CONTAMINATED SOILS, SEDIMENTS, WATER AND ENERGY

Volume 18

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CONTAMINATED SOILS, SEDIMENTS, WATER, AND ENERGY
Volume 18

Heavy Metals
Manufactured Gas Plants
NAPL
PCBs
Remediation
Risk Assessment
Sediments

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Paul T. Kostecki
Edward J. Calabrese
Christopher Teaf

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Contributing Authors

Mohamed S. Abdel-Rahman, University of Medicine and Dentistry of New Jersey, Pharmacology and Physiology Department, New Jersey Medical School, Newark, NJ

Michael Asselin, GZA GeoEnvironmental, Inc., 380 Harvey Road, Manchester, New Hampshire, USA, 03103

Denise Bartone, MS, CDW Consultants, Inc., 40 Speen Street, Suite 301, Framingham, MA, USA

Susan Cahalan, PG, CDW Consultants, Inc., 40 Speen Street, Suite 301, Framingham, MA, USA

Yoon-Jean Choi, U.S. Environmental Protection Agency, Region I, 5 Post Office Square, Suite 100, Boston, Massachusetts, USA, 02109

Frederic R. Coll, P.G., URS Corporation, Pittsburgh, PA

Gregory Council, Tetra Tech GEO, 1165 Sanctuary Parkway, Suite 270, Alpharetta, GA, 30009

Douglas J. Covert, Hazardous Substance & Waste Management Research, Inc., 2976 Wellington Circle West, Tallahassee, FL, 32309

Nianqiao Fang, School of Marine Sciences, China University of Geosciences, 100083 Beijing, China

Kenneth J. Gendron, Tighe & Bond Consulting Engineers, 446 Main Street, Worcester, MA 01608

Jonathan B. Higgins, CPG, LSP, Higgins Environmental Associates, Inc., 19 Elizabeth Street, Amesbury, MA 01913

Gordon Hinshalwood, Antea Group, 500 Summit Lake Drive, Valhalla, NY 10595

Brad A. Horn, PE, President, Redux Technology, 280 Callegari Drive, West Haven, CT 06516

Kun-Chang Huang, Antea Group, 2 Bridgewater Rd., Farmington, CT 06032
Richard Hull, U.S. Environmental Protection Agency, Region I, 5 Post Office Square, Suite 100, Boston, Massachusetts, USA, 02109
Talaat Ijaz, Tetra Tech GEO, One Salem Square, 295 Route 22 East, Suite 104E, Whitehouse, NJ, 08889
Michael Jasinski, U.S. Environmental Protection Agency, Region I, 5 Post Office Square, Suite 100, Boston, Massachusetts, USA, 02109
David Knowlton, City of Salem, 120 Washington Street, 4th Floor, Salem, MA 01970
Steven Lamb, GZA GeoEnvironmental, Inc., 380 Harvey Road, Manchester, New Hampshire, USA, 03103
Aaron Lapine, Antea Group, 500 Summit Lake Drive, Valhalla, NY 10595
Matthew Levinson, P.E., One Greenwood Ave, Suite 210, Montclair, NJ 07042
Baolin Liu, School of Marine Sciences, China University of Geosciences, 100083 Beijing, China
George Losonsky, Losonsky & Associates Inc., Glen Haven Drive, Baton Rouge, LA, USA.
Ximing Luo, School of Marine Sciences, China University of Geosciences, 100083 Beijing, China
James L. Marolda, Brown and Caldwell, 2 Park Way, Suite 2A, Upper Saddle River, NJ, USA, 07458
Michael E. Martin, Tighe & Bond Consulting Engineers, 4 Barlows Landing Road, Unit 15, Pocasset, MA, USA 02559
Nancy E. Milkey, Tighe & Bond, Inc., 53 Southampton Road, Westfield, MA 01085
Matthew D. Millias, PE, Principal, CDM Smith, 1 General Motors Drive, Syracuse, NY 13206
Robin Mongeon, New Hampshire Department of Environmental Services, 29 Hazen Drive, Concord, New Hampshire, USA, 03302
Richard A. Moore, P.G., URS Corporation, Pittsburgh, PA
David A. Murphy, Tighe & Bond Consulting Engineers, 177 Corporate Drive, Portsmouth, NH 03801
Matthew O’Neil, P.E., 220 West Exchange Street, Suite 107, Providence, RI 02903
Michael Sequino, Directional Technologies Inc., North Plains Industrial Drive, Wallingford, CT, USA
Steven P. Stucker, CPG,Senior Environmental Engineer, National Grid, 300 Erie Boulevard West, Syracuse, NY, 13202
Christopher M. Teaf, Center for Biomedical & Toxicological Research, Florida State University, 2035 E. Dirac Dr., Tallahassee, FL, 32310

Rita M. Turkall, University of Medicine and Dentistry of New Jersey, Pharmacology and Physiology Department, New Jersey Medical School and Clinical Laboratory Sciences Department, School of Health Related Professions, Newark, NJ

Garry Van Heest, Directional Technologies Inc., North Plains Industrial Drive, Wallingford, CT, USA

Foreword

The International Conference on Soils, Sediments, Water, and Energy began nearly 30 years ago as a modest, focused scientific forum about petroleum issues. It recently celebrated its 28th incarnation in October of 2012. Originated at and by the University of Massachusetts in Amherst, this prestigious annual conference, with its West Coast sibling, is among the most significant and influential environmental conferences in the world, regularly drawing 200 or more presenters, and as many as 700 participants year-in and year-out. This has translated to representation by over 40 countries and total 20,000 attendees. In the impressive three decades, attendees have come from nearly all 50 states.

With old problems continuing, new environmental events occurring with regularity, and important local, regional, or global events such as the Exxon Valdez, the Deepwater Horizon Spill, earthquakes and tsunamis, and many industrial events shaping Conference history, the Amherst meeting represent an essential and reliable service to the scientific community. Welcoming new ideas and approaches to environmental situations, as well as potential avenues of research and practical solutions, has been the strength of the Conference, whether in the platform sessions, the more informal and productive poster sessions, or even during breaks, lunches, and dinners. Those discussions serve as an essential vehicle for many of the intellectual connections that persist and develop long after the Conference adjourns. Its value was underscored once again this year by the breadth of subjects addressed at the 2012 Conference, including site investigation approaches, innovative remedial techniques, vapor intrusion, petroleum, indoor and outdoor air quality, environmental forensics, military installation impacts, human health and ecological risk assessment, heavy metals toxicology, nanotechnology, hydrogeology, historical manufactured gas plants (MGP), and many specific workshops, poster sessions and invited addresses during the week. Also well-represented in the presenters and the exhibitors in 2012 were the many experienced technical consultants, analytical laboratories, regulatory agency personnel, and members of the legal establishment. The manuscripts comprising Volume 18 of the Proceedings, which cover heavy metals, dioxins, PCBs, remediation of MGP sites and other facilities, groundwater quality, risk assessment, sediment quality, and regulatory applications, are a useful snapshot of the broad array of technical presentations that comprised the 28th annual Conference.

The Conference is extraordinarily well-done and, as in years past, it is my professional and personal privilege to preface this most recent edition in a long-running series which began in 1986. Presenters, sponsors, exhibitors, editors, conference staff, Scientific Advisory Boards, and especially the AEHS Foundation, all are to be commended for continuing and expanding this highly anticipated annual event which marks the beautiful fall of each year in the Northeast.

Christopher M. Teaf

Center for Biomedical & Toxicological Research
Florida State University
Tallahassee, Florida

About the Editors

Dr. Paul T. Kostecki's professional career has focused on research, education and training in environmental contamination with an emphasis on human and ecological risk assessment and risk management of soils. 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 55 conferences, workshops and courses both nationally and internationally, and has made 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 50 countries. Dr. Kostecki has published over 100 articles and reports, co-edited/co-authored 35 Books and secured over $15M 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 helped found Amherst Scientific Publishers and co-created seven peer-reviewed journals: Journal of Soil and Sediment Contamination (1990); Human and Ecological 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.

Dr. Kostecki served as Vice Provost for Research and Vice Chancellor for Research and Engagement at the University of Massachusetts Amherst from 2003 to 2009. He served as Special Advisor for the Clean Energy China Initiative, Office of the President, University of Massachusetts from 2009 – 2011. He briefly left the University of Massachusetts Amherst to establish the online education program for Simmons College, Boston, MA (2011 -2012). He is presently

Professor of Environmental Health in the School of Public Health and Health Sciences, University of Massachusetts, Amherst.

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.

Dr. Christopher Teaf is a Board-certified toxicologist with broad experience in evaluation of potential effects of chemical exposures in industry, agriculture, waste management, power generation, educational facilities, and commercial products. He has been on faculty at Florida State University's Center for Biomedical & Toxicological Research since 1979, and Director of Toxicology for Hazardous Substance & Waste Management Research since 1985. Chris' interests include risk assessment under environmental/occupational aspects of federal, state and local rules, risk communication, and development of risk-based targets for site remediation. He has extensive experience in evaluation of fate and potential health effects from petroleum, solvents, metals, pesticides, pharmaceuticals, biological agents (e.g., mold, microbes) and physical agents (*e.g., particulates, asbestos*).

For over 30 years, Chris has directed or conducted research in toxicology for World Health Organization, NATO, USEPA, Air Force, Department of Agriculture (USDA), Florida Department of Environmental Protection, Florida Department of Health, Florida Department of Community Affairs, and Agency for Toxic Substances & Disease Registry (ATSDR). He presently serves on the Human Health Peer Review Committee for Florida DEP. Chris served as Toxicologist for Technical Advisory Groups concerning Florida landfills and petroleum sites, as well as the Governor's Financial and Technical Advisory Committee. He chaired the Florida Department of Labor's Toxic Substances Advisory Council. He has organized and taught graduate/undergraduate courses and technical seminars for universities as well as international, federal, state and local agencies. He has chaired the Dog Island Conservation District since 2004.

Dr. Teaf has served on editorial boards or as peer reviewer for numerous journals and is Senior Human Health Editor for the international journal *Human & Ecological Risk Assessment.* In addition to training, research and advisory services to health agencies and private sector firms, he has provided environmental and toxicological services to the U.S. Attorney, Florida State Attorney, and Attorneys General of FL, OK, and WA. Chris has testified in federal or state court, and administrative matters, in about 15 states on issues of toxicology, health risk evaluation, and environmental chemistry.

PART I: Heavy Metals

Chapter 1

IRON REMOVAL AT REMEDIAL SITES: NEW REGULATIONS DRIVE THE SEARCH FOR MARKET-APPROPRIATE METHODS

Brad A. Horn[1 §], Matthew D. Millias[2], Steven P. Stucker[3]
[1]Redux Technology, 280 Callegari Drive, West Haven, CT 06516, [2]CDM Smith, 1 General Motors Drive, Syracuse, NY 13206, [3] National Grid, 300 Erie Boulevard West, Syracuse, NY, 13202

ABSTRACT

Over the past few years, new regulations limiting the discharge of iron to surface waters have become increasingly common. These regulations are particularly important in the groundwater remediation market where unique in-situ water chemistry results in elevated levels of iron as well as other minerals at a majority of sites with contaminated groundwater. Removal of iron from water tends to be challenging for a number of reasons, and commercially available methods have not been widely cost-effective in the remedial field.

The assessment criteria for iron removal technology at remedial sites is market-specific, and thus distinct from other markets where iron removal has been practiced. When assessing iron removal in remedial applications, key market-specific technical issues include: 1) space constraints; 2) operator requirements; 3) sludge generation, post-treatment and disposal costs; 4) head loss and operating pressure requirement; and 5) generation of backwash water requiring post-treatment units.

Since 2008, Redux has invested in an R&D effort to identify iron removal methods most appropriate for remedial applications, and to use our chemical knowledge to enhance promising techniques or develop new ones. This work has involved lab and bench-top studies, as well as pilot work in the field. Techniques studied include bag filtration, settlers, cross-flow micro-filters, sand, greensand

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[§] Corresponding Author: Brad A. Horn, PE, President, Redux Technology, 280 Callegari Drive, West Haven, CT 06516, Tel: 203-933-9071, Email: bhorn@reduxtech.com

and multi-media filters, and other specialty media filters, as well as all of these methods in conjunction with pretreatment chemicals.

This paper provides a review of iron removal technology alternatives and an assessment of their applicability to remedial applications. It presents bench-top and pilot scale work at many sites where these alternatives have been considered. Finally, it presents new technology, now in commercial application, which shows significant promise in being the most appropriate technique yet discovered by the authors for this niche treatment application.

Keywords: Groundwater, Iron Removal, Bead Filter

1. INTRODUCTION

Fouling of groundwater remediation systems by iron deposition and iron-related microbial biofilms is a common problem. Dissolved iron, in groundwater contaminated with anthropogenic organic materials, is often elevated, compared to nearby uncontaminated groundwater sources. This is due to a variety of factors, including pH and ORP (oxidation-reduction-potential) depression as a result of natural biodegradation of contaminants, making iron more soluble. During subsequent remedial operations, whether in-situ or ex-situ, iron can become insoluble, creating voluminous inorganic and microbial iron-related solids that interfer with treatment operations.

Control of iron deposition using blended water treatment chemicals has become more common as appropriate products have become available. However, in recent years, new regulations limiting the discharge of iron to surface waters have become increasingly common. These regulations essentially force site operators to consider alternatives for removal of iron as a pretreatment step. Removal of iron from groundwater is common in drinking water treatment, but methods used in this market are designed for iron levels that would be considered very modest in contaminated groundwater applications. In the drinking water market, total iron levels of one or two milligrams per liter are considered high, while contaminated groundwater often bears ten to a hundred milligrams per liter, and in some cases, more. Alternatively, higher levels of iron are treated in some industrial wastewater applications, but technology used in these applications tends to consume a very large footprint and is maintenance intensive.

In an effort to identify an iron removal method that is appropriate for the groundwater remediation market, the authors completed various literature reviews, bench-top analyses, and pilot studies. This work involved assessing existing iron removal alternatives used in a variety of applications in terms of their applicability to the groundwater remediation market. Thus, an important part of this work involved identifying design criteria, performance requirements, and operations requirements specific to the remedial field. Relevant considerations include: 1) space constraints; 2) operator requirements; 3) sludge generation, post-treatment and disposal costs; 4) head loss and operating pressure requirement; and 5) generation of backwash water requiring post-treatment units.

Techniques studied include bag filtration, settlers, cross-flow micro-filters, sand, greensand and multi-media filters, and other specialty media filters, as well as all of these methods in conjunction with pretreatment chemicals. Ultimately, pilot work and subsequent commercialization work were performed on several sites using an upflow media filter. This involved site-specific chemical pretreatment and subsequent solids separation. The solids separation unit is commonly called a bead filter and employs a floating plastic media, which can be treated to enhance removal.

This paper will provide a brief review of iron removal technology alternatives, with a focus on their applicability to remedial applications. Following this review, it presents data and analysis from three separate pilot studies performed using the upflow media filter.

2. MATERIALS AND PROCEDURE

2.1 Technology Review

The corresponding author's special focus on iron fouling since 1990 has enabled visits to many sites where iron deposition is a problem. This process has enabled observations of the various methods of iron removal. A brief description of the common techniques observed in use at remedial sites, along with obvious advantages and disadvantages (relevant to remedial applications), follows. Additional detailed information regarding these methods can be found in Tchobanoglous and Schroeder 1985, Eckenfelder 1989, Droste 1997, Green 2008, and Flynn 2009.

2.1.1 Chemical Treatment

All common methods of removing iron from water involve chemical treatment. The goal of chemical treatment is to convert any dissolved or ferrous iron to insoluble ferric iron salts, generally iron oxides and hydroxides. While treatment for each application is unique, this is typically achieved by chemically increasing ORP (using oxidizers), pH (using alkaline reagents), or both. Common oxidizers include oxygen, sodium hypochlorite, hydrogen peroxide, and chlorine dioxide. Common alkaline reagents include sodium hydroxide, hydrated lime, magnesium hydroxide, and sodium carbonate.

Iron solids initially formed are notoriously small (a fraction of a micron) and difficult to separate from the bulk water. Thus, in many cases, precipitant aids are used to build particle size and stability. Common precipitant aids include coagulants and flocculants. Coagulants serve to destabilize the charges that surround particles in suspension, which repel one another to form stable particulate suspensions. Historically, coagulants have been simple low molecular weight inorganics, such as alum, but newer, high performance organic coagulants are now common. Flocculants are polymers which essentially sorb (attach to) and "bridge" between particles formed by the coagulation process, creating larger agglomerated solids which settle faster and are easier to filter.

Typically, some method of solids separation is used in conjunction with chemical treatment. There are a variety of iron "oxy-hydroxides", all of which have slightly different physical characteristics. Chemical treatment can be "designed" using various reagents to produce those salts with characteristics which favor their removal by any particular solids separation technique. Similarly, precipitant aids can be selected from a great variety available to create the most desirable particulates. While common reagents work in many different applications, the optimum chemical treatment program tends to be specific to a particular groundwater.

Depending upon reagents used, chemical treatment can involve the handling of hazardous materials. Typically, reagent addition requires several stages involving multiple tanks, pumps, and mixers, which can be space consumptive, and operations intensive. In remedial applications, footprint and operations efforts can be reduced using static mixers, pipe flocculators, and proper controls.

2.1.2 Gravity Settling

Gravity settling, or sedimentation, is the most common method of separating iron solids from the bulk water. It is typically done in a specialized tank referred to as a settler, with various design features that minimize tank footprint, but allow quiescent flow for settling to occur. If space is not limited, large, open rectangular tanks are the simplest type of settler. Accommodations must be made to remove sludge from the bottom of the settler tank. In many cases, sludge removed from a settler may be further treated to increase solids concentration, and thus reduce disposal costs. This may be done by gravity thickening in a tall tank, or by various methods of active dewatering such as filter press, belt press, rotary filter, or centrifuge.

The primary disadvantage of gravity settling in remedial applications is the large space requirement. In addition, sludge withdrawn for a gravity settler has a low solids content. This increases disposal costs (assuming no sludge post-treatment occurs), particularly if sludge is considered hazardous.

2.1.3 Bag Filtration

Bag filtration is not commonly used in other markets for removal of iron, and is not, by any means, an ideal method of removing iron solids. However, bag filters are widely used at remedial sites in general, usually to prevent solids from fouling granular activated carbon (GAC) beds. GAC units and their associated bag filters often are used in a treatment train after an air stripper or oil-water separator. In cases where recovered groundwater is iron-bearing, bag filters often end up removing some or all of this iron. In these situations, filter bags tend to bind with iron solids rapidly (iron sludge is notoriously impermeable), requiring frequent bag replacements. In bags that are not replaced often enough, it has been widely observed that the resulting high pressure drop through the filter bags forces iron to "bleed" through the filter, fouling downstream units.

Though bag filters are not a very efficient way to remove iron solids, their pervasiveness at remedial sites has led the authors (and others) to experiment with employing chemical pretreatment to improve their viability for iron removal. The authors have found that chemical pretreatment can improve the usefulness of bag filters under certain situations. For example, precipitant aids (specifically, "dewatering" polymers) can reduce bag filter change-outs while retaining iron solids effectively. In spite of this, bag filtration does not compare favorably with other methods for iron removal at remedial sites.

2.1.4 Sand and Multimedia Filtration

Sand and multimedia filtration typically involves packed beds operating in down-flow mode under gravity or pressure. When employed with chemical pretreatment, they are effective at removing iron to low mg/l levels. Iron sludge accumulates on the sand or media until pressure drop, due to sludge cake, increases to some unacceptable level. At that point, the beds are backwashed and fluidized to remove iron solids. Backwash is typically collected and treated further, or it may be discharged to sanitary sewers in some cases.

Packed bed filters can be effective for iron removal and consume less space than gravity settlers of the same flow rating. While this smaller footprint is a big advantage in remedial applications, the requirement for clean backwash water, and the resultant generation of dilute iron-bearing backwash water, creates an operations challenge. Many remedial sites do not have clean water available unless treated water is stored, which requires large footprint storage tanks. Treatment of backwash water also creates an operations challenge, requiring storage tanks and further solids treatment of the dilute and voluminous backwash.

2.1.5 Greensand

Greensand is a naturally occurring, fine-grained material, which can be treated to remove iron in a packed bed arrangement. It is also referred to as manganese greensand since the treatment process to enable iron removal involves the application of potassium permanganate oxidizing agent. This oxidizer sorbs on the sand, oxidizing the iron to create insoluble ferric salts which then sorb to, and are physically filtered by, the media. The greensand media requires regular backwashing to remove iron solids, as well as subsequent regeneration by addition of potassium permanganate.

Greensand has been widely used in drinking water treatment for many years, and has been proven to be very effective in that application. Its use in remedial applications has been limited for several reasons: the requirement for clean backwash water and for treatment of dilute iron bearing backwash water creates challenges for many remedial sites. In addition, the economics of greensand regeneration and backwash at high iron loadings limits its window of appropriate application to what are considered low levels of iron (less than 5 mg/l) in the remedial market.

2.1.6 Specialty Media Filters

There are various specialty and proprietary media marketed specifically for iron removal. Most of these media are applied in packed beds and may require regeneration or backwash. One of the most common of these is BIRM (a tradename), widely used for iron removal in small drinking water applications. It requires a certain level of dissolved oxygen in influent water in order to insure iron oxidizes to the ferric state. Many groundwater remediation system influent waters do not contain appreciable amounts of dissolved oxygen, requiring the introduction of air or oxidizers to employ BIRM. Siemens (formerly US Filter) markets a specialty iron removal media which has been shown to be effective for removal of low levels of iron (several mg/l), but the authors do not have direct experience with this material.

2.1.7 Crossflow Microfilters

Several manufacturers offer filtration systems which avoid (or minimize) the common problem of membrane fouling by creating high shear rates parallel to the membrane surface. Some term these cross-flow microfilters, and these have been shown to be effective for removal of iron at the higher concentrations common on remedial sites with iron fouling. This method is necessarily used in conjunction with chemical pretreatment and involves recirculation of solids bearing water at a high ratio compared to the system throughput. While this technology is effective for iron removal at remedial sites, and its space requirement is less than most alternatives, the capital and operating costs are higher than alternatives.

2.2 Pilot Work

2.2.1 Technology Identification

Shortcomings of existing methods guided the authors' search for alternative techniques that might be adapted for remedial work. These criteria include compact footprint, minimal generation of backwash, maximum concentration of solids, and a general minimum of process sub-units. The use of packed bed separators offers a small footprint, but there are complications in separating solids from bed media. Literature searches suggested that packed beds employing floating beads might offer the benefit of a small footprint without the challenge of managing backwash: Certain configurations allow the use of air to stir and separate media from solids entrained in the bed. Bead filters have been widely used in the US in aquaculture water treatment, and to a more limited extent, overseas for municipal wastewater treatment (Malone and Gudipati 2005).

After a literature review and various discussions with academic investigators involved in bead filter work, the authors toured beadfilter installations to better assess feasibility in remedial applications. Based upon this work, the authors determined that adaptation to remedial work would require 1) different bead geometry than that used in prior applications; 2) pretreatment chemistry to create particles large enough to make bead size practical, targeting particle size of 50 microns; and 3) agglomerated particulates with a stability to endure the shear forces expected in packed bed flow. With these challenges in mind, several pilot study candidate sites were identified. Three pilot studies were run to assess feasibility of beadfilters for iron removal at two separate sites.

2.2.2 Pilot Study Site A

2.2.2.1 Site A – Phase I

This site is a very large superfund site in upstate New York. Two sequential pilot studies were run here, with the results of the first informing a redesign of the pilot apparatus for the second. The subject water is recovered from a single well which is one of two maintaining an inward gradient through a sheet-pile wall surrounding a fill area. The driving force for iron removal is expected discharge to surface waters, with an iron discharge limit of 0.5 mg/l. Various site specific conditions make the pilot work more challenging than would be expected at almost any remedial site: Total iron levels ranged from 350 mg/l to 400 mg/l with a good portion of this being dissolved. Iron removal is complicated by the addition of a blended deposit control agent to the well to prevent very rapid fouling of the recovery pump and transmission piping. Several bench-top studies were completed to determine if a chemical pretreatment program would be able to "break" the sequestered iron complexes and degrade the dispersants to allow creation of required iron particulates. These studies resulted in the development of a treatment protocol which included: 1) Fenton's chemistry to degrade deposit control components; 2) addition of a blended alkaline reagent to raise pH slightly from approximately 3.5 to about 6.5; 3) a high performance organic coagulant; and 4) a cationic flocculating polymer.

Using this pretreatment scheme, two sequential pilot studies were run. The first utilized a simple bead bed arrangement depicted in Figure 1.

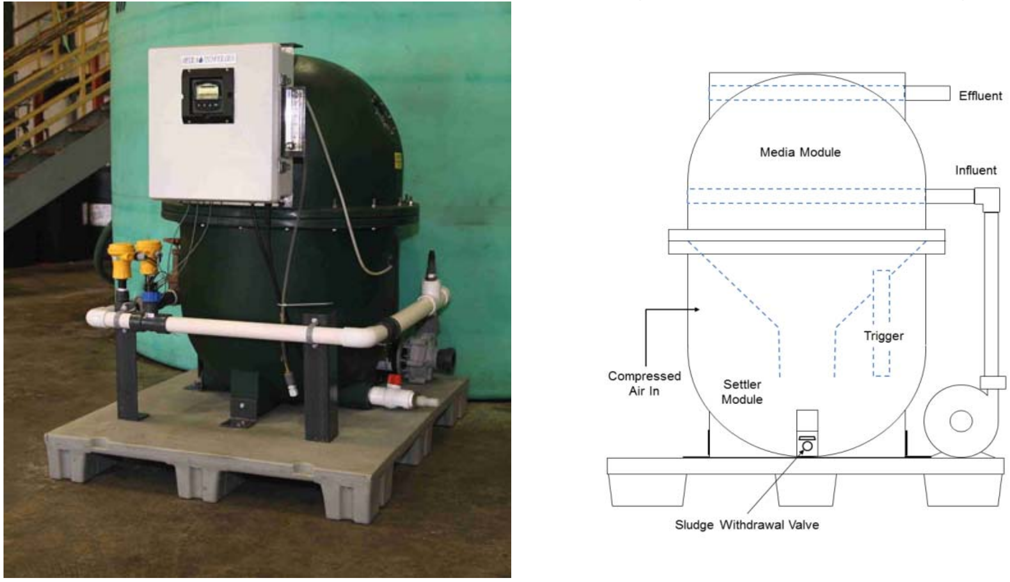

Figure 1. Photographic and schematic representations of initial pilot configuration

The schematic on the right is useful for understanding the basic operating concepts of this method. Various subsequent designs utilize the same basic components in different arrangements according to the performance criteria desired. The media module contains, and is partially filled with, the floating bead media. The feed pump introduces pretreated water into the bottom of the bead bed and water flows upward through the bed to the effluent pipe, constructed of slotted well screen. Solids are entrained in the media by flocculation, sorption and physical exclusion. Meanwhile, air is introduced slowly into the air chamber (in this case toroidally shaped, wrapping around the internal “sludge funnel”), lowering the water level in this chamber until it reaches the patented trigger, at which point air is rapidly transferred into the bead bed above, stirring it aggressively. The sludge/water mixture flows downward through the “sludge funnel” to fill the settler module completely (including the air chamber). Influent flow is uninterrupted during this bed purge, which has an adjustable cycle based upon the rate of compressed air introduced into the air chamber. After a bed purge, influent water refills the top of the unit, and another operating cycle begins, during which sludge settles in the bottom of the unit and can be periodically withdrawn.

Using this initial pilot arrangement, a three month pilot effort was completed. During the first two months of study the pilot unit was run during individual two or three day site visits, occurring every week or two. This phase of work involved extensive debugging of the pretreatment chemistry, recovery and transfer pumping systems, and various bead bed operating parameters. During each site visit, system operations were observed, monitored and documented in the site field book. With each visit, changes were made in configuration and operations as needed.

During the last month of field work the system operated continuously and periodic iron removal data was collected, along with extensive additional data reflecting status of operations.

2.2.2.2 Site A – Phase II

The second phase of pilot work at this site was conducted to incorporate lessons learned in the first phase. Figure 2 depicts the entire process set up for this phase of pilot work, including the pretreatment chemical feed, mixing and reaction manifolds, and a recirculation loop to recycle “stale” water upon each restart (added in the middle of this second phase). This second phase of pilot work lasted approximately seven months. During the first two months, data was collected using the same apparatus used in the first phase in order to enable design of an improved apparatus. Subsequently, this new bead filter, along with necessary controls to allow continuous operation, was installed, debugged, and operated for about five months.

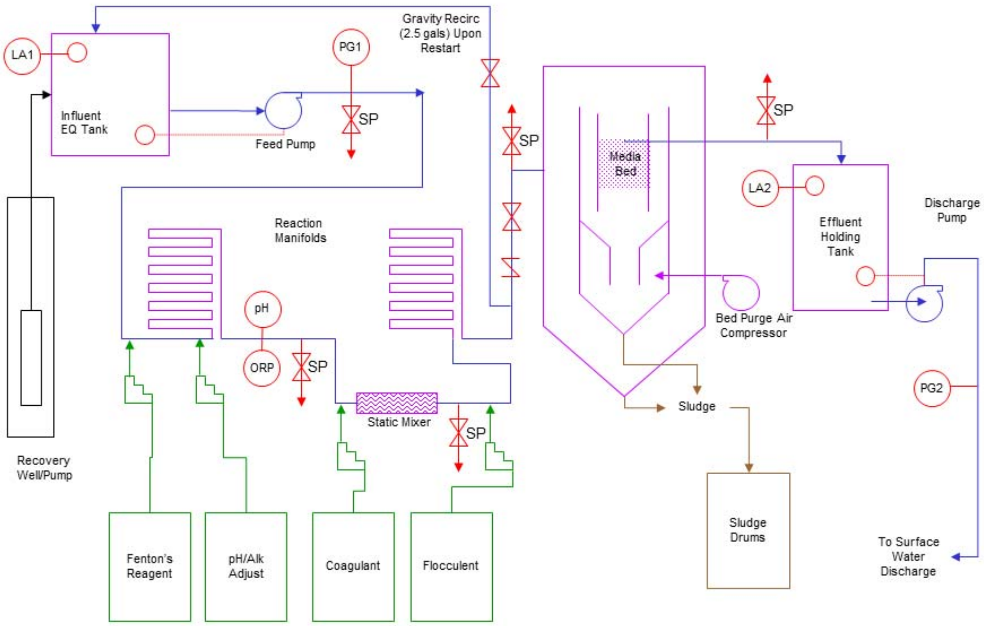

Figure 2. Entire process diagram for Site A – Phase II pilot work

There were two major improvements in the new pilot design: First, the use of a gear pump (rather than a centrifugal pump used in the first phase) enabled very accurate control of groundwater flow rate. This, in conjunction with fixed-feed chemical reagent pumps, eliminated the need for complicated chemical feed controls while still enabling accurate dosing. Second, the new design incorporates a “roughing chamber” for removing the largest solids: those which can be easily settled, rather than running all solids generated through the bead bed. This reduces unnecessary solids loading into the bead bed, allowing it to flocculate and remove smaller solids, or those that float. Figure 3 shows the top of the new pilot bead filter, with the outer “roughing chamber”, and an inner weir over which water flows to subsequently rise through the bead bed in the center section.

Figure 3. Top interior of redesigned Site A pilot bead filter

During the five months of operation, a dedicated site operator visited the site for several hours, three times per week to collect data regarding system performance and operation parameters.

2.2.3 Pilot Study Site B

This two week pilot study was completed at a landfill site located on a large air force base in Georgia. Work from the above pilot studies helped with redesign of a pilot apparatus most appropriate for the expected water characteristics. Iron removal was required, in this case, in order to effectively operate an ozonation unit without fouling it and to prevent iron from increasing oxidant demand. Influent water contained approximately 60 mg/l of total iron, virtually all dissolved. Preliminary bench-top studies derived an unusual treatment protocol: it involved addition of an inorganic poly-aluminum chloride coagulant followed by pH increase using caustic soda, followed by addition of high molecular weight anionic flocculating polymer. It is rare that coagulant is added before solids generation (in this case by increasing pH), but in this case it made a very significant difference in particle size development.

The apparatus used for solids separation is depicted in Figure 4. While this design is similar to that used in the Phase I work at Site A described earlier, it utilizes a bead size which is about one-third that used in the Site A work.

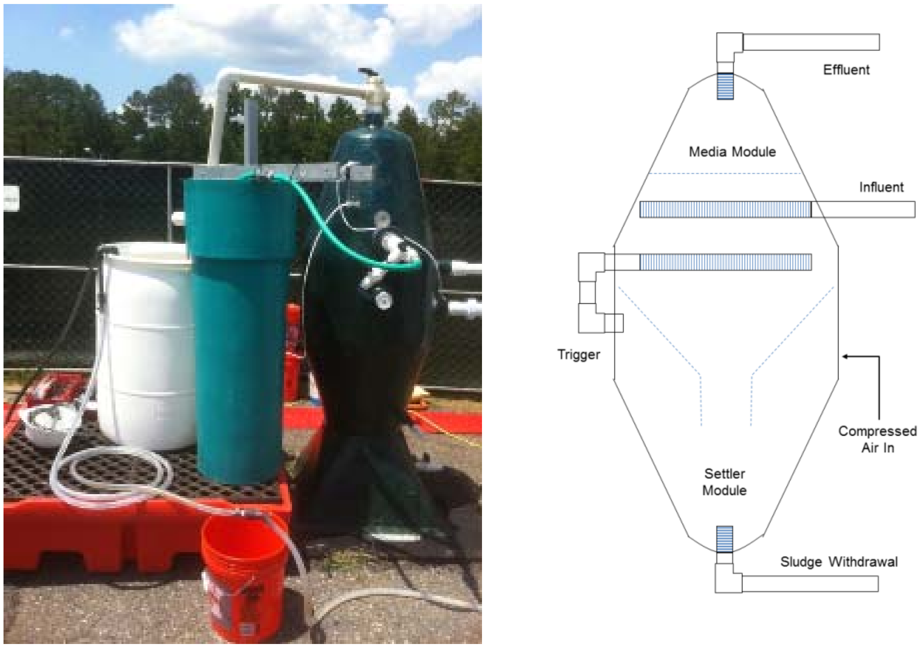

Figure 4. Photographic and schematic representation of Site B apparatus. Note in photo, bead filter is on right, along with recirculation and discharge tanks respectively to its left.

Site work for the pilot study involved an initial set-up and debug stage for several days, prior to the initiation of ozonation work. Iron removal and ozonation together operated for about two weeks, at a flow rate of one gpm. Iron removal and other operations parameters associated with filter operations were recorded regularly.

3. DATA AND ANALYSIS

This section provides data relating to iron removal for all three pilot efforts described previously. Though much additional data was collected relating to operations parameters, all of which ultimately relate to improving iron removal, the data presented here includes only measurements specific to iron concentrations in influent and effluent and certain sludge characteristics. This data is most critical to determining whether or not the subject iron removal technique merits further study. Other data which was collected in all three studies, but which is not directly germane to the iron removal performance and sludge production, includes bed pressure drop, iron particle size and stability measurements, settling tests, jar tests of samples taken at various points in the treatment train, reagent dosing tests, bed purging tests, and "upset" testing (where the bed was challenged, intentionally or unintentionally with poor pretreatment conditions), among other data. While this latter data constitutes the great majority of the testing data collected, and it enabled regular improvement in iron removal, detailed reporting and explanation of it is beyond the scope of this paper.

With the above caveat in mind, Table 1 is presented below, giving iron measurements taken during Phase I testing at Site A, along with relevant brief comments. In assessing this data set, it is important to understand that the influent contained blended deposit control agents (containing sequesterants and dispersants) which complicated proper pretreatment. During the initial test work of this phase, the groundwater fed to the filter was pumped directly from the well using the down-hole electric submersible well-pump, through the pretreatment manifold and filter. The recovery pump had been originally set up to cycle, feeding a relatively high flow rate periodically, with a ratio of on-time to off-time of about ten to one. This short-period, high-flow situation made accurate chemical dosing difficult, as compared to longer runs at lower flows. For various reasons, changing the pumping cycle was not feasible, so at mid study, an equalization tank was installed to allow a more desirable cycling pattern, greatly improving chemical dosing and subsequent iron removal.

By the end of this phase, enough sludge was generated to estimate sludge production and solids content. Sludge directly from the filter ranged around 3.5% solids content. Gravity thickening produced a sludge solids content in the range of 4.5%, with a final production rate of this material estimated to be about 1.6% of the groundwater volume treated.

Phase II of the Site A Pilot Work incorporated many lessons learned from the Phase I work. Treatment system upgrades included the incorporation of the equalization tank and positive displacement gear pump to enable long runs at low flow, with consistent reagent dosing. Once design data was collected and the redesigned pilot unit was installed, along with aforementioned changes, iron removal to low mg/l levels was consistently achieved, with complete oxidation of iron.

During Phase II pilot work, several process improvements incrementally increased average iron removal and improved sludge quality. These improvements included 1) the incorporation of a timer-controlled recirculation loop to send "stale" water back to the influent equalization tank for several minutes upon each cycle restart, and 2) better control of sludge level in the "roughing chamber" (aka influent atrium).

Table 1. Iron Removal Data for Site A – Phase I Pilot Work

Date & Sample ID	**Iron (mg/l)**		**Removal**	**Comment**
	Total	**Dissolved**	(total iron)	
11/3/2010				
Influent	430	310	95.3%	High flow, short duration runs, 6-8 gpm
Effluent	20	4		
11/16/2010				
Influent	390	300	99.0%	flow stabilized at 1-2 gpm
Effluent	4	2		
11/30/2010				
Influent	400	320	99.5%	Sludge Analysis: 4.5% solids w/w
Effluent	2	1		

After installation of the redesigned pilot unit, influent water chemistry changed somewhat (as it does periodically at Site A), which resulted in a sudden increase in floating iron solids. This upset highlighted one advantage of the bead bed approach over settlers depending upon gravity separation, as overall removal remained relatively stable. Subsequently, influent chemistry shifted back to original conditions (as indicated by the success of original optimized reagent feeds) and overall iron removal reached its best yet.

Table 2 presents iron removal data and relevant comments collected during Phase II work at Site A. While regular improvements in treatment occurred throughout both phases of the Site A work, the best effluent consistently produced contains one or two milligrams per liter of total iron.

Pilot work at Site B occurred subsequently to both phases of pilot work at Site A and incorporated adjustments in an attempt to improve iron removal. Media used in the Site B work was smaller and geometrically different than that used in the Site A work. Iron removal data collected from the Site B work consistently

Table 2. Iron Data for Site A – Phase II Pilot Work

Date & Sample ID	**Iron (mg/l)**		**Comment**
	Total	**Dissolved**	
3/16/2011			install gear pump
3/14/2011			
Influent	380	280	optimize chemistry
Effluent		<1	
3/28/2011			
Influent	390	300	1st full tote runs
Effluent		ND	
4/17/2011			
Influent	400	330	using settler only, removal of all particulate iron greater than 5 microns, <8 ppm colloidal
Effluent	5-8	ND	
5/22/2011			install new bead filter, restart
5/30-6/6/11			system upset, floating sludge
6/13/2011	390		
Effluent	3-4	ND	particulates 5-25 microns
7/1-9/13/11			
Effluent	1-2	ND	particulates 5-25 microns

gave an influent total iron level of sixty mg/l: all pilot work at this site was completed on a fixed volume of influent water contained in a single tank, resulting in very consistent influent quality. Once chemical pretreatment dosing was adjusted, iron filter effluent contained less than one milligram per liter of total iron in all cases. Influent and effluent iron measurements were collected at least twice per day over the two week period of operation.

While iron removal was very consistent during most of the Site B operations (allowing a very successful ozonation study to occur), particular attention was paid to bead bed operations parameters affecting iron removal. These included hydraulic loading, the advantages and effect of recycling through the iron filter, and loss of iron removal efficiency immediately after purging the bead bed of iron solids. From this work, various plans for improvement were borne, most significantly relating to loss of iron removal efficiency after bed purge: iron removal suffers after bed purge, for some period of flow (twenty to thirty minutes after bed purge). This effect can be minimized by recycling effluent back to the treatment system headworks, or by adding chemical “retreatment” to a recycle loop at the filter itself. These alterations are to be studied in upcoming pilot work.

4. CONCLUSION

The pilot work described in this paper proved that the use of bead beds for iron removal shows promise. Data collected helped greatly improve removal throughout the course of these three studies, as changes were implemented in response to data collected. The Site B pilot work results enabled the site owner to make the decision to proceed to full scale process development, and this system has now been in operation for over a year. Certain process problems identified in this pilot work have been addressed and others are still under study.

