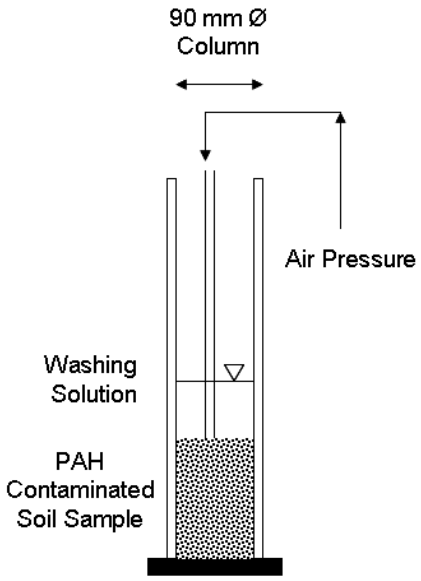

Figure 4. Laboratory experimental setup

The air flow started with the position of the pipe reaching the surface of the soil sample inside the tube. The air pressure rate was increased as the inlet pipe penetrated the soil sample. After the final depth was reached, air flow rate was kept constantly until the inlet pipe almost reached the bottom of the cylindrical tubes.

The soil inside the tube was allowed to settle to obtain clear water above the settled solids. The coarse fractions separated in this batch sedimentation experiment were analyzed for their particle size distribution. The wash water and the fine fraction were sampled through pipe by suctioning and the coarse fraction was sampled using a small spoon.

The segregation of coarse and fine fractions produced by IWS was investigated as a function of the washing duration, obtained by introducing air pressure into each tube for 1, 2, 3,4, 5, 10 and 15 minutes. The result shown in Table 3 indicated that the result of segregation in our batch sedimentation experiment was reliable, and the accuracy of segregation increase depending on the washing duration. A after 5 minutes washing, 92.2% of particles in the coarse fraction were separated as >0.075mm particles size diameter (fine to coarse sand) and fine fraction separated as <0.075mm particles size diameter (clay-silt). After 5 to 15 minutes, it seems that no significant difference occured in the results. Perfect segregation was expected in this method, but it showed that only about 90% of its grains were separated.

Table 3. *Values obtained by particles size analysis of coarse fraction separated by IWS*

Sample (observed fraction)	Washing Duration	Sand % (0.850 mm-0.250 mm)	Fine sand % (0.250 mm-0.075 mm)	Silt % (0.075 mm-0.005 mm)	Clay % (<0.005 mm)
Original	0	42.1	33.7	12.8	11.4
Coarse	1	44.7	47.6	5.0	2.6
Coarse	2	44.8	47.5	5.0	2.5
Coarse	3	43.5	49.1	4.9	2.3
Coarse	4	44.8	48.2	4.7	2.1
Coarse	5	44.2	49.7	4.0	2.0
Coarse	10	44.8	48.2	4.7	2.1
Coarse	15	44.2	49.7	4.0	2.0

The inaccurate result is attributed by the lack homogeneity in the particle size distribution of the coarse fraction. The sedimentation process is more complicated if several particles are present and the system becomes a sediment suspension in hindered settling reflected when the concentration of the suspension decrease, the homogeneity of the separated fraction will increase and therefore impossible to exclude small amounts of finer particles. Although the result of segregation by IWS was not perfect, the first important point of this study was that the process succeeded to separate the soil sample into a coarse fraction and a fine fraction. The segregation into coarse and fine fraction will affect the high and low concentration of the contaminant in each fraction.

2.2.2 Removal of PAHs in Contaminated Soil

As shown in the result of the previous experiment, the accuracy of particle segregation was influenced by the washing duration, and consequently it will affect the percentage removal of contaminant. In this experiment, the coarse fraction sampled was a representation of a clean fraction.

Figure 5 shows the experimental data by using the deionized (DI) water and DI water with addition of biosurfactant as washing solution. In the case of DI water washing, the result show that the removal process rapidly reaches equilibrium, at approximately 10 minutes for each PAH; after this period no considerable changes in the removal rates were observed. The PAH in the contaminated soil sample was mostly must found in the wash water and the fine fraction.

The fine fraction in the seven tubes was collected, combined and analyzed for PAH concentration. The results of the GC-MS analysis on the fine fraction showed that the concentrations of the PAH were very high. The accumulations of PAH in the fine fractions are attributed to the high specific surface area, the presence of clay minerals such as illite, and the high organic content.

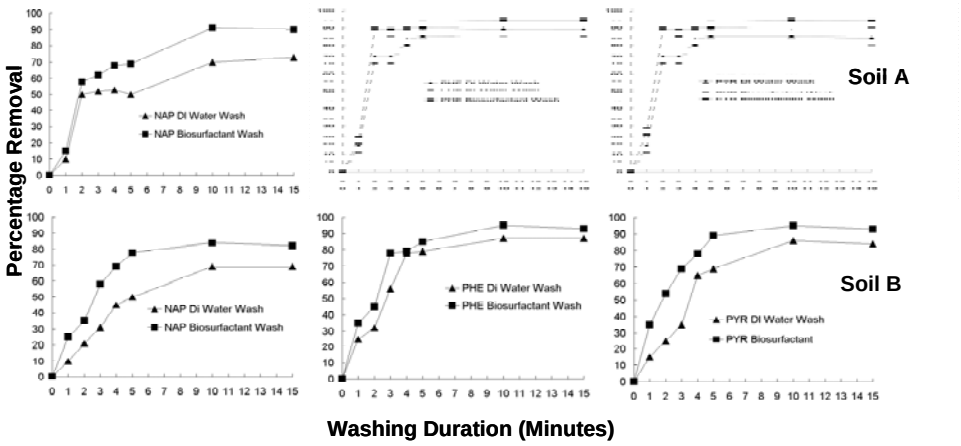

Figure 5. Percentage Removal PAH vs washing duration for soil A and B

The addition of biosurfactant (saponin) in order to enhance the percentage removal was also observed, by adding 0.25% by weight of saponin in the washing solution (Figure 5). In this stage, after fine fraction was removed, the wash water used was returned to the cylinder tube and saponin was added. The air pressure was then introduced into each tube for 1, 2, 3, 4, 5, 10 and 15 minutes to observe the effect of washing duration, the same as in the previous experiment. As shown in Figure 5, the removal percentage increased after the addition of saponin. The addition of saponin as an anionic biosurfactant was effective to assist in the solubilisation, dispersal and desorption of PAH from the contaminated soil fraction (Mulligan et. al., 2001).

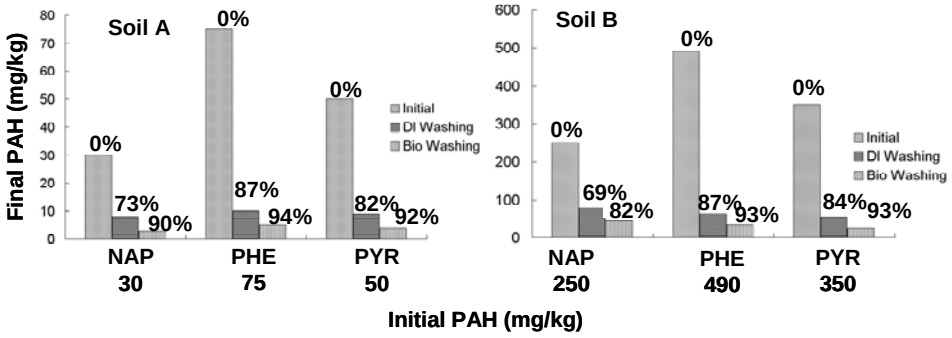

Figure 6. Removal efficiency of IWS on Soil A and Soil B

The result of the removal efficiency of PAH from soil A and B is shown in Figure 6. It shows that by using DI water only, approximately 80% of PAH retained in the

soil sample was removed. The addition of saponin has proven to be effective to enhance the removal efficiency up to more than 90%.

3. CONCLUSIONS

This study has addressed on the *in situ* soil remediation with an emphasis on the washing and segregation of soil particles by IWS. By using Ota District sandy soil as an object of this experiment, the following initial conclusions can be drawn from the results in this study:

The results of laboratory study on the effect of soil-water ratio on the effectiveness of particle segregation by IWS show that by using soil-water ratio 1:2 (v/v), the optimum for particle segregation on IWS was found. However, the result of laboratory study on the effect of diameter geometry of column on the effectiveness of particle segregation shows that generally the diameter geometry column will not affect the soil particle segregation.

The laboratory scale of in situ washing apparatus on IWS was able to produce a distinct size separation of the soil into coarse and fine and a significant reduction of Polycyclic Aromatic Hydrocarbon (PAH) such as Napthalene, Phenantrene and Pyrene level (90%) was achieved

The concentration of PAH contaminant was found to be a function of particle size; the coarse fraction were the cleanest and the fine fraction contained the highest PAH contaminant and a very small amount of the original contaminant was retained in the coarse fraction.

The removal efficiencies of remediation method proposed in this study depend on initial PAH concentration, the addition of biosurfactant in the washing solution and the duration of washing. Further treatment for the fine fractions and the wash water containing suspended solid particle and dissolve PAH contaminant need to be further investigated.

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Chapter 15

FAST-TRACK REMEDIAL DESIGN OF FULL-SCALE ISCO APPLICATION USING PILOT SCALE TESTING AND FIELD SCREENING PARAMETERS

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ABSTRACT

As a result of drum re-finishing operations, soil and groundwater at the Ottati and Goss Superfund Site in Kingston, NH, are contaminated with chlorinated volatile organic compounds (VOCs); benzene, toluene, ethylbenzene, and xylene (BTEX); and 1,4-dioxane. After re-evaluation of the selected remedy for groundwater, pump and treat, EPA changed the remediation approach to in-situ chemical oxidation (ISCO) through an Amended Record of Decision in September 2007. At that time, EPA established a goal for the site to attain construction complete status within one year, by September 30, 2008.

Activated persulfate was selected as the chemical oxidant for its capability to oxidize 1,4-dioxane, in addition to the other VOC contaminants of concern. Bench-scale and field pilot scale test were completed for three areas of the site to collect site-specific information to evaluate persulfate's ability to destroy the contaminants of concern and to optimize full-scale remediation design in three discrete source areas at the site. Base-activated persulfate was injected in Areas A and B in December 2007, and pilot test injection was completed in Area C in early February 2008, after vertical profiling was completed throughout Area C. Groundwater sampling for laboratory analysis was planned for 6 and 12 weeks after injection in each area; however, it was known during pilot test planning that the full-scale design would need to be completed by the end of March 2008, before all laboratory results would be available. In order to complete the design, an intensive evaluation of field geochemistry parameters and field screening chemical analysis was performed to assess radius of influence, oxidant

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persistence, and aquifer behavior. Field screening analyses included residual persulfate via a permanganate titration, sulfate via colorimetry, and sodium via an ion-selective electrode. The field screening and field geochemistry results were used heavily in completing the full-scale ISCO design. The laboratory analytical results noted significant decreases in concentrations of chemicals of concern in wells where geochemistry and field parameters were observed to change. This article discusses pilot test planning, performance monitoring, and full-scale design using data collected from the pilot test for this fast-track remediation. The full-scale application was completed between July and September 2008, and was the largest persulfate ISCO injection performed to date.

Keywords: in-situ chemical oxidation, sodium persulfate, pilot test, field screening analysis

1. INTRODUCTION

In-situ chemical oxidation (ISCO) has been demonstrated to be a robust remediation technology for treatment of numerous organic contaminants (Huling and Pivetz, 2006). Primary advantages of this technology are that degradation is rapid and that contaminants are treated in place in the subsurface, eliminating or minimizing extraction and ex-situ treatment (pump and treat).

In January 1987, EPA issued a Record of Decision (ROD) for the Ottati and Goss/Kingston Steel Drum Superfund Site in Kingston, New Hampshire that selected remedial actions for all areas of the site, including pump and treat for groundwater (USEPA, 1987). In 2006, EPA determined that the ROD-selected remedy for groundwater should be re-evaluated, to take into account the effects of remedial actions previously performed at the site that have changed the Site groundwater plumes, the revised conceptual site model since the 1986 Feasibility Study was prepared, and advances in remedial technologies. A Feasibility Study Addendum (FSA) Report for groundwater was completed in the spring of 2007 that evaluated the originally-selected remedy (pump and treat) in comparison to ISCO (M&E, 2007). Using investigation data collected between 2004 and 2007 to better delineate groundwater contamination, the FSA Report suggested that an ISCO remedy would be more cost-effective and timely than pump and treat. As a result, EPA issued an Amended ROD in September 2007 to change the selected remedy for groundwater to ISCO (USEPA, 2007). At that time, EPA established a goal for the site to attain construction complete status within one year, by September 30, 2008 (end of fiscal year 2008).

AECOM (formerly Metcalf & Eddy|AECOM) was tasked to perform bench-scale and field pilot scale testing to collect site-specific information to support the

remedial design for full-scale ISCO. Activated persulfate was the selected oxidant for pilot studies due to this oxidant's demonstrated ability to oxidize all site contaminants, including 1,4-dioxane, as well as its stability and longer anticipated residence time in the subsurface compared to ozone or Fenton's Reagent (which are also capable of breaking down VOCs and 1,4-dioxane) (Huling and Pivetz, 2006; ITRC, 2005). Bench-scale testing included estimating total oxidant demand (TOD) of site soils, as well as, conducting base demand tests to quantify base addition required to create alkaline conditions for base-activation of sodium persulfate. The pilot-scale treatability test consisted of injection of base-activated sodium persulfate into the saturated overburden in three pilot test areas (Area A, Area B, and Area C). The three pilot test areas lie within three distinct residual source areas that were targeted in the FSA Report (M&E, 2007) for full-scale groundwater remediation based on historical groundwater and soil sampling (Figure 1).

1.1 Site Setting and History

The Ottati & Goss/Kingston Steel Drum Superfund Site is located along Route 125 in Kingston, Rockingham County, New Hampshire. The 58-acre site is divided by Route 125 and is comprised of three distinct sections. The first section is a 5.89-acre parcel, historically referred to as the Great Lakes Container Corporation and Kingston Steel Drum (GLCC/KSD) area. This portion of the site is fenced and is now owned by the State of New Hampshire. The second section is 29 acres and is referred to as the Ottati and Goss (O&G) portion of the site. The third section is a 23-acre marsh located east of Route 125. From the late 1950's through 1980 drum reconditioning activities were performed at the site. The reconditioning operations included caustic rinsing of drums and disposal of the rinse water in a dry well near South Brook. Two leaching pits (lagoons) were also used at the site and were known as the "Kingston Swamp" and the "caustic lagoon." The Kingston Swamp and the caustic lagoon were reported to have been backfilled in 1973 and 1974, respectively.

Investigations of the site revealed that the soil throughout the site was contaminated with VOCs, polychlorinated biphenyls (PCBs), acid/base/neutral compounds (ABNs), metals, and cyanide at high concentrations at numerous locations and that groundwater was contaminated with VOCs, 1,4-dioxane, arsenic and other metals in several distinct plumes. VOCs and PCBs were measured in sediments in North Brook, South Brook.

Several remediation and removal actions were completed for contaminated soil and sediment at the site, including an EPA emergency removal action that processed and removed more than 4,000 drums and excavation and removal actions performed by potentially responsible parties (PRPs). In 1993, EPA, the

New Hampshire Department of Environmental Services (NHDES), and the PRPs entered into a Consent Decree. This agreement resulted in most parties contributing to a cash settlement, rendering the remainder of the costs at the site to be paid for by the Federal Superfund. In 2000, EPA contracted the U.S. Army Corps of Engineers – New England District to perform soil and sediment remediation at the site via excavation and treatment by low temperature thermal desorption (LTTD). Between August 2001 and June 2002, approximately 72,350 tons of VOC- and PCB-contaminated soil was excavated and treated in an on-site LTTD plant (ECC, 2003). In addition, remediation and restoration of six acres of wetland in Country Pond Marsh resulted in approximately 9,500 tons of sediment being excavated, transported, and disposed of off-site.

1.2 Conceptual Site Model

Soil and groundwater at the site were contaminated with chlorinated VOCs, BTEX VOCs, and 1,4-dioxane from both surface releases and a leachfield from former drum re-finishing operations that were conducted at the site. As noted in Section 1.1, contaminated unsaturated soil was excavated, treated on-site, and backfilled. However, contamination in saturated soil and groundwater remains. Additionally, some soil contamination located very close to Route 125 was not excavated due to concerns of undermining the road. Contamination is confined to the subsurface and therefore there is no current exposure pathway. Investigations of the site indicate that residual groundwater contamination at the site exists in three distinct residual source areas as shown on Figure 1.

Area A is located at the approximate center of the State-owned portion of the site. The residual plume from this area travels easterly toward Route 125, and groundwater contaminants include BTEX and chlorinated solvent compounds. The highest concentrations and potential source of VOC contamination have been noted in the western portion of Area A, in the vicinity of a former caustic lagoon. 1,4-Dioxane concentrations are generally low in Area A. Groundwater vertical profiling conducted prior to the ISCO pilot testing measured groundwater pH between 9.0 and 10.0 throughout most of Area A. Depth to bedrock ranges from approximately 20 to 36 feet below ground surface moving from west to east across this area, and no layer of weathered bedrock above competent bedrock has been observed in Area A. However a layer of smaller boulders/large cobbles was laid down in the western portion of Area A at a depth of approximately eight to ten feet below grade, at the bottom of the soil excavation pit during the remediation of the unsaturated zone soils by LTTD.

Area B is located in the southeast corner of the State-owned portion of the site, bordering Route 125. Soil borings advanced in Area B indicate that aquifer soils (~5 feet below ground surface to bedrock) are finer in texture and less

permeable than those observed in Area A. Contaminants were likely retained in the finer soils in this area and have been slowly migrating to the east beneath Route 125 or discharging to South Brook just before it flows under Route 125. Based on historical data prior to the ISCO pilot test, the highest site-wide concentrations of 1,4-dioxane (>200 ug/L) and total VOC concentrations greater than 20,000 ug/L have been measured in groundwater samples collected from Area B. Depth to bedrock ranges from approximately 18 to 33 feet bgs south to north across this area. Based on soil boring logs, a layer of weathered bedrock is present in the southern portion of Area B, with thickness between one and three feet.

Area C is located north of the State-owned portion of the site where a plume of lower total VOC concentrations lies roughly parallel to North Brook. Area C includes portions of palustrine forested, palustrine scrub/shrub and palustrine emergent wetlands, in addition to portions of forested wetland. There is standing water within some portions of Area C. The primary contaminant in Area C is 1,4-dioxane,which has been found at low concentrations (3 to 40 ug/L) in groundwater beneath a large area (greater than 2.5 acres). In addition, elevated concentrations of PCE (60 to 213 ug/L) and TCE (44 ug/L) were detected in groundwater at several vertical profiling locations sampled in January 2008.

Following the source soil removal action in 2002, soil texture is fairly consistent in the top five to eight feet (vadose zone) where soil was removed, remediated via thermal desorption and replaced. The replacement of the treated soils included compaction of the material before placing a final loam and topsoil cover over the site, and the permeability of the treated soils is poor such that after heavy rains most of the infiltrating water remains in the upper two feet consisting of loam and topsoil. Below five to eight feet, the textures range from fine-medium sand to coarse sand and gravel. Finer texture deposits appear to be located in the southeast corner of the site (Area B). Groundwater at the site generally flows from west to east, and eventually discharges to the marsh and Country Pond, located east of Route 125. Hydraulic conductivity values, estimated using the Waterloo profiler technique, ranged in Area A from 1.5×10^{-5} to 3.9×10^{-4} centimeters per second (cm/s). Hydraulic conductivity values estimated in Area B ranged between 9.3×10^{-6} and 1.6×10^{-4} cm/s.

To the north and south of the site are two easterly flowing brooks that drain the upland areas surrounding the site. North Brook and South Brook both travel through culverts beneath New Hampshire Route 125 and discharge to County Pond Marsh. Both North and South Brook are hydraulically connected with the shallow groundwater, and therefore, flow is subject to seasonal groundwater fluctuations.

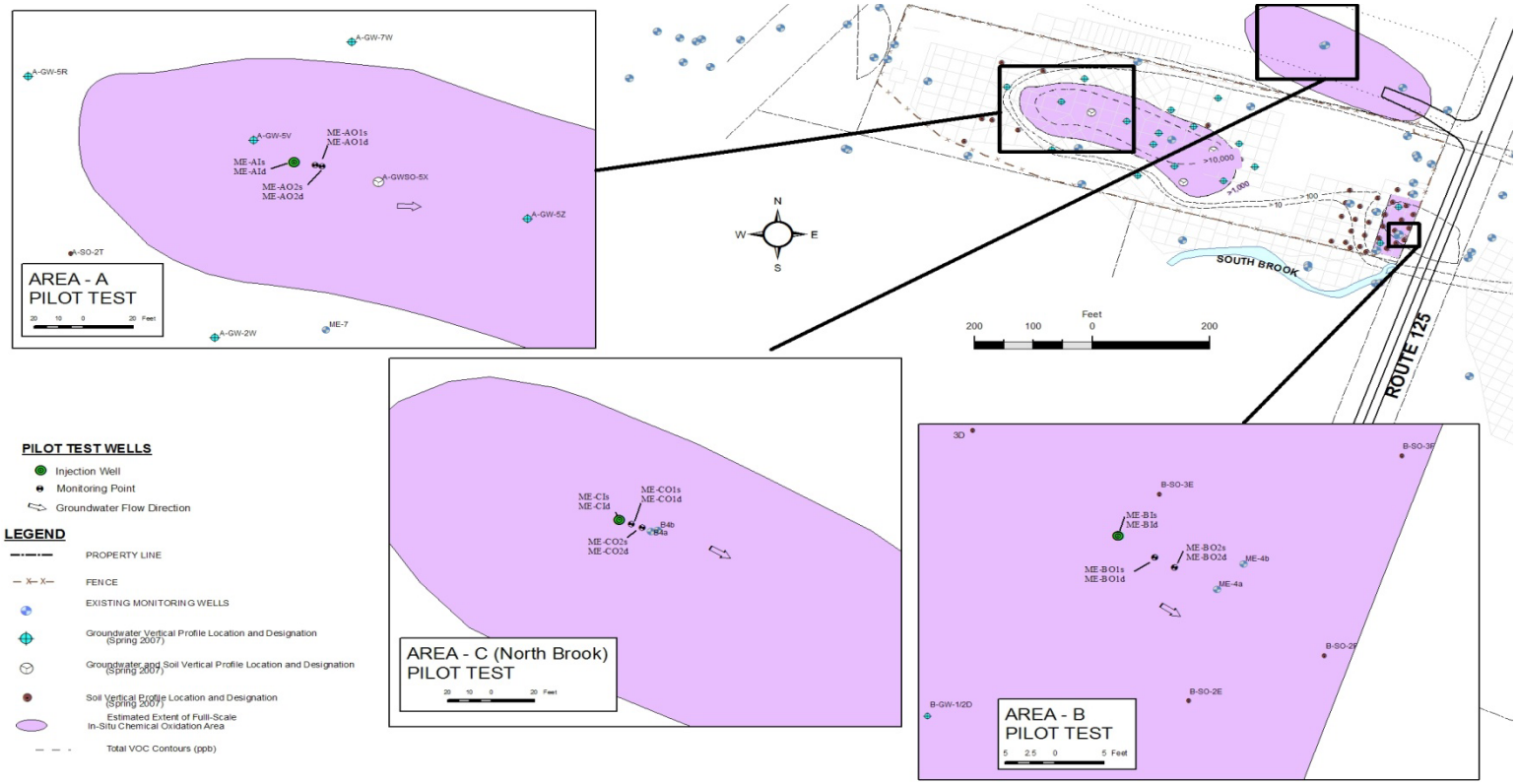

Figure 1. Site Map Showing Three Chemical Oxidation Pilot Test Areas

1.3 Treatability Pilot Test Objectives

The pilot-scale treatability test consisted of injection of chemical oxidant (activated persulfate) into the three discrete pilot test areas, one per residual source areas (Area A, Area B, and Area C). The bench-scale testing included quantifying the natural oxidant demand of site soils to assist in selecting oxidant dosages and estimating the quantity of base required to be added for alkaline activation for persulfate. The specific objectives for the field pilot treatability tests included:

1. Evaluating injection rates in each area of the site;
2. Estimating radius of influence (horizontal spread of injected oxidant);
3. Determining time of oxidant persistence in the subsurface;
4. Assessing contaminant rebound;
5. Evaluating changes in aquifer geochemistry and metals mobility;
6. Quantifying contaminant destruction;
7. Determining the oxidant dosage for full-scale remediation.

2. MATERIALS AND PROCEDURE

The treatability pilot test injections and subsequent performance monitoring were completed in three source areas between December 2007 and May 2008. Performance monitoring consisted of well-side measurements of field geochemical parameters, field screening analyses performed on-site, and fixed laboratory analyses on samples shipped off-site.

2.1 Well Installation

In each of the three pilot test treatability areas, an injection well pair (two target vertical intervals), and two monitoring well couplets were installed between November 20 and November 30, 2007. All injection wells and monitoring wells were constructed using two-inch diameter, schedule 40 PVC with 10-slot (0.010 inch) well screen. A well construction summary is provided as Table 1. The six wells were developed using whale pumps, and development volumes pumped from each well were approximately equal to estimated water volume lost to the subsurface during drilling and installation. After well development, a minimum of one week was allowed in each well before sampling as part of the pilot test baseline monitoring event.

Table 1. Chemical Oxidation Pilot Test Well Construction Summary.

Well	Function	Screen Interval	Notes
Area A			
ME-AIS	Injection	8-13	
ME-AID	Injection	14-19	
ME-AO1S	Monitoring	7.3-10.3	~ 6 feet east of ME-AIS
ME-AO1D	Monitoring	13.7-18.7	~ 6 feet east of ME-AID
ME-AO2S	Monitoring	8-13	~ 10 feet east of ME-AIS
ME-AO2D	Monitoring	15-20	~ 10 feet east of ME-AID
Area B			
ME-BIS	Injection	8-16	
ME-BID	Injection	18.5-23.5	
ME-BO1S	Monitoring	8-16	~ 5 feet east of ME-BIS
ME-BO1D	Monitoring	18-23	~ 5 feet east of ME-BID
ME-BO2S	Monitoring	9-17	~ 7 feet east of ME-BIS
ME-BO2D	Monitoring	19-24	~ 7 feet east of ME-BID
Area C			
ME-CIS	Injection	21-29	
ME-CID	Injection	32-40	
ME-CO1S	Monitoring	19-27	~ 6 feet east of ME-CIS
ME-CO1D	Monitoring	32-40	~ 6 feet east of ME-CID
ME-CO2S	Monitoring	21-29	~ 10 feet east of ME-CIS
ME-CO2D	Monitoring	32-40	~ 10 feet east of ME-CID

2.2 Treatability Bench-Scale Studies

During well installation, soil and groundwater samples were collected from each of the three pilot test areas for treatability bench-scale studies. Saturated soil samples were collected from each of the three pilot test areas, along with representative groundwater from existing monitoring wells each of the three areas. In total, 10 discrete soil samples were collected for 10 bench-scale tests. The bench tests were performed by RedoxTech's Cary, North Carolina laboratory. Total Oxidant Demand (TOD) reactors were prepared with approximately 200 grams of soil and 300 mL of representative groundwater (approximately 1:2 soil:water ratio), with sodium persulfate at a dosage of 10g/kg. The final persulfate concentration in the vessel was determined after 12 days, and the TOD value represents the total persulfate mass consumed per unit mass of soil. For the base demand analysis, a reaction vessel was prepared with approximately 100 grams of soil and 150 mL of water, and the initial pH was measured. Sodium persulfate at a dosage of 10g/kg was added, and a volume of sodium hydroxide (NaOH 25% volumetric basis) was added to increase the pH to greater than 10.5

for one hour. Additional base addition was performed two days later to again raise the pH above 10.5. The vessels were then allowed to react for 12 days after the second NaOH titration, at which time a final pH reading was taken.

2.3 Activated Persulfate Injection

Base-activated persulfate injection into Area A and Area B was completed December 17-18, 2007. Injection into Area C was completed on February 5, 2008 after planned additional investigation activities were completed in January 2008. Sodium persulfate (FMC Klozur) and sodium hydroxide dosages, injection pressure, and injection rates in each of the three areas are summarized on Table 2. Persulfate handling, preparation and injection for the field pilot injections were performed by Redox Tech, New England LLC, under contract to AECOM (formerly Metcalf & Eddy|AECOM). There is no source of potable water at the site, and water for mixing chemical oxidation solutions was transported to the site.

Table 2. Summary of Pilot Test Injections

Parameter	**Area A**		**Area B**		**Area C**	
	Shallow	**Deep**	**Shallow**	**Deep**	**Shallow**	**Deep**
Injection Well	ME-AIS	ME-AID	ME-BIS	ME-BID	ME-CIS	ME-CID
Vertical Interval (feet bgs)	8-13	14-19	8-16	Direct Push 22-23 / 19-22	21-29	32-40
Persulfate Dose	1,100 lbs per 500 gallon batch (26% by weight)		1,375 lbs per 600 gallon batch (~27% by weight)		910 lbs per 500 gallon batch (22% by weight)	
NaOH Dose (25% by weight)	~20 gallons per 500 gallon batch		~25 gallons per 600 gallons batch		20 gallons per 500 gallon batch	
Injection Volume (gallons)	500	500	530	300 / 350	495	500
Volume Per Vertical Foot (gallons)	100	100	66	150 / 117	62	63
Average Injection Rate (gallons per minute)	4	8	13	4 / 9	16	5
Injection Pressure (psi)	<5	25	20	25 / 25	20	20

In each pilot test area, injection was completed into two injection wells screened at different vertical intervals as shown on Table 1, with the exception of Area B. After attempting injection into the deep interval in Area B, it was determined that construction of the injection well was not satisfactory. Bottom-up, direct-push injection (1.25" diameter rods) was performed in Area B in the following intervals: 22 to 23 feet and 19 to 22 feet. Injection rates and injection pressures were recorded during the injection testing. A summary of pilot test injection parameters and observations, including sodium persulfate dose, sodium hydroxide base activation dose, total injection volume into each location, injection flow rate, and injection pressure for each of the three areas is summarized on Table 2.

2.4 Groundwater Performance Monitoring

Groundwater monitoring wells were purged and samples collected at a low rate using a variable speed pump (peristaltic pump) following USEPA low-flow sampling methods (USEPA, 1996). The following groundwater quality parameters were measured well-side using the YSI Model 6820: pH, specific conductance (μS/cm), temperature (^{o}C), oxidation reduction potential (ORP, mV), turbidity (NTU), and dissolved oxygen (DO, mg/L). Groundwater field measurements and sampling comments were recorded on field logs. Dedicated sampling tubing was used at each well. Turbidity was measured well-side using a Lamotte 2020 Turbidimeter. Collection of groundwater samples commenced after 30 minutes of purging.

Monitoring to evaluate the performance of the ISCO injection consisted of two types: contaminant monitoring and geochemical monitoring. For contaminant monitoring, groundwater samples were collected from pilot observation wells and sent to a fixed laboratory for analysis of the site contaminants of concern including VOCs, 1,4-dioxane, and select metals (arsenic, chromium, iron, manganese). One round was performed approximately 6 weeks after in-situ addition of activated persulfate, and a second round of samples was collected approximately 12 weeks after injection to evaluate potential rebound of contamination. Geochemical monitoring consisted of measurement of field geochemical parameters (pH, ORP, dissolved oxygen, specific conductance, turbidity, and temperature) and collection of a grab sample for field analysis of persulfate, sulfate (the breakdown product of persulfate), and sodium. Geochemical monitoring was performed at a higher frequency than contaminant monitoring to evaluate the persistence and distribution of the injected persulfate and temporal trends in aquifer geochemistry in the four pilot test monitoring wells in each pilot test area. In Area A and Area B, geochemistry performance monitoring was performed prior to injection (baseline) and approximately 0.5 weeks, 1.5 weeks, 3.5 weeks, 6 weeks, 8 weeks, and 12 weeks after injection. In

Area C performance monitoring was performed prior to injection (December 2007) and approximately 0.5 weeks, 1 week, 2 weeks, 4 weeks, 6 weeks, 8 weeks, and 12 weeks after injection. Additional geochemical monitoring was performed in Area B and Area C using existing monitoring wells (well ME-4A in Area B and wells B-4A and B4B in Area C). Geochemistry measurements in these wells were used to provide an additional lateral monitoring location for evaluation of radius of influence of the ISCO injections. Geochemistry performance monitoring was completed in these wells less frequently than in the four pilot test performance monitoring wells.

2.4.1 Field Screening Analysis

Groundwater samples were analyzed for sodium, sulfate, and persulfate on-site in a field laboratory trailer. Sulfate is a breakdown product of persulfate, while sodium acts as a conservative tracer upon dissociation of sodium persulfate. Elevated sulfate and/or sodium concentrations in monitoring wells, compared with baseline, were assumed to be a result of the influence of sodium persulfate injection. Field screening analyses were performed on all geochemistry performance monitoring events listed in the previous section.

Residual persulfate concentrations were measured via a potassium permanganate (0.5 N $KMnO_4$) titration into a solution containing known volumes of groundwater sample and ferrous ammonium sulfate (0.50 N $Fe(NH_4)_2(SO_4)_2.6H_2O$). Sodium concentrations in groundwater samples were quantified using a Fisher Scientific accumet Glass Membrane Sodium Combination ion-selective electrode. Sodium analysis was performed using the relative millivolt (mV) mode on a solution of 50 milliliters (mL) of sample and 2 mL of ionic strength adjuster (ISA). Three decadal standards (10 mg/L, 100 mg/L, and 1,000 mg/L) were used to develop a standard curve. Sulfate concentrations were measured using a Hach colorimeter (Model # DR 890).

2.4.2 Fixed Laboratory Analysis

Groundwater samples were collected and analyzed off-site as part of performance monitoring of contaminants of concern before injection (baseline), six weeks after injection, and 12 weeks after injection. VOCs analysis was performed through the EPA Contract Laboratory Program. 1,4-Dioxane analysis was performed by Columbia Analytical Services (Kelso, WA) by extraction and GC/MS SIM analysis using EPA Method 8270C. In addition, laboratory analysis was performed for arsenic, iron, manganese, chromium, and sodium by the USEPA Region 1 Office of Environmental Measurement and Evaluation (OEME)

laboratory in Chelmsford, MA per the USEPA Region 1 Standard Operating Procedure for metals analysis by Inductively Coupled Plasma Spectrometry.

3. DATA AND ANALYSIS

Bench-scale test results were conducted prior to the scheduled field pilot test injections to select appropriate dosages of persulfate and basic activator. Performance results and observations from the ISCO pilot test were used in the design of the site-wide remediation approach. Key design parameters for the full-scale design, based on pilot test data, include injection radius of influence, injection grid spacing, injection intervals, injection volumes, chemical dosages, and injection rates.

To ensure EPA Region 1 funding would be in place to meet the goal of construction complete in September 2008, the Basis of Design Report needed to be completed by March 30, 2008. Week 6 contaminant monitoring in Area C was performed on March 18, 2008, and Week 12 contaminant monitoring in Area A and Area B was performed on March 12, 2008. Therefore the design of the full-scale remediation approach needed to rely primarily on the frequent geochemistry monitoring completed in each area.

3.1 Bench-Scale Tests

Two discrete bench scale analyses were performed prior to the field pilot tests: total oxidant demand and soil base demand. TOD results were generally low and fairly consistent in all three pilot test areas of the site, generally between 1.6 and 2.8 g/kg. Slightly elevated TOD readings were measured from two samples: one collected from the eastern portion of Area A (22 feet deep; 6.2 g/kg) and one collected near the pilot test injection wells in Area B (12 to 15 feet deep; 5.4 g/kg). The TOD results are summarized on Table 3. Due to the observance of one elevated TOD result in both Area A and Area B and the higher contamination measured in these areas, slightly higher persulfate dosages were selected for the pilot test injections, as shown on Table 2.

From the base demand analysis, generally low doses of NaOH (25%), ranging between 0.8 and 2.3 milliliters (mL) per kg soil, were required to initially raise the pH to greater than 10.5. One soil-groundwater slurry from Area C required significantly more base to raise the pH (12.5 mL/kg); however, this sample location was outside of the Area C pilot test location as well as the area eventually targeted for full-scale ISCO in Area C based on the January 2008 groundwater vertical profiling investigation. After twelve days of persulfate-base-soil reaction time, the pH in five of the ten base demand vessels was circumneutral (between

6.0 and 8.0) and the pH of two samples (ME-AIP-18 and ME-BIP-22) remained above 8.0. These results suggested that the soil in the pilot test areas would likely have sufficient buffering capacity to maintain an elevated pH with persulfate addition and minimize extreme drops in pH due to sulfuric acid formation. Although, the post-reaction pH of two of the ten samples was approximately 3.0, no change was made to the base dosage for the pilot test based on the bench scale results. However, these two final acidic results did suggest that a low pH may be expected to be observed in monitoring wells in some portions of the site following a persulfate injection due to the breakdown of persulfate and the subsequent formation of sulfuric acid. The base demand results are summarized on Table 3.

3.2 Water Quality and Field Screening Parameters

Water quality parameters and field screening analyses were recorded to evaluate the persistence and the transport of the injected solution in the subsurface. Several consistent geochemical changes were noted in performance monitoring wells that were impacted by injection of base-activated sodium persulfate, including detection of residual persulfate, increase in ORP, increase in sulfate, increase in sodium, and increase in specific conductance.

Persulfate was observed to persist in the subsurface for a period of approximately four to six weeks in all three pilot test areas, which is consistent with observations from other similar injections based on discussions with FMC and literature (Huling and Pivetz, 2006). The persulfate persistence from the pilot test was not representative of the persistence observed at full-scale; however. After the full-scale injection performed from July to September 2008, residual persulfate was measured in performance monitoring wells four to seven months following injections. This longer persistence following full-scale injection may have been caused by a combination of factors: the large quantities injected, injection through a grid system compared to a single injection well location, and cold temperatures which decrease persulfate activation rates. However, low temperature is less likely related to the longer persistence observed at full scale, since the pilot test injections were performed during cold weather (December 2007 and February 2008), when groundwater temperatures were likely similar to those during the months following the full-scale injection (September 2008-March 2009).

In all three pilot test areas baseline ORP values were generally between -200 and -100 millivolts (mV). In wells where residual persulfate was measured to be greater than 1,000 ug/L, ORP values were observed to increase to between +200 and +500 mV.

Table 3. Summary of Bench Scale Studies.

Sample ID	Soil Sampling Location/Depth	Oxidant Demand (g S_2O_8 / kg soil)	Initial pH	Total NaOH Added (mL NaOH/kg soil)	Final pH (12 days)
AREA A					
ME-AIP-12	Area A pilot test area (depth 12-13 feet)	2.5	8.6	1.3	6.4
ME-AIP-12-Dup	Field Duplicate	2.3	9.0	0.8	6.0
ME-AIP-18	Area A pilot test area (depth 18 feet)	1.6	9.1	1.1	8.5
ME-AP1-16	Area A - eastern portion (depth 13.5-17 feet)	2.6	8.3	1.6	6.4
ME-AP1-24	Area A - eastern portion (depth 22 feet)	6.2	7.1	2.3	3.4
AREA B					
ME-BIP-14	Area B pilot test area (depth 12-15 feet)	5.4	7.9	2.3	3.0
ME-BIP-22	Area B pilot test area (depth 18-20 feet)	2.0	8.1	1.9	9.8
ME-BP1-16	Area B northwestern portion (depth 14-15 feet)	2.5	8.1	1.6	7.3
Area C					
ME-CIP-25	Area C pilot test area (depth 25 feet)	1.8	7.2	1.4	7.6
ME-CIP-36	Area C pilot test area (depth 36 feet)	2.0	7.0	1.2	6.0
ME-C08-30	East of Area C pilot test (depth 30 feet)	2.8	4.9	12.5	5.2

Groundwater pH increased to alkaline conditions shortly after injection due to the base activation in only three pilot test monitoring wells (ME-AO1S, ME-

AO1D, and ME-BO2D). However, alkaline pH in groundwater was only observed to persist for a period of 0.5 to 1.5 weeks. Therefore, the injection solution was likely transported as a result of pressurized injection into these three wells where alkaline pH values were measured. Generation of sulfuric acid in site groundwater as a result of the breakdown of added sodium persulfate caused the pH to drop in several monitoring wells to values between pH 3.0 and 4.0. During pilot test monitoring, the lowest pH readings in all three areas occurred between 1.5 and 3.5 weeks after injection, following which groundwater pH increased.

Significant increases from baseline of specific conductance, sulfate, and sodium in monitoring wells corresponds to those wells where residual persulfate was observed and ORP was measured to increase to oxidizing conditions (>200 mV). Geochemistry monitoring results in select pilot test monitoring wells are tabulated on Table 4. Temporal trends in these geochemical parameters are summarized graphically for Area A wells ME-AO1S and ME-AO2D on Figure 2 and for Area B wells ME-BO1S and ME-BO2D on Figure 3.

In the absence of fixed laboratory data, changes in water quality and field screening parameters were critical in assessing radii of influence and designing the injection grid spacing for full-scale ISCO injection in each area. For water quality parameters and field screening analyses, less importance was placed on specific values compared to relative changes from baseline conditions. In evaluating changes to the field screening and water quality parameters after pilot test injections, compared to baseline readings, were classified into three categories (Yes, Partially, and No) as shown on Table 5, with Parameter Assessment Criteria defined in Table 6. In addition, laboratory analysis results from the six week performance monitoring event were available for Area A and Area B when the full-scale design was finalized, and these analytical results were also operationally defined on Table 5 and were considered in estimating oxidant distribution and radius of influence. Radius of influence distance estimate in each area was inclusive of the monitoring wells where most parameters were classified as "Yes" or "Partially." Accordingly, radius of influence was estimated to be between six and ten feet in Area A, between five and eight feet in Area B, and greater than six but less than ten feet in the deeper portion of the Area C pilot test area.

Table 4. Summary of Groundwater Geochemical Parameters After Injection in Select Wells.
Water quality parameters and field screening parameters were measured frequently following injection to evaluate oxidant persistence and distribution.

Location	**ME-AO1D (13.7-18.7' bgs - 6 feet from Injection Well)**						**ME-AO2D (15-20' bgs - 10 feet from Injection Point)**					
Sampling Event	baseline	1/2 week	1.5 weeks	3.5 weeks	6 weeks	12 weeks	baseline	1/2 week	1.5 weeks	3.5 weeks	6 weeks	12 weeks
pH (standard units)	7.47	8.94	3.63	4.33	6.58	4.15	9.79	9.38	4.79	5.09	6.51	4.97
ORP (mV)	-174	18	369	410	-69	358	-273	-354	419	225	-158	235
Specific Conductance (µS)	360	568	7,738	4,246	835	3,872	643	1,795	5,423	4,656	1,954	3,207
Sodium (mg/L)	58	139	1809	1232	73	579	159	405	1,182	1,226	221	573
Persulfate (mg/L)	0	89	0	803	0	no sample	0	0	1,607	119	0	no sample
Sulfate (mg/L)	22	18	6,665	2,440	262	2,700	7	NR	2,758	3,050	801	2,700

Location	**ME-BO1S (8-16' bgs - 5 feet from Injection Well)**						**ME-BO2D (Screen 19-24' bgs - 8 feet from Injection Point)**					
Sampling Event	baseline	1/2 week	1.5 weeks	3.5 weeks	6 weeks	12 weeks	baseline	1/2 week	1.5 weeks	3.5 weeks	6 weeks	12 Weeks
pH (standard units)	8.20	4.64	4.41	3.32	3.86	5.11	9.24	12.57	8.95	4.11	3.15	4.66
ORP (mV)	-203	372	479	554	72	132	-151	278	255	502	456	210
Specific Conductance (µS)	1,071	20,170	19,290	18,290	13,745	7,180	779	6,243	2,036	18,380	13,960	17,170
Sodium (mg/L)	269	5,539	5,317	5,900	1,294	1,443	187	19,110	6,983	6,339	988	4,424
Persulfate (mg/L)	0	13,864	8,033	833	0	no sample	0	81,813	19,159	7,140	60	no sample
Sulfate (mg/L)	0	7,278	10,968	8,120	9,296	4,900	8	8,068	6,698	11,120	8,638	12,800

Table 5. Summary of Pilot Test Radius of Influence Assessment Parameters. Parameter Assessment Criteria were operationally defined for this site-specific pilot test.

Injection Interval	Shallow Injection (8-13')		Deep Injection (14-19')	
Well	ME-AO1S	ME-AO2S	ME-AO1D	ME-AO2D
Distance from Injection Point	6 feet	10 feet	6 feet	10 feet
↑ Residual Persulfate	□	□	□	■
↑ ORP	□	□	■	■
↑ Sulfate	□	□	■	■
↑ Sodium	□	□	■	■
↓ Concentration of chlorinated VOCs	■	■	□	□
↓ Concentration of BTEX VOCs	■	■	■	□

Injection Interval	Shallow Injection (8-16')		Deep Injection (18.5-23.5')	
Well	ME-BO1S	ME-BO2S	ME-BO1D	ME-BO2D
Distance from Injection Point	5 feet	7 feet	6 feet	8 feet
↑ Residual Persulfate	■	□	■	■
↑ ORP	■	□	■	■
↑ Sulfate	■	■	■	■
↑ Sodium	■	□	■	■
↓ Concentration of chlorinated VOCs	■	■	■	□
↓ Concentration of BTEX VOCs	■	□	■	□
↓ Concentration of 1,4-dioxane	◪	□	◪	□

Injection Interval	Shallow Injection (20-28')		Deep Injection (32-40')	
Well	ME-CO1S	ME-CO2S	ME-CO1D	ME-CO2D
Distance from Injection Point	6 feet	10 feet	6 feet	10 feet
↑ Residual Persulfate	□	□	■	□
↑ ORP	□	□	■	□
↑ Sulfate	□	□	■	□
↑ Sodium	□	□	■	□

Table 6. Site-Specific Definitions for Assessment Parameters.

	Persulfate	ORP	Sulfate	Sodium	↓ COC Concentration
■ – Yes	>1,000 mg/L	>200 mV	>500 mg/L	>1000 mg/L	>60%
◪ - Partially	>BL + 200 mg/L	≥ 0 mV	>100 mg/L	> 10 x BL	>30%
□ – No	≤BL + 200 mg/L	< 0 mV	≤100 mg/L	≤ 10 x BL	≤30%

3.3 Fixed Laboratory Results

The primary objective of the pilot test treatability study was to evaluate the extent that ISCO can reduce concentrations and mass of contaminants of concern in the ground at the Ottati and Goss Site. Contaminant concentrations were measured before the pilot test injections and destruction was quantified six and twelve weeks after the injection in each area. The ISCO pilot test demonstrated that BTEX and chlorinated VOC concentrations in groundwater could be effectively decreased in-situ. Overall, the concentrations of BTEX and chlorinated VOCs were reduced 50 to 95 percent from baseline concentrations following pilot-scale ISCO injection in pilot test monitoring wells in Areas A and B. Concentrations of PCE decreased in nearly all monitoring wells In several wells, VOC concentrations were noted to increase, and these increases are potentially due to desorption of contamination from soil particles and/or to contaminated water being pushed vertically to different depths or laterally to different areas. Concentrations of chloromethane and acetone, likely oxidation byproducts, were also noted to increase in some pilot test monitoring wells. Performance monitoring results from Week 12 indicated further reductions in concentrations of both BTEX and chlorinated VOCs in all four monitoring wells in Area A and in wells ME-BO1S and ME-BO1D between Week 6 and Week 12. Groundwater contaminant concentrations in wells ME-BO2S and ME-BO2D were observed to increase (compared to both baseline and Week 6 concentrations), and this is likely the result of desorption of VOCs from heavily contaminated soil. Concentrations of primary contaminants of concern prior to and after injection of persulfate in pilot test Area A are presented in Table 7. The effectiveness of persulfate in destroying 1,4-dioxane in-situ at the Ottati and Goss site was not clearly demonstrated from the activated persulfate pilot test injections. Baseline concentrations in performance monitoring wells in Areas A and C were nearly all less than the Interim Cleanup Level of 3 ug/L specified in the Amended ROD. In Area B, baseline concentrations of 1,4-dioxane ranged between 16 and 64 ug/L, and concentrations were reduced by 25 to 40 percent after the pilot test injections. In Area B, it is possible that the persulfate being consumed through oxidation of

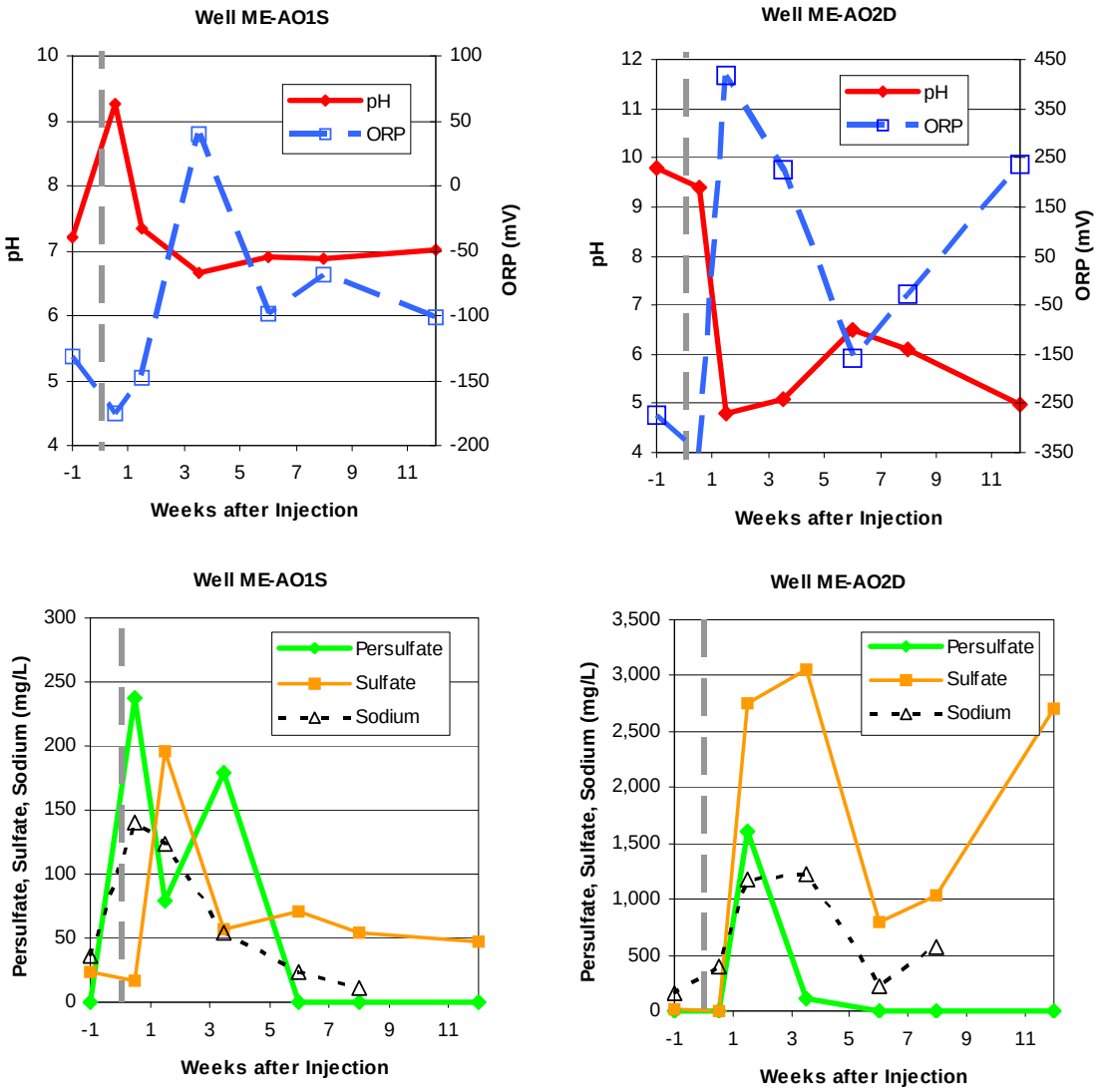

Figure 2. Temporal Summary of Water Quality and Field Screening Parameters Monitoring in Area A Monitoring Wells: ME-AO1S and ME-AO2D.

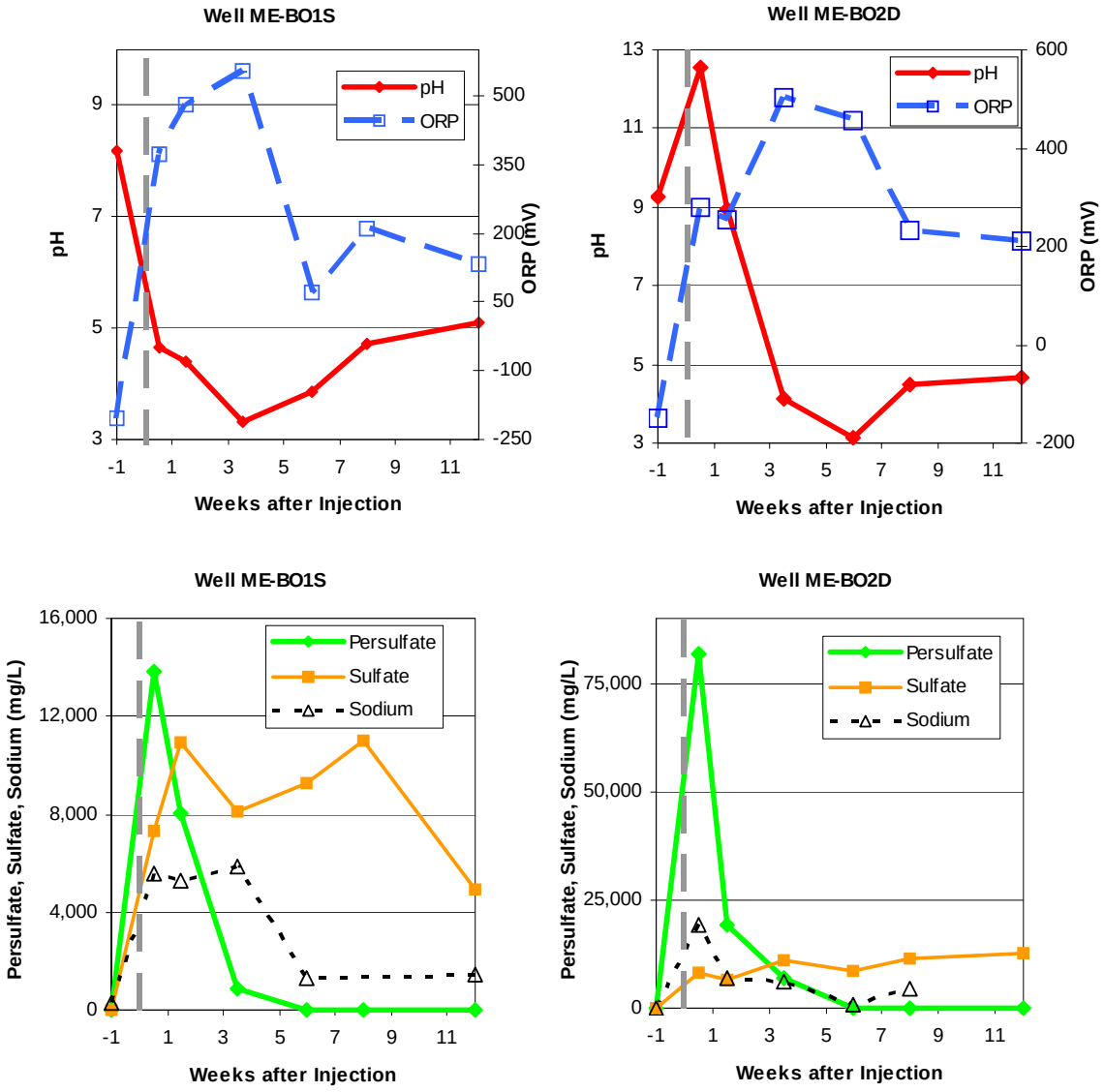

Figure 3. Temporal Summary of Water Quality and Field Screening Parameters Monitoring in Area B Monitoring Wells: ME-BO1S and ME-BO2D.

Table 7. Summary of Laboratory Analytical Results for Primary Contaminants of Concern Before and After ISCO Injection.

Concentrations shown in Area A and Area B pilot test monitoring wells. In the Area C pilot test area, concentrations of contaminants of concern were less than the Preliminary Cleanup Levels and no comparison was made between post-injection and baseline results. Total BTEX is the summation of benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene.

Location	**ME-AO1S**			**ME-AO2S**		
(ug/L)	baseline	6 weeks	12 weeks	baseline	6 weeks	12 weeks
PCE	51	7.6	1.1	17	1.2	<1
TCE	10	55	<1	5.9	<1	<1
TOTAL BTEX	326	220	0	116	14.2	1.7
Location	**ME-AO1D**			**ME-AO2D**		
(ug/L)	Baseline	6 weeks	12 weeks	baseline	6 weeks	12 weeks
PCE	67	2.1	42	650	290	200
TCE	13	120	15	250	220	500
TOTAL BTEX	372	496	75	7,200	3,430	4,030
Location	**ME-BO1S**			**ME-BO2S**		
(ug/L)	baseline	6 weeks	12 weeks	baseline	6 weeks	12 weeks
PCE	130	65	15	57	<10	<20
TCE	<25	5.4	<5	<50	<10	<20
cis-1,2-DCE	230	27	7.2	270	32	<20
vinyl chloride	<25	<5	<5	<50	<10	<20
TOTAL BTEX	3,040	844	782	6,480	3,580	4,840
1,4-Dioxane	50	32	30	53	41	36
Location	**ME-BO1D**			**ME-BO2D**		
(ug/L)	Baseline	6 weeks	12 weeks	baseline	6 weeks	12 weeks
PCE	1,400	330	190	130	57	100
TCE	1,500	670	600	190	140	230
cis-1,2-DCE	3,100	970	600	350	260	600
vinyl chloride	550	210	98	87	46	92
TOTAL BTEX	11,358	3,391	4,380	1,210	298	1,461
1,4-Dioxane	64	43	48	16	17	21

other contaminants of concern more amenable to oxidation (i.e., BTEX) and natural oxidant demand in soils limited oxidation of 1,4-dioxane. The acidification of groundwater in the vicinity of the injections may also have reduced the potential for 1,4-dioxane oxidation as alkaline conditions were not

maintained to generate sulfate free radicals. However, in a study by Felix-Navarro, it was observed that oxidation rates of 1,4-dioxane by persulfate were inversely proportional to pH (Felix-Navarro et al., 2007), and therefore basic pH may not be necessarily for 1,4-dioxane oxidation by persulfate.

Contaminant rebound was noted in the deep interval of Area B, where concentrations measured six weeks after injection were lower than baseline. However, in the twelve week performance monitoring samples, contaminant concentrations were higher than the Week 6 results, and for some contaminants concentrations were greater than baseline. The deep interval in Area B was the most contaminated pilot test interval, and rebound is likely due to desorption of organic contaminants from soil particles.

Shifts in aquifer geochemistry following the ISCO pilot test (generally more oxidizing and more acidic) were noted to impact the mobility of certain metals. Large iron and manganese concentration increases (one to two orders of magnitude) were observed in the deep interval in Area A, the shallow and deep intervals in Area B, and the deep interval in Area C after ISCO injection. The measured concentrations of arsenic were lower in all pilot test monitoring wells following the ISCO injection compared to baseline in Areas A and B; however, elevated laboratory reporting limits were greater than the baseline concentrations for some wells. In a few wells the arsenic concentrations decreased between the baseline and Week 6 sampling; however, the concentration then increased between the Week 6 and Week 12 sampling events. This may suggest that as groundwater geochemistry returns to baseline conditions, arsenic concentrations may return to pre-injection concentrations. Chromium concentrations were not detected in any well in baseline or post-injection monitoring in Area A or Area C. In Area B, well ME-BO2D, the concentration of chromium was measured to be 180 ug/L in the Week 6 sample, which exceeded the federal MCL (100 ug/L); chromium was not detected (reporting limit=110 ug/L) in the Week 12 sample from this well. The only other detection of chromium in Area B was in well ME-BO1D in the baseline sample (22 ug/L).

3.4 Other Observations

In the shallow interval of Area C, no indication of oxidant injection was noted in the two monitoring wells (ME-CO1S and ME-CO2S) during the one-half and one week geochemistry sampling events. Four additional one-inch PVC wells/piezometers screened from 20 to 30 feet deep were installed approximately five feet downgradient from the shallow injection well (ME-CIS) using a direct-push drill rig to provide additional groundwater monitoring sampling to assess the distribution of the injected solution in the subsurface. Water quality measurements and analysis of field screening parameters from the four additional

shallow piezometers provided no evidence of the persulfate injection or the destination of the persulfate injected into the shallow interval. Most of the injected solution likely traveled through a preferential pathway, potentially in an upgradient direction, that the pilot test monitoring well network (two monitoring wells ME-CO1S and ME-CO2S and four piezometers) in Area C did not capture. Two deep-interval piezometers were also installed approximately six feet from the deep injection well (to the northeast and southeast of injection well ME-CID). Elevated residual conductance and increases in ORP values were observed two weeks after injection in both of the deep interval piezometers, in addition to well ME-CO1D, indicating a good oxidant distribution in the subsurface that was at least six feet across at a distance six feet from the deep injection well.

3.5 Full-Scale Basis of Design

The ISCO remediation design was completed primarily using site-specific data collected during the pilot test. At the time of remedial design and submittal of the Basis of Design Report to USEPA Region 1, fixed laboratory analytical data was only available for the samples collected six weeks after injection in Areas A and B. Therefore, changes in water quality and field screening parameters were critical in assessing radii of influence, which was used in determining injection grid spacing, and selecting injection volumes and dosages. Site-specific, full-scale design parameters are summarized on Table 8. The horizontal and vertical extent of remediation was estimated using contaminant concentrations in soil and groundwater based on site investigations, most notably the vertical profiling of soil and groundwater in all three areas.

Injection for full-scale remediation was designed to be performed using a grid approach. Spacing within the injection grid was be designed to provide delivery of oxidant vertically and horizontally thoroughly throughout the portions of the site identified as needing active treatment to create contact between persulfate and the contaminants in soil and groundwater. Injection grid spacing in each area was primarily determined through the observed radius of influence from the pilot scale injection activities, where geochemistry changes and contaminant destruction were used to estimate radius of influence as summarized in Section 3.2 and on Table 5. Injection grid spacing also considered observed subsurface stratigraphy from soil boring logs, local hydrogeologic parameters (hydraulic conductivity and hydraulic gradient), and Metcalf & Eddy|AECOM in-situ injection experience at other sites in New England. To maximize potential contact between the chemical oxidant and contaminants, the injection grid spacing in each area was less than or equal to two-times the radius of influence to allow some overlapping in the subsurface of injected solutions. In Area A, where radius of influence was estimated to be between six and ten feet, a grid spacing of 16 feet was

Table 8. Full-Scale Remediation Basis of Design Parameters

Parameter	Area A	Area B	Area C
Depth to Ground Water	4.5 - 6 feet bgs	3 - 6 feet bgs	1-4 feet bgs
Depth to Bedrock	18 - 34 feet bgs	18 - 33 feet bgs	18 - 38 feet bgs
Treatment Thickness	11 - 22 feet	14 - 22 feet	4 - 19 feet
Targeted Remediation Area	30,000 sq. feet	6,000 sq. feet	15,000 sq. feet
Injection Volume	100 gallons / VLF	100 gallons / VLF	85 gallons / VLF
Sodium Persulfate Dosage	200 lbs / VLF (~24%)	205 lbs/VLF (~25%)	155 lbs/VLF (~22%)
Injection Grid Spacing	16 feet (within 10,000 ug/L TVOC isopleth) 20 feet (within 1,000 ug/L TVOC isopleth)	12 feet	16 feet (where PCE >100 ug/L) 20 feet
Injection Locations	107	55	42

incorporated into the full-scale design for the most contaminated center portion of the plume, and a grid spacing of 20 feet was chosen for the outer portions of the plume. In Area B, radius of influence was estimated to be between five and eight feet from the pilot test injections; due to the low permeability soils observed in Area B the full-scale ISCO design used a grid spacing of 12 feet throughout Area B. In the deeper portion of the Area C pilot test area, the radius of influence was estimated to be greater than six but less than ten feet; however, the pilot test area was located outside of the target area for full-scale remediation in Area C. Contamination concentrations were generally lower in Area C, so therefore 20 foot grid spacing was chosen for Area C, with the exception where PCE concentrations were noted to be greater than 100 ug/L in groundwater samples and a 16 foot grid was applied. It should be noted that the radius of influence in each area was based on injection volume and dosage used during the pilot test. Therefore for full-scale remediation design, it was assumed that using similar injection volumes for the full-scale as the pilot tests would affect the same mobile porosity in the groundwater aquifer. Volumes were designed to be approximately equivalent to the pilot test injections. Dosages were decreased slightly from the

high persulfate dosage used in the pilot test under the assumption that a grid injection approach would allow for increased contact between oxidant and contaminants.

With a successful pilot test injection in Area B using direct-push tooling, the design process evaluated performing injections through permanent injection wells and/or using temporary direct-push rods in each area of the Site To minimize time and cost associated with well installation, the design identified a large number of injection locations to be performed by direct-push injection. Similar to the single direct-push, pilot test point, the direct-push injections were designed to be "bottom-up," where injection rods are advanced to refusal (or the deepest target depth) and raised to the upper limit of the target depth interval. Semi-permanent injection wells were planned where contaminant concentrations were noted to be highest and follow-up ISCO injections were expected to be needed, including in the western portion of Area A within the 10,000 ug/L total VOC groundwater isopleth (which is near the presumed source), in Area B within the 100,000 ug/kg total VOC soil isopleth, and along the eastern boundary of Area B to reduce contaminant transport below Route 125. With this designed placement of PVC injection wells, approximately 80% of the injection points were designed to be direct-push with the remaining 20% of injection points to use injection wells.

4. CONCLUSION

The ISCO pilot test conducted at the Ottati and Goss Superfund Site successfully demonstrated that site contaminants, including chlorinated and BTEX VOCs and 1,4-dioxane, could be remediated in-situ with the injection of a strong chemical oxidant. Following the injection of base-activated persulfate through pre-constructed injection wells and through direct-push injection rods at one location, critical information was collected to design and optimize implementation of full-scale ISCO remediation. Due to the aggressive schedule required to achieve EPA's construction completion for the site, the remedial design needed to be completed without much of the fixed laboratory analysis for contaminants of concern. As a result, frequent monitoring for water quality parameters and field screening analyses was completed to evaluate the distribution and persistence of the chemical oxidant and the resulting changes in aquifer geochemistry. During remedial design for injection spacing, oxidant dosage, and volume, and it was assumed that significant destruction of site contaminants would occur in wells where persulfate, sodium, sulfate, and ORP changed significantly from baseline conditions. When all pilot test performance monitoring laboratory became available, this assumption was proved to be appropriate. The full-scale application was completed between July and September 2008, and was the largest persulfate

ISCO injection performed to date (FMC, personal communication with Phillip Block, May 26, 2010). Performance monitoring following full-scale remediation in January and April 2009 indicated significant reduction in contaminant concentrations in groundwater as well as reduction in plume area. As noted the full-scale design relied heavily on performance monitoring of water quality parameters and field analyses during the pilot test for the site's fast-track schedule. The reduction of contaminants as a result of full-scale injection suggests that the remedial design chose appropriate injection spacing and oxidant dosages based on pilot test monitoring.

5. ACKNOWLEDGEMENTS

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Chapter 16

REMEDIATION OF ACID TAR LAGOON

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ABSTRACT

Slovenia (20,000 km^2, 2 million inhabitants, 750,000 in employment) is industrialised to a medium extent. Many ecological problems have remained from past periods ('old ecological burdens'). Many of them are legal waste dumps resulting from the technology used in these past periods. One of these is the acid tar waste dump in the northeast of the country, close to the border with Austria ('Pesnicki Dvor', in operation from 1966 to 1983). In addition to mineral and sulphonated mineral oils, acid tar also contains well dispersed heavy metal salts of lead, zinc copper, arsenic and barium. The surface area of the acid tar at the dump was between 3,000 and 3,500 m^2. The total thickness of the acid tar and water was 5 m, and the pH value of the water below acid tar was approx. 1.5. In 2006 the clean-up of the dump began:

- Excavation of the tar and contaminated earth;
- Technological process of solidification of the tar;
- Loading and removal of the solidificate or the product of the incineration process;
- Capture and cleaning of waste acid gases;
- Cleaning of water from the dump at a treatment facility.

The process of solidification of the acid tar took place in a plate mixer (approx. 80 tonnes a day), the addition of active additives (CaO, $Ca(OH)_2$, $CaCO_3$) amounted to approx. 25 tonnes a day, and the total daily volume of all additives used was approx. 20–50 m^3. The daily production of solidificate from acid tar and contaminated earth was 90 m^3.

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More detailed results of the clean-up and cleaning from the polluted water process will be shown by individual stage of the process, with a timescale and the relevant measurements and data.

The end result of the clean-up is the removal of all acid tar and polluted soil, the removal of all surfaces and facilities used during the clean-up, the introduction of clean earth and the re-cultivation of the area ('greening').

Keywords: remediation, acid tar, lagoon, solidification

1. INTRODUCTION

Many ecological problems remain from the past in Slovenia. These are primarily contaminated sites, featuring a range of contaminants (e.g. heavy metals, acid tar, industrial wastes etc.). Remediation of some of them started years ago and is still the lastly still today. These activities go hand in hand with high costs. In most cases the owners or administrators no longer exist, so the high costs of remediation generally have to be provided by the state. A refinery company, Rafinerija Mineralnih Olj Maribor, was founded in 1947 near Maribor (an industrial city near the border with Austria) to process waste motor oil collected in Slovenian territory. The refining of waste, used technical motor and industrial oil with sulphuric acid produces a hazardous and unusable waste product – acid tar. In addition to mineral and sulphonated mineral oils, acid tar also contains exceptionally well dispersed free sulphuric acid, heavy metal salts (lead, zinc, copper), while process sulphuric acid contains barium and arsenic. In 1967 a landfill for residue from waste oil refining was built in Pesniski Dvor (a small village near the city of Maribor) in line with then applicable regulations. The landfill site operated until 1983. There are two more landfills nearby, which also represent an ecological burden on the environment. An attempt was made between 1983 and 1986 to add fly ash to the pit in addition to the embankment. The pit embankment was supported with iron (*sic*) sheet piling, and a trench was constructed to prevent the inflow of storm water into the acid tar pit. In 1994 the preparation of technical documentation for remediation of the landfill began, which defined the acid tar pre-treatment process with solidification. In 2000 measurements of geotechnical and seismic parameters were started at three acid tar landfills, which produced accurate data on the content, quantity, and contamination of earth and water. In 2001 waste process water treatment started, which used a process to isolate sulphuric compounds. In 2001 a plan for the complete remediation of the Pesniski Dvor landfill was included in projects financed from the national budget, which was set for completion by end of 2006. In 2003 physical, chemical and other applied tests of laboratory-prepared acid tar solids were carried out. This established the conditions of how the solidification,

incineration and final disposal of incineration residuals shall be performed. Location of the landfill is presented in Figure 1 (Resolution on National Programme of Environmental Protection in Period from 2005 to 2012, 2005).

Figure 1: Location of landfill

1. 1 State of landfill before remediation

The remediation area for the abandoned acid tar landfill is larger than the actual landfill pit and embankment itself. The project included construction of purpose-built remediation facilities in the wider remediation site, for which all the required permits under the legislation of the time were acquired. The site covers an area of 2.8 ha.

The overall site includes two sub sites:

1. the landfill location which includes the enclosed landfill pit within leachate collection trenches and the sheet piling-supported embankment and
2. the location with facilities for process equipment and handling areas.

The existing technical process equipment is intended to separate emulsions from previous remediation phases, and was installed on a reinforced concrete 540m^2 apron and including the following main technical devices:

- boiler with burner and chimney
- 2 heat-insulated decanting cisterns (50 m^3)
- cistern for eliminated oil (50 m^3)
- heating oil tank (50 m^3)
- 2 heat-insulated pre-decantors (50 m^3)

- heat exchanger
- emulsion, oil and water pumps.

Infrastructure facilities were constructed in parallel with technical facilities and equipment (Lipovsek and Kovac, 2007).

1.2 Basic characteristics of landfill

The landfill area enclosed within embankments covers 3000 to 3500 m^2. The surface layer of water was 4000 m^2. The (estimated) volume of contaminated land was 5000 m^3. The volume of sediment (highly viscous acid tar, fly ash, wastewater treatment sludge) was an (estimated) 15,000 m^3. The total thickness of the layer of water and the greatest depth of acid tar was 5 m. The land at the bottom of the landfill was clay. Profile of the landfill in presented in Figure 2.

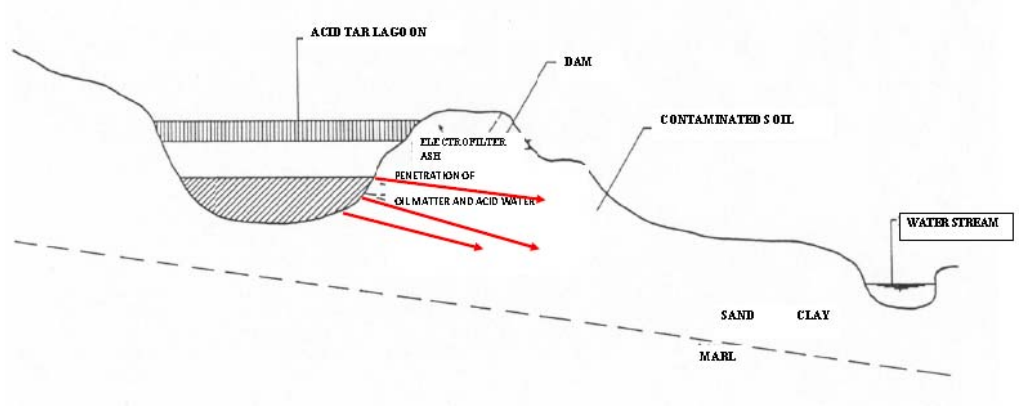

Figure 2: Profile of the landfill

2. MATERIALS AND METHODS

The technical process of acid tar solidification incorporates these technical processes:

- extraction of acid tar and contaminated land and internal transport of excavated material to the equipment which separates the largest items, such as timber, stone and others, from the material
- technical process of acid tar solidification
- capture and treatment of waste acid gas in scrubber
- solid material incineration

- revitalization of site through recultivation.

A rotating crane and excavator with telescopic arm are used to excavate acid tar and contaminated earth. The capacity of both machines is 10 tons per hour. After separating larger debris with the aid of a wheel loader, the acid tar is mixed at the loading point with additives, such as coal particulates, paper sludge, municipal waste treatment sludge, sawdust, etc. This ensures uniform granularity and flowability of the excavated material.

The solidification process starts with the transport of excavated and material mixed with additives past a magnetic separator (which removes any metal particulate present) to the mechanical mixer. This has a volume of 1.2 m^3, and is equipped with blades with a special form for stirring viscous and solid materials with controlled dosage of incoming components. Neutralising additives such as CaO, $Ca(OH)_2$ and $CaCO_3$, which neutralise the acidity, are added to the mechanical mixer on the basis of a preliminary analysis. Lengthy stirring and sufficient residence time ensure the best possible level of neutralisation. The mechanical mixer can mix approximately one tonne of material in a single batch. The quantities of neutralising additives may be changed, not only due to a low pH, but also due to moisture content or the energy value of the product. The residence time for the mechanical mixer is 2–3 minutes. Neutralisation in a mechanical mixer releases reaction heat, which depends on the neutralisation additives used. The increased temperature makes the mixture more viscous. Process water is added if required. The higher temperature also increases SO_2 emissions. The optimum temperature is 70°C and it cannot exceed 100°C, as H_2SO_4 and SO_3 also evaporate at that temperature, as do lighter fractions of oil and polycyclic hydrocarbons. The mechanical mixer is also equipped with an extraction device that removes harmful emissions to air caused by the process. Waste air is taken from the mechanical mixer to a reaction drum where dust particles are removed. From there gas emissions are conducted to the scrubber, where the neutralising liquid is NaOH. Cooled, stabilised, mainly small-grain material comes out of the reaction drum. This falls down a slope to a chute with a belt conveyor which moves the solidification product to a covered storage area. The addition of neutralisation additives during the solidification process releases heat which causes SO_2 and SO_3 to evaporate from the acid tar. At excess temperature (over 100°C), H_2SO_4 and lighter volatile fractions of mineral oils and polycyclic aromatic hydrocarbons also evaporate from acid tar. The total quantity of waste gases is around 3000 to 5000 m^3 per hour, which is conducted into a wet washing process and active carbon absorption (Hodalic et al, 2004).

Extraction takes place in this process equipment:

- acid tar and contaminated earth receiver: 250 to 500 m^3/h

- belt conveyor: 250 to 500 m^3/h
- mechanical mixer: 500 to 1000 m^3/h
- reaction drum: 1000 do 2000 m^3/h

Extraction is carried out using a fan, which has a capacity of 5000 Nm^3/h. Before entering the scrubber, waste gases are conducted via a solid particle isolator, which separates off particles.

The scrubber is placed above a tank of absorbent washing solution of NaOH, concentration 10%. The scrubber consists of two units: the first unit has a volume of 40 m^3, in which washing with a NaOH solution takes place, and has a pH regulation system and a chemical dosing device built in. The gases are conducted from the first unit into the second, in which there is a centrifugal fan that extracts the washed waste gases via an active carbon filter and into a container with H_2O_2, where Na_2SO_3 oxidises to Na_2SO_4. The scrubber's guaranteed SO_2 absorption rate is 98%. The initial concentration of SO_2 in the waste gas is approximately 5000 mg/m^3. Operational monitoring is carried out during remediation at the cleaned gas outlet point. If the legally permitted emissions of SO_2 are exceeded, solidification capacity is reduced.

The purpose of the active carbon filter is to remove volatile organic compounds (PAHs, lighter fractions of mineral oils, etc.).

2.1 Incineration of processed acid tar solids

After the solidification process, the neutralised acid tar is transported to Germany for incineration, where it will be processed into a secondary energy product suitable for co-incineration in a thermal power plant.

The thermal power plant uses coal with a high sulphur content. Transport takes place in containers. A short and simplified schematic illustration of the technical solidification process is shown in Figure 3.

Contaminated land is processed with reactive additives according to acidity levels. The earth is also transported to a processing plant where it will be processed into construction material. Scheme of technological process and scheme of mass flow are presented in Figures 4 and 5 (Lipovsek and Kovac, 2007).

The anticipated quantity of processed and transported solidified acid is around 50,000 tonnes, with the anticipated time scale for the entire process judged at around 3 years (Lipovsek and Kovac, 2007).

2.2 Revitalisation of site through recultivation

The revitalisation and recultivation of the area currently containing the acid tar pit will take place after conclusion of the technical process of acid tar solidification in line with landscaping norms. Revitalisation will be carried out in accordance with spatial planning acts. The pit will be covered and the surfaced turfed and planted with trees (Hodalic, et al, 2004).

3. RESULTS AND DISCUSSION

The average excavation rate was and still is 8 t of acid tar per hour. A smaller quantity of excavated acid tar makes it easier to manage SO_2 emissions from excavation, as well as the emission and neutralisation of sulphates and sulphides in the reaction drum during both solidification and neutralization.

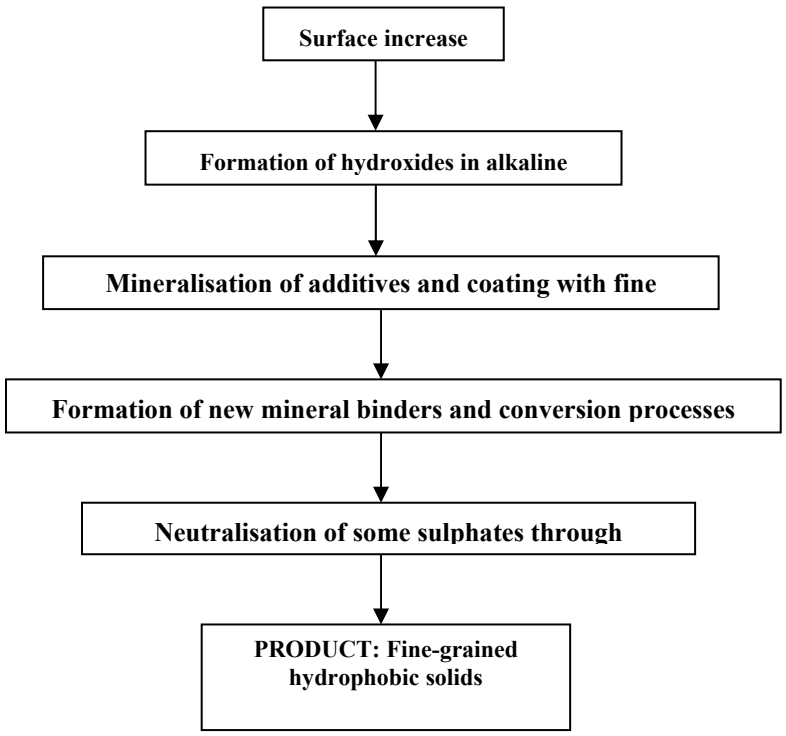

Figure 3. A schematic illustration of the technical solidification process

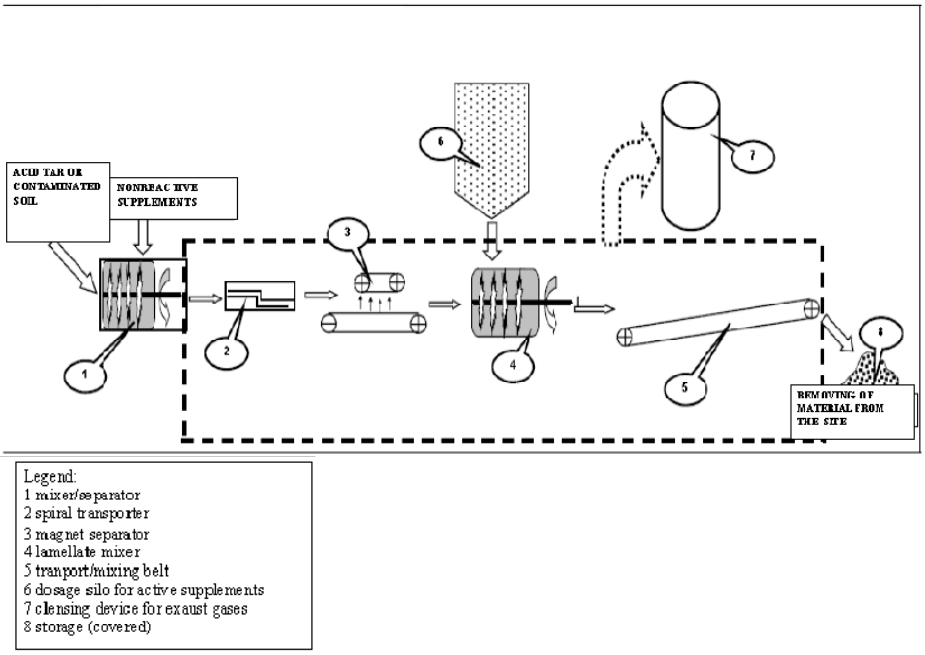

Figure 4. Scheme of technological process

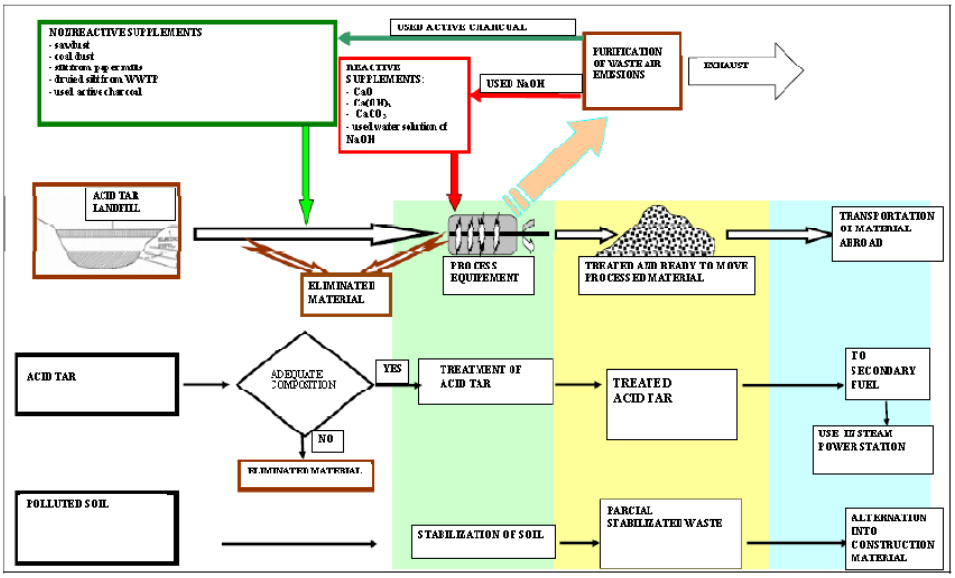

Figure 5. Scheme of mass flow

Table 1 indicates the mass balance for the acid tar excavation, solidification, neutralization of emissions, filling and removal of solid material.

Table 1. Mass balance for the acid tar excavation, solidification, neutralization of emissions, filling and removal of solid material

Quantity of acid tar excavated per hour	8 tonnes
Quantity of acid tar excavated per month	1600 tonnes
Acid tar density	1.1 to 1.3 t/m^3
Use of non-reactive additives per day	6 to 8 tonnes
Quantity of acid tar dosed into the mechanical mixer together with non-reactive additives	8.5 t/h
Quantity of neutralising additives (CaO, $Ca(OH)_2$, $CaCO_3$) per hour	2.7 tonnes
Use of neutralising additives per day	25 tonnes
Volume of all additives used per day	20 to 53 m^3
Total quantity of acid tar and additives dosed into the mechanical mixer per hour	8.2 to 9.6 m^3
Quantity of solid material produced per hour	10.5 to 14.2 tonnes
Quantity of solid material produced per hour	13.2 to 18.3 m^3
Solid material production per day	145 to 180 m^3
Number of (20 tonnes) lorries removing acid tar	5 to 7
Ratio dosed of acid to contaminated earth	2:1
Quantity of product per hour of processed contaminated earth during solidification	9 m^3
Quantity of solidified acid tar product and contaminated earth per day	90 m^3

3.1. Treatment of wastewater from acid tar pit

After excavation from the pit is complete, there will only be a pump placed in the pit, which will pump out all (storm) water to a wastewater treatment plant. The waste treatment plant in the acid tar pit areas is required to clean water produced during the solidification process as well as storm water contaminated by contact with acid tar. In the past storm water was already being treated before emission of the water into two water courses that run in the direct vicinity of the acid tar pit, just as treatment is required during the process. The water will continue to require treatment in future, until the revitalisation is completed. Ground water that has not passed to the water courses also requires treatment. The existing municipal treatment plant has a treatment capacity of 10 m^3/h and is intended to isolate mineral oils, for neutralisation of acidic process waters from the solidification process, neutralisation of metal oxides from the water-resistant layer of the acid tar landfill and for oxidisation of hydrogen sulphide. The waste treatment plant phases:

- oils and emulsions removed from water in gravitational oil-water separator
- contaminated water from the landfill site is then run off to a hopper

- the water is passed through an oil scraper and a settlement tank
- sulphide oxidation and pH regulation then takes place in baths
- the next phase is coagulation, flocculation, precipitation and sludge sedimentation followed by filtration in sand filters and active carbon absorption.

The treated water is released to a local stream, while part of the water is used for the technical needs of solidification and the waste treatment plant. Water samples are analysed before release. Table 2 indicates typical physical-chemical analysis of process monitoring before the start of the solidification process and before release to the Gacnik stream (Hodalic et al, 2004).

Table 2. Typical physical-chemical analysis of process monitoring before the start of the solidification process and before release to the Gacnik stream

Parameter	Limit value for release to water course	Sample 1	Sample 2
Flow on sampling (m^3)		56.2	51.3
Temperature (°C)	30	22.2	19.3
pH	6.5-9.0	9.1	9.3
Insoluble solids (mg/L)	60.0	11.2	4.8
Settled solids (mg/L)	0.5	≤ 0.05	≤ 0.05
COD (mg/L)	300	135	145
BOD_5 (mg/L)	30	10	23
Toxicity	4.0	3.0	1.0
Cu (mg/L)	5.0	≤ 0.05	≤ 0.05
Cd (mg/L)	0.1	50.005	≤ 0.005
Cr^{6+} (mg/L)	0.1	/	≤ 0.005
Ni (mg/L)	0.5	≤ 0.05	≤ 0.05
Pb (mg/L)	0.5	≤ 0.05	≤ 0.05
Hg (mg/L)	0.01	≤ 0.001	≤ 0.001
AOX (mg/L)	0.5	0.08	0.02
Ammonium nitrogen (mg/L)	50.0	3.6	0.8
Nitric nitrogen (mg/L)	35.0	0.40	0.25
Nitric nitrogen (mg/L)	5.0	/	2.0
Arsenic (mg/L)	0.1	≤ 0.01	≤ 0.02
Zinc (mg/L)	2.0	0.1	0.1
Total chrome (mg/L)	0.5	≤ 0.05	≤ 0.05
Chloride (mg/L)	30	20	22
Sulphate (mg/L)	300	500	340
Sulphide (mg/L)	0.5	≤ 0.05	≤ 0.05
Total hydrocarbons (mg/L)	10.0	≤ 0.1	≤ 0.1
BTX (mg/L)	0.1	≤ 0.05	≤ 0.05

The results of the physicochemical analyses indicate that the sulphate content is occasionally excessive and the pH value occasionally too high. The sulphate content was higher due to the solubility.

The results of the physicochemical analyses indicate that the ground water in the area is of good quality, with a notable reduction in mineral oil content.

The waste treatment plant has sufficient capacity to treat process water, water from the water-resistant layer, and for treatment of collected storm water from the surfaces around the process equipment.

Waste process water is produced during the washing of waste gas in the scrubber. Water use for wet cleaning in the scrubber is around 0.3 to 0.5 m^3/h due to recirculation of the washing liquid. Part of the process water arrives at the waste treatment plant from condensate and from the reaction drum. Part of the process water is returned to the solidification process.

3.2 Results of water monitoring for outflow and sediment in the Gacnik stream 2004

Analyses of Gacnik stream water were taken from two points – before the impact of the acid tar landfill and after output of the treated water, following processing at the acid tar landfill treatment plant. In addition to general parameters, a number

Table 3. The physicochemical analysis of water and sediment from the Gacnik stream – 2004

Parameter	Water (before outflow)	Water (after outflow)	Sediment (before outflow)	Sediment (after outflow)
Water temperature (°C)	19.0	19.5	/	/
pH	7.9	7.9	/	/
Elec. conductivity (μs/cm)	1250	650	/	/
Oxygen (mg/L)	7.6	8.4	/	/
O_2 saturation (%)	88	97	/	/
Insoluble solids (mg/L)	13	28	/	/
Dried solids (%)	/	/	100	97
Dried solids – wet filtration (%)	/	/	40	30
Sulphate (mg/L)	45	42	/	/
COD (mg/L)	≤ 5	≤ 5	/	/
PCB-28 (μg/kg)	/	/	≤ 1	≤ 1
PCB-52 (μg/kg)	/	/	≤ 1	≤ 1
PCB-101 (μg/kg)	/	/	≤ 1	≤ 1
PCB-138 (μg/kg)	/	/	≤ 1	≤ 1
PCB-153 (μg/kg)	/	/	≤ 1	≤ 1
PCB-18 (μg/kg)	/	/	≤ 1	≤ 1
EOX (mgCl/L)	/	/	≤ 1	≤ 1
Mineral oil (mg/L) (mg/kg)	≤ 0.005	≤ 0.005	66	70
Zn in water (g/L) in sediment. (mg/kg)	≤ 10	≤ 10	90	101
Pb in water (g/L) in sediment. (mg/kg)	≤ 1	≤ 1	25	20

of additional pollution parameters were selected that could indicate the impact of the acid tar landfill on water courses. The analysis was also performed on sediment from the same points. Table 3 indicates the physicochemical analysis of water and sediment from the Gacnik stream – 2004.

The similarity of the two sets of results in the table indicates that the quality of the water course at both sampling points is similar. Only the oxygen content is poorer, while the organic compound content is also higher, but the content of insoluble solids, sulphates, mineral oils and metals (Zn and Pb) are not higher.

The analysis of sediment, which is laid down over a lengthier period, indicates that the mineral oil content is higher.

3.3 Potential impact of acid tar landfill on ground water between drainage channels

In the potential area in which acid tar could threaten the ground water due to the penetration of pollutants through the embankment, holes were drilled from which ground water samples were regularly taken and the main acid tar pollution parameters were monitored. There were 7 such holes and in 3 of them there was an increased value for soluble solids, sulphate ion, mineral oils, volatile compounds, and partially barium and reduced pH values. This represents a threat to the ground water and the possibility of these pollutants penetrating to the Gacnik stream. Table 4 illustrates the chemical analyses for the holes in the acid tar landfill site in 2003.

Table 4. The chemical analyses for the holes in the acid tar landfill site in 2003

Parameter	Unit	VI	V2	V3	V4	V5	V6	V7
pH		7.9	7.5	6.8	7.5	7.3	6.3	7.5
Dried solids	mg/L	990	880	1400	1280	1900	2520	1340
Ash content	mg/L	960	780	1210	1020	1430	2000	1110
Total P	mg/L	0.5	0.5	0.2	0.3	0.1	0.1	0.1
Zn	mg/L	2.0	0.6	18.0	0.05	0.12	0.1	0.08
Cu	mg/L	≤ 0.4	≤ 0.4	≤ 0.4	≤ 0.4	≤ 0.4	≤ 0.4	≤ 0.4
Mn	mg/L	0.20	1.2	15	0.40	0.50	0.85	0.50
Mo	mg/L	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5
Ba	mg/L	1.6	2.5	4.5	4.0	5.8	5.7	3.5
Cr	mg/L	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
Pb	mg/L	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5
Ni	mg/L	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	0.1	≤ 0.05
Cd	mg/L	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
As	mg/l.	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
F	mg/L	0.36	0.65	0.20	0.20	0.14	0.14	0.18
SO_4^{2-}	mg/L	30	60	1000	760	1020	1950	1000
Cl	mg/L	380	200	20	35	50	50	35

Table 4. Continued

Parameter	Unit	VI	V2	V3	V4	V5	V6	V7
CN^-	mg/L	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01
$N0_2^{2-}$	mg/L	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01
Mineral oils	mg/L	0.05	0.03	0.20	0.10	0.25	2.30	0.05
VOC	mg/L	≤ 0.005	≤ 0.005	0.005	0.005	0.030	0.050	0.007
Halogenited organic compounds	µg/L	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
PCB	»g/L	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05

Samples were also taken in 2004, but only from these holes, where the analyses had deteriorated from the previous year, i.e. from holes V3, V5 and the new hole V8. Table 5 illustrates some chemical properties of ground water measured from 3 holes in 2004.

Table 5. Some chemical properties of ground water measured from 3 holes in 2004

Parameter	Unit	V3	V5	V 8
Hole depth	M	10.2 J	7,5	6,5
Water level	M	0.66	0.85	2.5
Air temp.	^oC	23	22	23
Water temp.	^oC	14.5	14.8	13.9
pH		7.5	6.8	5.9
Conductivity	µs/cm	1350	1080	120
O_2 saturation	%	25	44	60
Oxygen	(mg/L)	2.5	4.3	6.2
KPK	(mg/L)	15	60	≤ 5
Sulphates	$mgSO_4^{2-}/L$	10	320	25
Mineral oils	µg/L	≤ 6	7	≤ 6

The 2004 measurements indicate that the water insufficiently aerated, or that the oxygen content is relatively low. The sulphate content was also excessive and in some points the acidity level was also too high (hole V8, permitted pH value is from 6.5 to 9.5). Other parameters indicate that the water quality is improving and the impact of the acid tar landfill is falling, as the mineral oil and sulphate content was down.

3.4 Solidification process of waste

The abandoned acid tar landfill holds below water: highly acidic acid tar, mix of acidic acid tar and earth, fly ash and solid residue from the wastewater treatment process. These are all residue from previous remediation attempts (before 1990).

Table 6 indicates the estimated quantities of waste from previous remediation attempts.

Table 6. The estimated quantities of waste from previous remediation attempts

Surface layer of water (pH = 6 do 7)	4000 to 6000 m^3
Floating oil emulsion	Removed on an ongoing basis
Sediment volume: acid tar, fly ash, earth, waste treatment sludge	approx. 15,000 m^3
Volume of contaminated earth	approx. 5000 m^3

These forms of waste have been and will be processed in a similar manner to acid tar. It is expected that during processing some waste will appear that is not suitable for processing and solidification, such as pieces of iron, stones, barrels with unknown contents (due to illegal tipping), abandoned synthetic compounds and other. These will be separated off by a separator. This waste will be mixed with neutralising additives and handed over to an authorised waste management company. The anticipated quantity of such waste should not exceed 200 m^3 or 1% of the quantity anticipated for processing during remediation (Lipovsek and Kovac, 2007).

4. CONCLUSION

The remediation of acidic coal tar at Pesnica was successfully concluded in 2008. The entire broader area has been horticulturally landscaped and in that state put forward for its new use. In Slovenia there are 10 active industrial landfill sites and one hazardous waste landfill. In addition to the active landfills there is also a series of abandoned landfill sites, which came about due to inappropriate disposal of industrial waste. Some of them have already been remediated, e.g. foundry sand landfill at Crnomelj and the consequences of PCB pollution by electronic industry Iskra at Semic in the 1980s.

The greatest environmental threat at present is from the acid tar landfills near Maribor (Studenci and Bohova), the industrial waste landfill at Globovnik near Ilirska Bistrica, and a red mud and ash landfill at Kidricevo. These old polluted areas require special technical solutions and increased investment. Their remediation is planned as part of waste management strategy.

Remediation programmes have already been prepared for all the old polluted areas, and remediation work is already underway in Kidricevo and Globovnik, while the remediation of the coal tar landfills at Studenci and Bohova has been postponed due to administrative procedure, and primarily due to a lack of funds (Resolution on National Programme of Environmental Protection in Period from 2005 to 2012, 2005).

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Chapter 17

EX-SITU WELLHEAD TREATMENT OF 1,4-DIOXANE USING FENTON'S REAGENT

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ABSTRACT

At the U.S. Army Natick Soldier System Center (NSSC) in Natick, Massachusetts, groundwater is being pumped and treated to provide containment of a historical trichloroethene (TCE) plume. Upon discovering 1,4-dioxane (an emerging contaminant not previously monitored) at one of the monitoring wells above the Massachusetts Department of Environmental Protection drinking water goal of 3 µg/L, the existing on-site groundwater treatment system required augmentation to continue maintaining plume containment and meeting allowable discharge limits. Existing treatment consists of air-stripping and granular activated carbon, which both have a low efficiency for treating 1,4-dioxane. The concentration of 1,4-dioxane in the TCE plume requiring treatment is less than 100 micrograms per liter (µg/L) and approximately 10 to 20 µg/L in the 4 to 6 gallon per minute (gpm) combined discharge stream from three new extraction wells. Because 1,4-dioxane was only identified in a isolated portion of the TCE plume and not in the 75 to 90 gpm flow to the existing treatment system from this TCE plume and others, a goal was to provide in-situ or wellhead treatment for the 1,4-dioxane and not to treat the 75 to 90 gpm flow.

An engineering study was conducted to evaluate 1,4-dioxane and TCE treatment options, with key considerations being that 1,4-dioxane was detected at a low concentration, the extracted water was high in total suspended solids (TSS) and iron oxides, flow-rates needed for containment were small (< 6 gpm), 1,4-dioxane was highly localized, and the size of the physical plant had to be small. Viable options that were considered included the following Advanced Oxidation

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Processes (AOPs): Fenton's Reagent, hydrogen peroxide with ultraviolet (UV) light, hydrogen peroxide with ozone, and catalyzed persulfate.

Based on the engineering study, ex-situ application of Fenton's Reagent was selected as a practical cost-effective solution. Bench-scale jar testing demonstrated that naturally occurring iron found in the water was sufficient to provide the metal catalyst needed for the Fenton's reaction, and that stoichiometrically over-dosing hydrogen peroxide would decrease treatment residence-time necessary for achieving remediation goals and compensate for hydrogen peroxide dissipating side-competition reactions.

Keywords: advanced oxidation process (AOP), groundwater, 1,4-dioxane, trichloroethene (TCE), Fenton's reagent, hydrogen peroxide, and wellhead.

1. INTRODUCTION

Granulated activated carbon (GAC) and air-stripping (AS) treatment of groundwater extracted to provide containment of trichloroethene (TCE) and tetrachloroethene (PCE) plumes has been part of the on-going environmental restoration of the aquifer at the US Army Natick Soldier Systems Center (NSSC) in Natick, MA, since 1977. In 2005, with the concern over emerging contaminant 1,4-dioxane being discovered in chlorinated solvent plumes across the nation, a select group of NSSC long term monitoring program (LTMP) wells were sampled for 1,4-dioxane. The 1,4-dioxane sampling showed that 1,4-dioxane, an EPA group B2 probable human carcinogen, was present consistently in one monitoring well (MW-124B) and detected sporadically at other monitoring wells, and the 1,4-dioxane was co-mingled with TCE in the groundwater of Area of Concern (AOC) Buildings (Bldg) 63, 2, & 45.

Because NSSC is in a groundwater protection Zone 2 (that area of an aquifer which contributes water to a drinking water well under the most severe pumping and recharge conditions that can be realistically anticipated) with the underlying aquifer being considered GW-1 (i.e. drinking water aquifer), the chosen remedial action operation at this AOC was containment of the groundwater plume, which now included as a new requirement the containment of the 1,4-dioxane contaminated groundwater. Groundwater containment at the AOC was to be achieved by connecting the AOC extraction wells to the existing groundwater extraction and treatment system (GWETS), which treats influent from extraction wells that contain two other TCE/PCE groundwater plumes. The GWETS treatment train technology consists of GAC and AS both of which are known to have low efficiencies for removing 1,4-dioxane, because 1,4-dioxane has a low

octanol/water partition coefficient (0.537) and a low Henry's Law constant (4.88 X 10^{-6} atm m^3/mol) (Howard 1990).

Therefore neither of these technologies individually or in combination could achieve 1,4-dioxane removal from the extracted groundwater sufficiently to meet the GWETS 1,4-dioxane discharge limit (3 µg/L). The extent of 1,4-dioxane groundwater contamination is limited to the distal end of the previously characterized AOC 63, 2, & 45 TCE plume and is only detected in one extraction well, so wellhead treatment of 1,4-dioxane was to be performed instead of reconfiguring the GWETS treatment train, which treats influent water (90 gallons per minute [gpm]) from the other plumes, which have no 1,4-dioxane contamination.

An engineering feasibility and cost analysis study was performed to determine the optimum well-head treatment method. The key criteria for the basis of selection were the ability to treat by destruction co-mingled TCE and 1,4-dioxane found in the AOC 63, 2 & 45 plume with 1,4-dioxane levels ranging from 150 µg/L, the maximum historical detection, to 6 µg/L, the historical minimum detected in the groundwater. The 1,4-dioxane detections have shown a steady decrease since 2005, so there does not appear to be a steady source, which also factored into the need for a small and portable well-head treatment unit that could be moved or readily demobilized. 1,4-dioxane is a known solvent stabilizer in 1,1,1 trichloroethane (TCA); however, TCA has not been detected in groundwater at levels sufficient to be the cause for 1,4-dioxane detection. To achieve the remedial action objective of groundwater containment, an extraction flow-rate of less than 6 gpm was required. The typical groundwater extracted from this plume was high in turbidity and typically a translucent beige color from iron oxides.

Advanced oxidation processes (AOP), involving the generation of a free radical, were evaluated. The suspended solids and iron content made the ultraviolet (UV)/hydrogen peroxide AOP treatment impractical due to attenuation of the incident UV radiation and the need to constantly clean the UV lamps. Hydrogen peroxide with ozone was considered but this AOP uses proprietary reaction chambers, which are more cost effective for higher flow rate conditions and a permanent setting. Catalyzed persulfate treatment might have added sulfur compounds to the GWETs effluent, and some of the effluent is used for non-potable water purposes. Fenton's reagent was selected as the wellhead treatment technology based upon the demonstrated ability to destroy 1,4-dioxane and TCE under controlled reaction conditions with sufficient residence time and because of its relatively low-cost. Fenton's reagent is not a proprietary mixture and can be formulated from commercially available bulk reagents, which can be administered without a complex reaction chamber. Further, the main ingredient in Fenton's reagent hydrogen peroxide (H_2O_2) is consumed or breaks down to yield water.

1.1 Fenton's Reagent

Fenton's Reagent; Hydrogen peroxide in the presence of an iron catalyst yields strong oxidizing agents capable of 1,4-dioxane mineralization.

1.1.1 1,4-Dioxane Mineralization (Theoretical)

$C_4H_8O_2 + 10\ H_2O_2 \longrightarrow 4\ CO_2 + 14\ H_2O$ (10:1 ratio) (Klecha and Gonsior 1986)

Fenton's reagent catalytic reaction sequence involving iron that forms hydroxyl radical (·OH), which is one of the strongest oxidizing agents;

$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \cdot OH$

$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + \cdot OOH + H^+$

1.1.2 Prerequisite Conditions for Fenton's Reagent:

- Iron: Ferrous or ferric iron (US Peroxide 2009).
- pH range (3-5 Standard Units [SU]): This serves to dissolve iron making it available in solution as a catalyst that is not consumed in the reaction, but creates hydroxyl radicals from the hydrogen peroxide.
- Residence Time: Fenton's reagent as a function of concentration and reaction conditions will require a minimum contact time with 1,4-dioxane for removal.

Other AOPs utilize ozone or UV-light to create the hydroxyl radical, and these types of AOPs have been used successfully for ex-situ treatment of groundwater at several locations. According to an United States Environmental Protection Agency (USEPA 2006) literature survey, there were no sites where Fenton's reagent was used for ex-situ 1,4-dioxane treatment. The purpose of this paper is to describe how bench scale jar testing using Fenton's reagent led to a full-scale implementation of Fenton's reagent to successfully treat ex-situ TCE and 1,4-dioxane contaminated groundwater at the wellhead.

2. MATERIALS AND METHODS

2.1 Materials

Thirty-five percent hydrogen peroxide (H_2O_2), ferrous sulfate ($FeSO_4 \cdot H_2OX$), ferric sulfate ($Fe_2(SO_4)_3 \cdot H_2OX$), and sodium sulfite (Na_2SO_3) were obtained from Afla Aesar and were reagent grade. Concentrated hydrochloric acid was technical

grade. Various hydrogen peroxide solutions were prepared by dilution of 35% hydrogen peroxide by de-ionized (DI) water. Iron catalyst solutions were prepared using ferrous sulfate or ferric chloride solutions prepared by dissolving 7.9 grams of $FeSO_4 \cdot H_2OX$ or 2.9grams of $(Fe_2(SO_4)_3 \cdot H_2OX)$ solids respectively into 1-liter of DI water. Sodium sulfite, Fenton's reagent quenching reagent, was prepared by dissolving 75.6 grams of Na_2SO_3 solid into 1-L of DI water. 1,4-dioxane solutions were collected from NSSC groundwater monitoring (MW-124B) or extractions well (EW-3) by using low-flow sampling techniques (USEPA 1996) to obtain representative groundwater samples for the jar-testing. 1,4-dioxane concentrations in groundwater were determined by off-site laboratory analysis. Site groundwater solutions typically contain TCE and PCE as determined by 16 years of groundwater monitoring in addition to levels of 1,4-dioxane ranging from 6 µg/L to 150 µg/L collected from MW-124B and EW-3.

2.2 Analytical Methods

Aqueous 1,4-dioxane jar-testing sample aliquots were analyzed by Accutest Laboratory in Marlborough, Massachusetts, a Department of Defense Quality System Manual certified laboratory using EPA Region I 1,4-dioxane analysis method EIASOP-VOADIOXI (USEPA 2003), as modified to use selective ion monitoring (SIM), at m/z = 88 (parent ion) and m/z = 58 (secondary ion), to increase quantitative sensitivity. This method uses a heated purge block (EPA Method 5035) to increase the quantitative extraction efficiency, which yields a typical calibration response factor of 0.020. The method detection limit (MDL) was 0.18 µg/L with a calibration range from 1.0 µg/L to 100 µg/L

EM Quant peroxide test strip papers used to check the hydrogen peroxide levels during testing had a range of 0 to 25 mg/L and were obtained from EMD Chemicals Inc.(stock no. 10011-1).

YSI Inc. pH probe was calibrated using standard stock calibration solutions of pH 4 SU, pH 7 SU, and pH 10 SU.

2.3 Experimental Apparatus

Open topped 500-ml Kimax beakers were used as reaction vessels in the bench scale jar-testing and filled to a volume of 250 ml with the NSSC groundwater and dosed with amendments for the various trials. Intermittent mechanical stirring with was provided by using a glass rod.

2.4 Experimental Procedure

1,4-dioxane contaminated groundwater representative of the site condition to be treated was obtained from MW-124B or EW-3 at NSSC, as MW-124B represents a worse case scenario and EW-3 represents typical wellhead treatment plant (WTP) influent. Collected groundwater was stored with headspace in a 5-gallon carboy pending treatment trials. Groundwater used for all trials was acidified by the addition of 35% HCl until the pH was in the optimum acidity range for Fenton's reagent (3.0 to 5.0 SU) to be tested, as determined by a YSI pH probe monitoring the pH adjustment. The pH adjusted water was then divided into equal aliquots of 250-ml and placed into 500 ml open top beakers at atmospheric pressure and room temperature (ca. 25 °C). Either ferrous iron or ferric iron was spiked at the experimental trial levels and then hydrogen peroxide at concentrations ranging from 2.0 mg/L to 12,000 mg/L was added. Once hydrogen peroxide was added all of the conditions necessary for Fenton's reagent chemistry to yield hydroxyl radicals were present (low pH, dissolved ferric or ferrous ion, and hydrogen peroxide). Intermittent stirring was provided for all trials. Beakers were left open-topped and not temperature controlled. Initial reaction temperature was typically <20 °C, which is slightly above ambient groundwater temperature, as determined during the acidification step by the YSI probe. Residence time of the reaction was measured from the time hydrogen peroxide was added to the reaction beaker and ended upon collection of a sample aliquot. Reaction conditions were slowed for select sample aliquots by refrigeration (<6°C). For other sample aliquots the Fenton's reagent conditions were quenched by the addition of a sodium sulfite solution. Sample aliquots were collected by pouring the reaction vessel contents into an unpreserved (i.e no HCl) 40-ml volatile organic compound (VOC) sample vial with Teflon septum and leaving no headspace. Collected sample aliquots were stored at <6 °C pending analysis at the contract laboratory.

3. RESULTS AND DISCUSSION

Several experimental trials (A–D) were conducted to determine the applicability of using Fenton's reagent for remediation of 1,4-dioxane, and the optimal dosing levels of iron catalyst, acid, and hydrogen peroxide for remediation of 1,4-dioxane contaminated groundwater at NSSC.

3.1 Trial A Applicability of Fenton's Reagent to 1,4-Dioxane Remediation

Trial A: Objective was to establish the applicability of Fenton's reagent for removal of 1,4-dioxane from NSSC groundwater by dosing hydrogen peroxide at

concentrations ranging from 2 mg/L to 12,000 mg/L, which correspond approximately to 250% to 1,500,000% of the 10:1 stoichiometric ratio of hydrogen peroxide to 1,4-dioxane, see Figure 1 and Figure 2. An additional objective was to determine if longer residence times would remove 1,4-dioxane using lower hydrogen peroxide dosing levels, from 2 mg/L to 8 mg/L, which correspond to approximately 250% to 1,000% of the 10:1 stoichiometric ratio of hydrogen peroxide/1,4-dioxane, see Figure 3. Trial A conditions are provided in Table 1.

Table 1. Trial A Fenton's Reagent Experimental Conditions

Iron Species	Iron Catalyst Level (mg/L)	Residence Time (hours)	pH Levels	Initial 1,4-dioxane Level (µg/L)
Fe(II)	60	5, 24	3.1, 4.35, 6.07	30.1

Untreated groundwater from MW-124B had a slight translucent beige color typical of the ambient groundwater. Upon addition of Fenton's reagent at all pH values, the acidified solution color changed from clear to a characteristic ferric oxide red-orange color with the tint proportional to the hydrogen peroxide level dosed, and the 1,200 mg/L and 12,000 mg/L hydrogen peroxide dosed beakers yielded the most intense color change, which indicated that the Fenton's reaction was producing ferric iron species. After 1.5 hours of the 5-hour residence time elapsed, the hydrogen peroxide levels were determined using hydrogen peroxide test strips. All beakers dosed with less than 10 mg/L hydrogen peroxide were non-detect for hydrogen peroxide, and beakers dosed with 1,200 mg/L and 12,000 mg/L hydrogen peroxide had residual hydrogen peroxide in excess of 25 ppm (test strip maximum detection limit). Dosing hydrogen peroxide at levels <10 ppm did not yield sufficient 1,4-dioxane removal at 5 hours, and 1,4-dioxane removal measured after 24 hours, with similar hydrogen peroxide dosing levels, did not yield significant differences compared to 5-hours, see Figures 1 and 2. This suggests that 1,4-dioxane removal using Fenton's reagent occurs in a much shorter time-span for this media, and a longer residence time does not increase removal efficiency, most likely because the relatively lower levels of dosed hydrogen peroxide has been consumed. hydrogen peroxide dosed at 12,000 mg/L (1.2%) at pH 4.35 SU and at 1,200 mg/L (0.12%) at pH 3.2 SU resulted in complete 1,4-dioxane removal, and hydrogen peroxide doses at 12,000 mg/L at pH 3.2 had produced a 97% 1,4-dioxane reduction, see Figure 3, which demonstrated the applicability of Fenton's reagent to remove 1,4-dioxane from NSSC groundwater.

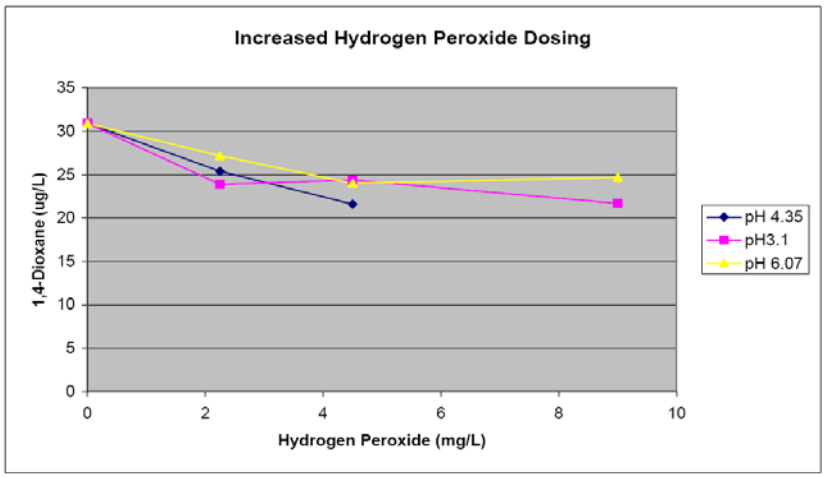

Figure 1. Removal of 1,4-dioxane from MW-124B groundwater treated ex-situ with Fenton's reagent at various pH levels (3.1, 4.35, and 6.07 SU) and hydrogen peroxide dosed at 2 mg/L, 4 mg/L, and 8 mg/L with dissolved ferrous iron (60 mg/L) and a 5-hour residence time.

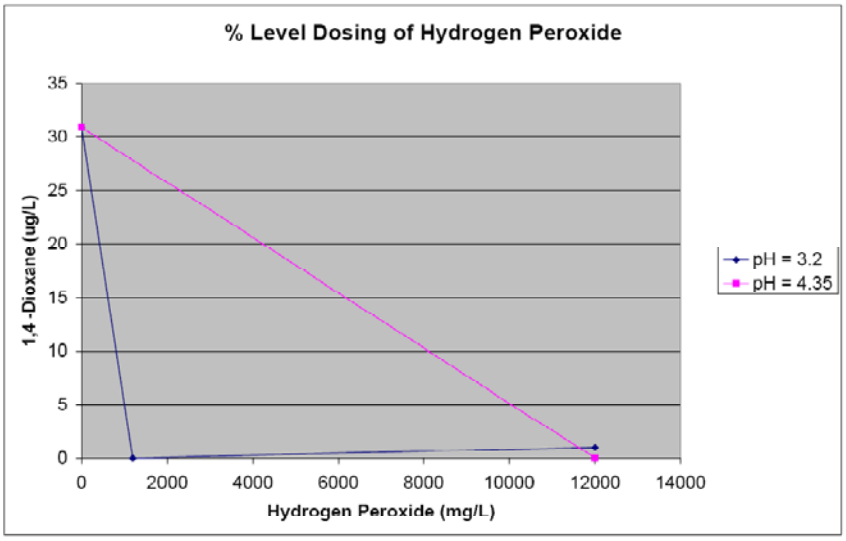

Figure 2. Removal of 1,4-dioxane from MW-124B groundwater treated ex-situ with Fenton's reagent at various pH levels (3.1 and 4.35 SU) and hydrogen peroxide dosed at 1,200 mg/L and 12,000 mg/L with dissolved ferrous iron (60 mg/L) and a 5-hour residence time.

3.2 Trial B Optimize Hydrogen Peroxide Dosing Level and Minimize Residence Time for 1,4-Dioxane Remediation

Trial B: Objective was to minimize hydrogen peroxide dosing levels and residence time needed for removal of 1,4-dioxane from NSSC MW-124B groundwater by dosing hydrogen peroxide at concentrations of 90 mg/L, 45 mg/L, 22.5 mg/L, 11.25 mg/L, 5.6 mg/L, and 2.8 mg/L, which correspond to

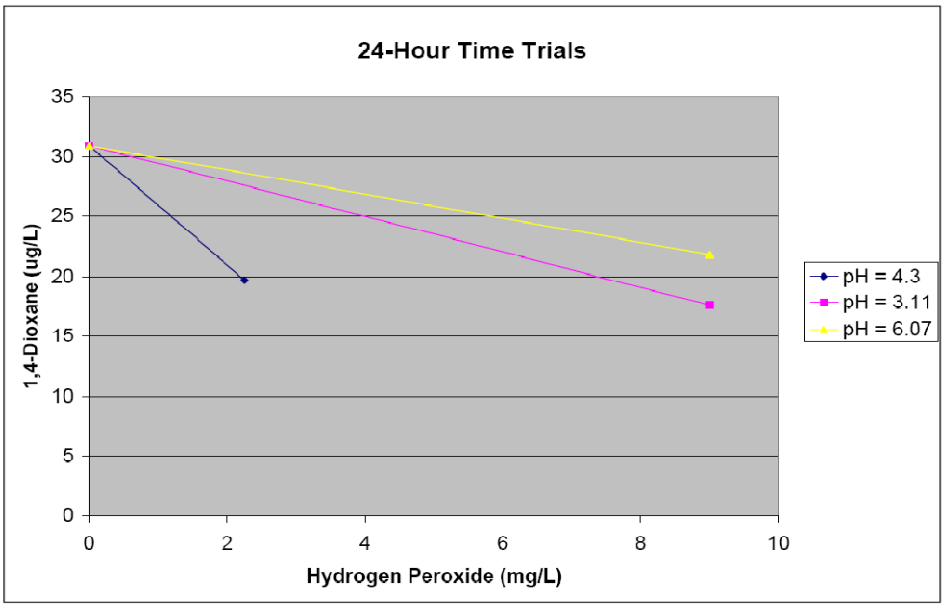

Figure 3. Removal of 1,4-dioxane from MW-124B groundwater treated ex-situ with Fenton's reagent at various pH levels (3.1, 4.35, and 6.07 SU) and hydrogen peroxide dosed at 2 mg/L and 8 mg/L with dissolved ferrous iron (60 mg/L) and a 24-hour residence time.

approximately 11,250% to 350% of the 10:1 stoichiometric ratio of hydrogen peroxide to 1,4-dioxane. Hydrogen peroxide removal as a function of residence time was conducted by dosing hydrogen peroxide concentrations of 90 mg/L, 45 mg/L, and 22.5 mg/L and taking sample aliquots every hour over a 5-hour duration, see Figure 4. The functional dependence of 1,4-dioxane removal at a 3-hour residence time for varying concentrations (90 mg/L to 2.8 mg/L) of dosed hydrogen peroxide is shown in Figure 5. Trial B conditions are provided in Table 2. For these trials the hydrogen peroxide was determined as a function of time using hydrogen peroxide test strips, see Table 3.

Table 2. Trial B Fenton's Reagent Experimental Conditions

Iron Species	Iron Catalyst Level (mg/L)	Residence Time (hours)	pH Levels	Initial 1,4-dioxane Level (µg/L)
Fe(II)	60	1, 2, 3, 4, 5	ca. 3.2	35

Table 3. H_2O_2 levels as a Function of Initial Hydrogen Peroxide Dosing and Elapsed Residence Time

Initial H_2O_2 Dose	Elapsed Residence Time		
(mg/L)	H_2O_2 levels at <1 Hour	H_2O_2 levels at 1.5 Hours	H_2O_2 levels at 2.5 Hours
90	>25 mg/L	>25 mg/L	>25 mg/L
45	> 10 mg/L	>10 mg/L	>5 mg/L
22.5	>2 mg/L	>2 mg/L	2 mg/L
11.25	0 mg/L	0 mg/L	0 mg/L
5.6	0 mg/L	0 mg/L	0 mg/L
2.8	0 mg/L	0 mg/L	0 mg/L

As in Trial A, untreated groundwater from MW-124B for Trial B had a slight translucent beige color typical of the ambient groundwater. Dosing hydrogen peroxide at 90 µg/L resulted in a relatively darker red-orange solution than lessor dosing levels as a function of hydrogen peroxide dosing, and as a function of time the solutions became less opaque to translucent, especially for relatively low-level hydrogen peroxide doses (2.8 mg/L). This change in color intensity with hydrogen peroxide dose and time corresponds to the hydrogen peroxide levels measured in the various reaction beakers, as the hydrogen peroxide levels decreased the color intensity decreased markedly for the reaction beaker dosed with 2.8 mg/L hydrogen peroxide. As shown in Figure 4 for hydrogen peroxide dosed between 22.5 mg/L to 90 mg/L, 1,4-dioxane removal is complete in 1-hour with residual unreacted hydrogen peroxide in excess of 2 to 25 mg/L respectively, which suggest that a 1-hour resident time is adequate for 1,4-dioxane removal under these conditions. The concentration dependence of 1,4-dioxane removal at a 3-hour residence time shows that 11.25 mg/L hydrogen peroxide, see Figure 5, is approaching the threshold of minimum hydrogen peroxide dosing needed for complete 1,4-dioxane removal. At <1 hour the hydrogen peroxide levels in the reaction beaker dosed with 11.25 mg/L hydrogen peroxide is 0 mg/L and 1,4-dioxane was completely removed, which demonstrates that hydrogen peroxide

was not rate limiting at this dosing level and the Fenton's reagent had adequate residence time for reaction completion.