5. REFERENCES

Droste, R.L. 1997. Theory and Practice of Water and Wastewater Treatment. New York, J Wiley

Eckenfelder, W.W. 1989. Industrial Water Pollution Control. New York, McGraw-Hill

Malone, R. F. and S. Gudipati. 2005. Polygeyser/Airlift Filtration of High Density Recirculating Aquaculture Systems. Proceedings of the 2nd International Sustainable Marine Fish Culture Conference, Fort Pierce, Florida

Flynn, DJ, ed. 2009. Nalco Water Handbook 3rd Edition. New York, McGraw-Hill

Green, DW, ed. 2008. Perry’s Chemical Engineers’ Handbook, Eighth Edition. New York, McGraw-Hill

Tchobanoglous, G. and Schroeder, E. 1985. Water quality: Characteristics, Modeling, Modification, Boston, Addison-Wesley

Chapter 2

ARSENIC CONTAMINATION IN SOIL, SEDIMENT AND WATER AROUND A GOLD MINE IN QINGHAI PROVINCE, CHINA

Baolin Liu[§], Ximing Luo, Nianqiao Fang
School of Marine Sciences, China University of Geosciences, 100083 Beijing, China

ABSTRACT

Contamination of the environment with arsenic (As) from both anthropogenic and natural sources has occurred in many parts of the world and is recognized as a global problem. In this study, 6 floodplain soil, 9 stream sediment and 9 surface water samples were collected in the vicinity of an active gold mine in Qinghai Province, China. All samples were analyzed for As by atomic fluorescence Spectrometry (AFS). Soil and sediment samples were also measured for pH, cation exchange capacity (CEC), and organic matter (OM). The objective of this study is to investigate the contamination level and dispersion pattern of As around the gold mine. Average As concentrations in stream sediment, floodplain soil, and water are 378 mg/kg, 30.93 mg/kg and 108.4μg/L, respectively. Arsenic is continuously dispersed downstream from the mining site at the Maridang Channel. Correlation analysis suggests OM content and CEC of soil and sediment have an influence on the distribution of As in the soil and sediment. A decrease of pH value of the soil and sediment will enhance the mobilization and migration of As. High enrichment factor (EF) values and Index of geoaccumulation (I_{geo}) values for As are found mainly in the stream sediments and parts of soils in the vicinity of the active mining site, suggesting that As has been at a strong pollution level. The arsenic contamination in surface water tends to be restricted to areas within a few kilometers of mine sites, probably because of the strong adsorption of arsenic by oxide minerals, especially iron oxide, under oxidizing and neutral conditions typical of many surface waters.

Keywords: Arsenic, contamination, sediment, gold mine

[§] Corresponding author: Baolin Liu, No 29, Xueyuan Road, Haidian District, Beijing, China, 100083. Tel: 8610-82332449; Email: liubaolin@cugb.edu.cn

1. INTRODUCTION

Heavy metal contamination has caused serious environmental and health-related problems around the world (Alloway and Ayres, 1997). Of heavy metals, Arsenic (As) is a toxic and carcinogenic element, which is usually present in coals or the ores with various sulfur-containing minerals (Zhu et al., 2010). Anthropogenic activities such as mining, smelting and coal combustion have resulted in the release of As into land surface environment, causing serious As-contamination (Xu et al., 1996). Contamination of the environment with arsenic (As) from both anthropogenic and natural sources has occurred in many parts of the world and is recognized as a global problem. Approximately 70% of total As deposits are distributed in China; however, an average of 70% of the exploited As remain in tailings during the mineral processes under current technique level in China (Xiao et al., 2008). The open pit dumping of As-containing tailings has released large amounts of hazardous matters into soils and surface waters through wind and hydraulic erosion (Zhu et al., 2010).

The Jiawu gold project is a mine field first operated in 2006. Geographically, the gold project was located in the Sanjiangyuan National Nature Reserve (SNNR), China, which contains the headwaters of the Yellow River, Changjiang River and Lantsang River. At the present, the gold project has been ranked as middle-scale level. However, due to execrable weathering and specific geographic condition, there were no reports related to environmental geochemistry of the Jiawu gold mine and the information on As contamination is not available in the area. It is necessary to assess the influence of the mining and milling operation of the gold mine on the local environment quality or even on the water quality of the Yellow River.

The present study will aim to investigate the contamination level and dispersion pattern of As around the gold mine, to identify main sources for the metal, and then to assess contamination level of the metal.

2. MATERIALS AND METHODS

2.1 Study Area

The Jiawu gold project is located in Jiawu Town, Qinhai Province, China (Fig.1). Hydrographically, the river system in the study area is a tributary of the Yellow River, flowing westerly directly into the Yellow River within a short distance. During the months from May to September, the region receives maximum precipitations. The annual average precipitation is 300 ~ 400mm. The annual average temperature is 0.4 ~ 0.6°C. There are no other industries in the area, except for mining activities. Geology of watershed largely consists of clastic rock and granite outcrops, with sandstone, slate and quartz veins prevalent in the mining areas. From historical point of view, except for some small geological explorations for the gold and antimony reported in the late 1980's on the site, there was no regular gold exploitation until 2006.

2.2 Sampling and Preparation

Sampling of soils, stream sediments, ground water and surface water in the vicinity of the active mine veins of the Jiawu gold mine in August, 2008 (see Fig.1). A total of six soil samples (H1-H6) were collected in a floodplain area at the downstream of the Maridang Channel. Each soil sample (0-20cm in depth) comprised a composite of five sub-samples taken within a 1×1m quadrate. In

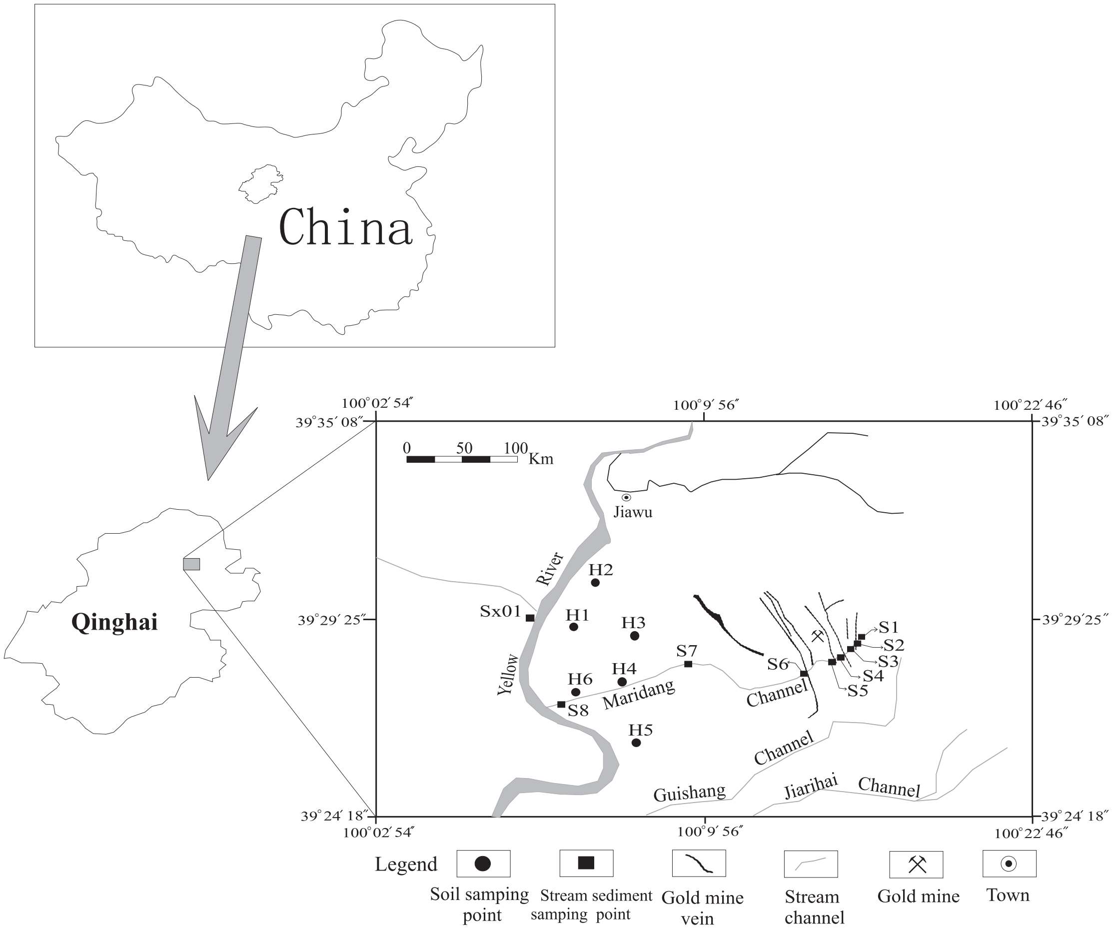

Figure 1. Study area and sampling site map

addition, nine stream sediment samples (S1- S8, SX01) were also collected from the Maridang Stream Channel located directly below the mine; this stream collected water running directly from the mine shaft opening. All soil and stream sediment samples were air dried at room temperature (about 25°C) for 1 week and sieved through a 2-mm nylon sieve to remove plant debris, pebbles, and stones. They were then grounded in agate mortar to a fine powder to pass a 200µm sieve for geochemical analyses. Nine surface water samples were collected from the Maridang Stream Channel.

2.3 Analytical Methods

The chemical analysis of metal was performed in the Analytical Laboratory Beijing Research Institute of Uranium Geology, China. Atomic fluorescence spectrometry (AFS-2202) was used to analyze the concentrations of Arsenic. Major element Al and Fe were analyzed by X-ray fluorescence (XRF) spectrometry (PW2404, Philips).

Water samples were filtered through 0.45 µm membrane and then acidified with concentrated HNO_3 for analyses of the cations using the HR-ICP-MS (Finnigan MAT, Germany).

The soil pH was determined by a pH meter with a soil/water ratio of 1:5. The cation exchange capacity (CEC) was measured using 1 mol/L ammonium acetate solution (Liu et al.,1996).

The soil organic matter was determined by the Walkey–Black method (Schnitzer, 1982).

3. RESULTS AND DISCUSSION

3.1 Physical and Chemical Properties of Stream Sediments and Soils

The physical and chemical properties of stream sediments and floodplain soils sampled near the Jiawu gold mine area are summarised in Table 1. Overall, some stream sediment samples from the vicinity of the mine have a relatively lower pH (7.8±0.38) than those of floodplain soils samples (8.45±0.26) due to the influence of the weathering of sulphide and gangue minerals. All of the studied soil pH (100%) is alkaline and/or strong alkaline. Analysis of the stream sediment sample demonstrates a narrow range of OM ranging from 0.52 to 2.13%. For OM, almost all of the studied soils have low organic matter contents (0.24–1.17%) which indicated that the soils in this area are not relatively fertile. Stream sediment and floodplain soil samples show a wide range of CEC ranging from 2.8 to 75.08 cmol kg^{-1}.

3.2 Concentration of Metals in Soil and Sediment

Concentration of As, Al and Fe in floodplain soil and stream sediment is also listed in Table 1. Overall, As content in the stream sediments are higher than those in soils. In the stream sediments, the contents of As decrease with the increase of distance to active mining site, while As concentration differences are not obvious in soil samples, except for a slightly high content in sample H1. This suggests that mining actives have a direct influence on enrichment of As in stream sediments. Compared to the Chinese Environmental Quality Standard for soils (GB15618-1995) (As: 15, 25 and 40 mg/kg for grade A, B and C, respectively), As concentration is significantly high in both soil and stream sediment. The concentration of As in stream sediments and soils is also significantly higher than world average values in uncontaminated soil (As: 6 mg/kg) reported by Bowen (1979).

3.3 Multivariate Analysis for Heavy Metals

Pearson's correlation coefficient can be used to measure the degree of correlation between the metal data and can provide suggestive information regarding heavy metal sources and pathways (Manta et al., 2002; Al-Khashman and Shawabkeh, 2006). The Pearson's correlation coefficients between heavy metal and soil, and sediment properties are summarized in Table 2. Close relationships were noted among As, Fe and CEC, suggesting a common source of these metals and their strong association with Fe oxides of the soils. As is negatively correlated with pH, suggesting that a decrease of pH value of the soil and sediment will enhance the mobilization and migration of As.

3.4 The Enrichment Factors (EF)

In order to better understand the sediment quality and discern the metal contamination in the stream sediments and soils, enrichment factor (EF) is used. EF was calculated using the following equation

$$EF = (X/Al)_{sample} / (X/Al)_{background}$$

where (X/Al)sample is the metal to Al ratio in the samples of interest and (X/Al)background is the natural background value of the metal to Al ratio (Sinex and Wright, 1988; Zhang et al., 2009).

In this study, the average shale concentrations of metals were selected as natural background values. Based on the research of Zhang and Liu (2002), if an EF value is between 0.5 and 1.5, it suggests that the metal may be entirely from crustal materials or natural weathering processes. If an EF is greater than 1.5, it suggests that a significant portion of the metal has originated from non-crustal or anthropogenic processes.

Table 1. The range and mean of metal concentration (mg/kg), pH, OM and CEC (cmol kg^{-1}) in soils and stream sediments (% for Al, Fe and OM).

Sample description		Al	Fe	As	pH	OM	CEC
Stream sediment (n=9)	Max	9.07	4.63	858	8.86	2.13	75.08
	Min	6.52	3.28	9.43	7.66	0.02	4.6
	Average	8.29	3.86	378	7.94	0.54	30.18
	STD	0.81	0.52	331.9	0.35	0.62	22.85
Soil (n=6)	Max	9.39	4.14	78.6	8.87	1.17	39.88
	Min	5.52	3.21	15	8.16	0.24	2.8
	Average	7.42	3.57	30.93	8.45	0.73	15.71
	STD	1.28	0.32	24.11	0.26	0.33	13.39
Surface water (n=9)	Max	—	—	231	—	—	—
	Min	—	—	8.78	—	—	—
	Average	—	—	108.4	—	—	—
	STD	—	—	79.2	—	—	—
Soil background of Qinhai province [a]		—	—	14	—	—	—
Chinese Environmental Quality Standard for Soil [b]	A	—	—	15	—	—	—
	B	—	—	25	—	—	—
	C	—	—	40	—	—	—

[a] *China Background values of Chinese soils (China Environmental Monitoring Station, 1990), A layer(0~20 cm), more than 4000 samples.*
[b] *Chinese Environmental Quality Standard for Soil (GB15618-1995)*

The EF values of As were computed with respect to the average shale concentration (Turekian and Wedepohl, 1961). High EF values for As were found both in the stream sediments and soils. The mean EF values of As in the stream sediments and soils are 28.21 and 2.58, respectively, suggesting that the stream sediments and soils have been heavily contaminated by As. Soils in the floodplain show a low degree of metal contamination with EF values being less than 1.5, suggesting that the mining activities had little influence on enrichment of these metals in the floodplain soils.

Table 2 Pearson's correlation matrix for the metal concentrations.

	As	Al	Fe
As	1.00[a]		
Al	0.29	1.00	
Fe	**0.87**	0.34	1.00
pH	-0.46	**-0.57**	-0.29
OM	0.43	-0.16	0.39
CEC	**0.52**	0.10	0.28

[a] *Linear correlation coefficient (r). Statistically significant correlation are indicated in bold where $P < 0.05$.*

3.5 Geoaccumulation Index

Index of geoaccumulation (I_{geo}) introduced by Muller (1969) was also used as a criterion in the heavy metal pollution assessment of the stream sediments and soils in the Jiawu gold mine area.

$$I_{geo} = \log_2[C_n/1.5\times B_n]$$

Where C_n is the measured concentration of the examined metal ‘‘n’’ in the sediment, and B_n is the geochemical background concentration of the metal ‘‘n’’. The I_{geo} is associated with a qualitative scale of pollution intensity; samples may be classified as unpolluted ($I_{geo} \leq 0$), unpolluted to moderately polluted ($0 \leq I_{geo} \leq 1$), moderately polluted ($1 \leq I_{geo} \leq 2$), moderately to strongly polluted ($2 \leq I_{geo} \leq 3$), strongly polluted ($3 \leq I_{geo} \leq 4$), strongly to extremely polluted ($4 \leq I_{geo} \leq 5$), and extremely polluted ($5 \leq I_{geo}$).

In this study, I_{geo} has been calculated using soil background values of Qinhai Province, as presented by China Environmental Monitoring Station (1990).

In most stream sediments, the I_{geo} values of As are between 2 and 5, corresponding to moderately to strongly contaminated sediments, especially near the active mine area. The highest I_{geo} values (5.15-5.35) for As are found near the active mine area, indicating that the mining activities have exerted an important influence on the contaminated environment. In most of floodplain soils, I_{geo} values of As are very low (<0), representing that there was no contamination of the metal in the soils.

The I_{geo} values for As in the stream sediments ranged from 2.08 to 5.35 (except for SX01). The highest I_{geo} values (>5) for As were found in these samples near the active mining area (e.g. S1, S2, S3), indicating an extremely contaminated environment.

It was notable that the degree of As pollution in stream sediments is generally higher than that in soils, as discussed in the previous section. It might be due to the fact that the stream sediments were collected in the Maridang Channel, where several gold mine veins are being exploited (Fig.1). Pyritization, limonitization, arsenopyrite, galenite and stibnite mineralization were existent locally. These minerals contained a large amount of heavy metals. A variety of other sulfide minerals such as orpiment As_2S_3, and realgar As_2S_2 also occur in association with gold deposits. All of these minerals oxidize rapidly upon exposure to the atmosphere releasing the arsenic and other heavy metals for partitioning between water and various secondary minerals, such as iron oxides. Oxidation of sulfide minerals can occur naturally or as a result of mining activity, resulting in the mobilization and migration of these metals with the running water, and finally depositing in the stream sediment in the channel.

Our results also showed that the arsenic contamination in surface water tends to be restricted to areas within a few kilometers of mine sites, probably because of the strong absorption of arsenic by oxide minerals, especially iron oxide, under oxidizing and neutral conditions typical of many surface waters.

4. CONCLUSION

In the vicinity of the Jiawu gold mine, Qinhai Province, China, As contents in the stream sediments are higher than that in soils. In the stream sediments, the As content decreases with the increase in distance to active mining sites, suggesting that mining activities have a direct influence on enrichment of As in stream sediment. As is continuously dispersed downstream from the mine site at the Maridang Channel.

Close correlation relationships were found among As, Fe and CEC, suggesting a common source of these metals and their strong association with Fe oxides of the soils.

High EF values for As were found both in the stream sediments and soils, suggesting that the stream sediments and soils have been heavily contaminated by As.

The I_{geo} values for As in the stream sediments ranged from 2.08 to 5.35 (except for SX01). The highest I_{geo} values (>5) for As were founded in these samples near the active mining area (e.g. S1, S2, S3), indicating an extremely contaminated environment, which might be related to the mining activities of gold.

5. ACKNOWLEDGMENTS

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6. REFERENCES

Al-Khashman, O.A., and Shawabkeh, R.A. 2006. Metals distribution in soils around the cement factory in southern Jordan. Environmen. Pollut. 140 (3), 387–394.

Alloway, B. J., and Ayres, D.C. 1997. Chemical Principles of Environmental Pollution. pp. 1-395. London, Blackie Academic & Professional.

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. New York, Academic Press.

China Environmental Monitoring Station. 1990. Natural Background Values of Soil Elements in China. Beijing: China Environmental Science Press (in Chinese)

Liu, G.S., Jiang, N.H., Zhang, L.D., and Liu, Z.L. 1996. Soil physical and chemical analysis and description of soil profiles. Beijing: Standa rd Press of China, pp 179–182 (in Chinese)

Manta, D.S., Angelone, M., Bellanca, A., Neri, R., and Sprovieri, M. 2002. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Sci. Total Environ. 300 (1–3), 229–243.

Muller, G. 1969. Index of geoaccumulation in sediments of the Rhine River. GeoJournal 2(3):108–118.

Schnitzer, M. 1982. Total carbon, organic matter, and carbon. In: Methods of soil analysis Part 2, Vol 9 (2nd edn), pp. 539–577. (Page, A.L., Miller, R.H., Keeney, D.R, Eds.), Agronomy Monograph, American Society of Agronomy, Madison.

Sinex, S.A., and Wright, D.A. 1988. Distribution of trace metals in the sediments and biota of Chesapeake Bay. Mar. Pollut. Bull. 19, 425–431.

Turekian, K.K., and Wedepohl, K.H. 1961. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Am. Bull. 72, 175–192.

Xiao, X.Y., Chen, T.B., and Liao X.Y. 2008. Regional distribution of arsenic contained minerals and arsenic pollution in China, Geogr. Res. 27 (1): 201–212.

Xu, H.N., and Xu, J.L. 1996. Cause of formation and distribution of arsenic in abnormal area of China, Soil 28: 80–84.

Zhang, W.G., Feng, H., Chang, J.N., Qu, J.G., Xie, H.X., and Yu, L.Z. 2009. Heavy metal contamination in surface sediments of Yangtze River intertidal zone: An assessment from different indexes. Environ. Pollut. 157, 1533–1543.

Zhang, J., and Liu, C.L. 2002. Riverine composition and estuarine geochemistry of particulate metals in China—weathering features, anthropogenic impact and chemical fluxes. Estuar. Coast. Shelf Sci.54, 1051–1070.

Zhu, Y.M., Wei, C.Y., and Yang, L.S. 2010. Rehabilitation of a tailing dam at Shimen County, Hunan Province: effectiveness assessment. Acta Ecol. Sin. 30, 178–183.

Chapter 3

HEAVY METAL SOIL REMEDIATION, MCGRATH PARK, SALEM, MASSACHUSETTS

Michael E. Martin[§1], Kenneth J. Gendron[2], David A. Murphy[3], David Knowlton[4]
[1]*Tighe & Bond Consulting Engineers, 4 Barlows Landing Road, Unit 15, Pocasset, MA, USA 02559,*[2]*Tighe & Bond Consulting Engineers, 446 Main Street, Worcester, MA 01608,* [3]*Tighe & Bond Consulting Engineers, 177 Corporate Drive, Portsmouth, NH 03801,* [4]*City of Salem, 120 Washington Street, 4th Floor, Salem, MA 01970*

ABSTRACT

McGrath Park consists of a 22.30 acre park located in Salem, Massachusetts containing two soccer fields (the upper and lower fields), a basketball court, two playgrounds and an asphalt parking lot. Prior to being developed as McGrath Park, the site was operated as a municipal, unlined burn dump from approximately 1946 until 1963. The dump reportedly received municipal solid waste (MSW) from 1946 until the early 1960's, when the City of Salem built an MSW incinerator on Swampscott Road. The ash from the burn dump, along with construction materials (e.g., bricks, concrete, scrap metal) was reportedly disposed in the dump until its closure in 1963.

During the assessment activities conducted at the site, heavy metals (arsenic, cadmium, lead and nickel) were detected in surficial soils, including arsenic at a concentration that could pose an Imminent Hazard (IH), resulting in the closure of the park. The overall goal of the soil remediation was to reduce metals exposure point concentrations in the surficial (accessible) soil at the Site to levels that do not pose a risk to human health and the environment. The work had to be conducted during the winter months, so the soccer fields would be ready for use for the Fall 2012 season. This paper describes the remediation activities performed at the Site to achieve the overall remediation goal, which included the construction of a landfill cap system to restrict access to residual heavy metals. This paper will also discuss the design considerations and additional improvements constructed as part of the capping project, including the improved storm water drainage system, new playground, basketball court and tennis court.

[§] Corresponding Author: Michael E. Martin, Tighe & Bond, 4 Barlow Landings Rd., Unit 15, Pocasset, MA, USA 02259, (508) 564-7285, MEMartin@tighebond.com

Keywords: Massachusetts Contingency Plan (MCP), Heavy Metals, Landfill Capping, Imminent Hazard, Recreational Open Space.

1. INTRODUCTION

The site is currently developed as McGrath Park, which consists of a 22.30-acre park located at 46 Marlborough Road in Salem, Massachusetts in a residential setting. McGrath Park formerly contained two soccer fields (the upper and lower fields), a basketball court, a tennis court, a playground and an asphalt parking lot (Figure 1). Following the detection of arsenic at a concentration that could pose an Imminent Hazard (IH), the Mayor of the City of Salem took immediate actions, which included the closing of the lower field, restricting access through the installation of a fence and posting signage notifying the public of the potential IH condition. The arsenic was detected in soil samples collected as part of a feasibility study for the installation of a sanitary sewer line and construction of a public restroom at McGrath Park (Tighe & Bond, July 2011).

To eliminate the potential IH condition, remediation activities consisted of the capping of the lower field to prevent direct contact with impacted soils. As part of the remediation activities, the City of Salem decided to improve the park aesthetics by reconfiguring the lower field of McGrath Park to include an additional asphalt parking lot to the west of the lower soccer field, a stone dust walking path along the perimeter of the park, a new asphalt basketball court, two new playground areas and stormwater drainage improvements (Tighe & Bond, September 2011). Since McGrath Park hosts all of the City of Salem youth soccer games and is the most active park in the City, the work had to be conducted during the winter months, so the soccer fields would be ready for use for the Fall 2012 season.

1.1 Conceptual Site Model

Prior to being developed as McGrath Park, the site was operated as a municipal, unlined burn dump from approximately 1946 until 1963. The dump reportedly received municipal solid waste (MSW) from 1946 until the early 1960’s, when the City of Salem built an MSW incinerator on Swampscott Road. The ash from the burn dump, along with construction materials (e.g., bricks, concrete, scrap metal) was reportedly disposed in the dump until its closure in 1963. During the assessment activities conducted at the site, the waste encountered in the lower field consisted of ash with some urban fill (e.g. brick and glass comingled with sand), with the cover material ranging in 0.1 feet to 1.5 feet in thickness. Waste in the upper field generally consisted of urban fill materials (brick, glass and porcelain comingled with sand) with trace amounts of ash, with the cover material ranging in 0.25 feet to 3 feet in thickness. The cover consisted of ash, coal and urban fill material mixed with smaller amounts loam and seed. Evidence of typical unburned MSW (e.g., newspaper, aluminum cans, plastics, etc) was not observed at the site (Tighe & Bond, May 2012).

Based on site reconnaissance observations and subsurface conditions encountered during the assessment activities, the site appears to have been a natural depression that was filled with waste. Bedrock outcrops were observed along northern extent of the park, as well as along the southern portion of the upper field. Additionally, bedrock outcropping was observed to the west of McGrath Park, on the west side of Marlborough Road. Refusal was encountered in the soil borings at depths ranging from approximately 2 feet below ground surface (BGS) to 36.5 feet BGS. A layer of peat, varying in thickness, was encountered in the borings at depths ranging from 12 feet BGS to 21 feet BGS, with a glacial till layer (gray fine sands and silts, with varying amounts of gravel and medium to course sands) underlying the peat layer (Tighe & Bond, July 2011).

1.2 Nature and Extent of Site Contamination

During a feasibility study for the installation of a sanitary sewer line and construction of a public restroom at McGrath Park, the City of Salem Department of Public Works (DPW) encountered fill materials associated with the former landfill operations conducted at the site. To characterize the fill material, 21 soil samples were collected from the upper and lower fields and analyzed for the landfill acceptance parameters. Elevated concentrations of arsenic, cadmium, lead and nickel were detected above their respective Reportable Concentrations (RCS-1) and Method 1, S-1/GW-3 Standards in soil samples collected from the lower field. Additionally, arsenic was detected in one soil exceeds the IH concentration, triggering a release condition that required 2-hour notification to the Massachusetts Department of Environmental Protection (MADEP) in accordance with (MADEP, MCP, 310 CMR 40.0000 et seq., April 2006). Due to the potential exposure to children utilizing the park for youth soccer, the Mayor of the City of Salem took immediate actions, which included the closing of the lower field, restricting access through the installation of a fence and posting signage notifying the public of the potential IH condition.

To delineate the horizontal and vertical extent of contamination, 39 soil borings were advanced across the upper and lower fields. The soil samples were submitted for RCRA 8 Metals, Extractable Petroleum Hydrocarbons (EPH) with target Polycyclic Aromatic Hydrocarbons (PAHs) and/or Polychlorinated Biphenyl (PCB) analysis. Soil results indicated that the elevated metal and PAH concentrations were limited to the ash fill on the lower field portion of the site, which ranged in depth between 12 feet BGS to 21 feet BGS (Tighe & Bond, May 2012).

1.3 Regulatory Programs

Based on the nature and location of the release, this project was subject to various regulatory programs including the MCP and the Wetlands Protection Act. Below is a brief summary of how each regulatory program applied to the Site:

- Concentrations of heavy metals present in soil exceeded the applicable Reportable Concentrations (RCs), therefore the release was reportable to the State (MADEP, MCP, 310 CMR 40.0000 et seq., April 2006).
- Regulated bordering vegetated wetlands (BVW) abuts the Site to the north and south, therefore project required approval from the Salem Conservation Commission (MADEP Wetlands Protection Act. 310 CMR 10.00 et seq., October 1997).

2. MATERIALS AND METHODS

2.1 Soil Remediation Methodology

The primary objective of the remediation efforts was to restrict access to the impacted soils through the construction of a cap system and to reduce the average metal concentration in the accessible soil layer (0-3 feet in unpaved portions of the site) to below the applicable Method 1, Risk Characterization Standards. Due to the potential IH condition at the site, the remediation activities were conducted as an Immediate Response Action (IRA) in accordance with 310 CMR 40.0410.

The capping of the lower field, asphalt parking lot, and playground areas commenced on December 26, 2011. The cap construction over the lower soccer field (unpaved portions of disposal site) consisted of 6 to 12 inches of granular borrow (grading materials), a woven geotextile separation/warning barrier, 18-inch drainage layer and 6-inch seed and loam layer (4-inch seed and loam layer on side slopes). The cap construction over areas paved with asphalt consisted of 12 inches of existing processed gravel and ground up and compacted pavement, a woven geotextile separation/warning barrier, 6-inch crushed stone sub-base, and 3 inches asphalt pavement (1.75 inches of binder course and 1.25 inches of top course). Approximately 295 cubic yards (442 tons) of common fill, 1,780 cubic yards (2,671 tons) of Title V sand fill material, 3,250 cubic yards (4,879 tons) of dense gravel, 100 cubic yards (150 tons) of stone, 96 cubic yards (144 tons) of stone dust and 1,740 (2,612 tons) of loam were used in the cap system construction at the site (Tighe & Bond, September 2012).

Due to the unconsolidated nature of the fill material and the stormwater structures being installed within the asphalt parking lot area, the woven geotextile fabric and fill material were initially placed to pre-load this area to minimize future settling of the stormwater infrastructure. One of the challenges encountered during the construction of the cap system and site drainage improvements was the generation of a significant volume of impacted fill material that needed to be placed beneath the cap system, when the majority of the cap system construction had been completed. Due to the elevated lead concentrations detected at the site, the off-site disposal of soil may have been subject RCRA regulations, due to potential leachable lead concentrations in the fill material that could have resulted in significant disposal costs. The decision to construct a cap system rather than dispose of the impacted fill material off-site was based on the fact that lead was not detected in the groundwater samples collected from the 13 monitoring wells installed at the site above the applicable Method 1, Risk Characterization Standards. Therefore, to meet the City's construction schedule and reduce the overall project costs, a soil disposal area was excavated along the northeastern portion of the lower field to accommodate this material, eliminating the need for off-site disposal. The final capping activities were completed in July 2012, meeting the construction schedule (Tighe & Bond, September 2012).

To minimize fugitive dust migration to the residential abutters, an air quality monitoring program, consisting of monitoring the ambient air in the vicinity of the work area for Total Volatile Organic Compounds (TVOCs) and total dust was implemented at the site. To minimize exposure to impacted dust by construction workers during construction activities and off-site migration of fugitive dust, dust monitoring was conducted during the construction activities. An action level of 0.15 milligrams-per-cubic-meter (mg/m^3) averaged over a 24-hour period, the National Ambient Air Quality Standard (NAAQS), for soil particles was established for the site. The air quality monitoring results were used to evaluate the need to implement dust suppression to be protective to both the construction workers and abutting residence (Tighe & Bond, September 2012).

3. DATA AND ANALYSIS

3.1 Confirmatory Soil Sampling Results

To confirm that the soils used to cap the site do not contain elevated contaminant concentrations, soil characterization sampling was performed at a frequency of 1 sample per 2,000 cubic yards for material generated from a virgin borrow source and 1 sample per 500 cubic yards for material originating from a non-virgin borrow source (i.e. construction source). The soil characterization sampling included the laboratory analysis of the cap materials for PCBs, RCRA-8 Metals, SVOCs, VOCs, EPH and VPH with target analytes.

To evaluate the metals of concern (arsenic, barium, cadmium and lead) in the accessible soils (0-3 feet BGS in the unpaved portions of the site), following the capping activities, 15 composite soil samples (S-1 through S-15) were collected from 100 by 100 feet grid and submitted for arsenic, barium, cadmium and lead analyses (Tighe & Bond, September 2012).

3.1.1 Post Cap Exposure Point Concentrations

To evaluate the risk of harm to health, safety, public welfare and the environment, post capping Exposure Point Concentrations (EPCs) were calculated for the unpaved portions of the lower field. The EPCs were calculated using a weighted average of the two feet of fill material being brought to the site for capping activities and the soil samples in the lower field that are considered accessible following capping activities. Based on the average metal concentrations for the cap material, (0-3 feet unpaved) no compounds exceeded the Method 1, S-1/GW-3 Risk Characterization Standards (Tighe & Bond, September 2012).

4. SUMMARY AND CONCLUSIONS

Residual metal concentrations remain in lower field portion of the Site at concentrations that could pose a risk to human health through direct skin contact or ingestion (per MCP). However, this exposure pathway was eliminated through institutional and engineering controls, which included the construction of a cap system to restrict access to residual soil contamination and implementation of a deed restriction to maintain the cap system. Laboratory analysis of the clean fill material used in the cap system construction demonstrated that following the completion of the cap system, all the contaminants of concern had been reduced to below the Method 1, Risk Characterization Standards. Therefore, the IRA activities conducted at the site were successful in eliminating the potential IH condition, as well as achieving a condition of No Significant Risk (NSR) for the release. In addition to achieving the remediation objective, pre-remediation construction sequence planning was successful in eliminating the need for off-site disposal of impacted fill material during the installation of the new stormwater infrastructure, reducing the overall project cost while also meeting the City’s construction schedule.

Figures 1 and 2. Before and after photographs of McGrath Park. The before photograph is looking northeast at the park prior site preparation and capping activities. The after photograph is looking southwest towards the where the before photograph was captured

5. REFERENCES

MADEP (Massachusetts Department of Environmental Protection). 2006. MCP (Massachusetts Contingency Plan). 310 CMR 40.0000 et seq., April 2006

MADEP (Massachusetts Department of Environmental Protection). 1997. Wetlands Protection Act. 310 CMR 10.00 et seq., October 1997

Tighe & Bond. 2011. Immediate Response Action Plan and Release Notification Form Submittal, McGrath Park, Salem, Massachusetts, July 2011

Tighe & Bond. 2011. Modified Immediate Response Action Plan and Status Report, McGrath Park, Salem, Massachusetts, September 2011

Tighe & Bond. 2012. Phase I Initial Site Investigation and Tier II Classification Report, McGrath Park, Salem, Massachusetts, June 2012

Tighe & Bond. 2012. Immediate Response Action Completion Statement, McGrath Park, Salem, Massachusetts, September 2012

Chapter 4

INFLUENCE OF SOIL AGING ON THE DERMAL PENETRATION OF ARSENIC AND CHROMIUM

Rita M. Turkall[1,2,§], Mohamed S. Abdel-Rahman[1]

[1]University of Medicine and Dentistry of New Jersey, Pharmacology and Physiology Department, New Jersey Medical School and [2]Clinical Laboratory Sciences Department, School of Health Related Professions, Newark, NJ

ABSTRACT

The potential health risk from exposure to metal contaminated soil is often based on the quantity of metal that can be removed from soil by vigorous extraction procedures. This approach can overestimate risk since it ignores complex interactions between metals and soil that can result in a reduction in the amount of metal that desorbs from soil and is subsequently absorbed by the body (bioavailability). The aim of this research was to determine the relative contribution of soil matrix and metal sequestration in soil with time ("aging") on the dermal penetration of pentavalent arsenic [As(V)], trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] as arsenic acid, chromium chloride and sodium chromate, respectively. *In vitro* flow-through diffusion cell studies were performed using dermatomed male pig skin and radioactive compounds to measure total penetration (sum of each metal in receptor fluid and skin). Immediate contact with the higher organic content soil reduced dermal penetration for Cr(III), As(V) and Cr(VI) by 88%, 78% and 60%, respectively. On the other hand, immediate contact with the higher clay content soil produced greater reductions in dermal penetration versus pure metal: Cr(III) and Cr(VI) (92%) and As(V) (87%). Aging in either soil further reduced dermal penetration for all metals by 93-97%. This study provided evidence that the bioavailability from dermal exposure to the metals examined can be significantly reduced by the soil matrix and aging in soil.

Keywords**:** arsenic, chromium, soil aging, dermal penetration

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[§] Corresponding Author: Rita M. Turkall, University of Medicine and Dentistry of New Jersey, Pharmacology and Physiology Department, New Jersey Medical School and Clinical Laboratory Sciences Department, School of Health Related Professions, Newark, NJ, (407)568-5122, turkalrm@umdnj.edu

1. INTRODUCTION

The potential health risk from exposure to chemically contaminated soil is related to the amount of chemical that desorbs from soil and that is subsequently absorbed by the body, i.e. bioavailability. Soil properties such as organic carbon content, clay content, particle size, and pH affect chemical sorption and desorption processes, and thus may have significant impacts on the bioavailability of chemicals from soils (NEPI, 2000a; Pu *et al.*, 2004). Another major determinant of bioavailability is chemical aging in soil (Alexander, 2000). Chemical aging in soil is the movement of chemicals from the surface of soil particles into less accessible sites with time (Linz and Nakles, 1997; Reid *et al.*, 2000). The mechanisms for chemical aging are not fully understood, however, it has been proposed that hydrophobic chemicals can partition into the solid phase of soil organic matter, as well as become entrapped within soil nanopores where they may be retained and become less accessible (Steinberg *et al.*, 1987; Brusseau *et al.*, 1991; Pignatello and Xing, 1996).

Most of the emphasis on chemical aging has been on organic chemicals in soil (Steinberg *et al.*, 1987; Scribner *et al.*, 1992; Hatzinger and Alexander, 1995; Kelsey *et al.*, 1997; Roy and Singh, 2001; Abdel-Rahman *et al.*, 2006). However, metals also age in soil (Lock and Janssen, 2003; Turpeinen *et al.*, 2003). The interaction of metals with soil is more complex than organic chemicals with soil. Metals may be associated with many components of soil in various ways (ion exchange, adsorption, precipitation, and complexation) or be present in the structure of minerals (Balasoiu *et al.*, 2001). The mechanism for the aging of metals in soil may be different than for organic compounds (Alexander, 2000). Proposed mechanisms include penetration into the mineral lattice of soil and diffusion through intraparticle pores (Yin *et al.*, 1997). Intraparticle diffusion may lead to the sequestration of metals within microporous solids, such as hydrous iron, aluminum, and manganese oxides, and some types of organic matter (Axe and Trivedi, 2002).

Compared to other routes of exposure to soil contaminants (oral, inhalation), the dermal route may not always be the most important route, but it can contribute significantly to total exposure. Because human skin comprises more than 10% of total body mass and 1.8 m^2 of body surface (Roberts and Walters, 1998; USEPA, 2001), it has the potential to absorb significant quantities of chemicals into the body during daily activities as well as occupational exposures. A chemical that cannot penetrate skin may be limited to local toxic effects on the skin, but if it readily penetrates skin and enters the circulation, it may have systemic effects. Therefore, it is necessary to know the capacity of a chemical for dermal absorption in order to assess its overall potential risk (Mattie *et al.*, 1994).

The studies reported in this paper were conducted to assess the dermal bioavailability of representative metal contaminants (pentavalent arsenic, trivalent chromium and hexavalent chromium, as arsenic acid, chromium chloride, and sodium chromate, respectively) in soil. These metals occur naturally in soil and are released into the environment due to erosion and/or weathering processes. However, additional and sometimes substantially higher amounts are also contributed to soil from human activities including mining, smelting, chemical production and use, and waste disposal (ATSDR, 2000, Palmer and Wittbrodt, 1991).

In soil, arsenic can occur as arsenates (AsO_4^{-3}) or arsenites (AsO_2^-), with trivalent arsenites being more toxic than the pentavalent arsenates. At high redox potential and acidic pH, the arsenate species predominates in soil. However, at low redox potential and alkaline pH, the arsenite species is more significant (Masscheleyn *et al.*, 1991; Peters *et al.*, 1996; Balasoiu *et al.*, 2001).

Regardless of the route of exposure to arsenic, the skin is a critical organ of arsenic toxicity because of local absorption and binding of sulfhydryl-group-containing proteins (Hostynek et al, 1993). Direct dermal contact with inorganic arsenicals may cause skin irritation and contact dermatitis. Usually the effects are erythema and swelling which may progress to papules, vesicles, or necrotic lesions in extreme cases (Holmqvist, 1951; ATSDR, 2000). Several types of carcinomas, namely basal cell carcinoma, squamous cell carcinoma and Bowen's disease (epidermal squamous cell carcinoma) are caused by arsenic (Magos, 1991).

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

Sensitive individuals can develop allergic contact dermatitis (ACD) from exposure to chromium. Symptoms include erythema, edema, and small vesicles (Ackerman, 1978; Adams, 1990). Because Cr (VI) compounds generally penetrate skin faster than Cr (III) compounds, they are more likely to produce a skin response in sensitized subjects (Samitz *et al.*, 1967). However, Cr (III) is considered to be the actual cause of allergic contact sensitization since only Cr (III) is capable of forming covalent bonds with skin proteins, which is a precondition for immunogenicity (Mali *et al.*, 1966; Polak *et al.*, 1973; Hansen *et al.*, 2003). Moreover, after Cr (VI) diffuses into the skin, that has limited capacity to reduce it to Cr (III) via complexation with proteins to produce the immunogenic antigen (Samitz and Katz, 1964; Samitz *et al.*, 1967, 1969; Polak *et al.*, 1973).