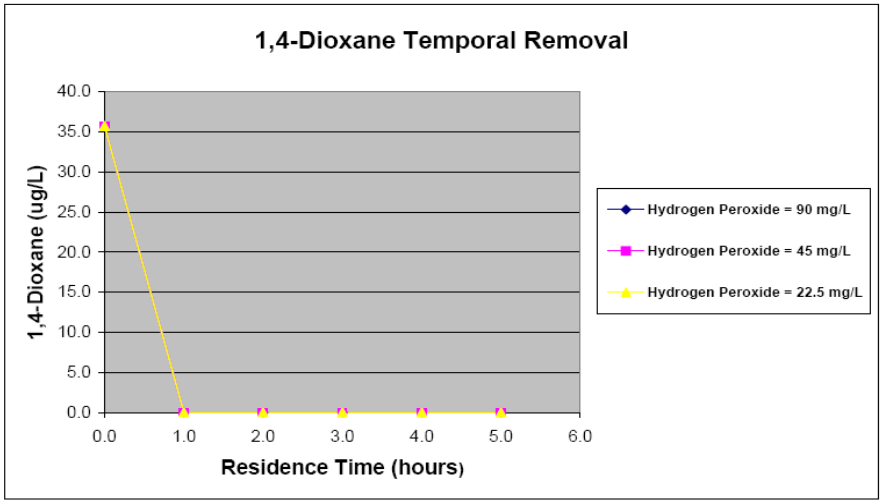

Figure 4. Removal of 1,4-dioxane as a function of time from MW-124B groundwater treated ex-situ with Fenton's reagent at pH 3.2 and hydrogen peroxide dosed at 22.5 mg/L, 45 mg/L, and 90 mg/L with dissolved ferrous iron (60 mg/L) and sample aliquots collected every hour for a 5-hour elapsed residence time.

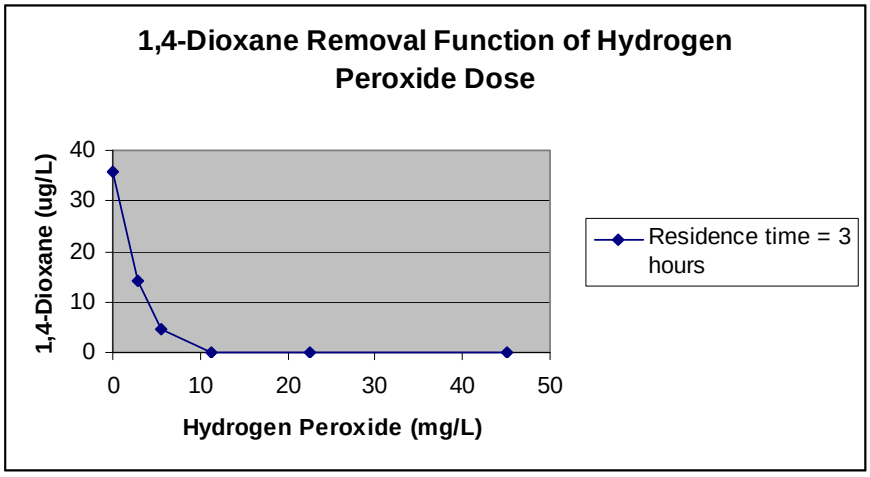

Figure 5. Removal of 1,4-dioxane from MW-124B groundwater treated ex-situ with Fenton's reagent at pH 3.2, and dissolved ferrous iron (60 mg/L) at a 3-hour residence time as a function of initial hydrogen peroxide dose.

3.3 Trial C Acidification Requirements and Acid Neutralization Evaluation

Trial C: Objective was to determine quantitatively the amount of acid required to lower the ambient NSSC Groundwater from EW-3 to pH 3.1, which is suitable for Fenton's reagent chemistry to remove 1,4-dioxane and determine the amount of base needed to restore the pH after treatment. Wellhead influent water from EW-3 was obtained and titrated with HCl to determine a typical dosing rate, which was determined to be approximately 3.17 gallons/day (gpd). Base titrations of EW-3 groundwater treated by Fenton's reagent (pH 3.1, hydrogen peroxide dose 45 mg/L, and 60 mg/L ferrous iron) showed that raising the pH by addition of 0.01 N sodium hydroxide would not be cost-effective.

The effluent from the WTP is transported to the GWETs in a pipeline shared by 4 other extraction wells and then combined in a header with groundwater from 3 additional extraction wells. The natural acid buffering capacity of all of this water was tested to determine if it was adequate to raise the WTP effluent pH, see Table 4.

Table 4. Demonstrated Groundwater Buffering Capacity to Raise Post Fenton's Reagent Wellhead Treatment Plant Effluent

NSSC EW-3 Groundwater	Fenton's Reagent pH Adjustment	Fenton's Reagent Effluent pH	Buffering by 4 Additional Extraction Wells	Buffering by All Extraction Wells
6.67 SU	3.1 SU	2.91 SU	4.8 SU	5.7 SU

By combining the WTP effluent with the all other extracted NSSC groundwater en-route to the GWETS for treatment and discharge, the natural buffering capacity of additional extracted groundwater is utilized resulting in raising the post Fenton's reagent pH to an acceptable level.

3.4 Trial D Optimize Iron Catalyst Dosing Levels for 1,4-Dioxane Remediation

Trial D: Objective was to determine the optimum ferrous or ferric iron dosing level required to provide the catalyst needed by Fenton's reagent to remove 1,4-dioxane from EW-3 groundwater. Iron dosing trials were conducted at pH 3.1 SU with a 22.5 mg/L hydrogen peroxide dose and a 1-hour residence time, see Table 5.

Table 5. Trial D Dependence of 1,4-Dioxane Removal on Iron Dosing Concentration and Iron Species

Iron Species Dosed	**Added Iron Catalyst Level (mg/L)**	**Post Treatment 1,4-dioxane Level (µg/L)**
Fe(II)	30	0
Fe(II)	15	0
Fe(II)	10	0
Fe(II)	2.5	0
Fe(III)	30	0
Fe(III)	15	0
Fe(III)	10	0
Fe(III)	2.5	0
No Iron Dosed	0	0

All iron dosing trials had complete removal of 1,4-dioxane, but most significantly the trial without any iron dosing also had complete 1,4-dioxane removal. The groundwater in the vicinity of MW-124B and EW-3 contains sufficient iron, most likely ferric iron due to the beige color of the groundwater and high oxidation reduction potential, to provide sufficient iron catalyst for Fenton's reagent without the need for additional dosing. The source of this iron is attributed to the aquifer geology of silty sands.

3.5 1,4-Dioxane Wellhead Treatment Plant

The 1,4-dioxane WTP consists of the following components, as illustrated on Figure 6:

1. WTP Spill Containment Features
2. pH Adjustment Tank
3. Hydrochloric acid feed line to pH adjustment tank
4. Fenton's Reagent Reaction Tank
5. Hydrogen peroxide and iron sulfate feed lines to Fenton's Reagent Reaction Tank
6. Discharge pump to convey water from the WTP to the GWETS

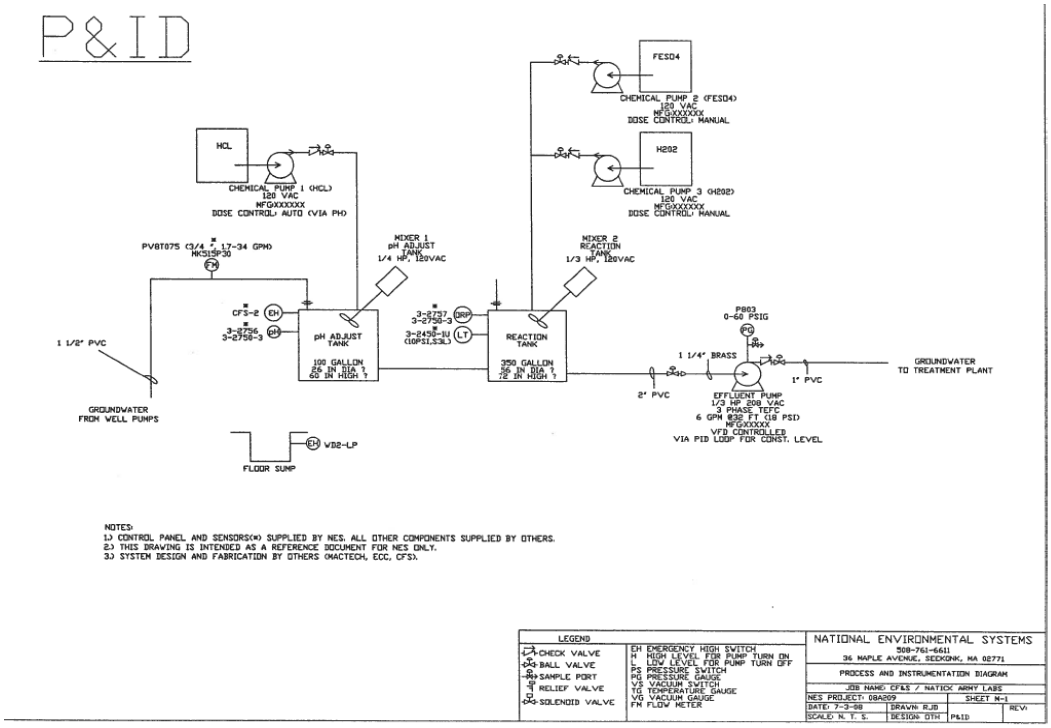

Figure 6. Wellhead Treatment Plant System Components.

3.5.1 1,4-Dioxane Wellhead Treatment Plant Spill Containment Features

The 1,4-dioxane WTP building was constructed to provide secondary spill containment in the event of a plumbing or component leakage and for weather protection. The WTP is housed in a wooden shed equipped with two heaters and a corrosion-resistant exhaust fan. Drums of chemicals are stored on polyethylene spill pallets. The pH Adjustment Tank and Fenton's Reagent Reaction Tank are placed within a polyethylene spill containment system, and the floor of the shed is lined with rubber matting. There is a floor sump, within the spill containment system for the pH Adjustment Tank and Fenton's Reagent Reaction Tank, equipped with a high water level indicator. If the high water level indicator is activated, the WTP will shut down and the system's telemetry module telephones the on-call WTP operator for notification.

3.5.2 pH Adjustment Tank

Combined groundwater pumped from extraction wells EW-2, EW-3, and EW-4 enters the WTP and is directed to a 100-gallon polyethylene pH Adjustment Tank, where HCl is dosed into the tank via a chemical metering pump. Flow entering the pH Adjustment Tank is monitored by a paddle-wheel flow sensor. When flow

is less than 1-gpm, a low-flow alarm is triggered and the WTP is shut down. A pH probe mounted in the pH Adjustment Tank controls the amount of HCl added by the metering pump in order to maintain a pH of approximately 3.5. Contents of the tank are mixed with a clamp mount mixer. The pH Adjustment Tank has approximately a 20-minute retention time, and it ensures a consistent flow rate and water quality to the Fenton's Reagent Reaction Tank. Water flows via a gravity overflow to the Fenton's Reagent Reaction Tank.

3.5.3 Hydrochloric Acid Feed Line to pH Adjustment Tank

A chemical metering pump feeds HCl from a 55-gallon drum to the pH Adjustment Tank. The speed of the pump is controlled by a pH sensor in the pH Adjustment Tank. HCl is transferred and discharged through low-density polyethylene (LDPE) tubing, which is suspended above the pH Adjustment Tank liquid level.

3.5.3 Fenton's Reagent Reaction Tank

Water in the 350-gallon Fenton's Reagent Reaction Tank is mixed via clamp mount mixer with hydrogen peroxide and, if necessary, iron sulfate can be dosed into this tank. Hydrogen peroxide is metered into the Fenton's Reagent Reaction Tank at a constant rate of 0.55 gpd via a variable speed chemical pump. An oxidation reduction potential (ORP) sensor continuously records tank ORP levels. High-water level and low-water level sensors will trigger alarms and WTP shut-down if the water level within the tank reaches a high water level. The 350-gallon Fenton's Reagent Reaction Tank provides a design retention time of approximately 60 minutes.

3.5.4 Hydrogen Peroxide and Iron Sulfate Feed Lines to the Fenton's Reagent Reaction Tank

Since start up of the WTP, only hydrogen peroxide has been dosed to the Fenton's Reagent Reaction Tank, via a variable speed chemical pump directly from the H_2O_2 chemical drum through LDPE tubing. Dose control is manual, and the pump is set at the lowest possible setting, which achieves a dosing rate of approximately 0.55 gpd. The discharge from the tubing is suspended above the liquid level in the Fenton's Reagent Reaction Tank.

3.5.5 Wellhead Treatment Plant Discharge

After treatment, water is pumped from the Fenton's Reagent Reaction Tank via a 3-phase effluent pump to a pipeline leading from the Buildings 63, 2, and 45 AOC

to the GWETS. The WTP effluent is controlled by the water level sensor in the Fenton's Reagent Reaction Tank.

The WTP effluent en-route to the GWETS is combined with groundwater from other extraction wells (not treated for or containing 1,4-dioxane), and the combined flow passes through an AS and GAC prior to discharge to the NSSC stormwater sewer.

3.6 1,4-Dioxane Wellhead Treatment Plant Operational Performance

The results of treatment of 1,4-dioxane by the WTP using Fenton's reagent are shown in Figure 7. The 1,4-dioxane influent concentrations to the WTP have decreased from 7.2 µg/L on September 9, 2008, to less than 1 µg/L on September 2, 2009. The WTP effluent has been consistently less than the Massachusetts Department of Environmental Protection drinking water goal of 3 µg/L and typically non-detect (<0.18 µg/L method detection limit). The typical operational parameters are shown Table 6.

Table 6. Wellhead Treatment Plant Design Operational Parameters

H_2O_2 Dose Rate	**Average H_2O_2 Level**	**Iron Dose Rate**	**Acid Dose Rate**	**pH**	**Retention Time**	**Base Dose Rate**	**WTP H_2O_2 Effluent (mg/L)**	**GWETS H_2O_2 Effluent (mg/L)**
0.55 gpd	19.1 mg/L	0 gpd	3.17 gpd	3.5	30 min	0 gpd	1.0	0.0

4. CONCLUSION

Ex-situ well-head treatment using Fenton's reagent been successfully removing 1,4-dioxane and TCE from contaminated groundwater during the last 1.5 years of operation. 1,4-dioxane influent levels of up to 8 µg/L have been reduced to levels below the MCP criteria (3 µg/L) and usually to non-detect (<0.18 µg/L) levels. The well-head treatment plant has the demonstrated capacity to treat influent 1,4-dioxane levels of 35 µg/L, and this unit with minimal changing of hydrogen peroxide dosing rates could treat influent with higher 1,4-dioxane levels and higher flow rates.

Iron and suspended materials, which may be detrimental to other treatment processes, are used here to great advantage, as ambient iron present in the site groundwater is used as the iron catalyst needed for Fenton's reagent. The low pH of the Wellhead Treatment Plant effluent is raised by the buffering capacity of the

untreated GWETs influent water combined with it en-route to the existing GWETs. Both of these adaptations of Fenton's reagent to NSSC conditions have resulted in significant economy in plant operations.

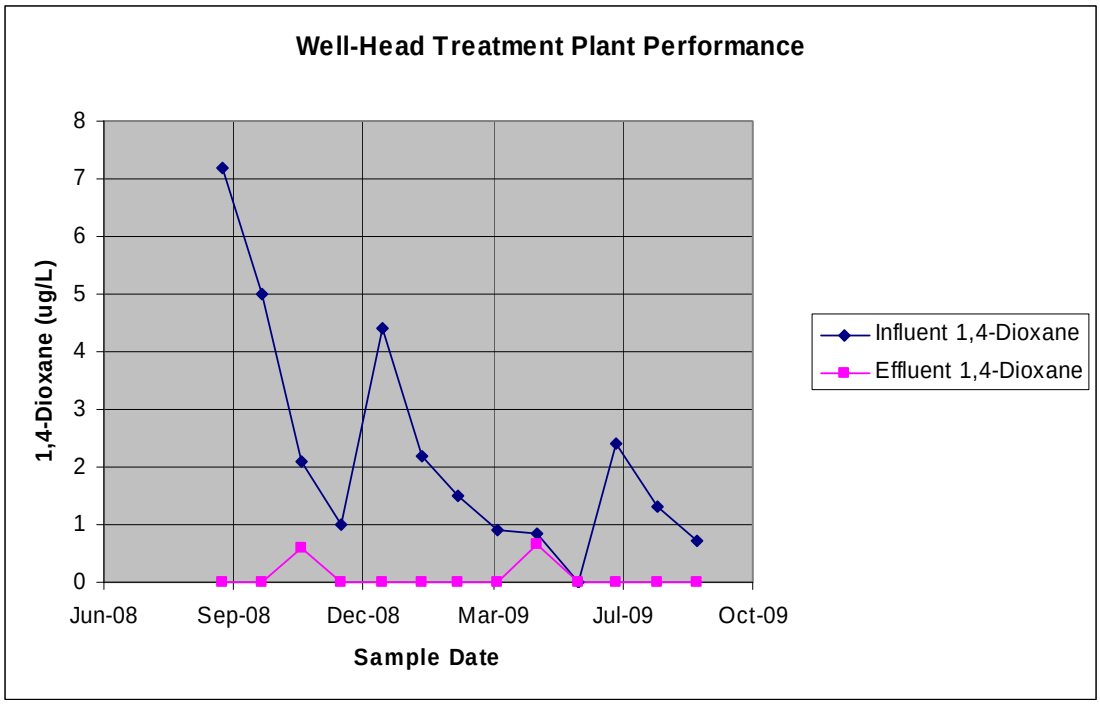

Figure 7. Wellhead Treatment Plant influent and effluent 1,4-dioxane levels since the plant start up.

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Chapter 18

REMOVAL OF PERCHLOROETHYLENE WITHIN A SILT CONFINING LAYER USING HYDROGEN RELEASE COMPOUND

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ABSTRACT

The Site is a former dry cleaning operation where a release of perchloroethylene (PCE) to soil and groundwater had occurred. Hydrogen Release Compound® (HRC) is being used for source control to mitigate vapor intrusion to the existing building. The Site is located in the Connecticut River basin with PCE up to 250 mg/L in perched groundwater above a silt-layer aquitard. Site risk is driven by the soil vapor intrusion pathway into the commercial building. Soil vapor extraction was implemented to mitigate vapor intrusion, with no appreciable change in the perched groundwater conditions and rapid rebound of PCE in soil gas to pre-treatment levels in four months. Our evaluation of soil data following multiple HRC applications over an 8-year period into the perched groundwater on top of a Connecticut River basin silt deposit finds that treatment in the sandy unit above the aquitard achieved significant reduction of PCE in the silt layer below. This discovery changed the project Conceptual Site Model and led to further evaluation of the source of PCE feeding into soil gas. With decreased groundwater concentrations of PCE but persistent soil gas concentrations, Membrane Interface Probe (MIP) work was done to further assess the extent of additional area within the perched groundwater that required treatment. The results indicated that the extent of significant concentrations of PCE was in a peripheral area around the initial treatment zones. Following the MIP results, additional in-situ HRC treatment in the perched aquifer over a broader area than previous injections was implemented with the intent of removing a significant mass of PCE. As we expected, there was a PCE source in the silt layer below the

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treatment area. Subsequent data show further decreases in PCE concentrations measured in perched groundwater and soil gas.

Keywords: vapor intrusion, soil, silt, aquitard, perchloroethylene, PCE, tetrachloroethylene, Hydrogen Release Compound®, HRC, in-situ, Membrane Interface Probe, MIP.

1. INTRODUCTION

The Site is the former location of a dry cleaning establishment that operated at the property from about 1958 to 1965. A release to soil and groundwater involving tetrachloroethylene (a.k.a. perchloroethylene or PCE) was discovered in 1989. The Site has since been subject to ongoing assessment, and implementation of a remedy involving soil vapor extraction (SVE) of soil gas that began in 1997. Additional remedial actions include excavation and off-Site disposal of approximately 45 tons of impacted soil and installation of a vapor-barrier membrane that was applied to the ground prior to installation of the concrete slab during reconstruction activities. Application of a liquid-based vapor sealant that utilized a reactive catalyst resulted in the formation of a pliable membrane that was able to seal utility penetrations into the building. The use of this technology allowed for the mitigation of the primary sources of subsurface vapor intrusion to buildings, cracks in the floor and utility penetrations.

The Connecticut River is located approximately 400 feet east of the Site, flowing in a southeast direction in the vicinity of the Site. It is not used as a drinking water resource. The Site has a perched layer of groundwater in a sand matrix over an aquitard of silt and clay. HRC was effective in reducing PCE concentrations in this layer. However, although the original spill strongly impacted this perched layer of groundwater, Membrane Interface Probe (MIP) results confirm that higher concentrations of PCE are directly on top of and within the silt layer in the area around the initial treatment zone. This new discovery was the cause of small quantities of PCE continually coming up from this reserve by diffusion. Although the PCE passes through the groundwater to reach soil gas, the significant pathway for possible risk posed to humans is through the soil gas rather than in the groundwater because there is no consumption or use of groundwater at the Site. Operating the SVE system controls the PCE in the soil gas and is still necessary, but does little to change the diffusion of PCE from the silt layer. Past injections of HRC have been completed in the perched groundwater zone and have been effective in reducing groundwater concentrations. HRC also appears to have decreased concentrations in the underlying silt layer even though injections were made at a shallower depth.

Additional contaminant mass reduction is expected with injection of more HRC over a larger area, resulting in source control in the periphery.

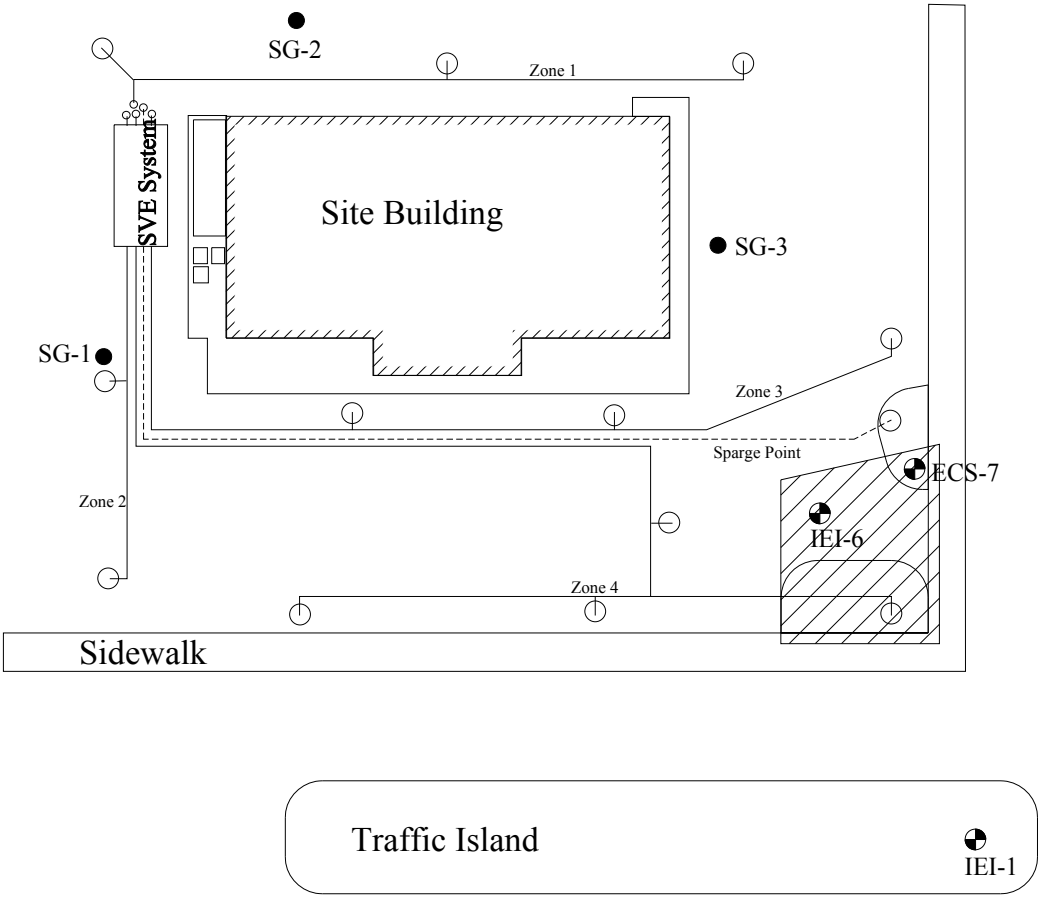

Figure 1. Site Map showing soil gas sample locations, groundwater monitoring wells, soil borings, and SVE System components. The area of the two initial HRC applications is illustrated by the hatched box.

2. MATERIALS AND METHODS

2.1 Hydrogen Release Compound® Application

Injection of over 2,000 pounds of Hydrogen Release Compound® (HRC) was conducted on three occasions over an 8-year period at 60 locations in an area

covering approximately 3,000 square feet. HRC was heated for lower viscosity and pumped through a grout pump for injection to target locations. The HRC was injected into the subsurface using four direct-push Geoprobe® units working simultaneously.

Hollow stainless steel rods were advanced to a depth of 15 feet below ground surface (bgs), which penetrated the surface of the silt layer underlying the Site. The HRC was applied through the end of the probe tip while the rod was retracted to a final depth of 5 feet bgs. Thirty pounds of HRC was applied at each location over a vertical profile of 10 linear feet.

2.2 Membrane Interface Probe

The Membrane Interface Probe (MIP) is a technology we used to address the question of PCE distribution in the subsurface. It provided relative contaminant concentrations with near continuous vertical resolution. Its high productivity also had an effect on horizontal resolution, in that it allowed for more assessment locations than could be obtained by traditional soil sampling.

In conducting MIP work, a heated probe was driven into the ground with a direct-push Geoprobe® unit. The probe has a resistive heating element to vaporize volatile compounds coupled with a membrane. Contaminant vapors diffuse through the membrane and enter a sweep gas stream which carries them to the surface where they are fed to an electron capture detector (ECD) and a photoionization detector (PID). At low concentrations the ECD has good response to chlorinated compounds (e.g. PCE), and the PID identifies organics in general. In this case, PCE concentrations tended to exceed the scale of the ECD, so the PID data was more useful for identifying the locations with the highest PCE concentrations.

Finally, the gas stream can be analyzed using a gas chromatograph (GC). A solid phase extraction needle captures contaminants from the stream and can be injected into a GC. The GC analysis provides accurate relative concentrations of different contaminants, but is not very accurate when total concentrations are compared to groundwater samples analyzed in the laboratory. For this reason, the data collected is not useful for risk characterization. The data is more suited to characterization of subsurface conditions.

The probe also had a conductivity sensor which gives some vague indication as to the presence of water and hydraulic conductivity on a near continuous vertical profile. These three parameters (contaminant concentration, groundwater, and hydraulic conductivity) are each shown on the same page for a given assessment location.

3. RESULTS AND DISCUSSION

Following two HRC applications into the perched groundwater table (less than 15 feet bgs), decreases in PCE concentrations in groundwater were observed. However, PCE concentrations in soil gas reached equilibrium to pre-treatment levels. This supported our conceptual site model that PCE from this region was diffusing up through the perched groundwater, causing the soil gas levels that were observed during SVE system shutdown periods. The MIP data also indicate that the PCE impact area may have been larger than the HRC application zones.

Membrane Interface Probe work to determine the spatial distribution of chlorinated compounds identified PCE in the silt layer below 15' bgs and above 30' bgs. An important finding was that the treatment of the shallow zone penetrated the silt confining silt layer.

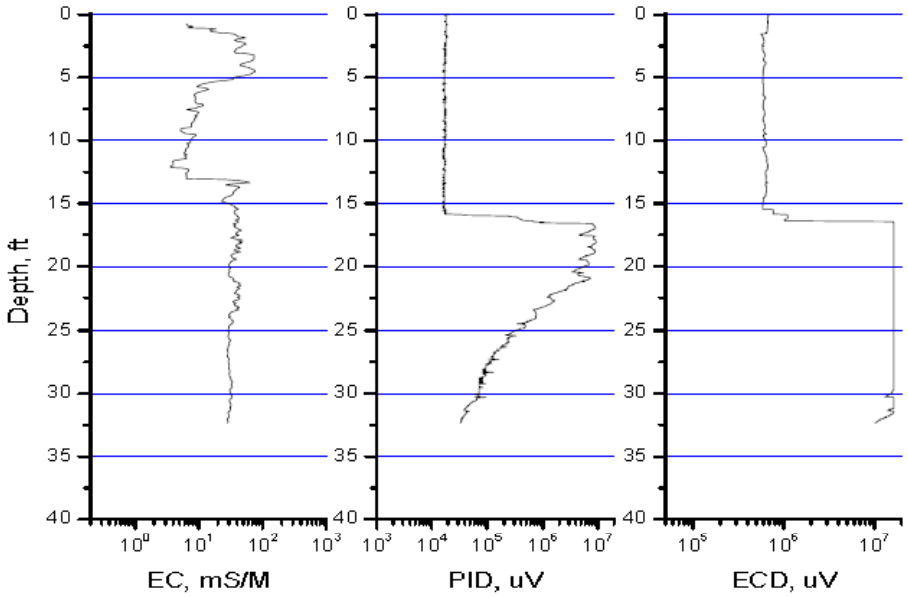

Figure 2. MIP results at IEI-103 assessment location (see Figure 4). The graphical representation illustrates increased PCE concentrations in the silt layer at approximately 15 feet below ground surface.

The data from nine MIP assessment locations were used to create a cross-section of the release area to illustrate the profile of PCE in the subsurface.

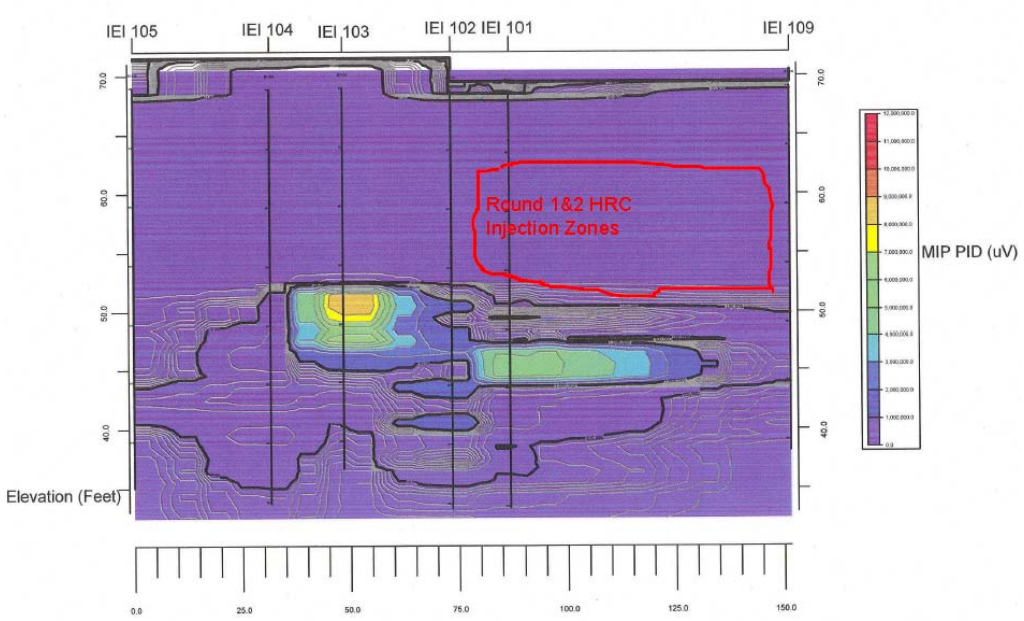

Figure 3. Cross-section of MIP results illustrating the treatment of PCE in the silt layer following an HRC application to the perched aquifer. The MIP data identify an area of higher PCE concentrations in the silt layer outside of the initial application areas.

Our evaluation of data following the second HRC injection indicated that decreasing PCE concentrations were measured in both soil gas and perched groundwater in the HRC application area compared to results collected prior to the first HRC injection. The ratio of TCE and DCE (PCE break-down products) to the amount of PCE in the source area increased following the second HRC application suggesting degradation, but subsequently dropped off suggesting that the HRC had been expended. Also, field screening of shallow monitoring wells in the source area for dissolved oxygen (DO), oxygen reduction potential (ORP), sulfate, and nitrate indicate that the HRC injected was likely expended. Groundwater results indicate that the HRC remedy was generally successful at reducing groundwater concentrations of PCE in the application area.

The results indicate that PCE is present in the silt layer and the extent of significant concentrations of PCE in the silt layer is broader in area than the initial HRC injection zone. IEI-101 and IEI-102 are the MIP points in the HRC injection area. We note the results in IEI-103 and IEI-108 were higher than in IEI-101 and IEI-102. Although a MIP baseline was not conducted before the HRC injection, we suspect that prior to HRC treatment, these concentrations would have been reversed, and that HRC injection into the perched groundwater caused PCE removal in the top part of the silt layer around IEI-101 and IEI-102.

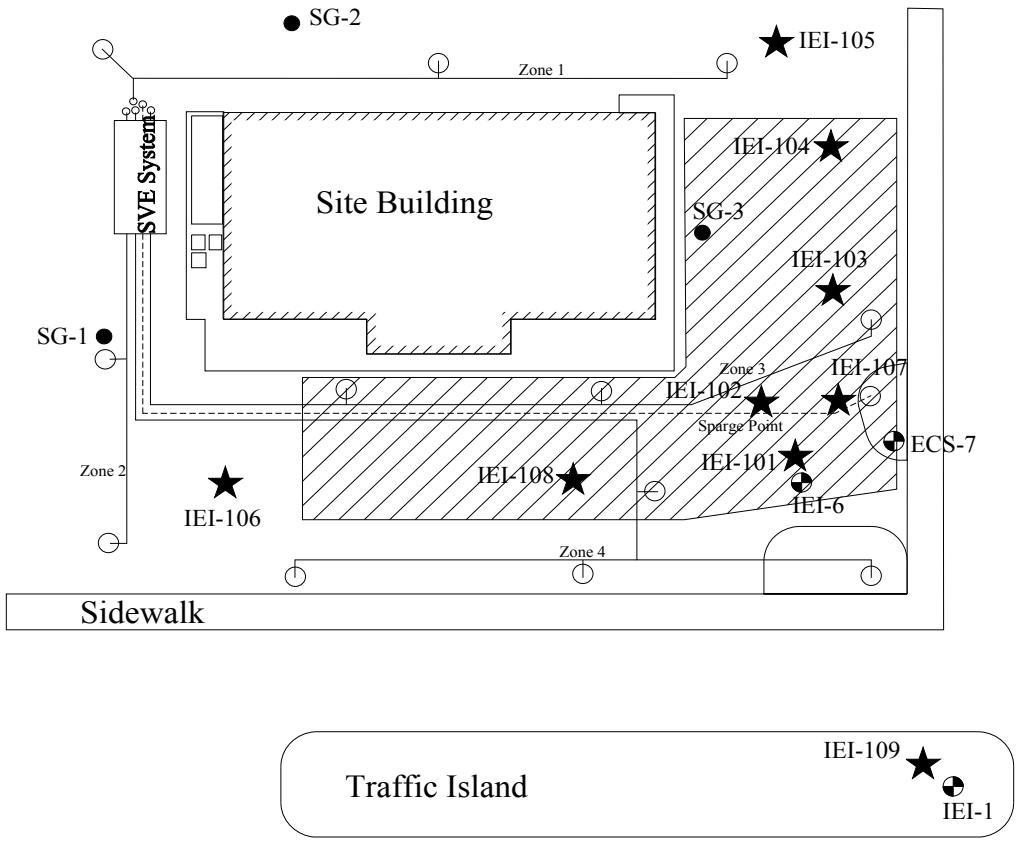

Figure 4. MIP assessment locations (star symbols) and HRC application zone (hatched area).

Table 1. PCE concentrations (milligrams per liter) in groundwater prior to 2007 full-scale HRC application ("Max PCE Since 2001") compared to current PCE concentrations ("Post-HRC").

Monitoring Well	Max PCE Since 2001	Post-HRC
IEI-1	41.8	17
IEI-6	22.4	1.8
ECS-7	40.6	0.03

Table 2. PCE concentrations (parts per billion by volume) in Soil Gas prior to 2007 full-scale HRC application ("Max PCE Since 2003") compared to current PCE concentrations ("Post-HRC").

Soil Gas Sample Port	Max PCE Since 2003	Post-HRC
SG-1	320	1.2
SG-2	380	11
SG-3	2,000	59

Operating the SVE system controls PCE in the soil gas and is still necessary, but does little to change the diffusion of PCE from the silt layer. Monitoring of environmental media is ongoing and additional contaminant mass reduction is expected following the recent application of HRC over a larger area.

4. CONCLUSION

Vapor intrusion was controlled by installation of a passive vapor barrier under the on-Site building and operation of a soil vapor extraction (SVE) system. Application of HRC to the subsurface was done to treat the source of the contamination, with the goal of turning off the SVE system. Following two HRC applications into the perched groundwater table (less than 15 feet bgs), decreases in PCE concentrations in groundwater were observed. However, PCE concentrations in soil gas rapidly reached equilibrium to pre-treatment levels. The MIP data indicated that the PCE impact area may have been larger than the HRC application zones. Another important finding was that the treatment of the shallow zone penetrated the silt confining silt layer. Traditional assessment using monitoring wells would not have offered this level of assessment, illustrating that MIP technology is a useful and cost effective tool.

Our evaluation of data following a subsequent HRC injection indicated that decreasing PCE concentrations were measured in both soil gas and perched groundwater in the HRC application area compared to results collected prior to the first HRC injection. The ratio of TCE and DCE (PCE break-down products) to the amount of PCE in the source area increased following the second HRC application suggesting degradation, but subsequently dropped off suggesting that the HRC had been expended.

Further analysis of the MIP results indicated that PCE was present in the silt layer and the extent of significant concentrations of PCE in the silt layer is broader in area than the initial HRC injection zone. This information was used to

design a Site-wide in-situ remediation to address PCE both vertically and laterally in the subsurface. Of particular interest was the ability of HRC to treat PCE in the confining silt layer when it was applied into the overlying perched aquifer. PCE in soil gas will be monitored to evaluate the impact of the remedy on the source area. We expect there would be no need for an active SVE system if there is a slow rebound in soil gas, as the passive vapor membrane would mitigate vapor intrusion to the building.

Chapter 19

NITRATE REMOVAL FROM SYNTHETIC HIGH NITRATE WASTE BY A DENITRIFYING BACTERIUM

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ABSTRACT

The work aims towards isolating organisms capable of treating high nitrate wastewater and optimizing the process for maximum denitrification rate. A denitrifying bacterium strain, isolated from the wastewater of a fertilizer denitrification plant (FDP), was screened from a total of 160 isolated cultures based on its high nitrate removal efficiency. Biochemical tests and 16S rDNA sequence analysis showed the bacterium genus to be *Pseudomonas* and close to *aeruginosa* species. The culture on acclimatization to high strength nitrate waste [10000 ppm NO_3 (2258 ppm NO_3-N)] in a sequence batch reactor, showed complete degradation in a time period of just 1.75 h. The specific nitrate and nitrite degradation rate of the process using the acclimatized culture was further increased by 54.4 % and 15 % respectively on optimizing the process using orthogonal array method. The applicability of this isolate for high rate denitrification process was investigated in a 4 L reactor and the two important enzymes involved in the first two steps of denitrification process, NaR and NiR were assayed. This provided an *invitro* index of the ability of the cells to reduce nitrate and nitrite. The reactor was run successfully for 2 months without any change in the activity.

Keywords**:** Denitrification; Sequence Batch Reactor; Orthogonal array; NaR; NiR

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1. INTRODUCTION

The high nitrogen level in wastewater has become a growing concern, which has increased the necessity to develop efficient N-removal techniques. High nitrate wastes (> 1000 ppm NO_3-N) are usually generated by fertilizer, metal finishing and nuclear industry (Glass and Silverstein, 1998; Glass and Silverstein, 1999) whose treatment has become a challenge for these industries. When such wastewaters are released into water streams, they cause various ill effects like methehemoglobinemia in infants and is also suspected to cause cancer (Forman et al., 1985). In USA the permissible level for nitrate in drinking water is 10 ppm NO_3-N (USEPA, 1987). Biological denitrification which is the reduction of oxidized nitrogen compounds like nitrate or nitrite to gaseous nitrogen compounds is the most important and widely used method to treat nitrate wastes as it enables the transformation of nitrogen compounds into harmless nitrogen gas. This process is performed by various chemorganotrophic, lithoautotrophic and phototrophic bacteria and some fungi (Shoun and Tanimoto, 1991; Zumft, 1997) especially under oxygen reduced or anoxic conditions (Focht and Chang, 1975). Denitrifiers can be naturally found in sediments, surface waters, soils, as well as in municipal and industrial wastes. The universality and common distribution of denitrifiers is related to their species complexity and different physiological requirements.

Focusing on biological nitrate removal, sequence batch reactor (SBR) is described as a very effective alternative to conventional activated sludge systems. SBR technology is based on the assumption that the microorganisms are exposed periodically to defined process conditions and this is effectively achieved in a fed batch system in which exposure time, frequency of exposure and amplitude of the respective concentration can be set independently of any inflow condition (Wilderer et al., 2001). From the process-engineering point of view, the composition and the metabolic properties of the microbial composition in the SBR system comes to a steady state by the enforcement of controlled short-term unsteady state conditions.

Biological denitrification of wastewater is usually a slow process and lasts several days. Efforts have been made to increase the nitrate removal rate. Adapted bacterial cultures from various industrial wastewater treatment plants have been proved to be very useful and observation suggests that cells need to be adapted to nitrate for full denitrifying ability (Hiraishi et al., 1995). Along with adaptation of the cultures, optimization of pH, temperature and carbon: nitrogen may also enable high rate of denitrification (Glass and Silvertsein, 1998; Nair et al., 2007).

Thus, if optimal conditions for denitrification processes can be defined, isolated cultures may be employed for N-waste removal in controlled conditions.

So far studies on denitrification of high nitrate waste using activated sludge (Glass and Silvertsein, 1998; Foglar et al., 2005; Dhamole et al., 2007; Nair et al., 2007) have been carried out, however not many studies have been carried out on treatment of high nitrate wastes (>7500 ppm NO_3) using pure cultures. The aim of this study was to determine the denitrification activity of a bacterium RS152, isolated from a FDP wastewater and its efficiency to denitrify high nitrate waste (10000 ppm NO_3). The identification of the strain was carried out using the ID 32 GN system (BioMerieux) and further confirmed using the 16S rDNA sequencing method. The studies were extended further to optimize the denitrification process for maximum denitrification rate using the orthogonal array method and by testing the isolate in bench scale experiments to establish optimal operational conditions for the treatment of wastewater. Simultaneously, the activity of the two important enzymes involved in the first two steps of denitrification process, nitrate reductase (NaR) and nitrite reductase (NiR) were also evaluated.

2. MATERIALS AND METHODS

2.1 Materials

All chemicals were purchased from M/S Hi-Media Limited, Mumbai, India and were of the highest purity available.

2.2 Isolation of denitrifiers

The arbitrarily named strain RS152 was isolated from the wastewater sample collected from a fertilizer industry. Soil and sludge samples were enriched in succinate nitrate medium (Disodium succinate hexahydrate 11 g; $NaNO_3$ 100 g; peptone 4 g in 1000 ml of deionized water, pH 7.2). The medium composition was modified by increasing the nitrate concentration, as our aim was to find an isolate capable of denitrifying high nitrate waste. Sludge sample (one ml) was inoculated in the media and incubated for 1 week under anaerobic conditions at 30^oC (Gamble et al., 1997). Loopful from the above enriched media was then directly inoculated into high concentration nitrate broth (100 g $NaNO_3$ l^{-1}) incubated for 1 week under anaerobic conditions at 30^oC and the tubes that showed growth were plated onto the same nitrate concentration agar plates. They were incubated anaerobically in anaerobic jars containing gas paks at 30^oC for 48 hr. Colonies of bacteria showing different morphological features were picked and isolated in pure culture.

2.3 Screening of denitrifiers

Different screening criteria's were used to categorize the isolated cultures and obtain the desired strain. The initial categorization was based on the study of their cultural characteristics. Cultures with similar cultural characteristics were grouped together and only one of the lot was selected. These cultures were then screened using the second categorization studies, which was based on their natural capabilities (without adaptation) to degrade nitrate. For degradation studies synthetic waste was used which had the following composition, Na_2HPO_4 7 g l^{-1}, K_2HPO_4 1.5 g l^{-1}, $MgSO_4$ 0.1 g l^{-1}, NaCl 0.3g l^{-1} and trace element solution 2ml l^{-1}. Trace element solution consisted of $CaCl_2$ 5.54 g l^{-1}, $FeSO_4$ $7H_2O$ 5.0 g l^{-1}, $MnCl_2$. H_2O 5.06 1 g l^{-1}, $ZnSO_4$ $7H_2O$ 2.2 g l^{-1}, $CuSO_4$ $5H_2O$ 1.51 g l^{-1}, $CoCl_2$ H_2O 1.61 g l^{-1}, EDTA 50 g l^{-1}, $(NH_4)_6MO_7O_{24}$ H_2O 1.1 g l^{-1} (Dhamole et al., 2007). Sodium acetate was used as a carbon source and sodium nitrate was used as nitrogen source. For screening out isolates with natural degradation capacity a nitrate concentration of 112 ppm NO_3-N (500 ppm NO_3) was used. The isolates which showed complete degradation at a lower time period were selected and were further screened. In this study the nitrate as well as the nitrite and ammonia levels were estimated. This screening was important, as a true denitrifier is the one, which doesn't accumulate nitrite or ammonia (Tiedge, 1994). The isolates which did not show any accumulation of NO_2 and NH_3 were screened out and were compared amongst each other to pick out the best desired isolate. This study was carried out in 250 ml flasks with 150 ml synthetic waste. The nitrate source used was sodium nitrate (1129 ppm NO_3-N) and carbon source was sodium acetate. 3 gL^{-1} MLSS culture was inoculated into the flasks and incubated at 30^oC under anaerobic conditions. Samples were withdrawn at regular time intervals from each of the flasks and the nitrate, nitrite and ammonia content was estimated.

2.4 Identification of isolated bacterium

Identification of the denitrifying bacteria was performed according to the ID 32 GN system (BioMerieux) for identification of nonfermenting rods. Identification was further confirmed using 16S rDNA sequencing of PCR products of extracted genomic DNA (Oyaizu, 1992). The bacterial DNA was amplified by polymerase chain reaction using thermal cycler (Eppendorf., Hamburg, Germany). The 50 µl reaction mixture contained the following compounds: 2 µl DNA template, 30 pmol each of the primers 5'-AAG GAG GTG ATC CAG CCG CA- 3', and 5'-AGA GTT TGA TCC TGG CTC AG- 3', 3 µl dNTP mix (10 mM), 4 µl of 10x PCR buffer (100 mM Tris (pH 9.0), 15 mM $MgCl_2$, 500 mM KCl), 1U of Taq polymerase. The amplification program of the PCR consisted of the following steps: denaturing for 1 min at 94^oC, annealing for 1 min at 56^oC and elongation

for 2 min at 72^{o}C, followed by a final synthesis step of 5 min at 72^{o}C. The PCR products (10µl) were analyzed on 1.5 % agarose gels and visualized by UV excitation after staining with ethidium bromide (0.5 mgL^{-1}). The PCR products were subsequently purified using Genei Quick PCR Purification kit. Nucleotide sequences were obtained by a sequencer (ABI PRISM model 377, Applied Biosystems, Foster city, CA). The partial 16S rDNA sequences (500- 800 bp) were compared with known sequences of 16S rDNA in the National Center for Biotechnology Information (NCBI) Genbank by using the Basic Local Alignment Search Tool (BLAST) algorithm (Aenson et al., 1999). The partial sequence of the 16S rRNA gene of the strain RS152 (822bp) was aligned with the sequences of other organisms described in the Fig.3, using CLUSTAL W (Thompson et al., 1994). Using the Kimura 2-parameter model developed by Kimura (1980), the pair wise evolutionary distances were calculated. The phylogenic tree was constructed using a tree-making algorithm (Neighbour Joining). This was carried out using the TREECON 3.1 program (Van de Peer and De Wachter, 1994). All the materials required for above studies were obtained from Bangalore Genei, Bangalore, India.

2.5 Acclimatization of isolate to high strength nitrate waste

To acclimatize the isolate RS152 to high strength nitrate concentration by a stepwise acclimatization procedure to increasing nitrate concentration was carried out in a SBR (Dhamole et al., 2007). A SBR was fabricated in the laboratory from borosil glass material having a total working volume of 1 L capacity. The reactor was operated in sequencing batch mode at a temperature of 37^{o}C ± 2^{o}C under anoxic conditions. Anoxic conditions were maintained by purging nitrogen gas from one of the pipes into the medium for 5 min and sealing the mouth of the reactor with parafilm. The total cycle period of 24 h consisting of 1.5 h of withdrawal and centrifugation phase, 0.5 h of filling phase and 22 h of reaction phase was employed throughout. All of these processes were carried out under aseptic conditions. The medium was under circulation using a magnetic stirrer. Reaction was initially started by inoculating 3 gL^{-1} MLSS of pure culture (obtained by growing in enrichment media) into 1 L synthetic nitrate waste (1125 mgL^{-1} NO_3- N). The C: N mole ratio was 2:1. After 24 h of reaction period, 500 ml of the media was withdrawn and centrifuged. The biomass was inoculated back into the reactor and 500 ml of sterile synthetic nitrate waste was filled into the reactor to make the total volume of 1 L. Nitrate, nitrite and ammonia of the decanted fluid were analyzed everyday. The isolate biomass was acclimatized to each nitrate concentration (224 ppm NO_3-N, 1128 ppm NO_3-N and 2258 ppm NO_3-N) for 15 days each.

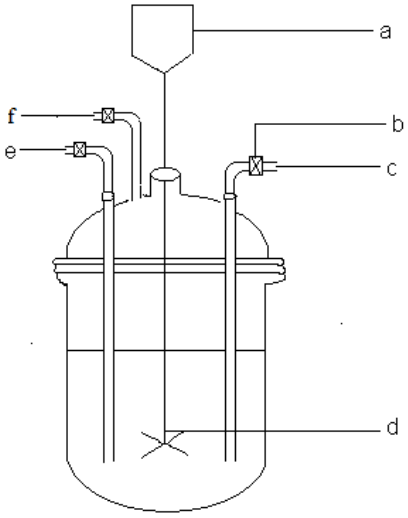

Fig. 1 A

Fig.1 B

Figure 1. 4 L stirred tank reactor. A: Schematic representation of the reactor a. Overhead agitator. b. Valve. c. Inlet for purging sterile N_2 gas. d. Impellar. e. Sampling port. f. vent to remove air during purging of N_2 gas. B: Photograph of the working bioreactor. Denitrification of 1129 ppm NO_3-N synthetic nitrate waste by the isolate was carried out for a period of 1 month.

2.6 Optimization of denitrification process

Using "MINITAB 13.30" software, the L25 (5^3) orthogonal array design was developed and analyzed. The design of L25 (5^3) orthogonal array and the different parameters (pH, temperature and carbon: nitrogen) that were optimized in the present study has been shown in Table 1. A 4 L reactor with 2 L working volume at a concentration of 1129 ppm NO_3-N and an acclimatized biomass concentration of 3 gL^{-1} MLSS was used to carry out all the 25 runs. The reactor was run under aseptic conditions and anoxic conditions were provided by purging sterile nitrogen gas from one of the vents for 5 min and sealing the mouth of the reactor with parafilm. The medium was kept under constant agitation using a stirrer at 140 rpm.

2.7 Application of the isolate in a bioreactor

A stirred tank reactor of 4 L capacity was fabricated in the laboratory from Borosil glass material. A schematic representation of the SBR is given in the Fig.1. The acclimatized biomass (3 gL^{-1} MLSS) was inoculated in the reactor. A headspace of 2 L was provided to prevent any solid loss generally caused because of foaming. An overhead stirrer with four-blade glass propeller was used for mixing. The stirrer speed was kept high (200 ± 50 rpm) enough to maintain a

Table 1. L25 (5^3) orthogonal array design for denitrification process using isolate RS152

(A) Temperature	(B) Carbon: Nitrogen	(C) pH	Total degradation time (min)
1	1	1	95
1	2	2	85
1	3	3	75
1	4	4	80
1	5	5	85
2	1	2	90
2	2	3	70
2	3	4	80
2	4	5	85
2	5	1	85
3	1	3	90
3	2	4	75
3	3	5	80
3	4	1	85
3	5	2	70
4	1	4	95
4	2	5	85
4	3	1	90
4	4	2	75
4	5	3	70
5	1	5	90
5	2	1	85
5	3	2	75
5	4	3	75
5	5	4	90

Level	(A) Temperature	(B) Carbon: Nitrogen	(C) pH
1	Room Temperature	1.90	6.5
2	32°C	2	7.5
3	37°C	2.25	8.5
4	42°C	2.5	9.5
5	47°C	2.75	10.5

homogenous suspension of biomass. Denitrification studies were carried out according to optimized conditions studied above. The reactor was operated as a batch system under anaerobic conditions. Samples were collected at regular time intervals using sterile syringe. These samples were analyzed for nitrate, nitrite, NaR and NiR enzyme.

2.8 Analytical methods

The nitrate and nitrite concentrations in the samples were analyzed using DIONEX Ion chromatograph fitted with an IC Pak anion column AS11 (2 x 250 mm) column. NaOH (12 mM) was used as eluent. Ammonia was estimated using Nesslers method (APHA, 1997). All the samples were centrifuged and filtered before analysis. Dilutions were carried out using deionized water. The NaR and NiR enzyme was assayed according to Kenji et al. (1981). The protein was determined by the Millers method (Miller, 1959). Mixed liquor suspended solids (MLSS) were determined by following standard methods (APHA, 1997). Anaerobic conditions in liquid medium were maintained by purging the medium with N_2 gas and sealing with an airtight rubber cork. Anaerobic conditions in solid medium were provided by incubating the agar plates in anaerobic jars (BBL Gas Pak systems) with gas paks.

2.9 Nucleotide sequence accession numbers

The 16S rRNA gene sequence from pure culture of RS152 has been deposited in the NCBI nucleotide sequence database under accession number DQ361030.

3. RESULTS

3.1 Isolation and screening

To isolate denitrifiers, sludge sample from a fertilizer industry and soil samples were enriched in succinate nitrate broth and the enriched samples were inoculated onto high nitrate concentration agar plates and incubated under anaerobic conditions. About 160 isolates capable of growing in high nitrate (2258 ppm NO_3-N) were obtained. To screen out the desired denitrifier from 160 cultures, their cultural characteristics were studied. 95 isolates having different characteristics were selected. These 95 isolates were brought down to 16 isolates, which were capable of degrading nitrate without accumulation of nitrite or ammonia and were thus termed as true denitrifiers (organisms which utilize nitrite further to produce either NO or N_2O or N_2 gas). From a total of 16 isolates, the numbers were brought down to 4 best isolates, which were capable of degrading about 90 % of 10000 ppm nitrate (2258 ppm NO_3-N). Measurements were made during the anaerobic growth on nitrate to compare the denitrification properties of these four cultures. The results (Fig. 2) clearly indicated that the isolate RS152 degraded both nitrate and nitrite effectively as compared to isolates RS16, RS17 and RS18 with only 4 ppm of residual NO_3-N and 23 ppm NO_2-N which eventually degraded in a period of 105 min. There was no accumulation of ammonia in any

of the cultures showing that denitrification was the route taken by all the isolates. For the isolates, RS16, RS17 and RS18 the residual nitrate were 79.3 ppm NO_3-N, 108 ppm NO_3-N and 121 ppm NO_3-N respectively. Thus the isolate RS152, which was capable of denitrifying high nitrate waste completely at a higher rate, was found to be superior to other isolates.

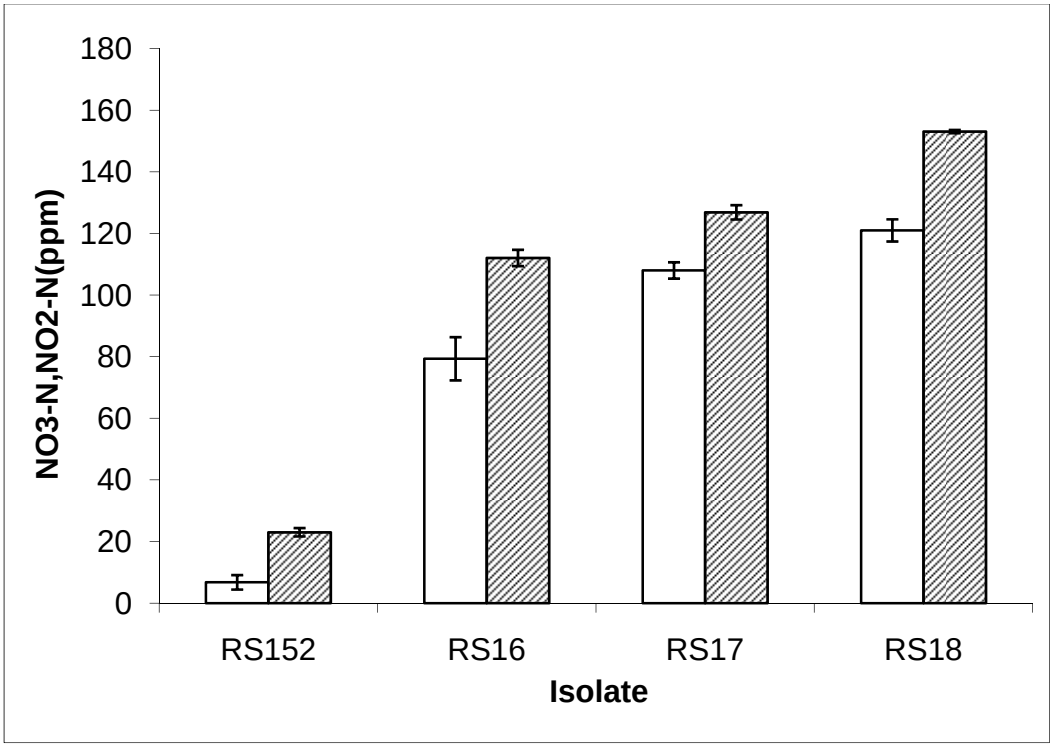

Figure 2. Comparison of the four cultures based on their nitrate degradation capability in 96 h. Medium: Synthetic nitrate waste; Nitrogen: Sodium nitrate (1129 ppm NO_3-N); Carbon: Sodium acetate; C: N: 2:1; Anaerobic condition: Purging of N_2 gas; Working volume: 150 mL; pH: 7; Temperature: 30^{o}C; Agitation: 100 rpm; MLSS: 3 gL^{-1}. Error bars indicate standard deviation of triplicate samples.

3.2 Identification and Biochemical characterization

The results of identification of the strain using the ID 32 GN system are shown in Table 2. The strain RS152 could grow on substrates like, N- Acetylglusosamine, D- Ribose, Itaconic acid, Sodium malonate, Sodium acetate, Lactic acid, L-Alanine, Potassium 5- Ketogluconate, Glygogen, D- Melibiose, L- Fucose, D-Sorbitol, L- Arabinose, Propionic acid, Trisodium citrate, L- Histidine, Potassium 2- Ketogluconate, 3- Hydroxybutryric acid, 4- Hydroxybutyric acid and L-proline. These results when compared with *Pseudomonas aeruginosa* showed 96.7 % identity. Similarly, comparative 16S rDNA gene sequence analysis

showed affiliation of the isolate RS152 to the genus *Pseudomonas* as seen in Figure 3. The strain RS152 showed 100 % similarity to *Pseudomaonas aeruginosa* strain DQ095913.1. Thus the genotypic studies further confirmed that the strain RS152 belonged to genus *Pseudomonas* and strain *aeruginosa*.

Table 2. Phenotypic characteristics of strain RS152 using the ID 32 GN system

Tests	Substrates	Qty (mg/cupule)	RS152 strain
RHA	L-RHAmnose	0.68	ND
NAG	N-Acetyl-Glucosamine	0.68	+
RIB	D-RIBose	0.70	+
INO	INOsitol	0.70	-
SAC	D-SACcharose	0.66	-
MAL	D-MALtose	0.70	-
ITA	ITAconic acid	0.23	+
SUB	SUBeric acid	0.35	-
MNT	SodiumMaloNaTe	1.20	+
ACE	SodiumACEtate	0.55	+
LAT	LacTic acid	0.32	+
ALA	L-ALAnine	0.68	+
5KG	Potassium 5-LetoGluconate	0.90	+
GLYG	GLYcogen	0.64	+
mOBE	3-hydOxyBEnzoic acid	0.23	-
SER	L-SERine	0.80	-
MAN	D-MANitol	0.68	-
GLU	D-GLUcose	0.78	-
SAL	SALicin	0.52	-
MEL	D-MELibiose	0.66	+
FUC	L-FUCose	0.64	+
SOR	D-SORbitol	0.68	+
ARA	L-ARabinose	0.70	+
PROP	PROPionic acid	0.29	+
CAP	CARic acid	0.11	-
VALT	VALeric acid	0.25	-
CIT	TrisodiumCITrate	0.57	ND
HIS	L-HIStidine	0.80	+
2KG	Potassium 2-Ketogluconate	0.98	+
3OBU	3-hydOXYBEnzoic acid	0.30	+
pOBE	4-hydOXYBEnzoic acid	0.23	+
PRO	L-PROline	0.52	+

3.3 Acclimatization studies

To acclimatize the isolate to high nitrate concentrations, the reactor was initially inoculated with 3 gL^{-1} MLSS .The isolate was acclimatized to increasing concentrations of nitrate (224 ppm NO_3-N, 1129 ppm NO_3-N and 2258 ppm NO_3-N) for 15 days each in a stepwise process. This process has been successfully

carried out in our laboratory using sludge (Dhamole et al., 2007; Nair et al., 2007).

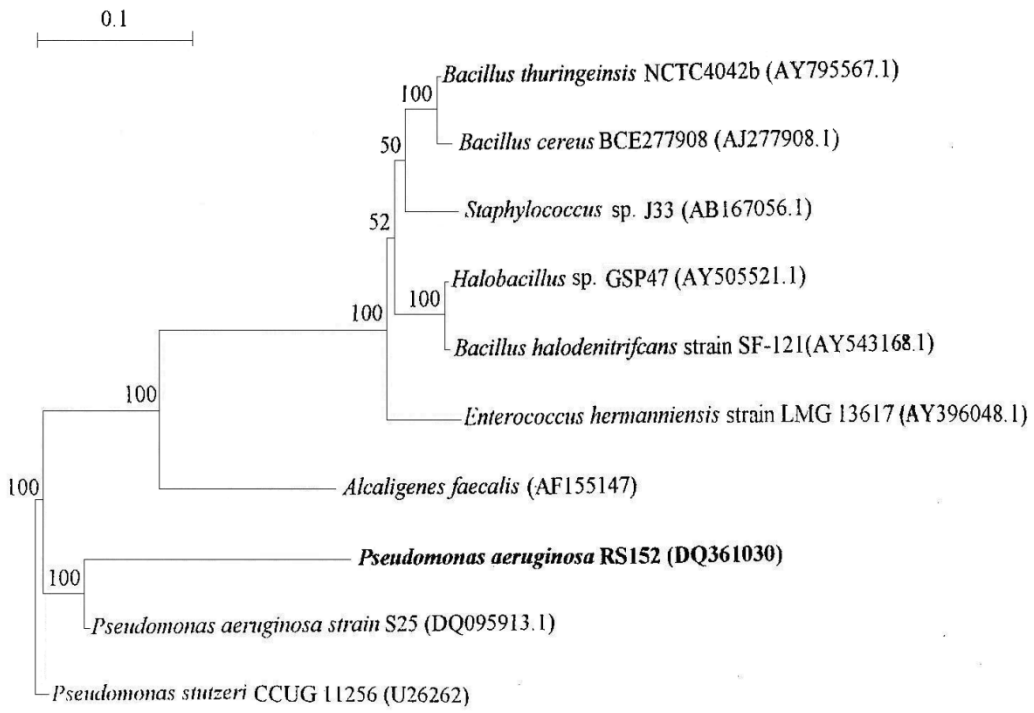

Figure 3. Phylogenic relationships of isolate RS152 and other organisms on the basis of 16S rDNA sequences. Bootstrap values (%) are given at the nodes. Scale bar, 10 inferred nucleotide changes per 100 nucleotides.

In the first stage, the isolate was acclimatized to 224 ppm NO_3-N synthetic nitrate waste for 15 days as described above. The nitrate and the nitrite profile for 224 ppm NO_3-N influent synthetic nitrate waste, which after dilution with the recycled culture and media becomes half, is depicted in Fig. 4. It is seen that 224 ppm NO_3-N synthetic nitrate waste was completely degraded by the isolate in a period of 1 h. Nitrite accumulation was low, because of the low nitrate concentration and high degradation rate of nitrate and nitrite (Dhamole et al., 2007). After a period of 15 days the same biomass was used in the second stage of acclimatization to 1129 ppm NO_3-N synthetic nitrate waste. Here the influent nitrate concentration was increased to 1129 ppm NO_3-N and the acclimatization was carried out in the same manner for another 15 days. Fig. 4 also shows the nitrate and nitrite profile during the degradation of 1129 ppm NO_3-N. Reduction

of entire nitrate was observed in 1.25 h, with a slight increase in build up of nitrite, which eventually got degraded in 1.25 h.

Acclimatization studies were further carried out for 2258 ppm NO_3-N for a period of 15 days using the same biomass. It can be seen from Fig. 4 that the nitrate was degraded completely to nitrite in a period of 1.5 h, with a build up of nitrite, which eventually got degraded in a period of 1.75 h. The reactor was operated for a period of 45 days at different nitrate concentrations and the acclimatized culture was used for optimization and enzymic studies.

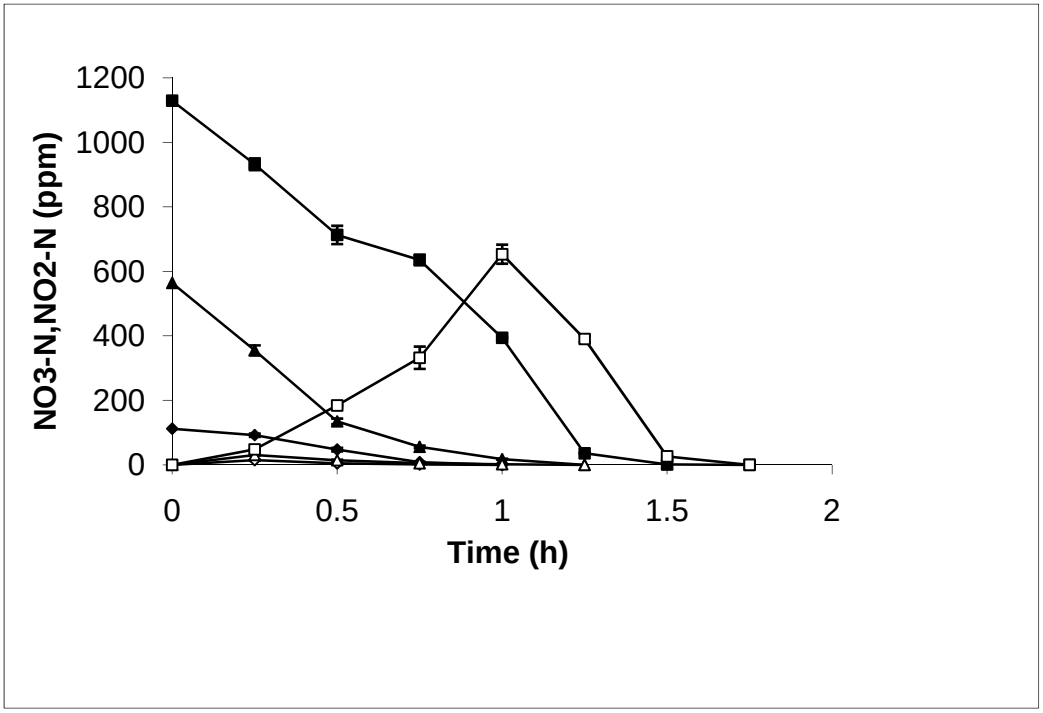

Figure 4. Nitrate and nitrite profile during denitrification of 224 ppm NO_3-N influent synthetic nitrate waste (actual concentration in the reactor = 112 ppm NO_3-N), 1129 ppm NO_3-N influent synthetic nitrate waste (actual concentration in the reactor = 564 ppm NO_3-N) and 2258 ppm NO_3-N influent synthetic nitrate waste (actual concentration in the reactor = 1129 ppm NO_3-N). MLSS for all concentrations = 3 gL^{-1}. Error bars indicate standard deviation of triplicate samples.

3.4 Orthogonal matrix method

The importance of parameters like pH, temperature and carbon to nitrogen ratio was determined using the orthogonal matrix method to get an optimum value for highest denitrification rate in a stirred tank reactor. L25 (5^3) orthogonal array was selected for this system with 3 different parameters. Temperature, Carbon: Nitrogen and pH are the variables optimized in the present study. Table 1

indicates the experimental set of L25 (5^3) orthogonal array for denitrification of synthetic nitrate waste using isolate RS152, along with the different variables and their factors used and the experimental results. These results were analyzed using MINITAB 13.30 software. The response table for means (smaller is better) obtained by analyzing the data for orthogonal array is shown in Table 3. It can be observed that the delta values of pH and carbon: nitrogen is higher than that of temperature. The main effect plots for the system, which shows the optimum levels of each factor obtained by statistical analysis, is shown in Fig. 5. It can also be observed that for each of the three variables at five levels, one level increases the mean compared to the other level. This difference is the main effect, i.e temperature at level 2, carbon: nitrogen at level 2, 3, 4 and 5 and pH at level 2. Thus the temperature at 37°C, carbon: nitrogen of 2:1 and above and a pH of 8.5 were the optimum levels for highest denitrification rate using the isolate strain RS152.

Table 3: Response table for mean

Level	(A) Temperature	(B) Carbon: Nitrogen	(C) pH
1	84	92	88
2	82	80	79
3	80	80	76
4	83	80	84
5	83	80	85
Delta	4	12	12

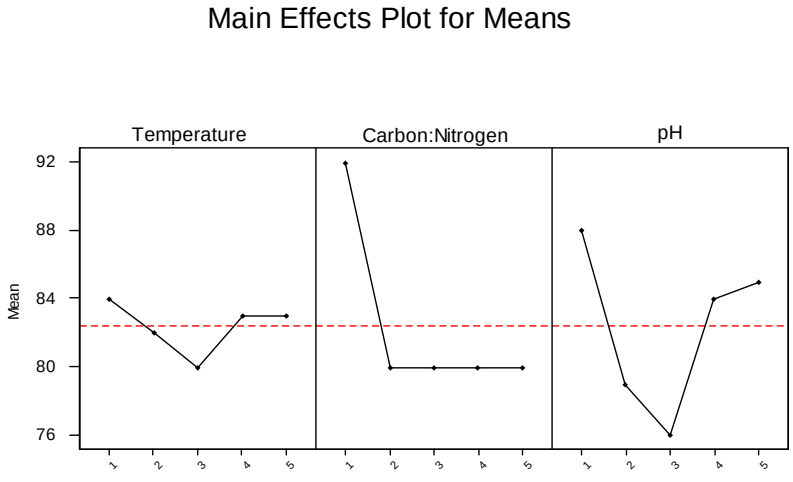

Figure 5. Main effect plot for denitrification by isolate RS152

3.5 Bioreactor studies

The denitrification activity of the isolate strain RS152 was observed in a stirred tank reactor of 4 L capacity fabricated in our laboratory. The reactor was run using the optimal conditions calculated from the orthogonal method and the specific denitrification rates were analyzed.

Biological denitrification can be depicted as

$$NO_3 \xrightarrow{K_{NO3}} NO_2 \xrightarrow{K_{NO2}} N_2$$

Where, K_{NO3} and K_{NO2} are zero order coefficients. Zero order data fit before and after optimization are shown in Fig. 6 and Fig. 7 respectively. The specific denitrification rate before optimization was found to be K^1_{NO3} = 263.5 mg NO_3–N g^{-1} MLSS h^{-1}, K^1 NO_2 = 157.6 mg NO_2–N g^{-1}MLSS h^{-1}, while after optimization it was found to be K^2_{NO3} = 388.2 mg NO_3–N g^{-1} MLSS h^{-1}, K^2_{NO2} = 182.2 mg NO_3–N g^{-1} MLSS h^{-1}. Specific rate of nitrate reduction was found to increase by 54.4 % on optimization, while the specific rate of nitrite reduction was found to increase by 15 % after optimization, thereby confirming the findings.

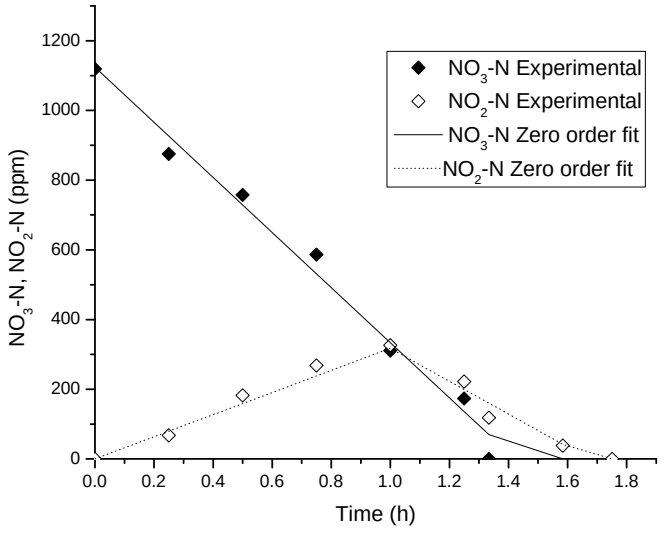

Figure 6. Experimental and zero order data fit for 1129 ppm NO_3-N synthetic nitrate waste before optimization. Medium: Synthetic nitrate waste; Nitrogen source: Sodium nitrate (1129 ppm NO_3-N), Carbon source: Sodium acetate; C/N: 2:1, pH: 7; Temperature: 30°C; Working volume: 2 L; Agitation: 140 ± 50 rpm; K^1NO_3= 263.5 mg NO_3–N g^{-1} MLSS h^{-1}; K^1_{NO2}= 157.6 mg NO_3–N g^{-1} MLSS h^{-1}; MLSS= 3 gL^{-1}.

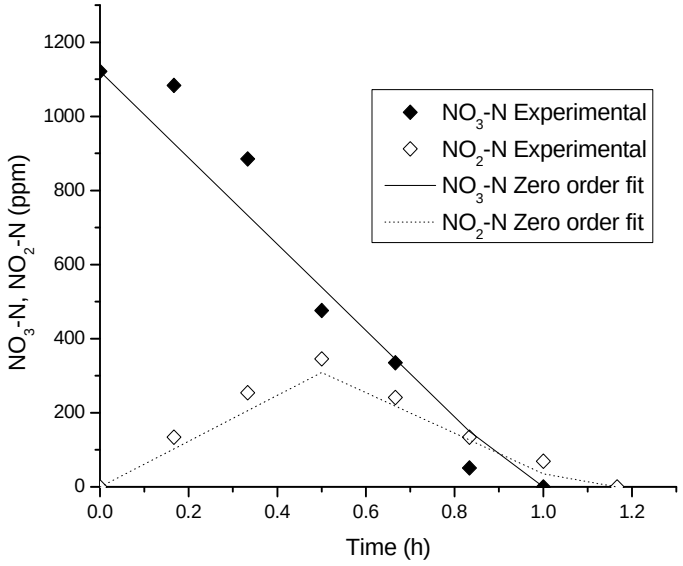

Figure 7. Experimental and zero order data fit for 1129 ppm NO_3-N synthetic nitrate waste after optimization. Medium: Synthetic nitrate waste; Nitrogen source: Sodium nitrate (1129 ppm NO_3-N), Carbon source: Sodium acetate; C/N: 2:1, pH: 8.5; Temperature: 37^oC; Working volume: 2 L; Agitation: 140 ± 50 rpm; K^2NO_3= 388.2 mg NO_3–N g^{-1} MLSS h^{-1}; K^2NO_2= 182.2 mg NO_2–N g^{-1} MLSS h^{-1}; MLSS= 3 gL^{-1}.

3.6 Enzyme studies

In vitro enzymatic activity of the isolate was carried out to understand the microbial metabolism physiology of high nitrate waste. Samples were assayed for NaR and NiR enzymes during the denitrification process of 1129 ppm NO_3-N in the stirred tank reactor. The enzyme assays show that the isolate strain RS152 contain activities of the denitrifying enzymes nitrate reductase and nitrite reductase, both of which are induced on cultivation with nitrate. On comparison with the nitrate and nitrite profiles (Fig. 7), the NaR and NiR specific activity also shows similar trend. As seen in Fig. 8, the NaR specific activity (1601 micromoles h^{-1} mg^{-1} protein) was found to be the maximum at a time period of 0.5 h, which eventually decreases, with the degradation of nitrate. Similarly the NiR specific activity (937 micromoles h^{-1} mg^{-1} protein) was found to be maximum at a time period of 0.6 h, which also reduces, with degradation of nitrite.

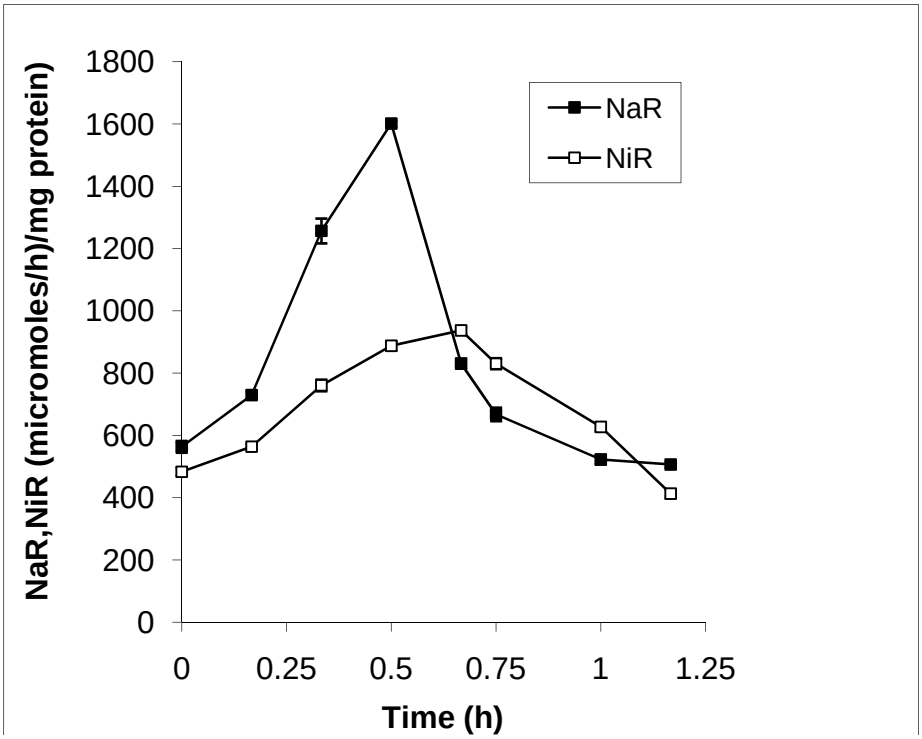

Figure 8. Nitrate reductase (NaR) and nitrite reductase (NiR) profile during the denitrification of 1129 ppm NO_3-N synthetic nitrate waste. Medium: Synthetic nitrate waste; Nitrogen source: Sodium nitrate (1129 ppm NO_3-N); Carbon source: Sodium acetate; Carbon: Nitrogen: 2:1, pH: 8.5; Temperature: 37^oC; Working volume: 2 L; Agitation: 140 ± 50 rpm; MLSS: 3 gL^{-1}.

4. DISCUSSION

Denitrification of high nitrate waste is still a challenge for industries producing nitrate wastes as high as 1000 ppm NO_3-N. Though treatments of such wastes have so far been reported using microbial consortia (Glass and Silverstein 1999; Foglar et al., 2005), very few studies have been carried out on nitrate waste treatment using an isolate, especially wastes containing high nitrate concentrations. In this study, to isolate a culture capable of denitrifying high nitrate, extensive screening of 160 cultures isolated from different habitats was carried out. Four denitrifiers capable of degrading about 90 % of 2258 ppm NO_3-N without any accumulation of NO_2 and NH_3 were isolated and compared amongst themselves. The results clearly indicated that the isolate RS152 degraded nitrate completely and more effectively as compared to isolates RS16, RS17 and RS18. The complete removal of nitrate as high as 2258 ppm NO_3 in a time period of just 105 min shows that this strain could play a substantial role in nitrogen

removal in sludge systems, and therefore was considered for further studies. This study showed that the isolated culture had the potential to be utilized in high rate denitrification processes which generally takes hours to degrade even low nitrate levels (< 100 ppm NO_3-N). Though denitrification using microbial consortia is a much known process as compared to isolate, these studies are important as (i) it gives a clear picture of the mechanism of the denitrification process which is obscure when a consortia is used. (ii) Accumulation of biomass which is a common problem faced during reactor studies using consortia can be avoided as isolate biomass can be used in low concentrations as compared to consortia.

Identification studies of the isolate RS152 using both biochemical characterization and 16S rRNA gene sequence analysis, indicated that the strain RS152 is closely related to *Pseudomonas aeruginosa* strain. Though biochemical studies have been proved to be successful in identifying the strains to the species level, using 16S rRNA gene sequence is a classic approach to detect and identify isolates accurately. The phylogenetic tree indicated that the strain RS152 forms a closest clade with *Pseudomonas aeruginosa* strain S25 with bootstrap resampling values of 100 %. The ID 32 GN system further confirmed the results by showing 96.7 % identity to *Pseudomonas aeruginosa*. On the basis of combined phenotypic and genotypic data, the strain RS152 belongs to the genus *Pseudomonas aeruginosa* which is also the most frequently isolated denitrifier from natural ecosystems (Gamble et al., 1977).

One of the methods used to biologically treat high nitrate wastes is by sequential adaptation to nitrate waste (Dhamole et al., 2007). Periodic exposure of microorganisms to defined process condition is found to be effective and this has developed into the SBR technology (Wilderer et al., 2001). Similar strategy was used to, wherein the isolate RS152 was acclimatized to high strength nitrate waste (224 ppm NO_3-N, 1129 ppm NO_3-N and 2258 ppm NO_3-N) in a stepwise manner for 15 days each in a SBR. The nitrate wastes were completely degraded without any accumulation of nitrite. The inoculum level remaining the same throughout the period of 45 days, during which the reactor was run, showed that the reactor was stable and efficiently denitrifying high nitrate wastes. This acclimatized culture was used for further studies on optimization of the denitrification process.

The denitrification rate, which is usually slow in any system, can be enhanced by optimizing various environmental conditions in which organisms degrade the nitrate. If optimal conditions for these processes can be defined, this isolate can be employed for high N waste removal in controlled conditions. Parameters like temperature, C:N, pH etc are some of the factors which contribute significantly to the denitrifying efficiency of the system. The Orthogonal array method, which has been used in various fermentation processes (Xu et al., 2003) to improve media for primary and secondary metabolite production, has been applied in wastewater

treatment systems to optimize conditions to get highest possible degradation rate (Nair et al., 2007). In the present study it was observed that the delta values for pH and C:N was the same while for temperature it was low. The magnitude of order of delta values shows the effect of the variables on the response characteristic of interest and the delta values being higher for pH and C:N ratio as compared to temperature, the most important factors controlling the denitrification activity of the isolate was pH at 8.5 and C:N of 2:1.

Using the optimum levels (temperature at 37^{o}C, carbon: nitrogen of 2:1 and a pH of 8.5), the specific denitrification rates were compared before and after the optimization process. For biological denitrification, zero order kinetics has been reported with respect to nitrate and nitrite (Moore and Schroeder 1971; Glass and Silverstein 1999; Foglar et al., 2005). The denitrification rate of the isolate RS152 was maximized by determining the most suitable denitrifying conditions. Also the specific denitrification rates of the isolate RS152 on comparison with that of a microbial consortium used in our previous studies (Dhamole et al., 2007; Nair et al., 2007), showed that the isolate showed a much higher denitrifying activity than microbial consortium thereby proving to be better. The specific denitrification rates for the isolate after optimization was found to be K^2_{NO3} = 388.2 mg NO_3–N g^{-1} MLSS h^{-1}, K^2_{NO2} = 182.2 mg NO_2–N g^{-1}MLSS h^{-1}, while the specific denitrification rates for microbial consortium after optimization was found to be K^2_{NO3} = 32.2 mg NO_3–N g^{-1} MLSS h^{-1}, K^2_{NO2} = 16.3 mg NO_2–N g^{-1} MLSS h^{-1}.

Many studies have been carried out in understanding the physiology of microbial metabolism of inorganic nitrogen compounds. Estimation of nitrate incorporation rates using stable isotope ^{15}N as a tracer are used for carrying out metabolic studies (Dugdale and Wilkerson 1986). But these studies often have problems with the loss of ^{15}N label. Berges and Harrison (1995) have shown that the measurement of enzyme activities is a good index of a biological rate. During enzymological studies of organisms, variability in enzyme immunochemical cross reactivity, efficiency and regulation within functional groups are often studied to a great extent (Korner 1993; Ka et al., 1997). Such results suggest that the regulation of ecosystem processes that are mediated by microbes may infact be affected by, and reflect, the community composition of functional groups. In the above studies it can be observed that (Fig. 8) the NaR and NiR specific activity show a similar profile as the nitrate and nitrite profiles (Fig. 7). The NaR activity was also found to be more (1601 micromoles/ h/ mg protein) as compared to NiR activity (937 micromoles/ h/ mg protein). This explains the rate of nitrate degradation to be faster as compared to nitrite reduction. The quantitative determination of the two enzymes nitrate reductase (NaR) and nitrite reductase (NiR), therefore gives an insight in understanding the metabolic activity during

the whole process of denitrification by the isolate which was not complete with the nitrate and nitrite degradation profiles.

5. CONCLUSIONS

Denitrification of high strength nitrate wastes by pure cultures is usually slow and lasts even several days. The isolate RS152 was found to be highly efficient in degrading nitrate wastes as high as 10000 ppm NO_3 (2258 ppm NO_3-N) in a time period of 1.75 h only, which to the best of authors knowledge is not reported for any isolate so far. Also comparative studies on the specific denitrification rates of the isolate RS152 and microbial consortium used in our previous studies as well as in other literatures showed that the isolate showed higher denitrifying activity thereby proving to be better (Glass and Silverstein 1999; Foglar et al., 2005; Dhamole et al., 2007; Nair et al., 2007). It can thus be applied for an efficient and economical high rate denitrification processes.

6. APPENDIX

SBR = Sequence batch reactor
NaR = Nitrate reductase
NiR = Nitrite reductase
K^1_{NO3} = Specific rate of nitrate reduction before optimization (mg NO_3–N g^{-1} MLSS h^{-1})
K^1_{NO2} = Specific rate of nitrite reduction before optimization (mg NO_2–N g^{-1} MLSS h^{-1})
K^2_{NO3} = Specific rate of nitrate reduction after optimization (mg NO_3–N g^{-1} MLSS h^{-1})
K^2_{NO2} = Specific rate of nitrite reduction after optimization (mg NO_2–N g^{-1} MLSS h^{-1})

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Chapter 20

THE CAPABILITY OF BINARY SYSTEM CONTAINING WATER-SOLUBLE IONIC LIQUIDS FOR TYPICAL ENDOCRINE DISRUPTOR CHEMICALS EXTRACTION FROM SEDIMENTS

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ABSTRACT

A binary system containing water and different water-soluble ionic liquids (WSILs) were considered for extraction of three typical endocrine disruptor chemicals (EDCs), 17β-estradiol (17β-E2), bisphenol A (BPA), and nonylphenol (NP), from three model sediments. Imidazolium and pyridinium based ionic liquids with different anions (tetrafluoroborate or chloride) were selected as representative WSILs to assess the extraction of EDCs from different sediments by the binary system containing water and WSILs at different molecular ratio. Comparing with extration of EDCs by water, the presence of 1-butyl-3-methyl imidazolium tetrafluoroborate ([bmim]PF_4) or N-butyl-3-methyl pyridinium tetrafluoroborate ([bmpy]PF_4) in the binary system at low molecular ratio could decrease the extraction of EDCs. However, at high molecular ratios, WSILs in binary system significantly increase the extraction of EDCs, especially for those from sediments with high organic matter content. At a molecular ratio of 5: 5 (WSIL: water), extraction by the binary system containing [bmim]PF_4 was more efficient than that by [bmpy]PF_4. However, at a molecular ratio of 1: 9, contrary results were gained. Cation-π, π-π, and hydrogen bond interaction of phenolic hydroxyl and "-N=C(H)-N-" were proposed to be the major interactions between WSILs and EDC molecules, while these interactions were greatly inhibited when water molecule presented in the binary system at high ratio. And also the adsorption of WSILs on sediments could affect the extraction efficiency when they presented at low ratio. At the same molecular ratio, the presence of [bmim]PF_4 and 1-butyl-3-methyl imidazolium chloride ([bmim]Cl) resulted in

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similar extraction efficiencies, which might suggest that anions of WSILs play minor role for extraction of EDCs in this study.

Keywords: water-soluble ionic liquid, sediments, extraction, 17β-estradiol, bisphenol A, nonylphenol

1. INTRODUCTION

Endocrine disruptor chemicals (EDCs), also called environmental hormone, have already become a threat to the global eco-system. As the typical EDCs, 17β-estradiol (17β-E2), bisphenol A (BPA), and nonylphenol (NP), are widely exist in environment, including soils and sediments.

Organic solvents have been used to extract organic contaminants from soil or sediment. Most of these organic solvents are volatile organic compounds (VOCs), which often exhibit high toxicity. Some techniques including soxhlet extraction, shaking extraction, microwave or ultrasound-assisted extraction, supercritical fluid extraction, and so on, use organic solvents to extract different organic contaminants from soils or sediments. Ionic liquids (ILs) are composed of organic cations and organic or inorganic anions, which remain liquid at the temperature below 100 ^{o}C (Fan et al., 2008). Recently, ILs were used as the alternatives of the traditional volatile organic solvents, to extract chemicals from water or solid phase (Pino et al., 2008). For example, 1-butyl-3-methyl imidazolium hexafluorophosphate ([bmim]PF_6) and 1-butyl-3-methyl imidazoliumchloride ([bmim]Cl) were used as the extractants, to assess the extraction of several organic contaminants, including DDT, dieldrin, hexachlorobenzene, and pentachlorophenol, from two different soils (Khodadoust et al., 2006).

In this study, two water-soluble ILs, 1-butyl-3-methyl imidazolium tetrafluoroborate ([bmim]PF_4) or N-butyl-3-methyl pyridinium tetrafluoroborate ([bmpy]PF_4), were selected as the representative imidazolium-based and pyridinium-based IL respectively, to compare the extraction of three typical EDCs from three different sediments by different binary systems containing water-soluble ILs and water. After that, the difference of extraction by the binary systems containing ILs with different anions at certain ratio (i.e. [bmim]PF_4 and [bmim]Cl) were also studied.

2. MATERIALS AND METHODS

2.1 Materials

[bmim]PF_4 was synthesized as described elsewhere (Zhao et al., 2006). Briefly, [bmim]Cl was prepared by adding equal amount (0.3 mol) of 1-methylimidazole and 1-chlorobutane to a round-bottomed flask fitted with a reflux condenser and reacting for 48 h at 70 ^oC until a yellow viscous liquid is formatted. The viscous liquid was then cooled and washed with ethyl acetate and dried under vacuum at 80 ^oC to remove the solvent. [bmim][PF_4] was prepared by slowly adding sodium tetrafluoroborate (0.1 mol) into [bmim]Cl (0.1 mol) in acetone. After stirring for 12 h, and dried under vacuum at 80 ^oC. [bmpy]PF_4 were provided by the Center for Green Chemistry and Catalysis, LICP, CAS.

Nonylphenol (NP, technical grade) was purchased from Tokyo Chemical Synthesis Ind. Co. Ltd, Japan. Standards of BPA and 17β-E2 were purchased from J&K Scientific Ltd. HPLC-grade methanol, acetone, dichloromethane, and acetonitrile were purchased from Biaoshiqi Company of Tianjin, China.

Three sediments, namely Liaohe River sediment, Yuqiao reservoir sediment, and Yellow River sediment, were used as the simulated sediments used in this study, with their properties shown in Table 1.

Table 1. Properties of sediments

Sediments	OC-%	Sand-%	Silt-%	Clay-%	pH
Liaohe River sediment	5.89	36.7	55.9	7.4	6.75
Yuqiao reservoir sediment	2.56	38.3	50.4	11.3	7.13
Yellow River sediment	0.27	82.62	9.80	7.58	7.03

2.2 Extraction experiments

Before extraction experiments, batch sorption experiments (48 h) were conducted to gain the polluted sediments by three EDCs, respectively. By accommodating the amount of analytes added to the water-sediments system, a pre-sorbed concentration of about 1 mg/kg was gained for all the three EDCs in three sediments. After the sorption experiments, the system was centrifuged at 3000 r/min for 30 min and the supernatant was replaced with the extracts containing [bmim]PF_4 or [bmpy]PF_4 and water at different molecular ratio from 1:9 to 5:5. [bmim]PF_4 was also compared with [bmim]Cl in the IL/water binary system at a ratio of 5:5, and the extraction percent of EDCs from the Liaohe River sediment and the Yellow River sediment were examined.

2.3 Analysis

Waters 1525 high-performance liquid chromatograph, with Waters 2475 fluorescence detector and 2487 UV detector (Waters Company, USA) was utilized for chemical analysis. Acetonitrile and water was used as mobile phase. Isocratic elution was carried out with a flow rate of 0.8 mL/min. For analysis of BPA and NP, excitation and emission wavelengths of the fluorescence detector were 233 and 302 nm, respectively. For analysis of 17β-E2, 205 nm was used by the UV detector.

3. RESULTS AND DISCUSSION

3.1 Effect of IL/water ratio

The extraction percent of BPA by pure water was 37.7 % (from the Yellow River sediment), 49.8 % (from the Yuqiao reservoir sediment), and 73.0 % (from the Liaohe River sediment), respectively. While the extraction percent of 17β-E2 was 9.3 % (from the Yellow River sediment), 26.2 % (from the Yuqiao reservoir sediment), and 55.0 % (from the Liaohe River sediment), respectively. For NP, the concentration in the pure water extractant was lower than its limit of detection. The exist of IL at a molecular ratio of 1:9 (IL:water) can further inhibit the extraction of BPA and 17β-E2 from all three sediments (Figure 1). However, the extraction percent increased with the increase of the IL ratio in the binary solution, when the ratio was larger than 2:8. At the ratio of 5:5, an extraction percent of ~80 % could occur for all three EDCs from three sediments by the binary system (Figure 1).

3.2 Effect of sediments property

As a whole, for sediments with high OC content, EDCs were difficult to be extracted, especially for NP (with highest K_{ow}). This suggests that presence of organic carbon components are adverse to the extraction of these EDCs by the IL-water binary system However, for chemicals in the Yellow River sediments, whose OC content was very low, the extraction percent of 17β-E2 and NP was lower than that in the other two sediments. This might be due to the possible stronger bond interaction between the analytes and the mineral surface of the Yellow River sediments.

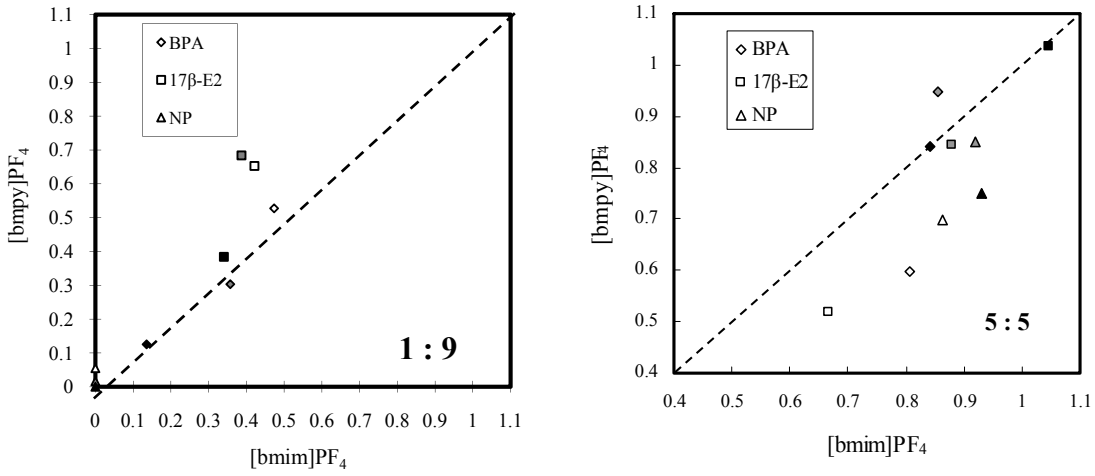

Figure 1. Comparison of extration percent with binary system containing $[bmim]PF_4$ or $[bmpy]PF_4$ and water at the ratio of 1:9 and 5:5 from three different sediments. Black points: Liaohe River sediements; Gray points: Yuqiao reservoir sediment; White points: Yellow River sediment.

3.3 Comparison of imidazolium-based and pyridinium-based IL

At the molecular ratio (IL:water) of 5:5 and 1:9, different extraction capability exhibited for binary system containing $[bmim]PF_4$ or $[bmpy]PF_4$ and water. At the ratio of 5:5, existence of imidazolium-based IL seems to be more propitious to the extraction of three EDCs, especially from the Yellow River sediment. This might because that, (i) the two "N" in the imidazolium structure enhance the probability of the happening of "cation-π" interaction; (ii) the "H" in the "-N=C(H)-N-" structure induces more stronger H bond interaction with the analytes; (iii) the five-membered ring of the imidazolium ring holds larger electron cloud density compared with that of six-membered pyridinium ring. However, for the binary system at the ratio of 1:9, contrary phenomenon was observed. It seems that the existence of [bmpy] based IL was more propitious to the extraction of the EDCs. This was attributed to the difference of sorption of two different IL. At the low ratio in solution, sorbed IL could enhance the sorption of EDCs. The sorption of $[bmim]PF_4$ was greater than that of $[bmpy]PF_4$. Therefore, the extraction was somewhat inhibited.

3.4 Comparison of ILs with different anions

At the same molecular ratio of 5:5, the presence of [bmim]PF_4 and 1-butyl-3-methyl imidazolium chloride ([bmim]Cl) resulted in similar extraction efficiencies from the sediments with low or high OC content (Figure 2), which might suggest that anions of WSILs play minor role for extraction of EDCs in this study.

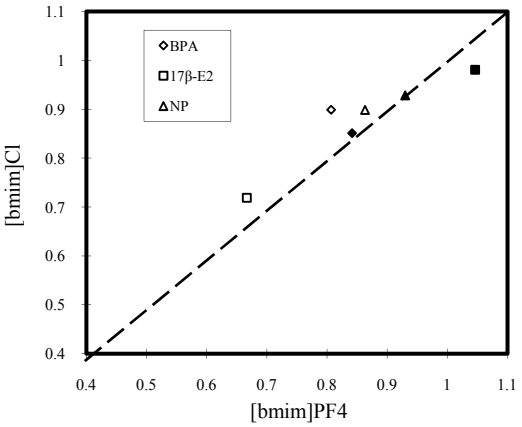

Figure 2. Comparison of extration percent with binary system containing [bmim]PF_4 or [bmim]Cl and water at the ratio of 1:9 and 5:5 from two different sediments. Black points: Liaohe River sediments; White points: Yellow River sediment.

4. ACKNOWLEDGMENTS

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PART VIII: Risk Assessment

Chapter 21

DETERMINATION OF ORAL OR DERMAL BENZENE EXPOSURE FROM CONTAIMINATED SOILS

Benzene Bioavailability from Soil

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ABSTRACT

Soil contamination with dangerous, toxic chemicals remains one of the most difficult problems in this era. Health risk assessments often do not consider the amount of chemicals in soil that are absorbed and their disposition (kinetics). The aim of these studies was to compare the extent to which adsorption to either a sand or clay content soil affects the kinetics and manner which benzene is subsequently handled in orally or dermally exposed rats. Dermal exposure increased absorption half-lives ($t_{1/2}$) by 25, 60 and 44-fold compared with oral exposure to benzene alone, or in the presence of sandy or clay soil, respectively. The elimination $t_{1/2}$ following dermal versus oral exposure were increased about 2-fold in benzene alone and sandy soil groups, while in the clay soil group the increase was 13-fold. The area under the blood concentration versus time curve (AUC) of benzene in the presence of either soil was increased after oral and decreased after dermal exposure compared with exposure to benzene alone. The urinary recovery, 48 hours following dermal exposure to benzene alone, was 3-fold greater than following oral exposure. Tissue distribution after all oral exposures resulted in the highest concentrations of radioactivity in gastric contents > stomach > fat > duodenum > adrenal. The highest tissue concentrations of radioactivity after

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dermal exposure to benzene alone were kidney > liver > treated skin; however, after exposure in the presence of either soil the highest tissue concentrations were treated skin > kidney > liver. The results of these studies reveal that the presence of sand or clay content soil produced qualitative and quantitative differences in the disposition of benzene in the body following oral or dermal exposures. These differences will impact the risk assessment of benzene.

Keywords**:** benzene, dermal or oral exposures, soil bioavailability effects

1. INTRODUCTION

Soil contamination with dangerous toxic chemicals remains one of the most difficult problems of this era. The hazardous chemical may persist in the environment; therefore, the potential for long-term health risk exists. The sources of hazardous chemical wastes are numerous. Industry, agriculture, and institutions such as hospitals and universities are all sources of materials that need to be discarded. People living in proximity to hazardous waste disposal sites or workers at these sites are at serious health risk if the sites are poorly managed or improperly designed. Contamination of soil and the leaking of these chemicals to both surface and ground water may lead to long-lasting toxicological problems. As industrial facilities are shut down, all too often they leave behind heavily contaminated soil. Furthermore, transportation of hazardous wastes to disposal sites also poses hazards since accidents are an ever-present possibility. If housing, schools, or office buildings are built over these areas, even in the distant future, exposure is likely to occur. Children who play in and around the soil in these areas will receive direct exposure. Children have been estimated to ingest 50-180 mg of soil per day (Clausing *et al*., 1987; Binder and Sokal, 1986).

Paralleling the growth of hazardous wastes, there has been an increasing interest in the development of procedures for assessing public health risks associated with exposures to hazardous materials. Estimates of health risk following exposure to contaminated soils have largely been based on results of studies performed with pure chemicals. However, the clay, mineral, and organic components of soil form complex, heterogeneous surfaces which are capable of adsorbing organic molecules (Hamaker and Thompson, 1972). The strength of the chemical-soil attractive forces can profoundly affect the reversibility of the adsorptive process. Therefore, the availability and the rate of chemical entering the body, its distribution to tissues, and the rate and amount of excretion may greatly differ from pure chemical investigation. Lucier *et al*. (1986) and McConnell *et al*. (1984) suggest that dioxin in soil from Times Beach and Minker Stout sites in Missouri was biologically available, as measured by

microsomal enzyme studies in guinea pigs. Umbreit *et al*. (1986) reported that despite the high concentration of dioxin from two manufacturing sites in New Jersey, this soil was unable to produce toxic effects in orally exposed guinea pigs compared with similar amounts of pure dioxin. Tight binding of dioxin to the soil matrix of the New Jersey sites correlated directly with its reduced bioavailability.

Widespread exposure to petrochemicals in dumping sites and groundwater has prompted an evaluation of the kinetics of benzene after oral and dermal treatment. Benzene is a common industrial chemical used for the synthesis of aromatic components (Baselt, 1982; Sandmeyer, 1981). It has been identified as the fourth most frequent substance recorded in 818 abandoned dump sites on the U.S. Environmental Protection Agency's 1985 National Priority List for Cleanup.

Frantz (1984) investigated the percutaneous absorption of benzene in animals and men. He reported that less than 0.2% of the applied doses were absorbed in all species studied. Other investigators (Susten *et al*., 1985) suggest that workers in tire plants may absorb 4-8 mg of benzene daily through the skin from a rubber solvent mixture containing 0.5% (v/v) benzene.

This study was conducted to compare the extent to which adsorption to either of two different soils (sandy and clay) affects the manner in which benzene is subsequently handled in orally and dermally exposed adult male rats.

2. MATERIALS AND METHODS

2.1. Chemicals

All studies were conducted using uniformly labeled ^{14}C–benzene 50 mCi/mmole (ICN Pharmaceuticals, Irvine, CA) with radiochemical purity >98%. Prior to use, dilution with HPLC-grade, unlabeled benzene (Aldrich Chemical Co.) was carried out to reduce specific activity to a workable range.

2.2. Soils

Studies were conducted on two different soils that are representative of soil types widely distributed in the United States (USDA, 1972, 1977). 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. The Keyport soil contains 50% sand, 28% silt, 22% clay, 1.6% organic matter; has a pH of 5; and was collected from the Woodbury formation near Moorestown in southwestern New Jersey. Soil particle size distribution was as follows: Atsion soil = 50-100 μm (22.2%), 100-250 μm (76.3%), > 250 μm (1.5%); Keyport soil = 50-100 μm (17%), 100-250 μm (65.3%), 250-500 μm

(13.6%), > 500 μm (4.1%). Soil analyses were performed by the Soil Testing Laboratory at Rutgers Cooperative Extension Resource Center, Rutgers University, New Brunswick, NJ. Organic matter content was measured by a modified Walkley and Black (1934) dichromate oxidation method. Because of the Atsion soil's higher sand content and the Keyport soil's higher clay content, these soils will be referred to as sandy and clay, respectively.

2.3. Animals

Male Sprague-Dawley rats weighing 250-300 g were purchased from Taconic Farms, Germantown, NY, and were immediately quarantined for one week. Animals were housed three per cage at a temperature of 25 ^{o}C and humidity 50% controlled environment with a 12 hour light/dark cycle. Food and water were provided *ad libitum*.

2.4. Benzene Administration

The oral administration of benzene was performed as follows: 150 μl of ^{14}C–benzene solution (5 μCi) alone or the same volume of radioactivity added to 0.5 g of soil, was combined with 2.85 mL of aqueous 5% gum acacia and a suspension formed by vortexing. This volume of benzene, or benzene soil suspension, was immediately administered by gavage to groups of rats which had been fasted overnight. Heparinized blood samples were collected at 5, 10, 14, 18, 20, 22, 30, 45, 60, 90, and 120 minutes by cardiac puncture of anesthetized rats. Immediately after the collection of the 120 minute blood sample, rats were sacrificed by an overdose of anesthesia and whole organs or samples of kidney, liver, lung, pancreas, spleen, bone marrow, brain, duodenum, adrenal, fat, esophagus, heart, ileum, skin, testes, thymus, thyroid, carcass, stomach, and gastric contents were collected and stored at -75 ^{o}C. Three hundred mg or smaller samples of tissues were used to determine the distribution of radioactivity as previously reported (Turkall *et al*., 1988).

In the dermal application, 30 minutes prior to the administration, five rats/group were shaved on their right costo-abdominal areas. A shallow glass cap (Q Glass Co., Towaco, NJ) circumscribing approximately a 13 cm^2 area was tightly fixed with Lang's jet liquid acrylic and powder (Lang Dental Manufacturing Corp., Inc., Chicago, IL) on the shaved skin of each animal. Rats were anesthetized during the cap attachment procedure. Either 300 mL of ^{14}C–benzene (40 μCi) alone or with 1 g of soil was introduced by syringe through an opening in the cap, which was immediately sealed. This volume of benzene coated the soil with no excess fluid remaining. Rats were rotated from side to side so that the soil-chemical mixture covered the entire circumscribed area.

Volatilization losses during administration of ^{14}C–benzene were determined and dosages were adjusted appropriately. Blood was collected by cardiac puncture under anesthesia at 2, 4, 8, 12, 24, 30, 48 and 72 hours. Blood samples from both routes of administration were processed and radioactivity was measured by liquid scintillation spectrometry, as previously described (Turkall *et al*., 1988; Skowronski *et al*., 1988).

2.5. Excretion and Metabolism Studies

In the excretion studies, groups of six rats each were administered benzene or benzene adsorbed to the soil, as described above. Pairs of animals were housed in all-glass metabolism chambers (Bioserve Inc., Frenchtown, NJ) for the collection of expired air, fecal and urine samples. Expired air was passed through activated charcoal tubes (SKC Inc., eighty-Four, FA) for the collection of ^{14}C–benzene, then bubbled through traps filled with ethanolamine:ethylene glycol monomethyl ether (1:2, v/v) for the collection of $^{14}CO_2$. Charcoal tubes and trap mixtures were collected at 1, 2, 6, 12, 24, and 48 hours, and fecal samples were collected at 24 and 48 hours. Samples were processed and radioactivity was measured as previously described (Turkall *et al*., 1988).

At the conclusion of the dermal excretion studies, rats were sacrificed by an overdose of anesthetic. The glass caps were opened, and 1.0 to 1.2 mL of ethyl alcohol was introduced through the cap opening. The animals were rotated from side to side and 100 μL aliquots of ethanol were removed to determine the percent of benzene dose remaining on the skin application sites (Skowronski *et al*., 1988). Then the glass caps were removed from the rats and tissue specimens were collected to determine the distribution of radioactivity as described above.

To determine benzene metabolism, urine samples were extracted and analyzed by high performance liquid chromatography, as established in our laboratory (Turkall *et al*., 1988).

2.6. Statistical Analysis

Exploratory data analysis was used to summarize replicate data in the plasma time course study. This approach allows a curve to be fitted to all data points, while providing resistance to those points which depart from the primary pattern (Tukey, 1977; Velleman and Hoaglin, 1981). The curve fitting procedure which was utilized is called smoothing. The curve fitting procedure "4235EH" smoother was utilized for these studies as described by Velleman and Hoaglin (1981). Each replicate was smoothed over all time points, a median value was calculated from all smoothed replicates at each time point, and a second smooth was applied to these median values. The final smoothed data was used to

calculate the rate constants and $t_{1/2}$ of absorption and elimination from plasma by regression analysis and the method of residuals (Gibaldi and Perrier, 1975) as well as to determine a maximum concentration was achieved. Plasma concentrations from 0 minutes to the time at which maximum concentration was achieved were used for absorption calculations.

For elimination calculations, 45 through 120 minute time point concentrations were used in oral route studies, while 12 through 72 hours and 24 through 72 hours time point concentrations were used in dermal route studies in the soil and pure groups, respectively. Since the rate constants and the $t_{1/2}$ are calculated from smoothed date, the standard errors (SE) of the rate constants were determined by the bootstrap method (Effron, 1982; Effron and Tibshirani, 1985). AUC was calculated by the trapezoidal rule using individual replicate data, reflects volatilization losses, and is reported as the mean $\pm$ SEM. Statistical differences between the treatment groups, were determined by analysis of variance (ANOVA), F test, and Scheffe's multiple range test. Comparison of slopes were determined using analysis of covariance.

3. RESULTS AND DISCUSSION

Absorption and elimination $t_{1/2}$ data following administration of ^{14}C–benzene orally and dermally to male rats is displayed in Table 1. The $t_{1/2}$ of absorption into plasma in the presence of either soil for oral or dermal treatment was not statistically altered compared to their respective pure group. However, dermal exposure increased absorption $t_{1/2}$ to 25, 60 and 44-fold compared to oral exposure in pure, sandy and clay groups, respectively. In oral treatment, the elimination $t_{1/2}$ of the clay group was significantly decreased ($p < 0.05$) compared to either sandy or pure groups. No significant change in elimination $t_{1/2}$ occurred after dermal exposure. In pure and sandy groups, the elimination $t_{1/2}$ of dermal treatment were increased about 2-fold versus oral treatments, while in the clay group the increase was 13-fold.

Table 1. Absorption and Elimination Half-Lives of Radioactivity in Male Rat Plasma

	$t_{1/2}$ (hr)[a]			
	Absorption		**Elimination**	
Treatment	**Oral**	**Dermal**	**Oral**	**Dermal**
Pure[b]	0.12	3.1	13.4	23.0
Sandy[c]	0.06	3.6	10.8	24.5
Clay[d]	0.10	4.4	1.4[e]	19.4

[a]Values calculated from five or six rats per group., [b]^{14}C–benzene alone.
[c]^{14}C–benzene adsorbed to sandy soil. [d]^{14}C–benzene adsorbed to clay soil.
[e] Significantly different from treatment with pure benzene ($p < 0.05$).

The AUC for the 2-hour period following oral administration was increased in both sandy and clay groups; however, only clay soil was significantly different ($p < 0.05$) compared to the pure group. Following dermal administration, both soils significantly ($p < 0.05$) decreased AUC values compared to pure group during the 72 hours studied (Table 2).

Table 2. Area Under Concentration Versus Time Curve of Radioactivity in Male Rat Plasma[a]

	Percent Initial Dose (mL/min)	
Treatment	**Oral**	**Dermal**
Pure[b]	1.53 ± 0.06	0.41 ± 0.21
Sandy[c]	2.60 ± 0.19	0.22 ± 0.08[e]
Clay[d]	3.64 ± 0.43[e]	0.17 ± 0.07[e]

[a]Values calculated from five or six rats per group.
[b]^{14}C–benzene alone.
[c]^{14}C–benzene adsorbed to sandy soil.
[d]^{14}C–benzene adsorbed to clay soil.
[e] Significantly different from treatment with pure benzene ($p < 0.05$)

Tables 3 and 4 display the patterns of urinary and expired air excretion of radioactivity following oral and dermal application of ^{14}C–benzene. In oral treatment the expired air represented the primary excretion route of ^{14}C–activity with lesser amounts eliminated in urine during the 48 hours following administration of benzene alone. Expired air and urine represented about equal excretion routes of ^{14}C–activity in the sandy soil treated group, while urine represented the primary route, with lesser amounts eliminated through the expired air in the clay soil group. The percentages of radioactivity in expired air of the clay soil group were significantly lower than those of the pure group at 0-12, 0-24, and 0-48 hours after oral treatment. Unmetabolized ^{14}C–benzene represented 98, 97 and 81% of the total radioactivity collected in the expired air of ^{14}C–benzene, sandy soil, and clay soil groups after oral treatment, respectively, with CO_2 comprising the remainder. With dermal application, the major route of excretion was the urine, and to a lesser extent, the expired air, in all treatment groups. During the 48-hour collection period, 86.2% of the initial dose was recovered in the urine of the pure benzene group. At the same time period, sandy and clay soil significantly decreased urinary excretion to 64.0% and 45.4%, respectively. The expired air recovery in dermal treatment was significantly decreased in the sandy soil group compared with the pure group, while the clay group was without significant change. Less than 1% of the administered dose was expired as $^{14}CO_2$ in all groups.

Table 3. Urinary Recovery of Radioactivity Following Oral or Dermal Administration of ^{14}C–Benzene[a]

Time (hour)	Oral			Dermal		
	Pure	Sandy	Clay	Pure	Sandy	Clay
0-12	23.2 ± 6.9	44.7 ± 21.5	37.9 ± 12.6	9.7 ± 3.8	16.2 ± 0.1	7.2 ± 1.7
12-24	2.3 ± 0.8	5.6 ± 1.9	7.2 ± 1.9	58.8 ± 2.8	31.3 ± 2.8[b]	25.1 ± 3.4[b]
0-24	25.5 ± 7.8	51.6 ± 20.7	45.1 ± 13.4	68.4 ± 2.9	47.4 ± 2.2[b]	32.3 ± 4.0[b]
24-48	0.5 ± 0.5	1.3 ± 0.7	0.8 ± 0.1	17.8 ± 1.8	16.6 ± 1.1	13.1 ± 1.9
0-48	26.0 ± 7.9	52.8 ± 21.4	45.9 ± 13.6	86.2 ± 2.1	64.0 ± 2.8[b]	45.4 ± 4.8[b]

[a]Values represent percentage of initial dose (mean ± SEM) of six animals per group.
[b]Significantly different than treatment with benzene alone ($p < 0.05$).

Table 4. Expired Air Recovery of Radioactivity Following Oral or Dermal Administration of ^{14}C–Benzene[a]

Time (hour)	Oral			Dermal		
	Pure	Sandy	Clay	Pure	Sandy	Clay
0-12	58.2 ± 7.2	50.0 ± 7.6	15.6 ± 10.0[b]	9.4 ± 1.0	3.9 ± 0.8[b]	8.5 ± 1.2
12-24	0.1 ± 0.0	0.2 ± 0.1	0.1 ± 0.0	2.5 ± 0.4	0.4 ± 0.1[b]	1.1 ± 0.2[b]
0-24	58.2 ± 7.2	50.2 ± 7.6	15.7 ± 10.1[b]	12.0 ± 1.4	4.3 ± 0.8[b]	9.6 ± 1.3
24-48	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0	0.8 ± 0.2	1.6 ± 0.5	0.5 ± 0.2
0-48	58.2 ± 7.2	50.2 ± 7.6	15.0 ± 10.1[b]	12.8 ± 1.1	5.9 ± 1.3	10.1 ± 1.4

[a]Values represent percentage of initial dose (mean ± SEM) of six animals per group.
[b]Significantly different than treatment with benzene alone ($p < 0.05$).

By comparing the excretion routes for the two different routes of administration, it can be seen that the urinary recovery in the dermal pure group after 48 hours from the administration exceeded the value of the oral pure group (86.2% versus 26.0%), but the other two treatments were almost without change. In the oral route, more than 82% of total radioactivity excreted in the urine of all treatment groups appeared during the 0-12 hour period following administration. However, in the dermal route, the highest amount of radioactivity in urine was recovered in the 12-24 hour interval (Table 3). Table 4 reveals that more than 98% of radioactivity excreted in expired air of all oral treatment groups appeared during the first 12-hour period following administration. In dermal application, the highest portion of radioactivity in expired air (approximately 75% of total) was also recovered in the 0-12 hour period following the administration. The total activity recovered in expired air following oral administration far exceeded the values following dermal administration in the period studied. During the 48-hour period, the radioactivity in the feces of oral treatment was 0.6, 1.3 and 1.4% of initial doe in pure, sandy and clay groups, respectively. In the dermal route < 0.5% fecal recovery occurred in all groups during the same time period.

Tissue distribution of radioactivity after oral administration is displayed in Table 5. Gastric contents contained the highest concentration of radioactivity in all groups, with the mean activity (as percentage of initial dose/g) of the clay

group (18.7) being about 6-fold higher than that of either the sandy soil (2.8) and pure benzene (2.1) groups. Stomach contained the highest tissue concentration of radioactivity, with fat the second highest in all treatments, followed by the duodenum an adrenal. No statistically significant differences were detected in the tissue concentrations of radioactivity between the oral treatment groups.

Table 5. Tissue Distribution of Radioactivity in Male Rat Following Oral Administration of ^{14}C–Benzene

Gastric Contents[a]	
Pure Benzene	2.1 ± 1.8
Sandy Soil	2.8 ± 0.7
Clay Soil	18.7 ± 10.8[b]
In All Treatment Groups:	
Gastric Contents > Stomach[c] > Fat > Duodenum > Adrenal	

[a]Values represent percent initial dose per gram (mean ± SEM) from five rats per group, 2 hours following oral administration.
[b]Significantly different than treatment with pure benzene ($p < 0.05$)
[c]No statistical differences between treatment groups.

In the dermal route, soil-related differences were observed in tissue distribution. The distribution patterns of ^{14}C–activity for pure and soil-adsorbed benzene are demonstrated in Table 6. ^{14}C–activity 48 hours post administration of soil-adsorbed benzene was greatest in the treated skin followed by kidney, liver, duodenum, spleen treated fat, and untreated fat, as well as bone marrow in both soil groups. In the pure benzene group, kidney contained the highest amount of radioactivity, followed by liver, treated skin, duodenum, treated fat, and untreated fat as well as bone marrow. Clay soil treatment statistically increased radioactivity (10-fold) in treated skin, while statistically decreasing radioactivity (4-Sfold) in treated fat compared to benzene alone. It is worth noting that at necropsy, ethanol extraction of all dermal application sites contained only 0.1% of the initial dose indicating loose retention of chemical.

Table 6. Tissue Distribution of Radioactivity in Male Rat Following Dermal Administration of ^{14}C–Benzene

Pure Benzene Group:
Kidney > Liver > Treated Skin > Duodenum > Treated Fat > Untreated Fat > Bone Marrow
Sandy and Clay Groups:
Treated Skin[a] > Kidney > Liver > Duodenum > Spleen > Treated Fat[b] > Untreated Fat > Bone Marrow

[a]Significantly increased in the clay group compared to the pure benzene group ($p < 0.05$).
[b]Significantly decreased in the clay group compared to the pure benzene group ($p < 0.05$).

Data showing the urinary metabolites of ^{14}C–benzene in the male rat after oral and dermal application are given in Table 7. Phenol was the major urinary

metabolite detected in the 0-12 hour urines of all treated groups in both routes of administration. Smaller quantities of hydroquinone, catechol, and benzenetriol compared to phenol were also detected. The type and percentage of benzene metabolites produced were not altered in the presence of either soil after oral administration, while after dermal administration, hydroquinone was statistically decreased in the 0-12 hour interval in the presence of sandy soil compared to the pure group. Similar metabolite percentages were detected in 12-24 hour urines of all treated groups (data not shown). The parent compound was not detected in the urine of any treatment group. Use of acid hydrolysis in the preparation of urinary extract did not permit identification of conjugation products.