Further, the relative contribution of the soil matrix and chemical aging in soil on the dermal bioavailability of the representative chemicals were determined to better evaluate the impact of the results on health risk. Bioavailability was assessed by measuring dermal penetration. Specifically, the dermal penetration of each of the chemicals aged in soil was compared to the respective pure chemicals (without soil) and to the chemicals added freshly to soil, and the effects of soil composition (percent sand, clay, organic matter) on dermal penetration were examined.

2. MATERIALS AND METHODS

2.1 Chemicals

Arsenic in the form of arsenic acid (H_3AsO_4) (Sigma/Aldrich Chemical Co., St. Louis, MO) was used as a carrier and labeled with arsenic-73 (Los Alamos National Laboratory, Los Alamos, NM). Chromium-51 as chromium chloride ($CrCl_3$)(588.9 mCi/mg specific activity, 99.9% purity) or as sodium chromate (Na_2CrO_4)(477.6 mCi/mg specific activity, 99.9% purity) was purchased from New England Nuclear (NEN) Life Science Products, Boston, MA.

2.2 Soils

Studies were 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, and 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.

2.3 Chemical Aging in Soil

Individual chemicals were added to each of the soils that were previously autoclaved and hydrated to 11% (w/w) with sterile distilled-deionized water. This is the maximum amount of water that could be used to lightly moisten the soils without there being an excess of water when each chemical was added to the soils. Arsenic acid and each of the chromium compounds were added to soil at a ratio of 83 and 0.3 μg/g soil, respectively. After each chemical was mixed thoroughly with the soils to ensure uniform distribution of chemical, treated soils were added to Teflon-sealed vials and aged in the dark at room temperature for three (As) or four (Cr) months.

2.4 Animal Model

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

2.5 *In Vitro* Dermal Penetration Studies

Excised skin was cut to a thickness of 200 μm with a dermatome (Padgett Electro-Dermatome Model B, Padgett Instruments Inc., Kansas City, MO) and circular pieces were mounted into Teflon flow-through diffusion cells (Crown Bio Scientific, Inc., Somerville, NJ). The exposed skin surface area (0.64 cm^2) was maintained at a temperature of 32°C. The dermal side of each skin sample was perfused with HHBSS containing 10% fetal bovine serum (Sigma/Aldrich) at a flow rate of 3 ml/h and aerated continuously with oxygen (Collier *et al.*, 1989). Each chemical was applied separately to the stratum corneum surface of the skin either alone in 5 μl of vehicle (ethanol for As; sodium phosphate butter, pH 6.8 for Cr), immediately after the addition of 30 mg of soil, or after aging in 30 mg of each of the two soils. The chemical doses/cm^2 of skin surface area were arsenic acid (3.9 μg), chromium chloride (15.5 ng), and sodium chromate (15.5 ng), while the elemental doses/cm^2 of skin surface were arsenic (2 υg) and chromium (5 ng). Immediately after the skin was treated, diffusion cells were capped.

Receptor fluid (perfusate) was collected in scintillation vials containing 10 ml of Formula-989 liquid scintillation cocktail (Packard Instruments Co., Inc., Meriden, CT) up to 16 h postdosing. After 16 h of exposure to the chemical alone or in soil, the loosely adsorbed chemical was washed from the surface of the skin with soap and water (once with 1 ml of a 1% aqueous soap solution and twice with 1 ml of distilled-deionized water). Skin samples were completely solubilized in Solvable (Packard) for 8 h at 50^{o}C to determine the amount of radioactivity remaining in the skin. Radioactivity in all samples was counted by liquid scintillation spectrometry (LS 7500, Beckman Instruments, Inc., Fullerton, CA). Sample quench was corrected by using the H-ratio method.

2.6 Statistical Analysis

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

3. DATA AND ANALYSIS

Dermal penetration of the chemicals is reported in Tables 1 and 2 as total penetrations. Total penetration represents the sum of chemical penetrating into receptor fluid and the amount in skin that potentially can penetrate into receptor fluid with time (Chu *et al.*, 1996). Percent total penetration equals: (the amount of the initial dose that penetrated skin divided by the amount of the initial dose applied to skin) X 100. Immediate contact with either soil significantly decreased the total penetration of each chemical versus treatment with the pure chemical; Keyport was more effective than Atsion soil (92, 92, and 87% decrease versus 60, 88 and 78% decrease, respectively for Cr(VI), Cr(III) and As(V)). Aging in either soil further reduced the total penetration of each chemical compared to the chemical immediately added to soil and by 93-97% compared to pure chemical.

Table 1. Effects of Time in Atsion Soil on the Dermal Penetration of Metal Compounds

Metal Compound	Pure	Immediate	Aged
Arsenic (V)	44.6 ± 2.8 [a]	10.0 ± 2.0 [b]	1.5 ± 0.3 [b]
Chromium (III)	35.6 ± 2.4	14.1 ± 2.4 [b]	2.4 ± 0.2 [b,c]
Chromium (VI)	33.5 ± 2.2	4.1 ± 0.6 [b]	1.3 ± 0.2 [b]

[a] Percent total penetration (mean ± SEM) = (amount of dose that penetrated skin divided by amount of dose applied to skin) X 100. For each chemical, n = 8-11 replicates per treatment from three pigs.

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

[c] Significantly different from chemical immediately added to Atsion soil ($p < 0.05$, ANOVA)

Table 2. Effects of Time in Keyport Soil on the Dermal Penetration of Metal Compounds

Metal Compound	Pure	Immediate	Aged
Arsenic (V)	44.6 ± 2.8 [a]	6.0 ± 0.8 [b]	1.8 ± 0.1 [b,c]
Chromium (III)	35.6 ± 2.4	3.0 ± 0.3 [b]	1.8 ± 0.2 [b]
Chromium (VI)	33.5 ± 2.2	2.8 ± 0.6 [b]	1.2 ± 0.1 [b]

[a] Percent total penetration (mean ± SEM) = (amount of dose that penetrated skin divided by amount of dose applied to skin) X 100. For each chemical, n = 8-14 replicates per treatment from three pigs.

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

[c] Significantly different from chemical in freshly spiked Keyport soil ($p < 0.05$, ANOVA)

Individual data for receptor fluid and skin are not presented in Tables 1 and 2. However, penetration into receptor fluid represents only a small component of total penetration ($\leq$ 0.4% As(V), $\leq$ 2% Cr(III), $\leq$ 0.8% Cr(VI)) for all treatments. On the other hand, the percentage of metal dose bound to skin predominated for all treatments. The percentages of metal bound to skin were highest for treatments with pure chemicals as follows: 44.2% As(V); 33.6% Cr(III); and 32.7% Cr(VI). Immediate and aged soil treatments reduced the skin binding component of total penetration as to the following: 0.6-9.8% As(V); 1.2-12.8% Cr(III); and 0.8-3.3% Cr(VI). The remainder of the initial dose that did not penetrate skin was found in the skin wash for all treatments (data not shown). A range of 60-67% of the initial dose was detected in the skin wash for the pure chemical treatments. In the presence of soils, chemical in the skin wash increased to 83–98% of the initial dose.

Total penetration ratios calculated for the time that the chemicals were in soil demonstrated that the penetration ratios between immediate and pure treatments were lower for Keyport than for Atsion soil (Table 3). The difference was greatest for Cr(III) (5-fold), followed by As(V) (1.7-fold), and Cr(VI) (1.5-fold).

There were no differences between the soils for penetration ratios between aged and pure treatments for any of the chemicals.

Table 3. Dermal Bioavailability Ratios of Metal Compounds Added Immediately to or Aged in Soil Versus Pure Compound

Metal Compound	Atsion Soil		Keyport Soil	
	Immediate/Pure	Aged/Pure	Immediate/Pure	Aged/Pure
Arsenic (V)	0.22 [a]	0.03	0.13	0.04
Chromium (III)	0.40	0.07	0.08	0.06
Chromium (VI)	0.12	0.04	0.08	0.04

[a] Ratio of percent of initial dose (mean) for total penetration.

This study demonstrated that the presence of soil reduced the dermal penetration of all three metal compounds studied versus penetration in the absence of soil. The time of metal-soil contact was a factor, since each metal aged in soil produced a smaller penetration than that which occurred for metal immediately added to soil. Further, Keyport versus Atsion soil produced a greater reduction in dermal penetration for metal immediately added to soil and both forms of Cr were more affected than As.

Arsenic sorption to soil is strongly related to iron, manganese, and aluminum oxides, clay content, and organic matter content (Galba and Polacek, 1973; Thanabalasingam and Pickering, 1986; Yan-Chu, 1994; Balasoiu *et al.*, 2001). Soils with higher clay content have been shown to retain more arsenic than soils with lower clay content (Woolson and Kearney, 1973; Elkhatib *et al.*, 1984). This is consistent with results of the current study where nearly a 2-fold larger reduction in total penetration occurred with immediate addition to Keyport than Atsion soil with Keyport soil having an 11-fold higher clay content than Atsion soil. Further, the additional reduction in penetration that occurred with aging in either soil suggests that adsorption to soil surface sites predominated after immediate contact followed by a slower sorption to remote sites with aging.

Similarly, the total penetration of Cr(III) immediately added to Keyport soil was reduced to a greater extent than with Atsion soil. Furthermore, the reduction in dermal penetration achieved with Atsion soil only reached that of Keyport soil after aging. The data suggest that in Atsion soil, Cr(III) initially adsorbed to the surface of soil particles following immediate application, then slowly continued to diffuse into the soil becoming less bioavailable with aging. It has been suggested that slower adsorption and decreased resistance to desorption of some metals may be due to diffusion through intraparticle micropores of soil organic matter (Yin et al, 1997; Strawn and Sparks, 2000). This is consistent with the 2.75-fold higher organic content of Atsion than Keyport soil. On the other hand, rapid adsorption of Cr(III) to Keyport soil during the 16 hours after immediate addition of the chemical to soil is suggested by similar dermal penetration results for immediate and aging treatments. Several investigators have demonstrated that Cr(III) is strongly and rapidly adsorbed to soil by iron and manganese oxides, clay minerals and sand (Schroeder and Lee, 1975 Bartlett and Kimble, 1976a; Korte *et al.*, 1976; Griffin *et al.*, 1977; Rai *et al.*, 1984; Dreiss, 1986; Stanin, 2005). Therefore, while an aging effect was predominant for Cr(III) in the Atsion soil, surface adsorption was important for the Keyport soil.

On the other hand, there was no difference in total dermal penetration for Cr(VI) between the two soils either following immediate addition to soil or with aging in soil. At low Cr(VI) concentrations, like those used in this study, adsorption to soil increases as pH decreases no matter what the sorbent (Griffen *et al.*, 1977; Bartlett and Kimble, 1979; Rai *et al.*, 1984; Stanin, 2005). Thus, with the acidic pH of both soils in this study (4.2 for Atsion and 5.0 for Keyport soils), similar adsorption of Cr(VI) to the soils would be expected and account for the lack of difference in total penetration. Further, Cr(VI) can be reduced to Cr(III) in acidic soils (Bartlett and Kimble, 1976b; Palmer and Puls, 1994; Jardine *et al.*, 1999, Kotas and Stasicka, 2000), with reduction nearly complete after 200 days for soils in the pH range 4-7 (Stewart *et al.*, 2003). In this study, Cr(VI) may not have been completely reduced to Cr(III) during the 120 aging period.

The soil load (47 mg/cm^2) that was used in these studies was based on soil adherence values reported in the literature (10^{-3} to 10^2 mg/cm^2), which depended on soil properties, occupational and recreational activities, and different parts of the body (Kissel *et al.*, 1996, 1998; Holmes *et al.*, 1999). However, Yang *et al.* (l989), Duff and Kissel (l996), and Roy and Singh (2001) showed that only chemical in the monolayer of soil that is in direct contact with the skin surface is likely to be absorbed by skin. Monolayers of 3-9 mg/cm^2 were reported by those investigators, and their studies showed that increasing the soil load decreased the percent of the applied dose of chemical absorbed. However, the soil loading that will achieve a monolayer is dependent on the particle size distribution of the soil being tested (Driver *et al.*, 1989; NEPI, 2000b). For example, a soil load of 40 mg/cm^2 was used in Wester *et al.*'s (1993) studies on sodium arsenate in soil. The study showed a total penetration of 0.8% from soil on human cadaver skin and a dermal bioavailability of 3.2-4.5% in monkeys. Because the soil particle sizes were very large (180-300 μm) in their studies, the soil loading was only slightly higher than a monolayer (Duff and Kissel, 1996). Particles less than 150 μm in diameter have been shown to have greater adherence to skin than larger size fractions (Driver *et al.*, 1989; NEPI, 2000b). For the two soils used in the studies reported here, only 17-22% of the soil particles have an arithmetic mean particle size diameter less than 150 μm. This suggests that monolayer coverage was slightly exceeded, and with a lower soil load, the dermal penetration of the studied chemicals may be a little higher.

Another factor that must be considered in addition to the soil load is the amount of chemical applied per unit area of skin. Although there were no significant differences in the percutaneous absorption of arsenic between a trace dose of arsenic in soil (4 X 10^{-5} µg/cm^2) and a higher dose (0.6 µg/cm^2) in Wester *et al.*'s (1993) study in monkeys, the penetration rate of pure mercuric chloride through human skin *in vitro* was shown by Wahlberg (1965) to be concentration dependent.

4. CONCLUSIONS

Health risk assessments are often based on exposure to the total concentration of a chemical in a contaminated site. The total concentration is usually determined by rigorous extraction procedures such as acid digestion, sonication, or Soxhlet extraction to remove the chemicals from soil (USEPA, 1986, 1992; Tang *et al.*, 1999). This approach can result in an overestimation of risk because when humans are exposed to contaminated soil, only a fraction of the total concentration (the bioavailable fraction) may be absorbed into the systemic circulation. The data presented in this paper highlight the need to incorporate bioavailability data into the health risk assessment of exposure to contaminated soils. The overall conclusion from this study is that soil decreased the dermal bioavailability of the metal compounds examined. Moreover, differences in soil composition and residence time in soil produced significant quantitative differences in bioavailability.

5. REFERENCES

Abdel-Rahman, M.S., Skowronski, G.A., and Turkall, R.M. 2006. Impact of aging time on the dermal penetration of phenol in soil. Soil and Sediment Contam. 15, 47-60.

Ackerman, A.B. 1978. Histologic Diagnosis of Inflammatory Skin Disease, pp.223-226, Philadelphia, PA, Lea and Febigger.

Adams, R.M. 1990. Allergic contact dermatitis. In: Occupational Skin Disease, 2nd edition, pp. 26-31(Adams, R.M., Ed.) Philadelphia, PA, W.B. Saunders.

Alexander, M. 2000. Aging, bioavailability, and overestimation of risk from environmental pollutants. Environ. Sci.Technol. 34, 4259-4265 .

ATSDR (Agency for Toxic Substances and Disease Registry). 2000. Toxicological Profile for Arsenic, pp. 15-132, 172, 243-299. U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA.

Axe, L. and Trivedi, P. 2002. Intraparticle surface diffusion of metal contaminants and their attenuation in microporous amorphous Al, Fe, and Mn oxides. J. Colloid Interface Sci. 247, 259-265.

Balasoiu, C.F., Zagury, G.J., and Deschênes, L. 2001. Partitioning and speciation of chromium, copper, and arsenic in CCA-contaminated soils: Influence of soil composition. Sci. Total Environ. 280, 239-255.

Bartek, M.J., LaBudde, J.A., and Maibach, H.I. 1972. Skin permeability in vivo: Comparison in rat, rabbit, pig, and man. J. Invest. Dermatol. 58, 114-123.

Bartlett, R.J. and Kimble, J.M. 1976a. Behavior of chromium in soils. I. Trivalent forms. J. Environ. Qual. 5, 379-383.

Bartlett, R.J. and Kimble, J.M. 1976b. Behavior of chromium in soils. II. Hexavalent forms. J. Environ. Qual. 5, 383-386..

Bartlett, R.J. and Kimble, J.M. 1979. Behavior of chromium in soils. III. Oxidation. J. Environ. Qual. 8, 31-35.

Bronaugh, R.L. and Stewart, R.F. 1985. Methods for *in vitro* percutaneous absorption studies. IV. The flow-through diffusion cell. J. Pharm. Sci. 74, 64-67.

Brusseau, M.L., Jessup, R.E., and Rao, P.S.C. 1991. Nonequilibrium sorption of organic chemicals: elucidation of rate-limiting processes. Environ. Sci. Technol. 25, 134-142.

Chu, I., Dick, D., Bronaugh, R. *et al.* 1996. Skin reservoir formation and bioavailability of dermally administered chemicals in hairless guinea pigs. Food Chem. Toxicol. 34, 267-276.

Collier, S.W., Sheikh, N.M., Sakr, A. *et al.* 1989. Maintenance of skin viability during *in vitro* percutaneous absorption/metabolism studies. Toxicol. Appl. Pharmacol. 99, 522-533.

Dreiss, J. 1986. Chromium migration through sludge treated soils. Ground Water 24, 312-321.

Driver, J.H., Konz, J.J., and Whitmyre, G.K. 1989. Soil adherence to human skin. Bull. Environ. Contam. Toxicol. 43, 814-820.

Duff, R.M. and Kissel, J.C. 1996. Effect of soil loading on dermal absorption efficiency from contaminated soils. J. Toxicol. Environ. Health. 48, 93-106.

Elkhatib, E.A., Bennet, O.L., and Wright, R.J. 1984. Arsenite sorption and desorption in soils. Soil Sci. Soc. Am. J. 48, 1025-1029.

Galba, J. and Polacek, S. 1973. Sorption of arsenates under kinetic conditions in selected soil types. Acta Fytotech. 28, 187-197.

Griffin, R.A., Au, H.K., and Frost, R.R. 1977. Effect of pH on adsorption of chromium from landfill leachate by clay minerals. J. Envir. Sci. Health Ser. A 12, 431-449.

Hansen, M.B., Johansen, J.D., and Menne, T. 2003. Chromium allergy: significance of both Cr(III) and Cr(VI). Contact Dermatitis, 49, 206-212.

Hatzinger, P.B. and Alexander, M. 1995. Effect of aging of chemicals in soil on their biodegradability and extractability. Environ. Sci. Technol. 29, 537-545.

Holmes, K.K., Jr., Shirai, J.H., Richter, K.Y. *et al.* 1999. Field measurement of dermal soil loadings in occupational and recreational activities. Environ. Res. A 80, 148-157.

Holmqvist, I. 1951. Occupational contact dermatitis: A study among employees at a copper ore smelting work including investigations of skin reactions to contact with arsenic compounds. Acta Derm. Venerol. 31 (Suppl. 26), 26-29, 44-45, 110-112, 195-204.

Hostynek, J.J., Hinz, R.S., Lorence, C.R. *et al.* 1993. Metals and the skin. Crit. Rev. Toxicol. 23, 171-235.

Jardine, P.M., Fendorf, S.E., Mayes, M.A. *et al.* 1999. Fate and transport of hexavalent chromium in undisturbed heterogenous soil. Environ. Sci. Technol. 33, 2939-2944.

Kelsey, J.W., Kottler, B.D., and Alexander, M. 1997. Selective chemical extractants to predict bioavailability of soil-aged organic chemicals. Environ. Sci. Technol. 31, 214-217.

Kissel, J.C., Richter, K.Y., and Fenske, R.A. 1996. Field measurement of soil load attributable to various activities. Implications for exposure assessment. Risk Anal. 16, 115-125.

Kissel, J.C., Shirai, J.H., Richter, K.Y. *et al.* 1998. Investigation of dermal contact with soil in controlled trials. J. Soil Contam. 7, 737-752.

Korte, N.E., Skopp, J., Fuller, W.H., *et al.* 1976, Trace element movement in soils: influence of soil physical and chemical properties. Soil Sci. 122, 350-359.

Kotas, J. and Stasicka, Z. 2000. Chromium occurrence in the environment and methods of its speciation. Environ. Pollut. 107, 263-283.

Linz, D.G. and Nakles, D.V. 1997. Executive Summary. In: Environmentally Acceptable Endpoints in Soil, pp. 22-40. (Linz, D.G. and Nakles, D.V., Eds.). Annapolis, MD, American Academy of Environmental Engineers.

Lock, K. and Janssen, C.R. 2003. Influence of aging on metal availability in soils. Rev. Environ. Contam. Toxicol. 178, 1-21.

Losi, M.E., Amrhein, C., and Frankenberger, W.T., Jr. 1994. Environmental biochemistry of chromium. Rev. Environ, Contam. Toxicol. 136, 91-121.

Magos, L. 1991. Epidemiological and experimental aspects of metal carcinogenesis: physiochemical properties, kinetics, and the active species. Environ. Health Perspectives 95, 157-189.

Mali, W.H., Malten, K., and van Neer, F..C.J. 1966. Allergy to chromium. Arch. Dermatol. 93, 41-44.

Masscheleyn, P.H., Delaune, R.D., and Patrick, W.H., Jr. 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environ. Sci. Technol. 25, 1414-1419.

Mattie, D.R., Grabau, J.H., and McDougal, J.N. 1994. Significance of the dermal route of exposure to risk assessment. Risk Anal. 14, 277-284.

Monteiro-Riviere, N. and Stromberg, M. 1985. Ultrastructure of the integument of the domestic pig (Sus scrofa) from one through fourteen weeks of age. Anat. Histol. Embryol. 14, 97-115.

NEPI (National Environmental Policy Institute). 2000a. Assessing the Bioavailability of Organic Chemicals in Soil for Use in Human Health Risk Assessments. Washington, DC.

NEPI (National Environmental Policy Institute). 2000b. Assessing the Bioavailability of Metals in Soil for Use in Human Health Risk Assessments. Washington, DC.

Palmer, C.D. and Puls, R.W. 1994. Natural attenuation of hexavalent chromium in groundwater and soils. Ground Water, EPA/540/S-94/505.

Palmer, C.D. and Wittbrodt, P.R. 1991. Processes affecting the remediation of chromium-contaminated sites. Environ. Health Perspect. 92, 25-40.

Peters, G.R., McCurdy, R.F., and Hindmarsh, J.T. 1996. Environmental aspects of arsenic toxicity. Crit. Rev. Clin. Lab. Sci. 33, 457-493.

Pignatello, J.J. and Xing, B. 1996. Mechanisms of slow sorption of organic chemicals to natural particles. Environ. Sci. Technol. 30, 1-10.

Polak, L., Turk, J.L., and Frey, J.R. 1973. Studies on contact hypersensitivity to chromium compounds. Prog. Allergy, 17, 145-226.

Pu, X., Lee, L.S., Galinsky, R.E. *et al.* 2004. Evaluation of a rat model versus a physiologically based extraction test for assessing phenanthrene bioavailability from soils. Toxicol. Sci. 79, 10-17.

Qiao, G. and Riviere, J.E. 2000. Dermal absorption and tissue distribution of 3,3',4,4'-tetrachlorobiphenyl (TCB) in an ex-vivo pig model: assessing the impact of dermal exposure variables. Int. J. Occup. Environ. Health, 6, 127-137.

Rai, D., Zachara, J.M., Schwab, A.P., *et al.* 1984. Chemical attenuation rates, coefficients and constants in leachate migration. Volume I, A Critical Review, Final Report Electric Power Research Institute (EPRI) EA3356, Palo Alto, Ca, EPRI.

Reid, B.J., Jones, K.C., and Semple, K.T. 2000. Bioavailability of persistent organic pollutants in soils and sediments – a perspective on mechanisms, consequences, and assessment. Environ. Pollut. 108, 103-112.

Reifenrath, W. and Hawkins, G. 1986. The weanling Yorkshire pig as an animal model for measuring percutaneous penetration. In: Swine in Biomedical Research, pp. 673-680. (Tumbelson, M.E., Ed.). New York, Plenum.

Roberts, M.S. and Walters, K.A. 1998. The relationship between structure and barrier function of skin. In: Dermal Absorption and Toxicity Assessment, pp. 1-42. (Roberts, M.S. and Walters, K.A., Eds.). New York, Marcel Dekker.

Roy, T.A. and Singh, R. 2001. Effect of soil loading and soil sequestration on dermal bioavailability of polynuclear aromatic hydrocarbons. Bull. Environ. Contam. Toxicol. 67, 324-331.

Samitz, M.H. and Katz, S.a. 1964. A study of the chemical reaction between chromium and skin. J. Invest. Dermatol., 43, 35-43.

Samitz, M.H., Katz, S.A., Scheiner, D.M. *et al.* 1969. Chromium-protein interactions. Acta Derm-Venereol. 49, 142-146.

Samitz, M.H., Katz, S., and Shrager, J.D. 1967. Studies of the diffusion of chromium compounds through skin. J. Invest. Dermatol. 48, 514-520.

Schroeder, D.C. and Lee, G.F. 1975. Potential transformation of chromium in natural waters. Water Air Soil Pollut. 4, 355-365

Scribner, S.L., Benzing, T.R., Sun, S. *et al.* 1992. Desorption and bioavailability of aged simazine residues in soil from a continuous corn field. J. Environ. Qual. 21, 115-120.

Stanin, F.T. 2005. Transport and fate of chromium (IV) in the environment. In: Chromium (IV) Handbook. pp 165-214. (Guertin, J., Jacobs, J.A., and Avakian, C.P., Eds.) Boca Raton, FL, CRC Press.

Steinberg, S.M., Pignatello, J.J., and Sawhney, B.L. 1987. Persistence of 1,2-dibromoethane in soils: Entrapment in intraparticle micropores. Environ. Sci. Technnol. 21, 1201-1208.

Stewart, M.A., Jardine, P.lM., Brandt, C.C. *et al.* 2003. Effects of contaminant concentration, aging, and soil properties on the bioaccessibility of Cr (III) and Cr (VI) in soil. Soil Sediment Contam. 12, 1-21.

Strawn, D.G. and Sparks, D.L. 2000. Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil. Soil Sci. Soc. Am. J. 64, 144-156.

Tang, J., Robertson, B.K., and Alexander, M. 1999. Chemical-extraction methods to estimate bioavailability of DDT, DDE, and DDD in soil. Environ. Sch. Technol. 33, 4346-4351.

Thanabalasingam, P. and Pickering, W.F. 1986. Arsenic sorption by humic acids. Environ. Pollut. 12, 233-246.

Turpeinen, R., Virta, M., and Häggblom, M.M. 2003. Analysis of arsenic bioavailability in contaminated soils. Environ. Toxicol. Chem. 22, 1-6.

USDA (U.S. Department of Agriculture). 1972. National Cooperative Soil Survey: Official Series Description, Keyport Series, Soil Conservation Service, Washington, DC.

USDA (U.S. Department of Agriculture). 1977. National Cooperative Soil Survey: Official Series Description, Atsion Series, Soil Conversation Service, Washington, DC.

USEPA (United States Environmental Protection Agency). 1986. Test Methods for Evaluating Solid Wastes. Office of Solid Wastes, Washington, DC. SW-846.

USEPA (United States Environmental Protection Agency). 2001. Risk Assessment Guidance for Superfund (RAGS), Volume 1: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment), Interim Guidance. Office of Emergency and Remedial Response, Washington DC, EPA/540/R- 99/005.

Wahlberg, J.E. 1965. Percutaneous absorption of sodium chromate (^{51}Cr), cobaltous (^{58}Co), and mercuric (^{203}Hg) chlorides through excised human and guinea pig skin. Acta Dermato-Venereol. 45, 415-426.

Walkley, A. and Black, I.A. 1934. An examination of Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 37, 29-37.

Wester, R.C., Maibach, H.I., Sedik, L. *et al.* 1993. In vivo and *in vitro* percutaneous absorption and skin decontamination of arsenic from water and soil. Fund. Appl. Toxicol. 20, 336-340.

Woolson, E.A. and Kearney, P.C. 1973. Persistence and reactions of ^{14}C-cacodylic acid in soils. Environ. Sci. Technol. 7, 47-50.

Yan-Chu, H. 1994. Arsenic distribution in soils. Adv. Environ. Sci. Technol.: Arsenic in the Environ. 26, 17-49.

Yang, J.J., Roy, T.A., Krueger, A.J. *et al.* 1989. *In vitro* and *in vivo* percutaneous absorption of benzo(a)pyrene from petroleum crude-fortified soil in the rat. Bull. Environ. Contam. Toxicol. 43, 207-214.

Yin, Y., Allen, H.E., Huang, C.P. *et al.* 1997. Kinetics of mercury (II) adsorption and desorption in soil. Environ. Sci. Technol. 31, 496-503

PART II: Manufactured Gas Plants

Chapter 5

ACCELERATED ATTENUATION OF MGP CONTAMINANTS IN GROUNDWATER USING SOURCE CONTROL, OZONE, AND OXYGEN “CURTAIN WALLS”

Matthew Levinson[1§], Matthew O’Neil[2]
[1]One Greenwood Ave, Suite 210, Montclair, NJ 07042, [2]220 West Exchange Street, Suite 107, Providence, RI 02903

ABSTRACT

Source control, ozone injection, and multiple oxygen “curtain walls” are being used to treat DNAPL coal tar and stimulate and sustain an aerobic environment to bioremediate a groundwater plume containing BTEX and PAH contaminants at a former MGP site in New York. The source area contains free-phase DNAPL coal tar and the dissolved-phased portion of the plume migrates beneath a mixed commercial and residential community for approximately ¾ of a mile (1.2 kilometers) to its discharge point in a tidal bay. Site investigations and subsequent groundwater sampling events have bounded the width of the plume to an approximate 500 foot (152.4 meters) path. The bottom depth of the plume varies between 30 and 70 feet (9.1 and 21.3 meters) below the ground surface (bgs), and the water table fluctuates between 3 and 7 feet (0.9 and 2.1 meters) bgs.

A 70 foot (21.3 meter) deep perforated barrier wall was installed to contain and control source material while being treated with ozone; and multiple oxygen injection “curtain walls” were installed downgradient to stimulate and sustain an aerobic environment to bioremediate the dissolved-phase groundwater plume. This paper will discuss the critical importance of controlling a DNAPL source and the efficacy of promoting an attenuating environment to achieve remediation goals; the design methods and specifications of the barrier wall, ozone injection system, and the oxygen injection “curtain walls,” and how they complement each other. The results from the monitoring program have indicated that this remedial

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[§] Corresponding Author: Matthew Levinson, PE, One Greenwood Ave, Suite 210, Montclair, NJ 07042, Email: MLevinson@geiconsultants.com strategy has significantly reduced the extent and reach of the groundwater plume, and decreased the BTEX and PAH concentrations by approximately 60 to 99%.

Keywords: Manufactured Gas Plant, MGP, Ozone Injection, Oxygen Injection, Bioremediation, Aerobic, Source Control, BTEX, PAH, DNAPL, Coal Tar, Remediation, Groundwater Plume, Attenuation

1. INTRODUCTION

The former MGP operations began in the late 1880s and continued into the 1970s. Most of the MGP facilities were demolished in 1973. Various remedial investigations, interim remedial measures, and remedial actions have been completed or implemented at the Site. The Site is broken into 4 operable units (OU) as depicted on Figure 1; however, this paper will focus on the remedial activities in OU-1 and OU-2 and their integration into a cohesive remedial strategy. OU-1 represents the former MGP facility and is the location of the primary source area. OU-2 represents the dissolved phase contaminant plume emanating from OU-1 which ultimately discharges into a tidal creek. (GEI, Consultants 2007; GEI Consultants, 2008)

A series of groundwater and soil investigations were conducted between 1999

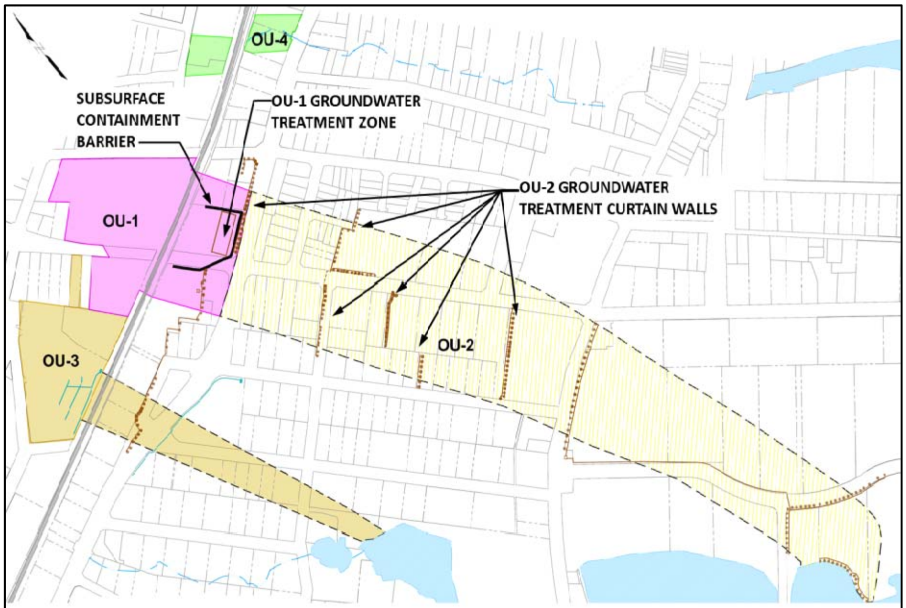


Figure 1 : Site Plan

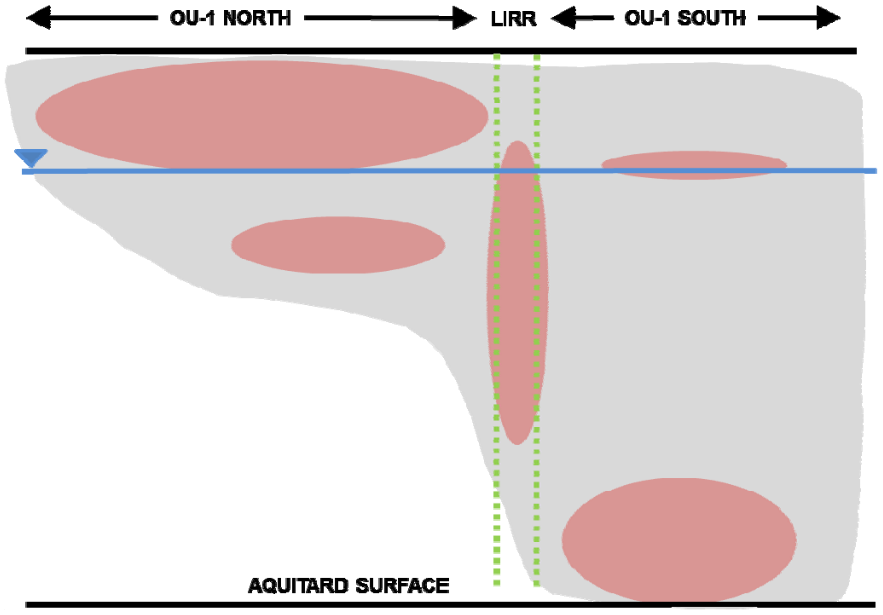


Figure 2 : Distribution of MGP Soil Contamination

and 2004 to collect the required analytical data to characterize the site and develop a remedial strategy. Within OU-1, the MGP-related soil contamination was present in five general areas as depicted on Figure 2. The majority of the impacts were located in shallow soils within the northern section of OU-1. The remaining contamination was located in isolated hot spots located in the intermediate soils, below the LIRR tracks, and at the water table surface and the surface of the aquitard in southern section of OU-1. In OU-2, the impacts were limited to the dissolved phase. The boundary of the dissolved phase plume in OU-2 as shown in Figure 1 is based on concentration isopleths of the contaminants of concern (COCs) or total BTEX and total PAHs greater than 100 micrograms per liter (ug/L) established during the remedial investigations. The plume extends approximately 3,400 feet (1036 m) from OU-1 to the discharge point at the tidal creek, and is approximately 500 feet (152.4 m) wide. To date, the groundwater plume in OU-2 has not penetrated the deeper confined aquifer at approximately 60 to 70 feet (18.2 to 21.3 m). (GEI, Consultants 2007; GEI Consultants, 2008)

In 2004, a remedial action plan was developed to remediate the source areas in OU-1. The remedy included shallow source removal, installation of a containment barrier wall with a perforated window, groundwater treatment, and deep in-situ chemical oxidation. Initial groundwater modeling of the OU-1 remedy indicated that the source control and treatment measures would reduce the contaminent flux into OU-2. Based on that model, the groundwater plume would take approximately 10-15 years to be remediated following the completion of the OU-1 remedy.

In OU-2, two oxygen injection lines were installed in 2004 as an interim remedial measure to treat impacted groundwater at the toe of the plume prior to the discharge into the tidal creek while the remedy in OU-1 was conducted. These lines were able and continue to reduce COC concentrations by approximately 95% at the discharge point within three to six months of operation. The success of that interim remedial measure at cutting off the plume prompted calls for additional treatment systems throughout the community to hasten the degradation of the plume. A remedial plan was developed for OU-2 which included the installation of multiple oxygen injection curtain walls. The remedial plan included a series of pre-design investigations, which further defined the horizontal and vertical definition of the plume. The results of the investigations were used to estimate the contaminant flux in the vicinity of the proposed curtain wall locations, determine the required depth of the injection, specify the injection system components, and determine the location of permanent monitoring well clusters for system performance monitoring. The conceptual plan for the overall remedy in OU-1 and OU-2 is depicted in Figure 3.

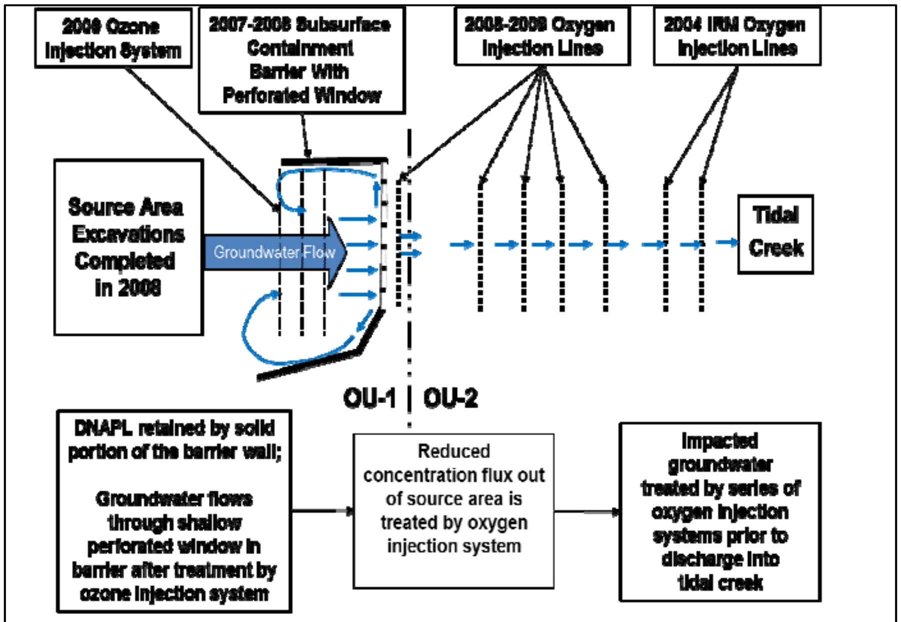


Figure 3 : Conceptual Remedial Plan

2. MATERIALS AND PROCEDURES

2.1 Technology Evaluations

A number of potentially applicable technologies were screened for the groundwater treatment zone upgradient of the perforated window in the barrier wall and for the OU-2 plume. Based on the screening, in-situ chemical oxidation (ISCO) was identified as the best-suited technology upgradient of the gate and biostimulation via oxygen injection was selected for the OU-2 plume.

2.1.1 Ozone Injection Technology Selection

Pilot tests for various oxidants including hydrogen peroxide, sodium persulfate, potassium permanganate, and ozone had been conducted at the site with varying levels of success. The choice of oxidant and its specific long-term delivery technique are keys to success at each site. For the OU-1 treatment zone location, a powerful fast-acting oxidant was required that could be delivered with minimal operator supervision and storage and handling issues. In addition, the system will operate for a number of years and will be at a highly visible location adjacent to residential and commercial properties. Based on these criteria, ozone was selected as the oxidant. A treatment system was installed to generate ozone on-site from fresh air. Due to the instability of ozone it is delivered to the injection points directly with no on-site storage. (GEI, Consultants 2009d)

2.1.2 Oxygen Injection Technology Selection

Oxygen injection was previously in use at the site in OU-3 and as part of an IRM in OU-2 completed in 2004. Although these systems had already proved effective at remediating the plume, an evaluation of other technologies was completed. Five technologies were identified as potentially viable for remediation of the OU-2 plume: Oxygen Injection, Oxygen Release Compound (ORC) Injection, In-Situ Vapor Stripping, In-situ Chemical Oxidataion (ISCO), and Groundwater Pump & Treat. These five technologies were selected because each has been demonstrated either at this or at other similar sites as being effective in the remediation of BTEX and naphthalene in groundwater. For purposes of the technology evaluation, the time of the remedy period was assumed to be five years based on the estimate of the remediation using the existing oxygen injection system. Following the completion of the technology evaluation, New York State Department of Environmental Conservation, selected oxygen injection technology for the locations within the community.