Table 7. Urinary Metabolites of ^{14}C–Benzene in the Male Rat[a]

	Oral			Dermal		
Metabolite	**Pure**	**Sandy**	**Clay**	**Pure**	**Sandy**	**Clay**
Phenol	39 ± 1	41 ± 3	34 ± 2	38 ± 3	44 ± 4	46 ± 3
Catechol	14 ± 1	15 ± 3	18 ± 2	13 ± 1	14 ± 5	12 ± 1
Hydroquinone	17 ± 3	25 ± 3	26 ± 1	19 ± 2	10 ± 1[b]	25 ± 1
Benzenetriol	12 ± 3	14 ± 3	20 ± 4	5 ± 2	17 ± 7	13 ± 2

[a]Values represent percent of total radioactivity in the 0-12 hour collection period from 6 animals per group (mean ± $SEM_{)}$

[b]Statistically different than treatment with benzene alone ($p < 0.05$).

4. CONCLUSIONS

This study revealed that the presence of sandy and clay soil produced qualitative and quantitative differences in the manner of the availability of benzene in the body following oral or dermal treatments. Although the soil group in oral treatment did not significantly alter the rate of benzene absorption ($t_{1/2}$), AUC for 0-2 hour post-administration was increased in both soil groups. Because the density of benzene is less than water, some gavaged material could be vaporized out of the gastrointestinal tract directly without absorption into the body. Adsorption of benzene to the soil decreased the vaporization of benzene. Detection of the bulk of radioactivity excreted in expired air as unmetabolized benzene during the same time period supports this conclusion. The relatively stronger adsorption of benzene to clay soil is supported by significantly increased AUC, significantly decreased excretion in expired air, as well as relatively high concentration of radioactivity in the gastric contents 2 hours after the oral administration.

Dermal exposure of pure and soil-adsorbed benzene produced plasma concentration of radioactive compound comparable to those generated by oral administration only when rats were exposed to eight times the concentration of ^{14}C–benzene used in the oral route (40 versus 5 μCi). Also, this laboratory

reported that peak plasma concentrations after dermal treatments were delayed about 36-fold compared to those which occurred following oral administration (Turkall *et al*., 1988; Skowronski *et al.,* 1988). The absorption and elimination $t_{1/2}$ in all groups after dermal treatment were much longer compared to their respective oral groups. The result of this study is in agreement with those of Frantz (1984) and Susten *et al.* (1985), that indicated benzene was not readily absorbed through the skin. After dermal application, both soil groups demonstrated a significantly lower amount of ^{14}C–activity in urine compared to the pure group, while radioactivity in expired air was decreased significantly after sandy soil administration.

Routes of excretion and amount excreted by the various routes were changed in the presence of the soils in both routes of administration. Expired air recoveries were decreased in all dermal treatments compared to the oral experiments, while the urine was the primary route of excretion in all dermal groups as well as the oral clay group. The fecal route remains a minor excretion route in the presence or absence of soils.

The quantity and quality of benzene metabolites produced were almost without change, except the amount of hydroquinone in the dermal sandy group was significantly decreased. Phenol was the primary urinary metabolite in all the treatments studied.

Malkinson and Gehlmann (1977) reported that the most important factors related to chemical persistence in soil are organic matter and clay content of the soil. In both the dermal and the oral soil-adsorbed benzene studies, altered bioavailability results revealed that a higher percentage of clay rather than organic matter is controlling the retention of benzene in soil. Particle sizes, and thus surface area of the two soils are essentially equivalent and do not appear to be a factor in this study.

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Chapter 22

THE ICE STORM OF 2008 AND EMERGENCY RESPONSE COORDINATION THROUGHOUT WESTERN AND CENTRAL MASSACHUSETTS

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ABSTRACT

On December 11, 2008, an ice storm devastated the Northeast causing critical damage to the utility infrastructure leaving over a million residents without power. Storm damage throughout the region was mostly related to fallen trees, power lines and utility poles. The storm made national headlines and prompted public officials to declare a state of emergency in Massachusetts, New Hampshire, New York, Vermont and Maine. This case study will focus on the emergency response efforts in Massachusetts related to the cleanup of environmental impacts caused by the release of transformer oil (mineral oil dielectric fluid) contained within utility pole mounted transformers. Mineral oil dielectric fluid (MODF) is a highly refined mineral oil which is stable at high temperature and has excellent insulating properties. However, MODF does pose environmental risks and, as a result, is regulated under the Massachusetts Contingency Plan (MCP, 310 CMR 40.0000). Additionally, polychlorinated biphenyls (PCBs) were routinely used in oil-filled transformers well into the 1970's. Massachusetts regulations require the notification and remediation of MODF releases to the environment. Reportable quantities, governing reporting requirements, and cleanup standards for MODF releases have been established based on the PCB content of the transformer oil. The widespread nature of the storm damage caused a logistical nightmare when coordinating emergency response activities. With over 100 reported releases of MODF, release sites were continually reevaluated to determine which posed the greatest threat to the environment, human health and public safety. Prioritization of release sites was accomplished only after careful consideration of various factors, including the

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PCB concentration of the transformer oil, impacted environmental receptors (wetlands, surface water, private water supplies, etc.) and the accessibility of each release site. In fact, accessibility may have proven to be the most crucial of factors when prioritizing cleanups, since many releases were not immediately discovered.

Keywords: Ice Storm, Emergency Response, Transformer Oil, MODF, PCB

1. INTRODUCTION

On December 11, 2008, an ice storm devastated the Northeast causing critical damage to the utility infrastructure, leaving up to a million residents without power in Massachusetts alone. The storm event affected over 30 cities and towns in central and western Massachusetts where heavy ice accumulations caused innumerable fallen trees, power lines and utility poles. Residents were left without critical utility services for days. In many of the hill towns, lack of electricity also meant lack of running water and/or lack of heat. The ice storm may have dissipated the following day but the aftermath was felt for days, weeks and even months by some.

In addition to leaving residents without power, the Ice Storm of 2008 also left utility companies scrambling to not only restore services but also to manage the environmental impacts related to fallen, ruptured and otherwise compromised transformers and their related contents. While the "little gray cans" hanging from utility poles rarely receive a second glance by passers-by, these transformers are oil-filled and pose varying degrees of risk associated with their hazardous contents. Mineral Oil Dielectric Fluid (MODF) is routinely used in transformers and also regulated as a hazardous material under Massachusetts regulations.

As Western Massachusetts Electric Company (WMECO) and National Grid's environmental consultants, Tighe & Bond, Inc. managed the assessment, remediation and ultimate site closure of 112 MODF releases associated with downed pole-mounted transformers throughout Berkshire, Hampshire, Hampden, Franklin, Worcester and Middlesex counties. While the ice storm may have dissipated on December 12, reports of ruptured transformers continued through January 12, 2009. With a continuously growing list of MODF releases, release sites were continually evaluated to determine which posed the greatest threat to the environment, human health and public safety.

1.1 MODF Usage and Regulation

Mineral oil dielectric fluid (MODF) is a byproduct of petroleum distillation. MODF is often used in oil-filled electrical transformers due to its stability at high

temperatures and excellent insulating properties. The most commonly used liquid in a transformer is a mineral oil known as transformer oil that has a continuous operating temperature rating of 105º C, a flashpoint of 150º C, and fire point of 180º C (Dorf 1997). A good grade transformer oil has a breakdown strength of 86.6 kV/cm (220 kV/in), that is far higher than the breakdown strength of air, which is 9.4 kV/cm (25 kV/in) (Dorf 1997). MODF is regulated under the Massachusetts Contingency Plan (MCP, 310 CMR 40.0000) and as a result, releases of MODF to the environment require assessment and/or remediation. Additionally, polychlorinated biphenyls (PCBs) were routinely used in oil-filled transformers well into the 1970's. As a result, releases of MODF to the environment may require action under state and federal regulations.

1.1.1 MODF Regulation under the MCP

The MCP establishes requirements for the notification, assessment, alternatives evaluation and remediation of releases of oil or hazardous materials to the environment. Notification requirements are based upon contaminant concentrations (Reportable Concentrations) or quantities released (Reportable Quantities). Reportable Concentrations (RCs) and Reportable Quantities (RQs) are established at 310 CMR 40.0300 of the MCP and are listed at 310 CMR 40.1600, the Massachusetts Oil and Hazardous Materials List. If a contaminant is detected in soil or groundwater at a concentration greater than its associated RC, by definition this detection constitutes a reportable release to the environment. If the quantity of oil or hazardous material released to the environment within a 24 hour period exceeds the associated RQ, by definition the incident constitutes a reportable release.

The MCP establishes a RQ of 25 gallons for MODF containing a PCB concentration less than 2 parts-per-million (ppm). Additionally, 310 CMR 40.0352 establishes RQs for materials containing PCB concentrations less than 500 ppm as well as materials containing PCB concentrations greater than 500 ppm. The RQ for MODF containing a PCB concentration greater than 2 ppm but less than 500 ppm is 10 gallons and the RQ for MODF containing a PCB concentration greater than 500 ppm is one gallon. Table 1 below identifies the number of releases in each PCB category.

Table 1. PCB Concentrations of Release Sites

PCB Content of MODF	Number of Release Sites
Less than 2 ppm PCB	78
Between 2 ppm and 500 ppm PCB	32
Greater than 500 ppm PCBs	2

The MCP establishes RCs for both soil and groundwater and each media is given two RC categories: RCS-1 and RCS-2 for soil and RCGW-1 and RCGW-2 for groundwater. RCS-1 applies to all soil samples collected within 500 feet of a residential dwelling, residentially zoned property, school, playground, recreational area or within the boundaries of a groundwater resource area categorized as RCGW-1. RCS-2 applies to all soil samples not obtained from an RCS-1 area. RCGW-1 applies to all groundwater samples collected within a current or potential drinking water source area. RCGW-2 applies to all groundwater samples that are not collected from a RCGW-1 area.

RCs associated with MODF are those which regulate the relevant constituents associated with MODF. For the purposes of assessment or remediation of MODF releases, the Massachusetts DEP Extractable Petroleum Hydrocarbon (EPH) analysis is used to characterize MODF impacts to surrounding media (soil, groundwater). EPH analysis quantifies concentrations of hydrocarbons that fall within the ranges of C_9-C_{18} Aliphatics, C_{19}-C_{36} Aliphatics and C_{11}-C_{22} Aromatics. Table 2 below identifies the RCs associated with EPH analysis.

Table 2. MCP Reportable Concentrations

EPH (mg/kg)	**GW1 (mg/l)**	**GW2 (mg/l)**	**S1 (mg/kg)**	**S2 (mg/kg)**
C_9-C_{18} Aliphatics	0.7	5	1,000	3,000
C_{19}-C_{36} Aliphatics	14	50	3,000	5,000
C_{11}-C_{22} Aromatics	0.2	5	1,000	3,000

Once a release is determined to be reportable, assessment and remediation of that release must be conducted in accordance with the applicable provisions of the MCP.

1.1.2 MODF Regulation under the EPA

MODF has been known to contain PCBs and as a result, MODF is to some extent regulated by the Environmental Protection Agency (EPA) under the Toxic Substances Control Act (TSCA). Title 40 of the Code of Federal Regulations (CFR) regulates PCBs under Part 761. Title 40 CFR Part 761 requires that a release to surface water, vegetable gardens, farm land or grazing land of any quantity of PCB material, with a concentration greater than 50 ppm, be reported

to the EPA within 24 hours. Additionally, releases of a material with a PCB concentration between 50 and 499 ppm, must be reported to the EPA within 24 hours if the quantity released exceeds 2,700 gallons and releases of a material with a PCB concentration of 500 ppm or greater must be reported to the EPA if the quantity released exceeds 270 gallons.

2. CASE STUDIES

During the Ice Storm, several scenarios evolved for the 112 spill sites that were reported. Several reports of a transformer down revealed no loss in fluid. Several revealed total loss of a transformer's contents, while still many others revealed lost volumes between these two extremes. In addition, any one (or more) of several different media types (soil, surface water, sediment, etc.) were impacted at a given release site. The sections below describe typical release scenarios and media impacted by the releases as well as describing response actions required to establish compliance with the MCP.

Table 3. Environmental Media Impacted by Release

Media Impacted	**Number of Release Sites**
No Actual Release	33
Pavement/Snow/Ice	3
Soil	69
Wetland	3
Surface Water	4

2.1. No Actual Release

In this scenario, a downed transformer was observed to be intact with no loss of oil from the unit. As an example, U.P. No. 4, located on Carr Street in Westminster, Massachusetts met this criterion. Upon arrival at the reported release site, the transformer was observed to lying on its side in a snow bank. Upon further inspection, the unit was observed to be intact, failures were not identified in the bushings, the knock-outs or the main seal. The transformer was righted, photographed and removed from the "required cleanup" list and subsequently picked up by either National Grid/WMECo crews or their environmental contractor crews for disposal. In this scenario, Tighe & Bond was responsible for developing a summary report of the critical elements of the event and documenting the exemption from reporting under the MCP.

2.2. Release to Pavement/Snow/Ice

A release of MODF to pavement, snow or ice was the least complex of reportable scenarios, requiring minimal remedial actions. In this scenario, a downed transformer released a portion of its contents to snow/ice and pavement in the vicinity of the damaged utility pole. An example for this scenario is a release on East Hoosac Street in Adams, Massachusetts. National Grid and Tighe & Bond mobilized to the site and discovered a 15-kVA transformer at the edge of the roadway. Subsequent laboratory analysis of the transformer oil confirmed that the transformer contained less than 1 ppm, which is considered non-PCB, in accordance with Environmental Protection Agency (EPA) CFR Part 761.3 and Massachusetts DEP (310 CMR 40.0000) regulations. Approximately 15 gallons MODF had flowed in a northeasterly direction down the sloped asphalt road. In addition, automobile traffic had spread the oil along a 98 foot long × 21 foot wide section of road. Response actions associated with this release scenario involved the deployment of oil absorbent materials to contain the release as well as the collection and offsite disposal of spent oil absorbent material. Additionally MODF-impacted snow, ice required removal and offsite disposal. Following the implementation of initial response actions, the asphalt roadway was found to be free of significant cracks and as such confirmatory sampling of subsurface soils was not required. Response actions resulted in post remediation conditions which would be consistent with those required for a Class A-1 Response Action Outcome (RAO) scenario under the MCP, however the volume of the release did not constitute a reportable condition under the MCP. As a result, Tighe & Bond developed a Non-Reportable Summary Report to document the event and response actions associated with the release.

2.3. Release to Soil

In this scenario, a downed transformer (or damaged and still attached to a utility pole) released some or all of its contents to soils in and around the vicinity of the UP. An example for this scenario (the most common scenario for the Ice Storm cleanups) includes a release at 62 Main Street in Orange, Massachusetts. A 50-kVA transformer was dislodged from its mount on U.P. No. 7 and fell to the ground. Upon impact with the ground surface, the transformer released all of its 19 gallons of PCB-MODF to the soil. After conducting a visual survey of the release area, Tighe & Bond personnel and National Grid's environmental contractor mobilized to the site to excavate soil, conduct confirmatory soil sampling and field-screening activities and render the site ready for restoration. Upon receipt of acceptable analytical data for the site, Tighe & Bond coordinated with National Grid's landscape contractor to have the site restored to its original condition for the property owner. Tighe & Bond was responsible for notification

and reporting requirements including a Class A-2 Response Action Outcome (RAO) Statement to fulfill National Grid's obligations under the MCP.

2.4. Release to Wetlands

In this scenario a downed transformer (or damaged and still attached) released some or all of its contents to soil, pavement or snow/ice and ultimately impacted an adjacent wetland system. The release associated with U.P. No. 23/122 on Old North Road in Worthington, Massachusetts was one such release. Heavy ice accumulation caused U.P No. 23/122 to break, rupturing the attached transformer, resulting in the release of approximately 12 gallons of MODF to the driveway at 1081 Old North Road, the asphalt road surface and the adjacent stormwater culvert, which ultimately discharges to a wetland area across Old North Road. Laboratory analytical data confirmed the MODF exhibited a PCB concentration of less than 2 ppm. Initial visual inspection of the release area indicated that the release had impacted three separate areas in the vicinity of U.P. 23/122, an area approximately 10 feet long by 5 feet wide, which included a stormwater drainage culvert adjacent to the point of impact; a wetland area approximately 55 feet long by 15 feet wide downgradient of the stormwater drainage culvert; and an area approximately 160 feet long by 10 feet wide adjacent to Old North Road. The vertical extent of contamination varied from surficial impacts to one foot below surface grade. Oil absorbent materials were deployed to the roadway surface to capture remaining MODF impacts and oil-absorbent booms were deployed at locations downgradient of the stormwater drainage culvert to contain visible MODF impacts to stormwater run-off. Response actions included the excavation of impacted media (soil, snow and ice) for offsite disposal as well as confirmatory sampling of soil and stormwater run-off within the release area.

Despite impacts to an adjacent wetland system, surface water and sediment were not impacted by this release. Standing water within wetland system at the time of the release was a function of the stormwater management system in the area and in the absence of a storm event, surface water was not present within the release area. This distinction carries with it varying compliance requirements. While stormwater sampling was conducted and compared to the Recommended Surface Water Quality Guidelines, pursuant to DEP Policy WSC-02-411, soil samples collected from within the impacted wetlands did not classify as sediment. While someone initially responding to a release may classify media being sampled as sediment based on the presence of what appears to be surface water; an important distinction needs to be made between stormwater run-off and surface water to determine whether the impacted media was soil or sediment.

The MCP defines sediment as "detrital and inorganic or organic matter situated on the bottom of lakes, ponds, streams, rivers, the ocean, or other surface water bodies". The MCP further defines surface water as "all waters other than groundwater within the jurisdiction of the Commonwealth, including, without limitation, rivers, streams, lakes, ponds, springs, impoundments, estuaries, wetlands, coastal waters and vernal pools. The release area is at times heavily influenced by the local stormwater drainage system. In the absence of a storm event, the soils are not located on the bottom of a surface water body. Tighe & Bond personnel conducted numerous site reconnaissance visits over the course of approximately three months and documented that the impacted wetlands did not contain surface waters. As a result, soil samples collected from the impacted wetland were classified as soil rather than sediment.

This release required the submittal of an Immediate Response Action (IRA) Plan, prior to the submittal of a RAO Statement to allow for adequate documentation related to classification of impacted media as soil rather than sediment.

2.5. Release to Surface Water

In this scenario, a sudden release occurred on Orpin Road in Peru, Massachusetts when ice buildup damaged power lines and broke a utility pole causing a pole-mounted transformer to fall, resulting in a release of 16 gallons of non-PCB MODF to soil, surface water and sediment. The released MODF flowed through a drainage swale/culvert, into a stream and discharged to a wetland. Initial visual inspection of the release area indicated that the release had impacted two separate areas in the vicinity of the utility pole, which would require remediation. Impacted areas included an area of soil which included a stormwater drainage culvert adjacent to the point of impact and a forested wetland area located downgraident of the surface water drainage culvert outfall. Response actions included the excavation of MODF-impacted soil, field-screening activities, confirmatory sampling (soil, surface water and sediment) and the recovery of 2,500 gallons of impacted surface water from the drainage culvert outfall area.

Observations made during subsequent site reconnaissance visits confirmed the presence of surface waters within the wetlands area. As a result, sediment samples were compared to available DEP sediment screening criteria for PCBs. In the absence of available sediment screening criteria for extractable petroleum hydrocarbons (EPH), a Stage I Environmental Screening was conducted to evaluate "readily apparent harm" and "potentially significant exposures". No visible impacts to surface water, sediment or adjacent soils and no signs of stressed vegetation or wildlife were observed during subsequent site

reconnaissance visits. Upon receipt of acceptable analytical data for the site, Tighe & Bond completed and submitted the appropriate reporting documentation (Class A-2 RAO)to DEP to complete site closure.

3. PRIORITIZATION OF RELEASES

Once the scale of ice storm devastation became known, it was obvious that a large number of transformer releases had occurred and would require cleanup. Tighe & Bond personnel worked closely with National Grid and WMECo personnel to determine reported release locations, gleaning over whatever details could be gathered from the reports and investigating each reported spill location. As reports of releases were received from National Grid and WMECo, Tighe & Bond located and visited each location to determine the severity of the release, if a reportable condition existed, what response actions would be required for each location and the sensitivity of the release site, in order to triage the site accordingly. In many cases, cleanup crews would be re-routed while on their way to a spill location if, for example, a more severe release was identified, or if roadways proved impassible due to downed lines, poles, trees or other obstructions. All told, the triaging portion of the cleanup took approximately 3 weeks to obtain the reports, visit each site and categorize each release for cleanup, reporting to DEP, etc. The cleanups, restoration and reporting was completed by the end of April 2009 for the 100 plus spills that were identified, remediated, documented and closed out between the day of the ice storm and the completion of the last cleanup which occurred on April 6, 2009.

In addition to responding to spill reports, Tighe & Bond was also provided with a list of transformers which had been retrieved and returned to area work centers prior to implementation of response actions. After cross-checking the list of retrieved transformer locations with the spill cleanup locations and locations which had been documented to not constitute a release, Tighe & Bond personnel visited the remainder of the retrieved transformer locations to assess whether a release had occured. Where spills could be identified, the sites were triaged; cleanups were completed, and closed. It should be noted that every spill site identified has been closed via either the submittal of a Non-Reportable Release Summary Report to National Grid/WMECo or submittal to DEP of a RAO Statement.

4. CONCLUSION

The Ice Storm of 2008 left in its path a wake of destruction that not only damaged property and critical infrastructure but also resulted in various environmental risks. Along with the obvious strains associated with repairing critical infrastructure, National Grid and WMECo demonstrated the utmost concern for remediating environmental impacts resulting from the ice storm. Support crews were mobilized from out of state to assist with infrastructure repair as well as environmental response and remediation activities progressed with a "whatever it takes to get the job done right" approach. In retrospect, one could easily envision a scenario in which impacts to the environment could have persisted for much longer causing significant deterioration of resource areas, had the responsible parties (National Grid and WMECo) not placed such a great deal of emphasis on the importance of comprehensive environmental response actions.

In Massachusetts, the Ice Storm of 2008 involved an unprecedented number of releases over a short period of time and dispersed over a large geographical area, with varying environmental impacts. At times environmental response activities may have seemed ad hoc, but the situation required the continual adaptation of response strategies to best minimize risk associated with such expansive and varied environmental impacts. It is uncertain whether Massachusetts will ever experience a similar storm event causing such widespread environmental impacts. However should this scenario repeat itself, or should a similar event occur, there is at least one lesson that can be learned from the Ice Storm of 2008. The ability to adapt is the most critical component of a successful emergency response effort.

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Chapter 23

COMPARISON OF INTERNATIONAL RISK-BASED SCREENING LEVELS

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ABSTRACT

In response to a growing public concern over the potential environmental and human health-related effects associated with impacted sites, many countries have launched national frameworks for remediation of high priority sites. Some countries have developed Risk-Based Screening Levels (RBSLs) as part of a national framework. RBSLs are numerical media concentrations used to inform decision making about land contamination. Many countries have yet to develop their own RBSLs. Those countries often require that the regulated community to use RBSLs developed for other countries and, in some cases, to select and defend the most appropriate RBSLs for use.

Understanding the underlying assumptions used in developing internationally available RBSLs and their intended purpose is essential to making informed decisions regarding their use to manage contamination and mitigate risk. This paper evaluates some of the underlying assumptions used by a representative group of countries in developing RBSLs.

This analysis was, by necessity, done at the level of primary assumptions, methods and technical elements. Despite this fact, some general conclusions regarding use of internationally available RBSLs have been drawn in the paper.

Keywords: International, Risk-assessment, RBSL, Screening Level

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1. INTRODUCTION

Derivation methods for RBSLs differ from country to country, and consequently, the numerical values can vary significantly. Insight into the reasons for the differences will help the regulated community and regulatory agencies alike in making informed decisions about the most appropriate RBSLs in making decisions about management of land contamination in specific regions.

Differences in the regulatory contexts under which RBSLs are developed internationally has lead to diverse terms to describe them, such as screening values, guidance values, action levels or intervention values, maximum acceptable concentrations and maximum permissible risk levels, cut off values, trigger values, and environmental quality objectives. Some RBSLs are set at risk levels deemed to be negligible or insignificant. Other RBSLs are established as warning levels, while others still are set at levels that represent potentially unacceptable risk.

Understanding the underlying assumptions used in developing internationally available RBSLs and their intended purpose is essential to making informed decisions regarding their use to manage contamination and mitigate risk. This paper will evaluate some of the underlying assumptions within the RBSLs used by a representative group of countries. Specific objectives of the review include:

- Describing the state of the science of RBSL derivation methods and their application; and
- Assessing commonalities and differences amongst international methods and the resulting numerical values.

2. PRACTICES AND PRINCIPLES

The derivation of an RBSL has both political and scientific bases. A major political issue that arises during this process is the definition of “permissible” or “tolerable” risk. The underlying questions of how to set RBSLs for deciding between “acceptable” and “unacceptable” risk has been challenging risk assessors, regulators and the public in the U.S. and European countries for several decades now. It is important to recognize, however, that decisions about levels of risk that are considered “acceptable” or “unacceptable” can be made without ever identifying the hazard, measuring the actual hazard posed (risk assessment), or addressing how best to regulate it (risk management). In other words, decisions about the risk level at which RBSLs are set are “policy” decisions, not scientific ones.

The science of RBSL development entails risk estimation, which in turn, involves exposure and toxicity assessment. Actual exposure is largely dependent on site-specific conditions, (e.g. soil type and soil properties, depth of groundwater table, etc) and on the land-use (e.g. receptor characteristics, activity on the site, type of buildings at the particular site in question). Exposure assessment is generally considered a "soft science" as it depends on conjecture (sometimes called hypothesis), qualitative analysis of data and uncertain experimental results and sometimes, anecdotal information. Toxicity is an inherent property of the contaminants present at the site in question. The science of toxicology is considered a "hard science" as it relies on experimental, empirical, quantifiable data and is intended to be objective. However, toxicology data are often interpreted differently, even by knowledgeable scientists.

The policy and scientific issues that bear on RBSL development are discussed below.

3. STATE OF THE POLICY

The question of "How safe is safe enough?" has been at the forefront of environmental decision making in the U.S., Canada, Europe, Australia and New Zealand for several decades now. Despite the longstanding debate, the question of determining "context-specific" risk acceptance criteria below which no (further) control is warranted continues to challenge the environmental community and require global attention in the urban renewal and consolidation subject area. Part of the reason is that, in spite of efforts by regulatory entities that have "blazed the trail" for risk-based decision making to carefully define their procedures and assumptions in developing RBSLs, the message is often misinterpreted by referencing the risk level set by these initial agencies as the level of "acceptable risk", implying that any higher risk is "unacceptable." Frequently the misquoted risk level is one in a million risk (1×10^{-6})

The level of risk to which RBSLs are set usually depends on the intended application within the regulatory framework, although application is inconsistent. While there are no fixed rules, there are some common practices, which are briefly discussed below.

3.1 Negligible Risk

Derivation of RBSLs that correspond to negligible risk levels are intended to maintain soil concentrations at levels such that, even under the most sensitive land use scenarios, exposure will result in negligible or de minimis risk. RBSLs established at negligible risk levels are generally used in defining long term

environmental objectives. Long term objectives for soil quality, for example, are usually based on what is considered to be a negligible risk level.

3.1.1 Unacceptable Risk

On the other hand, RBSLs set at potentially unacceptable or intolerable risk levels aim at preventing significant adverse effects from occurring. Action levels are often set at levels that correspond to a potentially unacceptable risk level.

3.1.1.1 Actions Required

While in the past, RBSLs were widely applied for forcing remediation works, RBSLs are now generally used as trigger values for some type of action, whose outcomes are then considered in relation to site-specific needs and objectives.

Actions can include remediation, but they may also take the form of:

- Restrictions in land use;
- Further investigations; and/or
- Conduct of site specific risk assessment.

4. STATE OF THE SCIENCE

4.1 Exposure Assessment

In developing RBSLs to protect human health, the intent is to ensure that exposure to contaminants at the guideline concentration will not result in adverse human health effects. Therefore, exposure assessment entails estimating daily intake. In the derivation of generic RBSLs, generic exposure scenarios are assumed that are often designed to be protective even in highly unrealistic worst-case circumstances (i.e. where highly unlikely conditions may lead to the highest possible exposure). For example, in setting residential standards for soil, it is typically assumed that the potentially exposed population has daily contact with soil via incidental ingestion, dermal contact, and inhalation over a lengthy period of time (i.e., 30 years for adults in the U.S.).

Use of overly conservative default scenarios represents “hyper vigilance” on the part of the regulators, because in setting RBSLs based on these exposure combinations, land use that is unlikely to occur is protected, in addition to land use that is likely to occur. This approach has the benefit of allowing the regulators to state categorically that contaminated land is not permitted to pose a health risk. This simplifies the complex question of “how safe is safe enough” for the

regulators, but there is cause for concern with this over-simplified approach. If these generic RBSLs are broadly misapplied as remediation goals, the result can be high economic cost for very little, if any, reduction in "actual" risk to the end user.

4.2 Toxicity Assessment

During the toxicity assessment, estimates of the tolerable daily intake (TDI) of individual compounds are made. One of the key issues in toxicology data interpretation is making sure that the toxicological information is relevant to the specific problem under investigation, in this case the potential for human health effects. Because reasonable scientists sometimes disagree about the meaning of toxicity data, different regulatory entities have developed different sets of toxicity benchmarks. These toxicity benchmarks underpin the discipline of health and environmental risk assessment and are, along with the differences in the definition of "permissible" or "tolerable" risk, a primary contributor to differences amongst the RBSLs that have been developed internationally.

One major difference between the U.S. and other countries is in the way that carcinogens are evaluated and regulated. In countries such as the Canada, the United Kingdom (U.K.), and the Netherlands, chemical carcinogens are regulated using a case-by-case approach. Known or suspected chemical carcinogens are subjected to an individual review that considers both the mechanism of action and epidemiology data. This process usually involves the formation of expert advisory committees that make the decisions regarding exposure standards or regulations, rather than an agency. The advisory body commonly uses a "weight-of-the-evidence" approach, in which all of the available information and test data are used to formulate a scientific position for consideration as the basis for a regulatory decision. This approach has historically been poorly received in the U.S. due to pressure to establish public policy that errs on the side of safety. In the wake of unrelenting financial pressure from competing social needs, and the European experience, the weight-of-evidence approach has gained momentum within the U.S. Environmental Protection Agency (EPA) in recent years (http://www.fplc.edu/risk/vol6/fall/pausten.htm).

4.3 Country-Specific Risk-Based Screening Levels:

AECOM has developed a prototype International RBSL database. The prototype database has been generated to allow comparison of human health protective RBSLs for a variety of the most common compounds across the globe. For the comparisons to be meaningful, it was important to ensure that the environmental application of the values was similar. For this reason the database currently contains RBSLs for the residential soil scenario only. Residential RBSLs have been

included for both a lower tier of "Permissible" or “Acceptable” levels and an upper tier of "Intervention" or “Action” levels. The dataset includes approximately fifty compounds representative of several different chemical classes.

Unfortunately, the methodology used in deriving the RBSLs is published for relatively few countries, and in some cases, background documentation is published but not accessible. Therefore, derivation methodology is often not transparent, which significantly hampered efforts to do a meaningful comparison amongst the various country-specific RBSLs. As a result, the reason for differences in RBSLs developed by different countries is not always evident.

For the purposes of this paper, comparisons have been made between lesser known RBSLs developed by Asian countries and those developed by several of the countries for which risk-based contaminated land management is well established and RBSLs are fairly well documented.

4.3.1 Australia and New Zealand

The approach to deriving Health-Based Investigation Levels (HILs) in Australia/New Zealand is based on the concept of tolerable daily intake (TDI), which is a dose that humans may be exposed to everyday without experiencing appreciable risk. The HILs are established for “toxic effects other than cancer” and “cancer toxic effects” as opposed to being based on mechanistic distinctions (threshold vs. non-threshold) like the other countries discussed in this paper. In developing the HILs, a portion of the TDI is allocated to each medium that may contribute to overall exposure for a particular COPC, although the proportion is not fixed. In addition, HILs are set so that total exposure (i.e., background + soil) does not to exceed the TDI. Therefore, the HILs address cumulative exposure (across all media) (NEPC, 1999a; NEPC, 1999b).

Australian Acceptable Daily Intakes (ADIs) for agricultural and veterinary chemicals (http://www.health.gov.au/internet/main/publishing.nsf/Content/ocs-adi-list.htm) have been developed and are the recommended as the primary source of toxicity information for use in establishing HILs (NEPC, 1999a), (NHMRC, 1999). For other chemicals, World Health Organization (WHO) ADIs are typically used. The target risk level at which the HILs are set is not clearly stated in the technical support documents. However, based on the fact that WHO ADIs are based on a 1 x 10^{-5} for carcinogens, and they are the primary source of toxicity values when Australian ADIs are not available, it is assumed that the Australian HILs also correspond to a cancer risk of 1 x 10^{-5}. HILs have been developed for about 40 COPCs and are defined as the concentration above which further appropriate investigation will be required (NEPC, 1999a).

4.3.2 Canada

Recommended Soil Quality Guidelines (SQGs) were published by the Canadian Council Ministers of the Environment (CCME) in 1997 (CCME, 2006). Health Canada has developed its own reference doses (TDIs for threshold substances and Risk Specific Doses or RSDs associated with risks of 10^{-4}, 10^{-5}, 10^{-6} and 10^{-7} for non-threshold substances) for a variety of contaminants and uses those in establishing SQGs.

The Canadian guidelines indicate that human health SQGs representative of both a 1×10^{-5} and a 1×10^{-6} incremental cancer risk have been developed (CCME, 2006). However, it appears from the lookup tables that the only COPC for which a SQG corresponding to a 1×10^{-5} risk level has been developed is benzene. Values for other COPCs appear to correspond to a 1×10^{-6} (one in a million) cancer risk goal. A distinguishing feature of the Canadian SQGs is the way in which background contamination is approached. Background is set at 80% of the SQG for all compounds, causing the SQG to be reduced to 20% of the original calculation.

The Canadian SQGs are defined as "numerical limits or narrative statements recommended to support and maintain designated uses of the soil environment" (CCME, 2006). SQGs have been developed for 65 COPCs.

4.3.3 China

The Chinese values are officially called Environmental Quality Standards (EQS). They were developed to the protect soil and groundwater, environment, and people who work at, visit, or live neighboring an industrial facility. They are referred to as maximum (permissible) values (PRC, 1999).

Chinese EQS values for have been developed for about 90 COPCs. Standards for Class A are defined as "target values" for soil that is suitable for all uses. Standards for Class B are intended as "action levels" above which remedial action should be taken to bring the concentrations back to Class A standards (PRC, 1999). The EQS values referenced in this paper are the Class A target values.

The EQSs designed to protect against cancer endpoints are based on an excess lifetime cancer risk of 1×10^{-5} (one in 100,000). Those established on the basis of non-cancer endpoints correspond to a hazard quotient of one (PRC, 1999). Anecdotal information suggests that the EQS values represent a translation of the U.S. values with exposure assumptions changed to better describe the Chinese population. Therefore, it is assumed that U.S. toxicity factors were used in their derivation, although this has not been confirmed.

4.3.4 Hong Kong

The Hong Kong Environmental Protection Department (EPD) recently published Risk-Based Remediation Goals (RBRGs) for Contaminated Land Management (EPD, 2007a). RBRGs are intended as site assessment criteria that are appropriate for most sites in Hong Kong, where humans are the only significant receptors that require protection.

The Hong Kong RBRGs were developed as threshold contaminant concentrations, below which exposure is considered minimal. However, despite the definition of the RBRGs as levels below which exposure is considered minimal, the Guidance Manual for the Use of Risk-Based Remediation Goals (RBRGs) for Contaminated Land Management (EPD, 2007a) states that when concentrations of soil or groundwater are detected above the RBRGs, "cleanup" is required.

The Guidance Manual indicates that relevant overseas methodologies, such as ASTM (1995 and 2000) and CCME (NEPC, 1999) were used in developing RBRGs with input of local data insofar as possible. Toxicity data used in deriving the RBRGs were derived from a number of sources, but primarily from the U.S. EPA's Integrated Risk Information System (IRIS) at http://www.epa.gov/iriswebp/iris/subst/index.html. RBRGs protective of cancer endpoints are based on an excess lifetime cancer risk of 1×10^{-6}. Those established on the basis of non-cancer endpoints correspond to a hazard quotient of one (EPD, 2007a; EDP, 2007b).

4.3.5 Netherlands

Human health based RBSLs developed by the Netherlands are called Dutch Intervention Values (DIVs). The DIVs are intended to be used in a defined policy framework (i.e., the Dutch Soil Protection Act) to identify areas that are "Seriously Contaminated" and are only intended for use in evaluating polluted properties. A distinguishing feature of the DIVs is that they are to be applied on a spatial scale. For there to be an instance of serious contamination, the average concentration of a minimum of 25 m^3 of soil must exceed a DIV. In instances where serious contamination is defined, it then needs to be determined whether action to deal with the contamination is urgently required. The factors which dictate urgency are the actual risks to which man and ecosystems are currently being subjected, and the risks of migration. These are highly dependent on land use (RIVM, 2000).

The source of human toxicity values is the Re-Evaluation of Human-Toxicological Maximum Permissible Risk Levels (RIVM, 2001). Dutch toxicity values are expressed as Maximum Permissible Risk (MPR) values, which quantify

the human-toxicological risk limits (i.e., TDI, tolerable concentration in air (TCA), oral cancer risk and/or inhalation cancer risk) for approximately 50 chemicals. For compounds that exhibit threshold effects, the MPR has been defined as a TDI. For genotoxic carcinogens (using the non-threshold approach), the MPR is defined as the exposure level with an excess lifetime cancer risk of 1×10^{-4} (1 in 10,000) for the oral (CR_{oral}) or inhalation ($CR_{inhalation}$) pathways. DIVs have been developed for 130 COPCs.

4.3.6 Thailand

The Pollution Control Department of Thailand has published Soil Quality Standards (SQS) for a limited number of compounds (PCD, 2004). Thai SQSs have been developed for 36 COPCs.

The Thai standards for non-carcinogens correspond exactly to the U.S. EPA Region 9 Preliminary Remediation Goals (PRGs) from 2000. SQSs for carcinogens are a factor of 10 higher than the U.S. EPA Region 9 PRGs, which were set at a target cancer risk goal of 1×10^{-6}. Therefore, the SQSs for carcinogens correspond to a target cancer risk of 1×10^{-5}.

4.3.7 United Kingdom

The official values for England and Wales, are the Soil Guideline Values (SGVs) published by the Environment Agency (EA, 2010). The SGVs derived for non-threshold substances are derived on the basis of a hierarchy of authoritative sources developed specifically for soil contamination, and a target risk of 1×10^{-5} where methods as defined by the EA are applicable. Additionally the principal of "As Low As Reasonably Practicable" or ALARP is applied for genotoxic carcinogens (EA, 2009a; EA, 2009b). A total of eleven SGVs have been developed by the EA at this point following a recent review of underlying assumptions and four additional reports are in process. SGVs and associated guidance previous to 2008 were formally withdrawn as of August 2008 (EA, 2010).

4.3.8 United States

The U.S. EPA recently harmonized RBSLs formerly published by U.S. EPA Regions 3, 6, and 9 by publishing a single table of generic Regional Screening Levels (RSLs) at http://www.epa.gov/reg3hwmd/risk (U.S. EPA., 2010a).

The primary source for toxicity values used in deriving the U.S. RSLs is the Integrated Risk Information System (IRIS) (U.S. EPA., 2010b), an on-line computer database of toxicological information (http://www.epa.gov/iris/index.html), which contains toxicity values for hundreds

of compounds. Constituents with known or potential noncarcinogenic effects are assumed to have a dose below which no adverse effect occurs. This dose is called the threshold dose. The Reference Concentration (RfC) is the corresponding inhalation toxicity benchmark for noncarcinogens. The underlying assumption made by U.S. EPA during regulatory risk characterization for constituents with known or assumed potential carcinogenic effects is that no threshold dose exists (i.e., some finite level of risk associated with each non- zero dose). This differs from other International agencies, which consider the possibility that some carcinogens act through a threshold mechanism. The U.S. EPA also differs from other International agencies in considering toxicological effects other than carcinogenicity (i.e., structural chromosome aberrations, DNA damage/repair, and in vitro transformation) as supportive evidence for a chemical's potential carcinogenicity in classifying compounds as carcinogens (U.S. EPA., 2003). Therefore, more COPCs are considered potential carcinogens under the U.S. risk assessment framework.

The RSLs correspond to either a 1×10^{-6} risk level for carcinogens or a hazard quotient of one for non-carcinogens. The EPA RSLs are defined as chemical-specific concentrations for individual contaminants in soil that may warrant further investigation or possibly, site cleanup. The technical support document for the RSLs emphasizes that RSLs should not be considered cleanup standards until other response options have been evaluated and considered (U.S. EPA., 2010a).

4.4 Comparison of Risk-Based Screening Levels

Table 1 shows a side-by-side comparison of country-specific RBSLs for a select group of COPCs. These compounds were selected because they tend to be some of the COPCs of most public concern and they often drive contaminated land management decisions. Values in bold represent the lowest COPC-specific RBSL across the represented countries. Italicized values represent the highest COPC-specific RBSL amongst all of the countries. Table 2 is a comparison of exposure assumptions implicit in the country-specific RBSLs.

4.4.1 Most Conservative RBSLs

As shown in Table 1, the Canadian SQGs (Soil Quality Guidelines) represented the lowest of the RBSLs for eight out of the 15 COPCs. The conservative nature of the Canadian SQGs is the result of several highly conservative assumptions made by the CCME in their derivation. Those assumptions (CCME, 2006) are:

- Guidelines developed considering all relevant pathways and media (only 20% of the tolerable daily intake allocated to soil);
- SQGs are calculated after considering the sum of the background soil exposure; and
- With the exception of benzene, all SQGs for carcinogens correspond to a 1 x 10^{-6} cancer risk.

4.4.2 Least Conservative RBSLs

The DIVs (Dutch Intervention Values) had the highest RBSL for six out of the 15 COPCs.

The liberal nature of the DIVs is due primarily to:

- DIVs for carcinogens correspond to a 1 x 10^{-4} cancer risk; and
- Carcinogenic potency is expressed as a MPR (Maximum Permissible Risk) level that recognizes that non-genotoxic carcinogens have a threshold below which carcinogenic effects do not occur (by contrast to the non-threshold approach assumed in the U.S.).

The DIVs for soil were developed for use in determining whether land that is "already contaminated" poses a serious threat to public health. In addition, the DIVs are intended to be applied on a spatial scale, not for comparing to individual sample results. For there to be an instance of "serious contamination", the average concentration of a minimum of 25 m^3 of soil or sediment, must be higher than the DIV for at least one substance. Dutch Target Values, which are intended to protect sustainable soil quality and have an ecological health basis, are intended for use in evaluating "uncontaminated" land (RIVM, 2000).

4.4.3 Sources of Variability

Some sources of variability in the RBSLs presented in this paper are illustrated in Table 2 and discussed below.

5. EXPOSURE PATHWAYS

The exposure pathways considered in deriving RBSLs are fairly consistent amongst the countries evaluated in this paper. However, several of the country-specific RBSLs (Australia, Netherlands, U.K.) appear to include the additional pathway of produce ingestion (JRC, 2007) (NEPC, 1999b) (RIVM, 2007) (EA, 2009a). However, it is not entirely clear whether the default RBSLs include produce

ingestion for all COPCs or if the pathway is only included for those COPCs for which produce ingestion has the potential to be a risk driver. Again, the lack of clarity in many of the support documents makes such issues difficult to resolve.

Table 1. Comparison of Country-Specific Risk-Based Screening Levels

Country:	Australia New Zealand	Canada	China	Hong Kong		Netherlands	Thailand	United Kingdom	United States
				Urban	Rural				
Reference:	NEPC, 1999a	CCME, 2006	PRC, 1999	EPD, 2007a		RIVM, 2000	PCD, 2004	EA, 2010	U.S. EPA, 2010a
METALS									
Arsenic	*100*	12	20	22.1	21.8	55	3.9	32	**0.39**
Chromium VI	100	0.4	NA	221	218	*380*[1]	300	NA	**0.29**
Lead	300	**140**	**140**	248	255	*530*	NA	NA	400
PETROLEUM RELATED CONSTITUENTS									
Benzene	1.1	**0.0068**	0.2	0.704	0.279	1	*6.5*	0.33	1.1
Toluene	68	**0.08**	26	1440	704	130	520	610	*5000*
Ethyl-benzene	48	**0.018**	10	*709*	298	50	230	350	5.4
Xylenes	48	**2.4**	5	95	36.8	25	210	230[8]	*630*
MTBE[3]	NA	NA	NA	**6.88**	**2.8**	*100*[4]	NA	NA	43
PERSISTENT ORGANIC POLLUTANTS									
Total Dioxin/ Furans	NA	**0.000004**	NA	0.001	0.001	0.001[4]	NA	*0.008*[2]	0.0000045[5]
Aldrin	NA	NA	0.04	NA	NA	*4*[9]	NA	NA	**0.029**
DDT[6]	NA	**0.7**	1	NA	NA	4[9]	*17*	NA	1.7
Total PCBs[7]	*10*	1.3	**0.2**	0.236	0.226	1	2.2	NA	0.22
CHLORINATED SOLVENTS									
Trichloro-ethene	NA	**0.01**	12	0.523	0.211	*60*	28	NA	2.8
Tetrachloro-ethene	NA	0.2	4	**0.101**	**0.044**	4	*57*	NA	0.55
Vinyl Chloride	NA	NA	NA	NA	NA	0.1	*1.5*	NA	**0.06**

NA – Not available

Bolded values represent the lowest COPC-specific RBSL.

Italicized values represent the highest COPC-specific RBSL.

[1] Value for total chromium, not chromium VI.

[2] U.K. - Value should be compared to the sum of all dioxins, furans and dioxin-like PCBs.

[3] MTBE - Methyl-tert butyl ether

[4] Netherlands - No reliable value could be derived. Value given is called an "indicative level for serious soil contamination".

[5] USA - Value for 2,3,7,8-TCDD.

[6] DDT - p,p'-Dichlorodiphenyltrichloroethane

[7] PCBs - Polychlorinated biphenyls

[8] Value for p-Xylenes, as this is the most conservative of the three xylene values given.

[9] Netherlands – Values represent sum of aldrin, eldrin & dieldrin, and sum of DDT, DDE & DDD respectively.

Table 2. Comparison of Country-Specific Assumptions for Development of Residential Risk-Based Screening Level

Country:	Australia New Zealand	Canada	China	Hong Kong		Nether-lands	Thailand	United Kingdom	United States
				Urban	Rural				
Reference:	NEPC, 1999b	CCME, 2006	PRC, 1999	EPD, 2007b		RIVM, 2007	PCD, 2004	EA, 2009a	U.S. EPA, 2010a
EXPOSURE PATHWAYS									
Soil Ingestion	√	√	√	√	√	√	√	√	√
Dermal Contact w/Soil	√	√	√	√	√	√	√	√	√
Inhalation of Outdoor Air	√	√		√	√	√	√	√	√
Inhalation of Indoor Air	√	√		√	√	√	√	√	√
Consumption of Produce	√					√		√	
TARGET CANCER RISK									
1 X 10^{-4}						√			
1 X 10^{-5}	√		√				√	√	
1 X 10^{-6}		√		√	√				√
EXPOSURE ASSUMPTIONS (Adult/Child[1])									
Adult Body Weight Child (kg)	64 13.2	71 16.5	55.9	50 15	50 15	70 15	NS	71 5.6-20[4]	70 15
Adult Inhalation Rate Child (m^3/day)	22 15	15.8 9.3	NA	20-21[2] 10	20-21[2] 10	20 7.6	NS	12-16.4[4] 8.5-12.7[4]	20 20
Adult Soil Ingestion Rate Child (mg/day)	25 100	20 80	50	200 100	200 100	50 100	NS	50 100	100 200
Adult Skin Surface Area Child (m^2)	NA	2500 2600	2550	2300 1200	2950 1500	900-1700[3] 500-2800[3]	NS	1610-2200[4] 300-870[4]	5700 2800
Adult Exposure Duration Child (years)	70 Age	30 4	40	30 6	30 6	70 6	NS	70 6	30 6
Regulatory Action Required Upon Exceedance									
Intervention						√[5]			
Remediation		√		√[6]	√[6]				
Action (further investigation, risk assessment, restrict landuse)	√		√				√[7]		√
Not Specified								√[8]	

NS – Thai exposure assumptions "not specified".

[1]Exposure assumptions for the child are specific to children between the ages of birth to six years (or closest age group for specific regulatory agency).

[2]Different inhalation rates for indoor and outdoor air.

[3]Different exposed skin surface area assumed for indoor and outdoor.

[4]CLEA model divides a lifetime into eighteen age intervals (or age classes) to account for variations in exposure characteristics with age.

[5]For there to be an instance of serious contamination, the average concentration of a minimum of 25 m^3 of soil must exceed a Dutch Intervention Value. In instances where serious contamination is defined, it then needs to be determined whether action to deal with the contamination is "urgently" required. Factors which dictate urgency are the actual risks to which man and ecosystems are being subjected, and the risks of migration.

[6]Defined as levels below which exposure is considered minimal, but the guidance (EPD, 2007a) states that when concentrations of soil or groundwater are detected above the RBRGs, "cleanup" is required.

[7]Action required upon exceedance of Thai standards is not specified, but since they are based on U.S. EPA Region 9 Preliminary Remediation Goals (recently superseded by EPA Regional Screening Levels), it is assumed that they represent action levels, similar to the U.S. exposure assumptions.
[8]Soil Guideline Values (SGV) are described as an "acceptable" level of soil contamination, but U.K. guidance does not indicate that concentrations above the SGV are "unacceptable". Required action is not specified.

The Chinese EQSs (Environmental Quality Standards) do not appear to consider the inhalation pathway (PRC, 1999), which seems sets these RBSLs apart from the others.

In setting SQGs, the CCME (Canadian Council Ministers of the Environment) only allocates 20% of the residual acceptable daily intake (ADI) to soil because it is assumed that there are other media to which people are exposed (air, water, food, and consumer products) that must be taken into account in setting an RBSL (CCME, 2006). Australia takes a similar approach in developing its HILs (Health-Based Investigation Levels) except that the allocation is not fixed (generally, the HIL allocation has been higher than 20%) (NEPC, 1999a).

6. EXPOSURE ASSUMPTIONS

The soil ingestion rate is usually the most sensitive input parameter to the equations used to derive soil RBSLs for most COPCs. Exceptions to this general rule of thumb, however, include highly lipophilic or fat soluble COPCs (i.e., POPs), for which dermal uptake can sometimes represent a more significant exposure pathway than soil ingestion. There are a few highly volatile COPCs for which the inhalation pathway dominates the soil RBSL (e.g., trimethylbenzenes), but these are rare.

Interestingly, the soil ingestion rates assumed in developing the Canadian SQGs (lowest RBSLs for eight out of 15 COPCs) are amongst the least conservative (lowest) of all the featured countries. The exposed skin surface area assumed in development of the Canadian SQGs is in the range of that assumed by the other countries, although the area assumed for children, age five to 11 years, could be considered somewhat high relative to the other countries. Of the country-specific RBSLs compared in this paper, the U.S. exposure assumptions are generally the most conservative. U.S. RSLs represented the lowest of the RBSLs for four out of 15 COPCs.

There is variability in other exposure assumptions used by different countries as well. For example, the body weight assumed in developing the Chinese EQS and Hong Kong RBRGs are lower (50 – 55 kg) (PRC, 1999), (EPD, 2007b) than the body weight assumed by western countries (≈ 70 kg) (CCME, 2006), (U.S. EPA., 2010a), (RIVM, 2007), (EA, 2009a) and Australia/New Zealand (64 kg) (NEPC, 1999b).

7. TOXICITY BENCHMARKS

An underlying assumption made by U.S. EPA in developing toxicity benchmarks for constituents with known or assumed potential carcinogenic effects that differs from other International agencies is that, for carcinogens, no threshold dose exists (i.e., there is some finite level of risk associated with each non-zero dose) (U.S. EPA., 2003). International agencies in many other countries (Australia/New Zealand, Canada, U.K., Netherlands) (NEPC, 1999a), (CCME, 2006), (EA, 2009b) (RIVM, 2001) consider the possibility that some carcinogens act through a threshold mechanism, which is generally considered to be the scientifically accurate assumption.

The area of cancer assessment is one where different national strategies in environmental policies are often reflected. For example, Health Canada classifies benzene as carcinogenic to humans but does not derive an oral cancer risk value because it considers exposure by the oral route to be negligible (CCME, 2006). On the other hand, the Dutch National Institute of Public Health and the Environment (RIVM) and the U.S. EPA have both developed an oral cancer toxicity factor by doing a route extrapolation from inhalation unit risks based on leukemia incidence in occupationally-exposed humans (RIVM, 2001; U.S. EPA, 2003).

It is not possible to say definitively whether one agency or another is consistently more or less conservative than the others in deriving toxicity benchmarks, just that toxicity information is often interpreted differently from one country to the next and these interpretations influence the level at which RBSLs are set.

8. TARGET RISK GOALS

Target risk goals used in establishing country-specific RBSLs reflect policy decisions made by the individual international regulatory entities regarding what represents an "acceptable" or "tolerable" risk. All of the RBSLs described in this paper correspond to a non-cancer hazard quotient of 1, while the RBSLs for carcinogens correspond to a range of target cancer risk goals from 1×10^{-4} to 1×10^{-6}. The DIVs (Dutch Intervention Values) correspond to a cancer risk of 1×10^{-4} and the U.S. RSLs, Canadian SQGs (except for benzene), the Chinese EQS, and Hong Kong RBRGs correspond to a cancer risk of 1×10^{-6}. The remaining RBSLs (Australia/New Zealand, Thailand, U.K.) correspond to a target cancer risk goal of 1×10^{-5}. As the target risk goal represents the starting point from which RBSLs are calculated, the variances amongst different countries clearly influences the level at which RBSLs are set.

The ITER (International Toxicity Estimate for Risk) is a free Internet database of human health risk values and cancer classifications for over 600 chemicals of environmental concern from several organizations worldwide (TERA, 2008). The ITER database is available at http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?iter and presents risk data in a tabular format along with a synopsis explaining differences in data and a link to each organization for more information. This database represents an excellent source of information on the differences between toxicity factors used to set country-specific RBSLs. However, care must be taken to compare risk values that are expressed in the same terms. To do this, it is necessary to read the text below the summary tables in the database, as the tables express the health risk values in different units of measure.

9. CONCLUSIONS

The speed and ease of application are amongst the greatest benefits of applying generic default RBSLs and are the primary reason why the use of RBSLs has become so common. Their use can provide clarity, comparability and transparency to non-specialist stakeholders. However, their inappropriate use can, and often does, lead to misleading results and misallocation of funds.

Countries that have formally developed or adopted RBSLs have done so under different National regulatory frameworks and exceedance of RBSLs requires different response actions from one country to the next. Most countries use generic RBSLs as part of a broader approach that includes the option of conducting a site-specific risk assessment as one of several possible actions in circumstances where a RBSL has been exceeded. However, there are some exceptions, such as Hong Kong where an exceedance requires cleanup. Exceedance of Chinese Class B "action levels", which are not discussed in this paper, also requires remediation. However, a key aspect of all programs should be evaluation of the applicability of the generic RBSLs to individual contaminated sites. It is important to note, however, that RBSLs are developed for evaluating and setting priorities for impacted sites on a consistent risk basis. They are rarely intended to be considered as thresholds above which health effects are inevitable or to be used as "de facto" cleanup goals.

The significance of exceeding a RBSL, whether it corresponds to a maximum permissible concentration or an action level, should be judged in relation to the conservative assumptions adopted during development. The significance of a RBSL exceedance should also consider the target risk level at which the RBSL is set relative to the level of risk posed by other sources (e.g. risk of inhalation of contaminated air or risks from smoking).

Understanding the underlying assumptions used in developing internationally available RBSLs is essential to making informed decisions regarding their use to manage contamination and mitigate risk, even if they are used outside of the National regulatory framework under which they were developed. This paper has attempted to explain some of the apparent differences between a subset of the internationally available RBSLs. In some cases, differences can be attributed to different national strategies in environmental policies (e.g., whether background or cumulative exposure across multiple media is considered). Moreover, the RBSLs have been set at different target risk goals, which reflect differences in what is considered an "acceptable" risk from one country to the next. In other cases, the reasons for differences between internationally accepted RBSLs are not clearly understood due to poor documentation.

There are a number of important considerations in determining the appropriateness of using of the generic RBSLs discussed in this paper outside of the regulatory framework for which they were intended. For example, the Canadian SQGs were developed considering all other media (air, water, food, consumer products) and background concentrations. As a result, only 20% of the tolerable daily intake was allocated to soil in establishing the SQGs. This, may or may not be an appropriate allocation depending on the site and the regulatory framework in which these SQGs are used.

The Dutch Intervention Values (DIVs) were developed for use in determining whether land that is "already contaminated" poses a "serious" threat to public health. However, the DIVs are intended to be applied on a spatial scale, not for comparing to individual sample results. For there to be an instance of "serious contamination" under the regulatory framework for which the DIVs are intended, the average concentration of a minimum of 25 m^3 of soil must be higher than the DIV for at least one substance. However, even when a situation of "serious contamination" is properly identified based on exceedance of the DIV by the recommended volume of soil, a number of factors should still evaluated, such as the actual risks to which man and ecosystems are subjected and the potential for migration, in determining the urgency of intervention.

Thai SQS values appear to be based on U.S. EPA PRGs (preliminary remediation goals) from 2000. The EPA Region 9 website (http://www.epa.gov/region09/waste/sfund/prg/index.html) indicates that the Region 9 PRGs should no longer be used for contaminant screening of environmental media because they have been replaced with the more current U.S. EPA Regional Screening Levels (RSLs). The EPA Region 9 PRGs had not been updated in years and, therefore, for a number of COPCs, the PRGs are no longer based on up-to-date toxicity information. Therefore, the Thai standards are out of date.

The U.K. SGVs have been the subject of much confusion and controversy amongst both regulators and practitioners regarding the U.K. SGVs (Soil Guideline Values). The problem identified with the SGVs is that they essentially provide an "acceptable" level of soil contamination, but do not necessarily indicate whether concentrations at or just above the SGV are "unacceptable". This called into question whether the SGVs achieve their primary objective, which was to help identify contaminated land. The SGVs were formally withdrawn as of August 2008, however since early 2009 new risk assessment documentation has been published in the U.K. in an attempt to clear up some of the earlier confusion.

Finally, in deriving or choosing RBSLs for carcinogens, it is necessary to take a view about the acceptability of levels of additional risk. What is considered to be the acceptable level of risk can vary over orders of magnitude (usually between 1 x 10^{-4} and 1 x 10^{-6}) between different organizations. As shown in Table 2, out of the eight countries for which RBSLs have been evaluated in this paper, three have established RBSLs for carcinogens at a 1 x 10^{-6} cancer risk; four have established RBSLs at 1 x 10^{-5}, and one at 1 x 10^{-4}. Despite the differences in target cancer risk goals used by different authoritative organizations, there appears to be growing consensus for selecting a target risk of 1 x 10^{-5} as the upper-bound "acceptable" risk (JRC, 2007). The consensus may be moving toward selecting 1 x 10^{-5} as the upper-bound "acceptable" risk from one COPC and 1 x 10^{-4} as the upper-bound "acceptable" risk from any one source.

The following conclusions regarding the use of internationally available RBSLs discussed in this paper are provided:

- Canadian SQGs only allocate 20% of the tolerable daily intake to soil and are set at an "acceptable" risk goal of 1 x 10^{-6}, making them amongst the more conservative internationally available RBSLs;
- DIVs are amongst the least conservative of the RBSLs and are not generally appropriate for use in Tier 1 screening assessments where maximum soil concentrations are compared to "generic" RBSLs as they are intended for application to a minimum of 25 m^3 of "impacted" soil;
- Thai SQS values are out of date as they are based on U.S. EPA PRGs from 2000, and all PRGs have been replaced by U.S. RSLs;
- The U.K. SGVs have been fluctuating rapidly for several years, but some consensus has now been reached and SGVs are being published again.
- There appears to be growing consensus for selecting a target risk of 1 x 10^{-4} as the upper-bound "acceptable" risk from any one source and 1 x 10^{-5} as the upper-bound "acceptable" risk from any one COPC.

This analysis was, by necessity, done at the level of primary assumptions, methods and technical elements. A detailed comparison of algorithms and input

values has not yet been undertaken. This is primarily because many of the RBSLs that have been developed are not well documented. A detailed analysis of this sort will likely require surveying the regulators in countries for which risk-based management of contaminated land is relatively new to gain better insight into the bases for the RBSLs that have been developed in those countries.