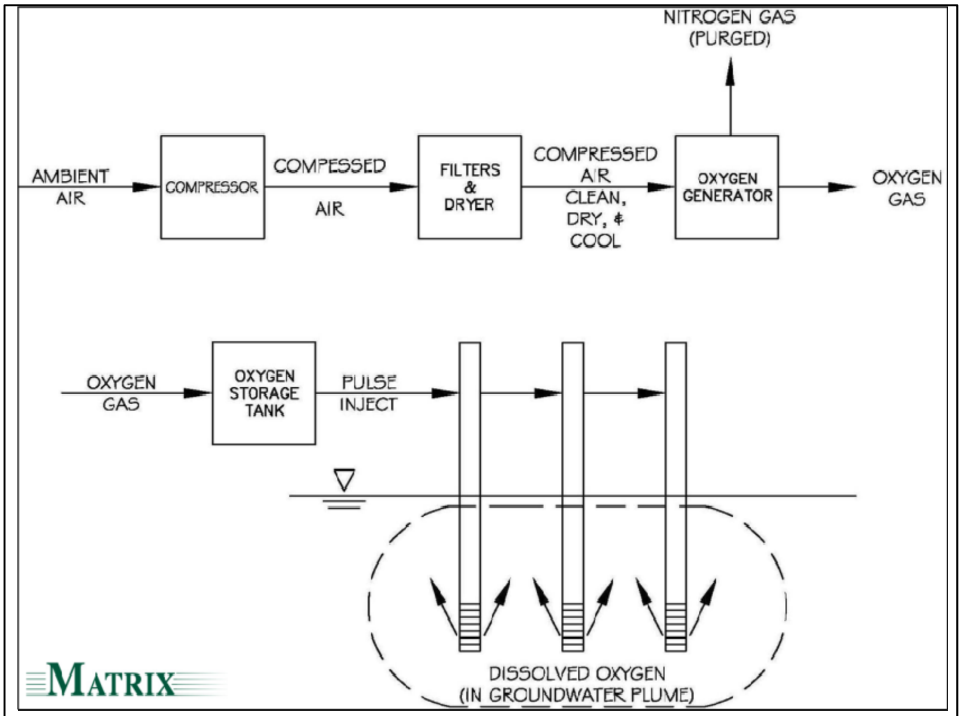


Figure 4 : Oxygen Injection Process Flow Diagram

Oxygen injection technology involves the injection of a 90 to 95 percent pure oxygen gas into groundwater to increase the dissolved oxygen concentration and enhance aerobic biodegradation of COCs. The technology filters ambient air to generate a 90 to 95 percent pure oxygen gas, which is then injected in pulsed intervals into the subsurface through a series of injection wells at low flow rates. The low flow rates and pulsed injection intervals are cycled to allow for the maximum transfer of vapor-phase oxygen into dissolved-phase oxygen. A schematic of the process flow is provided in Figure 4. The system is patented and built by Matrix Environmental Technologies, Inc. In general, it consists of a rotary screw air compressor, refrigerated air dryer, pressure-swing adsorption oxygen generator, and automated oxygen delivery manifold. Ambient air is compressed to 110 pounds per square inch (PSI; 758 kilopascals) and conditioned through a series of filters and the air dryer. The compressed air flows to an oxygen generator where the nitrogen is removed through a process called pressure swing adsorption. This process uses a molecular sieve (synthetic zeolite) which adsorbs nitrogen at high pressure and releases it at low pressure. The resulting gas stream has an oxygen purity of 90 to 95 percent and is stored in a receiver tank for injection into the aquifer. By slowly injecting oxygen at 90 to 95 percent purity, dissolved oxygen concentrations can increase to a maximum of approximately 40 mg/L. (GEI Consultants, 2009b)

3. DATA AND ANALYSIS

3.1 Ozone Injection Design

The design of the ozone injection system was based on the flux of COCs through the treatment zone. As the other components of the remedy were implemented and the overall COC mass available for transfer to the aqueous phase decreased, the mass flux varied. The ozonation system was designed before implementing the aggressive COC mass removal actions of excavation and ISCO. As a design baseline, the ozonation system should have the capacity to treat the pre-excavation/treatment COC flux. Over time, as COC flux decreases, the operation of the ozonation system can be adjusted to inject at a reduced rate, matching the decreased flux.

COC flux was assessed by analyzing groundwater quality data and calculating groundwater flow rates. Historical groundwater quality data at eight wells in the treatment zone vicinity were analyzed to assess COC concentrations and the site groundwater model was used to predict groundwater flow rates. Data from the RI and subsequent quarterly groundwater monitoring events were used to estimate the range of dissolved-phase BTEX and PAH levels in the treatment zone. The average concentration of BTEX at the wells ranges from 23 µg/L to 26,947 µg/L, with an overall average of 7,081 µg/L. The average concentration of PAHs at the wells ranges from 2,768 µg/L to 8,281 µg/L, with an overall average of 5,160 µg/L. These overall average concentrations of BTEX and PAH were used to design loading of the ozonation system as they represented a reasonable estimate of the expected COC concentrations during initial operation of the system. (GEI Consultants, 2009d)

A design safety factor of 3 was calculated and applied to the design loading to account for variations in the COC loading, other organic compounds not captured by BTEX and PAH laboratory analyses, COCs sorbed onto soils and naturally occurring organic matter (characterized by TOC analysis) in soil and groundwater. A site groundwater model was used to predict groundwater flow rates through the treatment zone. Using the proposed barrier wall configuration with a perforated window, the estimated flow rate through the treatment zone was calculated at 2,000 cubic feet per day (cfd). Multiplying the concentration by the flow rates and applying the appropriate conversion factors yields an estimated baseline COC loading for design purposes of 0.9 lb/day (0.4 kg/day) of BTEX and 0.6 lb/day (0.3 kg/day) of PAHs. (GEI Consultants, 2009d)

The stoichiometric ozone demand was calculated based on groundwater and soil constituents to determine the amount of ozone required to oxidize each of the constituents completely to carbon dioxide and water. Based on this evaluation, an average 7,000 g/day (~16 lb/day) of ozone was calculated for delivery in the treatment zone. To confirm these calculations, a series bench tests were performed to identify oxidation intermediates and determine the residence time required to oxidize. The findings showed that the ozone completely destroyed all dissolved constituents in the aqueous phase within 30 minutes. (GEI Consultants, 2009d)

3.2 Oxygen Injection Design

The data sets generated from the pre-design investigations were used to create a snap shot in time of the plume and construct an approximate cross section for each proposed treatment area. The vertical and horizontal plume boundary was estimated and defined by the 100 µg/L concentrations of the COCs. Figure 5 depicts the plan and cross-sectional view of one area in OU-2. Due to access agreements and the location of the road, this curtain wall was designed to only

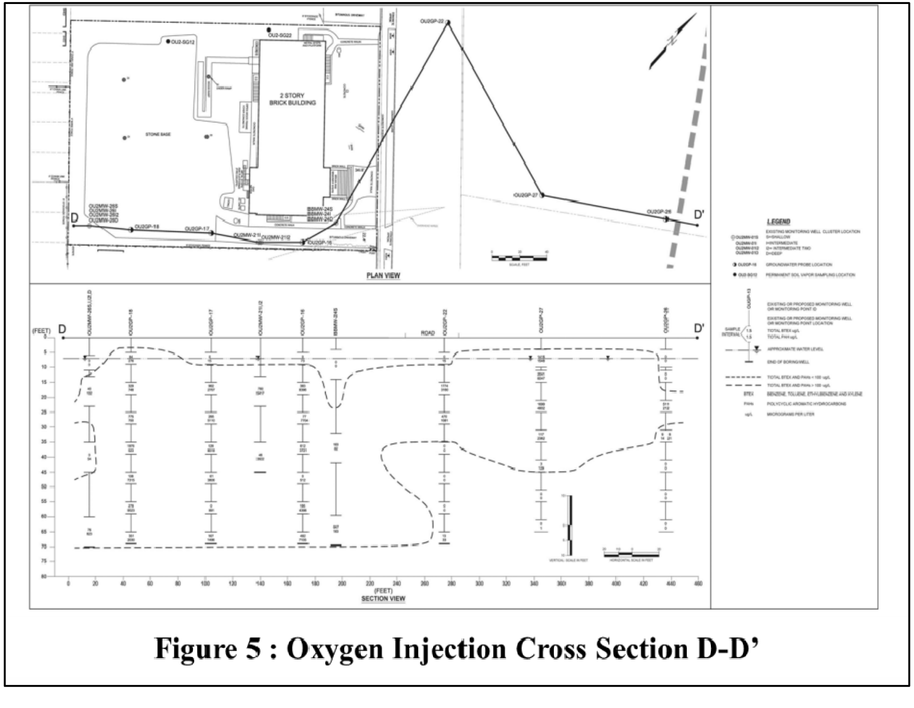


Figure 5 : Oxygen Injection Cross Section D-D’

treat the left portion of the cross-section. Therefore, the volumetric flow rate of this portion was estimated using the following assumptions:

- The cross-sectional shape of the targeted portion of the plume is equivalent to a rectangle 235 feet (72 m) wide by 70 feet (21.3 m) deep.
- The formation porosity is 30%.
- The groundwater seepage velocity is approximately 1 foot per day (ft/day)(0.3m/day).

Using the data and these assumptions, the volumetric flow rate of the groundwater plume passing through the injection area was estimated at 4,935 cubic feet per day (CF/day) or 0.037 million gallons per day (MGD) (140 kiloliters/day (kl/d)). (GEI Consultants, 2009b)

3.2.1 Average Concentration Load

The average concentration load of total VOCs, total SVOCs, and total metals was estimated using data collected from a combination of temporary groundwater probes and permanent monitoring well clusters. Temporary groundwater probe samples were collected at 5 foot intervals from the water table to the aqutard.. Monitoring well clusters consisted of 2 to 4 wells installed within 5 feet (1.5 m) of each other and screened at different depths (i.e. shallow (water table), intermediate, deeper intermediate, and/or deep) The estimated average contaminant (VOCs and SVOCs) concentration load ranges between 0.08 and 2.78 mg/L across the above cross-section. (GEI Consultants, 2009b)

However, because a large portion of the oxygen demand is derived from the amount of oxygen consumed by the amount of carbon in a compound, this load is converted to a carbon load. Assuming that the estimated concentration load for oxygen consumption is comprised of 94% carbon, the average carbon load for this cross-section is 0.07 and 2.61 mg/L. Applying the average carbon concentration load to the estimated plume flow rate of 0.037 MGD (140 kl/d)) as found above with a unit conversion factor of 8.34 (lbs)(L)/(MG)(mg), the average carbon mass load can be estimated using Equation 1 below:

EQUATION 1: *Mass Loading (lbs/DAY) =*

$$2.61 mg/L * 0.037 Mgal/Day * 8.34 lbs \cdot L/Mgal \cdot mg = 0.81 lbs/D$$

Using Equation 1, the total carbon mass load for this plume ranges from 0.02 to 0.81 lbs/day (0.009 to 0.37 kg/d) (Table 1). Assuming a percentage of dissolved metals will also consume oxygen as it passes through the curtain wall, the average compound mass load is then estimated by adding the carbon mass load to the mass load due to dissolved metals. For the above cross-section, 50% of the average dissolved total metals, or 40.5 mg/L, is assumed to be available for oxygen consumption. Using equation 1, the average metals mass load contributing to the compound mass load is 12.5 lbs/day (5.7kg/d). When added to the carbon mass load, this value yields a range of average compound mass loads of 12.52 to 13.30 lbs/day (5.7 to 6.0 kg/d) (Table 1). (GEI Consultants, 2009b)

Table 1. Calculation Summary

Sample Depth Interval (ft bgs) (m bgs)	Ave. Contaminant Concentration Load (mg/L)	Ave. Carbon Concentration Load (mg/L)	Ave. Carbon Mass Load (lbs/day)(kg/day)	Ave. Total Metals Concentration (mg/L)	Percent of Total Metals Consuming Oxygen (mg/L)	Ave. Total Metals Concentration Load (mg/L)	Ave. Total Metals Mass Load (lbs/day)(kg/day)	Total Compound Mass Load (lbs/day)(kg/day)
6 to 10(1.8 to 3)	0.08	0.07	0.02(0.01)	81	50	40.5	12.5(5.63)	12.52(5.7)
15 to 19(4.5 to 5.7)	2.78	2.61	0.81(0.36)	81	50	40.5	12.5(5.63)	13.30(6.0)
25 to 29(7.5 to 8.7)	2.22	2.09	0.64(0.28)	81	50	40.5	12.5(5.63)	13.14(5.9)
35 to 39(10.5 to 11.7)	2.15	2.02	0.62(0.27)	81	50	40.5	12.5(5.63)	13.12(5.9)
45 to 49(13.5 to 14.7)	1.62	1.53	0.47(0.21)	81	50	40.5	12.5(5.63)	12.97(5.8)
55 to 59(16.5 to 17.7)	2.18	2.05	0.63(0.28)	81	50	40.5	12.5(5.63)	13.13(5.9)
65 to 69(19.5 to 20.7)	1.60	1.50	0.46(0.21)	81	50	40.5	12.5(5.63)	12.96(5.8)

3.2.2 Estimated Oxygen Demand

For the purpose of design, oxygen to carbon ratio was used to estimate the required oxygen demand. This ratio is estimated from the reaction of oxygen with naphthalene producing entirely carbon dioxide and water. Based on this reaction, this calculates a ratio of approximately 3.0 grams of oxygen per gram of naphthalene. (GEI Consultants, 2009b)

A small percentage of injected oxygen will either not dissolve or be consumed by cations or other organic matter. Therefore, a factor of safety of 2.0 was applied to oxygen in the 3:1 oxygen to naphthalene ratio in order to ensure that

Oxidation Reaction for Naphthalene

$$C_{10}H_8 + 12O_2 \rightarrow 10CO_2 + 4H_2O$$

the required amount of oxygen is available. As a result, a minimum 6.0 pounds of oxygen per pound of carbon must be injected into the treatment zone to accommodate the compound mass in the plume. Using the highest average compound load of 13.30 lbs/day (6.0 kg/d), approximately 80 pounds (36.3 kg) of oxygen is required for daily injections. (GEI Consultants, 2009b)

3.2.3 System Capacity and Design

Based on pilot testing performed during Interim Remedial Measure (IRM) activities, typical well spacing within each curtain wall is approximately 20-25 ft. The curtain wall depicted in Figure 6 was designed using 40 injection points spaced approximately 18-20 feet apart.. Using a flow rate of 120 SCFH (3.4 cubic meter per hour (cmh)), the corresponding mass flow rate of oxygen into the aquifer was estimated at approximately 10.68 lbs (4.8 kg) of oxygen per hour or 256.3 lbs/day (115.3 kg/d) across all injection points. However, the oxygen transfer efficiency to groundwater is not 100%. This transfer is dependent on

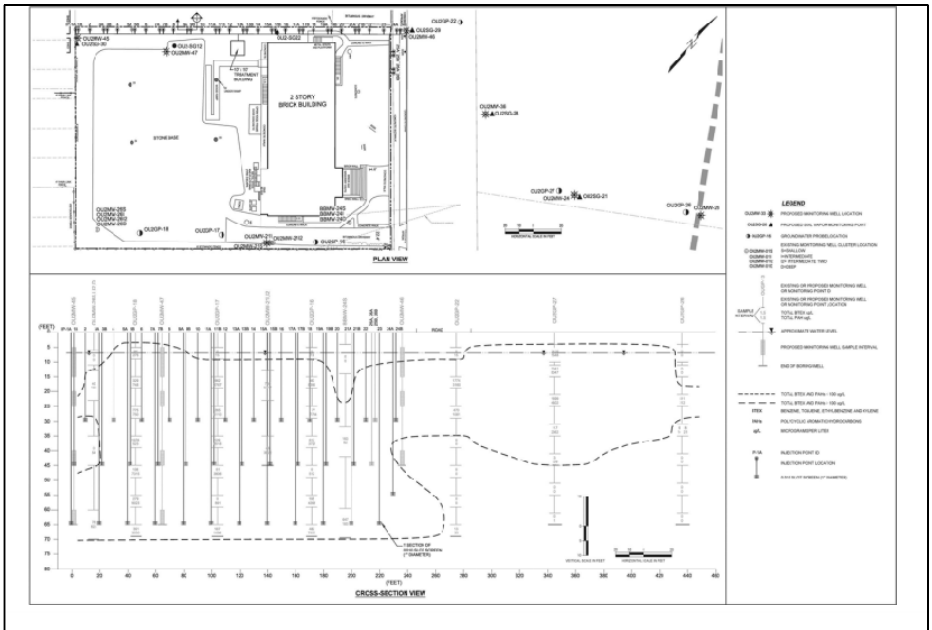


Figure 6 : Oxygen Injection Curtain Wall

both the oxygen solubility and the depth of injection. The deeper the point of injection is installed below the water table, the higher the transfer efficiency due to a longer contact time between the oxygen gas molecule and the groundwater. For injection points at depths of 25 to 70 feet (7.5 to 21 m) bgs, a transfer efficiency of between 75-95%, respectively, is assumed. Therefore, approximately 8.0 to 9.6 lbs (3.6 to 4.3 kg) of oxygen per hour is available. This equates to a supply rate of approximately 192 to 230.4 lbs (86.4 to 103.7 kg) of oxygen or 0.16 lbs/min (0.07 kg/min) across all injection points. At this rate, approximately 6.4 lbs (2.9 kg) of oxygen per minute is injected by the 40 injection points installed at this location [0.16 lbs/min (0.07 kg/min) x 40 injection points = 6.4 lbs/min (2.9 kg/min)]. To achieve the 80 pounds (36.3 kg) of oxygen as estimated above to treat the highest average compound load of 13.30 lbs/day (6.0 kg/d), the system pulses oxygen into the plume for approximately 12.5 minutes every hour. (GEI Consultants, 2009b)

3.2.4 Performance Monitoring

The groundwater concentrations in OU-1 and OU-2 are monitored by a series groundwater monitoring well clusters located up-gradient, side-gradient and down-gradient of the each treatment line. In OU-1 this includes monitoring wells located downgradient of the injection lines both before and after the perforated window in the barrier wall. Monitoring well clusters were sampled under low-flow conditions for COCs and a suite of inorganics prior to startup, monthly for 3 months after startup, and then quarterly. Low-flow parameters including Dissolved Oxygen (DO), Oxidation-Reduction Potential (ORP), pH, and specific conductance were collected during each sampling event. The frequency of monitoring at many of the OU-2 well clusters has since been reduced to annual or discontinued based on the dramatic reduction of the plume. (GEI Consultants, 2009b)

4. CONCLUSION

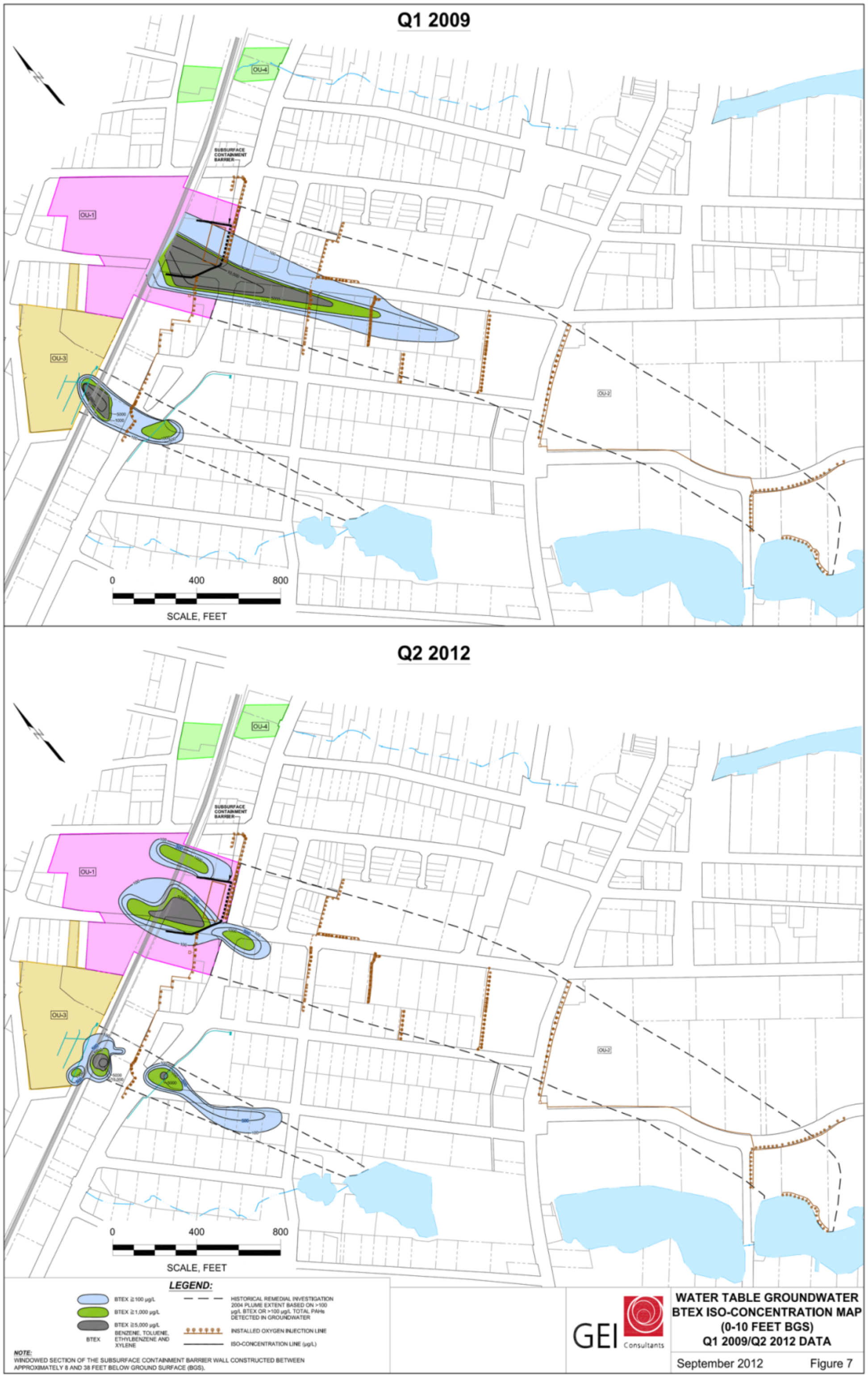
In general, any successful remediation campaign for an extensive groundwater plume requires a source area remediation strategy that will ultimately augment and facilitate a full-scale plume remediation and vice-versa. Conceptually, the success of the remedial strategy to eliminate the plume in OU-2 is directly contingent with the success of the remedial actions implemented at its source area (OU-1). Both strategies were designed and implemented to integrate and complement each other. The success of each individual component provided opportunities to enhance the original source control and treatment remedy and speed up the original timeline for remediating the groundwater plume in the community.

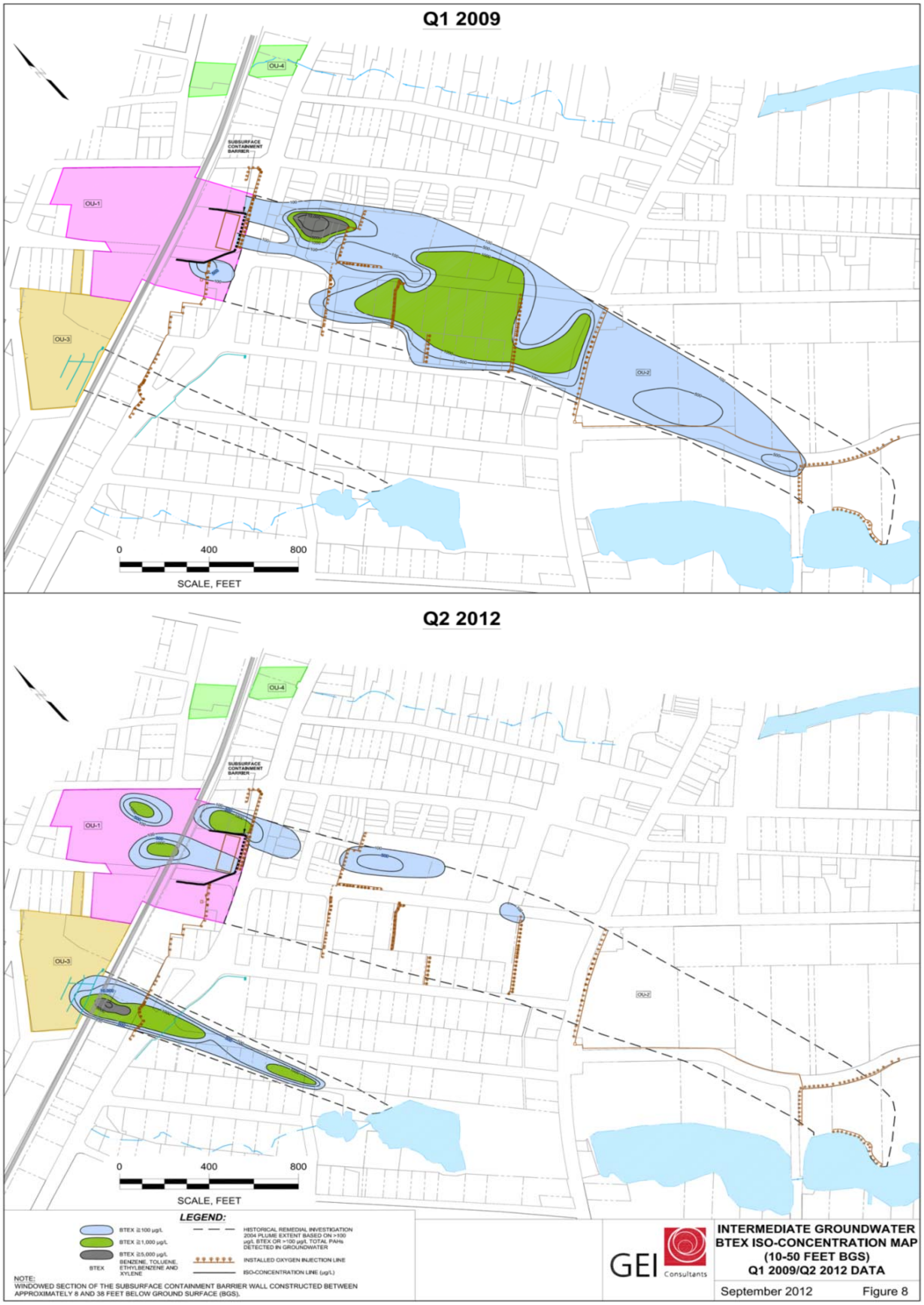
The rapid success of the oxygen injection lines installed as part of the OU-2 IRM to reduce concentrations of COCs at the discharge point allowed time to design and coordinate the subsurface barrier wall installation with local officials. The oxygen injection line installed in 2008 immediately downgradient of the barrier wall provided treatment of groundwater discharging through the perforated gate while the ozone injection system was installed and tested. Over the first year of operation while the ozone injection building and system were being installed, the concentrations of total BTEX and total PAHs were reduced by up to 90% and and 68%, respectively, approximately 220 ft (67 m) down-gradient of the oxygen injection system.

Based on the success of the initial oxygen injection systems, three more oxygen curtain walls were designed and installed in OU-2. These curtain walls were spaced as evenly as possible throughout the middle of the plume extent to accelerate the cleanup of the plume. Installed in this fashion, the curtain walls created and maintained multiple aerobic environments along the flow path of the plume. As a result, each curtain wall supplemented one another by reducing the dissolved contaminant mass as the groundwater flows through each curtain wall towards the discharge point.

After the D-D' curtain wall depicted in Figure 5 operated for approximately 2 months, reductions in total BTEX and total PAH concentrations ranged between 75-99% and 21-99%, respectively. Within the same timeframe, standard plate counts of bacteria populations increased 1 to 3 orders of magnitude. Within one week of operation, dissolved oxygen (DO) concentrations ranged between 20 and 40 mg/L; and have since remained above 20 mg/L. The curtain walls installed in OU-2 are proving very effective at reducing the COC concentrations within the groundwater plume.

The following figures present a comparison of the plume between Q1 2009 and Q2 2012. Figures 7 to 9 illustrate Total BTEX concentrations within the three aquifer depth zones; and Figures 10 to 12 – Total PAH (GEI Consultants, 2009c; GEI Consultants, 2012). As illustrated by the figures, there have been significant reductions in the footprint of the groundwater plume within 3 years of full operation of the oxygen injection curtain walls. By expanding the oxygen curtain wall systems in concert with the barrier wall and ozone system, the groundwater plume is being remediated in a fraction of the time initially estimated.


Q1 2009
OU-4
SUBSURFACE CONTAINMENT BARRIER
OU-1
OU-3
OU-2
0
400
800
SCALE, FEET
Q2 2012
LEGEND:
BTEX ≧100 µg/L
BTEX ≧1,000 µg/L
BTEX ≧5,000 µg/L
BTEX
BENZENE, TOLUENE, ETHYLBENZENE AND XYLENE
HISTORICAL REMEDIAL INVESTIGATION 2004 PLUME EXTENT BASED ON >100 µg/L BTEX OR >100 µg/L TOTAL PAHs DETECTED IN GROUNDWATER
INSTALLED OXYGEN INJECTION LINE
ISO-CONCENTRATION LINE (µg/L)
NOTE:
WINDOWED SECTION OF THE SUBSURFACE CONTAINMENT BARRIER WALL CONSTRUCTED BETWEEN APPROXIMATELY 8 AND 38 FEET BELOW GROUND SURFACE (BGS).
GEI Consultants
WATER TABLE GROUNDWATER BTEX ISO-CONCENTRATION MAP (0-10 FEET BGS) Q1 2009/Q2 2012 DATA
September 2012
Figure 7


Q1 2009
OU-1
OU-2
OU-3
OU-4
SUBSURFACE CONTAINMENT BARRIER
0
400
800
SCALE, FEET
Q2 2012
OU-1
OU-2
OU-3
OU-4
SUBSURFACE CONTAINMENT BARRIER
0
400
800
SCALE, FEET
LEGEND:
BTEX ≧100 µg/L
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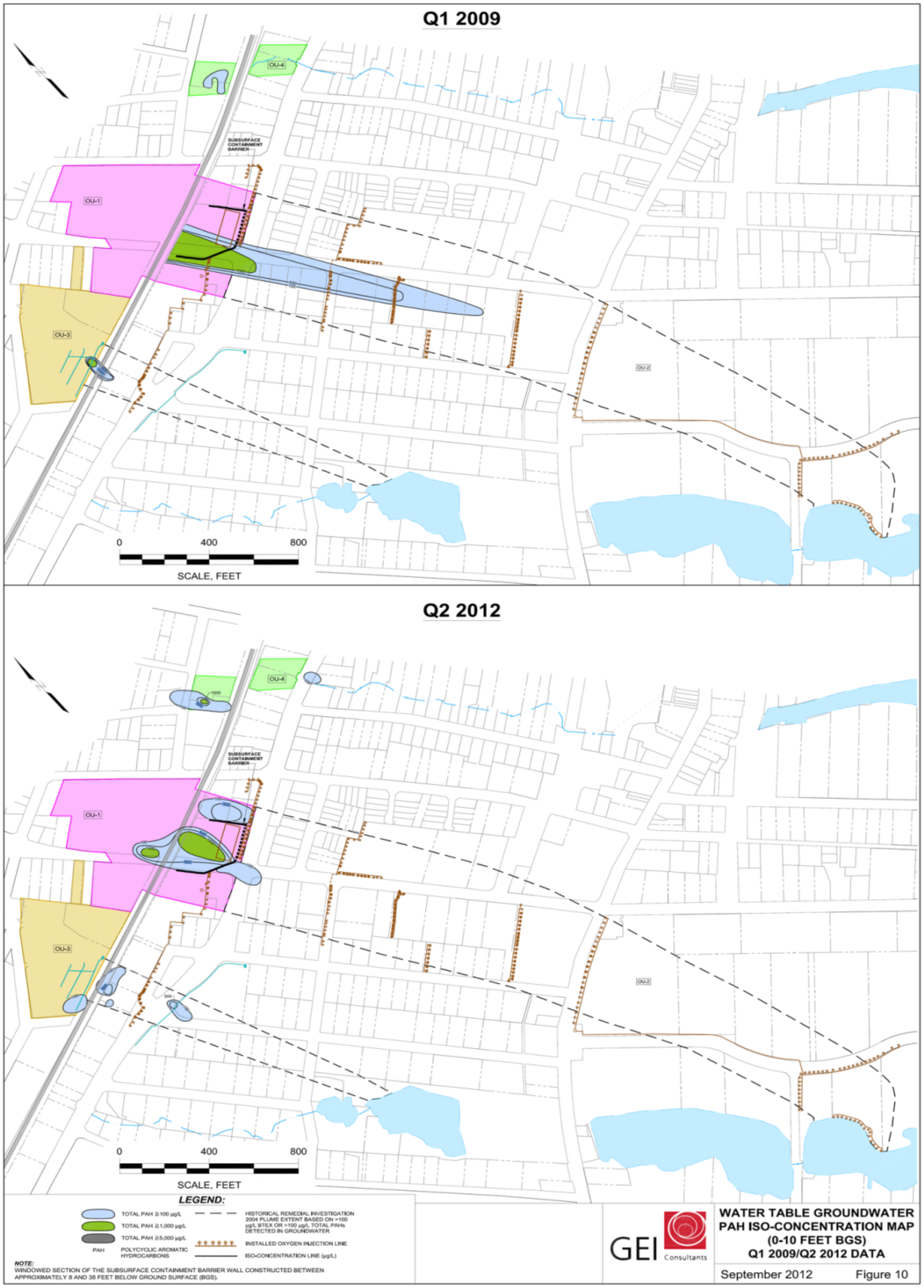
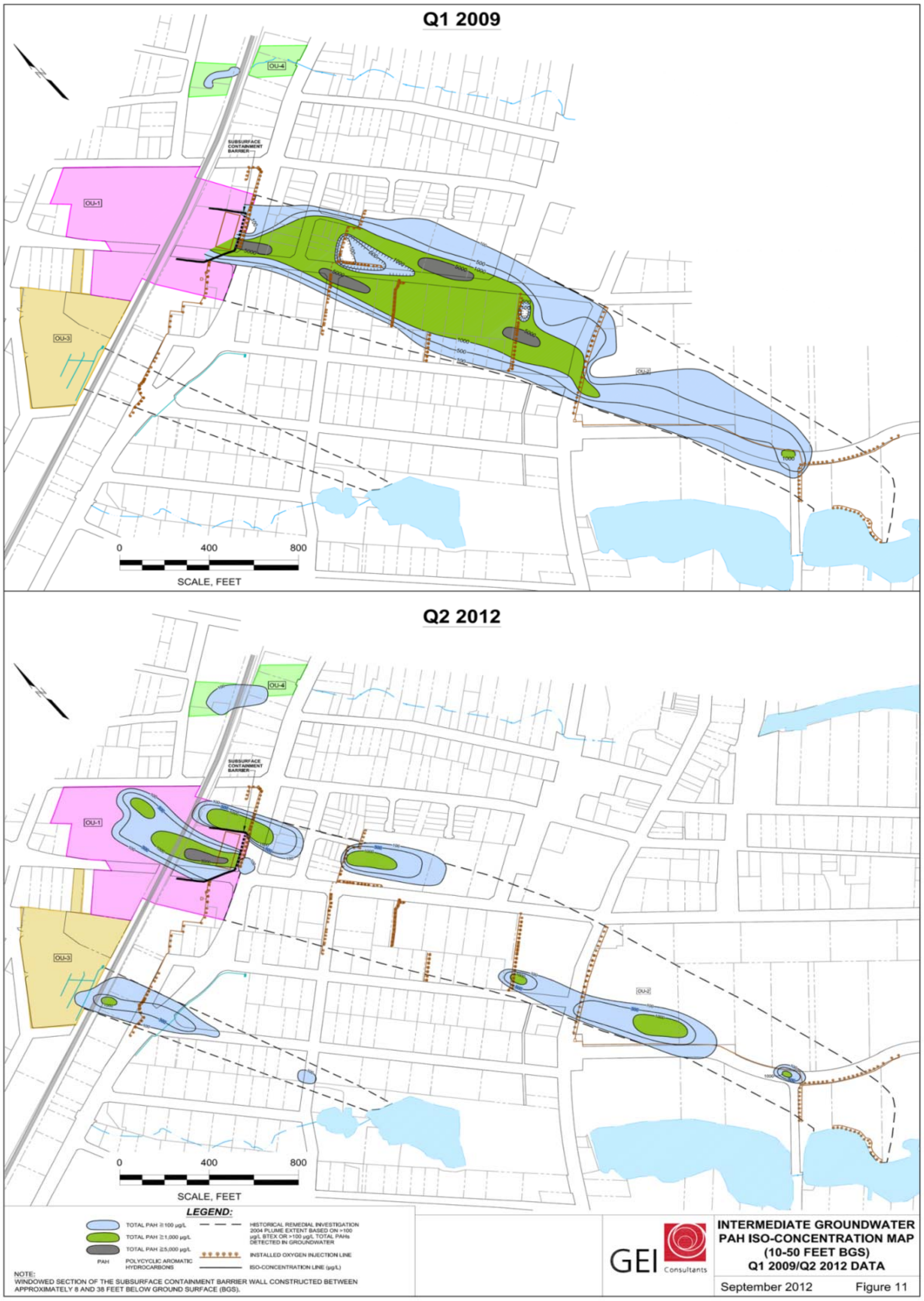
BTEX ≧5,000 µg/L
BTEX
BENZENE, TOLUENE, ETHYLBENZENE AND XYLENE
HISTORICAL REMEDIAL INVESTIGATION 2004 PLUME EXTENT BASED ON >100 µg/L BTEX OR >100 µg/L TOTAL PAHs DETECTED IN GROUNDWATER
INSTALLED OXYGEN INJECTION LINE
ISO-CONCENTRATION LINE (µg/L)
NOTE:
WINDOWED SECTION OF THE SUBSURFACE CONTAINMENT BARRIER WALL CONSTRUCTED BETWEEN APPROXIMATELY 8 AND 38 FEET BELOW GROUND SURFACE (BGS).
GEI Consultants
INTERMEDIATE GROUNDWATER BTEX ISO-CONCENTRATION MAP (10-50 FEET BGS) Q1 2009/Q2 2012 DATA
September 2012
Figure 8

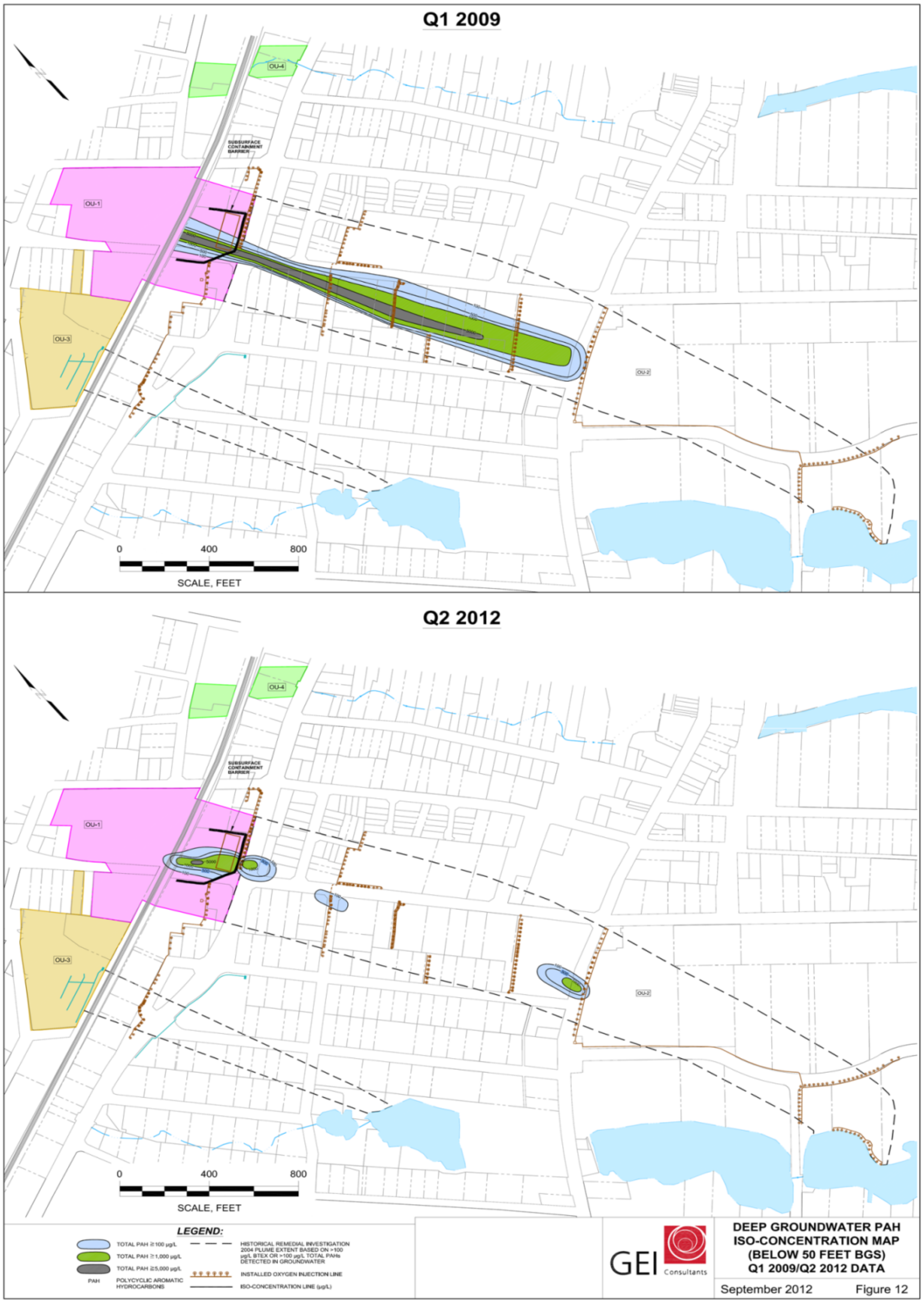

Q1 2009
SUBSURFACE CONTAINMENT BARRIER
OU-1
OU-2
OU-3
OU-4
0
400
800
SCALE, FEET
Q2 2012
SUBSURFACE CONTAINMENT BARRIER
OU-1
OU-2
OU-3
OU-4
0
400
800
SCALE, FEET
LEGEND:
BTEX ≧100 µg/L
BTEX ≧1,000 µg/L
BTEX ≧5,000 µg/L
BTEX BENZENE, TOLUENE, ETHYLBENZENE AND XYLENE
HISTORICAL REMEDIAL INVESTIGATION 2004 PLUME EXTENT BASED ON >100 µg/L BTEX OR >100 µg/L TOTAL PAHs DETECTED IN GROUNDWATER
INSTALLED OXYGEN INJECTION LINE
ISO-CONCENTRATION LINE (µg/L)
GEI Consultants
DEEP GROUNDWATER BTEX ISO-CONCENTRATION MAP (BELOW 50 FEET BGS) Q1 2009/Q2 2012 DATA
September 2012
Figure 9


Q1 2009
OU-4
SUBSURFACE CONTAINMENT BARRIER
OU-1
OU-3
OU-2
0
400
800
SCALE, FEET
Q2 2012
OU-4
SUBSURFACE CONTAINMENT BARRIER
OU-1
OU-3
OU-2
0
400
800
SCALE, FEET
LEGEND:
TOTAL PAH ≧100 µg/L
TOTAL PAH ≧1,000 µg/L
TOTAL PAH ≧5,000 µg/L
PAH POLYCYCLIC AROMATIC HYDROCARBONS
HISTORICAL REMEDIAL INVESTIGATION 2004 PLUME EXTENT BASED ON >100 µg/L BTEX OR >100 µg/L TOTAL PAHs DETECTED IN GROUNDWATER
INSTALLED OXYGEN INJECTION LINE
ISO-CONCENTRATION LINE (µg/L)
NOTE:
WINDOWED SECTION OF THE SUBSURFACE CONTAINMENT BARRIER WALL CONSTRUCTED BETWEEN APPROXIMATELY 8 AND 38 FEET BELOW GROUND SURFACE (BGS).
GEI Consultants
WATER TABLE GROUNDWATER
PAH ISO-CONCENTRATION MAP
(0-10 FEET BGS)
Q1 2009/Q2 2012 DATA
September 2012
Figure 10



INTERMEDIATE GROUNDWATER PAH ISO-CONCENTRATION MAP (10-50 FEET BGS) Q1 2009/Q2 2012 DATA

September 2012 Figure 11



DEEP GROUNDWATER PAH ISO-CONCENTRATION MAP (BELOW 50 FEET BGS) Q1 2009/Q2 2012 DATA

September 2012 Figure 12

5. REFERENCES

GEI Consultants, Inc., 2007, *Hydrologic Study, Confidential Site*.

GEI Consultants, Inc., 2008, *Quarterly Operations, Maintenance & Monitoring Report, First Quarter (Q1) 2008, Confidential Site.*

GEI Consultants, Inc., 2009a, *Quarterly Operations, Maintenance & Monitoring Report, Fourth Quarter (Q1) 2008, Confidential Site.*

GEI Consultants, Inc., 2009b, *Remedial Design Document, Confidential Site.*

GEI Consultants, Inc., 2009c, *Quarterly Operations, Maintenance & Monitoring Report, First Quarter (Q1) 2009, Confidential Site.*

GEI Consultants, Inc., 2009d, *Phase 1A Remedial Design Report, 100 % Submission, Confidential Site.*

GEI Consultants, Inc., 2012, *Quarterly Operations, Maintenance & Monitoring Report, Second Quarter (Q2) 2012, Confidential Site.*

Chapter 6

THE IMPORTANCE OF PRE-DESIGN INVESTIGATIONS IN REMEDIATION OF FORMER MANUFACTURED GAS PLANT SITES

James L. Marolda[§]
Brown and Caldwell, 2 Park Way, Suite 2A, Upper Saddle River, NJ, USA, 07458

ABSTRACT

Prior to conducting the construction activities for environmental remediation, multiple phases of investigation work including Pre-Design Investigation (PDI) activities are typically completed in an effort to improve remedial designs. This improvement results in development of more accurate remedial cost estimates and more effective remediation implementation. The results and findings from PDI activities are intended to provide additional data and information, supplementary to that provided in investigations completed prior to remedy selection, to support preparation of the remedial design as well as contractor procurement and remedial construction.

Excavation and off-site treatment/disposal of soils often is a major component of remedial alternatives at former manufactured gas plant (MGP) sites. However, excavation at former MGP sites can prove to be challenging to implement due to the presence of subsurface remnants of former MGP structures and other subsurface obstructions. At former MGP sites in New York State, various methods were employed during the completion of PDI work to refine the certainty of the presence and dimensions of subsurface structures/obstructions that would require demolition/removal to implement the excavation component of the remedy including: compilation and review of historical MGP drawings; review of previous investigation findings; conventional investigation techniques such as excavation of test pits and advancement of test borings; and surface geophysical surveys. Data and information obtained from the subsurface evaluation would also serve to refine volumes of impacted soils requiring removal.

[§] Corresponding Author: James L. Marolda, Brown and Caldwell, 2 Park Way, Suite 2A, Upper Saddle River, NJ, USA, 07458, Email: JMarolda@Brwncald.com

Characterization of the substantial subsurface impediments at former MGP sites is essential for developing an accurate estimation of the scope and costs associated with their demolition/removal and to more effectively implement the remedy selected for the site.

Keywords: MGP, excavation, structure, remediation.

1. INTRODUCTION

Environmental remediation is a challenging and often costly process which is further complicated at former MGP sites due to the extensive subsurface infrastructure that exists at these sites. The infrastructure at former MGP sites often obstructs areas of planned subsurface remediation, thereby inhibiting effective implementation of remedial alternatives. Specifically, alternatives that include excavation as a component of the remedy, whether it be as the selected remedial process or a requirement for completing other remedial processes (e.g., pre-excavation prior to application of in-situ stabilization/solidification [ISS] to remove subsurface obstacles and to accommodate material swelling as a result of the ISS treatment), can be difficult to efficiently execute. In order to better evaluate the subsurface obstructions in areas of remediation, an uncharacteristic approach for implementation of a PDI was developed. PDI activities are commonly performed to fine tune remediation boundaries (e.g., limits of soil removal) and to collect data to support the design of a selected remedy (e.g., collection of samples for treatability and waste characterization). However, at former MGP sites, estimation of quantities of subsurface obstructions that would require demolition/removal to implement a selected remedy should also be considered when preparing remedial designs.

Understanding the potential subsurface obstacles through a carefully planned PDI can be extremely valuable as the resultant data provides information critical to developing accurate remedial cost estimates and better quantifying volumes of soil that will require removal and off-site treatment/disposal. The approach incorporates collection of data through both desktop and field methods.

Provided in the following sections is a brief background describing the general history of MGP operations and characteristics of the MGP sites that were investigated, a description of the investigation approach, findings from the investigation, and conclusions regarding the investigation approach.

2. BACKGROUND

Operations at MGP sites for the production and distribution of gas manufactured from coal or oil began in the mid-1800s and spanned an entire century. Manufactured gas production began to decline and virtually ended in the mid-1900s with the continually expanding development and use of natural gas supplies and other fossil fuels (Calabrese and Kostecki, 1991). Gas produced at MGP sites was ultimately used to light and heat homes, commercial establishments, industries, and street lamps. Waste residuals from the production processes, including tar, were introduced into the subsurface and thus, investigation and remediation of these sites is now necessary to address the resulting impacts. Tar encountered at MGP sites is typically denser than water, behaving as a dense non-aqueous phase liquid (DNAPL) in the subsurface and having a very low aqueous solubility.

Historic releases of tar/DNAPL from MGP operations can be traced back to subsurface relief holders or other subsurface structures where waste residuals from the manufacturing processes had accumulated. Materials remaining in these subsurface structures along with soils contaminated with tar/DNAPL outside of the structures are commonly targeted for removal and/or treatment as part of the selected remedies for former MGP sites.

In general, most MGP sites tend to be small, on the order of a few acres (Calabrese and Kostecki, 1991). Therefore, MGP structures were constructed immediately adjacent to one another to maximize operational space (see Figure 1). Process related structures at MGP sites included facilities such as retorts, gas holders, gas generators, purifiers, and several related structures. Above-grade structures at most MGP sites have been razed. The subsurface foundations for these structures as well as remnants of former subsurface MGP structures (e.g., gas holders, tar wells, sumps, etc.) and associated process piping remain in-place within the subsurface. As a consequence, access to the subsurface materials requiring remediation is difficult.

3. APPROACH

The investigation approach described herein was completed at two separate MGP sites in New York State to provide data for refining the certainty of the presence and, if present, the dimensions and composition of subsurface structures/obstructions that would require demolition/removal to facilitate implementation of the selected remedy at these sites. Investigation activities were completed in two stages: a desktop evaluation, followed by a field program.

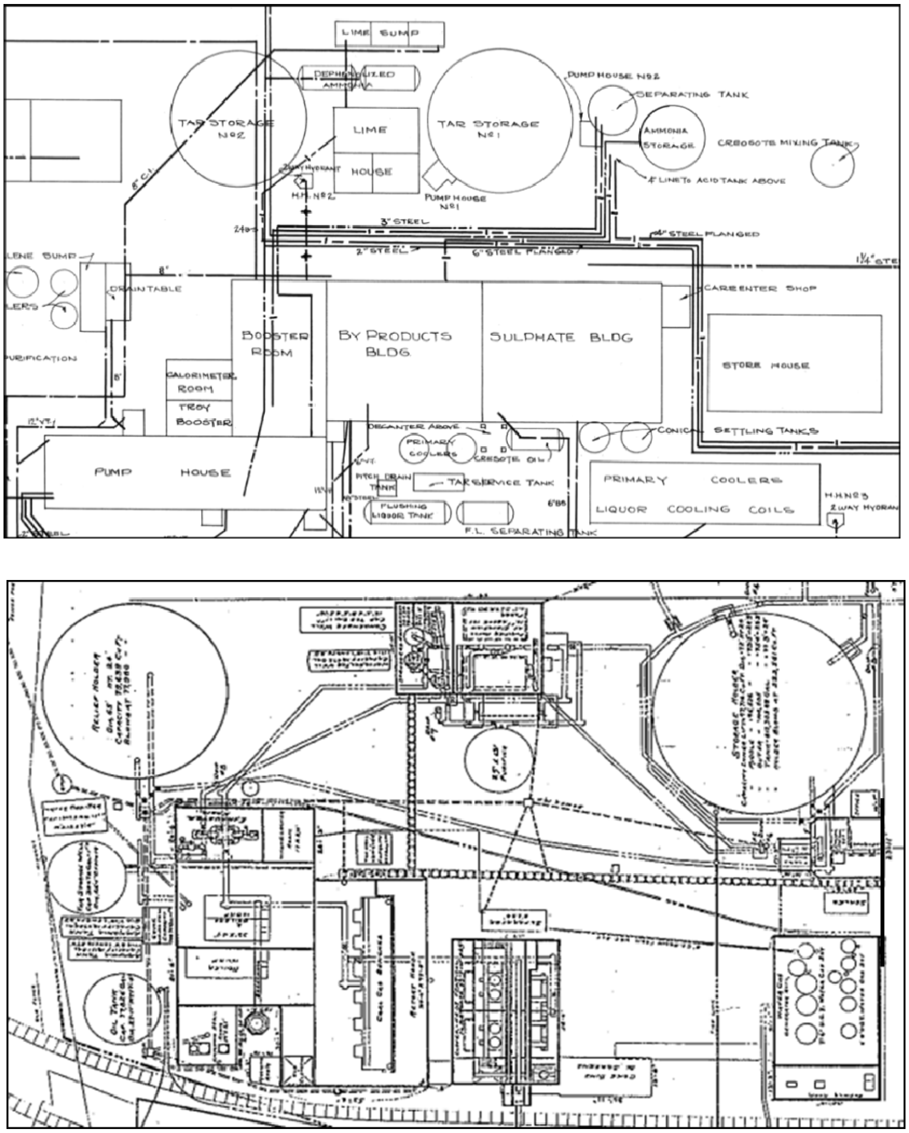


Figure 1. Historical MGP drawings depicting arrangement of process structures and associated piping.

3.1 Desktop Evaluation

Components of the desktop evaluation included identification of potential structures within areas of planned remediation, compilation and review of historic plant drawings, and review of previous investigation findings as they relate to dimensions of subsurface structures/obstructions.

Initially, structures within areas of remediation were assigned identification numbers (see Figure 2). A review of information available for the structures was then conducted using historical plant drawings acquired from site owners, Sanborn® Fire Insurance Maps and observations documented during historical investigation locations (e.g., borings, test pits, etc.) positioned within or proximal to identified structures. In some instances, review of the plant drawings and observations from intrusive activities conducted at the site produced enough information for determining the size and construction of a particular structure. However, for the majority of the structures, only partial dimensions were determined through review of the abovementioned sources.

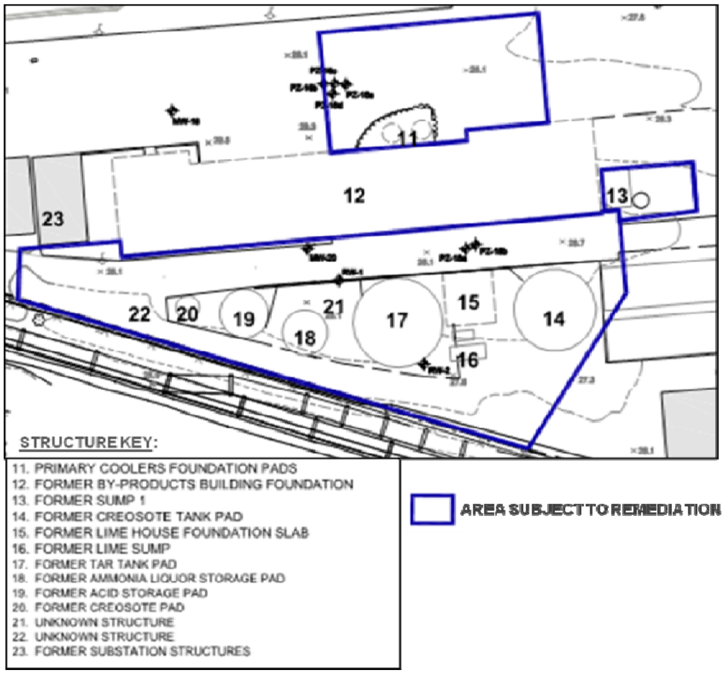


Figure 2. Structures identified within remediation areas.

Following the desktop review process, a table was then generated to summarize information acquired to date for each structure identified in areas subject to remediation. The table also provided a summary of proposed PDI activities, if any, required to adequately characterize the dimensions and materials of construction of a structure. Figure 3 provides an example of the types of materials that were reviewed to establish the dimensions of a former gas holder foundation. Based on the review, it was determined that further field investigation was not required to obtain additional information associated with this particular structure. Conversely, Figure 4 depicts a basement floor plan of a former MGP structure. Review of this historical plant drawing resulted in identification of a data gap to assess the basement foundation.

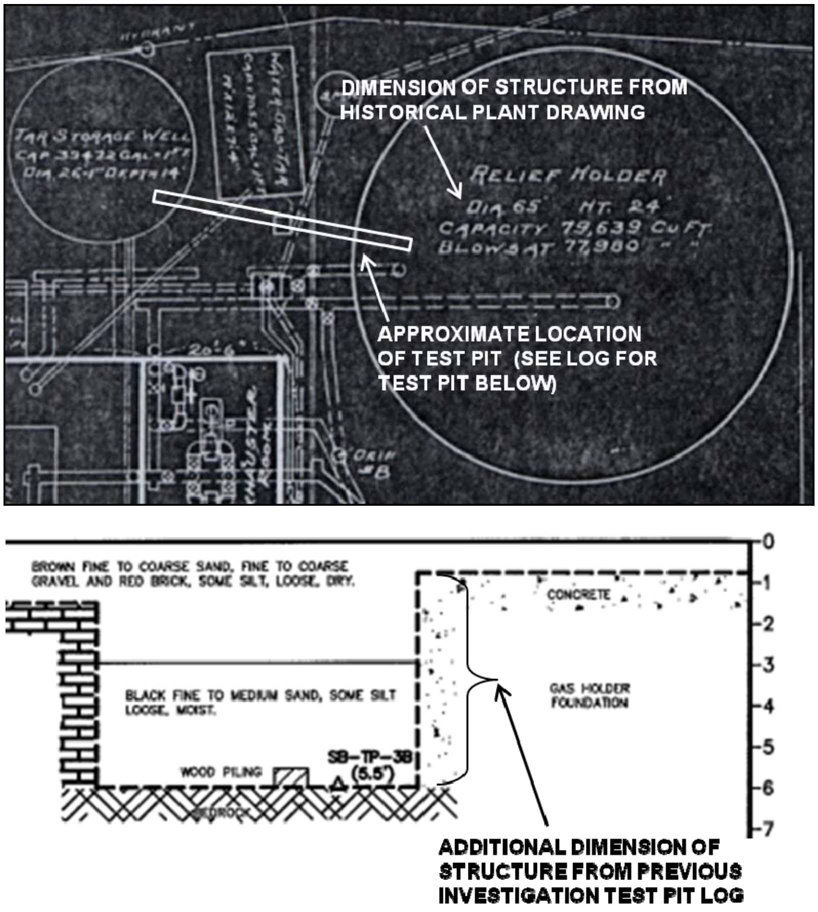


Figure 3. Additional investigation of structure <u>not</u> required based on review of available data.

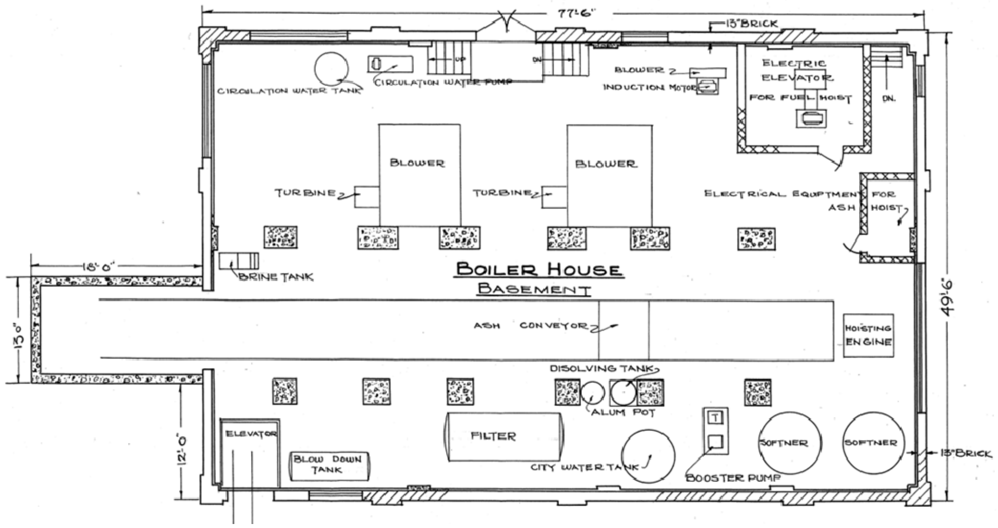


Figure 4. Additional investigation of structure required based on review of available data.

Results of the desktop evaluation were used to formulate a field program with its main objective being the collection of data associated with subsurface structures/obstructions identified during the desktop study where additional information was required to adequately confirm the presence of and characterize the dimensions of these features.

3.1 Field Investigation

The structures/obstructions that required further assessment, as determined during the desktop study, were evaluated using both non-intrusive and intrusive field methods.

3.1.1 Non-Intrusive Methods

A non-intrusive survey was performed prior to conducting intrusive PDI activities to identify potential utilities and other obstructions (i.e., former structures, foundations, etc.) adjacent to and within areas where remediation is planned. The identification of utilities/obstructions is intended to allow for the preparation of contingencies to remove and/or relocate obstructions prior to implementation of the remedy. The findings of the subsurface obstruction survey were used to confirm the locations identified during the desktop study as well as assess the presence/absence of additional potential subsurface structures, piping, and utilities not identified on existing site drawings.

The geophysical techniques used for the subsurface obstruction survey activities included ground-penetrating radar (GPR) using a GSSI SIR-2000 system, electromagnetics (EM) using a Geonics Ltd. EM-61MK2 metal detector and other potential subsurface obstruction identification methods (e.g., pipe and cable tracing). Once identified, geophysical anomalies interpreted to represent potential subsurface obstructions to remedy implementation were surveyed and plotted on an existing site plan.

3.1.2 Intrusive Methods

3.1.2.1 Coring through Structures

If a concrete structure was visible at the ground surface that will need to be removed to facilitate remedy implementation (e.g., foundation of a former above grade MGP-related structure, in order to determine its approximate thickness and characteristics), coreholes were drilled. Coreholes were drilled by means of conventional drilling techniques using a rotary drilling rig. Cores were collected until the base of the concrete structure was penetrated. Once penetrated, a spilt-spoon sampler was driven a few feet below the structure to verify that the structure did not extend further into the subsurface.

3.1.2.2 Soil Borings

Soil borings were completed for the purposes of estimating approximate thicknesses of foundation slabs and to characterize soils below building foundations adjacent to previously identified target areas for excavation. The soil borings were advanced using hollow stem augers and sampled with a split-spoon sampler from ground surface to a depth determined in the field based on the objective for the location.

3.1.2.3 Test Pits

Test pits were excavated at several locations to determine approximate dimensions of former MGP structures and foundations for existing site buildings. Annotated photographic logs were prepared to document observations from the test pits.

4. DATA AND ANALYSIS

4.1 Desktop Evaluation

As discussed above, results of the desktop evaluation were used to plan a field investigation to collect additional data to characterize dimensions of subsurface structures/obstructions. Table 1 provides an example of the process used for determining whether or not additional data collection was necessary to adequately characterize a subsurface structure/obstruction.

Table 1. Structure evaluation and design investigation activities.

Structure ID	Structure Description	Information Acquired To-Date	Information Source(s)	Planned Design Investigation Activity
1	Former Gas Holder/Relief Holder	Holder pad is composed of concrete and is approximately 5.25' thick; base of pad encountered at approximately 6' BGS and is set on top of rock. Diameter of holder pad: 65'.	Previous Investigation Locations: TP-3; Drawings: Drawing No. 1900-40.	Additional data collection not necessary.
18	Former Ammonia Liquor Storage Pad	Approximate 1' thick concrete footings encountered along perimeter of tank pad; approximate diameter of tank pad: 30'; thickness of pad unknown.	Previous Investigation Locations: TP-101A; Drawings: Site Plan.	Collect concrete cores to determine approximate thickness of pad.

4.2 Field Investigation

Results and findings from the field activities described in Section 3.1 are summarized in the following subsections.

4.2.1 Geophysical Survey

An EM-61 MK2 metal detector was used to conduct an EM survey. This detector records four measurements spaced by time (time gates) after an initial transmit pulse is emitted. Since the objective of the survey was to detect and delineate remnant structures and either abandoned or active utilities, a time gate that reads responses from large metal targets and shows the least interference from smaller targets was selected for displaying potential targets of interest.

Figure 5 presents the results of the EM survey next to a portion of a historical plant drawing that depicts the former MGP structures. In appearance, outlines and interior areas of remnant concrete pads, the majority of which are likely associated with former MGP operations, are evident from the data produced. This is due to the mere absence or relatively low amount of metal within the subsurface concrete associated with the former MGP structures. The apparent traces of the remnant concrete pads display a low metallic response, whereas areas outside of the former MGP structures exhibit a substantially greater metallic response as a result of buried utilities and/or metal objects in the subsurface or simply earth materials that are moderately conductive (i.e., electrolytic soils).

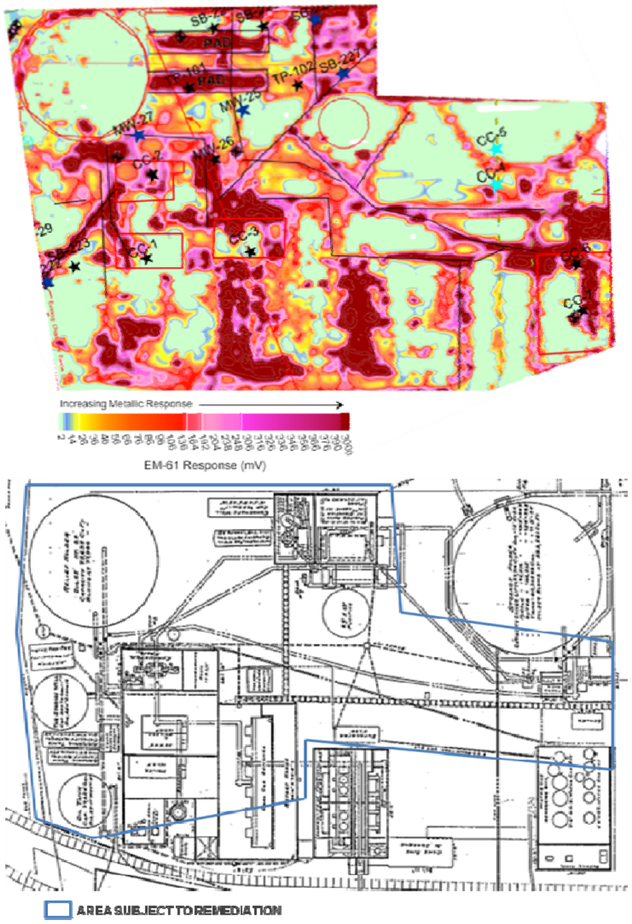


Figure 5. Geophysical survey results.

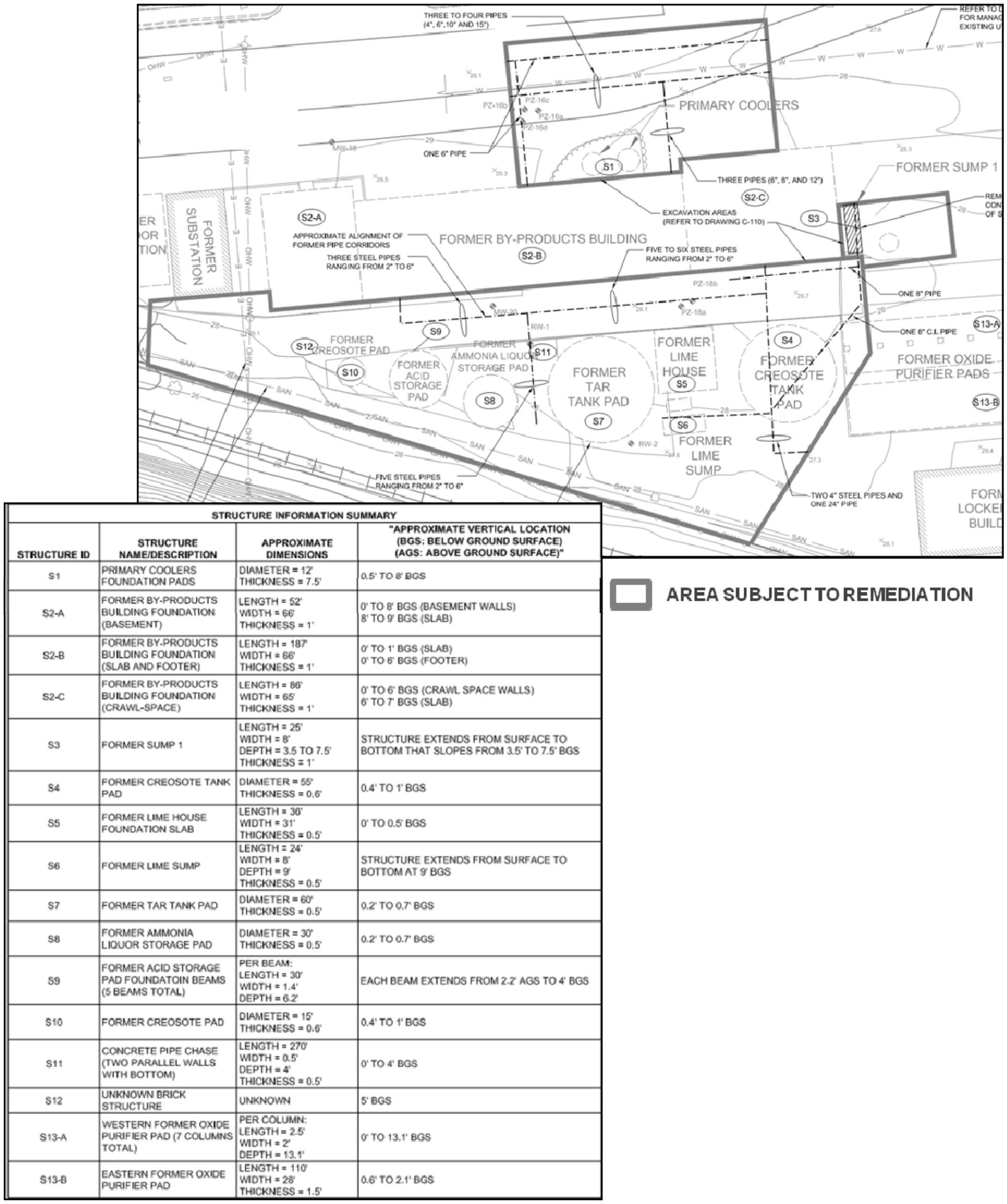
4.2.2 Structure, Pad, and Foundation Investigation

Written and photographic documentation of observations made during the intrusive investigation was prepared. Observations pertaining to the construction and dimensions of structures, pads and foundations were summarized in tabular form (see Table 2) for eventual incorporation into the final remedial design for the site.

Table 2. Structure, pad and foundation findings.

Structure ID	Structure Description	Structure, Pad and Foundation Findings
S9	Former Acid Storage Pad	5 east-west oriented concrete columns, approximately 1.4' wide and 30' long and extending from 2.2-0' above ground surface to 4' bgs; 4' bgs: split-spoon, auger, core barrel refusal on possible metallic bottom of former acid storage pad.
S13-A	Western Former Oxide Purifier Pad	0-13.1' bgs: Concrete, core was completed on a 2.5' x 2' concrete pad, approximately 5-7 pads exist in the area of the western former oxide purifier, pads presumably extend to top of rock surface.

Following completion of the pre-remedial design investigation activities, the findings from the investigation and data obtained previously were compiled to facilitate calculation of estimated structure demolition quantities. The findings resulted in calculation of approximately 860 cubic yards of concrete/masonry demolition for one of the former MGP sites that was evaluated. The compilation of the findings from the investigation activities conducted at the second MGP site is currently in progress. As demolition of these structures will be performed to facilitate implementation of the remedy, the volumetric estimate of the concrete to be removed during the remediation process will be included as part of the design documents to be provided to the remedial contractor. This will allow for the contractor to account for the effort to address these subsurface obstacles in their cost estimates. Structure demolition is typically accounted for by the remedial contractor in line items for mobilization and the use of equipment appropriate for demolishing structures (e.g., hoe ram, hydraulic hammer or equivalent attachment mounted on an excavator, backhoe or other conventional excavation equipment). In addition to the estimated structure demolition quantities, a structure demolition and decommissioning plan was generated (see Figure 6) as part of the final Remedial Design Report included as a component of the remedial contractor bid package.



STRUCTURE INFORMATION SUMMARY			
STRUCTURE ID	STRUCTURE NAME/DESCRIPTION	APPROXIMATE DIMENSIONS	"APPROXIMATE VERTICAL LOCATION (BGS: BELOW GROUND SURFACE) (AGS: ABOVE GROUND SURFACE)"
S1	PRIMARY COOLERS FOUNDATION PADS	DIAMETER = 12' THICKNESS = 7.5'	0.5' TO 8' BGS
S2-A	FORMER BY-PRODUCTS BUILDING FOUNDATION (BASEMENT)	LENGTH = 52' WIDTH = 66' THICKNESS = 1'	0' TO 8' BGS (BASEMENT WALLS) 8' TO 9' BGS (SLAB)
S2-B	FORMER BY-PRODUCTS BUILDING FOUNDATION (SLAB AND FOOTER)	LENGTH = 187' WIDTH = 66' THICKNESS = 1'	0' TO 1' BGS (SLAB) 0' TO 6' BGS (FOOTER)
S2-C	FORMER BY-PRODUCTS BUILDING FOUNDATION (CRAWL-SPACE)	LENGTH = 86' WIDTH = 65' THICKNESS = 1'	0' TO 6' BGS (CRAWL SPACE WALLS) 6' TO 7' BGS (SLAB)
S3	FORMER SUMP 1	LENGTH = 25' WIDTH = 8' DEPTH = 3.5 TO 7.5' THICKNESS = 1'	STRUCTURE EXTENDS FROM SURFACE TO BOTTOM THAT SLOPES FROM 3.5' TO 7.5' BGS
S4	FORMER CREOSOTE TANK PAD	DIAMETER = 55' THICKNESS = 0.6'	0.4' TO 1' BGS
S5	FORMER LIME HOUSE FOUNDATION SLAB	LENGTH = 36' WIDTH = 31' THICKNESS = 0.5'	0' TO 0.5' BGS
S6	FORMER LIME SUMP	LENGTH = 24' WIDTH = 8' DEPTH = 9' THICKNESS = 0.5'	STRUCTURE EXTENDS FROM SURFACE TO BOTTOM AT 9' BGS
S7	FORMER TAR TANK PAD	DIAMETER = 60' THICKNESS = 0.5'	0.2' TO 0.7' BGS
S8	FORMER AMMONIA LIQUOR STORAGE PAD	DIAMETER = 30' THICKNESS = 0.5'	0.2' TO 0.7' BGS
S9	FORMER ACID STORAGE PAD FOUNDATOIN BEAMS (5 BEAMS TOTAL)	PER BEAM: LENGTH = 30' WIDTH = 1.4' DEPTH = 6.2'	EACH BEAM EXTENDS FROM 2.2' AGS TO 4' BGS
S10	FORMER CREOSOTE PAD	DIAMETER = 15' THICKNESS = 0.6'	0.4' TO 1' BGS
S11	CONCRETE PIPE CHASE (TWO PARALLEL WALLS WITH BOTTOM)	LENGTH = 270' WIDTH = 0.5' DEPTH = 4' THICKNESS = 0.5'	0' TO 4' BGS
S12	UNKNOWN BRICK STRUCTURE	UNKNOWN	5' BGS
S13-A	WESTERN FORMER OXIDE PURIFIER PAD (7 COLUMNS TOTAL)	PER COLUMN: LENGTH = 2.5' WIDTH = 2' DEPTH = 13.1'	0' TO 13.1' BGS
S13-B	EASTERN FORMER OXIDE PURIFIER PAD	LENGTH = 110' WIDTH = 28' THICKNESS = 1.5'	0.6' TO 2.1' BGS

Figure 6. Structure demolition and decommissioning plan.

Using an estimated duration for demolishing the structures, which was based on an approximate demolition rate per volume of material from previously completed demolition activities at one of the MGP sites as part of an interim remedial measure (IRM), an approximation of cost can be made. For the site requiring demolition/removal of 860 cubic yards of concrete, it was estimated that the duration of the demolition work would be approximately five weeks. Use of an excavator with demo attachment (e.g., hoe ram or hydraulic hammer) for this period of time was estimated at approximately \$4,500 per week (including the labor cost for the excavator operator at approximately \$60 per hour) resulted in a cost of approximately \$37,500 to address the structures. When factoring in other costs associated with the demolition work such as Construction Quality Assurance inspection (labor and expenditures: approximately \$50,000) and air quality monitoring (approximately \$10,000), the total cost increase as a result of the need to address the structures could be as much as approximately \$100,000.

5. SUMMARY AND CONCLUSIONS

Using the above-described approach, characterization of the substantial subsurface impediments at two former MGP sites was accomplished. Results of the characterization process were used to estimate demolition/removal volumes related to the subsurface structures/obstructions. These volumes will eventually be provided as part of a remedial contractor bid package for use in developing a scope and cost to implement the remedy considering the structure demolition/removal. Refinement of the estimated volume of soil slated for removal and off-site treatment/disposal as part of the site remedies will also be performed based on the data from the structure characterization effort. The estimated volume of soils requiring removal will noticeably decrease from previous estimates prepared prior to conducting a PDI similar to the approach described above. This estimate would have been prepared when the volume of the subsurface structures/obstructions occupying areas of remediation is taken into account.

A higher level of cost certainty for remediation of former MGP sites where the need to address subsurface structures as a component of the remedy can be achieved through implementation of investigation activities such as those discussed above. Results from this type of investigation can be used to provide the entity responsible for remediation an increased assurance level of their cost certainty prior to initiating remedial construction at these sites. Recognition of the magnitude of the potential subsurface impediments prior to remediation will ultimately allow for the construction contractor to properly develop a scope and cost estimate, including the appropriate equipment for implementing remedial activities. Thus, the potential for remedial schedule delays and cost increases during the construction process will be substantially decreased.

6. REFERENCES

Calabrese, E.J., and Kostecki, P.T., 1991. Chapter 3, Issues at Manufactured Gas Plant Sites: An Overview of Research Programs. In: Hydrocarbon Contaminated Soils Volume I. (Menzie, C.A., Unites, D.F., and Nakles, D.V.). Lewis Publishers, Boca Raton, FL.

PART III: NAPL

Chapter 7

LASER INDUCED FLUORESCENCE INVESTIGATION OF LIGHT NON-AQUEOUS PHASE LIQUID, TROY MILLS LANDFILL SUPERFUND SITE, TROY, NEW HAMPSHIRE

Michael Asselin[1], Steven Lamb[2§], Robin Mongeon[3], Richard Hull[4], Michael Jasinski[5], Yoon-Jean Choi[6]

[1]GZA GeoEnvironmental, Inc., 380 Harvey Road, Manchester, New Hampshire, USA, 03103, [2]GZA GeoEnvironmental, Inc., 380 Harvey Road, Manchester, New Hampshire, USA, 03103, [3]New Hampshire Department of Environmental Services, 29 Hazen Drive, Concord, New Hampshire, USA, 03302, [4]U.S. Environmental Protection Agency, Region I, 5 Post Office Square, Suite 100, Boston, Massachusetts, USA, 02109, [5]U.S. Environmental Protection Agency, Region I, 5 Post Office Square, Suite 100, Boston, Massachusetts, USA, 02109, [6]U.S. Environmental Protection Agency, Region I, 5 Post Office Square, Suite 100, Boston, Massachusetts, USA, 02114.

ABSTRACT

This abstract has been prepared to summarize the findings from the Laser Induced Fluorescence (LIF) investigation of the Light Non-Aqueous Phase Liquid (LNAPL) area located near the LNAPL interceptor trenches at the Troy Mills Landfill Superfund Site in Troy, New Hampshire. The LIF field work was performed on September 9 through 11, 2011 in accordance with the August 2011 LNAPL Investigation Work Plan (Work Plan) approved by the New Hampshire Department of Environmental Services (NHDES) and the United States Environmental Protection Agency, Region 1 (EPA). This work was performed by GZA GeoEnvironmental, Inc. (GZA) with support from Columbia Technologies, Inc., Dakota Technologies, Inc. and GeoSearch, Inc. The strategy, planning, and field work were assisted by NHDES and EPA.

Keywords: Soil, pollution, soil investigation, light non-aqueous phase liquid, LNAPL, laser induced fluorescence, LIF, remedial strategies

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[§]Corresponding Author: Steven Lamb, GZA GeoEnvironmental, Inc., 380 Harvey Road, Manchester, New Hampshire, USA, 03103, Email: Steven.Lamb@gza.com

1. INTRODUCTION

The objectives of the LNAPL investigation were to:

- Estimate the current LNAPL extent (area of coverage);
- Measure the thickness of LNAPL / LNAPL-impacted soil in areas where encountered; and
- Further evaluate the potential source of the LNAPL plume.