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PART IX: Sediments

Chapter 24

CHEMICAL CHARACTERISTICS OF SEDIMENT OF THE LOWER HACKENSACK RIVER, NEW JERSEY

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ABSTRACT

The sediments of the Lower Hackensack River provide a record of contamination from ongoing and historical processes in a highly urbanized watershed in northern New Jersey. This estuarine river runs through suburban and small cities in its northern, freshwater reaches; passing south through 8,500 acres of wetlands known as the Hackensack Meadowlands to its mouth at Newark Bay. The goal of this review is to depict the environmental quality of this ecosystem using data derived from sediments collected in 2003 during a Fishery Resource Inventory. This study replicated a similar inventory conducted in 1988, allowing for elucidation of spatial and fifteen-year trends. In the sediments, heavy metal concentrations, grain size distribution and carbon content were analyzed.

Based on sediment guidelines published by NOAA in 1995, the estuary is in "poor" ecological condition; the average concentration of one contaminant, mercury, exceeds the ERM (ERM is the median concentration of a contaminant observed to have adverse biological effects in the literature values examined). It is also apparent that enrichment of mercury and other metals occurs in the Hackensack River north of the mouth of Berry's Creek, a major tributary known for its legacy of industrial contamination. In addition to this spatial trend, a good predictor of metal concentrations in the sediments appears to be the amount of organic matter present; preservation of organic matter in the river increases as tidal influence is diminished. The sulfate/sulfide cycle, driven by the reaction between seawater and the organic matter, appears to be the primary mechanism.

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Between 1988 and 2003, the average sediment concentrations were reduced significantly for cadmium (71%), chromium (63%), copper (73%) and lead (22%); zinc concentrations remained approximately the same (mercury was not analyzed in 1988). These results suggest a natural attenuation process at work, as burial preserves sulfide rich contaminated sediments.

Keywords: contamination, estuary, organic matter, sediments

1. INTRODUCTION

In 1987 the Hackensack Meadowlands Development Commission (HMDC) initiated a two-year fishery study of the lower Hackensack River. The purpose of the study was to provide an inventory of the fishery resources within the boundaries of the Hackensack Meadowlands District. The data was used to asses the fish population that was using the River, and to determine the extent to which the River and its tributaries provided habitat and refuge for those species. The data from the 1987-88 study was presented in the HMDC's 1989 fishery resource inventory report (HMDC, 1989), which is frequently requested by the State and Federal resource agencies, environmental consultants and the public (Bragin et al., 2005).

The HMDC, which was renamed the New Jersey Meadowlands Commission (NJMC) on August 29, 2001 had always envisioned repeating the fishery inventory periodically to determine whether the fish community would respond to perceived water quality improvements that were occurring within the District. Therefore, in 2001, the NJMC began a new fishery resource inventory of the Hackensack River, the goal of which was to repeat the earlier study and compare the results.

Rather than simply repeat the inventory, the NJMC decided that additional studies would be beneficial. The additional studies included: an investigation of selected contaminants in fish tissue; a study of the reproductive health of the white perch; a food habits study of the white perch; an investigation of the benthic invertebrates that live in and on the river bottom; and a chemical and textural analysis of the river bottom sediments. The results of each of these companion studies are reported under separate cover, and can be obtained from the MERI library.

1.1 Study Design

A total of 21 sampling locations were established during the 1987-1988 fisheries study (HMDC, 1989). The locations were selected with the assistance of the New Jersey Department of Environmental Protection (NJDEP) Bureau of Marine

Fisheries. Sites were selected based on their spatial distribution along the River (within the HMD) and the suitability of deploying and retrieving each of the gear types in order to sample subtidal and shallow inshore areas of the River. The gear types were selected to match what the NJDEP Bureau of Marine Fisheries used in making collections for other fisheries studies in estuarine waters around the State.

The locations sampled during the 2001-2003 fisheries study depicted in Figure 1 replicated the 1988 sites. Due to changes in site conditions during the intervening 13 years, two sampling sites, T9 and TN1, were slightly re-located from their original 1987-1988 locations. Sediment samples were collected by the MERI fisheries team once from each sampling location during the study. Three replicate samples were collected from each location, for a total of 78 sediment samples (river trawl locations were sampled at the shallow and deep end). Table 1 lists the sediment sampling sites, indicating lower Hackensack River segment, river mile or tributary, and fisheries gear type used at each location.

This report focuses solely on the chemical and textural analysis of the river bottom sediments. Sediments were characterized by parameters helpful for measuring ecological-risk and for making comparisons between sampling locations. In the sediments, heavy metal concentrations, grain size distribution and total organic carbon content were analyzed. "These data confirm whether samples were collected in depositional zones, as indicated by relatively higher carbon values and a higher percentage of fine-grained particles, and provide a qualitative indication of bioavailability. Depositional zones are areas of highest potential contamination" (Frasco, 1997). The metals arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel and zinc were analyzed in all sediment samples.

2. MATERIALS AND METHODS

2.1 Field Methods

Sediment samples were collected using a standard 316-stainless steel Ponar grab sampler (sampling area of 0.05 m^2, weight ~50 lbs.), deployed from a 21 foot Privateer work skiff via a davit equipped with a battery-operated winch. The collection of sediments for chemistry and textural analyses occurred over six days between July and December of 2003, with the majority of the samples collected in December. The first step of the sediment collection process was to anchor the boat above the sampling location. Water depth was ascertained using a Garmin model 160 Blue depthfinder. Next, the Ponar grab was arranged in the open position and it was slowly lowered through the water column using a sufficient length of 5/8 inch line until it contacted the sediment. Once the Ponar grab was on the bottom,

the line was allowed to go slack, and was then given a sharp tug to release the closing mechanism. As the Ponar grab closed, it scooped up approximately 8.2 liters of sediment (i.e., for a full grab in soft sediments. At locations where the substrate was clay or hard-packed sediments, the Ponar was dropped from a

Table 1. Sediment Sampling Sites

	River Mile	Sampling Site	Net Type
Upper River	12.5	TN 6	Trap Net
	12.0	GN 3	Gill Net
	10.9	T5-S	Trawl Shallow
	10.9	T5-D	Trawl Deep
	10.9	TN 5	Trap Net
	10.6	S 3	Seine
	9.3	T4-S	Trawl Shallow
	9.3	T4-D	Trawl Deep
	9.2	TN 4	Trap Net
Middle River	7.4	S 2	Seine
	7.1	TN 3	Trap Net
	7.0	T3-S	Trawl Shallow
	7.0	T3-D	Trawl Deep
	6.8	GN 2	Gill Net
Lower River	5.4	T2-S	Trawl Shallow
	5.4	T2-D	Trawl Deep
	3.8	T1-S	Trawl Shallow
	3.8	T1-D	Trawl Deep
	3.6	TN 1	Trap Net
	3.5	S 1	Seine
	3.0	GN 1	Gill Net
Tributary	Sawmill	T6	Trawl
	Sawmill	TN2	Trap Net
	Berry's	T7	Trawl
	Mill	T8	Trawl
	Cromakill	T9	Trawl

height of one to two feet above the sediment surface in an attempt to collect a sufficient volume of material for the required laboratory analyses in one grab). The winch was then used to raise the Ponar grab containing the collected sediment to the surface. The davit was swung over the deck of the boat and the

Ponar grab was slowly lowered into a laboratory cleaned plastic tub (18.5 inches long x 14 inches wide x 7 inches high). Water overlying the sediment sample (if any) was slowly decanted through the screens at the top of the Ponar grab sampler and was discarded. The Ponar grab was then opened, releasing the collected sediments into the plastic tub. Any sediment adhering to the walls of the Ponar grab were scraped into the tub using a plastic scoop. The sediments were homogenized using the same plastic scoop, and were transferred to properly labeled, pre-cleaned, three-liter glass jar with a Teflon lid, and placed on ice in coolers for transfer to the Meadowlands Environmental Research Laboratory (MERI) laboratory. Three replicate samples were collected at each sampling location. Details regarding the collection location, date and time of sample collection, water depth, observations related to the sediments collected in each replicate sample, and any other pertinent observations were recorded in a field notebook, and are summarized in Table 2.

Table 2. Sediment Sampling

SITE	Date Sampled	Water Depth (ft)	Visual Description of Sediment	Additional Notes
GN1	12/04/03	~15	grey sandy mud (Rep 2 produced a sheen)	Rep.1 required 3 grabs, and Rep 2 required 2 grabs
GN2	12/29/03	9	sticky grey clay	Needed 2 grabs for each replicate
GN3	08/05/03	8.4	very soft black mud (consistency of mayonnaise)	Each replicate was a full grab
S1	12/04/03	4	mud underlain by sand & gravel (mud produced a sheen)	Replicate 1 required 3 grabs
S2	12/04/03	3	sandy mud	Replicate 1 required 3 grabs
S3	12/12/03	2.5	soft black mud w/ thin brown surface layer	Each replicate was a full grab
T1 deep	12/18/03	16	stiff blackish-grey clay w/ a thin brown surface layer w/ sand & shell hash	Amphipods noted in samples
T1 shallow	12/18/03	11	stiff grey clay	Each replicate was between 1/2 to 3/4 full
T2 deep	12/18/03	19	brown mud w/ some sand. Rep. 1 produced a slight sheen	Replicates 2 & 3 required 2 grabs each
T2 shallow	12/18/03	11	brown sandy mud w/ organic matter & silvery sheen	Each replicate was ~1/4 full
T3 deep	12/18/03	15	soft black mud w/ thin (~1.5 - 2 inch thick) brown surface layer	Each replicate was a full grab

Table 2. Sediment Sampling (continued)

SITE	Date Sampled	Water Depth (ft)	Visual Description of Sediment	Additional Notes
T3 shallow	12/18/03	4	soft black mud w/ thin brown surface layer	Each replicate was a full grab
T4 deep	12/12/03	14	hard sticky grey clay	Needed 2 grabs for each replicate
T4 shallow	12/12/03	~7	soft black mud	Each replicate was a full grab
T5 deep	07/11/03	16.8	brownish-black mud (consistency of mayonnaise) (no odor)	Each replicate was a full grab
T5 shallow	07/11/03	8.3	black mud (consistency of mayonnaise) (with a slight chemical odor)	Replicates 1&2 were full grabs, Rep 3 was 3/4 full
T6	12/04/03	12 to 15	hard grey clay	~6 grabs needed for each replicate
T7	12/29/03	18	soft black mud w/ thin brown surface layer, anaerobic odor, Phrag stalks	Each replicate was a full grab
T8	12/29/03	9.8	brownish-grey soft mud w/ many Phragmites stalks, anaerobic odor	Amphipods and chironomid larvae noted
T9	12/29/03	10	very soft black mud (consistency of mayonnaise) w/ worm tubes on surface	Each replicate was a full grab
TN1	08/05/03	4.2	brownish-grey clayey mud	Each replicate was ~3/4 full
TN2	08/05/03	5.1	greyish-black mud with thin brown layer on top	Each replicate was a full grab
TN3	12/04/03	5	blackish-grey mud w/ thin brown surface layer	Each replicate was a full grab
TN4	12/12/03	3	sticky black mud	Each replicate was between 1/2 to 3/4 full
TN5	12/12/03	4	sticky black mud w/ a very soft top layer	Each replicate was a full grab
TN6	08/05/03	2	soft black mud (consistency of mayonnaise) (no odor or sheen)	Each replicate was a full grab

The Ponar grab sampler was cleaned using site water and a hard-bristle scrub brush to remove any visible sediment before the next replicate sample was collected. After the third replicate sediment sample was collected at a particular sampling location, the Ponar grab sampler was decontaminated using a triple-step wash procedure that included an initial wash and scrub using site water, followed by an Alconox detergent wash/scrub and distilled water rinse, followed by a 10% nitric acid rinse, distilled water rinse, and finally an acetone rinse followed by a final distilled water rinse. The Ponar grab was then placed in a laboratory cleaned plastic tub, ready to be used at the next sediment collection location.

2.2 Physical Properties of Sediment

Sediment texture (particle-size), percent moisture and organic matter were determined for each sample in order to characterize the sediment and to help clarify the difference between site metal concentrations. Statistics performed to discern differences between sites normalized metal concentrations to the percentage of fine material contained in each sample. The American Society for Testing and Materials and (ASTM 2003) standard methods D 422 (particle-size) and D 2974 (moisture and organic matter) were utilized.

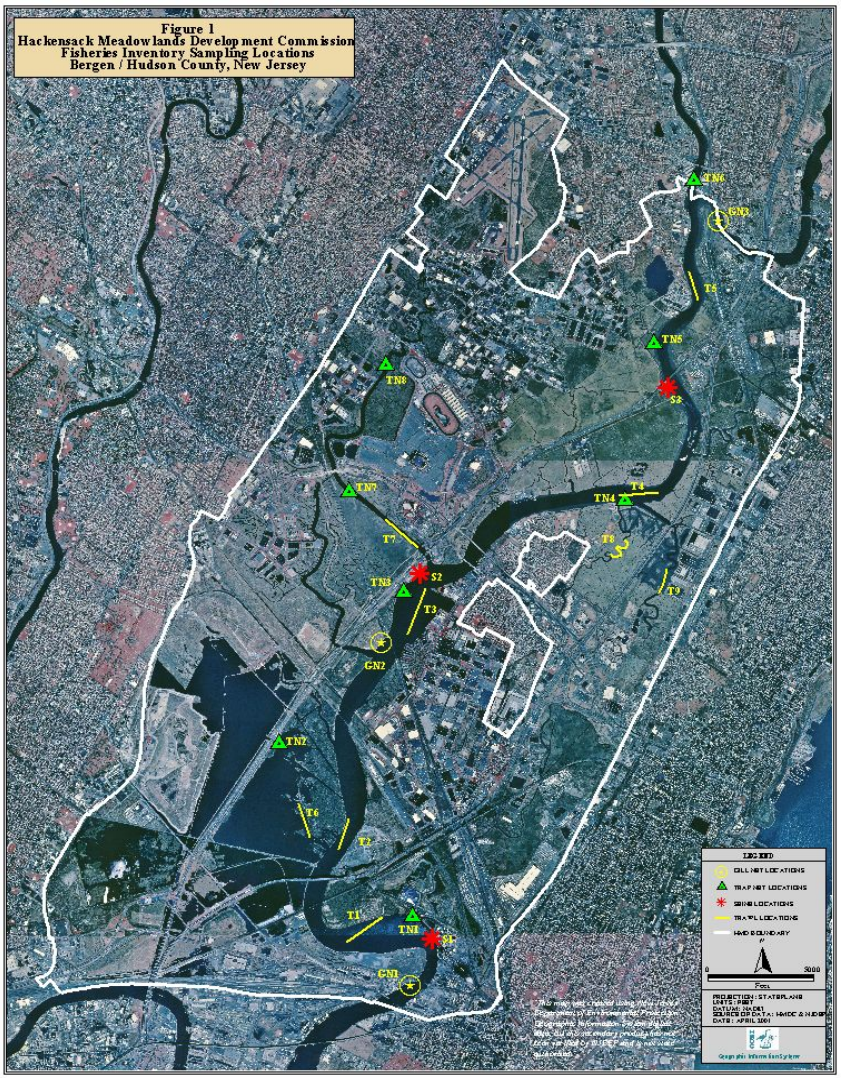

Figure 1. Map of Fisheries Inventory Sampling Locations

Appendix 1 contains the standard operating procedure for particle-size analysis. In summary:

1. The soil sample is dried at room temperature.
2. Sieve the ground sample through a No. 10 (2 mm) sieve using the Rotasift for 5 minutes. This material when weighed is the coarse fraction.
3. The material passing through the sieve is mixed with a dispersing agent until homogenized.
4. Transfer soil-water slurry (sample in dispersing agent) from its beaker into a glass sedimentation cylinder and fill to 1000mL with DI/distilled water.
5. Record both hydrometer (specific gravity) and temperature readings at intervals of 2, 5, 15, 30, 60, and 150 minutes after sedimentation begins.
6. When the hydrometer/temp readings are finished, pour the cylinder through a No. 230 (63 um) sieve. Dry the material retained on the No. 230 sieve at 105^{o} C.
7. Once dried, break up aggregations and perform a final sieve analysis of the material through a No. 40 (425 um), No. 60 (250 um), and a No. 120 (125 um) sieve (simultaneously) for 20 minutes. Weigh and record the mass of material retained on each sieve and the material that passed through all three sieves. This is the mass of sandy material.

A calculator using Excel (Appendix 2 contains a sample spreadsheet) was devised to convert hydrometer readings to grain size classifications. This is necessary to distinguish between clay and silt size material (collectively referred to as % fines).

Table 3. Grain Size Classes

Sieve	Grain Size	Classification
4	4.75 mm	Pebble
10	2.00 mm	Granule
40	425 um	Coarse Sand
60	250 um	Medium Sand
120	125 um	Fine Sand
230	62.5 um	Very Fine Sand
<230	5 um	Silt
	<5 um	Clay

ASTM Method D 2974 describes the gravimetric determination of both moisture content and organic matter. Percent moisture was determined by drying

the sample for 16 hours at 105° C. Organic matter (ash content) was determined by igniting the oven dried sample from moisture content in a muffle furnace at 550 °C.

2.2 Metals Analysis

A sufficient amount of sediment (1-2 g wet weight, yielding 0.4-0.8 g dry weight) was oven-dried, weighed, and mineralized in 10 ml Trace Metal Grade HNO_3 in Teflon bombs in a microwave digester. The resultant mineralized solution was boiled off to near dryness, restored to 25 ml volume with 1% HNO_3, and divided. Twenty ml were used by the MERI laboratory for analysis of Cr, Cu, Cd, Fe and Pb by flame atomic absorption spectrophotometry (AAS). The remaining 5 ml were used by UMDNJ for Hg analysis by cold-vapor AA in a Bacharach MAS-50D mercury analyzer and for As analysis by hydride generation AA in a Perkin-Elmer 603 spectrophotometer. All metal analyses in 1988 were performed in the HMDC Laboratory (now MERI Laboratory) using AAS. Instrumentation in the MERI laboratory was upgraded in 2001.

One Standard Reference Material (SRM) was analyzed with every ten samples. Table 4 is a summary of the percent recovered, which ranged from 72.4% for Chromium to 103% for Cadmium in 2003, and 69.9% for Zinc to 120% for Cadmium in 1988. Arsenic, Mercury and Iron were not analyzed in 1988.

Table 4. Summary of SRM Recovery

Metal	**% Recovery**	
	1988	2003
Arsenic		75.7
Cadmium	120	103
Chromium	105	72.4
Copper	92.4	99.7
Mercury		91.2
Lead	108	95.9
Nickel	115	95.6
Zinc	69.9	82.0
Iron		81.9

3. RESULTS AND DISCUSSION

3.1 Sediment Texture

Table 5 summarizes the average percent fine material (sum of the silt and clay fractions), organic matter (OM) and moisture content grouped by net type. On

average, the seine locations had the least amount of fine sediment. This is an artifact of the manner in which the sites were selected. Since the seine net was walked through the water and the net hauled up onto the shoreline at each seine location, sites that could not be easily traversed (i.e., those with thick mud) were not selected. Areas chosen as seine collection locations generally had a firm bottom (i.e., were lacking in fines). On the other hand, the trap net sites were selected to sample nearshore areas which were too muddy to seine. The trap nets were staked into mudflats at the selected locations that were close to shore, hence the high average percentage of fine material in the trap net samples. Intermediate between the seine and trap net locations were the gill net and trawl locations, which were generally located in deeper waters of the Hackensack River, or in the tributaries. The higher energy of the flowing river at some locations does not allow for the settlement of much fine material (e.g., GN1 and T2), while other sampling locations were clearly in areas of lower energy which were depositional in nature (e.g., T1 and T5).

Table 5. Net Type Averages of Physical Properties

Net Type	# of Locations	% Fines	% OM	% Moisture
Seines	3	40	7.7	50
Gill Nets	3	61	7.9	51
Trawls	14	70	9.8	60
Trap Nets	6	82	12.0	65

The surface area of particles increases as the size of particles decreases; as organic matter is often found as coatings on particles, it is reasonable for fine material and organic matter to co-vary as demonstrated by the net type averages. The moisture content of samples introduces the notion that opportunities for interchange between solid and liquid phases in the benthic environment are plentiful. In fact, the complexity of the system described by these parameters plays a strong role in the metal concentrations found in our samples.

Table 6 describes the texture of material sampled in the current and previous studies. Overall, the percentage of fines in the samples has remained relatively consistent; averaging 72% in 1988 and 69% in 2003. A plot of the data in Figure 2 reveals the temporal relationship in better detail. At Site T5 Deep, for example, fine material was relatively depleted in 1988 compared to 2003. This site is located in the channel of the River opposite the PSE&G Bergen Generating Station power plant; between 1988 and 2003 the cooling regime for this plant was converted from using river water to self contained cooling towers. This removed a thermal discharge plume which likely scoured the fine material from the river channel, providing a possible explanation for this change. Site S1 is also relatively depleted in fine material. The site is located along the bank of the river where a

strong current provides persistent scouring; but no change in conditions has occurred to explain the difference between the intervening years. Figure 2 also illustrates that one goal in the sampling design was met; collection sites were successfully replicated. This conclusion is supported by calculation of the population correlation coefficient between the two data sets: r = 0.73.

Table 6. Comparison of Fine Material Collected, 1988/2003

Sample Site	1988	2003	Difference
GN1	11.5%	19.1%	7.6%
GN2	73.0%	73.7%	0.7%
GN3	98.2%	89.0%	-9.2%
S1	41.5%	1.80%	-39.7%
S2	40.3%	27.7%	-12.6%
S3	97.3%	91.3%	-6.0%
T1 (deep)	55.1%	70.6%	15.5%
T1 (shallow)	56.4%	74.6%	18.2%
T2 (deep)	17.6%	19.5%	1.9%
T2 (shallow)	11.0%	40.2%	29.2%
T3 (deep)	92.8%	87.5%	-5.3%
T3 (shallow)	91.0%	81.2%	-9.8%
T4 (deep)	88.9%	60.9%	-28.0%
T4 (shallow)	93.9%	68.6%	-25.3%
T5 (deep)	14.8%	84.7%	69.9%
T5 (shallow)	96.7%	79.6%	-17.1%
T6	94.8%	76.6%	-18.2%
T7	94.6%	84.6%	-10.0%
T8	91.4%	84.0%	-7.4%
T9	92.5%	86.4%	-6.1%
TN1	76.3%	83.6%	7.3%
TN2	94.8%	86.5%	-8.3%
TN3	96.0%	78.6%	-17.4%
TN4	89.4%	76.7%	-12.7%
TN5	77.6%	80.1%	2.5%
TN6	84.8%	85.6%	0.8%
Average	72.0%	68.9%	-3.1%

The percentage of fine material helps describe the sedimentary character of the estuary, both spatial and temporal. The sampling sites covered nine miles of the river and the major tributaries that are within the Hackensack Meadowlands

District. Grouping the river sampling sites spatially can reveal differences between the lower, middle and upper part of the river within the District. Refer to Table 1 for the grouping of sites. Note that each river segment is separated by at least 1.5 river miles. Because of the strong influence of net type on sediment characteristics, an attempt was made to include a sampling from each net type in each segment. Exceptions are the absence of a gill net in the upper part of the river and a seine in the tributaries.

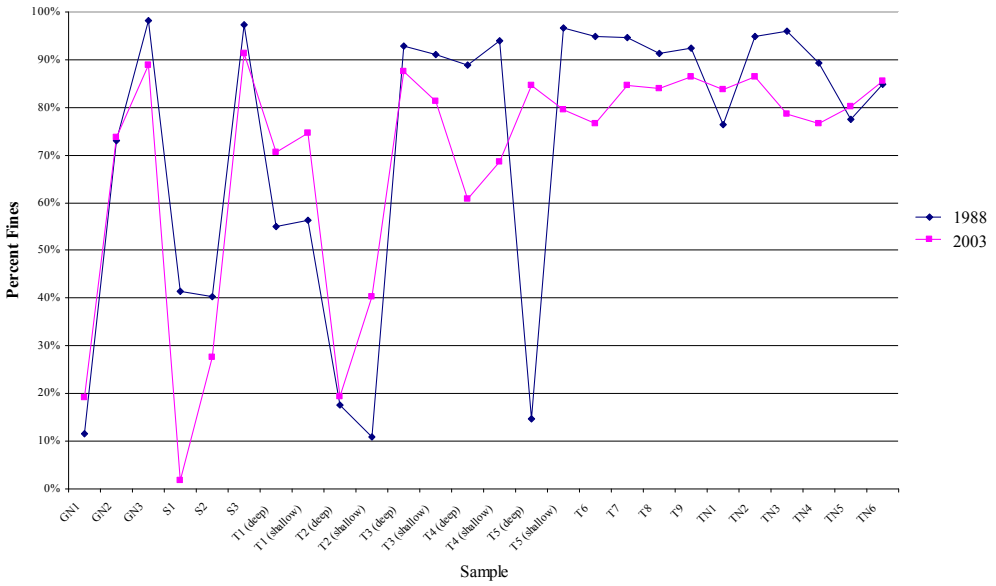

Figure 2. Plot of Site Textures

Figure 3A compares the average of fine percentages found in the tributaries and river in 1988 and 2003: Tributaries contain finer material then the river; the river hasn't changed during the 15 year interval between sampling; and there has been a 12% reduction in the percentage of fine material found in tributary samples. The composition of fine material is a function of hydrodynamics. As energy in the water column dissipates, finer material is deposited. The River would naturally have higher energy, with finer material being carried until deposition occurs in mudflats, along the shorelines and in the tributaries. Because the relative amount of fine material is very dynamic, it is difficult to draw conclusions from this data; for example, the increased energy from storm events can redistribute fine material in the short term that would mask long term changes in the River.

Figure 3B is a comparison between the average of fine percentages found in the three segments of the river in 1988 and 2003: The average percentage found in

the lower river has increased 13%; the middle part of the river has decreased by 13%; and the upper part of the river has remained relatively unchanged (2% decrease). Appendices 3 and 4 contain the complete grain size analysis for sediments collected in 1988 and 2003.

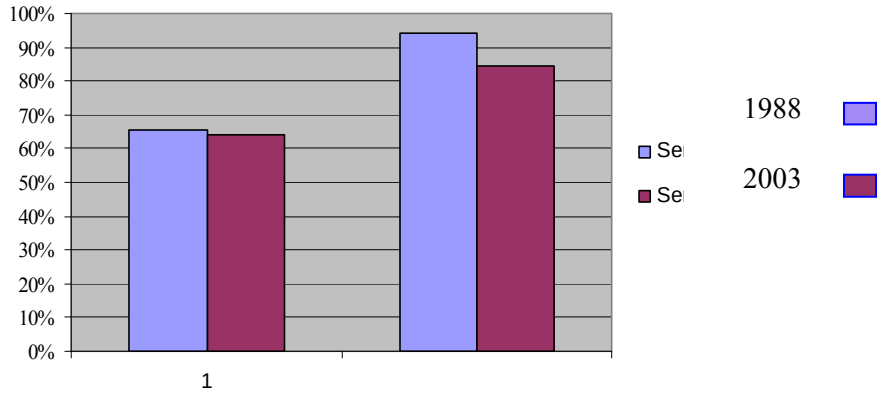

Figure 3A. Spatial Distribution of Percent Fines: River vs. Tributaries

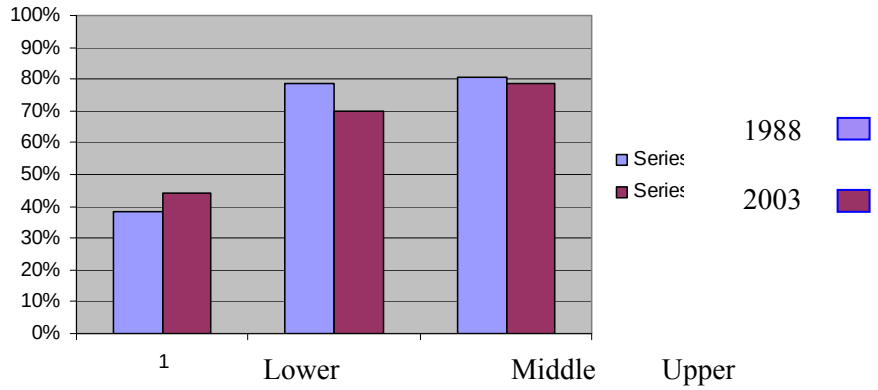

Figure 3B. Spatial Distribution of Percent Fines: River Segments

3.2 METALS

The metals and organic chemicals selected for analysis are contaminants known to bioaccumulate. The organics and mercury bioconcentrate, i.e., accumulating to higher levels (typically an order of magnitude) with each trophic level, making them of special concern (Weis 2005). The discussion which follows will include a description of the spatial distribution of metal concentrations collected in 2003

and the factors affecting that distribution; and a comparison between data collected in 2003 and 1988 using sediment quality criteria as a measure of ecosystem quality. A complete listing of concentrations obtained in 2003 and 1988 appears in Appendices 5 and 6.

There are no absolute chemical concentrations that correspond to sediment toxicity, but "Effects Range Low" (ERL) and "Effects Range Median" (ERM) values are used as guidelines in assessing sediment contamination. ERM is the median concentration of a contaminant observed to have adverse biological effects in the literature studies examined (Long et al 1995). A more protective indicator of contaminant concentration is the ERL criteria, which is the 10th percentile concentration of a contaminant represented by studies demonstrating adverse biological effects in the literature. Ecological effects are not likely to occur at contaminant concentrations below the ERL criterion (USEPA 2004, p. 12).

Table 7 describes qualitative ratings for sites based on ERM and ERL criteria. Based on the EPA's sediment contamination assessment criteria, the ecological condition of the Hackensack River estuary sediments in 2003 was Poor; the average concentration of one contaminant, mercury, exceeds the ERM. Table 8 provides a comparison of average metal concentrations obtained in 1988 and 2003 to the ERM and ERL criteria. Metals which exceeded the ERM criteria are printed in red. In 1988, three additional metals cadmium, copper and nickel exhibited concentrations that would have exceeded the ERM criteria. The improvement in sediment quality in the 15 years between studies is depicted in the table as the high concentrations of cadmium, copper and nickel are no longer experienced in these estuarine sediments.

Table 7. Criteria for Assessing Sediment Contaminants by Site (USEPA 2004, p. 17)

Rating	**Criteria**
Good	No ERM concentrations are exceeded, and less than five ERL concentrations are exceeded.
Fair	Five or more ERL concentrations are exceeded
Poor	An ERM concentration is exceeded for one or more contaminants.

Six of the 21 river samples, collected primarily at sites below the mouth of Berrys Creek, exhibit Good sediment quality: the mercury ERM is not exceeded and less than five ERLs are exceeded (See Table 9). None of the tributary sites meet this criteria. Other contaminants that exceed ERM criteria in individual samples are cadmium, lead, nickel and zinc. The average concentration of all of the metals exceed ERL criteria; 60% of the sampling sites exceed more than five ERLs.

It is apparent that the sediments can be considered contaminated by all of the metals studied. Superimposing a semi-qualitative stacked bar graph on the map of the estuary, Figure 4, reinforces this spatial trend. In this urban estuary, multiple sources for the metals are likely; Newark Bay, the Passaic River, historical industrial discharges, hazardous waste sites, landfills, power plant emissions and run-off from combined sewer outfalls and transportation arteries contribute.

Table 8. Hackensack River: Average Metal Concentrations (As and Hg were not analyzed in 1988)

ERM and ERL Guidance Values in Sediments (Long et al., 1995)				
Constituent	**ERL mg/kg**	**ERM mg/kg**	**Hackensack Estuary Mean**	
			1988	2003
Arsenic	8.2	70		8.89
Cadmium	1.2	9.6	10.5	3.0
Chromium	81	370	347	130
Copper	34	270	429	115
Mercury	0.15	0.71		3.55
Lead	47	218	164	128
Nickel	21	52	110	42.9
Zinc	150	410	243	263

The sediments are mobile, capable of absorbing contaminants anywhere in the estuary, carrying their load of metals until being deposited.

The distribution of the mercury in the sediments of the estuary is depicted in Figure 5. The maximum concentration of the mercury occurs in Berry's Creek. It is apparent that enrichment occurs in the Hackensack River above the mouth of Berry's Creek Canal (Site T7). A chemical processing plant located at the head of the tidal portion of Berry's Creek operated from 1929 until 1974. Although the Ventron/Velsicol facilities were abandoned and demolished in 1974, contaminants still remain on site and potential pathways for migration are re-distribution of sediments, groundwater and air. Discharges from the facility are known to have contaminated the Creek with mercury and other chemicals. Mercury levels in the sediment adjacent to the property are among the highest known in freshwater ecosystems nationwide. (USEPA 2006). It is clear that the mercury contamination is no longer confined to Berry's Creek. Statistical analysis supports the conclusion that there is no significant difference between mercury concentrations found throughout lower, middle and upper river segments (Filipiak and Johnson 2007).

Table 9 represents the average metal concentration of three replicates collected at each site. The organization of the table by river miles and tributaries with coloration of concentrations exceeding the ERL sediment criteria (See Table 8), allows for a visual representation of spatial trends. The distribution of ERL exceedences (five or more per site) suggests that with two exceptions, S-2 at mile 7.4 and T-4 Deep at mile 9.3, the river north of mile 7.0 is likely to suffer negative ecological effects.

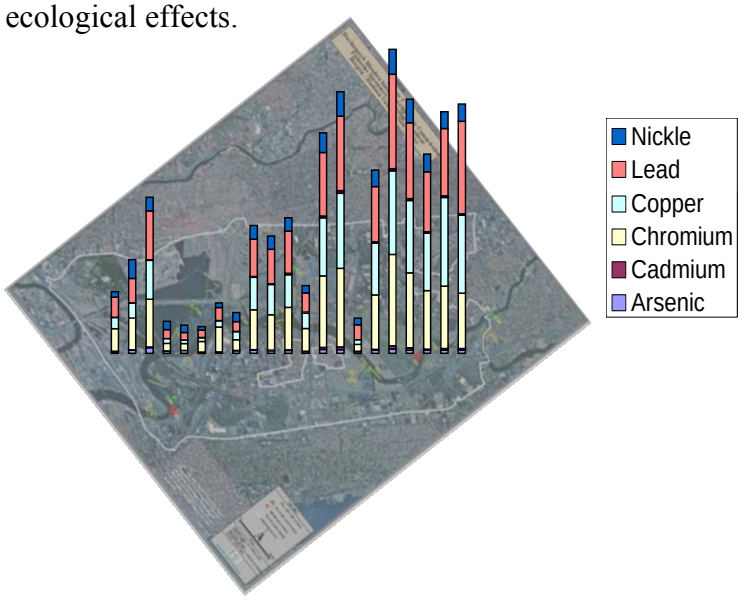

Figure 4. Visual Depiction of metal spatial trend

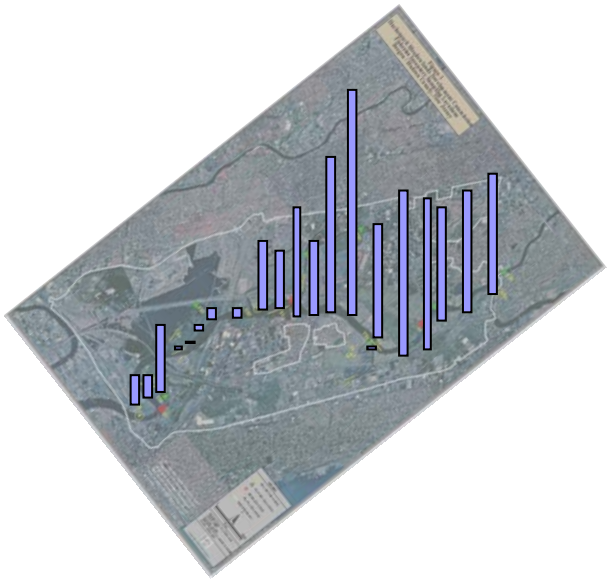

Figure 5. Visual Depiction of mercury spatial trend

Table 9. Hackensack River metal concentrations obtained in 2003
Values exceeding the ERL are typed in boldface; values exceeding the ERM are bolded and italicized.

		Metals (mg/kg)								
		Arsenic	Cadmium	Chromium	Copper	Mercury	Lead	Nickel	Zinc	Iron
	ERL	8.2	1.2	81	34	0.15	47	21	150	
	ERM	70	9.6	370	270	0.71	218	52	410	
Sampling Sites	River Mile									
GN 1	3.0	5.13	0.80	68.9	**33.9**	***1.11***	**61.5**	16.2	101	12472
S 1	3.5	**10.4**	0.42	**96.1**	**46.6**	***0.85***	**73.7**	***57.8***	113	34720
TN 1	3.6	**17.1**	**2.48**	**145**	**118**	***2.57***	**148**	**41.7**	**230**	29198
T1-S	3.8	7.01	0.14	23.2	14.5	0.09	27.3	**25.2**	59.2	26463
T1-D	3.8	**8.76**	0.13	20.6	11.2	0.05	22.6	**22.6**	56.4	27471
T2-S	5.4	3.68	0.29	32.4	11.8	**0.20**	22.7	10.8	54.7	11997
T2-D	5.4	3.58	0.46	76.0	19.5	**0.43**	39.4	14.0	68.6	12139
GN 2	6.8	**8.26**	0.34	33.3	24.9	**0.38**	29.1	**28.1**	82.0	34512
T3-S	7.0	**9.65**	**1.69**	**121**	**99.1**	***2.65***	**113**	**41.9**	**213**	33966
T3-D	7.0	**8.16**	**1.45**	**108**	**92.5**	***2.22***	**105**	**40.2**	**210**	30418
TN 3	7.1	**8.92**	**1.62**	**130**	**99.3**	***4.19***	**129**	**40.5**	**236**	34945
S 2	7.4	5.68	0.90	69.1	47.4	***2.86***	**58.0**	**22.4**	130	19859
TN 4	9.2	**11.8**	**5.95**	**218**	**177**	***5.99***	**193**	***59.8***	**390**	36687
T4-S	9.3	**11.1**	**8.43**	**240**	**228**	***8.65***	***227***	***74.3***	***437***	38166
T4-D	9.3	5.79	0.36	21.3	13.8	0.09	45.3	20.2	61.2	24987
S 3	10.6	**9.64**	**2.95**	**165**	**158**	***4.36***	**168**	**49.9**	**359**	37232
T5-S	10.9	**13.4**	*9.88*	**278**	**255**	***6.34***	***287***	***76.2***	***660***	35524
T5-D	10.9	**9.87**	**7.28**	**228**	**220**	***5.79***	***231***	***71.8***	***522***	36034
TN 5	10.9	**9.11**	**3.90**	**178**	**175**	***4.35***	**182**	53.8	**384**	36923
GN 3	12.0	**9.63**	**5.30**	**190**	**270**	***4.67***	**205**	**51.2**	527	37760
TN 6	12.5	**10.1**	**5.08**	**168**	**237**	***4.65***	282	**52.3**	494	37772
TN2	Sawmill	**9.33**	**2.03**	**190**	***270***	***2.06***	**205**	**51.2**	527	37760
T6	Sawmill	6.36	0.13	**123**	**106**	**0.20**	**130**	**41.1**	**244**	32817
T7	Berry's	**13.8**	***13.05***	23	13	***20.8***	22	**25.8**	66	29304
T8	Mill	**22.8**	**1.93**	**297**	**237**	***3.41***	***227***	***73.4***	***536***	38060
T9	Cromakill	**11.6**	**2.19**	**170**	**133**	***3.28***	**141**	**52.2**	**283**	38843

3.3 Sediment Metal Behavior

We can look to the relative concentration of total carbon and fine grained particles to discern why the metals reside where they do. Concentration distributions presented to show patterns of regional contaminant distributions and metal co-variances imply common sources or behaviors (Mecray et al 2001). Table 10 displays the Pearson product-moment coefficient (R^2) which depicts the strength of the correlation of the values of independent variables obtained at each sampling

site. With the exception of iron and arsenic, the sediment correlation matrix displays the close affinity of all of the metals. A general linear model was used to measure the relationship between each of the metals as independent or predictor variables and other metal as dependent or criterion variable (Filipiak and Johnson 2007). The significant model equations for each of the metals confirmed the strong interaction between the metals (Filipiak and Johnson 2007). Because correlation does not imply causation, it cannot be inferred from this information that the metals share a common source. It is more likely that their observed distributions result from the influence of hydrodynamics reflected by sediment texture and organic content.

Table 10. Sediment Correlation Matrix (R^2)
* Correlation coefficients > 0.77

	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury	Nickel	Zinc	River mile	% Fines
Cadmium	0.47										
Chromium	0.58	0.93*									
Copper	0.50	0.91*	0.92*								
Iron	0.63	0.55	0.63	0.66							
Lead	0.56	0.91*	0.94*	0.96*	0.65						
Mercury	0.43	0.89*	0.93*	0.88*	0.60	0.90*					
Nickel	0.67	0.80*	0.87*	0.78*	0.83*	0.82*	0.76*				
Zinc	0.47	0.94*	0.93*	0.99*	0.65	0.97*	0.89*	0.80*			
River mile	0.13	0.77*	0.71	0.85*	0.62	0.79*	0.81*	0.60	0.85*		
% Fines	0.55	0.54	0.54	0.65	0.70	0.62	0.58	0.47	0.63	0.61	
% TOC	0.62	0.85*	0.89*	0.92*	0.79*	0.95*	0.87*	0.82*	0.92*	0.80*	0.79*

Particulate size and resulting total surface area available for adsorption are both important factors in adsorption processes… smaller particles can both be more widely dispersed by water and can also serve as sites of enhanced adsorption (John and Leventhal 1995 p. 13). In this estuary dominated by the tidal regime, depositional environments occur when energy dissipates. One would expect the percent of fine material to increase as the distance increases from the mouth of the river; a moderate correlation ($R^2 = 0.61$) between % fines (silt and clay fraction) and river mile does exist. The strength of the correlation between the metals and % fines is moderate as well (average $R^2 = 0.59$). A confounding factor which diminishes the strength of the river mile/ percent fines correlation relates to the differing substrate requirements for the four net-types used for sampling fish which provided the sites for sediment collections as well (Table 5).

A better predictor of metal concentrations in the sediments appears to be the amount of organic matter present in the sediments. In organic carbon-rich sediments, trapped interstitial fluids can commonly form a strongly reducing (anoxic) environment. The sediment samples in this study averaged almost 60% water. Low redox potential in this environment can promote sulfate reduction and sulfide mineral deposition. During diagenesis, much of the potentially toxic metals, such as arsenic, cadmium, copper, mercury, lead, and zinc, can form insoluble sulfides; a change to an oxidizing environment caused by disturbance of the sediment and exposure to the atmosphere or with the influx of oxygenated (sea) water can result in rapid reaction of this anoxic sediment and thereby release significant proportions of these metals (John and Leventhal 1995 p. 13). The sulfate/sulfide mechanism appears to effect metal concentrations, helping to explain the enrichment in the upper reaches of the river and depletion as oxygenated sea water interacts the organic matter in sediments.

3.4 1988/2003 Comparison

Between 1988 and 2003, the average sediment concentration of cadmium, chromium, copper, lead and nickel was reduced by between 22% and 71%; zinc concentrations remained relatively constant (8% increase). This dramatic improvement suggests a natural attenuation process is burying contaminated sediments with cleaner material. Perhaps the naturally high background concentration of zinc found in this region provides a continuous supply of this metal to the sediments.

Table 11. Metal Comparison 1988/2003

Average Metal Concentrations (mg/kg)			
Metal	**1988**	**2003**	**Difference**
Cadmium	10.5	3.0	-71%
Chromium	347	130	-63%
Copper	429	115	-73%
Lead	164	128	-22%
Nickel	110	42.9	-61%
Zinc	243	263	+8%

Statistical analysis was performed on the sediment metal concentrations as well (Filipiak and Johnson 2007). Three sites, S1, S3 and TN5, were not included in the year to year comparison. S3 was excluded because there was no data in 1988; it had been identified as S4. S1 and TN5 were excluded as the site identification was recorded incorrectly. To test whether there were significant different between studies done in 1987-88 and 2003 a paired t test was used. The justification for using the paired t experimental design was the methodology of having samples collected at approximately the same geographical locations where

the only factor is the time in between collections (Filipiak and Johnson 2007).

Significant difference in concentrations was found for the following metals in sediments when comparing 1987-88 and 2003 using a paired t-test:

- Cadmium (Cd), levels higher for 1987-88
- Chromium (Cr), levels higher for 1987-88
- Copper (Cu), higher for 1987-88
- Lead (Pb), higher for 1987-88.

When the sites were grouped according to their location in the main river or tributaries, the following metals exhibited significant differences in the main river:

- Cadmium (Cd), higher for 1987-88
- Copper (Cu), higher for 1987-88
- Lead (Pb), higher for 1987-88

The main river levels of Chromium, Nickel and Zinc did not have a statistically significant change between 1987-88 and 2003. In the tributaries, there were no significant differences for any of the metals studied.

Statistics were also applied to the Lower, Middle and Upper segments of the Hackensack River (see Table 1 and Figure 1). The only statistically significant result was the higher value of cadmium concentrations in the Lower River in 1987-88 compared to 2003.

4. CONCLUSIONS

Sampling and analytical methods applied to the sediment study of 2003 successfully replicated the 1988 effort, allowing for spatial and temporal comparisons between physical and chemical properties. The ecological quality of the Hackensack River Estuary was discerned using guidance criteria applied to metal concentrations.

The texture of bottom sediments has not changed greatly during the 15 year interval between studies and the sediment quality has clearly improved. Between 1988 and 2003, the average sediment concentration of cadmium, chromium, copper, lead and nickel was reduced by between 22% and 71%. However, since 60% of the sampling sites exceed more than five ERLs the estuary continues to exhibit metal contamination.

Mercury concentrations once thought to be confined to Berry's Creek, have now reached all parts of the estuary. Since Mercury was not determined in the 1989 study, it was not possible to determine trends over time.

Finally, the majority of the metals seem to be correlated. This correlation however does not conclusively show that they share a common source. The study indicates that their observed distributions are also closely related to sediment texture and organic content.

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APPENDIX 1. Grain-Size Analysis SOP

Standard Test Method for Particle-Size Analysis of Soils, D422-63(2002). ASTM International, 2003.

(Nicole Quinn, MERI)

Procedure:

Expose the soil sample (about 130g out of jar for silt/clay soils, about 200g for sandy soils) to air at room temperature until dry. Use the blower under the hood. This could take 2-7 days.

Break up aggregations in a mortar with a rubber-covered pestle, trying not to crush the grains.

Sieve the ground sample through a No. 10 (2 mm) sieve using the Rotasift for 5 minutes.

Break up aggregations retained on No. 10 sieve, using mortar and pestle. Sieve the ground material again through the No. 10 sieve for 5 minutes.

After sieving the sample twice through the No. 10 sieve, remove the sieve and wash with DI/distilled water anything retained on the sieve. Put this sieve in the oven to dry at a temp. of 100 – 105 degrees Celsius. This is the coarse material.

Get a 250mL beaker and a spatula and measure out 50g into the beaker for silt/clay soils and 100g for sandy soils. Use at least 32g for silt/clay and 82g for sandy soils. Use the PB3002-S DeltaRange scale.

Add 125mL of the dispersing solution (40g/L sodium hexametaphosphate) to the beaker and stir until homogenized. Cover with parafilm, label, and leave for at least 16 hours.

To make more dispersing solution, measure 40g of sodium hexametaphosphate and add to about 800mL DI/distilled water in a 1000mL beaker. Place on stir plate, and using stir bar, mix for about 20 minutes or until homogenized.

Remove the sieve with the coarse material from oven when the sample is dry and sieve it for 5 minutes through both a No. 10 and a No. 4 sieve, simultaneously. Weigh and record the masses for each sieve. These are the masses of coarse material for the sample. Use the PB221S Sartorius scale.

After 16 hours, begin the hydrometer readings for the samples. Use the same 151H hydrometer that was used throughout this project, for which a composite correction has already been made.

Transfer soil-water slurry (sample in dispersing agent) from its beaker into a glass sedimentation cylinder and fill to 1000mL with DI/distilled water. Rinse all soil from beaker into cylinder. Label the cylinders. Only two tests can be run at a time, and it is possible to finish four in a day.

Use a rubber stopper to cap the cylinder. Record both hydrometer (specific gravity) and temperature readings at intervals of 2, 5, 15, 30, 60, and 150 minutes after sedimentation begins. Hold both ends of the cylinder and mix for one minute. Setting down the cylinder is the beginning of sedimentation. Record your start time.

When you have finished the hydrometer/temp readings for the sample, pour the cylinder through a No. 230 (63 um) sieve over the sink and run tap water though it until clear. Dry the material retained on the No. 230 sieve in an aluminum weighing dish in the oven at 105 degrees Celsius. This will take about 1.5 – 2 days for most samples to completely dry.

Once dried, break up aggregations in mortar with rubber-covered pestle. Perform a final sieve analysis of the material through a No. 40 (425 um), No. 60 (250 um), and a No. 120 (125 um) sieve (simultaneously) for 20 minutes. Weigh (on the Sartorius scale) and record the mass of material retained on each sieve and the material that passed through all three sieves. This is the mass of sandy material.

APPENDIX 2. GRAIN-SIZE CALCULATOR

PARTICLE-SIZE ANALYSIS OF SOILS ASTM D 422

Start by recording data from notebook or worksheet.

Hit [F9] to calculate.
Save to a new file name and repeat.

Sample #	78816 GN2-
Location	3
Weight (g)	50.0
Temperature	
C	21.0
K	0.014

Sieve Analysis	
Sieve	**Weight (g)**
4	0.000
10	0.124
40	0.000
60	2.681
120	2.013
230	0.000
<230	45.18

Size Classification and %	
Pebble	0.00%
Granule	0.25%
Coarse Sand	0.00%
Medium Sand	5.36%
Fine Sand	4.03%
Very Fine Sand	0.00%
Silt	62.6%
Clay	27.8%

		Hydrometer Analysis				
Time (T)	**Hydrometer reading**	**% in Suspension**	**Depth L**	**L/T**	**Diameter (D)**	**Ln D**
2	1.020	65.0%	11.0	5.500	0.032	-3.439
5	1.017	55.2%	11.8	2.360	0.021	-3.862
15	1.014	45.5%	12.6	0.840	0.013	-4.378
30	1.012	39.0%	13.1	0.437	0.009	-4.705
60	1.011	35.7%	13.4	0.223	0.006	-5.041
150	1.009	29.2%	13.9	0.093	0.004	-5.480
		Silt diameter	**Ln**		**Trend Coefficient**	
		0.005	-5.298		0.308	

APPENDIX 3. SEDIMENT SAMPLE TEXTURES 2003

Location	Pebble 4 MM	Granule 2 MM	Coarse Sand 0.5 MM	Medium Sand 0.25 MM	Fine Sand 0.125 MM	Very Fine Sand 0.0625 MM	Silt 0.005 MM	Clay < 0.005 MM
TN1-1	0.72%	0.31%	0.96%	1.37%	0.03%	21.0%	33.3%	42.4%
TN1-2	0.34%	0.71%	0.00%	0.00%	0.00%	0.00%	47.5%	51.4%
TN1-3	0.00%	0.33%	0.45%	2.07%	0.03%	20.8%	38.0%	38.3%
S1-1	16.4%	11.3%	33.8%	17.5%	0.01%	18.2%	1.76%	1.01%
S1-2	29.5%	12.1%	31.3%	9.21%	0.06%	17.4%	0.31%	0.18%
S1-3	21.7%	19.4%	17.1%	9.78%	0.02%	29.6%	1.31%	1.06%
GN1-1	0.02%	0.50%	1.50%	12.9%	15.9%	50.6%	9.15%	9.54%
GN1-2	1.13%	1.07%	2.51%	13.6%	0.01%	65.1%	9.87%	6.65%
GN1-3	0.05%	0.67%	2.92%	12.8%	0.01%	61.4%	12.0%	10.2%
T1-1 Deep	6.85%	2.11%	1.17%	3.68%	0.02%	35.4%	25.8%	24.9%
T1-2 Deep	0.00%	0.00%	0.46%	1.97%	0.01%	25.4%	21.4%	50.8%
T1-3 Deep	0.00%	0.00%	2.95%	3.29%	5.00%	0.0%	42.3%	46.5%
T1-1 Shallow	0.00%	0.00%	0.36%	2.46%	0.03%	11.9%	26.3%	58.9%
T1-2 Shallow	1.01%	2.52%	3.29%	2.33%	0.06%	15.5%	28.5%	46.7%
T1-3 Shallow	7.41%	2.15%	3.22%	3.46%	0.02%	20.5%	23.3%	40.0%
TN2-1	0.00%	0.06%	1.17%	1.93%	3.06%	13.0%	29.6%	51.3%
TN2-2	0.00%	0.04%	0.17%	0.36%	0.00%	4.39%	35.2%	59.9%
TN2-3	0.00%	0.15%	0.72%	1.40%	0.09%	14.1%	25.2%	58.3%
S2-1	13.3%	5.55%	6.26%	10.2%	0.04%	23.6%	22.2%	18.9%
S2-2	27.4%	8.64%	0.00%	27.0%	18.8%	12.2%	3.4%	2.62%
S2-3	27.4%	8.14%	8.22%	5.85%	1.53%	12.9%	12.1%	23.9%
GN2-1	5.43%	0.70%	1.42%	8.90%	0.03%	17.4%	21.3%	44.8%
GN2-2	0.00%	0.35%	0.61%	3.45%	0.02%	30.9%	27.8%	36.9%
GN2-3	0.00%	0.25%	0.00%	5.36%	4.03%	0.00%	23.9%	66.4%
T2-1 Deep	11.9%	1.89%	10.2%	26.7%	0.01%	49.1%	0.17%	0.07%
T2-2 Deep	4.07%	2.55%	9.79%	12.7%	0.02%	16.8%	42.2%	11.9%
T2-3 Deep	3.69%	1.87%	21.9%	30.4%	0.05%	38.0%	3.17%	0.88%
T2-1 Shallow	0.11%	0.51%	8.30%	2.39%	0.01%	83.7%	3.6%	1.44%
T2-2 Shallow	2.48%	0.75%	0.55%	2.10%	0.01%	69.4%	16.8%	7.92%
T2-3 Shallow	0.00%	0.01%	1.64%	2.56%	0.02%	86.5%	8.22%	1.10%
TN3-1	0.00%	0.07%	12.3%	9.87%	6.94%	21.0%	28.2%	21.5%
TN3-2	0.60%	0.02%	0.36%	0.37%	0.00%	5.29%	31.7%	61.7%
TN3-3	0.99%	0.17%	0.37%	0.38%	0.00%	5.43%	15.8%	76.9%

Location	Pebble 4 MM	Granule 2 MM	Coarse Sand 0.5 MM	Medium Sand 0.25 MM	Fine Sand 0.125 MM	Very Fine Sand 0.0625 MM	Silt 0.005 MM	Clay < 0.005 MM
S3-1	0.00%	0.30%	0.42%	1.02%	0.01%	3.34%	18.7%	76.2%
S3-2	0.07%	0.56%	1.39%	2.76%	0.01%	6.03%	31.9%	57.3%
S3-3	0.00%	0.48%	1.24%	2.92%	0.03%	5.57%	25.5%	64.2%
GN3-1	0.00%	0.00%	11.6%	0.79%	0.05%	1.66%	45.7%	40.2%
GN3-2	0.00%	0.18%	3.22%	0.64%	0.00%	1.55%	51.0%	43.4%
GN3-3	0.00%	0.00%	7.02%	1.10%	0.04%	5.25%	42.1%	44.4%
T3-1 Deep	0.00%	0.00%	2.21%	3.22%	0.08%	17.4%	20.1%	57.0%
T3-2 Deep	0.00%	0.29%	0.27%	0.29%	0.00%	6.47%	26.8%	65.9%
T3-3 Deep	0.22%	0.07%	0.19%	0.33%	0.02%	6.55%	22.7%	69.9%
T3-1 Shallow	0.00%	12.6%	0.16%	0.39%	0.03%	6.04%	25.4%	55.4%
T3-2 Shallow	0.00%	0.14%	0.26%	0.42%	0.02%	7.15%	27.3%	64.7%
T3-3 Shallow	0.00%	0.00%	1.50%	3.88%	0.03%	23.7%	28.4%	42.6%
TN4-1	0.00%	0.01%	1.76%	0.87%	0.02%	4.31%	26.3%	66.8%
TN4-2	0.00%	0.02%	13.7%	0.84%	0.23%	4.08%	27.1%	54.0%
TN4-3	0.00%	0.00%	3.74%	8.69%	0.07%	31.5%	19.7%	36.3%
T4-1 Deep	0.00%	0.18%	0.19%	1.53%	0.03%	36.6%	24.9%	36.6%
T4-2 Deep	0.00%	0.13%	1.90%	2.23%	0.04%	46.7%	22.1%	26.9%
T4-3 Deep	0.19%	0.05%	0.22%	1.95%	0.02%	25.5%	30.2%	41.8%
T4-1 Shallow	0.00%	0.00%	5.41%	8.22%	0.06%	30.2%	14.0%	42.1%
T4-2 Shallow	0.00%	0.11%	3.04%	0.98%	0.01%	4.83%	32.0%	59.0%
T4-3 Shallow	0.00%	0.00%	8.01%	6.98%	0.08%	26.3%	18.6%	40.1%
TN5-1	0.00%	0.00%	9.64%	6.26%	0.13%	26.9%	18.6%	38.4%
TN5-2	0.00%	0.00%	0.00%	8.85%	2.07%	0.00%	23.8%	65.3%
TN5-3	0.00%	0.07%	3.68%	1.84%	0.47%	0.00%	34.4%	59.6%
T5-1 Deep	0.00%	0.00%	5.14%	1.02%	0.01%	5.10%	45.0%	43.7%
T5-2 Deep	0.00%	0.06%	1.10%	1.12%	0.01%	8.29%	34.8%	54.6%
T5-3 Deep	0.00%	0.21%	4.45%	2.81%	0.09%	16.6%	28.1%	47.8%
T5-1 Shallow	0.00%	1.95%	1.46%	1.68%	0.17%	6.93%	41.6%	46.2%
T5-2 Shallow	0.00%	0.00%	8.96%	3.26%	0.26%	14.4%	32.0%	41.1%
T5-3 Shallow	0.00%	0.07%	7.61%	1.99%	0.01%	12.4%	35.8%	42.2%
TN6-1	1.47%	0.08%	9.00%	2.38%	0.02%	6.80%	35.1%	45.2%
TN6-2	0.00%	0.06%	1.21%	0.79%	0.29%	5.82%	27.0%	64.8%
TN6-3	0.01%	0.25%	3.14%	4.04%	0.24%	7.54%	41.1%	43.7%
T6-1	0.00%	0.96%	6.29%	4.34%	1.76%	0.00%	22.9%	63.7%
T6-2	2.98%	1.90%	6.82%	10.1%	0.02%	20.3%	20.3%	37.5%
T6-3	0.00%	0.06%	0.03%	2.04%	0.02%	12.4%	11.5%	74.0%

Location	Pebble 4 MM	Granule 2 MM	Coarse Sand 0.5 MM	Medium Sand 0.25 MM	Fine Sand 0.125 MM	Very Fine Sand 0.0625 MM	Silt 0.005 MM	Clay < 0.005 MM
T7-1	0.00%	0.04%	4.77%	0.92%	0.01%	5.24%	41.7%	47.4%
T7-2	1.52%	5.12%	9.30%	2.31%	0.02%	7.78%	46.7%	27.3%
T7-3	0.56%	0.53%	2.23%	1.04%	0.33%	4.47%	37.7%	53.1%
T8-1	2.38%	4.07%	2.44%	1.37%	0.04%	5.10%	40.2%	44.4%
T8-2	0.08%	1.03%	1.40%	1.74%	0.01%	8.56%	31.7%	55.4%
T8-3	3.34%	4.53%	4.38%	2.14%	0.47%	4.91%	51.0%	29.3%
T9-1	0.02%	0.07%	5.73%	2.43%	0.01%	6.64%	53.6%	31.5%
T9-2	0.19%	0.15%	2.72%	1.85%	0.01%	5.91%	44.4%	44.8%
T9-3	0.00%	0.14%	4.26%	2.10%	0.02%	8.70%	43.7%	41.1%

APPENDIX 4. SEDIMENT SAMPLE TEXTURES (PERCENTAGE) 1988

Location	Pebble 4 MM	Granule 2 MM	Very Coarse Sand 1 MM	Coarse Sand 0.5 MM	Medium Sand 0.25 MM	Fine Sand 0.125 MM	Very Fine Sand 0.0625 MM	Silt and Clay < 0.0625 MM
TN1	0	0.2	1.6	2.8	6.1	7.7	5.3	76.3
S1	8	6.4	6.2	10.4	12.8	12.2	4.6	39.4
GN1	0	0.3	0.3	0.7	22.2	58.5	6.5	11.5
T1 Deep	3.6	3.7	1.7	2	5.9	16.2	11.8	55.1
T1 Shallow	0.32	0.5	0.4	1.3	3.8	20.9	16.4	56.4
TN2	0	0.3	0.8	0	0.4	2.2	1.5	94.8
S2	0.7	1	2.2	4.4	8.8	24.4	18	40.3
GN2	0	0.7	0	0.8	10	8.6	6.7	73
T2 Deep	0.1	1.9	2	10.1	27.8	30.8	9.8	17.6
T2 Shallow	54.1	6.5	2.9	3.5	8.2	10.1	3.6	11
TN3	0	0.2	0.7	1.3	0.2	0.9	0.7	96
S3	0	0.1	0.5	0	0.2	1.3	0.5	97.3
GN3	0	0	0	0	0.2	0.1	1.5	98.2
T3 Deep	0	0	0.8	0	0.1	1.6	4.7	92.8
T3 Shallow	0	0.7	0.1	0	0.4	2.1	5.8	91
TN4	0	0.7	0.3	0	0	1.5	2.8	89.4
T4 Deep	0	0	0.4	0	0.2	2.1	8.3	88.9
T4 Shallow	0	0.7	0.3	0	0.1	1.7	3.3	93.9
TN5	0	0	0.7	0	1	14.8	5.8	77.6
T5 Deep	0	0.3	3.5	7.9	29.8	38.3	5.4	14.8
T5 Shallow	0	0.1	0	0	0.1	0.3	2.8	96.7
TN6	0	0.3	0.5	1.6	1	7.5	4.3	84.8
T6	0	0	0.6	0	0.5	2.1	2.1	94.8
T7	0	0.2	0.8	0.2	0.3	1.7	2.3	94.6
T8	0	0.1	0.3	0	0.4	5.8	2	91.4
T9	0	0.1	0.8	0.1	1	2.9	2.6	92.5

Note: Percentages reflect the results obtained from one sample collected at each location.

APPENDIX 5. METAL CONCENTRATIONS OF SEDIMENTS COLLECTED IN 2003 (MG/KG DRY WT.)

Site - Rep. #	Collection Date	T.O.C. (%)	% Fines (silt & clay)	METALS (ug/g) Dry Weight								
				As	Cd	Cr	Cu	Hg	Pb	Ni	Zn	Fe
T5 Shallow-1	7/11/03	N.D.	87.8	12.3	7.36	134	203	4.64	230	52.0	469	37348
T5 Shallow-2	7/22/03	13.7	73.1	13.3	11.7	316	294	5.84	306	95.9	738	35332
T5 Shallow-3	7/22/03	13.2	77.9	14.5	10.6	384	268	8.55	327	80.6	773	33892
T5 Deep-1	7/22/03	14.3	88.7	10.0	4.22	142	189	4.28	185	55.1	436	37593
T5 Deep-2	7/22/03	15.9	89.4	9.3	6.18	145	197	4.43	202	63.3	453	38317
T5 Deep-3	7/22/03	15.9	75.8	10.3	11.4	398	274	8.66	306	96.8	675	32193
GN3-1	8/5/03	13.1	85.9	9.1	5.24	190	258	4.85	144	50.2	521	39472
GN3-2	8/5/03	12.8	94.4	8.4	5.03	198	261	4.46	221	47.3	505	35780
GN3-3	8/5/03	11.8	86.6	11.4	5.63	183	289	4.69	250	56.1	555	38029
TN6-1	8/5/03	16.4	80.3	10.0	5.58	174	234	4.56	239	55.2	510	38999
TN6-2	8/5/03	15.8	91.8	10.1	4.94	173	243	4.55	241	49.0	516	38106
TN6-3	8/5/03	13.6	84.8	10.2	4.71	159	234	4.83	366	52.7	455	36209
TN1-1	8/5/03	9.39	75.6	11.9	1.39	124	101	2.49	125	38.3	196	28208
TN1-2	8/5/03	10.3	99.0	18.0	3.92	146	114	2.58	161	43.0	244	27904
TN1-3	8/5/03	10.7	76.3	21.4	2.13	166	140	2.63	158	43.9	251	31481
TN2-1	8/5/03	9.42	80.8	9.40	1.63	119	104	1.77	115	37.8	239	32867
TN2-2	8/5/03	10.2	95.0	9.30	2.52	127	106	2.31	136	46.2	243	31953
TN2-3	8/5/03	9.65	83.6	9.30	1.96	123	109	2.11	139	39.2	251	33632
GN1-1	12/4/03	2.17	18.7	4.85	0.83	62.9	35.4	1.43	52.7	16.5	98	13214
GN1-2	12/4/03	4.50	16.5	4.50	0.71	72.1	26.1	0.73	51.5	13.1	86	10119
GN1-3	12/4/03	5.54	22.1	6.04	0.88	71.8	40.2	1.19	80.5	19.0	118	14085
S1-1	12/4/03	3.71	2.77	10.7	0.29	118	36.4	0.30	54.1	71.9	91	35598
S1-2	12/4/03	4.76	0.49	11.2	0.43	80.6	45.7	1.28	76.9	42.0	116	39712
S1-3	12/4/03	8.15	2.37	9.2	0.54	89.9	57.8	0.98	90.2	59.6	133	28849
T6-1	12/4/03	6.04	86.7	6.11	0.14	24.1	13.1	0.10	25.4	28.1	71.2	30114
T6-2	12/4/03	4.86	57.8	6.37	0.09	17.0	11.2	0.45	15.2	19.6	50.0	22551
T6-3	12/4/03	6.09	85.4	6.59	0.16	27.1	15.8	0.05	24.1	29.7	76.1	35248
S2-1	12/4/03	5.35	41.1	7.23	1.03	97.5	65.2	2.81	81.4	30.1	175	24612
S2-2	12/4/03	4.41	5.98	3.98	0.67	46.0	30.0	2.06	39.6	15.7	89.1	14593
S2-3	12/4/03	4.66	36.0	5.84	0.99	63.7	47.0	3.72	52.8	21.5	126	20371
TN3-1	12/4/03	10.5	49.7	8.38	1.61	125	98.3	5.03	117	38.8	225	33847
TN3-2	12/4/03	7.04	93.4	9.06	1.62	127	100	3.36	143	40.3	241	34899
TN3-3	12/4/03	10.6	92.7	9.32	1.62	137	99.3	4.18	126	42.2	242	36088
TN5-1	12/12/03	12.5	57.0	9.01	4.27	184	183	4.47	189	56.8	401	36467
TN5-2	12/12/03	12.7	89.1	9.16	3.24	163	162	3.79	170	50.4	386	38544
TN5-3	12/12/03	12.7	93.9	9.15	4.18	187	181	4.79	187	54.3	363	35759
S3-1	12/12/03	12.5	94.9	9.79	3.01	179	157	5.11	177	49.6	373	37568

Site - Rep. #	Collection Date	T.O.C. (%)	% Fines (silt & clay)	METALS (ug/g) Dry Weight								
				As	Cd	Cr	Cu	Hg	Pb	Ni	Zn	Fe
S3-2	12/12/03	12.7	89.2	9.33	3.31	158	169	4.32	163	51.0	347	36712
S3-3	12/12/03	12.8	89.8	9.79	2.52	159	147	3.66	163	49.2	356	37417
T4 Deep-1	12/12/03	6.52	61.5	6.28	0.20	19.7	13.1	0.11	27.6	22.2	58	24479
T4 Deep-2	12/12/03	5.74	49.0	7.90	0.18	19.8	12.9	0.15	30.5	17.0	54	26222
T4Deep-3	12/12/03	6.89	72.1	3.18	0.71	24.6	15.5	0.02	77.7	21.5	71	24260
T4 Shallow-1	12/12/03	13.0	56.1	10.7	8.01	241	248	9.58	232	74.6	426	39234
T4 Shallow-2	12/12/03	11.9	91.0	11.6	8.87	226	210	8.69	223	75.3	451	37175
T4Shallow-3	12/12/03	13.5	58.6	11.1	8.41	253	225	7.66	225	72.8	434	38090
TN4-1	12/12/03	13.6	93.0	11.7	5.38	214	185	5.23	187	60.2	396	37472
TN4-2	12/12/03	15.1	81.2	12.4	6.49	224	180	6.24	199	62.0	396	39010
TN4-3	12/12/03	11.1	56.0	11.2	5.97	217	165	6.49	193	57.1	377	33579
T1 Shallow-1	12/18/03	7.10	85.2	8.80	0.10	22.4	13.8	0.06	22.1	26.8	63.5	29156
T1 Shallow-2	12/18/03	5.10	75.3	6.71	0.20	27.2	16.3	0.16	36.4	25.6	64.6	24839
T1 Shallow-3	12/18/03	8.50	63.3	5.51	0.14	20.0	13.4	0.05	23.5	23.0	49.5	25396
T1 Deep-1	12/18/03	6.79	50.7	8.89	0.11	18.8	12.4	0.13	25.3	21.7	48.1	28642
T1 Deep-2	12/18/03	6.01	72.2	8.02	0.12	20.7	9.66	0.00	20.9	25.5	61.0	27684
T1 Deep-3	12/18/03	4.00	88.8	9.38	0.17	22.4	11.5	0.03	21.8	20.6	59.9	26087
T2 Shallow-1	12/18/03	2.48	5.03	3.44	0.30	34.9	10.9	0.20	14.9	10.3	52.6	11720
T2 Shallow-2	12/18/03	2.00	24.7	3.85	0.20	31.6	11.0	0.21	25.9	10.8	57.5	12256
T2Shallow-3	12/18/03	2.60	91.0	3.74	0.35	30.7	13.4	0.19	27.4	11.3	54.0	12015
T2 Deep-1	12/18/03	2.61	0.25	3.79	0.43	83.8	17.1	0.40	24.6	13.1	66.9	12197
T2 Deep-2	12/18/03	2.63	54.1	3.30	0.34	45.0	15.2	0.35	48.9	11.7	52.8	9580
T2 Deep-3	12/18/03	1.92	4.06	3.64	0.63	99.3	26.2	0.55	44.6	17.2	86.0	14639
T3 Shallow-1	12/18/03	9.05	80.8	9.41	1.68	113	96.6	2.53	111	42.6	206	35249
T3 Shallow-2	12/18/03	10.2	92.0	9.18	1.74	127	103	2.74	115	42.1	214	33548
T3 Shallow-3	12/18/03	10.6	70.9	10.3	1.65	124	97.8	2.69	114	41.1	220	33101
T3 Deep-1	12/18/03	10.4	77.1	8.47	1.29	109	97.3	1.83	104	40.2	224	30968
T3 Deep-2	12/18/03	10.2	92.7	7.62	1.46	104	88.6	2.29	99.2	38.6	197	28276
T3 Deep-3	12/18/03	9.88	92.6	8.39	1.60	111	91.5	2.56	112	41.9	208	32010
GN2-1	12/29/03	7.03	66.1	9.36	0.45	41.7	33.7	0.55	35.0	31.3	98.3	37439
GN2-2	12/29/03	4.78	64.6	10.1	0.27	23.7	17.2	0.30	25.4	29.1	76.7	34499
GN2-3	12/29/03	5.12	90.4	5.38	0.31	34.4	23.9	0.30	27.0	23.9	71.0	31598
T7-1	12/29/03	9.09	89.0	13.9	11.57	308	240	15.09	234	73.2	519	35445
T7-2	12/29/03	19.0	74.0	14.2	13.70	287	224	25.24	215	72.6	535	45747
T7-3	12/29/03	12.5	90.8	13.3	13.88	296	247	22.19	231	74.4	554	32987
T8-1	12/29/03	21.0	84.6	11.4	1.98	168	136	3.53	138	50.4	289	39307
T8-2	12/29/03	15.6	87.2	1.30	1.45	160	130	2.65	136	52.7	276	36831
T8-3	12/29/03	20.4	80.2	55.6	2.35	181	133	4.04	149	53.5	283	40390
T9-1	12/29/03	16.4	85.1	12.0	2.04	158	144	3.08	162	53.0	328	39216
T9-2	12/29/03	16.5	89.2	11.2	1.97	159	149	3.33	144	50.6	271	46105
T9-3	12/29/03	16.1	84.8	11.5	2.56	157	145	3.44	152	51.0	337	35251

		T.O.C. (%)	% Fines (silt & clay)	METALS (ug/g) Dry Weight								
				As	Cd	Cr	Cu	Hg	Pb	Ni	Zn	Fe
	MIN	1.92	0.25	1.30	0.09	17	10	0.00	15	10.3	48	9580
	MAX	21.01	99.0	55.6	13.9	398	294	25.2	366	96.8	773	46105
	AVG	9.78	68.9	9.64	3.05	130	115	3.55	128	42.9	263	31095
	ST DEV	4.69	28.1	6.26	3.47	87	88	4.30	86	20.3	185	8756

***** The T.O.C. values shown are the mean of two samples.

+ The T.O.C. value shown is the mean of three samples.

APPENDIX 6. METAL CONCENTRATIONS OF SEDIMENTS COLLECTED IN 1988 (MG/KG DRY WT.)

Sample	N	Ni	Cu	Pb	Cd	Zn	Cr
T1 (shallow)	4	37.3 ± 4.3	176 ± 10.8	151.3 ± 39.8	2.8 ± 0.5	140.5a	256.5 ± 26.1
T1 (deep)	2	49.5	371	28.5	1.7	114b	35
T2 (shallow)	2	86.5	1128.5	101	2.9	367b	71
T2 (deep)	2	127.5	836.5	196	3.7	402b	251
T3 (shallow)	2	22.5	121.5	116.5	2.9	96b	115
T3 (deep)	2	38	163.5	119.5	3.8	112b	145.5
T4 (shallow)	3	61.7 ± 2.4	303 ± 11.5	235.3 ± 46.5	8.9 ± 0.7	225b	430.3 ± 95.1
T4 (deep)	3	60.3 ± 6.3	271 ± 9.9	219.7 ± 25.2	8.0 ± 1.1	180a	302.7 ± 104.9
T5 (shallow)	2	92.5	235.5	212.5	13	307	313.5
T5 (deep)	3	306.3 ± 27.6	1063 ± 216.0	328.3 ± 88.3	8.7 ± 2.1	481.3 ± 59.7	821.3 ± 80.0
T6	3	71.0 ± 6.5	175.7 ± 9.0	23.7 ± 3.7	1.7 ± 0.3	109.7 ± 71.7	39.7 ± 27.1
T7	1	49	172	125	8.5	118	195
T8	1	52	110	25	2.8	75	25
T9	2	91.5	491	324	13.5	563.5	1196
GN1	3	502.3 ± 327.7	1917 ± 378.2	215.3 ± 40.4	4.2 ± 0.4	569.3 ± 78.2	920.3 ± 424.8
GN2	2	84	259.5	190.5	6.2	187	284.5
GN3	2	133	586.5	258	13.9	497.5	415.5
TN1	3	128.3 + 61.5	166 ± 7.1	115.7 ± 15.8	3.9 ± 1.0	100.7± 4.1	309.7 ± 136.7
TN2	2	63.5	156.5	100.5	4.7	134	189
TN3	1	61	156	106	4.9	129	198
TN4	1	52	151	97	4.7	123	151
TN5	5	124.2 ± 40.3	229.4 ± 16.8	174.6 ± 24.5	5.5 ± 1.1	171.4 ± 53.5	459 ± 175.9
TN6	2	133	350	233.5	9.2	276.5	366
SI	3	218 16.5	529 + 28.5	164.3 + 21.3	5.9 + 0	332.7 + 102.8	917.3 + 175.1
S2	2	124	424.5	154	8	271.5	285
S3/S4	1	87	602	249	120	241	334
MIN		22.5	110	23.7	1.70	75.0	25.0
MAX		502	1917	328	120	569	1196
AVG		110	429	164	10.5	243	347
ST DEV		100	412	82.5	22.6	153	299

PART X: Site Assessment

Chapter 25

DYE TRACER STUDY—TRIED AND TRUE METHOD YIELDS SURPRISING RESULTS

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ABSTRACT

The use of tracer dyes is a technically valid and cost-effective method for characterizing contaminant fluxes and hydraulic properties in complex hydrogeologic systems. Dye tracing methods were successfully employed at a site in New Jersey to evaluate the effectiveness of the groundwater containment system and to update the conceptual site model (CSM). The data has driven a reevaluation of the groundwater containment system and CSM, including a review of interim alternative technologies to increase efficiency while a new approach capping the remedial action timeframe at 15 years is tested and implemented.

Uncertainty with regard to the persistence of constituents in downgradient monitoring wells and the influence of long-term pumping from the interconnected overburden and basalt bedrock aquifers led to the evaluation of methods that would both address multiple hypotheses on contaminant flux and update the CSM. The property contains several distinct features that add to its complexity, including a former surface impoundment underlain by alluvial sediments and fractured bedrock, and the immediate presence of water bodies.

The fluorescent dyes fluorescein, eosine, and rhodamine WT were selected for the Dye Tracer Study (DTS) and individually injected at three locations following

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baseline sampling. The injection locations considered the presence of source material (former surface impoundment), hydraulic properties of the aquifers (pumping induced gradients, travel times, heads from adjacent water bodies), and parent/daughter compound concentration relationships. The DTS was conducted over 14 months and involved the collection of grab and composite samples from monitoring and extraction well networks, and along an adjacent brook.

A single dye, fluorescein, was identified over the course of the DTS. The fluorescein was injected in the former surface impoundment and travelled south at an approximate rate of ten feet/day. The DTS illuminated flow pathways that were unexpected in terms of speed of groundwater migration and extent laterally and vertically.

Keywords: dye tracing, groundwater tracer, fluorescein, eosine, rhodamine WT, contaminant flux, groundwater flow, site assessment, site characterization.

1. INTRODUCTION

Tracer dyes have been used to aid understanding of complex systems for at least the last century, with applications ranging from characterizing human disease vectors to anthropomorphic contributions to environmental degradation (USGS, 1986). Tracer dyes are used to understand receptor pathways related to an identified condition. The following discussion focuses on the use of tracers at an environmental remediation project where contaminant flux was poorly understood, including uncertainty with regard to groundwater containment and the applicability of the working conceptual site model (CSM).

Dye tracer methods were employed to test three hypotheses on groundwater flow and contaminant migration mechanisms. The data revealed flow pathways that proved the least anticipated hypothesis, which is now the basis for the revised CSM.

2. PROJECT BACKGROUND

Soil and groundwater contamination was identified at a former organic pigments manufacturing plant located in northern New Jersey in the mid-1980s. The contamination consists of chlorinated ethenes and benzenes, primarily tetrachloroethylene (PCE) and 1,2-dichlorobenzene (IT Corporation, 1990). Lime neutralization sludge was disposed in surface impoundments located in the northern half of the property (North Yard) prior to 1940 (earliest records available) and continuing through the mid-1970s. Manufacturing was located in the southern half of the property (South Yard).

Remedial investigations revealed contamination in soil and groundwater. The remedial action construction consisted of demolishing the manufacturing plant, capping the North Yard and South Yard, and startup of a groundwater and soil vapor extraction and treatment system. Prior to activation of the groundwater extraction and treatment system (GETS), volatile organic compounds (VOC) exhibited concentrations exceeding the New Jersey Department of Environmental Protection (NJDEP) Ground Water Quality Standards (GWQS) at overburden compliance wells located to the east across a brook. Since GETS startup, VOC concentrations in the overburden compliance wells have been reduced by three orders of magnitude. However, several compounds continue to exhibit concentrations above GWQS despite extraction system upgrade programs. Consequently, it remained unclear as to whether VOC migrated to compliance wells from the west beneath the brook (working CSM) or via an upward gradient from the underlying bedrock (remedial investigation finding). A third hypothesis proposed contaminant migration from the North Yard along the shallow fractured basalt bedrock.

As a result of the extraction system upgrade outcomes and the competing hypotheses on groundwater flow and contaminant migration mechanisms, GETS effectiveness remained uncertain. Dye tracing was considered the most efficient method for characterizing groundwater flow and contaminant migration to compliance wells (OUL, 2002). A Dye Tracer Study Work Plan was therefore developed and implemented in October 2005 and the field phase completed in December 2006. Two additional rounds of dye tracer data have since been collected: November 2007 and January 2009.

3. PHYSICAL AND GEOLOGIC SETTING

The property is situated in the valley formed by the First Watchung and Second Watchung mountain ranges (NJGS, 2003). Property topography ranges from approximately 206 feet above mean sea level (msl) to 170 feet above msl, with the topographic gradient toward the southeast. The topographic high is the North Yard and the topographic low is a brook channel at the southeastern corner of the South Yard. Storm water infiltration is limited by an impermeable liner incorporated into the cap across the property and is instead conveyed to the brook.

The brook, which drains a watershed between the crests of the two mountain ranges, runs into the northern limit of a man-made pond (dammed). The pond is situated adjacent to the north border of the North Yard. The brook then exits the southern side of the pond via a dam spillway and enters the property at the northeastern corner, adjacent to the North Yard. The elevation of the brook transitions from approximately 179 feet msl at the northeastern corner of the

property to approximately 175 feet msl at a second spillway located approximately 900 feet south of the dam. The brook elevation drops approximately four feet at the spillway and exits the property near the southeastern corner of the South Yard at an approximate elevation of 170 feet msl.

The head in the pond likely drives water as seepage into the local sediments at and surrounding the dam and, where the brook leaves the pond, the heads are still held artificially higher. The pond potentially forces a southerly gradient locally. In addition, being situated in the valley between the two Watchung Mountains increases the potential that higher-velocity depositional environments existed during glacial episodes. Therefore, glacio-fluvial deposits are likely to exist in the native sediments (NJGS, 2003). Where glacial or post-glacial streams were running, coarse sediments would have been deposited. These features, called "paleo-channels", now buried by subsequent sedimentation and artificial fill, would create a significant permeability contrast with typical till sediments and could act as important conduits for overburden groundwater flow.

Bedrock across the property consists of two distinctly different formations: Metamorphosed sedimentary rock (of the Triassic Newark Basin), including shale and sandstone layering, and Jurassic Age basalts of igneous origin that were intruded into and flowed over the shale and sandstone (Geraghty & Miller, Inc., 1993). Erosion and folding/faulting of the rock formations produced the current subsurface conditions, along with surface weathering and erosion. Basalt bedrock outcrops in and along the brook at the northeastern section of the property. The basalt outcropping transitions to a gravelly stream bed as the brook flows from the North Yard to the South Yard. This transition is complete in the vicinity of the concrete spillway and indicates that glacial-alluvial sediments may extend under and across the brook.

The basalt is encountered at varying depths across the property, but tends to be present at shallower depths in the northern and eastern portions and ranges from approximately 25 feet to 45 feet below ground surface (bgs). The bedrock surface generally slopes to the southwest, with minor undulations. The shallow basalt is in contact with alluvial sediments, and was observed to have a highly weathered zone—boring logs indicate the presence of significant vertical joints or fractures (IT Corporation, 1990). The exposed shallow basalt at the northeast corner of the property exhibits a high degree of weathering and fractures. The deeper basalt unit was shown via boring logs to have generally lesser amounts of fracturing and thus appears to have lower (or significantly lower) permeability than the shallow basalt (Geraghty & Miller, Inc., 1993). Significant decreases in head measured during drilling and in ongoing water level monitoring indicate that this layer acts generally as a confining unit. Primary porosity in the Watchung

Basalt is negligible. Secondary porosity is provided by joints. This is exemplified by the presence of a lineament located along the western portion of the property. The lineament has revealed a bedrock fault or fracture system that is under the direct influence of the deep bedrock groundwater extraction system as evidenced by pumping induced hydraulic gradients in South Yard wells.

Groundwater is approximately 20 feet deep in the overburden aquifer and shallower in the immediate vicinity of the brook. Depth to groundwater in the fractured bedrock is generally similar. Depth to water in the deep bedrock beneath the South Yard is much deeper, ranging from more than 75 feet to almost 200 feet. The lower water levels in the deep bedrock are attributed to the long-term remedial pumping. The vertical gradient between the overburden and the shallow fractured bedrock groundwater is typically downward and low, indicating a strong hydraulic connection. The vertical gradient between the shallow and deep bedrock groundwater is high, indicating a weak hydraulic connection.

The North Yard was constructed over time as a series of surface impoundments and contains an estimated 94,000 cubic yards of lime neutralization sludge, including some with pigments and residues (IT Corporation, 1990). The sludge has a relatively low permeability and is in direct hydraulic connection with native sediments (alluvium) and weathered/fractured basalt. Remediation features in the North Yard include four overburden and shallow bedrock groundwater extraction wells on the eastern perimeter, west of the brook, 40 dual-phase vapor extraction (DPVE) wells installed in the former surface impoundment, and two deep bedrock groundwater extraction wells.

The South Yard includes a former equalization basin and its predecessor, an unlined process lagoon, as well as thick, reworked sediments and fill, and the slabs/foundations of former manufacturing buildings. Based on boring logs, artificial fill and/or constructed features comprise almost all of the shallow subsurface materials above bedrock in the South Yard. Remediation features in the South Yard include six overburden and shallow bedrock groundwater extraction wells on the eastern perimeter, west of the brook, and a network of 20 soil vapor extraction (SVE) wells installed in the vicinity of the former lagoon.

4. DYE TRACER STUDY METHODS

The Dye Tracer Study (DTS) was designed to test hypotheses on groundwater flow and contaminant transport mechanisms from three sections of the property: North Yard, South Yard, and the topographic and hydraulic high point at the western edge of the property. The objectives of the DTS were to evaluate groundwater flow conditions and contaminant flux within and between the

alluvium and the shallow fractured bedrock, identify discharge zones and estimate travel times, and evaluate the degree of mixing.

4.1 Tracer Dye

Three tracer dyes were employed for the DTS: fluorescein, eosine, and rhodamine WT. The tracers are of a class of fluorescing compounds known collectively as xanthenes dyes (i.e., derived from xanthene). Xanthene dyes are water soluble, stable (i.e., not easily affected by geochemical changes), readily disperse (i.e., not adsorbed by formation materials), and are not known to cause toxicological impacts. They are strongly fluorescent, making detection possible even under highly dispersive conditions. For these reasons, xanthene dyes are considered conservative tracers in a groundwater environment (Flury and Wai, 2003).

Fluorescein and eosine were procured as a powder containing approximately 75 percent dye equivalent and 25 percent diluent. Diluent (typically starch) in dye mixtures is a standardizing material used by manufacturers to ensure that different batches of dye have the same fluorescence intensity. Diluents may also improve the mixing performance of the dye. The fluorescein was received in six, 22-liter carboys, while the eosine was received in three, 22-liter carboys. Each carboy was filled with four pounds of powdered dye. To each carboy, four gallons of municipal water were gradually added to thoroughly dissolve the dye. Fluorescein was introduced to the North Yard lime sludge/alluvial sediments at six randomly selected DPVE wells. Eosine was introduced via an overburden monitoring well (hydraulic high point) located along the western border of the property.

Rhodamine WT (water tracing) was received pre-mixed in four, 1-quart Nalgene bottles (20 percent dye equivalent and 80 percent water). Nothing additional was required for this dye in terms of preparatory work. Rhodamine WT was introduced via an SVE well located in the western portion of the South Yard.

4.2 Background Data

The DTS design considered the potential for interference (analytical peaks in or near acceptable wavelength ranges) by naturally fluorescing substances or similar manmade dyes that may be associated with former production (OUL, 2002). To investigate potential sources of fluorescence interference in groundwater and surface water, two rounds of background sampling were conducted. Background concentrations of a compound with a fluorescence wavelength similar to that of fluorescein (approximately 515 nanometers [nm]) were identified in wells and brook monitoring stations. Neither eosine or rhodamine, nor substances which

fluoresce at or near the wavelengths of these dyes, were detected above analytical method detection limits.

A second unknown fluorescing substance was identified during background sampling. Wavelength peaks of this substance were in the 483 nm range. This compound was labeled the 483 dye and was identified in several monitoring stations that exhibited background concentrations of the compound fluorescing at 515 nm. However, while background concentrations of the 515 nm substance were exhibited widely across the property, the 483 dye was limited to locations in the vicinity of the former unlined process lagoon and the northern section of the North Yard. Final deposition in the North Yard occurred in the northern section and reportedly consisted of materials excavated from the unlined process lagoon. The identification of the 483 dye at the two distinct locations suggests that it may have been associated with former production, whereas the 515 nm background substance is either from naturally occurring processes or is an artifact of historic production, which has had a longer period to disperse. Sampling of upgradient groundwater to determine true background quality was not performed due to a lack of monitoring wells (NJDEP, 2005).

4.3 Field Methods

The dyes were introduced on November 1, 2005. The injection wells were tested with potable water prior to dye introduction to measure the rate of intake. Due to the sensitivity of the analytical method and the high potential for false positives from cross-contamination, care was taken in the transport and handling of the dyes during introduction. Each dye was transferred to its respective injection point in dedicated poly-sheeting. Dedicated funnels were used at each injection point to introduce the dyes. All disposables used during dye introduction at a given injection point were disposed afterwards and replaced with new disposables prior to commencing dye introduction at the next well. A dilute solution of bleach was available to neutralize spilled dye. No injection location was subsequently used for monitoring.

Prior to introducing a dye, water was added through a funnel to wet the well casing/riser pipe. This helped to prevent dye loss to the inside surface of the well casings. The entire volume of the dye was introduced as a single slug. Each well was flushed with ten gallons of municipal water at a rate equivalent to the observed intake.

Monitoring of dye transport through the aquifer system was accomplished by setting carbon composite samplers at each station for a period of one week. Grab samples of water were also collected to provide dye concentrations at a known point in time. The one week period was maintained throughout the DTS to ensure

consistency in the analytical data. After one week, the carbon samplers were collected from their respective stations along with the water grab samples. Groundwater levels were measured prior to sample collection. To prevent cross-contamination, new latex gloves were used at each sample station. All samples were shielded from sunlight during collection to prevent the dyes from degrading. Carbon composite samplers were bagged separately from the water vials. All samples were documented/tracked using chain of custody procedures (NJDEP, 2005) and shipped on ice directly to Ozark Underground Laboratories (OUL).

The carbon samplers were supplied by OUL and constructed of a fiberglass mesh (1.3 millimeters [mm] to 1.5 mm). Each sampler was pre-filled with a standardized 4.25 grams of Barnebey and Sutcliffe Type AC Activated Carbon and heat sealed. In preparation for deployment, each carbon sampler was triple-soaked in distilled water for ten minutes per soak.

The first round of carbon samplers were deployed on October 31, 2005, one day prior to dye introduction to ensure that any rapid movement through the aquifer system would be identified. During the first six weeks after dye introduction, carbon samplers were set and retrieved on a weekly basis. After the initial six rounds of weekly sampling, carbon samplers were set biweekly until August 22, 2006. The carbon samplers were set once per month thereafter, beginning in September 2006, until field phase termination on December 19, 2006.

4.4 Analytical Methods

The carbon composite samplers were washed at OUL (Aley, 2003) with dye-free, unchlorinated water to remove sediment and organic matter. After washing, the packets were shaken to remove excess water, and the carbon emptied into new disposable plastic beakers. The dyes were then eluted from the carbon with a solution of five percent aqua ammonia (29 percent ammonia) and 95 percent isopropyl alcohol (70 percent alcohol, 30 percent water), and enough potassium hydroxide flakes to supersaturate the solution. The potassium hydroxide was added until a supersaturated layer was visible at the bottom of the container. The supersaturated layer was not used for the elution. Fifteen milliliters of the solution were poured over the washed charcoal, the beaker capped, and the sample allowed to stand for one hour. The liquid was subsequently decanted into a new disposable beaker.

Three milliliters of elutant were extracted using a disposable polyethylene pipette and transferred to a disposable polystyrene cuvette specifically designed for fluorometric analysis. The cuvette was then placed in the spectrofluorophotometer for analysis. The spectrofluorophotometer performs a

synchronous scan of the sample and generates a plot. Emission fluorescence is depicted on the plot. The fluorescence peak represents the concentration of a given dye in parts per billion (ppb), which is calculated by separating fluorescence peaks due to dyes from background fluorescence and then calculating the area of the peak. The area is proportional to the area obtained from a standardized solution. The wavelength emitted indicates which type of dye is present.

Water grab samples were normally tested without pre-treatment, unless extremely turbid. In instances where samples were turbid, the laboratory let the solids settle from the sample, centrifuged the sample, or diluted the sample.

Ozark Underground Laboratory has established normal emission fluorescence wavelength ranges for the dyes used. A range is equivalent to mean values plus and minus two standard deviations. Detection limits for the dyes were determined by OUL based on the concentration necessary to produce emission fluorescence peaks where the signal to noise ratio is three. For OUL to deem a concentration a positive dye recovery, the following conditions must be met:

In the elutant and the water, there must be at least one fluorescence peak at the station between the minimum and maximum wavelength peak for a given dye**.**

A positive dye detection in elutant must be at least three times the detection limit and at least ten times the concentration detected in a given background sample. The peak must resemble the typical shape exhibited by the dye.

For a peak to be deemed a positive recovery of dye in water (grab sample), there must be a corresponding positive recovery of dye in the elutant (composite sample) from the same station. The concentration must be at least three times the detection limit.

5. RESULTS AND DISCUSSION

Fluorescein was the only tracer dye to exhibit concentrations during the DTS. Eosine exhibited low concentrations at one downgradient location during post-DTS sampling. The groundwater flow and contaminant flux pathways that are now established by way of the DTS findings have driven significant revisions to the CSM.

5.1 Groundwater Flow and Discharge

Fluorescein was injected into North Yard DPVE wells, which are constructed through the alluvial sediments to the top of the shallow fractured bedrock surface. Fluorescein was subsequently detected in a majority of the monitoring points,

exhibited a wide range of travel times and concentrations, and followed a north to south transect across the property. The relative concentrations of fluorescein observed during the DTS and VOC observed during quarterly groundwater sampling mirror each other at all monitoring points. The fluorescein travel time correlated with the presence and relative concentrations of VOC daughter products at a given monitoring well. Only extraction wells were available for sample collection from the overburden and shallow fractured bedrock. Therefore, dye travel times and relative concentrations are influenced by placement of the screened interval, formation characteristics, and extraction rates.

Fluorescein was positively identified in an overburden extraction well located at the southeast corner of the North Yard during week 4 and peaked during week 18 (February 28, 2006). Fluorescein was positively identified in an overburden extraction well located at the northeast corner of the South Yard during week 16 (February 14, 2006). The approximate distance between these two points is 355 feet. Fluorescein was also positively identified in overburden and shallow bedrock extraction wells along the eastern edge of the South Yard during week 16. These points form a north to south transect (South Yard transect) from the North Yard, with the shallow bedrock extraction well situated the furthest, approximately 725 feet, from the closest fluorescein injection point.

Fluorescein velocities were calculated by dividing the distance between the closest North Yard injection point and a given monitoring point by the time elapsed between injection and the first positive dye concentration at that given monitoring point. This equated to a velocity of approximately 6.1 feet per day (ft/d) for fluorescein to reach the southeast corner of the North Yard. Velocities between the closest North Yard injection point and the extraction wells along the South Yard transect ranged from 4.3 ft/d to 6.9 ft/d (shallow bedrock). The velocities drop by a factor of roughly two if calculated based on when the maximum concentration is observed and by a factor of roughly three when the mid-point of the decreasing concentration is used for the calculation. The change in velocity at a given monitoring point was a function of the trend, which in turn is a function of well location, formation in which the well is screened, extraction rate, and tracer dye dispersion.

The fluorescein trend lines, which reflect relative concentrations, travel time, and dispersion, can be related to VOC concentration data. For example, each well along the South Yard transect exhibits high concentrations of parent (PCE) and daughter compounds (trichloroethylene, cis-1,2-dichloroethylene, vinyl chloride) in groundwater samples. Conversely, an overburden extraction well located at the southern edge of the South Yard, which exhibited low concentrations of fluorescein late in the DTS (week 36, July 3, 2006), but high concentrations of 483 dye, also exhibits high concentrations of daughter products in groundwater

samples (parent compounds are typically not observed). The location of this well may represent a low velocity overburden plume, which is undergoing biodegradation and may or may not be isolated from shallow bedrock.

The data collected from two bedrock monitoring wells located at the northeast and southeast corners of the South Yard demonstrate the preferential flow in the shallow fractured bedrock. These wells are situated at the northern and southern extent of the South Yard transect. Each of these wells is installed below the shallow fractured zone of the basalt. The bedrock well located at the northeast corner of the South Yard did not exhibit positive detections of fluorescein until late in the DTS (week 34, June 19, 2006). The highest fluorescein concentration was exhibited in samples collected at the end of the DTS (December 19, 2006). The well is situated in a portion of the property from which past groundwater elevation data has demonstrated a strong downward vertical gradient between the overburden and shallow basalt zones and the deep basalt as a function of the extraction system. The bedrock well located at the southeast corner did not exhibit fluorescein during the DTS. Instead, the well consistently exhibited concentrations of the 483 dye and the 515 nm background substance. These data indicate that groundwater flow and contaminant migration occurs through the shallow fractured basalt, while the deeper competent basalt has low primary and secondary permeability.

Variability of flow and location were key drivers for whether the brook acted as a discharge or recharge boundary for groundwater. Data indicate that the section of the brook lying above the spillway acts as a recharge boundary except in periods of very low flow. This observation is verified by the fact that VOC are generally not observed during monitoring events in samples collected from the brook and the compliance well situated above the spillway. During low flow conditions, combined with the change in hydraulic head on the downstream side of the spillway, the southern reach of the brook is a groundwater discharge zone. This is verified by surface water and compliance well analytical data which intermittently exhibit low VOC concentrations. Fluorescein was detected in the compliance well located below the spillway late in the DTS.

5.2 Contaminant Flux

Sampling results from the remedial investigations and subsequent monitoring has demonstrated that contaminated groundwater persists in portions of the bedrock. The North Yard continues to emanate significant contaminant fluxes to the groundwater extraction system. While groundwater concentrations have dropped from initial operations, contaminant fluxes measured at the extraction points have been relatively steady over the past several years. Based on the dye-tracer testing and the observed pattern of highest concentrations in the shallow groundwater

flow system, the contact zone between the overburden and upper basalt appears to be of the highest transmissivity and fastest groundwater flow zone. The breakthrough of fluorescein to the South Yard transect indicates that the prevailing velocity could be as high as 10 ft/d and the estimated horizontal hydraulic conductivity could be on the order of 100 ft/d.

A significant finding during the DTS was the presence of the 483 dye. The 483 dye is considered a marker for historic contaminant migration since it has been identified only at locations that represent longer periods of contaminant flux than for the DTS injected tracers. The presence of 483 dye in extraction wells along the South Yard transect is a strong indicator of contaminant migration in the shallow fractured bedrock from the North Yard. With several exceptions, the shallow bedrock extraction well on the South Yard transect exhibited the highest concentrations of the 483 dye over the course of the DTS. While the presence and higher concentrations of the 483 dye in the shallow bedrock extraction well may be due to its proximity to the former unlined process lagoon, its presence in all extraction wells along the South Yard transect is a strong indication of a North Yard flux.

5.3 Extended Period Dye Tracer Data

Two additional rounds of dye tracer data were collected: November 2007 and January 2009. The January 2009 round had the advantage of incorporating wells installed during a groundwater remedial investigation conducted between November and December 2008.

The fluorescein concentration exhibited in a new shallow bedrock well installed in the central portion of the South Yard was high compared with other wells sampled in January 2009. The 483 dye was also present at a relatively high concentration, indicating a long-term flux from the North Yard. The contaminant concentrations in this well are the highest of any well on the property. This is consistent with preferential flow in the uppermost portion of the fractured basalt where the well was constructed.

Fluorescein was detected at higher concentrations in new shallow bedrock compliance wells installed to the east of the brook than in the corresponding overburden wells. Similarly, contaminant concentrations across the brook are higher in the shallow bedrock wells than in the overburden wells. Since GETS startup, contaminant concentrations in the overburden wells east of the brook have decreased by up to three orders of magnitude. There are no baseline analytical data available for the shallow bedrock groundwater east of the brook. It is important to note that, as with the fluorescein concentrations, contaminant concentrations in the wells to the east of the brook are several orders of magnitude

below concentrations in the extraction wells and the monitoring wells located to the west in the South Yard. Therefore, though the primary groundwater flow direction in the shallow fractured bedrock is south, parallel to the brook, based on dye and contaminant trends across the brook, preferential flow in the bedrock is the likely mechanism for contaminant migration east of the brook.

Based on hydraulic head data and observations during pumping, the bedrock monitoring well located at the southwest corner of the South Yard is hydraulically connected to a deep bedrock extraction well in the North Yard. The bedrock monitoring well exhibited increasing fluorescein concentrations, nearly tripling between November 2007 and January 2009. This indicates that fluorescein is reaching deeper bedrock strata over time. The two North Yard deep bedrock extraction wells also exhibited increasing fluorescein trends, indicating further downward migration over time.

The presence of low fluorescein, and for the first time eosine, concentrations in a shallow bedrock monitoring well located near the western border of the South Yard during the January 2009 sampling event is considered a model for groundwater flow and contaminant flux at the property. Neither dye was detected in the overburden well of the well pair. The well pair is located south of the North Yard and the eosine injection point. As with the low concentrations in the shallow bedrock wells to the east of the brook, the fluorescein and eosine at this well represents preferential migration from the North Yard, albeit at very low concentrations. Contaminant concentrations are correspondingly low. The migration of eosine (injected in the overburden at the western edge of the property) demonstrates the interconnection between the overburden and shallow bedrock and the preferential flow in the fractured zone. Eosine has moved vertically under the influence of the prevailing hydraulic head from the overburden to the shallow fractured bedrock and migrated to the south.

6. CONCLUSIONS

Dye tracer methods identified and correlated source area contaminant flux, groundwater concentrations, groundwater discharge locations, and travel times as related to the presence of parent compounds and daughter products. Based on the results of the tracer sampling, the established CSM has been revised. The revised CSM now recognizes the contaminant flux from the North Yard and its southerly migration with the predominant hydraulic gradient.

Summarily, the North Yard contaminant flux migrates along the contact zone between the alluvial sediments and the underlying shallow fractured basalt. This contact is not impervious but slightly leaky, as fluorescein eventually did migrate

into the competent basalt under stressed (pumping) conditions. While the presence of a South Yard source area cannot be discounted, the tracer data indicate that once in the South Yard, the contaminant flux migrates vertically through primary fractures under the influence of the deep bedrock groundwater extraction system.

Dye tracer methods were selected over more traditional means, such as monitoring wells/piezometers, due to the complexity of the aquifer system. Dye tracer methods allowed the testing of three hypotheses, essentially eliminating the need to conduct three separate, albeit interrelated, remedial investigations. The DTS yielded valuable data on groundwater flow and contaminant migration at a low cost when compared to traditional means. Compounding the value was the fact that the least anticipated hypothesis is now the basis for the revised CSM.

7. NEXT STEPS

Modification of the North Yard DPVE well containment system will be required to control contaminant flux to the alluvial sediments/shallow fractured bedrock interface. Control of the South Yard contaminant flux vertically to the deep bedrock must also be considered. The first step in this process was the completion of a State of the Art Technology Evaluation and Economic Analysis Report, which identified alternatives for North Yard source control and outlined a pre-design investigation work plan.

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Chapter 26

FLOATER/SINKER SITE ASSESSMENT COMPLICATED BY ASBESTOS

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ABSTRACT

This paper is a case study of how soil and groundwater investigations were conducted at a site containing building asbestos and having access limitations. While previous evaluations of site conditions utilized time-consuming conventional soil boring and monitoring well procedures, continuing investigation necessitated more advanced screening techniques. Since the principal site contaminants are hydrocarbons (both light and dense), Cone Penetration Testing (CPT) and Ultraviolet Induced Fluorescence (UVIF) technologies were chosen to evaluate subsurface conditions. The first round of CPT/UVIF testing indicated groundwater contamination may have extended under the plant buildings which led to building asbestos removal and structural demolition. The second round of CPT/UVIF field work completed in four days appears to have successfully delineated the hydrocarbon contamination.

Keywords: Cone Penetration Testing (CPT), Ultraviolet Induced Fluorescence (UVIF), asbestos, fuel oil, Dowtherm®, heat transfer fluid, LNAPL, DNAPL

1. BACKGROUND

Owens Corning (OC) previously manufactured a high-temperature pipe/equipment insulation product in Berlin, New Jersey. Prior to 1972 the calcium silicate insulation product contained 11% to 14% asbestos, making it an asbestos-containing material (ACM). The manufacturing plant closed in 1993 which triggered New Jersey's Industrial Site Recovery Act (ISRA) program

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within the Department of Environmental Protection (NJDEP). The Department directed that the Technical Requirements for Site Remediation (TRSR) be followed in evaluating site conditions and potential areas of environmental concern (AOCs).

The site is located within the New Jersey Pinelands Commission boundary and occupies approximately 45 acres consisting of production and warehouse buildings and other support structures which cover about 20 percent of the property. Another 5 percent of the property is paved with the remainder undisturbed woods. The water table under the plant buildings ranges from 10-15 feet bgs (below ground surface) and the soil lithology is sand, gravelly sand and silty sand extending more than 70 feet bgs. The site's topography includes some relief with the low spot near the center of the site. Storm water in this area is collected in an infiltration pond called the Lower Pond. When this pond filled, excess water was pumped to a second infiltration pond located at a higher elevation known as the Upper Pond. The former manufacturing process required curing and drying of the molded wet process pipe insulation material using curing ovens heated with heat transfer fluid with temperature ultimately maintained by natural gas firing and fuel oil backup.

Initial site investigation activities under the ISRA program identified soil and groundwater impacts related to the former manufacturing operations. Most of the identified impacts were primarily related to the historic use of Dowtherm® (a heat transfer fluid), fuel oil and various lubricants. Groundwater is affected by the Dowtherm® (sinker) and fuel oil (floater). Initially thirteen areas of concern (AOCs) were established around the site outside of the plant buildings. Subsequent investigations determined that no further action was warranted for eight of the thirteen AOCs. This paper will focus on investigative techniques for two of the AOCs addressed in the Remedial Action Workplan (RAW) namely: AOC #3 (former Dowtherm® storage and transfer area) and AOC #8 (the Lower Pond and adjacent alley). The site plan (Figure 1) shows the AOC and monitoring well locations in relation to the building footprint.

2. SUBSURFACE INVESTIGATION TECHNIQUES-THEN AND NOW

Numerous site investigations prior to 2003 indicated the presence of LNAPL (light non-aqueous phase liquid) in some soil and groundwater samples at AOC #3. The principal VOC (volatile organic compound) contaminant is benzene (from fuel oil). Also, limited direct investigation within the aquifer [one deep

monitoring well (MW-11D) between AOC #3 and AOC #8] indicated the presence of DNAPL (dense non-aqueous phase liquid) in groundwater samples.

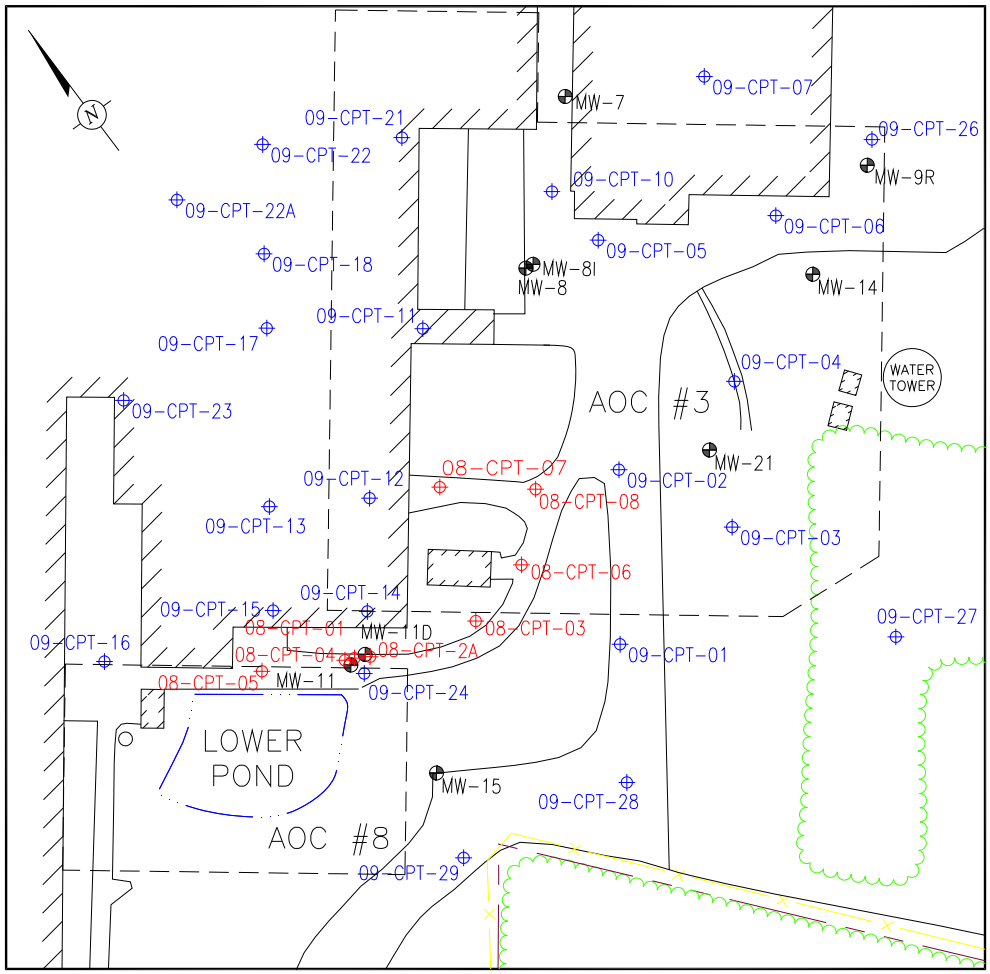

Figure 1. Site plan showing AOC, monitoring well and CPT/UVIF boring locations

The principal SVOC (semi-volatile organic compound) contaminants are diphenyl and diphenyl ether (from Dowtherm®) (New Jersey Department of Environmental Protection, 2003).

All previous subsurface investigations were conducted using traditional soil boring procedures. These include the collection and inspection of numerous soil/groundwater samples followed by costly laboratory analysis and data evaluation. Beginning in 2008 OC implemented more advanced screening technologies to accelerate data collection/analysis and to reduce sampling and

analytical costs. Environmental consulting services are supplied by ARCADIS U.S., Inc. of Newtown, Pennsylvania.

Undertaking advanced screening technologies can help reduce or even replace extensive and costly soil sampling programs. The screening technologies have the unique advantage of providing essential information about the source and extent of contamination in real time. Advanced screening technologies can determine subsurface heterogeneity within the geologic formations. Also, the technologies can estimate the relative magnitude of contamination within underground formations.

2.1. Cone Penetration Testing

Cone Penetration Testing (CPT) is a technology that can be used to delineate soil types and permeability for unconsolidated formations to depths exceeding 100 feet. By eliminating traditional soil borings, costly waste disposal associated with soil cuttings can be eliminated. CPT measurements are derived by continuous penetration resistance as the CPT probe is driven to depth. Soil deformation is interpolated by measuring probe tip resistance, friction sleeve resistance and dynamic pore pressure. CPT provides real-time results and continuous logs of soil borings. In addition, since CPT soil borings interpret subsurface lithologies, possible biases and interpretation differences by field technicians/geologists are eliminated.

2.2. Ultraviolet Induced Fluorescence

Ultraviolet Induced Fluorescence (UVIF) utilizes fluorescent radiation to identify hydrocarbons present in soil and groundwater. UVIF technology incorporates a sensor that is deployed by direct push methods. High intensity ultraviolet light is emitted through a sapphire window in the side of the UVIF probe. The UV light is absorbed by hydrocarbons in the subsurface and re-emitted, or fluoresced, at a different wavelength. This fluorescence is captured by a fiber optic cable within the probe and transmitted to the surface. Since fluorescence intensity is proportional to hydrocarbon concentration, this technology is able to effectively delineate the presence and vertical extent of hydrocarbon-impacted soil in the borehole (Roux Associates Inc., 2007).

2.3. Combining Cone Penetration Testing With Ultraviolet Induced Fluorescence

The amalgamation of the cone penetrometer and the ultraviolet induced fluorescence module produces a powerful site characterization tool for geo-environmental investigations. The CPT/UVIF probe (Figure 2) combines the

UVIF module with the cone penetrometer to detect fluorescence and soil mechanical properties. As the UVIF module collects information on contaminant characteristics, the CPT probe characterizes the ground in terms of soil type, soil permeability, soil strength and phreatic surface. Therefore, at each test location an integrated vertical profile of contaminant location, relative contaminant concentration, soil stratigraphy and soil permeability are generated in real time on site. Having all of this information allows for on-site assessment and decision making resulting in optimization of the site investigation and ultimately a reduction in site characterization costs (ConeTec, 2006).

3. REMEDIAL INVESTIGATION RESULTS

3.1. CPT/UVIF Results in 2008

In the summer of 2008 the CPT/UVIF investigation technique was employed to evaluate the horizontal and vertical extent of DNAPL in the vicinity of MW-11D near the Lower Pond (AOC #8). The site plan (Figure 1) shows the 2008 CPT/UVIF sounding (boring) locations in red. In conjunction with the eight CPT/UVIF borings, soil samples were collected using direct push drilling at select intervals in two soil borings collocated with the CPT/UVIF borings. The samples were used to confirm select UVIF responses and to allow visual and analytical confirmation of soil impact. Each sample was visually inspected, logged and field screened with a photoionization detector (PID) prior to being submitted to the laboratory for analysis for diphenyl and diphenyl ether. Upon completion the boreholes were backfilled to comply with NJDEP requirements. Prior to initiating the drilling work, a utility locating service was used, in conjunction with site-specific information to clear the proposed drilling locations. During drilling, soil cuttings were containerized in 55-gallon steel drums and were shipped off-site for disposal/recycling.

CPT data confirmed soil lithology to be sand, gravelly sand or silty sand to a depth of 70 feet bgs. Groundwater is located at 10-12 feet bgs. UVIF data showed a hydrocarbon mixture (fuel oil and Dowtherm®) that straddles the water table between 10 and 15 feet bgs. UVIF data also confirmed the presence of a DNAPL zone approximately 50 feet bgs particularly near MW-11D. However, due to the close proximity of the plant buildings this series of borings did not completely determine the physical extent of the DNAPL associated with AOC #3. All available data indicated the groundwater contamination may have extended under the plant buildings. Conducting groundwater investigations from inside the buildings were stymied due to loose ACM insulation (walls, ceiling, etc.) falling down and low overhead room to maneuver field equipment. Therefore the

buildings and equipment were abated for asbestos and the structures demolished by mid-2009 to facilitate continued field investigation.

3.2. Preliminary CPT/UVIF Results in 2009

In the summer of 2009 CPT/UVIF field work commenced to further delineate the extent of the DNAPL observed in MW-11D and LNAPL observed in the area directly east of the former manufacturing building. Thirty borings were advanced in areas identified as requiring further delineation. Fifteen of the borings were located in the previously existing building footprint. The site plan (Figure 1) shows the 2009 CPT/UVIF sounding (boring) locations in blue. As in 2008 in conjunction with the CPT/UVIF borings, a direct push drilling rig (i.e. Geoprobe®) was utilized to collect sixteen confirmatory soil lithology and analytical samples from 8 borings. The CPT/UVIF borings took four days to complete and the Geoprobe® samples covered two days.

CPT data shows top of groundwater at 9-12 feet bgs. UVIF data appears to complete the delineation of the LNAPL and DNAPL plumes. The data plots for Sounding (Boring) #10 (Figure 3) show typical CPT/UVIF borehole profiles. The UVIF profile shows hydrocarbon detections at the groundwater interface and at approximately 50 feet bgs. The "**qt**" plot represents cone tip resistance in tsf (tons per sq ft), the "**fs**" profile portrays sleeve friction in tsf, the "**u**" plot shows pore pressure in ft, the "**UVIF"** profile represents UVIF fluorescence intensity in volts and the "**SBT**" plot is the soil behavior type based upon computerized interpretation of the geo-physical parameters **qt, fs** and **u.**

4. POTENTIAL REMEDIAL APPROACH

Since the site is within the New Jersey Pinelands Commission boundary the soil/groundwater cleanup goal will be background conditions. A number of potential remedial strategies have been evaluated for OC to gain insight into an overall remediation plan for the site. Likely remediation scenarios include excavation with off-site disposal or on-site treatment and other aggressive source area in-situ stabilization/treatment options. Longer term remediation alternatives suggest air sparging and soil vapor extraction or chemical treatment.

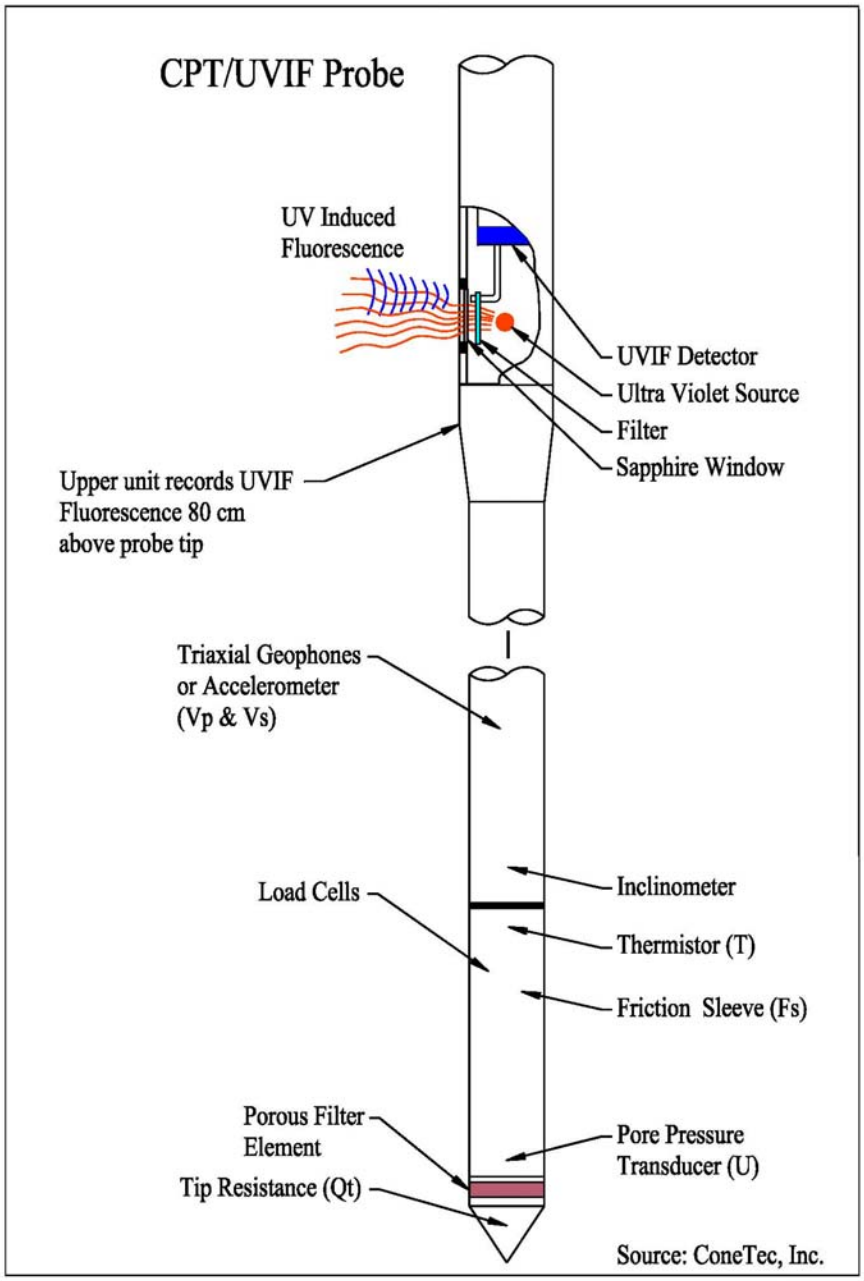

Figure 2. Details of cone penetrometer coupled to UVIF module

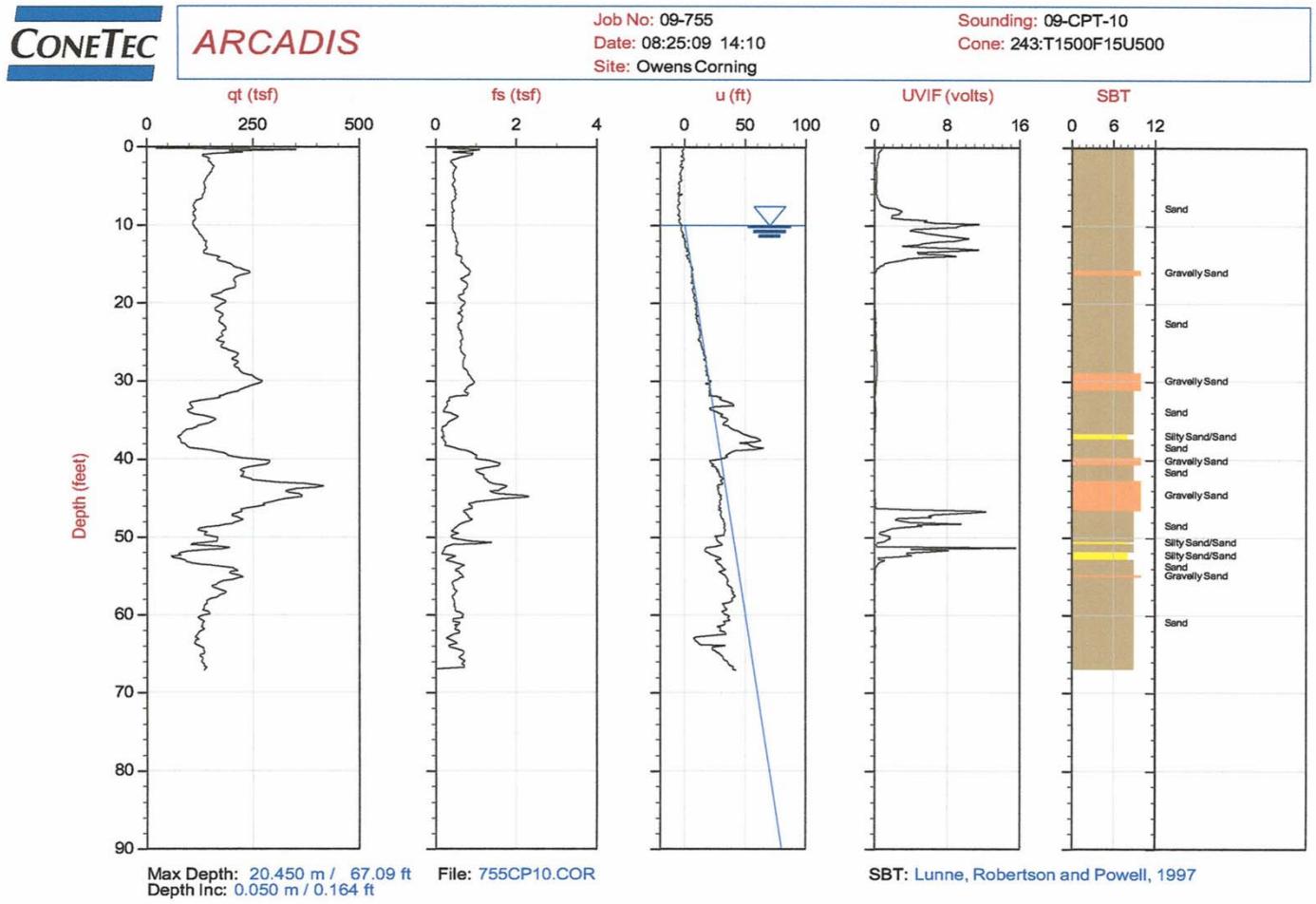

Figure 3. Typical CPT/UVIF borehole profiles

5. CONCLUSIONS

The implementation of CPT/UVIF soil investigation technology at an existing impacted site has allowed OC to rapidly delineate LNAPL and DNAPL contamination at varying elevations within the same location. The straight-forward operation i.e. direct-push drilling, no soil cuttings, real-time data and continuous interpretation of subsurface conditions were major reasons the CPT/UVIF approach was selected. The remedial investigation results demonstrate that CPT/UVIF technology provides essential subsurface information rapidly thus allowing field personnel the ability to manage remedial investigations more efficiently and at lower cost. Overall, the CPT/UVIF methodology provides significant visualization into site stratigraphy, is a useful tool to delineate hydrocarbon contamination and increases insight into contaminant migration. The application of advanced in-situ soil testing equipment with continuous data interpretation appears efficient, economical and a flexible method to achieve better soil/groundwater understanding and has a bright future with all stakeholders (owners, consultants and regulatory agencies).