Columbia Technologies of Baltimore, Maryland provided LIF testing services to address the objectives of this project. The fiber-optic-based fluorescence LIF system was deployed with standard direct push geoprobe equipment (which was provided and operated by GeoSearch, Inc.). The LIF system used a laser to induce a pulse of monochromatic light through a fiber optic line to a probe where the light is emitted and excites any polycyclic aromatic hydrocarbon-containing compounds in the subsurface, causing them to fluoresce with a characteristic wavelength signature. The induced fluorescence signal is returned over a separate fiber optic line to the surface where it is quantified using a detector system. The peak wavelength and intensity provide information about the type of petroleum product or potential interferences. The two types of technologies that were considered for investigating the LNAPL area at the Site were the UVOST® *(Ultraviolet Optical Screening Tool)* and TarGOST® *(Tar-specific Green Optical Screening Tool).* The UVOST® is a system for detecting residual-phase semi-volatile organic compounds (gasoline, diesel, kerosene, aviation fuel, machine oils, lubricants, and some crude oils). The uniqueness of UVOST® is the use of an exciter light rather than a solid state laser and the integration of the laser and detecting systems into a compact system. Use of the exciter and the system integration provides greater reliability, better reproducibility, and less room for operator error. (GZA, 2011)

TarGOST® is a system that is optimized for refractory petroleum products (coal tars, creosote, heavy crude) and other DNAPLs. The feasibility of using the LIF technology (including both *UVOST*® and *TarGOST*® technologies) at the Site was evaluated in June 2011. GZA collected a product sample from well TRY_MW-201S and submitted the sample to Dakota Technologies, (Fargo, North Dakota, (701) 237-4908) for testing. Testing results indicated that while both *UVOST*® and *TarGOST*® technologies had a good response signal, it was concluded by Dakota Technologies that the *UVOST*® system was more appropriate for the Site based on misleading scatter in the data results from the *TarGOST*® testing. (GZA, 2011)

2. MATERIALS AND PROCEDURE

Columbia Technologies operated the *UVOST*® system with a geoprobe system to investigate the subsurface LNAPL impacted soil. An initial soil boring grid was laid out at the site. Depending upon the real time LIF screening results of each investigation location, iterations of LIF soil screening were performed to identify where the LNAPL impacted soil was located. Sampling in an outward pattern away from the monitoring well where the thickest amount of LNAPL was performed until no LNAPL was detected. The area extent of LNAPL was identified and the highest LIF response signals identified the migration path of the LNAPL. The vertical thickness of the LNAPL impacted soil was measured at each LIF investigation location, and LNAPL thickness was measured at the LNAPL monitoring wells at the Site. The location of each LIF investigation location was recorded by using global positioning system (New Hampshire State coordinate system). (GZA, 2011)

3. DATA AND ANALYSIS

Table 1 summarizes the investigation findings for each subsurface LIF screening location. “LNAPL Impact” is defined as the presence of LNAPL and / or the LNAPL smear zone in the subsurface soil. The table also includes the impacted soil depth, the indicated thickness of the impacted soil, and the elevation of the top layer of impacted soil. The LIF maximum response signal, also included in Table 1, documents the maximum LIF response signal obtained at each probe location.

Figure 1 attached illustrates the locations of the LNAPL monitoring wells (TRY_MW-C1S through TRY_MW-C8S, plus TRY_MW-201S and TRY_MW-201P) and LIF soil investigation locations (A-1 through A-31) near the trench area. NHDES had requested GZA to evaluate the data in such a way as to define two areas of impacted soil (one area being considered a low impact area; and the other area being considered a higher impact area where the majority of the LNAPL contamination was located). The thickness of the LNAPL-impacted soil (as determined by the LIF system) was evaluated to determine the area of relative LNAPL smearing. GZA evaluated the data and considered a smeared thickness of one foot to be a differentiator. Area #1 shown on Figure 1 represents the area where the LNAPL smeared soil is less than a foot thick. In many parts of Area #1, the LNAPL smeared soil thickness is only 0.3 foot thick. Area #2 shown on Figure 1 represents the area where the LNAPL smeared soil is more than 1 foot thick and is the area that contains the majority of the LNAPL-impacted soil.

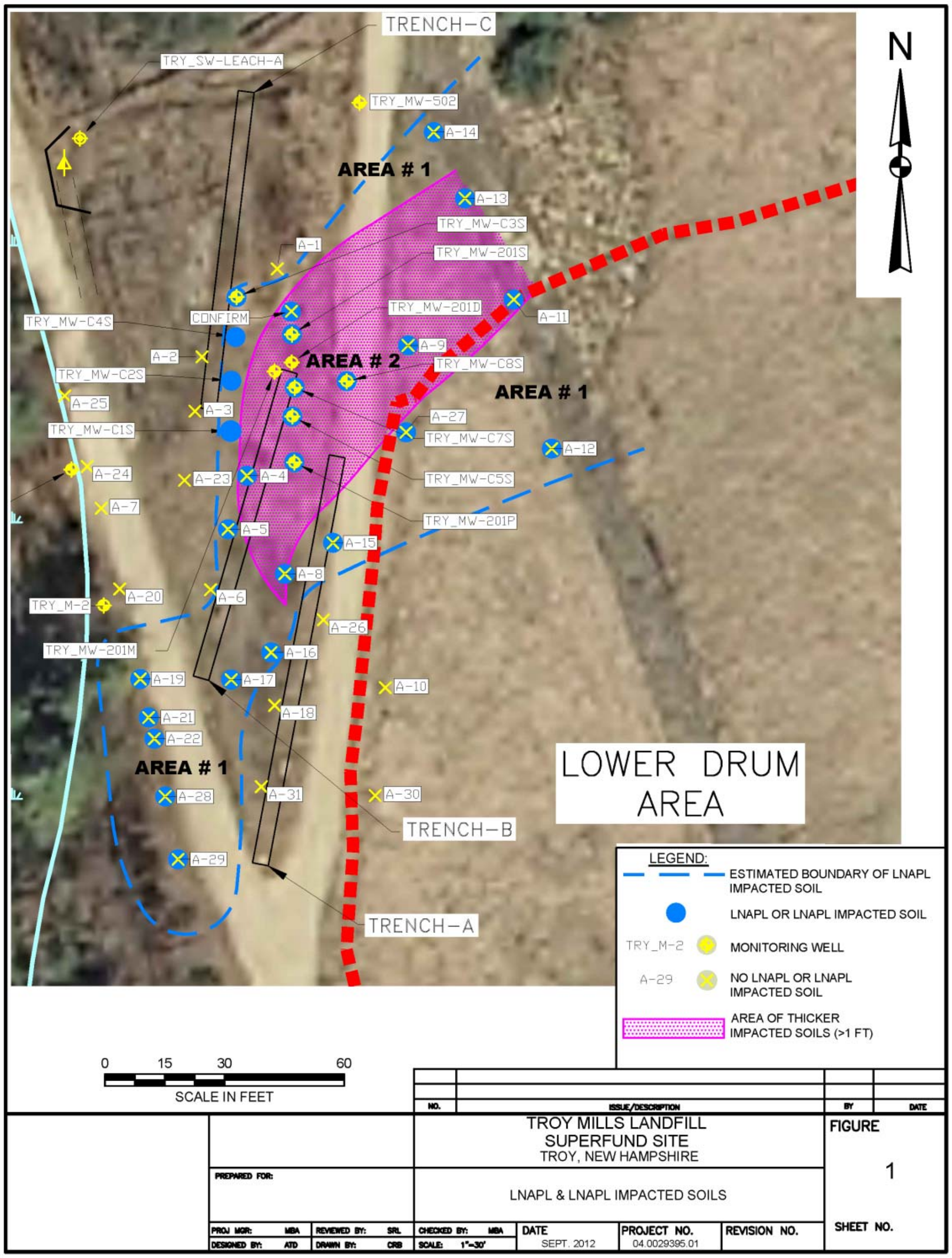

Figure 1. Troy Mills Landfill Superfund Site, Troy, New Hampshire

Table 1. LIF Findings of LNAPL AreaTroy Mills Landfill Superfund Site September 2011

LIF Investigation Location	**LNAPL Impact Detected ?**	**Impacted Soil Depth**	**Top of Impacted Soil**	**Impacted Soil Thickness**	**LIF Max Response Signal**
(See Figure X)	(Yes or No)	(Feet below ground surface)	(Elevation)	(Feet)	(Percent)
A1	No	---	---	---	5.2
A2	No	---	---	---	1.5
A3	No	---	---	---	1.5
A4	Yes	5.2 – 7 ft	1040.36	1.8 ft	26.4
A5	Yes	5.8 – 6.4 ft	1040.18	0.6 ft	5.2
A6	No	---	---	---	1.5
A7	No	---	---	---	1.4
A8	Yes	5.4 – 7.1 ft	1042.36	1.7 ft	5.8
A9	Yes	11 – 12.2 ft	1042.31	1.2 ft	6.2
A10	No	---	---	---	2.6
A11	Yes	11.5 – 14.4 ft	1045.37	2.9 ft	52.8
A12	Yes	14.4 – 14.7 ft	1044.23	0.3 ft	8.4
A13	Yes	12.1 – 13.4 ft	1043.56	1.3 ft	28.1
A14	Yes	13.6 – 13.9 ft	1042.14	0.3 ft	9.1
A15	Yes	6.2 – 6.5 ft	1044.37	0.3 ft	10
A16	Yes	5.5 – 6.2 ft	1042.20	0.7 ft	12.9
A17	Yes	6.4 – 6.7 ft	1040.79	0.3 ft	29.8
A18	No	---	---	---	2.6
A19	Yes	6.1 – 6.4 ft	1039.98	0.3 ft	6.3
A20	No	---	---	---	1.8
A21	Yes	7.2 – 7.5 ft	1039.71	0.3 ft	9.5
A22	Yes	6.2 – 6.5 ft	1041.11	0.3 ft	6.6
A23	No	---	---	---	1.5
A24	No	---	---	---	3.1
A25	No	---	---	---	1.8
A26	No	---	---	---	3.2
A27	Yes	7.8 – 8.7 ft	1045.19	0.9 ft	3.9
A28	Yes	7.8 – 8.3 ft	1040.65	0.5 ft	28
A29	Yes	6.5 – 6.8 ft	1043.67	0.3 ft	5.9
A30	No	---	---	---	2.5
A31	No	---	---	---	3.1
Confirm	Yes	7 – 10 ft	1040.53	3 ft	11.3
BAC	No	---	---	---	2.5

"Confirm" is confirmation sample near MW-201S; "BAC" is background sample located out of trench area and close to back gate.

Area #1 (approximately 3,100 square feet) shown on Figure 1 is represented by a blue dashed line on the figure to indicate the approximate area of LNAPL-impacted soil area outside of Area #2 and therefore is viewed as a low impacted area. Using the average thickness of LNAPL-impacted soil in Area #1 (0.42 feet average thickness), the estimated volume of LNAPL-impacted soil in Area #1 is approximately 1,302 cubic feet or 48.2 cubic yards. Area #2 (red / purple shaded area) shown on Figure 1 represents the estimated area where the LNAPL-impacted soil thickness was 1 foot or greater. This area would most likely represent the more contaminated soil that would contain the majority of the current liquid LNAPL material. This area is estimated to be approximately 2,900 square feet. Using the average thickness of LNAPL-impacted soil in Area #2 (1.98 feet), the estimated volume of LNAPL-impacted soil in Area #2 is approximately 5,742 cubic feet or 212.7 cubic yards.

The data generated during the investigation indicates that the LNAPL migration path originates from an area east by northeast of Trench C (which implies that the former drum burial area is the likely the former source of the LNAPL). The geoprobe was unable to investigate the area east / northeast of investigation locations A-11 and A-13 due to the steep slope of the former drum burial area and the increased depth of the groundwater table (30 feet below ground surface) from the top of the former drum burial area. There may have also been subsurface obstacles buried in this area (i.e., subsurface liner, textile materials, etc.). Soil sampling performed at a later date did not detect LNAPL in the former drum burial area. (GZA, 2011)

4. CONCLUSION

The LNAPL impacted soil area in the trench area is approximately 6,000 square feet, and based on the average thickness assumptions presented above, would contain approximately 261 cubic yards of LNAPL-impacted soil.

The LIF investigation results shown on **Figure 1** indicates that the LNAPL material has historically flowed toward the wetland at LIF investigation locations A-19, A-21, A-22, A-28, and A-29 (at least after the installation of the trenches). These locations contain LNAPL-impacted soil and border the wetland area.

Based on a projection of the LIF response signal data in an upgradient direction, the historic source of the LNAPL observed in the trench area appears to be east of the trench area.

5. REFERENCES

GZA. 2011. GZA GeoEnvironmental, Inc., Summary of LNAPL Investigation, Troy Mills Landfill Superfund Site, NHDES Site No. 198405082, CERCLIS ID No. NHD980520217, NHDES One-Stop Document Storage System, Final Report, December 19, 2011.

Chapter 8

RELATIONSHIP OF LIGHT NONAQUEOUS PHASE LIQUID THICKNESSES VERSUS GROUNDWATER ELEVATION TRENDS AT A REMEDIATION SITE IN WESTERN MASSACHUSETTS

Nancy E. Milkey[§]
Tighe & Bond, Inc., 53 Southampton Road, Westfield, MA 01085

ABSTRACT

In 1968, a release of petroleum was identified at an undeveloped property downgradient of a former drop forge which operated from approximately 1900 through 1979. Subsequent delineation of the release determined that the source was within the industrial building area housing the drop forge. In August 1990, nine fuel oil underground storage tanks (USTs) were removed from the industrial complex. While installation dates are not clearly documented, the tanks may have been installed as early as 1909. During the removal, large holes were identified in the USTs where gauging sticks had punctured the bottom of the tanks.

The site is surrounded by water on three sides and historically sheens have been observed on the surface water. In 1992, three 36-inch recovery wells were installed in two areas of the site to prevent future outbreaks of fuel oil to the adjacent surface water. These initial three wells were supplemented with 20 additional recovery wells in the 1990s and early 2000s.

Prior to installing the additional recovery wells, a detailed hydrogeologic investigation was completed to identify the presence of preferential pathways and provide data for the design of a comprehensive hydraulic and physical barrier. An extensive soil boring program, including the use of a cone penetrometer, was undertaken. The results of the investigation indicated that the majority of contaminant transport is occurring through a sand and gravel layer located at depth.

Extensive gauging of light nonaqueous phase liquid (LNAPL) thicknesses has been conducted at the site since assessment and remediation were initiated at the property. Over 80 monitoring and recovery wells are located throughout the site

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[§] Corresponding Author: Nancy E. Milkey, P.G., LSP, Tighe & Bond, Inc., 53 Southampton Road, Westfield, MA 01085, Email: NEMilkey@tighebond.com

providing an extensive network of monitoring points. The data has been evaluated to identify trends in the LNAPL thicknesses to assist with the remedial efforts and evaluate plume migration.

Keywords: groundwater, pollution, petroleum, light nonaqueous phase liquid, remediation

1. INTRODUCTION

The subject property is a former drop forge located on Depot Street in Chicopee, Massachusetts. The site and much of the surrounding area has a long history of industrial use. Historically, the subject parcel had been used by the Moore Drop Forge Company (MDF) for forging steel parts and related operations. Operations at the facility included die machining, shearing, hot forging, heat treating, shot blasting, pickling, metal washing, grinding, welding and salt bath heat treating. MDF and its successors operated on the property from approximately 1900 to 1979.

In 1968, a release of petroleum was identified at an undeveloped property downgradient of the former drop forge. Subsequent delineation of the release determined that the source was within the industrial building area housing the drop forge. In August 1990, nine fuel oil underground storage tanks (USTs) were removed from the industrial complex. While installation dates are not clearly documented, the tanks may have been installed as early as 1909. During the removal, large holes were identified in the USTs where gauging sticks had punctured the bottom of the tanks.

The site is located at the confluence of the Chicopee and Connecticut Rivers and is surrounded on three sides by water. It consists of approximately 16-acres of land which is primarily undeveloped open space. The industrial buildings, which were located on the northeastern portion of the site, were demolished between 2003 and 2004.

1.1 Release History

The earliest record of environmental releases being identified at the site was a 1968 Field Memorandum prepared by the Massachusetts Water Resources Commission/Division of Water Pollution Control (WRC/DWPC) dated September 25, 1968. The Memorandum indicated that the ground in an unidentified excavated area of the MDF site was "deeply saturated with oil." The memorandum stated that a superintendent for MDF had arranged to have a pit excavated with a bulldozer near the flood control dike to determine the source of the previously reported oil outbreaks. Water flowing into the pit from the berm area was observed to have oil on the surface.

Since that time, extensive investigation has been conducted at the site to identify the source of the petroleum and a limited pump and treat system began operating in the early 1990s. Initial remedial efforts focused on preventing free phase petroleum outbreaks to surface water (the Depot Street Ponds, seasonally-flooded wetland areas on the west side of the site, and an adjacent hydroelectric canal). One recovery well, operating with a two pump system, was installed upgradient of each of these surface water receptors. In the late 1990s, this system was expanded and the two recovery wells on the south side of the site were supplemented with a 350-foot Waterloo Barrier® and seven additional recovery wells which effectively stopped additional releases to the adjacent ponds and Dwight Canal.

Six additional recovery wells were installed in the "RW-3 Area," to the west of the former industrial area, and once the buildings were demolished, additional recovery wells were installed in the source area.

Prior to installing the additional recovery wells, a detailed hydrogeologic investigation was completed to identify the presence of preferential pathways and provide data for the design of a comprehensive hydraulic and physical barrier. An extensive soil boring program, including the use of a cone penetrometer, was undertaken. The results of the investigation indicated that the majority of contaminant transport is occurring through a sand and gravel layer located at depth. The locations of the recovery and monitoring wells in the RW-3 Area of the site are shown in Figure 1.

1.2 LNAPL Monitoring

As part of the operation and maintenance of the remediation system, 53 monitoring wells are gauged on a monthly schedule. These wells are located across the site at varying distances from the adjacent surface water bodies. The depth to groundwater and LNAPL thicknesses are measured and recorded in each well. If LNAPL is identified in a monitoring well, it is removed with a bailer and disposed of in the oil/water separator of the remediation system.

Due to the long-term operation of the system, we have over 20 years of gauging data from numerous wells at the site. While evaluating this data, several trends have been identified which will be discussed in subsequent sections of this article.

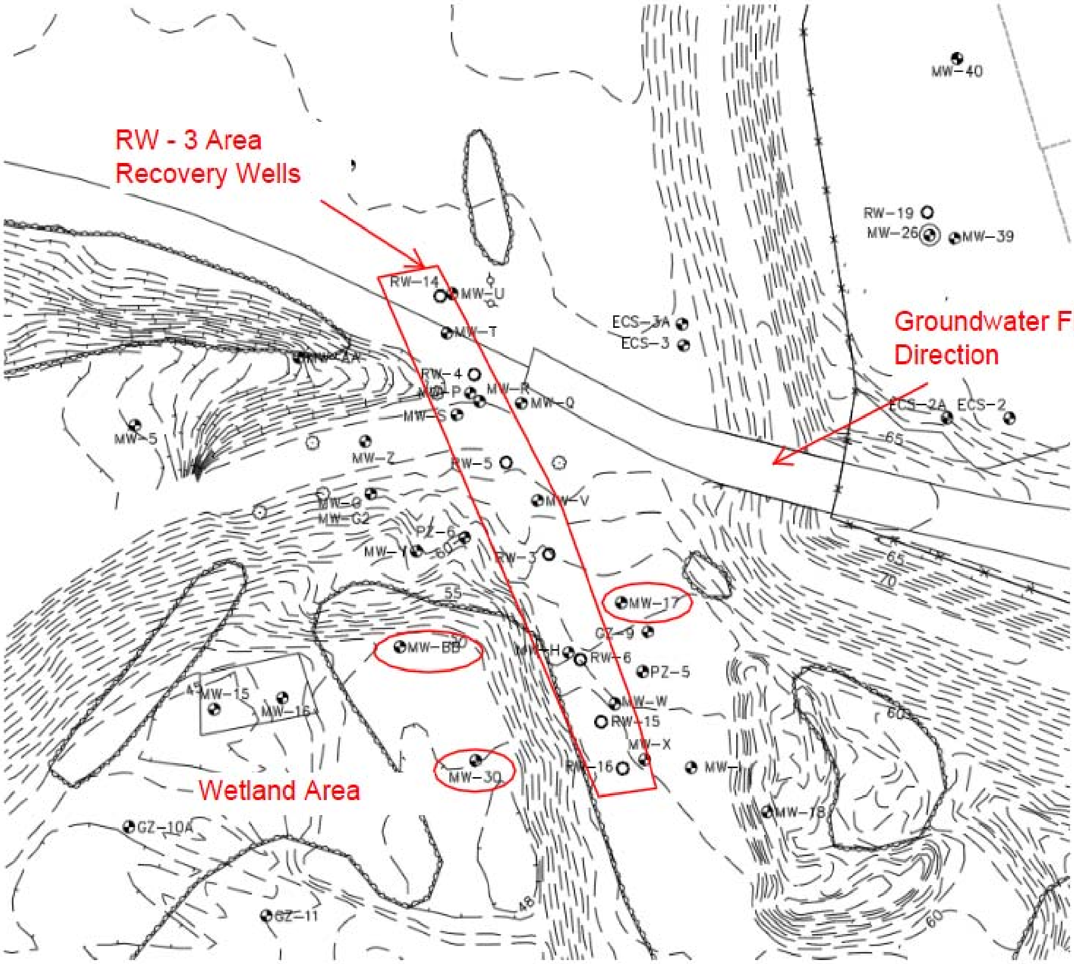

Figure 1. Monitoring and Recovery Well Locations – RW-3 Area

2. LNAPL BEHAVIOR

Numerous regulatory guidance documents and research have been published regarding the behavior and migration of LNAPL in various subsurface environments. The assessment and remediation of LNAPL releases is complicated because they are influenced by the physical characteristics of the LNAPL (viscosity, volatility, etc.) and the characteristics of the subsurface environment (hydraulic gradient, porosity, grain size, hydraulic conductivity, etc.).

One of the characteristics of LNAPL that has generated a lot of interest is fluctuations in the thickness of LNAPL in monitoring wells. Numerous states and regulatory agencies base their remedial goals and the ability to close a LNAPL site on the thickness of measureable product in "a groundwater monitoring well or otherwise observed in the environment" (Massachusetts Contingency Plan, 1993).

However, research has shown that the thickness of LNAPL fluctuates within wells based on changes in groundwater elevations. These fluctuations correspond to changes in the volume of mobile and residual LNAPL in the formation. As the water table rises, the LNAPL is displaced from the pore spaces, and oil becomes trapped as isolated droplets. As the water table drops, the LNAPL is able to drain from the pore spaces. However, some of the oil remains as residual oil, creating the typical smear zone that is observed at many LNAPL sites (API, 2004).

3. SITE-SPECIFIC OBSERVATIONS

The data from January 2010 through June 2012 for three monitoring wells (MW-17, MW-BB, and MW-30) located in what is referred to as the RW-3 Area (named for the original recovery well installed in this area of the site) has been graphed in Figures 2, 3, and 4, respectively. The locations of the monitoring wells in relation to the recovery wells and groundwater flow are shown on Figure 1. The LNAPL thickness in each well was graphed versus groundwater elevations as measured at each location. As can be seen in each of the figures, large fluctuations in LNAPL thickness are regularly measured in each well.

Monitoring wells MW-BB and MW-30 are located in a seasonally-flooded wetland area on the downgradient side of a hydraulic barrier in the RW-3 Area. Both of these wells exhibit large fluctuations in groundwater elevations due to the shallow depth to groundwater and their proximity to the adjacent surface water bodies (which fluctuate seasonally and with precipitation events). As the groundwater table fluctuates, the LNAPL thicknesses vary.

As is referenced throughout the literature, the LNAPL thicknesses typically increase as groundwater levels drop (API, 2004). As the water table drops, the LNAPL may increase in thickness in a monitoring well due to drainage from the unsaturated zone. This will result in an increased apparent thickness in that well (Newell et al. 1995).

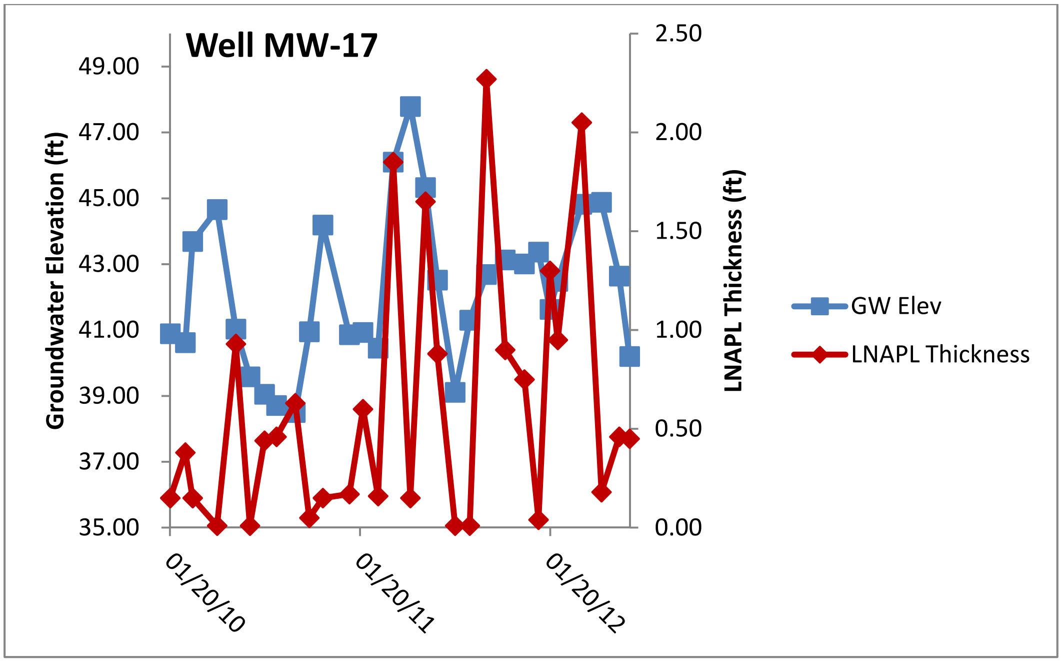

Figure 2. LNAPL Thickness versus Groundwater Elevation – Monitoring Well MW-17

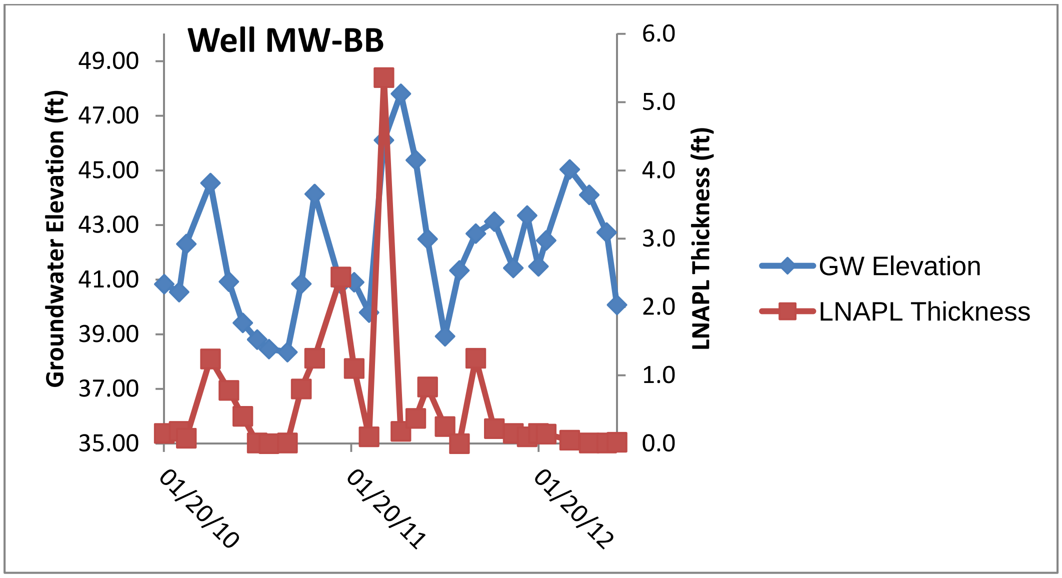

Figure 3. LNAPL Thickness versus Groundwater Elevation – Monitoring Well MW-BB

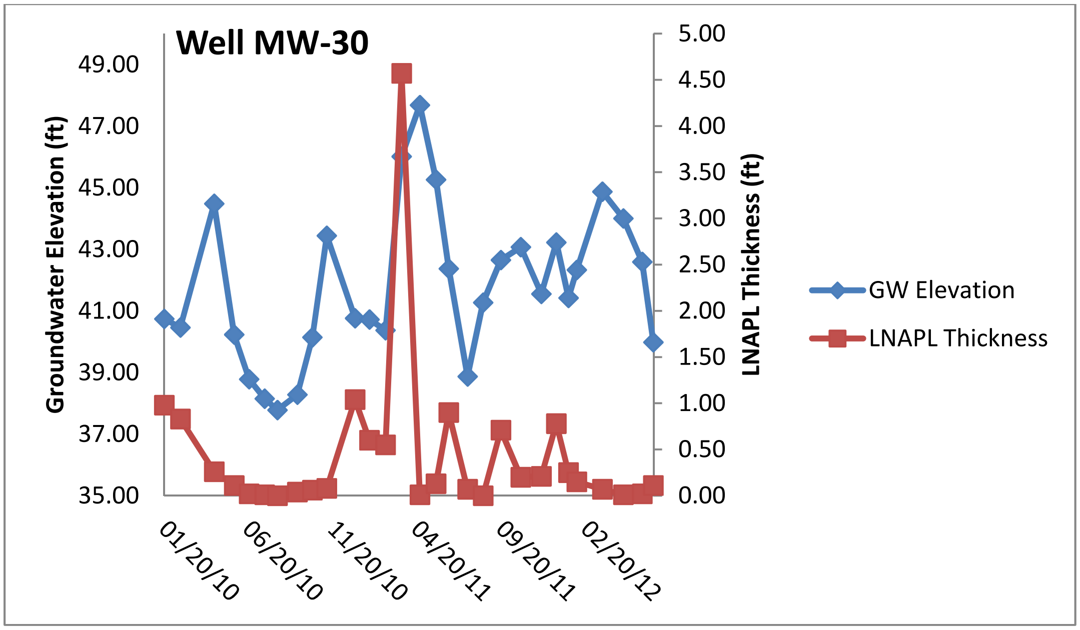

Figure 4. LNAPL Thickness versus Groundwater Elevation – Monitoring Well MW-30

4. CONCLUSIONS

The Delta Park site is located in close proximity to multiple surface water bodies (Chicopee and Connecticut Rivers and a hydroelectric canal) that cause large fluctuations in groundwater elevations at the site. Due to a long history of petroleum releases at the subject property, LNAPL has been detected in numerous wells across the site. The LNAPL thicknesses exhibit a typical pattern of fluctuation in relation to groundwater elevations.

Many regulatory agencies determine the ability to "close" a site with LNAPL based on the thicknesses of LNAPL measured in wells. As is demonstrated in the examples presented from this site, LNAPL thickness is a poor indicator of the quantity or mobility of LNAPL present in the formation at a site.

5. REFERENCES

API (American Petroleum Institute). 2004. *API Interactive LNAPL Guide*. Release 2.0.2.

Massachusetts Department of Environmental Protection, 1993. *Massachusetts Contingency Plan.* 310 CMR 40.0000. As amended.

Newell, C.J., S.D. Acree, R.R. Ross and S.G. Huling. 1995. Light *Nonaqeous Phase Liquids*. Environmental Protection Agency Ground Water Issue, EPA/540/S-95/500.

PART IV: PCBs

Chapter 9

POLYCHLORINATED BIPHENYLS IN BUILDING MATERIALS AS A SOURCE OF SOIL CONTAMINATION: ENVIRONMENTAL IMPACTS OF REMEDIAL OPTIONS AND CASE STUDY

Susan Cahalan[§], Denise Bartone
CDW Consultants, Inc., 40 Speen Street, Suite 301, Framingham, MA, USA

ABSTRACT

Polychlorinated biphenyls (PCBs) can be present in buildings that were constructed or renovated from the mid-1950s to the late 1970s. Substantial concentrations of PCBs can exist in paints, caulking around windows and doors, and expansion joints. The Toxic Substances Control Act (TSCA, 40 CFR Part 761) prohibits material with PCB levels exceeding 50 parts per million (ppm), and the U.S. Environmental Protection Agency considers this to be an “unauthorized use” of PCBs. Building materials containing PCBs are a known source of contamination in building interiors and surrounding soil. Soil contamination around buildings occurs from disturbance during renovations, natural weathering and deterioration of the building materials. PCBs mobilize from sealants to surrounding materials, air and to the ground.

Remedial action is critical for the management of PCB contaminated sites. However, the practice of disposing of PCB remedial waste (soils) in landfills should be reconsidered due to the mobility of PCBs. Volatilization of PCBs can occur through surrounding air channels. Furthermore, the potential failure of leachate collection systems can result in PCB migration into groundwater. There are several evolving remedial options for PCB contaminated soils that can be grouped into two basic categories: incineration and non-incineration. There are environmental implications of the remedial method chosen. For example, high

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[§] Corresponding Author: Susan Cahalan, CDW Consultants, 40 Speen Street, Suite 301, Framingham, Massachusetts, USA, 01756, Tel: 508-875-2657,
Email: scahalan@cdwconsultants.com

temperature incineration is energy intensive, and produces greenhouse gases and toxic emissions. Other remedial methods can mobilize additional contaminants present, and chemicals added for dechlorination may impact groundwater supplies. Therefore, remedial options for PCB contaminated soils should be evaluated for environmental impacts, as well as monetary costs.

Keywords: Polychlorinated biphenyls, soil, building materials, remediation

1. INTRODUCTION

Polychlorinated biphenyls (PCBs) are synthetic chlorinated chemicals that are persistent and widespread in air, water, soils and sediments. PCBs are ubiquitous in the general environment and are transported by wind and water. PCBs bind strongly to organic particles in the water column, atmospheric particulates, sediments, and soil. The deposition of particulates from the atmosphere is largely responsible for their accumulation in sediments and soils. Another source of PCB contamination is the use of PCBs in building materials, which are found in a wide variety of commercial/industrial buildings, schools and hospitals. Weathering and volatilization of PCBs from building materials contaminate surrounding soils that can lead to exposures to humans and animals. Most concerning, because of their toxicity, is the PCB contamination of soil around schools. There are existing and emerging remediation technologies for PCB contaminated soil; however, the method of remediation chosen however can have deleterious results.

2. MATERIALS AND METHODS

A literature review of PCBs in building materials such as caulking, glazing and expansion joints as a source of PCBs in surrounding soils was explored. Documented and emerging remedial options were reviewed. The literature search was conducted within the Harvard Library electronic journals system. The search yielded journal articles summarizing evidence that PCBs in building materials are a source of contamination to soils. Furthermore, the search yielded numerous experimental studies and evaluations of existing remediation processes. Reviewed below are a few of the latest studies.

3. DISCUSSION

3.1 Building Materials as a Source of PCB Contamination in Soil

PCBs do not occur in nature; therefore, all PCBs found in the environment originate from man-made materials. PCBs are classified as persistent organic pollutants (POPs) due to their chemical and physical properties. The chemical formula for a PCB is $C_{12}H_{10-x}Cl_x$ and the molecular structure consists of 2 to 10 chlorine atoms attached to two benzene rings (biphenyl) (ATSDR, 2000). There are 209 congeners, which are a variation of the number and position of the chlorine atoms. The physical properties of PCBs include: a low flash point, low partition coefficient, and is not readily soluble in water, but is soluble in oils. The solubility in water decreases with an increase in the degree of chlorination (Cornelissen et al., 2009). These properties are favorable for use in industrial applications because of chemical inertness, high electrical resistivity, and thermal stability. Most PCBs were added to reduce the flammability and increase the stability of mineral oils used as dielectric fluids in electrical transformers and capacitors, including the small transformers in fluorescent light fixtures. PCBs were also commonly used as a plasticizer in building materials such as joint sealers, window caulking, glazing, paint, and plaster (Herrick et al., 2007).

PCBs were commercially produced from 1929 to the 1970s. Due to growing public and scientific concerns about their toxicity, persistence, and global distribution, PCBs were phased out of production by the late 1970s (EPA, 1998a). Since PCBs are no longer being manufactured or used in large quantities (ATSDR, 2000), the compounds are predominantly redistributed from sources such as landfills, hazardous waste sites, old equipment, and building materials, to the soil, water, air and sediments. The release of PCBs into the environment from building materials comes from volatilization, weathering, or abrasion from eolian forces (Herrick et al., 2004).

PCBs are a ubiquitous environmental contaminant that are known or suspected to cause a wide range of human health and ecosystem effects. PCBs have significant toxic effects on the immune system, reproductive system, nervous system, and the endocrine system (ATSDR, 2012).

There are numerous studies that focused on the contamination of the surrounding environment from buildings where PCBs are present in building materials. Overall, the sources of PCBs in the soils were attributed not only to the process of renovation, but also from weathering and deterioration. One benchmark study in Bergen, Norway had results showing that the PCB product used in building materials is reflected in the adjacent surface soils (Andersson et al., 2004). This was determined when the PCB congeners in the building material showed the same relative pattern as the adjacent surface soil. Additionally, the PCB concentration in the surface soil was higher than the corresponding building material, which was due to the high organic matter content of the soil.

The Toxicity Characteristic Leaching Procedure (TCLP) is a soil extraction chemical analysis method used to simulate chemical leaching through a landfill. This method is also used to evaluate the mobility of PCBs from building materials to soil. In another study (Herrick et al., 2007), PCB contaminated soil had levels ranging from 3.3 to 34 milligrams per kilogram (mg/kg) around buildings with undisturbed caulking, which contained 10,000 to 36,200 mg/kg PCBs. The results of the TCLP (leachate concentrations of 76–288 mg/L) suggest that PCBs in caulking can be mobilized with dissolved organic matter that also leach off the caulking material (Herrick et al., 2007).

3.2 Case Studies

A pre-demolition hazardous building assessment was conducted at a high school, where approximately 200 faculty/staff and 1,300 students attended. The building is approximately 234,000 square feet and consists of the original 1938 high school structure and numerous additions (1955, 1963, 1979 and 2002). As part of the hazardous building assessment, samples of suspect PCB-containing caulking/expansion joints throughout the interior and exterior of the building were sampled for laboratory analysis of PCBs via Environmental Protection Agency (EPA) Soxhlet extraction 3540C/8082 (EPA, 1998b). Window caulk from the 1955 and 1963 wing contained PCBs at an average concentration of 6,800 mg/kg.

Soil samples were collected from beneath the window banks where the caulking contained an average PCB content of 6,800 mg/kg. A total of 129 soil samples were collected in a grid pattern (0.5’, 5’ and 8’ from the building). The soil samples were collected for laboratory analysis of PCBs via EPA Soxhlet extraction 3540C/8082. Soils ranged in concentration from 1.5 to 3.4 mg/kg PCBs, but nearly all samples had detectable concentrations of PCBs. The aroclor (1548) detected in the soil was similar to the aroclor in the caulking material, indicating that the mobilization of PCBs from the caulk to the soils is from weathering.

At another school property, a pre-renovation hazardous building assessment was conducted. The 67,000 square foot elementary school opened in 1963, with an addition built in 1988. Window and curtain wall caulking was collected for laboratory analysis of PCBs via EPA Soxhlet extraction 3540C/8082. PCBs concentrations of the window caulking averaged 10,000 mg/kg and the curtain walls averaged 6,000 mg/kg. The curtain wall caulking was installed in 1999, according to school officials. Thus, even though the production and use of PCBs were banned in the 1970s, building products from foreign markets can contain

PCBs, and at high concentrations. Post abatement soil samples collected from the school property did not contain any detectable concentrations of PCBs. This may be because the topography surrounding the school protected the building, and the PCB containing caulk was not highly weathered.

4. REMEDIAL TECHNOLOGIES AND ENVIRONMENTAL EFFECTS

4.1 Land Filling

In many cases, soil concentrations of PCBs from building material leaching are not characteristic of hazardous waste (>50 ppm); therefore, the soils are excavated and transported offsite to a non-hazardous landfill. Excavation and disposal of PCB contaminated soil in landfills is a cost effective and proven technology for remediation. The landfilling POPs, such as PCBs, can have significant adverse environmental consequences because of their mobility and persistence. PCBs will persist in landfills for long periods of time and eventually leach into groundwater, surface water, and air. Leachate is formed when rainwater percolates through the waste and mobilizes pollutants. Often the PCBs in the leachate can reach the environment relatively unchanged and pollute groundwater, surface water and sediments. Over extended time periods, the engineered landfill systems may degrade before the POPs, posing a future risk of releasing large quantities to the environment (Weber et al., 2011).

In a study by (Ham et al., 2008), it was found that the concentration of PCBs can eventually decrease with landfill age and changing precipitation patterns. Also, the leachate concentration of PCBs increased with an increasing ratio of biodegradable wastes, thus the leachability of POPs from landfills is influenced by the dissolved organic matter from biodegradable wastes (Ham et al., 2008).

PCBs can also become dechlorinated under anaerobic conditions in landfills. In a study by (Rodenburg et al., 2010), water samples of all 209 PCB congeners demonstrated strong dechlorination signals. This analysis suggested that under the right conditions, PCBs can be inadvertently be remediated to a less toxic form.

4.2 Incineration

PCB impacted soils can be remediated by incineration. Incineration occurs at high temperatures (870 to 1,200 °C), and the PCBs are volatilized in the presence of oxygen. The destruction removal per PCBs is 99.9999%. Most of the operating incinerators in the United States are rotary kiln or fluidized bed incinerators (Asher et al., 2012).

Incinerator off-gas requires treatment by an air pollution-control system to remove particulates and neutralize and remove acid gases (HCl, NO_x, and SO_x). Incineration is subject to a numerous regulations, including; CAA (air emissions), TSCA, RCRA, NPDES, and NCA (noise) (Asher et al., 2012).

The waste streams produced by incineration include solids, cooling water and emissions from the incinerator. Ash is commonly either air-cooled or quenched with water after discharge from the combustion chamber. Dewatering or solidification/stabilization of the ash may also have to be applied since the ash could contain leachable metals at concentrations above regulatory limits (FRTR, 2012). However, the general acceptance of incineration as a means of disposal for PCB-contaminated materials has declined because of concerns about incomplete incineration and the possible formation of highly toxic by-products, such as hydrogen chloride and polychlorinated dibenzodioxins (Rivera-Austrui et al., 2011).

In one study in Canada (Asher et al., 2012), a signatory country to the Stockholm Convention on Persistent Organic Pollutants, is destroying all of its remaining stockpiles of PCBs, including soils. Most of these wastes are incinerated at the Swan Hills Treatment Center, a permanent incinerator facility. Despite destruction efficiencies of 99.999%, numerous air and soil study data has shown significant PCB contamination in the region around the treatment plant.