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Chapter 27

A COMPARISON OF THREE SOIL CHARACTERIZATION METHODS ON A SOIL FORMED IN SANDY GLACIAL OUTWASH

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ABSTRACT

A field scale test was performed to evaluate three different soil sampling approaches. These included a USDA-NRCS pedon approach, a multiple increment approach, and a five-point composite approach. A 484 ft^2 plot in an upland glacial outwash plain in Falmouth, Massachusetts was subjected to these three soil characterization methods. The USDA-NRCS approach involved the excavation of a soil pit (or pedon) with soils described according to the methods outlined in the Soil Survey Manual (Soil Survey Staff, 1993). Natural soil horizons were identified and samples were collected to a depth of 4 ft. For the multiple increment samples, a 30-point grid was installed and samples were collected using a 1 in push probe. For the five-point composite, a five-point grid was installed within the plot and samples were collected with a 2.5 in bucket auger. Both the multi-increment and the five-point composite samples were taken at arbitrary depths of 0-3 in, 3-6 in, 9-12 in, 21-24 in, and 33-36 in. All samples were subjected to particle size and organic carbon analyses. The upland soil shows the effects of podzolization with some translocation of organic matter with depth in the pedon. The particle size analysis of the pedon confirms a sandy glacial outwash with a thin layer of loess in the upper horizons. The particle size analysis also shows a clear pattern of decreasing silt content with depth in the pedon. The organic carbon analysis shows both compositing approaches have greater organic carbon contents at depth compared to the soil pedon. The compositing approaches also show higher silt contents with depth compared to the

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soil pedon. The enrichment of organic carbon and silt in the lower samples may indicate a mixing of surface materials with depth for both composite methods.

Keywords: pedology, pedon, podzolization, particle size analyses, organic carbon analysis, multiple increment sampling

1. INTRODUCTION

Soil characterization is an essential part of the determination of the nature and extent of contamination in soils. Not only is it necessary to evaluate the areal distribution of contamination across a land surface, but the depth of soil contamination is also key to understanding how that contaminant is distributed in three-dimensional space. Depth characterization also provides a key parameter in determining volumes of contaminated soil. Understanding how contamination is distributed vertically requires a method that not only provides a reasonable estimate of contamination, but also elucidates the depositional and post-depositional processes responsible for the distribution of contamination with depth. This investigation compares a method used by soil scientists to describe and map soils with two methods utilized in environmental investigations; a multiple point composite approach and a multiple increment approach.

A soil formed in sandy glacial outwash was selected for sampling using the three soil characterization methods. The pedon approach entailed excavating a pedon or a roughly 1 x 1 meter (m) pit where the soil face was described using methods outlined in the *Soil Survey Manual* (Soil Survey Staff, 1993). The pedon approach characterizes a soil based on physical soil properties such as texture, structure, consistence, etc. These characteristics identify soil horizons which then determine the location of the soil samples. The composite and multiple increment approaches use arbitrary depths, and samples are collected without regard for subsurface soil properties. In this investigation a comparison of these methods is used to determine the more appropriate method of defining the distribution of soil contamination with depth.

2. SITE SETTING

The soil investigation was conducted in Falmouth, Massachusetts on Cape Cod in an upland location on a glacial outwash unit known as the Mashpee Pitted Plain (Figure 1). The geologic setting of the site is dominated by Late Pleistocene deposits attributed to a Late Wisconsinan ice front advance and retreat. Deposits on Cape Cod normally date no older than 18,000 to 22,000 years ago when the Laurentide Ice Sheet reached its maximum southward extent to the islands of

Martha's Vineyard and Nantucket (Oldale, 2001; Dyke and Prest, 1987; Fletcher, 1993). The Mashpee Pitted Plain was formed by streams that drained the Buzzards Bay and Cape Cod Bay glacial lobes whose terminal extents are marked by the Buzzards Bay and Sandwich moraines (Oldale, 2001). Many of the upland outwash plain landscapes are covered with a thin (1 to 4 ft) mantle of loess derived from the drying of abandoned braided stream channels and deposition of silt eastward as a result of prevailing westerly winds.

The investigation was conducted in a soil mapped as the Carver soil series (Fletcher, 1993). The Carver series is a very deep, excessively drained soil in broad areas primarily on outwash plains, but can also be found in areas of sandy glacial lake deposits. Slopes range from 0 to 35 percent. The Carver soil series generally has an organic surface composed of approximately 2 inches (in) of loose, undecomposed pine needles, leaves, and twigs with one inch of matted, partly- to well-decomposed organic material. The soil surface is light brownish gray very friable loamy coarse sand about 3 inches thick. The subsoil is coarse sand approximately 33 inches thick. The upper 10 inches of this subsoil is strong brown and very friable, the next nine inches is yellowish brown and very friable, and the lower 14 inches is brownish yellow and loose. The soil below 65 inches is a light yellowish brown, loose coarse sand. The Carver series is similar to the Enfield and Merrimac series with the exception that it has a lower silt content in the surface. The Carver soils are classified as mesic, uncoated Typic Quartzipsamments (Fletcher, 1993).

This investigation examined a soil developed in sandy glacial outwash in Falmouth, Massachusetts. The soil is located in an upland position on the Mashpee Pitted Plain east of the Buzzards Bay Moraine. The plain is pitted with several kettle lakes, the closest being Boa Swamp located to the east of the investigation site (Figure 2). The investigation area is located in a wooded setting consisting of scrub pine, white pine, northern red oak, and white oak with an understory of low-bush blueberry and gooseberry. The area has not been known for agricultural production, but has likely been logged at least once. Boa Swamp had been used for production of peat in the early 20th century. Based on the soil development and the expression of subsurface horizons, the soil has been relatively undisturbed by human activity.

3. BACKGROUND

Soils are natural bodies as defined in *Soil Taxonomy* (Soil Survey Staff, 1999) that are composed of solids (mineral and organic materials), liquids, and gases that occur on the land surface, occupy space, and are characterized by either horizons (layers) that are distinguishable from the parent material (original

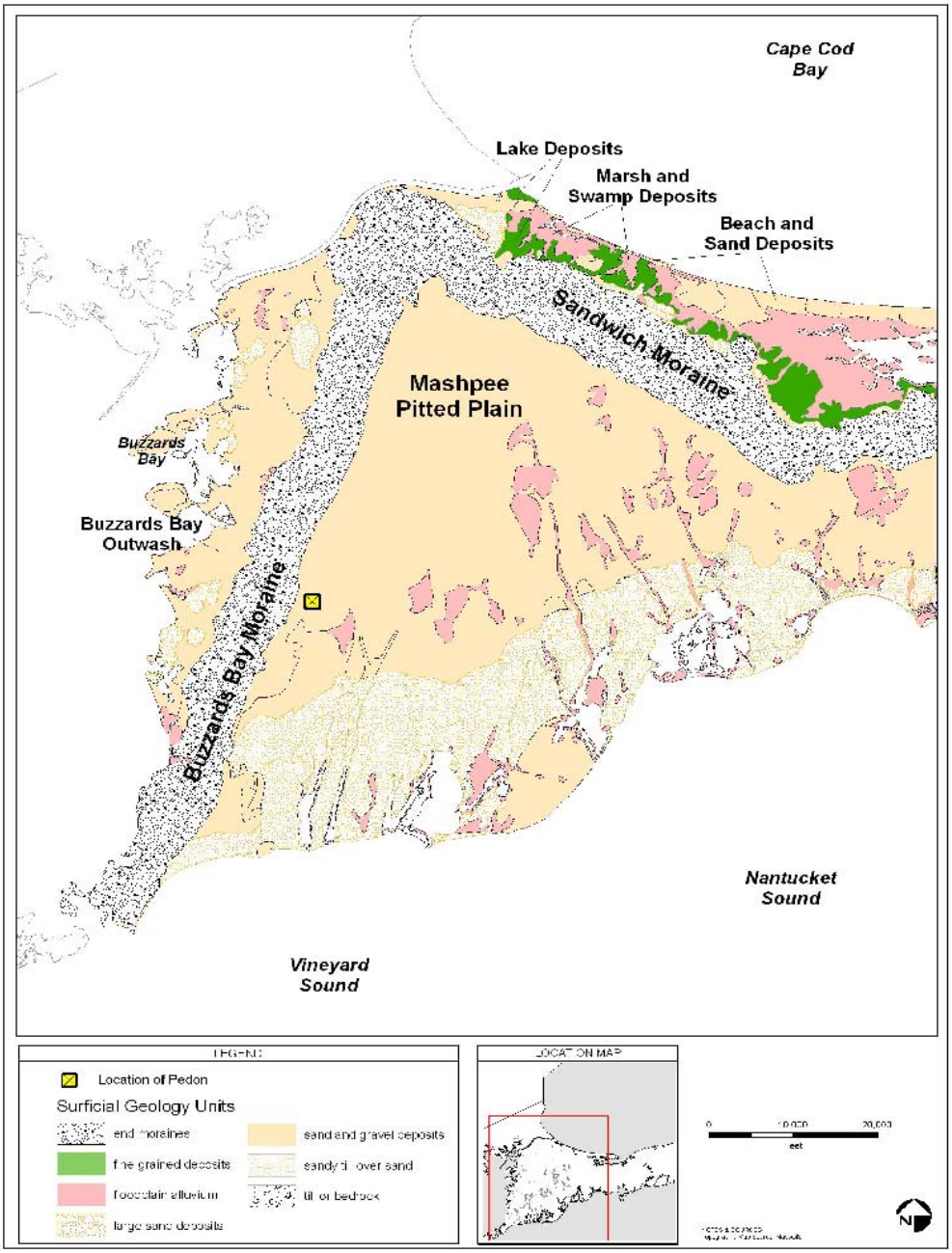

Figure 1. Cape Cod geology.

Figure 2. Location of Falmouth soil investigation.

material) as a result of additions, losses, transformations, and/or translocations of energy and matter; or the ability to support rooted plants in a natural environment.

The challenge in defining the variability in the soil is not only how to define these natural bodies, but also how to quantify the constituents within the soil. For example, soil amendments such as lime or fertilizer require a knowledge of the soil surface across a two-dimensional area of given depth to determine the quantities required to produce a crop without under- or over-amending the soil. For soil contamination, it is necessary to understand the distribution of contaminants across a soil area in order to more effectively develop a strategy for remediation. There have been a number of studies that show how soil constituents can be quantified across a soil area (Jenkins, et al., 1997; Jenkins, et al., 1999; Hewitt et al., 2005; Jenkins, et al., 2006). However, there are fewer studies on how these soils vary across an area at depth (Hewitt et al., 2007). In this investigation, three soil characterization methods will be used to define soil variability at depth: the pedon approach, and two compositing approaches; the multiple increment approach and the five-point composite approach.

The USDA-NRCS pedon approach is used primarily by soil scientists for the development of soil maps, usually on a county level survey. A pedon as defined in *Soil Taxonomy* (Soil Survey Staff, 1999) is a unit of sampling within a soil. The pedon is considered the smallest body of soil large enough to represent the nature and arrangement of horizons. A pedon has three dimensions, and its lower limit is the arbitrary limit between the soil (pedogenically altered material) and the non-soil (parent material). Its lateral dimensions are large enough to represent the nature of any horizons and variability that may be present across space. The minimal areal extent of a pedon is roughly 1 m^2, but can range to 10 m^2 depending on the variability in the soil across space. The polypedon is a unit of soil classification homogeneous at the soil series level and large enough to exhibit all the soil characteristics considered in the description and classification of soils (Soil Survey Staff, 1993). In practice, soil scientists generally use the pedon as the central concept of the polypedon or soil mapping unit. The pedon incorporates soil properties, site setting, vegetation, engineering properties, etc. into consideration of the mapping unit. Therefore, the pedon is the prototype of the soil that is characterized and mapped in space.

The second approach considered in this investigation is the multiple increment approach. While the pedon approach is more of a discrete sampling approach, the multiple increment approach is used to characterize surface soils for amendments and/or soil contaminants. In this approach, an area of interest or decision unit is identified and a number of "increments" of subsamples are collected and composited into a single sample. These samples can be collected using a random sampling or grid technique allowing for adequate coverage of the investigation area. In agricultural studies, it is recommended that 15 to 30 individual cores within an investigation area be collected to develop a representative sample (Clay

et al., 2008). Multiple increment samples have also been used in studies of military ranges to characterize surficial deposition of explosives in and around military targets. Many of these studies have occurred in association with the Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, New Hampshire (Hewitt et al., 2007), but have also been used in Canada (Thiboutot et al., 2004), Alaska (Walsh et al., 2005), and Louisiana (Jenkins et al., 2005). The approach used at CRREL is a systematic grid sampling approach (USEPA, 2002) where a decision unit is defined and a grid is established to sample surface soils across that area. In this method, a number of sub-samples (or increments) are collected across a decision unit, usually consisting of short cores 2-3 cm in depth that are composited into a single sample to represent the soil surface of that decision unit (Hewitt et al., 2007). The rationale for using this approach is to reduce the amount of variability between samples in a decision unit. The technique was developed to address the heterogeneous distribution of explosive particles on the surface of soils in the areas of targets and firing points (Jenkins et al., 2000a, 2000b, 2001a, and 2001b). It has been noted that discrete samples in these target areas often yield results that are not reproducible and fail to adequately account for all explosive mass that may be present in and around these target areas. A multiple increment strategy yields more reproducible results and provides estimates of contaminant mass that are suitable for the development of conceptual site models and support risk assessments for surface soils (Hewitt et al., 2007; Jenkins et al., 2005).

A third method used for sampling soils in both the horizontal and vertical dimensions is the five-point composite approach (AMEC, 2003). The five-point composite approach uses a five-point configuration where an 11 x 11 foot (ft) square is established with four points plus an additional point in the center of the square. Each point is sampled with a bucket auger at arbitrary depths, and each point is composited with the other four for the same depth interval. In theory, the five-point composite characterizes an area 22 x 22 ft to a depth designated at the time of sampling.

All three soil characterization field methods can be used for surface soils. However, has been some discussion on the utility of the multiple increment approach in characterizing soils at depth (Hewitt et al., 2007). The pedon approach characterizes soils at depth based on properties observed in the soil profile where the investigator describes the natural horizons as they occur; but the multiple increment approach was designed for surface soils and, in most cases, at very small vertical intervals (1-3 cm). This method was designed to evaluate the mass of explosive particles that are heterogeneously dispersed across a soil surface in the vicinity of range targets. The limitations of using the multiple increment method with depth has been noted, and some recommendations include

reducing the number of increments in a decision unit (Hewitt et al., 2007). It has also been cautioned that subsurface characterization across large decision units results in considerable uncertainty (Hewitt et al., 2007). The U.S. Environmental Protection Agency (USEPA) has suggested that multiple increment samples can be collected at depth based on the type of target (e.g., grenade ranges and disposal areas) where energetics can be found below the surface (USEPA, 2006). However, other agencies have recommended not applying the multiple increment approach to soils at depth greater than six inches (USACE, 2009). In general, the multiple increment approach has not been tested extensively for soil contamination at depths greater than those characterized for surface soils. The five-point composite approach does evaluate soils at depth, but it does so only at arbitrary intervals that are pre-determined (AMEC, 2003). The purpose of this investigation is to compare the three methods and evaluate how they characterize a soil at depth.

4. METHODS AND MATERIALS

The investigation was conducted on a small plot in a wooded area in Falmouth, Massachusetts. A study area was plotted that was 22 x 22 ft in area consistent with the dimensions of a soil grid based on the five-point composite approach (AMEC, 2003). A series of 30 points were established within this 22 x 22 ft grid. The 30 points were selected based per Hewitt et al. (2007); i.e., decision units less than 100 m^2 require only 30 increments for characterization. The method deviates from Hewitt et al. (2007) in that each point was measured and marked rather than placed at the discretion of the sampler walking in a serpentine pattern along the rows of each grid line. A diagram of the grid is presented in Figure 3, and the site grid is presented in Figure 4. After the grid was established, samples were collected using a 1 in. stainless steel push probe. Arbitrary depths of 0-3 in, 3-6 in, 9-12 in, 21-24 in, and 33-36 in were selected for the samples. For each interval, with the exception of the first, a 2.5 inch bucket auger was used to clean a hole for each sample increment. This was done to avoid cross-contamination of samples at depth. The 30 increments from each depth were composited into a single sample container. All soil collected from the 30 increments were included in the sample per Hewitt et al. (2007).

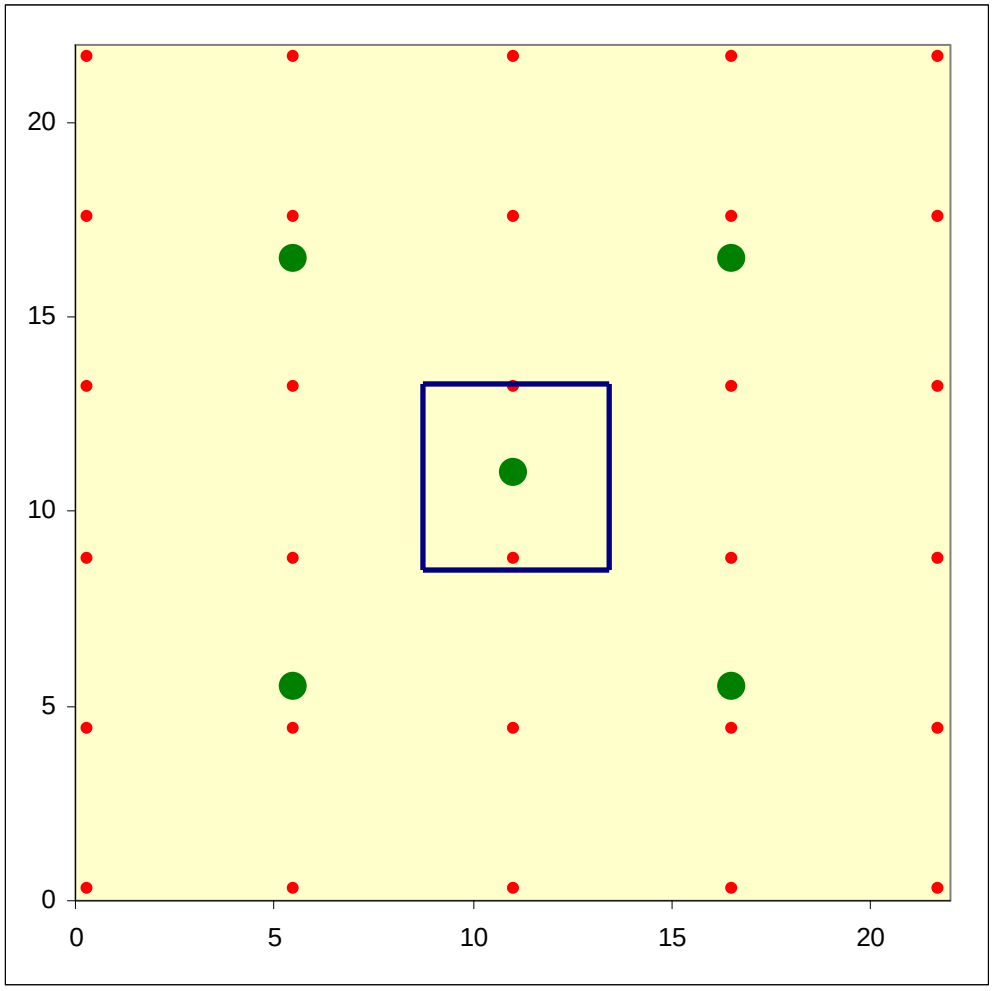

Figure 3. Diagram of soil sample locations within the 22 x 22 ft investigation area for multiple increment, five-point composite, and pedon.

Figure 4. 30 point grid in investigation area.

For the five-point composite approach, an 11 x 11 ft grid was established with the 22 x 22 ft decision unit (Figure 3). This included four points on the corners of the 11 x 11 ft grid and a point located in the center of the grid (Figure 3). Samples were collected at the arbitrary depths of 0-3 in, 3-6 in, 9-12 in, 21-24 in, and 33-36 in. A 2.5 in bucket auger was used to collect these samples. The five subsamples from each depth interval were composited into a single sample.

After completion of sampling by the multiple increment and five-point composite methods, a 1 x 1 m soil pit was excavated within the 22 x 22 ft grid unit (Figure 3). The pedon was described and sampled based on methods outlined in the *Soil Survey Manual* (Soil Survey Staff, 1993). A photograph of the finished pedon is presented in Figure 5.

Collected samples were subjected to particle size analysis and organic carbon analysis. The samples were air dried and ground to pass a 10 mesh sieve (2.00 mm limiting diameter). The particle size analysis consisted of a combination of sieving and sedimentation techniques as outlined in Gee and Bauder (1986). Samples with greater than 1 percent organic carbon were pretreated with a 30 percent H_2O_2 solution. Approximately 10 g of the less than 2.00 mm fraction of

Figure 5. Soil pedon in investigation area.

each sample was dispersed in Na-hexametaphosphate-Na-carbonate solution, and the sand size fraction of each sample was separated from the smaller fractions by wet sieving. The sand fraction was dried and fractionated by dry sieving into very

coarse sand (2.00-1.00 mm), coarse sand (1.00-0.50 mm), medium sand (0.50-0.25 mm), fine sand (0.25-0.10 mm), and very fine sand (0.10-0.050 mm) fractions. The remaining silt and clay size fractions of each sample were retained in a 1000 ml capacity sedimentation cylinder and placed in a water bath. Pipette analysis was performed on these samples to determine silt (50-2 μm) and clay (less than 2 μm). Organic carbon was determined using the Walkley Black method (Nelson and Sommers, 1996).

5. RESULTS

The pedon for this investigation is presented in Figure 6, and the description of the pedon is presented in Table 1. The soil exhibits an organic layer (5-0 cm) that is situated on the surface of the soil pedon. According to soil survey convention, the contact between a surface organic layer and the underlying mineral layer is the origin of the soil description or 0 cm. The organic layer was highly decomposed, and those parts that could be identified consisted of oak leaves and pine needles. Below the organic layer was a transitional AE horizon that showed properties of a surface horizon with properties of an albic or eluvial horizon. The horizon is thin (4 cm), has a dark grayish brown (10YR 4/2) color, and a loamy coarse sand texture. Below the AE horizon is an eluvial horizon (E) that exhibits a lighter color (light brownish gray, 10YR 6/2) and is thin (3 cm). The lighter colors indicate a horizon from where organic materials plus aluminum and iron sequioxides have leached due to the combination of coarse textures and the chelating effect of acid-producing vegetation. The removal of these soil constituents is evident in the underlying Bhs_1 horizon which exhibits darker and redder colors (dark reddish brown, 5YR 3/3). These colors indicate translocation of humus and iron with depth from the AE and E horizons. This is also evident in the thin reddish coatings noted on the ped faces in this horizon. The lower boundary is wavy and, in some cases, irregular with fingers of this material noted as deep as 38 cm. However, the horizon is approximately 3 cm thick in general. This translocation of humus plus aluminum and iron sequioxides is a pedogenic process known as podzolization and is commonly found in coarse textured soils that form in environments with fulvic acid-producing vegetation (Stobbe and Wright, 1959; McKeague and St. Arnaud, 1969; Petersen, 1976). The underlying horizon, or Bhs_2 horizon, is also an illuvial horizon where translocation of humus and sequioxides are apparent in the morphology. The horizon is lighter in color than the overlying horizon (strong brown 7.5YR 5/6) with the redder colors represented as mottles (yellowish red, 5YR 4/6). The consistence in this horizon is more firm in the mottled zones and indicates an accumulation of iron sesquioxides. This horizon is thicker (18 cm) than the overlying horizons and does not have the wavy lower boundary noted in the Bhs_1 horizon. The BC

horizon is a transitional horizon and exhibits the combined morphological characteristics of the glacial outwash parent material and the pedogenically altered soil material. This horizon is lighter in color (strong brown, 7.5YR 4/8) and has a texture (loamy coarse sand) similar to the overlying horizons. This horizon is thicker (21 cm) with a friable consistence. The soil structure is weak subangular blocky, which is weaker than the structure in the overlying horizons, but still indicates soil properties dominating over the looser parent material. The CB horizon exhibits more parent material properties and less soil properties than the BC horizon. The horizon is lighter in color (yellowish brown, 7.5YR 5/6) and the texture is coarser (coarse sand) than the more loamy overlying horizons. It was noted that many upland locations in Barnstable County have a 1 to 4 ft thick layer of silty loess on the surface (Fletcher, 1993). This pedon has more loamy textures in the upper horizons to a depth of 59 cm. This probably represents a loess cap that is partially in place in the upper horizons and may have translocated to the lower horizons. The CB horizon is looser in consistence and is lacking in mottles, coatings, and concretions. There are also few rounded gravels present in this horizon. The C horizon is the parent material and consists of pedogenically unaltered glacial outwash. This horizon is lighter in color (brownish yellow, 10YR 6/6) and has no soil structure (structureless single grain). The color is due primarily to the expression of the rounded quartz sand grains. In addition, there are more rounded gravels and cobbles in this lower horizon. There was also some remnant fine stratification in the lower portion of the pedon. This horizon had no coatings, mottles, or concretions noted.

Laboratory results for the soil pedon are presented in Table 2. The distribution of particle size and organic carbon with depth help to illustrate the pedogenic processes that are represented in the soil profile. Analysis shows that between 33 and 44 percent of the sand fraction is a coarse sand, which is consistent with soils derived from glacial outwash. The clay content is relatively uniform with an increase from 3.29 to 7.42 percent between the Bhs_2 and the BC horizons. The increase is likely due to the parent material because there is no evidence of illuviation of clay in the profile at that depth. The parent material (C horizon) is more than 90 percent sand with much less silt and clay. The silt fraction is the most revealing of the three particle size types because it represents the addition of loess on top of the glacial outwash and comprises between 15 and 22 percent silt content in the matrix. The silt profile decreases between the AE and E horizons from 15.29 to 14.56 percent and increases again to 21.46 percent in the Bhs_1 horizon. This shows that some silt is moving from the AE and E horizons into the lower horizons as a consequence of translocation of silt particles with infiltrating water (Figure 7). The silt content decreases in the Bhs_2 horizon (17.51 percent) and again in the BC horizon (14.48 percent). This decrease in silt content with depth indicates the limit of silt translocation in this particular medium. The parent

Figure 6. Soil pedon and horizons.

Table 1. Pedon description.

Area:	Falmouth, Barnstable County, Massachusetts
Classification:	Typic Quartzipsamments
Location:	70°34'53" W, 41°37'51"N
Native Vegetation:	northern red oak, white oak, white pine, scrub pine, lowbush blueberry
Physiography:	upland outwash plain
Parent Material:	loess over glacial outwash
Elevation:	81 ft
Infiltration:	rapid
Available Water:	low
Hydraulic Conductivity:	high
Soil Wetness Class:	class 1
Soil Slope:	nearly level
Erosion:	none to slightly eroded
Surface Runoff:	very slow
Sampled by:	Michael Morris, 16 November 2008

Horizon	**Depth (cm)**	**Description**
Oa	5-0	highly decomposed organics consisting of oak leaf and pine with a sphagnum consistence; very dusky red 2.5YR 2.5/2
AE	0-4	dark grayish brown 10YR 4/2 (moist) loamy coarse sand; weak fine subangular blocky structure; loose consistence; clear, smooth boundary; common medium roots; common fine pores; no mottles or concretions; no coatings on ped surfaces; displays some salt and pepper characteristics of organic plus sand
E	4-7	light brownish gray 10YR 6/2 (moist) loamy coarse sand; weak, fine subangular blocky structure; very friable consistence; no concretions; no coatings; common fine and few medium roots; common fine pores; one fingering of albic material; extended as deep as 17 cm; clear, smooth boundary
Bhs_1	7-10	dark reddish brown 5YR 3/3 (moist) loamy coarse sand; moderate medium to fine subangular blocky structure; friable consistence; very thin, discontinuous coatings on ped faces (segregated iron); very few fingers of this material as deep as 38 cm; white, rounded quartz grains are visible in peds; common fine and few medium roots; clear, wavy boundary
Bhs_2	10-28	strong brown 7.5YR 5/6 (moist) loamy coarse sand with common medium mottles of yellowish red 5YR 4/6; moderate, medium, subangular blocky structure; friable to firm consistence, firm particularly in the mottled zones; common fine roots; common fine and medium pores in the root zones; clear, smooth boundary
BC	28-49	strong brown 7.5YR 5/8 (moist) loamy coarse sand; few fine rounded quartz gravels; weak coarse subangular blocky structure; friable consistence; no concretions; no coatings; few fine roots; few fine pores; clear, smooth boundary

Table 1. Pedon description. (con't)

Horizon	Depth (cm)	Description
CB	48-73	yellowish brown 10YR 5/6 (moist) coarse sand; weak medium subangular blocky structure; friable to loose consistence; no coatings; no concretions; few fine rounded quartz gravels; few fine roots; few fine pores; clear, smooth boundary
C	73-103+	brownish yellow 10YR 6/6 (moist) coarse sand, color derived primarily from expression of quartz grains; common medium rounded quartz and granite gravels with few rounded quartz and granite cobbles; structureless single grain structure; very few fine roots; no visible pores; no concretions; no coatings

material (CB and C horizons) contains considerably less silt (7.65 and 3.01 percent, respectively). The translocation of silt sized particles has been documented in bench scale studies and is generally more prevalent in soils with coarser sand textures (Wright and Foss, 1968). This particular soil pedon likely represents a soil developed from glacial outwash with a loess cap that has been mostly eroded from the soil surface and partially translocated into the sandy matrix.

The organic carbon analysis of the pedon also shows the evidence for podzolization. The Oa horizon is defined as one that has well decomposed organic material that comprises more than 50 percent of the soil matrix (Soil Survey Staff, 1993). This is why the organic carbon content was not determined for this horizon (Table 2). The organic carbon content decreases considerably in the AE horizon to 0.75 percent, but represents the highest organic carbon content of the mineral horizons (Figure 8). There is another considerable decline in organic carbon content in the E horizon which represents some translocation of organic matter from the E horizon into the underlying horizons. This is shown by the increase in organic carbon in the Bhs_1 horizon to 0.42 percent and the greater increase in the Bhs_2 horizon to 0.54 percent. This increase represents organic matter than has been translocated from the upper A and E horizons into the lower horizons. In horizons below the Bhs_2 horizon the organic carbon content decreases by almost half (0.27 to 0.25 percent). This decrease may represent some translocation but may also be indicative of carbon that occurs naturally in the parent material. This is more evidence that the pedogenic process of podzolization is active at this site.

Table 2. Laboratory results.

Sample	Lower Depth	Organic Carbon	Sand	Silt	Clay	VCoS	CoS	MS	FS	VFS	USDA
	Ft	%	%	%	%	%	%	%	%	%	
Oa	0.16	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
AE	0.29	0.75	81.73	15.29	2.98	7.12	35.61	23.46	22.91	10.90	LCoS
E	0.39	0.42	81.48	14.56	3.96	7.37	34.83	23.96	22.92	10.92	LCoS
Bhs_1	0.49	0.49	76.03	21.46	2.51	8.15	33.35	23.31	21.73	13.46	LCoS
Bhs_2	1.11	0.54	79.20	17.51	3.29	14.43	41.15	21.53	14.54	8.34	LCoS
BC	1.77	0.27	78.10	14.48	7.42	13.25	36.06	21.89	18.55	10.25	LCoS
CB	2.56	0.20	86.46	7.65	5.89	13.01	36.19	20.53	20.42	9.84	CoS
C	3.54	0.25	92.73	3.01	4.26	18.81	43.55	18.72	14.48	4.44	CoS
MI 1	0.25	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
MI 2	0.50	1.44	77.79	17.82	4.39	14.11	30.75	22.98	22.38	9.78	LCoS
MI 3	1.00	0.40	76.90	13.46	9.64	11.16	33.58	22.56	23.95	8.75	LCoS
MI 4	2.00	0.31	78.60	13.13	8.27	10.73	28.72	23.71	24.03	12.81	LCoS
MI 5	3.00	0.25	86.80	8.62	4.58	10.24	28.67	22.82	23.72	14.55	CoS
5-pt 1	0.25	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
5-pt 2	0.50	0.18	78.29	12.69	9.02	12.26	29.40	24.88	23.21	10.24	LCoS
5-pt 3	1.00	0.49	75.17	16.3	8.53	9.79	31.26	21.63	24.53	12.79	LCoS
5-pt 4	2.00	0.39	79.54	13.68	6.78	12.69	34.34	21.19	18.39	13.39	LCoS
5-pt 5	3.00	0.51	86.75	9.88	3.37	30.04	20.93	18.56	19.61	10.86	CoS

ft = feet
MI = multiple increment
5-pt = five-point composite
% = percent
Sand = 2.00-0.050 mm
Silt = 0.050 mm – 2 µm
Clay = < 2 µm
USDA = U.S. Department of Agriculture
VCoS = very coarse sand, 2.00-1.00 mm
CoS = coarse sand, 1.00-0.50 mm
MS = medium sand, 0.50-0.25 mm
FS = fine sand, 0.25-0.10 mm
VFS = very fine sand, 0.10-0.050 mm
LCoS = loamy coarse sand
NA = not analyzed due to high organic carbon content

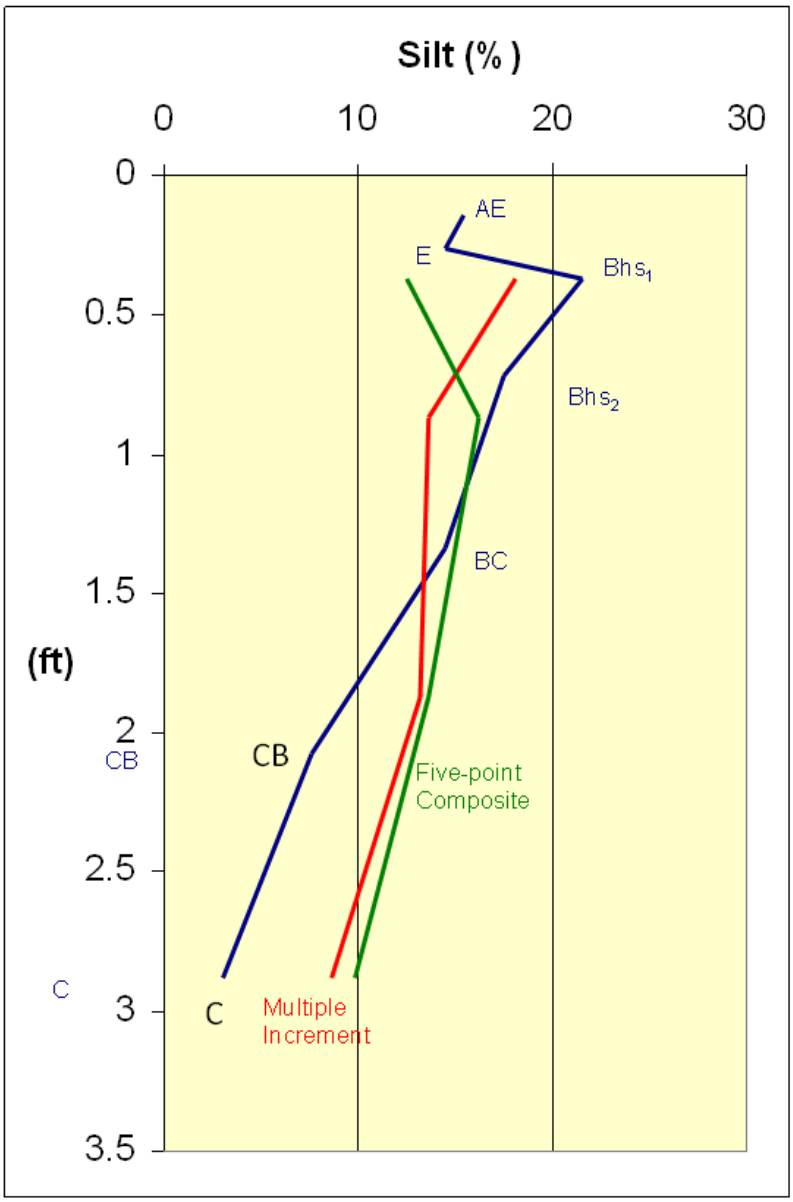

Figure 7. Silt content with depth for pedon, multiple increment, and five-point composite approaches.

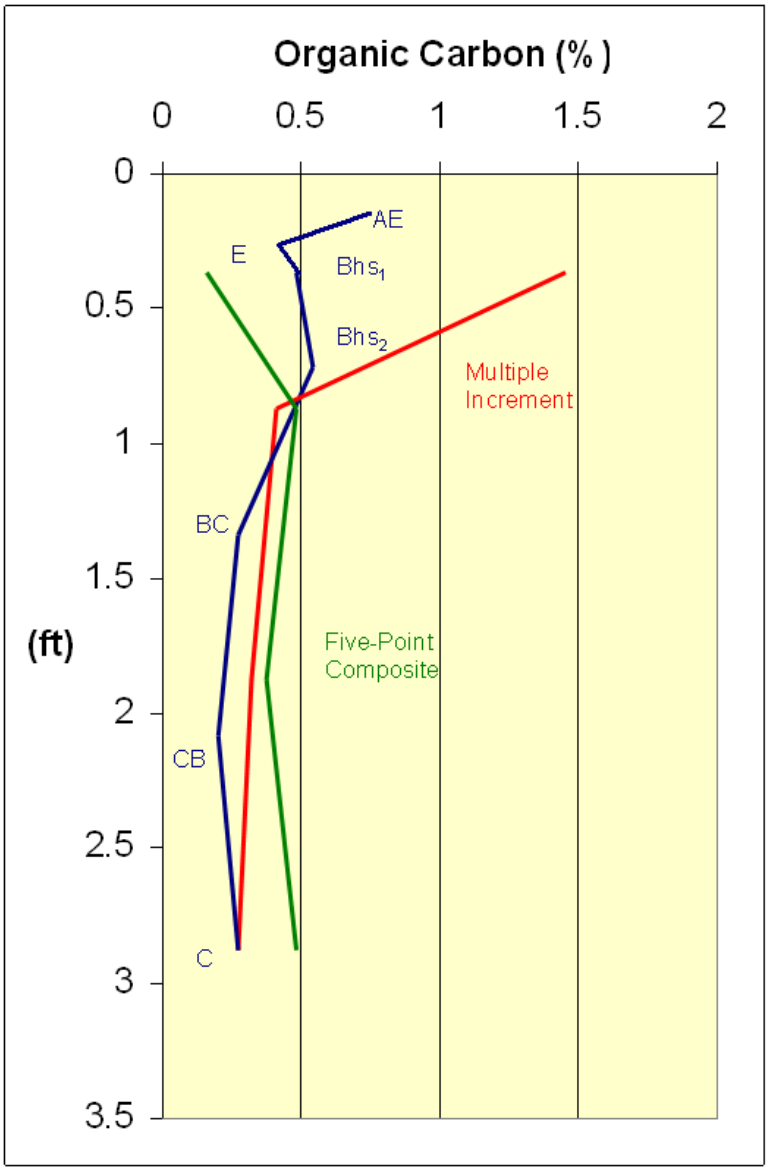

Figure 8. Organic carbon content with depth for pedon, multiple increment, and five-point composite approaches.

The multiple increment approach used arbitrary intervals for characterizing the soil decision unit. As expected, the physical descriptions and laboratory analytical results indicate a profile that is a homogenized version of the pedon approach results. The 0-3 in interval has the dark color of the organic matter (dark reddish brown, 5YR 2.5/2) but shows some mixing with the underlying mineral horizon expressed as white sand grains (Table 3). This is expected because the organic horizon is less than 3 inches thick (approximately 2 inches). The 3-6 in interval intercepts at least three soil horizons (AE, E, and Bhs_1), and this is evident in the mix of colors described in this interval including brown (10YR 3/2, AE horizon), very dark grayish brown (10YR 3/2, E horizon), and strong brown (7.5YR 5/6, Bhs_1 horizon). The texture of loamy coarse sand is consistent with these three horizons. The 9-12 in interval would represent one illuvial horizon (Bhs_2) and one transitional horizon (BC). The moist color is strong brown (7.5YR 5/6) and is consistent with the Bhs_2 horizon, and the loamy coarse sand texture is consistent with both horizons. The 21-24 in interval would correlate with the CB transitional horizon and has a brownish yellow color (10YR 6/6) and a weak medium subangular blocky structure which is also consistent. However, the loamy coarse sand texture is not consistent with the CB horizon's coarser texture. The 33-36 in interval correlates with the C horizon and has a light yellowish brown color (10YR 6/4) and a coarse sand texture that is consistent. The consistence is loose, and the sample contained common rounded quartz gravels. The C horizon has this, but also contains rounded quartz cobbles that would be too large to sample with a 1 in push probe. In general, the multiple increment approach does not account for the subtle variability in the surface soil horizons.

The laboratory analyses for the multiple increment approach also show that the method homogenizes the soil (Table 2). The coarse sand fraction is still shown to be dominant using this approach, but it only varies between 29 and 34 percent in the column. The silt content in the intervals varies from the samples collected in the pedon approach (Figure 7). The finer textures that would indicate possible presence of residual loess in the soil are present in the 3-6 in interval at 17 percent, which is consistent with the top three mineral horizons of the pedon; however, the subtle translocation of silt in the profile is missed due to the larger sampling interval. Additionally, the 21-24 in interval shows a silt content of approximately 13 percent, which is double what the pedon shows at the same interval (CB horizon, 8 percent silt). Even the lowest interval of 33-36 in shows triple the silt content (9 percent) of the corresponding C horizon (3 percent). One possible explanation for this phenomenon is cross-contamination of soil samples in the lower horizons with the upper horizons as a result of poor bore-wall integrity and increased traffic across the study area to collect 30 subsamples.

Table 3. Soil description for multiple increment sampling approach.

Area:	Falmouth, Barnstable County, Massachusetts
Sampled by:	Michael Morris and Aimee Comeau, 9 November 2008
Depth (in)	**Description**
0-3	dark reddish brown (5YR 2.5/2) organic material with flecks of white quartz sand with common medium mottles of dark brown (10YR 3/3); weak medium crumb structure; common fine and medium roots
3-6	brown (10YR 5/3) loamy coarse sand with common medium mottles of strong brown (7.5YR 5/6) and very dark grayish brown (10YR 3/2); weak fine crumb structure; common fine roots, very friable consistence
6-9	no description
9-12	brownish yellow 7.5YR 5/6 loamy coarse sand; medium fine subangular blocky to structureless single grained structure; few fine and medium roots
12-21	no description
21-24	brownish yellow (10YR 6/6) loamy coarse sand with few fine brownish yellow (10YR 6/8) mottles; weak fine subangular blocky to structureless single grain structure; very friable; few fine roots
24-33	no description
33-36	light yellowish brown (10YR 6/4) coarse sand; structureless single grain structure; loose consistence; no visible roots; common fine rounded quartz gravels

The organic carbon content in the multiple increment approach shows some signs of cross-contamination as well. The first interval (0-3 in) had too much organic matter to measure using the Walkley Black method (Nelson and Sommers, 1996) (Table 2). However, the 3-6 in interval had an organic carbon content of 1.44 percent which is almost double the highest of the top three mineral horizons in the soil pedon (Figure 8). Although the lower intervals are more consistent with the pedon, the 21-24 in interval is slightly elevated in comparison to the pedon organic carbon content (0.31 percent compared to 0.20 percent in the CB horizon). If the organic horizon on the surface were contamination, this would show that the soil was contaminated for at least the top 6 inches rather than in the top 3 inches as the pedon would indicate.

The five-point composite approach also homogenized the soil in comparison to the pedon approach. The 0-3 in interval is a dark black (5YR 2.5/1) organic horizon that is consistent with the Oa horizon of the pedon and has a fraction of AE's mineral horizon mixed into it (Table 4). The 3-6 in interval is a mixture of the top three mineral horizons described in the pedon as revealed by the multiple

colors. The dominant color is strong brown (7.5YR 5/6), which is consistent with the Bhs_1 horizon and is mottled with very dark grayish brown (10YR 3/2) of the AE horizon and grayish brown (10YR 5/2) of the E horizon. The loamy coarse sand texture is also consistent with these three horizons, and the subangular blocky structure shows some remnant soil structure in the upper mineral horizons. The 9-12 in interval exhibits a strong brown color (7.5YR 4/6) and a loamy coarse sand texture, which is consistent with the Bhs_2 horizon. However, there is no structure left in the sample, and that is not consistent with the Bhs_2 or BC horizon. The 21-24 in interval has a yellowish brown color (10YR 5/6) that is consistent with the CB horizon, but the lack of soil structure and the loamy coarse sand texture is not consistent. The 33-36 in interval has a brownish yellow color (10YR 6/6), a coarse sand texture, and a structureless single grain structure that is consistent with the C horizon.

Table 4. Soil description for five-point composite sampling approach.

Area:	Falmouth, Barnstable County, Massachusetts
Sampled by:	Michael Morris and Siobhan Morris, 14 November 2008
Depth (in)	**Description**
0-3	black (5YR 2.5/1) organic plus sand mixture; many medium and fine roots
3-6	strong brown (7.5YR 5/6) loamy coarse sand with many medium grayish brown (10YR 5/2) and very dark grayish brown (10YR 3/2) mottles; weak fine subangular blocky structure; common fine and medium roots
6-9	no description
9-12	strong brown (7.5YR 4/6) loamy coarse sand; structureless single grain structure; very friable to loose consistence; common fine roots
12-21	no description
21-24	yellowish brown (10YR 5/6) loamy coarse sand; structureless single grain structure; loose consistence; few fine roots
24-33	no description
33-36	brownish yellow (10YR 6/6) coarse sand; structureless single grain structure; loose consistence; very few fine roots

The laboratory analysis results for the five-point composite approach are similar to that observed for the multiple increment approach (Table 2). The major particle size fraction is sand (75 to 87 percent) with coarse sand dominating (21 to 34 percent). The silt profile is somewhat consistent with the pedon, but does show some elevated contents in the lower portions of the profile (Figure 7). The 3-6 in interval has a silt content that is comparable to the E horizon of the pedon (13 and 15 percent, respectively). The 9-12 in interval is also consistent with the Bhs_2

horizon with silt contents of 16 and 18 percent, respectively. However, the 21-24 in interval's silt content is almost double that of the CB horizon (14 and 8 percent, respectively). The 33-36 in interval's silt content is also elevated (10 percent) compared to the corresponding C horizon (3 percent). This shows the possible cross-contamination of samples that was observed in the multiple increment approach. Borehole integrity would also be an issue with the five-point composite approach, particularly in sandy, unstable soils.

The organic carbon content of samples collected using the five-point composite approach shows some enrichment of organic carbon with depth compared to the pedon approach. The first interval (0-3 in) had too high an organic carbon content to measure with the Walkley Black method (Nelson and Sommers, 1996), consistent with the Oa horizon (Table 2). The 3-6 in interval, however, had an anomalously low organic carbon content (0.18 percent) that was well below the lowest of the upper three mineral horizons (E horizon, 0.42 percent) (Figure 8). The 9-12 in interval (0.49 percent) is consistent with the Bhs_2 horizon (0.54 percent). The 21-24 in (0.39 percent) and 33-36 in (0.51 percent) intervals are double their corresponding mineral horizons (0.20 and 0.25 percent, respectively). These results indicate that there could be some cross-contamination of samples with depth using the five-point composite method.

6. DISCUSSION

The soil description for the pedon approach was used to establish the taxonomy of the soil pedon. The primary consideration in classifying this pedon was whether the illuvial horizons (Bhs_1 and Bhs_2) qualified as spodic horizons, the diagnostic horizon of the Spodosols order. The illuvial horizons did not meet the criteria for a spodic horizon because neither had an organic carbon content greater than 0.60 percent (the Bhs_2 was 0.54 percent). This placed the soil in the Entisols order, and the subgroup was classified as a Typic Quartzipsamments (Soil Survey Staff, 2006). The Spodic Quartzipsamments was a possibility, but there was neither enough cementation in the illuvial horizon nor laboratory data to substantiate this classification. The soil in this soil mapping unit is classified as a Typic Quartzipsamment according to the soil survey conducted for Barnstable County (Fletcher, 1993). Therefore, the pedon description was consistent with the survey.

One of the considerations in the development of a conceptual site model is to determine the presence and/or intensity of soil disturbance in a soil decision unit. In this case, a soil that exhibits properties of podzolization has likely been undisturbed for a period of time. There are several ideas of how podzolizaton is expressed as a function of time. Schaetzl (2002) found that more intensive podzolization formed well developed Spodosols in areas of Michigan dominated

by hardwood forest, low fire frequencies, and deep snowpacks in comparison to areas with jack pine and oak barrens with smaller snow packs that formed Psamments. Wang et al. (1986) found that Spodosols in Canada varied from enriched sequioxide and depleted organic matter content in the northern spruce forests to lower sequioxide and higher organic matter content in the southern maple forests. In glaciated terrain, Spodosols are relatively young. Spodosols have been estimated at 10,000 years in Sweden (Olsson and Melkerud, 1989), 3,000-8,000 years in Michigan (Franzmeier and Whiteside, 1963), and 500 years in Menomee, Wisconsin under hemlock vegetation (Hole, 1975). Podzols with well developed albic (E) horizons ranging in age from 230 to 11,300 years were studied in Finland (Buurman and Jongmans, 2005). Spodosol development was determined to be a minimum of 1,520 years to meet the organic matter content and 4780 years to meet the accumulation of sequioxides (Mokma et al., 2003). Therefore, to develop soils with the characteristics observed in the study pedon would require a minimum of 230 years. This relative time estimate would pre-date any recent activities on Cape Cod, including military training (with the exception of the Revolutionary War). Thus, if sampling were needed to quantify the amount of explosive residue across this decision unit, the sampling would only require a depth of a few inches to characterize the mass deposited across the site.

A separate study was conducted on the results of this method comparison. The organic carbon profiles of the three methods were used in a Seasonal Soil Compartment Model (SESOIL) (Bonazountas and Wagner, 1984; Hetrick et al., 1993) simulation to understand how contaminants might be transported through this profile assuming a surface deposition of readily available explosive compounds. Because of the great variability in the organic matter contents at the surface and the variability in the methods used to describe this organic layer, all three approaches assumed a uniform distribution of organic carbon (1.50 percent) in the top 3 in of soil. Table 5 shows the input parameters used in the simulation for each soil sampling method. In this exercise, the compounds hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitroluene (TNT) were loaded into the surface of each profile for each soil method. The results showed that RDX was transported through the profile by 1.2 years in the pedon method compared to 1.4 years in the multiple increment and 1.5 years in the five-point composite approaches. TNT was transported through the profile in 1.1 years in the pedon approach as compared to 1.3 and 1.5 years in the multiple increment and five-point composite approaches respectively. The difference in these three methods is the enrichment of organic carbon with depth in the composite approaches which retards the transport of organic compounds through the soil profile. Therefore, for RDX and TNT, the pedon approach provides a more conservative estimate of

transport and predicts a more rapid groundwater impact by these explosive compounds.

Table 5. Input parameters used in SESOIL analysis.

Source Thickness (cm)	4.06			
Source Area (cm^2)	450,000			
Contaminant	RDX		TNT	
Source Concentration (mg/kg)	126.5		126.5	
Water Solubility (mg/L)	59.7		130	
Diffusivity in Air (cm^2/s)	NA		0.0245	
Henry's Law Constant (m^3-atm/mole)	0.000000063		0.00000046	
Organic Carbon Partition Coefficient (L/kg)	195.4		1834	
Molecular Weight (g/mole)	222.12		227.13	
Source Loading Type	Instantaneous			
Number of Soil Layers	4			
	Layer-1	Layer-2	Layer-3	Layer-4
Layer Thickness (cm)	7.62	7.62	15.24	60.96
Number of Sublayer	4	8	5	10
Intrinsic Permeability (cm^2)	1.00E-08	1.00E-08	1.00E-08	1.00E-08
Soil Density (g/cm^3)	1.66	1.66	1.66	1.66
Disconnectedness Index	3.7	3.7	3.7	3.7
Porosity	0.3	0.3	0.3	0.3
Organic Carbon Content (percent) Pedon	1.50	0.49	0.54	0.24
Organic Carbon Content (percent) Multiple Increment	1.50	1.44	0.40	0.28
Organic Carbon Content (percent) Five-point Composite	1.50	0.18	0.49	0.45

cm = centimeters
cm^2 = square centimeters
RDX = hexahydro-1,3,5-trinitro-1,3,5-triazine
TNT = 2,4,6-trinitrotoluene
mg/kg = mg/kg
mg/L = milligrams per liter
cm^2/s = square centimeters per second
m^3-atm/mole = cubic meters –atmospheres per mole
L/kg = liters per kilogram
g/mole = grams per mole
g/cm^3 = grams per cubic centimeter
NA = not available

One of the primary differences among the pedon, the multiple increment, and the five-point composite approaches is the documentation of soil morphology. The assessment of soil morphology is critical to the pedon approach and aids in the interpretation of soil-forming processes. In contrast, both the multiple increment and the five-point composite approaches pay little or no attention to

soil morphology. Because these approaches use arbitrary depth intervals, both methods assume that the soil is uniform across the increments for each depth interval. When applied to surface sampling, this is clearer because there is a well defined, natural boundary between the soil surface and the non-soil above the surface. However, as noted by the U.S. Army Corps of Engineers (2009), the uncertainty with depth is a major concern and should not be applied to any sampling effort other than surface characterization. If the 5 cm organic layer on the surface of this soil had been contamination, it could be interpreted in the multiple increment and five-point composite approaches that contamination was evident at 2 ft or more based on the carbon profile. These approaches also show that the silt content was enriched at depth when the pedon approach shows the higher silt contents much closer to the surface. This cross-contamination likely occurs as a result of the movement of soil materials from the surface to the sample below due to the instability of the walls of the soil borings. The pedon approach uses a clean soil profile, and sampling occurs from the bottom to the top to avoid this cross contamination of samples. Based on the profiles of the two composite methods, a disturbed soil could be interpreted based on the available data. The pedon approach, however, shows that the soil was not disturbed, the organic layer was clearly limited to the surface, and the translocation of organic carbon in the profile was natural (not due to human impact). The pedon approach focuses on soil morphology, makes interpretations based on the characteristics of the soil, and provides a more clear conceptual site model for the decision unit. This approach can be applied to disturbed soils as well because there are soil characteristics that are expressed in the profile due to soil-forming processes such as human activity or disturbance. Activities such as plowing, burials of items, burning, disposal, treatments, and amendments can be found in the morphology of the soil.

The multiple increment and five-point composite approaches do not address the position of the decision unit in the context of the landscape in considering the boundaries of a decision unit. Because the five-point composite approach considers only a relatively small unit, this aspect is not as critical because there is less chance that the unit will traverse a major physiographic boundary. In this investigation, for example, the decision unit was limited to an upland position with a nearly level terrain. However, the multiple increment approach can be applied to decision units as large as 2,500 m^2 (Hewitt et al., 2007). A unit this size could easily be placed across multiple soil or geomorphological units (upland, backslope, footslope, terrace, floodplain, etc.) that have different soil properties and require different conceptual site models to account for deposition and subsequent burial and transport. If such a large unit were used in this investigation, the unit would cross the upland into the backslope, footslope, and perhaps the toe slope and bottom (bog). Each of these landscapes have different

factors regarding erosion, deposition, slope adjustment, and stability that would affect how a contaminant might express itself in the soil profile. A rule of thumb for placing large decision units across a landscape is the larger the decision unit, the greater the uncertainty. Therefore, a more detailed approach to soil morphology will provide a more detailed conceptual site model and in turn reduce the uncertainty of interpreting the impact of human activities (or lack thereof) in a soil at depth.

Another consideration is the time that is spent to characterize soils in a given decision unit. In this investigation, a relatively small decision unit (484 ft^2) located entirely in an upland position on a nearly level landscape was assessed. The soil was sandy and relatively stone-free making the excavation and coring of the soil relatively easy. For the pedon, it took one person approximately four hours to excavate, clean, photograph, describe, and sample. The five-point composite approach took one person approximately one hour to establish the grid, collect the soil samples, and take soil descriptions of the five samples. For the multiple increment approach, it took two people approximately five hours to establish the grid and collect and describe the five samples for a 30 increment composite. Given that the multiple increment and the five-point composite approaches were almost equally effective in cross-contaminating the soil samples with depth thus producing results of similar quality, the five-point composite approach would be the more cost effective of the two arbitrary interval, compositing approaches for characterizing this decision unit. The pedon approach provided much more information and is the established method for characterizing a given soil unit, making the time investment to reduce uncertainty more valuable. Therefore, applying a composite method to characterize anything but a soil surface would be meaningless without some knowledge of the soil morphology at depth of the decision unit under investigation.

7. CONCLUSIONS

A comparison of three soil characterization methods showed that among a USDA-NRCS pedon method, a multiple increment composite method, and a five-point composite method, the pedon method was the one that provided the most reasonable and complete information on soil variability at depth. The investigation of a 22 x 22 ft decision unit on a soil developed from loess over an upland glacial outwash plain showed that the soil had undergone podzolization with translocation of organic matter plus iron sesquioxides from the surface horizons into the subsoil horizons. This pedogenic process developed a soil with an irregular carbon distribution with depth. There is enrichment of organic matter in the surface horizon, depletion of organic matter in the albic horizon, and

subsequent enrichment of organic matter in the illuvial horizons. Translocation of organic matter was estimated at approximately 1.0 ft in depth. A particle size analysis showed that a loess cap likely worked into the sandy outwash matrix and was partially translocated as a result of infiltrating water. Depth profiles compiled from both multiple increment and a five-point composite approaches showed that there was relatively little variability in organic carbon and silt with depth. Moreover, the compositing methods showed enrichment of organic carbon and silt with depth below 1.5 ft indicating cross-contamination of deep samples by shallow soils. This was likely due to instability of boreholes with depth in an unstable, sandy matrix. The pedon approach provided a more detailed assessment of soil variability with depth and a more comprehensive conceptual site model of depositional and post-depositional processes. The two compositing approaches were designed to evaluate soils with contaminants that were deposited as surface debris. It is recommended that the compositing approaches be used exclusively for characterizing surface soils only (0-3 cm). Care should be taken to limit the extent of these decision units to landscapes of similar physiographic characteristics. These compositing methods should only be used at depth in concert with the evaluation of soil morphology for any decision unit, particularly if trying to evaluate the nature and extent of soil contamination at depth.

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