In another study in India (Thacker et al., 2012), numerous air samples were collected for laboratory analysis of PCBs and dioxins during 2009-2010. The air samples were collected in cities where incinerators and thermal treatment plants were located. The concentrations of dioxin-like PCBs ranged from 0.0070 to 26.8140, the toxicity equivalent in nanograms per meter squared (ng TEQ/Nm3). The concentration range of dioxin-like PCBs were higher than the regulated limit of (0.1 ng TEQ/Nm3) (Thacker et al., 2012) permitted in emission gases from large waste incinerators. The results of the air sampling suggests that there is unstable combustion in incinerators and thermal processes, and “imply that the gas cooling facilities of most incinerators cannot control general pollutants in emissions, let alone dioxin-like PCBs” (Thacker et al., 2012).

4.3 Solidification/Stabilization

Waste stabilization involves the addition of a binder, cement, asphalt or fly ash to a waste product to convert contaminants into a less soluble, mobile, or toxic form. Solidifying waste reduces permeability, which coincides to less leaching. This form of encapsulation, when applied to PCB contaminated soil, may reduce mobility, but does not concentrate or destroy them (USEPA, 2012).

4.4 Bioremediation

Biodegradation refers to the breakdown of compounds by microorganisms. Bioremediation uses existing bacteria that are stimulated by the addition of oxygen and nutrients. Additionally, augmentation is done by making use of exogenous bacteria. Bacteria and prokaryotes are documented to biodegrade complex organic compounds to simpler ones, and completely mineralize others. Bioremediation of contaminated soil and sediment can occur in the presence of oxygen (aerobically) or under near oxygen-free conditions (anaerobically) (McDermott et al., 1989).

PCBs are considered resistant to biodegradation. Several ongoing laboratory and field studies indicate that PCBs can biodegrade even with a high degree of chlorination, but at a slow rate (Anyasi and Atagana, 2011). However, the potential direct emissions from anaerobic and aerobic PCB decomposition were not known nor considered. Though some studies show promise, a process for accelerating PCB biodegradation rates are not commercially viable at this time. Furthermore, literature search on bioremediation processes for PCBs in soil either were bench scale with laboratory contaminated soils, or in situ for soils contaminated by PCB-laden carrier oils. Laboratory created contaminated soils may not show the same properties as those in the field due to age, weathering, and non-homogeneous distribution of PCBs.

4.5 Vitrification

Vitrification can be used to treat soil and sediment containing organic, inorganic, and radioactive contaminants. Vitrification technology uses heat (1600-2000°C) to melt the contaminated soil or sediment, which forms an obsidian-type glassy end product. PCBs can be destroyed by the high temperatures used during vitrification. The glass-type waste will mostly pass TCLP tests and resists corrosion (Dàvila et al., 1993).

In-situ vitrification is successfully used to treat PCB-contaminated soils. One such project involved a Superfund site in EPA Region 10, Washington State. According to the EPA, "the maximum PCB concentration in the soil was 17,860 ppm. The project was used as an official demonstration for the EPA under the provisions of the TSCA. The contaminated soil and debris were collected from around the site and staged into a treatment cell to a depth of approximately five meters. The volume was processed by five melts to create one contiguous monolith. This process satisfied all performance criteria established for the project as follows:

- stack gas emissions requirements were fully satisfied; independent stack sampling determined that the total destruction/removal efficiency for the PCBs was greater than 99.9999% and there were no PCBs or congeners detected in the stack gases;
- the vitrified product was determined to be free of PCBs (in the ppb range);
- and the process did not result in the contamination of the surrounding soil (USEPA, 2012)."

Vitrification, however, uses large amounts of energy (800-1,000 kwh per ton). Emissions associated with vitrification require sophisticated off-gas treatment to meet the removal efficiency of PCBs (99.999%). The off-gas treatment components may also need further treatment or disposal. Scrubber water also needs carbon treatment and disposal (Dàvila et al., 1993).

5. EMERGING TECHNOLOGIES

5.1 Iron Nano Particles

Zero-valent iron has long been used as a soil remediation reagent and is successfully applied as a dehalogenation reagent for various chlorinated organics. However, zero-valent iron has been less useful for treating PCBs (Grieger et al., 2010). Scientific research has multiplied with investigations into the remediation capacity and reductive ability of zero-valent iron (ZVI), and more recently nano-scale zero-valent iron (nZVI). Zero-valent iron is elemental iron that has an excess of electrons being characteristically stable as Fe2+ and Fe3+. This zero-valent form acts as an electron donor, facilitating the reduction of a variety of contaminants (Grieger et al., 2010). At the nano-scale (particle diameter <100 nm), the reductive capacity is greatly increased due to the much larger surface area that accompanies a reduction in particle diameter (Mueller and Nowack, 2010).

Varanasi, et al. describes a process wherein low temperature thermal desorption treatment of PCBs can be made more economically viable by the addition of nZVI prior to treatment. The reaction equation shown below describes the process whereby PCBs are dechlorinated by nZVI in water:

$2Fe^{\circ} \rightarrow 2Fe^{2+} + 4e^{-}$
$3H_2O \rightarrow 3H^{+} + 3OH^{-}$
$2H^{+} + 2e- \rightarrow H2\ (g)$
$RCl + H^{+} + 2e^{-} \rightarrow RH + Cl^{-}$

(Varanasi et al., 2006)

The preliminary treatment phase that saw the mixture of contaminated soil with iron nanoparticles and water ultimately produced a 95% destruction efficiency of PCB contaminants (Varanasi et al., 2006). Though effective, iron nano-particles needed thermal treatment to assist in PCB destruction via dechlorination. High destruction of PCBs was not observed at room temperature, most likely due to the slow transfer of PCBs from soil to catalyst surface. Both lowering the pH and adding surfactant had no effect on PCB destruction. Though this treatment shows promise, high energy inputs are needed for the thermal treatment (Varanasi et al., 2006).

5.2 Microwave Radiation

The decomposition of PCBs in soil using microwave energy and graphite fibers was studied, as well as creating a model for in situ remediation using condensers, and either pencil lead or iron wire (Abramovitch et al., 1999). The results showed 100% decomposition of PCBs in the soil, and the collection of desorbed PCBs in condensate was collected and remediated. Although this study showed promise for in situ remediation, the PCB contaminated soil used in the study was created in the laboratory rather than using actual contaminated soil.

The use of incineration is a proven and widely used technology for remediating soils contaminated with PCBs, yet this process has the potential to release dioxin into the atmosphere. Another study used microwave heating and granular activated carbon (GAC) for remediation (Liu and Yu, 2006). The microwave power used to increase the soil temperature was improved with the use of GAC to degrade PCBs in soil, and dioxin was not created during the reaction; however, PCBs were added to the soil in the laboratory.

5.3 Phytotechnology

Phytoremediation is a strategy that uses plants to degrade, stabilize, and/or remove soil contaminants. Phytoremediation is an effective and non-intrusive means of remediating soils. Flavonoids and other compounds released by roots can stimulate growth and activity of PCB degrading bacteria. Furthermore, root growth and death promotes soil aeration, which can enhance oxidative degradation of PCBs (Anyasi and Atagana, 2011).

The ability of PCBs to be degraded or be transformed in the environment depends on the degree of chlorination of the biphenyl. Biodegradation is done in two ways, mineralization and co-metabolism. Mineralization is a process whereby the organic pollutant is used as a source of carbon and energy by the organism resulting in the reduction of the pollutant daughter products. Co-metabolism requires a second substance as its source of carbon and energy for the microorganisms, but the target pollutant is transformed at the same time (Anyasi and Atagana, 2011). When the products of co-metabolism further degrade they can be mineralized into incomplete degradation, and this may result in the formation of metabolites that are more toxic than the PCB compound (Dobbins, 1995).

Rhizoremediation, a type of phytoremediation that involves both plants and their associated rhizosphere microbes, can occur naturally or can be augmented by introducing microbes (Gerhardt et al., 2009). Microbes can be contaminant degraders or can act symbiotically with plants to degrade pollutants. Phytoremediation research has showed great promise as a cost-effective and environmentally friendly remedial strategy. However, there are numerous inconclusive and unsuccessful attempts at phytoremediation in the field (Gerhardt et al., 2009). Because of promising laboratory and laboratory results, further research for field applications are necessary.

Numerous reports of unsuccessful and inconclusive field trials for the degradation of PCBs by phytoremediation have revealed that the rate of remediation is very slow. This is because plant growth is hard to achieve in heavily impacted soils. Another challenge is that there are stressors that affect phytoremediation in the field such as variations in temperature, nutrients, precipitation, and herbivory (Dobbins, 1995). There is still promising research in plant PCB remediation, however, it is declining due to the lack of successful, large scale field outcomes (Anyasi and Atagana, 2011).

6. CONCLUSION

PCBs are known to be present in building materials and mobilize from these materials to the soil. Because PCBs have significant toxic effects, including effects on the immune system, reproductive system, nervous system, and endocrine system, remediation must occur at PCB contaminated sites, especially in the presence of schools. Several remedial options are available for PCB in soils. Besides costs, the environmental effects of the remedial technology should be evaluated, since some options have deleterious results. This is especially true when evaluating under Sustainable Remediation guidelines, in which the remedial alternative is protection of human health and the environment, and produce limited emissions. A life cycle analysis of remedial considerations can be conducted in the remedial technology selection. Factors to be considered in the life cycle assessment are: soil transport including machine use, energy and emissions for incineration and vitrification, landfill and leachate emissions, emissions and odors from bioremediation and phytoremediation, and energy and emissions for nZVI thermal treatment.

Of the remedial technologies summarized above, bioremediation and phytoremediation are more environmentally friendly if done in-situ, however, these methods are the least efficient at destroying PCBs. Though phytoremediation has shown promise, further study is needed to bridge from the laboratory to the field. Incineration is the most efficient at PCB destruction, but has the most impacts.

In selecting a remedial alternative for PCB soil abatement, a balance should be made between economics, effectiveness, the results of a life cycle assessment, ecological and health risks, and social acceptability.

7. REFERENCES

Abramovitch, R. A., Bangzhou, H., Abramovitch, D., and Jiangao, S. 1999. In situ decomposition of PCBs in soil using microwave energy. *Chemosphere*, *38*(10), 2227-2236.

Andersson, M., Ottensen, R., and Volden, T. 2004. Building materials as a source of PCB pollution in Bergen, Norway. *Science of The Total Environment*, *325*, 139-144.

Anyasi, R., and Atagana, H. 2011. Biological remediation of polychlorinated biphenyls (PCB) in the environment by microorganisms and plants. *African Journal of Biotechnology*, *10*(82), 18916-18938.

Asher, B., Ross, M., and Wong, C. 2012. Tracking chiral polychlorinated biphenyl sources near a hazardous waste incinerator: fresh emissions or weathered revolatilization? *Environmental Toxicology and Chemistry*, *21*(7), 1453-1460.

Agency for Toxic Substances and Disease Registry (ATSDR). 2000. Toxicological profile for Polychlorinated Biphenyls (PCBs). Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

ATSDR. (n.d.). Toxic Substances - Polychlorinated Biphenyls (PCBs). (n.d.). *ATSDR Home*. Retrieved August 1, 2012, from http://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=26.

Cornelissen, G., Okkenhaug, G., Breedveld, G., and Sorlie, J. 2009. Transport of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in a landfill: A novel equilibrium passive sampler to determine free and total dissolved concentrations in leachate water. *Journal of Hydrology*, *369*, 253-259.

Davila, B., Whitford, K., and Saylor, E. 1993. Technology alternatives for the remediation of PCB contaminated soil and sediment, *540/S-93/506*. Washington D.C.: U.S. Environmental Protection Agency.

Dobbins, D. 1995. Biodegradation of Pollutants. *Encyclopedia of Environmental Biology* (p. 128). New York: Academic Press Inc.

Federal Remediation Technologies Roundtable (FRTR). (n.d.). 4-22 Incineration. Retrieved August 1, 2012, from http://www.frtr.gov/matrix2/section4/4-23.html.

Gerhardt, K., Huang, X., Glick, B., and Greenberg, B. 2009. Phytoremediation and rhizoremediation of organic soil contaminants: potential and challenges. *Plant Science*, *176*, 20-30.

Grieger, K., Fjiordbage, A., Hartmann, N., Erikksson, E., Bjierg, P., and Baun, A. 2010. Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for in situ remediation: Risk mitigation or trade-off?. *Journal of Contaminant Hydrology*, *118*, 165-183.

Ham, S., Kim, Y., and Lee, D. 2008. Leaching characteristics of PCDDs/DFs and dioxin-like PCBs. *Chemosphere*, *70*, 1685-1693.

Herrick, F., McLean, M., Meeker, J., Baxter, L., and Weymouth, G. 2004. An Unrecognized Source of PCB Contamination in Schools and Other Buildings. Environ Health Perspect. 112(10): 1051–1053.

Herrick, R. F., Lefkowitz, D. J., and Weymouth, G. A. 2007. Soil contamination from PCB-containing buildings. *Environmental Health Perspectives*, *115*(2), 173-175.

Liu, X. and G. Yu. 2006. Combined effect of microwave and activated carbon on the remediation of polychlorinated biphenyl-contaminated soil. *Chemosphere* 63: 228-235.

McDermott, J., Unterman, R., Brennan, M., Brooks, R., Mobley, D., Schwartz, C., and Dietrich, DK.. 1989. Two strategies for PCB soil remediation: biodegradation and surfactant extraction. *Environmental Progress*, *8*(1), 46-51.

Mueller, N.C., and B. Nowack. 2010. Nanoparticles for Remediation: Solving Big Problems with Little Particles. *Elements* 6 (2010): 395-400. Print.

Rivera-Austrui, J., Borrajo, M., Martinez, K., Adrados, M., Abalos, M., Van Bavel, B., Rivera, J., and Abad, E. 2011. Assessment of polychlorinated dibenzo-p-dioxin and dibenzofuran emissions from a hazardous waste incineration plant using long term sampling equipment. *Chemosphere*, *85*, 285-291.

Rodenburg, L., Du, S., Fennell, D., and Cavallo, G. 2010. Evidence for Widespread Dechlorination of Polychlorinated Biphenyls in Groundwater, Landfills, and Wastewater Collection Systems. ***Environ. Sci. Technol.***, *44*, 7534-7540.

(n.d.). Test Methods | Wastes | US EPA. *US Environmental Protection Agency*. Retrieved September 20, 2012, from http://www.epa.gov/SW-846/pdfs/8082.pdf

Thacker, N., Sheikh, J., Tamane, S., Bhanarkar, A., Majumdar, D., Singh, K., et al. 2012. Emissions of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (PCBs) to air from waste incinerators and high thermal processes in India. *Environmental Monitoring and Assessment*, 2012 March 2 (epub ahead of print). *0167*, 1-5.

U.S. EPA, 1998a. EPA TSCA Final Rule. Federal Register, 63(124), 1.

U.S. EPA 1998b. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. EPA publication SW-846, Washington, DC:U.S. Environmental Protection Agency.

Varanasi, P., Fullana, A., and Sidhu, S. 2006. Remediation of PCB contaminated soils using iron nano-particles. *Chemosphere*, *66*(207), 1031-1038.

Weber, R., Watson, A., Forter, M., and Oliaei, F. 2011. Review Article: Persistent organic pollutants and landfills - a review of past experiences and future challenges. *Waste Management Resources*, *29*, 107-121.

PART V: Remediation

Chapter 10

PA ACT 2 CLOSURE OF A MULTIPLE-REMEDY UST SITE

Frederic R. Coll[§], Richard A. Moore
URS Corporation, Pittsburgh, PA

ABSTRACT

URS Corporation (URS), under contract with the Pennsylvania Department of Environmental Protection (PADEP), completed remedial closure of a former leaking underground storage tank (LUST) Site contaminated with BTEX and MTBE. Aquifer impacts resulting from former leaking USTs threatened the local water supply. Significant issues at the Site include challenging geology, constituent distribution and fate, public health, and land use. Aquifer impacts resulting from former leaking USTs at the Site, located in Sewickley, PA, threatened the local water supply.

The former source area presented significant remedial challenges including a large vadose zone, aquifer impacts to 90 feet, and land use. The former gas station property is presently an integral part of an existing profitable retail business, presenting further challenges and limiting potential remedial options. Operation of nearby public water supply wells generated a gradient reversal leading to significant migration and diving of the MTBE plume towards the supply wells.

In-situ oxidation via the Kerfoot Technologies, Inc. patented combined ozone-hydrogen peroxide process, termed Perozone™, was implemented in the former source area, replacing a formerly installed SVE system that proved ineffective. The remedial technology and design implemented resulted in significant source area concentration reductions and the development of subsurface conditions conducive to bioremediation. Additional remedial measures undertaken at the Site include passive oxygen addition and plume cut-off for the off-site MTBE plume.

[§] Corresponding Author: Frederic R. Coll, P.G., 681 Andersen Drive, Pittsburgh, PA 15220, Tel: 412-503-4675, Email: Frederic.Coll@URS.com

The application of these multiple remedies at the Site provided for an effective, site-wide remedial strategy to achieve corrective action.

Keywords: In-situ oxidation, MTBE, water supply protection, Perozone™, ozone remediation, plume cut-off, PA Act 2, UST site closure.

1. INTRODUCTION

1.1 Site Setting

The Site is located in Sewickley Borough, Allegheny County, Pennsylvania, within the Allegheny Plateau Physiographic Province of southwestern Pennsylvania. The Site is situated on the northern bank of the Ohio River, which is located approximately 400 feet south of the Site (Figure 1).

The Site setting is mixed land use, surrounded by commercial and residential properties, as well as public lands including a middle school and the local Water Authority. The Water Authority, which operates water supply wells that withdraw approximately one million (1 MM) gallons of groundwater per day, is located approximately ½ mile upstream of the Site along the banks of the Ohio River, within the Well Head Protection Area (WHPA) (Moody, 1995) of the Water Authority well field (Figure 2).

The property had been used for retail gasoline sales and auto repair since the 1940s. The USTs were in operation for an unknown number of years until operations ceased in December 1998, prior to the closure of the USTs in May 1999. The current use of the Site is high-end automobile retail sales and represents a significant revenue base for the local borough.

1.2 Conceptual Site Model

The Site overlies unconsolidated materials that comprise the Ohio River Sand and Gravel Aquifer, a prolific aquifer with hydraulic conductivities estimated at 600 feet per day and determined to be on the order of 100 feet thick in the vicinity of the Site. The water table is encountered at approximately 40 feet below ground at the Site, yielding a saturated thickness on the order of 60 feet at the Site. The unconfined aquifer water table approximates the water elevations of the nearby Ohio River, indicating hydraulic communication between the aquifer and the Ohio River (URS, 2003). A comprehensive monitoring well network was established during site investigative activities completed between 2000 and 2004, as illustrated in Figure 2. Groundwater flow direction at the Site was determined to be generally south, towards the Ohio River at low gradients (0.0005 ft/ft).

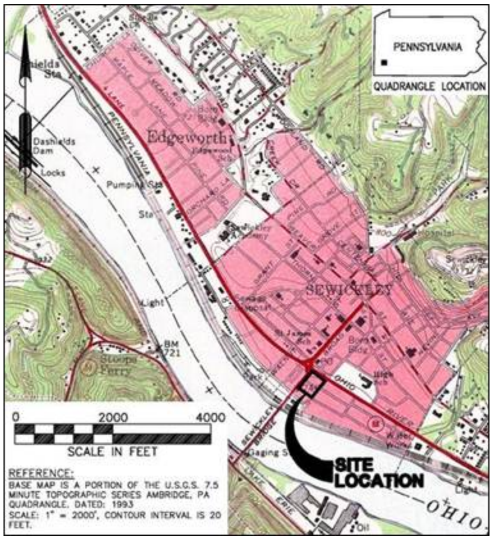


Figure 1. Modified Site Location Map (USGS, 1993).

At distances removed from the Site, the groundwater flow direction is influenced by the operation of the Water Authority supply wells, resulting in southeasterly groundwater flow directions, as portrayed in Figure 3.

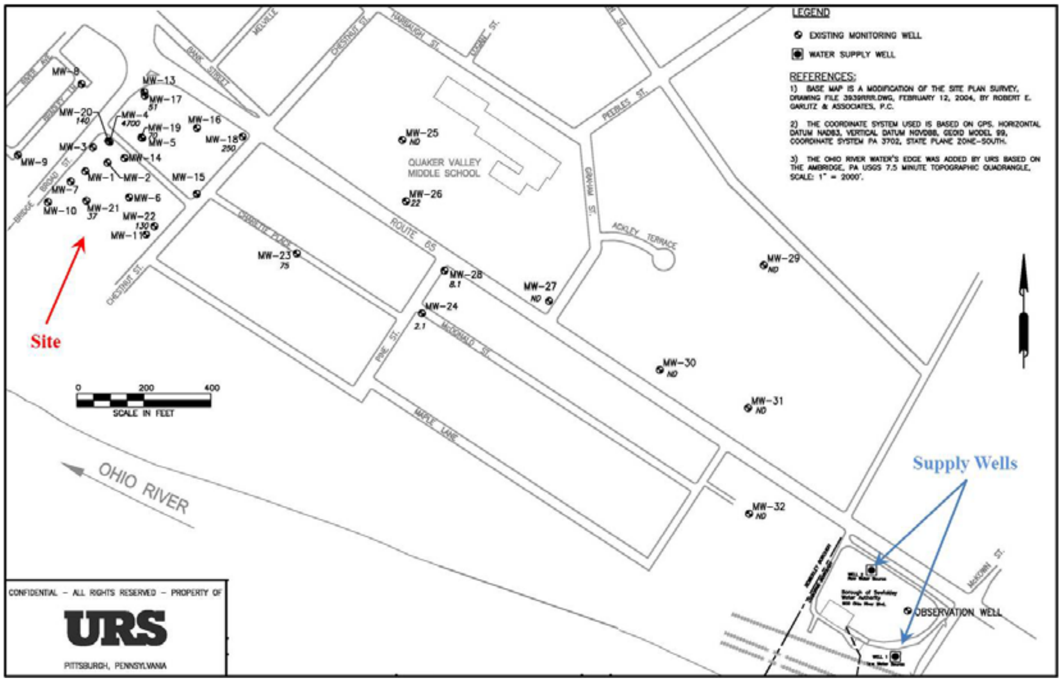


Figure 2. Site Plan Depicting Monitoring Well Network and Supply Wells.

The results of the investigative activities indicated significant source area impacts dominated by BTEX and MTBE throughout the saturated thickness of the aquifer. Additionally, MTBE impacts were identified to have migrated far from the Site. Preliminary investigative work completed by former site engineers defined impacts limited to the vadose zone and smear zone (e.g. shallow groundwater).

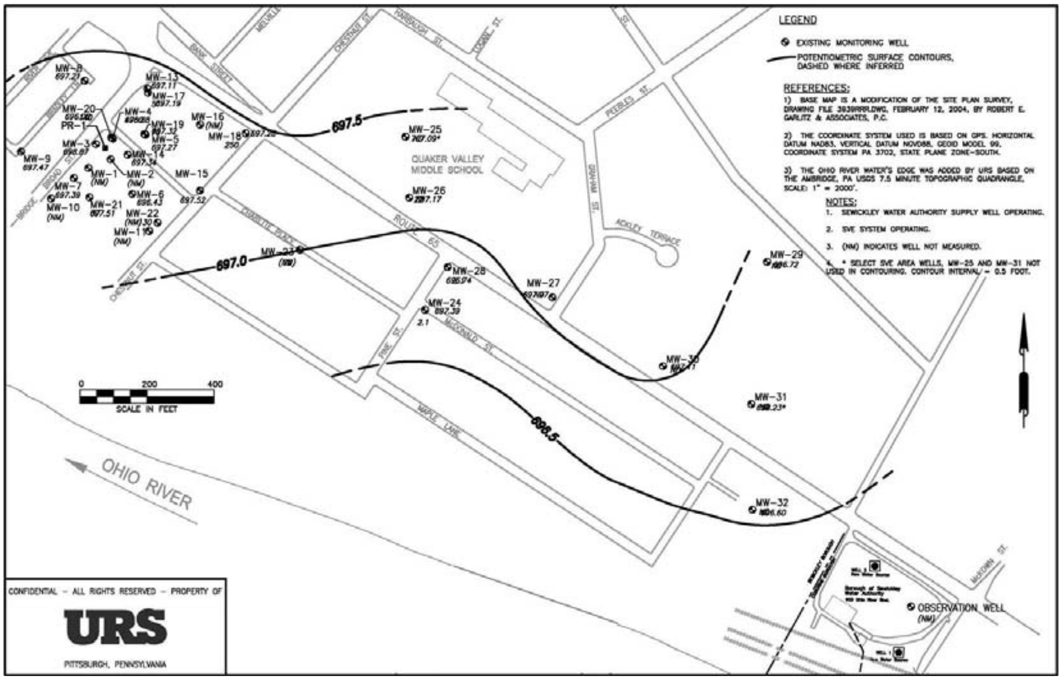


Figure 3. Site Plan Depicting Monitoring Well Network and Potentiometric Surface.

1.3 Previous Source Area Remediation

A soil vapor extraction (SVE) system was installed and operated within the source area in 2000 by former site engineers. Free product recovery from the water table was initiated in 1999 and an SVE system was selected as a source area remedial action in 2000. Consistent with the preliminary investigative findings, these on-site interim remedial measures served to address only the impacted, shallow source area. The SVE system targeted the vadose zone (up to 40 feet below ground). Asymptotic volatile organic compound (VOC) recoveries were realized by late 2005, with persistently high source area concentrations remaining. Figure 4 presents a plan depicting site details, including the vapor extraction points.

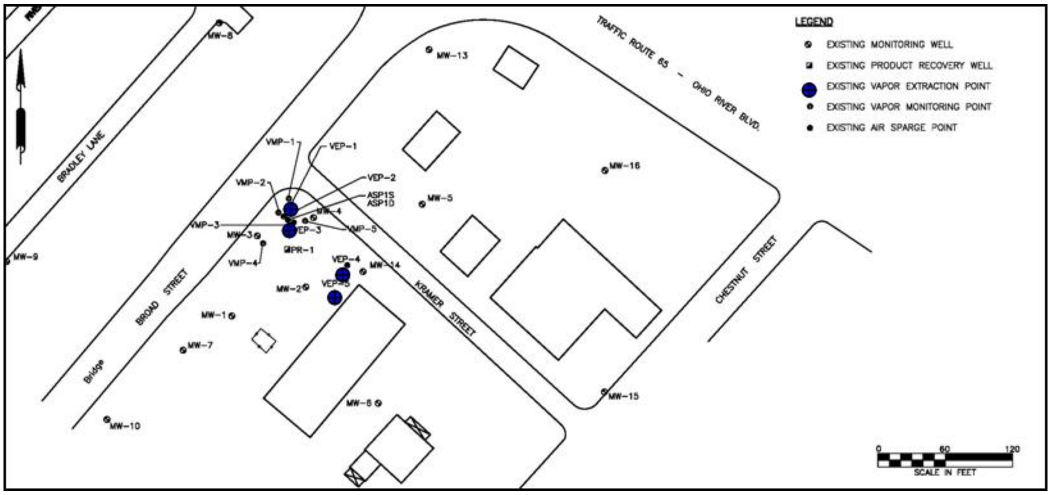


Figure 4. Site Plan Depicting SVE Locations Within Former Source Area.

Figure 5 presents the persistent BTEX impacts, portrayed in parts per billion (ppb), within the former source area between 2004 and 2006, supporting the need for the development of an alternate remedial strategy.

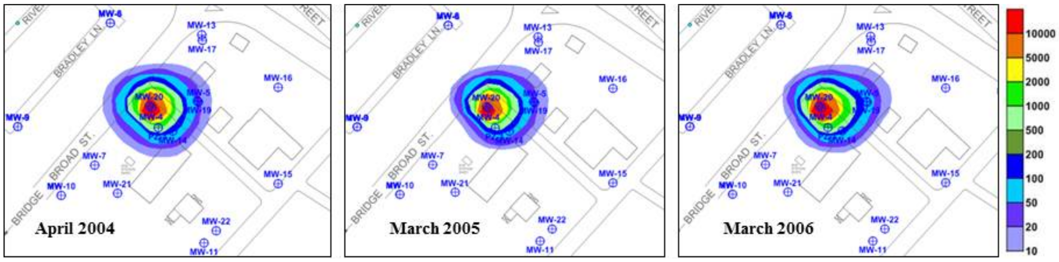


Figure 5. Persistent BTEX (Benzene contours shown) Impacts in Former Source Area (ppb).

1.4 Revised Conceptual Site Model

URS revisited the preliminary conceptual site model and completed additional investigative activities during 2004 and 2005. The findings of these additional investigations included the following:

- Benzene, toluene, ethyl benzene and xylene (BTEX) impacts were predominantly confined to the area immediately surrounding the former source area, and were observed throughout the aquifer to depths of 90 feet below ground, based upon discrete-depth sampling results.
- Methyl tert butyl ether (MTBE) impacts were also identified to be present throughout the saturated thickness of the aquifer and extending to a significant downgradient distance from the Site, migrating under influence of the Water Authority supply wells.

- The MTBE dissolved phase plume was determined to dive to greater depths along the off-site migration pathway, due to density and hydraulic conductivity effects.
- The SVE system was ineffective for source area contaminant reduction.
- The aquifer contained sufficient biological capacity to support in-situ bioremediation, however, depressed availability of dissolved oxygen (DO) in groundwater was determined to be the main limiting factor.

2. REMEDIAL TECHNOLOGY IMPLEMENTATION

2.1 Source Area Remedial Action - In-situ Oxidation

Following a technical evaluation, it was determined that the application of in-situ oxidation technology best suited remediation of the former source area. Additionally, the remedial strategy for the Site included the delivery of DO to the downgradient aquifer to provide the necessary electron acceptor to stimulate the in-situ bioremediation of the MTBE dissolved phase plume.

In order to properly remediate the entire thickness of the unconsolidated aquifer, including the 40-foot thick vadose zone, a gaseous-based oxidation technology was selected. Perozone™ Remediation System, manufactured by Kerfoot Technologies, Inc., was designed and installed in the former source area. The Perozone™ oxidation process represents an enhanced ozone oxidation and includes patented technology in which the generated ozone bubbles are coated with liquid hydrogen peroxide. The Perozone™ System utilizes an ozone sparging process termed C-Sparger™, which employs the generation of nano- to micro-sized bubbles of air-encapsulated ozone created by forcing an air/ozone mixture through specialized delivery points, termed Spargepoints®, to treat subsurface impacts in soil or groundwater.

The oxidation technology was installed to target persistent source area impacts and included the installation of ten Spargepoints®, designated as SP-1 through SP-10. Each Spargepoint® was installed at a depth of 55 to 60 feet below grade using standard hollow-stem auger drilling techniques. Two (2) Spargepoints®, SP-8 and SP-10, were installed at a depth of approximately 80 feet below grade, to treat deep aquifer impacts.

The existing SVE remediation shed was refurbished to house the Perozone™ System. The Perozone™ System construction included the installation of underground conduit to convey the individual ozone and peroxide delivery lines to each Spargepoint® location. Figure 6 presents the layout of the source area

Perozone™ System at the Site. Figure 7 presents the typical vault installation with the underground conduits and the individual Spargepoint® locations.

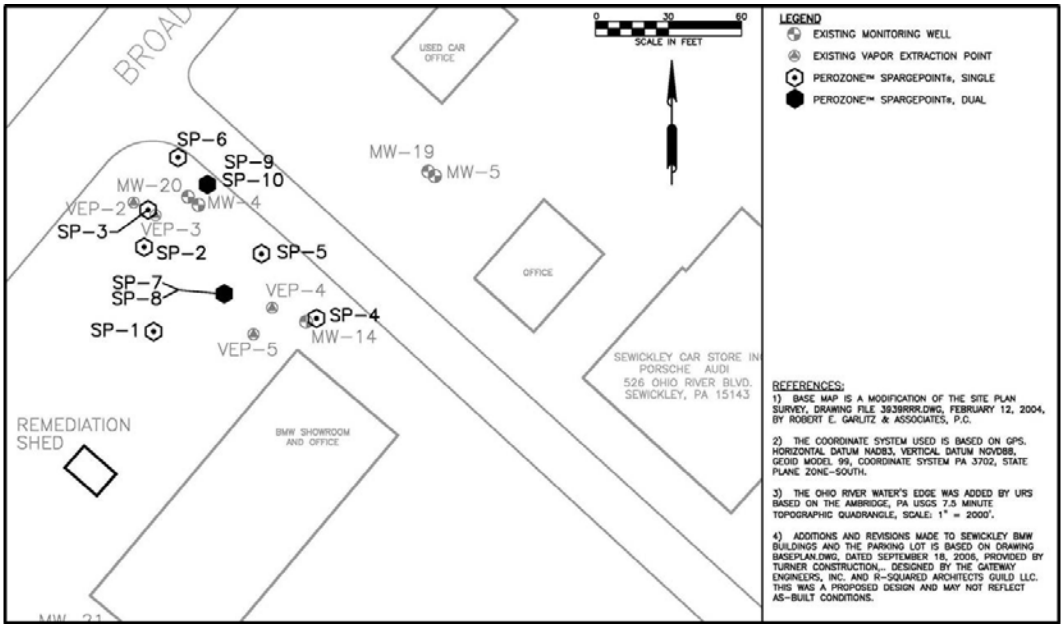


Figure 6. Perozone™ System Layout.

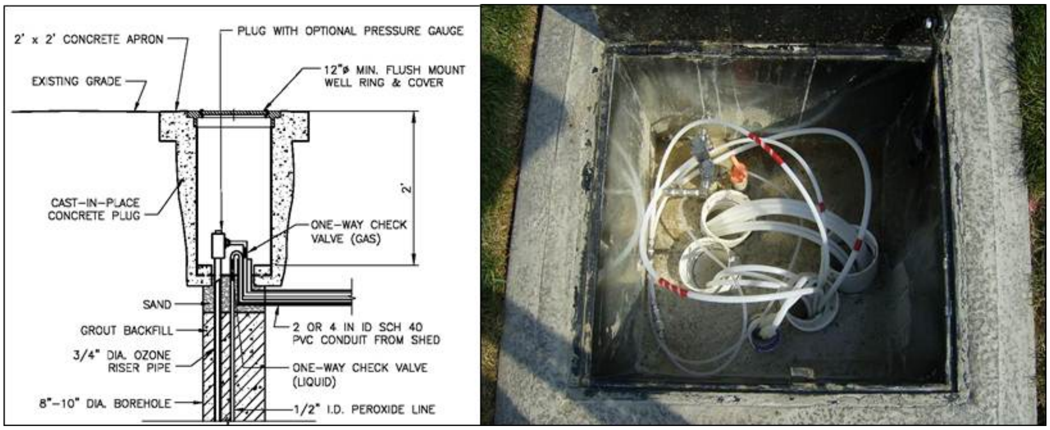


Figure 7. Typical Perozone™ System Well-Head Detail and As-Built Vault.

The start-up of the Perozone™ System was initiated in May 2007 following system component installations and included a shakedown period in which system optimization related to delivery was completed. Figure 8 presents the final installation surface completions with minimal impact to the current property operations.

Figure 8. Minimally Invasive Installed Perozone™ System - As-Built Photographs.

The Perozone™ System components within the remediation shed include two wall-mounted panels that control the peroxide and ozone injections. The Perozone™ System components were installed within a climate-controlled room within the existing SVE remediation shed. Figure 9 depicts the system panels and other components.

Figure 9. Main Components of the Perozone™ System.

The ozone-hydrogen peroxide oxidation system is fully automated and only requires the periodic re-supply of hydrogen peroxide to the work tank. The Perozone™ System was initiated in May 2007 through June 2010, when operation ceased. A total of 1,450 gallons of 10% by weight hydrogen peroxide was delivered to the subsurface Spargepoint® network at an average of 1.5 gallons per day, with accompanied ozone gas delivery at an average concentration of 800 parts per million (ppmv).

The in-situ oxidation results have provided for significant contaminant concentration reductions in the source area including BTEX constituents and MTBE. Tert butyl alcohol (TBA), an aerobic degradation byproduct of MTBE, was not previously detected at the Site, therefore, its presence suggests active MTBE degradation processes at the Site. The successfulness of the Perozone™ System is evidenced by the benzene reductions, portrayed in Figure 10.

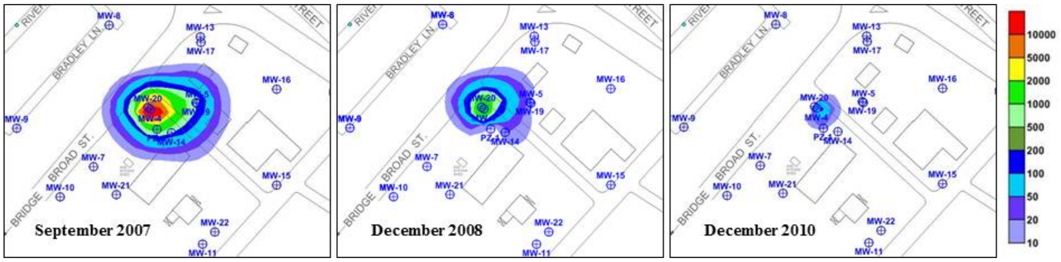


Figure 10. Source Area Benzene Reductions (ppb).

Figure 11 presents time-series results for source area monitoring wells MW-4, MW-14, MW-20 and PZ-1, which depicts the remedial effectiveness of the source area in-situ oxidation remediation.

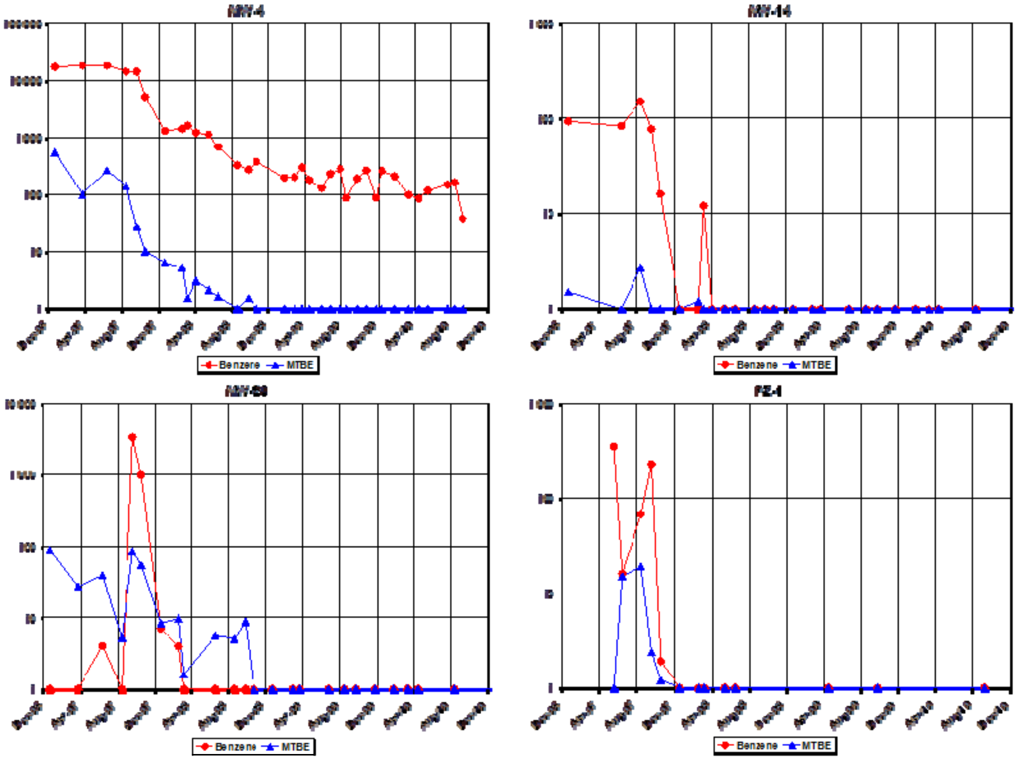


Figure 11. Source Area Monitoring Well Time Series Trends (ppb).

2.2 Downgradient Remedial Actions

As noted, the dissolved phase MTBE plume was determined to be threatening the local Water Authority supply wells with observed MTBE plume diving. MTBE impacts were detected up to 1,500 feet east-southeast of the Site, migrating under influence of the operating water supply wells. Figure 12 presents the 2004 MTBE iso-concentrations of the shallow aquifer, mid-aquifer, and deep aquifer zones, demonstrating the off-site impacts and the MTBE plume diving, as the core of the plume is observed to shift in an easterly direction with depth.

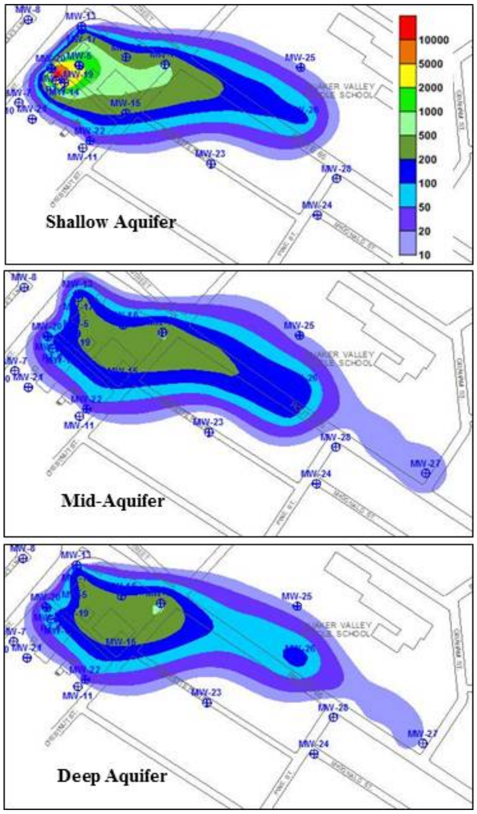


Figure 12. Downgradient MTBE Impacts (ppb) and Plume Diving.

In order to address the immediate threat to the Water Authority supply wells, an MTBE plume cut-off action was initiated in February 2005. The groundwater extraction cut-off remedy was implemented within residential area monitoring well MW-28. The pumping system operates at the designed pumping rate of 35 gallons per minute (gpm), with discharge to the local authority. The cut-off pumping well provided for an additional level of protectiveness for the downgradient water supply wells. Following installation, hydraulic testing was performed to determine the aquifer conditions during operating conditions of the cut-off pumping system. The apparent capture zone was determined to be approximately 500 feet at 35 gpm. Figure 13 presents photographs of the completed installation of the plume cut-off remedy, which was required to be minimally invasive in this residential area. Figure 14 demonstrates the operational effectiveness of the MTBE plume cut-off remedial action.

Figure 13. Installed MTBE Cut-off Pumping Well System - As-Built Photographs.

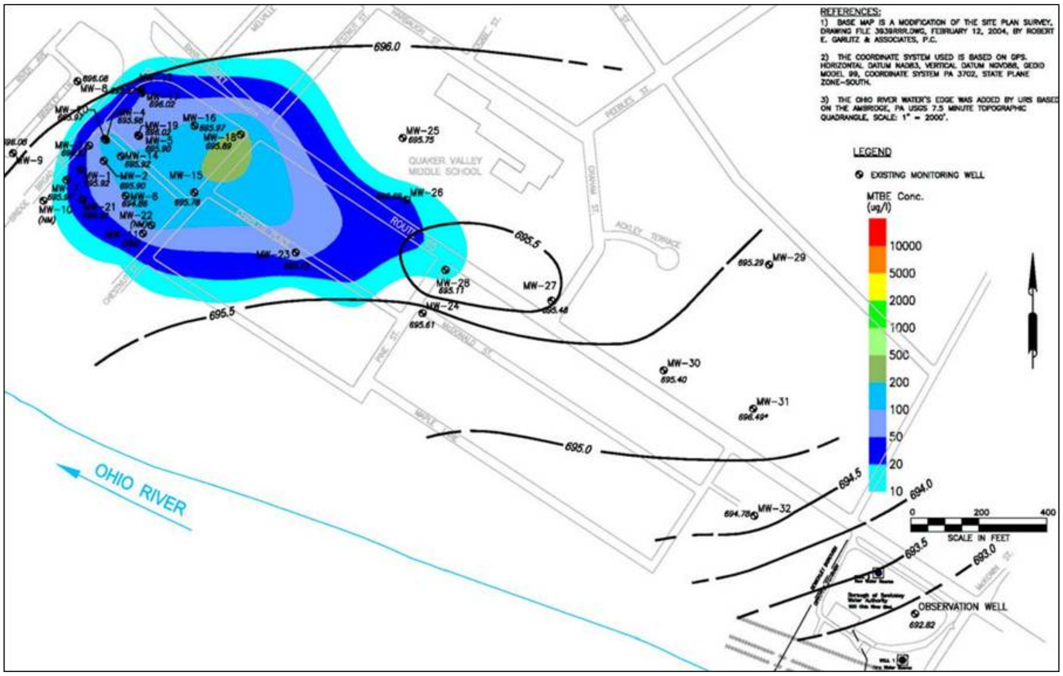


Figure 14. MTBE Plume and Apparent Capture Zone of Groundwater Cut-off Remedy.

In order to further address off-site MTBE impacts to groundwater, a passive oxygen infusion technology was applied at downgradient monitoring well MW-18, located mid-way between the source area at the Site and downgradient plume cut-off well MW-28. The passive oxygen addition via diffusion was initiated in January 2007, and included the installation of an oxygen concentrator that supplies oxygen to a specially developed micro-porous delivery device that generates miniscule oxygen gas bubbles, designed to diffuse directly into groundwater, providing the limiting DO source to groundwater to support biodegradation of MTBE. The overall system design limited impacts to the surrounding property, as portrayed in Figure 15. The results have proved highly beneficial at reducing MTBE concentrations within the downgradient plume, as evidenced in Figure 16. The MTBE plume cut-off remedy was eliminated in early 2011 following verification of MTBE plume remediation.

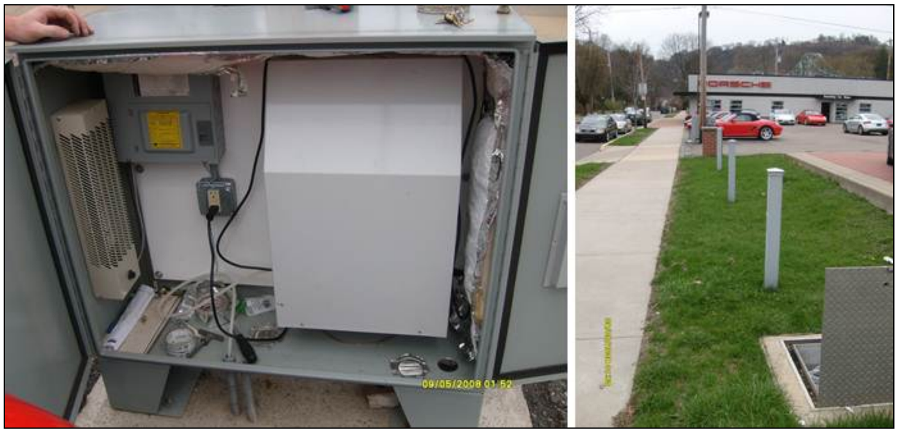


Figure 15. Passive Dissolved Oxygen Generator and MW-18 Vault - As-Built Photographs.

3. CLOSING

Prior to URS’ involvement, an SVE system was installed and operated for five years, yielding ineffective results. URS designed and implemented an in-situ chemical oxidation remedy in 2007, featuring an ozone-based injection delivery manifold system installed in the former source area and passive oxygen addition in the downgradient plume. The ozone-based remedy was operated for a period of three years and resulted in >95% reductions of UST-related constituents in source area groundwater. The application of dual-source area and downgradient plume management remedies provided an effective remedial strategy to affect site-wide remedial closure.

In late 2010, URS developed a site-specific standard (SSS) (URS, 2010) approach for the Site utilizing the PA Land Recycling Program (Act 2) Guidance

(PADEP, 2002). Specifically, URS completed risk assessment and characterization activities that documented that the remedial actions implemented at the Site met the SSSs for soil and groundwater for all exposure pathways, including dermal contact and inhalation of indoor air. Potable use of the groundwater constituted a persistent, unacceptable risk, however, based upon the local borough zoning classification, the Site property is required to connect to the public water supply; therefore, withdrawal of groundwater from beneath the Site is prohibited, constituting an incomplete exposure route. Notwithstanding, an Environmental Covenant was completed under PADEP guidelines and is currently in place for the Site.

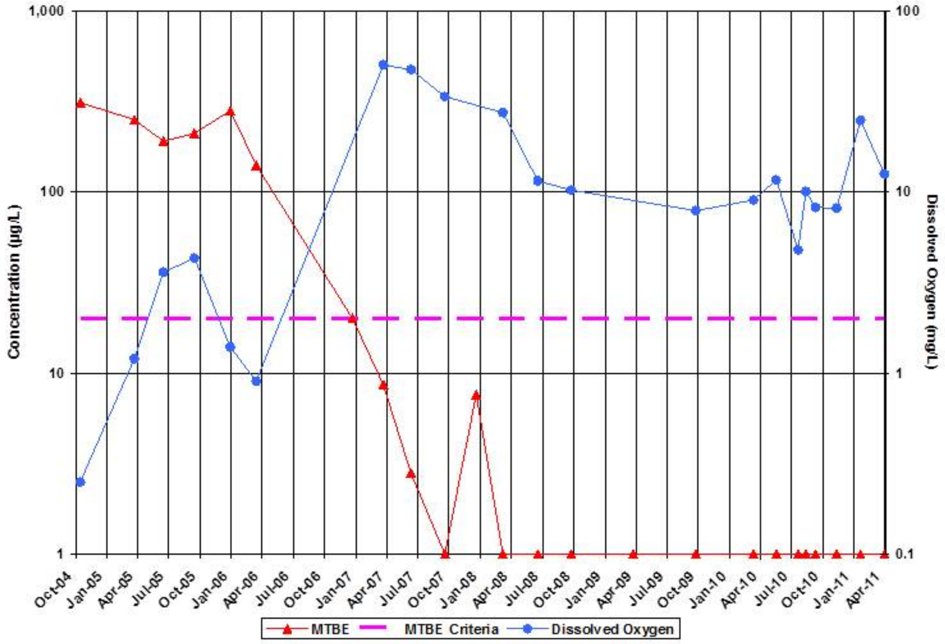


Figure 16. MTBE Plume Remedy Time-Series Results for MW-18.

Remedial completion was further verified by the results of fate and transport modeling and statistical evaluations completed for the comprehensive dataset, as documented in the Remedial Action Completion Report (URS, 2011). The remedial system and infrastructure was dismantled in late 2011 and the property was returned to an unencumbered use for the current owner.

4. REFERENCES

Moody and Associates, Inc., 1995, Well Head Protection Program, Allegheny County, Pennsylvania.

Pennsylvania Department of Environmental Protection, 2002, Land Recycling Program Technical Guidance Manual, Bureau of Land Recycling and Waste Management, Document Number: 253-0300-100.

URS Corporation, 2003, Site Characterization Report, Former W.V. Hovis Sunoco Site, Sewickley, PA, prepared for the Pennsylvania Department of Environmental Protection under Contract IRRSC-4 #5-064.

URS Corporation, 2010, Site-Specific Standard Determination Report, Former W.V. Hovis Sunoco Site, Sewickley, PA, prepared for the Pennsylvania Department of Environmental Protection under Contract IRRSC-6 #5-131.

URS Corporation, 2011, Remedial Action Completion Report, Former W.V. Hovis Sunoco Site, Sewickley, PA, prepared for the Pennsylvania Department of Environmental Protection under Contract IRRSC-6 #5-131.

Chapter 11

REMEDIATION AND REDEVELOPMENT OF A GASOLINE-IMPACTED SITE USING THE ISCO-SSD COUPLING APPROACH

Kun-Chang Huang[1§], Gordon Hinshalwood[2], Aaron Lapine[2]
[1]Antea Group, 2 Bridgewater Rd., Farmington, CT 06032, [2] Antea Group, 500 Summit Lake Drive, Valhalla, NY 10595

ABSTRACT

In Situ Chemical Oxidation (ISCO) in conjunction with Sub-Slab Depressurization (SSD) is evaluated as the approach for remediation and redevelopment of a gasoline impacted site in a high-value urban area. In the first phase of the evaluation, laboratory and field pilot ISCO feasibility studies (FS) were conducted to evaluate the degradation of contaminants of concern (COCs) including benzene, toluene, ethyl benzene and xylenes (BTEX), methyl tertiary-butyl ether (MtBE) and naphthalene (NAP).

In the laboratory FS, degradation of the COCs using activated sodium persulfate (ASP) with chelated-iron and sodium hydroxide was conducted at various dosages at 20 °C for 14 and 28 days in groundwater and soil slurry matrixes, respectively. The results indicated that the applied ASP processes were highly effective in degrading the COCs. In groundwater matrixes, BTEX and NAP were degraded to below 0.5 µg/L by ASPs at SP 5 g/L (21 mM) within 14 days, corresponding to a COC destruction percentage of 99.9%.

The ISCO pilot FS results indicated that total COC concentration in the treatment area was significantly reduced during a 15-day testing period. Variation in pH, ORP and sulfate concentrations in nearby monitoring wells indicated that the ASP radius of influence (ROI) extended over 18 feet. However, significant reduction in total BTEX in the monitoring wells was not observed, reflecting a limited influence of the ASP treatment at the area, most likely due to the behavior of the density-driven downward flow of the injected 30% (w/w) ASP solution that limited the ROI of the ASP treatment.

[§] Corresponding Author: Kum-Chang Huang, Antea Group, 2 Bridgewater Rd., Farmington, CT 06032, Email: ken.huang@anteagroup.com

Keywords: Site Remediation, Sodium Persulfate, Chemical Oxidation, Redevelopment

1. BACKGROUND

Redevelopment of contaminated sites undergoing soil and groundwater remediation is a common occurrence in highly urban settings, which frequently presents significant challenges to those implementing the remediation program. While the excavation, commonly needed for basements and foundations of new buildings, often presents the opportunity of removing large volumes of impacted soils, redevelopment projects can be difficult to accommodate in that their schedule is often significantly accelerated compared with remediation schedules, resulting in post-redevelopment challenges for the remediation team (i.e., performing remediation under the floor of a new building). A feasible remedial strategy, developed to facilitate both the remediation and the redevelopment processes uses a combined approach: ISCO to actively destroy/control the COCs underlying the development area, and SSD to eliminate the intrusion potential of contaminated soil vapors migrating inside the buildings.

ISCO using ASP has been widely applied for remediation of contaminated sites impacted by organic contaminants in recent years. ASP processes, like other radical-driven oxidant processes such as Fenton's reagent and ozone applications, have been reported to be effective in degrading numerous organic contaminants through the formation of free radicals (e.g., sulfate, hydroxide and organic free radicals) generated in the ASP processes (Huang, et al., 2002; Watts R.J., 2011). The results of recent research and site remediation projects have demonstrated that ASP with heat, chelated metals and high pH is highly effective in degrading chlorinated solvents, oxygenates and a wide variety of recalcitrant organic compounds (Huang et al., 2005; Nadim et al., 2006, Liang et al., 2008; Johnson et al., 2008; Tsitonaki et al., 2010).

ASP processes used in remediation of petroleum-contaminated sites are less reported in the literature. This paper presents part of the findings obtained from both laboratory and pilot scale ISCO FS conducted to select the chemical oxidant best suited for destruction of the site-specific COCs. The degradation effectiveness of the COCs including BTEX, MtBE and NAP using ASP with chelated iron (Fe^{2+}) and high pH is presented. Results and implications are discussed in the paper.

2. SITE CHARACTERIZATION

The subject site is located in an urban environment where native soils have been extensively disturbed and fill materials historically predominate. The site soils were characterized to a depth of approximately 30 feet below ground surface (bgs) through a combination of groundwater monitoring well installations and direct-push soil sampling probes. Silty sand predominates across the northern and southern areas of the site, with sandy lenses intermixed. The middle portion of the site is predominantly sand, with some silty sand and several silt lenses. A peat layer is located approximately 30 feet bgs, underlying most of the site. Groundwater at the subject site has historically ranged between 12 and 15 feet bgs. A localized mounding effect from the infiltration has raised the water table to less than 5 feet bgs on some portions of the site. Groundwater flow follows local topography, which generally decreases in elevation from northeast to southwest.

The site was historically used as a gasoline service station prior to the redevelopment activities. Soil and groundwater impacts from this historical use primarily included BTEX and MtBE. These impacts were compounded by a #2 fuel oil release from a neighboring residential complex, which led to fuel oil soil and groundwater impacts (by semi-volatile organics) spread across the subject site in addition to the gasoline-range organics identified from the service station site use. The areas of impact range throughout the site, but are most concentrated on the central and western portions of the site.

3. EXPERIMENTAL MATERIALS AND APPROACH

Laboratory and pilot-scale FSs were conducted for evaluation of effectiveness and selection of the ASP processes to provide active COC destruction and migration control mechanisms for the subject site. Contaminated soil and groundwater were collected, characterized and used in the laboratory FS.

In the laboratory FS, a series of experiments were conducted to investigate the effectiveness of degrading the site-specific COCs with two ASP processes: 1) Fe-EDTA ASP (i.e., SP activated by ferrous sulfate-ethylenediamine tetra acetate sodium salt, Fe-EDTA) and 2) Alkaline ASP (i.e., SP activated by high pH with sodium hydroxide (NaOH). Homogenous groundwater and soil slurry batch experiments were conducted to acquire key engineering parameters including degradation efficiency, needed treatment time, oxidant demand, reaction variables (e.g., pH, ORP and SP conc.) for the design and optimization of the full-scale site remediation.

Two sets of batch experiments were conducted with the testing conditions presented in Tables 1A and 1B. In each set of the tests, control experiments (i.e., reactors without adding SP and activators) were included and used to obtain the baselines for determining the extent of destruction of the COCs. The experiments were run under minimum headspace (to avoid the VOC loss due to evaporation) at 20 ºC and 100 rpm for 14 or 28 days. Post-treated soil and groundwater samples were collected at the end of the tests to determine the effectiveness of total COC destruction. Relevant reaction parameters (i.e., residual SP concentration, pH and ORP) were determined at the end of the test.

Table 1A. Degradation of COCs in Groundwater with ASPs (20 ºC and 100 rpm for 14 days)

Test	Test Goals	Initial SP	Site Groundwater	SP/(COCs+TPH)	pH	Fe-EDTA
Number		(g/L)	(mL)	(g/mg)	SU	(mg/L as Fe)
A1	Degradation of target COCs with Alkaline ASP at SP 5 g/L	5	250	0.059	> 10.5	None
A2	Degradation of target COCs with Alkaline ASP at SP 20 g/L	20	250	0.235	> 10.5	None
A3	Degradation of target COCs with Fe-EDTA SP at SP 5 g/L	5	250	0.059	None	250
A4	Degradation of target COCs with Fe-EDTA SP at SP 20 g/L	20	250	0.235	None	250
A5	Reaction Control- Site groundwater only	None	250	None	None	None

Table 1B. Degradation of COCs in Soil Slurry System with ASPs (20 ºC, 100 rpm for 14 days)

Test	Test Goals	Site Soil	Liquid	Initial SP	SP/Soil	Fe-EDTA	System
Number	Soil-Groundwater Slurry System	(g)	/Soil Ratio	(g/L)	Ratio (g/kg soil)	(mg/L as Fe)	pH
B1	Degradation of target COCs in soils with Alkaline ASP at 50 g/L	80	2.5:1	50	135	None	> 10.5
B2	Degradation of target COCs in soils with Fe-EDTA ASP at 50 g/L	80	2.5:1	50	135	250	No Control
B3	Reaction Control	80	2.5:1	None	None	None	No Control
B4	Reaction Control Duplicate	80	2.5:1	None	None	None	No Control

A small scale pilot study was conducted, primarily aiming to investigate transport and control of the ISCO application within the site property boundaries.

A 500-gallon solution of SP (2.2 lb/gal) and chelated Fe (0.022 lb/gal Fe-EDTA as Fe) was injected into the treatment zone through two application points (namely AW-1 and AW-2). Both chemicals were obtained from FMC Corp. The two injection wells were constructed of 10 feet 4-inch diameter, Schedule 40, 0.040-inch slot size PVC screens and riser pipes. The points were finished to 14 feet bgs, with 10-ft screen intervals and 5-foot risers and Morie #2 well sand packs to two feet above the well screen with a bentonite seal above the filter pack.

ISCO solutions were applied using diaphragm pumps at ground surface, which was connected to both the reagent drum and the wellhead with 1-inch reinforced PVC tubing secured with camlock fittings at all end points. Application pressure was monitored using an Ashcroft sprinkler system pressure gauge. Following the ASP injection, the application points and three surrounding observation wells were sampled for COCs and various geochemical parameters (e.g., pH, ORP, sulfate concentration) at desired treatment stages including pre-application, during injection and post-application (including 1 day, 7 days and 15 days).

4. RESULTS AND DISCUSSION

Soil and groundwater characterization has confirmed that the site is contaminated by gasoline-related compounds. In the average of two replicate groundwater samples collected for the laboratory FS, benzene (146 µg/L), toluene (3,705 µg/L), ethyl benzene (3,450 µg/L), total xylenes (18,800 µg/L) and naphthalene (68 µg/L) were detected above the applicable regulatory criteria. High concentrations of total petroleum hydrocarbons (TPH; TPH_{GRO} 58,100 µg/L and TPH_{DRO} 375 µg/L) were found in the collected groundwater used in the laboratory FS. Contaminated site soil was also characterized prior to use in the FS. Key results are presented below.

4.1 Degradation of COCs in Groundwater with ASP Processes

In Alkaline ASP testing reactors, the degradation percentage of total targeted COCs reached 99.95% and 99.97% after a 14-day treatment with Alkaline SP at 5 g/L and 20 g/L, respectively (Figure 1). All the detected COCs including BTEX and NAP were degraded to below 0.5 µg/L after a 14-day treatment with Alkaline SP at 5 g/L and 20 g/L. TPH_{GRO} and TPH_{DRO} were degraded from 34,450 µg/L to below 50 µg/L, and from 290 µg/L to 75 µg/L with Alkaline ASP at 20 g/L, indicating that gasoline-related compounds with a higher carbon number (generally more persistent) were also degraded with Alkaline ASP under the testing conditions.

In Fe-EDTA ASP reactors, the degradation percentage of total targeted COCs achieved 99.86% and 99.89% after a 14-day treatment with Fe-EDTA ASP at 5 g/L and 20 g/L, respectively (Figure 1). Primary targeted compounds BTEX and NAP were degraded to below the applicable regulatory criteria after a 14-day treatment period. TPH_{GRO} and TPH_{DRO} were degraded from 34,500 µg/L to 188 µg/L and from 292 µg/L to 209 µg/L with Fe-EDTA ASP at 20 g/L.

The concentrations of target COCs, TPH_{GRO} and TPH_{DRO} in the post-treated groundwater of the 14-day COC destruction tests are summarized in Table 2. The results indicate that both Alkaline ASP and Fe-EDTA ASP processes were highly effective in degrading the COCs including BTEX, NAP and other non-targeted compounds (detected as TICs-tentative identification compounds) that were detected in the control reactor (Column A1 data).

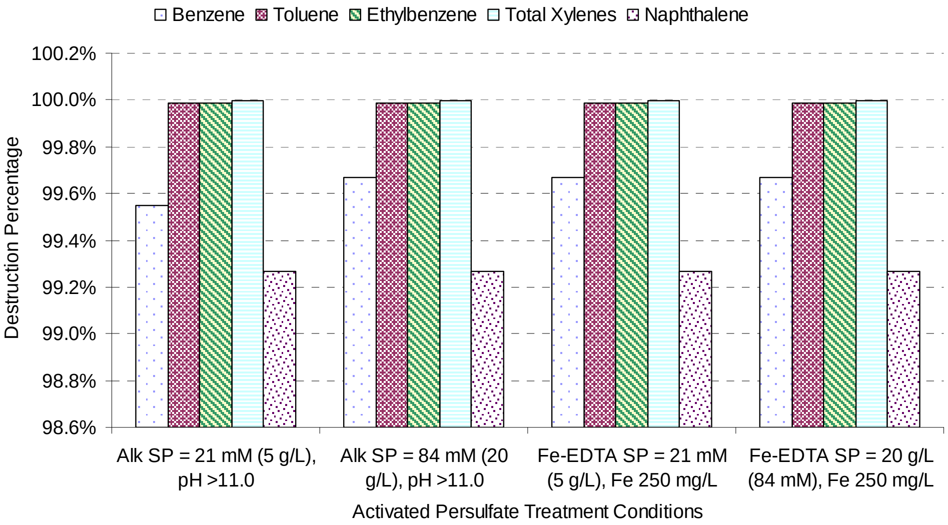


Figure 1. Degradation of Target COCs (BTEX and NAP) with Alkaline ASP and Chelated- Fe(II) ASP in Groundwater; Reactions at 20 ºC and 100 RPM for 14 days

4.2 Degradation of COCs in Soil Slurry Matrixes with ASPs

The soil characterization indicated that the collected soil contained high levels of target COCs, TPH and organic content. A higher SP dose (i.e., 203 g- SP/kg wet soil) and a longer treatment period (i.e., 28 days) were thus applied in the soil slurry FS for the treatment of the impacted soils. The results indicated that the two selected ASP processes at the SP dose of 203 g/kg wet-soil were capable of degrading the COCs including BTEX, NAP and MtBE. After a 28-day treatment with ASP at 203 g/kg wet soil, significant degradation of MtBE (67% and 50%, xylenes (40% and 38%) and NAP (13%, and 50%) were observed with

Table 2. Degradation of BTEX, NAP and TPH with Alkaline ASP and Chelated- Fe(II) ASP in Groundwater; Reactions at 20 ºC for 14 days

Degradation of COCs in Site Groundwater with ASP	A1	A2	A3	A4	A5
Treatment Conditions	Experimental Control	Alk SP = 21 mM (5 g/L), pH >11.0	Alk SP = 84 mM (20 g/L), pH >11.0	Fe-EDTA SP = 21 mM (5 g/L), Fe 250 mg/L	Fe-EDTA SP = 84 mM (20 g/L), Fe 250 mg/L
VOCs (Method 8260B)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)
Benzene	151	0.68	BRL (<0.5)	BRL (<0.5)	BRL (<0.5)
Toluene	3780	BRL (<0.5)	BRL (<0.5)	BRL (<0.5)	BRL (<0.5)
Ethylbenzene	3570	BRL (<0.5)	BRL (<0.5)	BRL (<0.5)	BRL (<0.5)
Total Xylenes	17800	BRL (<0.5)	BRL (<0.5)	BRL (<0.5)	BRL (<0.5)
Methyl tert-butyl ether (MTBE)	BRL (<15)	BRL (<2)	BRL (<2)	BRL (<2)	BRL (<2)
Naphthalene	68	BRL (<0.5)	BRL (<0.5)	BRL (<0.5)	BRL (<0.5)
Temtative IdentifiedI Compounds (TICs)	690	13	7	37	29
VOCs+TICs	25991	14	7	37	29
Degradation percentage of Targeted VOCs		99.95%	99.97%	99.86%	99.89%
TPH-GRO	34450	--	BRL (<50)	--	190
TPH-DRO	290	--	75	--	210

Alkaline ASP and Fe-EDTA ASP, respectively (Figure 2). As indicated by the results, the applied ASP treatment conditions (e.g., SP dosage and treatment time) was insufficient to achieve the desired treatment goal. The data revealed the influence of soil matrixes on the destruction efficiency of the COCs with ISCO processes whose reactions were non-selective towards all reactants in the soil slurry systems.

Incomplete reactions, resulting in increases in concentration of reaction intermediates such as benzene and toluene, were observed in Fe-EDTA ASP reactors. Nonetheless, it should be noted that the reaction intermediates such as benzene (a site contaminant and a oxidation intermediate of toluene and naphthalene) can be further degraded given sufficient dosage and treatment time.

The variation in pH, ORP and SP levels during the soil slurry FS were monitored. The pH level in the Fe-EDTA ASP reactors decreased significantly from near neutral (pH 6.9, referred to the experimental controls) to an acidic condition (pH 2.3) These data are not provided here. The results elucidate the influence of persulfate chemistry on the treatment systems. In contrast, in the Alkaline ASP reactors, the dosed NaOH maintained the pH level in the reactors within the desired range (pH >10.5) during the testing period.

As with pH, the ORP level was significantly influenced by both the ASP concentration and treatment processes. In the Fe-EDTA ASP reactor, the ORP with ASP at 203 g/kg wet soil, significant degradation of MtBE (67% and 50%, xylenes (40% and 38%) and NAP (13%, and 50%) were observed with level

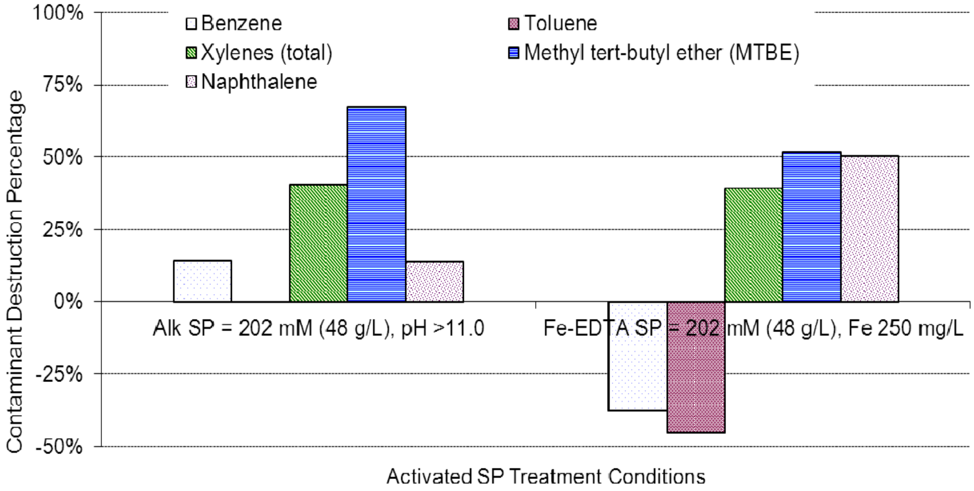


Figure 2. Achieved Degradation of BTEXs, MtBE and NAP with Alkaline ASP and Chelated-Fe ASP in Soil Slurry Systems; Soil-Liquid Ratio 2.5:1 at 20 ºC and 100 rpm for 28 days

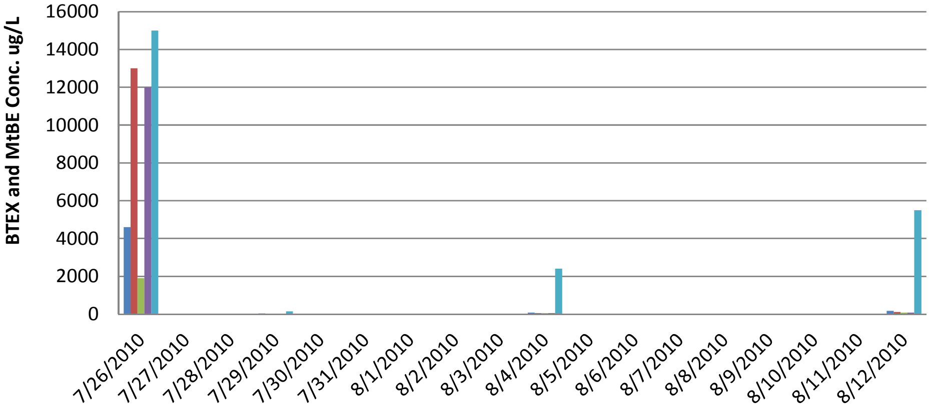
increased from - 93 mV (referred to the controls) to 660 mV in the end of the test, reflecting a highly oxidative condition in the treatment systems. In contrast, a low ORP level of 50 mV at the end of the test was observed in the Alkaline SP reactor. The results revealed the difference in treatment mechanisms between Alkaline ASP and Fe-EDTA ASP processes.

There was 93.5% of the dosed SP consumed in the Alkaline ASP reactor during the 28-day test. In contrast, 28.2% of the dosed SP remained in the Fe-EDTA ASP reactor. The results indicate a faster reaction rate of SP with the site soil constituents in the Alkaline ASP process than those in the Fe-EDTA ASP treatment.

4.3 Pilot Scale FS Results- Degradation of COCs and ASP Transport

The pilot study conducted at the subject site indicated that total BTEX and MtBE concentrations were significantly reduced in the ISCO application areas during the 15 day testing period (Figure 3). Total BTEX (from 31,500 µg/L at pre-injection to 223 µg/L) and MtBE (from 15,000 µg/L at pre-injection to 2400 µg/L) were degraded by 99% and 84%, respectively, in the treatment area 7 days after the Fe-EDTA ASP injection. The observed results are consistent with the laboratory FS findings that the Fe-EDTA ASP process is effective in degrading gasoline-related COCs including BTEX and MtBE.

ISCO application radius of influence extended over 18 feet, evidenced by the variation of reaction parameters including pH, ORP and sulfate levels in an observation well, located 18 feet equidistant from the two injection points. Variation in pH and ORP levels in two additional observation wells indicated the influence of the ISCO application beyond 18 feet. However, these wells showed no significant changes in total BTEX or sulfate concentrations over the study period, mostly likely due to the impact from the density-driven downward flow behavior of the injected 30% (w/w) ASP solution (Huling and Pivetz, 2006). The density-driven vertical flow effect, in addition to the volume of the ASP dosage, is considered and incorporated into the full-scale field ISCO design.



	7/26/2010	7/29/2010	8/4/2010	8/12/2010
■ Benzene (µg/L)	4600	40	84	170
■ Toluene (µg/L)	13000	10	50	120
■ Ethyl-benzene (µg/L)	1900	10	50	81
■ Xylenes (µg/L)	12000	10	50	85
■ MTBE (µg/L)	15000	150	2400	5500

Figure 3. Degradation of BTEX and MtBE in the ISCO Treatment Area after the Fe-EDTA ASP Injection

5. CONCLUSIONS

This study demonstrated the effectiveness of degrading gasoline-related COCs including BTEX, MtBE and NAP with Fe-EDTA ASP and Alkaline ASP processes. In both groundwater and soil slurry matrixes, BTEX, MtBE and NAP were rapidly degraded by the two evaluated ASP processes. The COCs in groundwater were degraded to below 0.5 µg/L with the applied ASPs within 14 days, corresponding to a COC destruction percentage of 99.9%. The results indicate the ASP process can be used as the remedial approach to provide active COC destruction and migration control mechanisms for the subject site.

The results of the small scale pilot testing demonstrated that BTEX and MtBE were significantly degraded with the applied ASP process. Monitoring of reaction parameters (i.e., pH, ORP and sulfate levels) showed that the ROI with ASP treatment extended over 18 feet. The data also revealed the need of optimizing the field design with respect to the ASP dosage, oxidant transport, depths of injection wells/observation wells, etc.

The ASP-SSD coupling approach appears to be a promising cost-effective remedy for the subject site. The remedial systems are designed to provide both active ISCO treatment mechanisms and passive SSD indoor air pollution controls. A full-scale ASP application is being implemented for cleanup and in support of the site redevelopment plan. A SSD system consists of 4-inch slotted PVC pipe placed directly beneath the floor slab, with vapor barrier, across the entire redevelopment building footprint. A bed of gravel 6 inches thick is placed under the entire floor slab area, with a deeper gravel bed located beneath/around the slotted pipe. Three venting piping systems are constructed in “H” configurations and connected to 4-inch risers going up the interior walls of the building and terminating in vents on the roof. A long-term performance monitoring program will be implemented for evaluation of the proposed remedial approach at the site.

6. REFERENCES

Huling, S.G. and Pivetz, B.E. 2006. In Situ Chemical Oxidation. Environmental Protection Agency Engineering Issue.

Huang, K.C., Couttenye, R., and Hoag, G.E. 2002. Kinetics of Heat-Assisted Persulfate Oxidation of methyl tert- butyl ether (MTBE). Chemosphere. Vol. 49/4, PP 413-420.

Huang, K.C., Zhao Z., Hoag, G.E., Dahmani, A., and Block, P.A. 2005. Degradation of Volatile Organic Compounds with Thermally Activated Persulfate Oxidation. Chemosphere. Vol. 61, PP 551-560.

Johnson, R. L., Tratnyek, P. G., O'Brien Johnson, R. 2008. Persulfate persistence under thermal activation conditions. Environ. Sci. Technol. 42, 9350-9356

Liang, C.J., Huang, C.F., Yan-Jyun Chen, Y.J. 2008. Potential for activated persulfate degradation of BTEX contamination. Water Res. 42, 4091–4100.

Nadim, F., Huang, K., Dahmani, A. 2006. Remediation of soil and groundwater contaminated with PAH using heat and Fe(II)-EDTA catalyzed persulfate oxidation. Water Air Soil Pollut. Focus 6, 227-232

Tsitonaki A., B. Petri, M. Crimi, H. Mosbæk, R.L. Siegrist, and P.L. Bjerg. 2010. In situ chemical oxidation of contaminated soil and groundwater using persulfate: A review. *Critical Reviews in Environmental Science and Technology,* 40(1):55-91.

Watts, R.J. 2011. Enhanced Reactant-Contaminant Contact through the Use of Persulfate In Situ Chemical Oxidation (ISCO). SERDP Project ER-1489

Chapter 12

DIRECTIONALLY DRILLED AND ENGINEERED HORIZONTAL REMEDIATION WELL SCREENS ACCELERATE SITE CLOSURE

Garry Van Heest[1 §], Michael Sequino[1], George Losonsky[2]
[1]Directional Technologies Inc., North Plains Industrial Drive, Wallingford, CT, USA, [2]Losonsky & Associates Inc., Glen Haven Drive, Baton Rouge, LA, USA.

ABSTRACT

Environmental regulators increasingly prefer in situ remediation technologies and active vapor intrusion (VI) mitigation. Vapor mitigation and in situ source removal represent the primary concern at sites where water table or vadose zone hydrocarbon volatilization can affect indoor air quality.

Horizontal directional drilling (HDD) technology and engineered horizontal well screens are applied at sites where in situ remediation strategies and/or VI drive site closure strategy. Where chlorinated solvents are the issue, horizontal wells enable soil vapor extraction (or multiple in situ chemical oxidation injections) and provide subslab depressurization with appropriately sized/controlled blower systems.

Free phase light non-aqueous phase liquid (LNAPL) accumulations can pose significant in situ remediation challenges. Vertical wells cannot supply sufficient oxygen to maintain vigorous bacteria populations required for successful biosparging and free phase biosparging is generally not considered feasible. However, horizontal well screens and blower systems for biosparging have been successfully applied at a site with thousands of gallons of free product (Sequino et al, 2011).

HDD coupled with engineered horizontal well screens are used to reach inaccessible locations and achieve site closure more rapidly than vertical technology. Horizontal screens hundreds of feet long are installed beneath structures and other locations inaccessible to vertical equipment. More rapid site closure is achieved via two principal factors: zone of influence (ZOI); and the

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[§] Corresponding Author: Garry Van Heest, Directional Technologies Inc., North Plains Industrial Drive, Wallingford, CT, 06492, Tel: 203-294-9200, Email: gvanheest@directionaltech.com

stratified nature of typical target zones of sedimentary origin (Raghupathi et al, 2010). Horizontal screens develop significant elliptically-shaped ZOI. Vertical anisotropy resulting from the sedimentary stratification causes channeling and impedes fluid flow through the porous formation to the vertical screen in the most efficient pattern, producing the greatest rate of pore volume exchange. Horizontal screens placed largely within a single sedimentary unit will develop the most efficient flow pattern within that sedimentary unit.

Keywords – biosparging, horizontal well, horizontal directional drilling.

1. INTRODUCTION

Remediation professionals have for many years used horizontal remediation wells (HRWs) to successfully address technically challenging problems such as: 1) employing air sparge or biosparge/soil vapor extraction (AS/SVE) remediation to large subsurface LNAPL releases; 2) vapor intrusion mitigation beneath occupied commercial structures; 3) reaching inaccessible contaminant masses located beneath structures and civil infrastructure; and 4) dependably achieving rapid site closure.

2. MATERIALS AND PROCEDURE

Horizontal directional drilling technology was developed for the oil and gas industry to enhance recovery and more recently employed along with hydraulic fracturing to produce hydrocarbons from shale formations. The technology was subsequently adapted for shallow applications including subsurface utilities, such as fiber optic cable installation beneath roads.

Horizontal drilling technology employs specialized drill rigs, high tensile strength tubulars, special drill bits and battery operated sonde and locator instruments. A HDD drill rig is compact, maneuverable, capable of exerting considerable hydraulic horizontal thrust and designed for robust production rates, enabling the driller to operate the rig from a console without manually manipulating tubulars.

Directional Technologies Inc. began designing and installing HRWs over 20 years ago. Well materials used in HRWs include polyvinyl chloride (PVC), high density polyethylene (HDPE), fiberglass reinforced epoxy (FRE) and stainless steel. The driller has two options for HRW installation: continuous (entry-exit) well and blind (no exit) well. For a continuous well, the drill bit enters the ground, reaches a specified target depth, breaches the surface ("daylights") and the riser and screen are pulled into the bore. For a blind well, the drill bit enters the ground, reaches the specified target depth, the drill bit is withdrawn and the screen and riser are pushed into position. Blind wells are very useful where surface space is limited or there is no real estate in which to daylight.

Horizontal well screen design is critical to successful HRW performance. In other words, it is essential that the screen provide uniform flow (or vacuum) across the entire screen length. Directional Technologies Inc. achieves screen design uniformity by using hydrogeologic software to model fluid flow through the riser, screen slots and into/through the formation.

Directional Technologies Inc. regularly mitigates VI by installing HRWs under buildings to depressurize the floor slabs. In many cases one HRW is sufficient to depressurize the entire slab. A significant advantage afforded by this technology is that the HRW can be installed in occupied buildings without enduring costly business interruptions. Vapor intrusion mitigation HRWs can be designed to also efficiently distribute in situ chemical oxidation (ISCO) reagents or bioamendments for enhanced biodegradation of contaminants within target soil volumes that are either too large or inaccessible for vertical injection methods to be successful (Raghupathi et al, 2012).

Conventional wisdom teaches that biosparging technology is ineffective at sites with significant free phase LNAPL accumulations because subsurface oxygen concentrations cannot be adequately maintained to sustain bacteria populations that use LNAPL as a nutrition source. Owing to substantially greater screen length, HRW screens provide significantly greater contact area with impacted media than vertical wells (Sequino et al, 2011). This concept is illustrated in Figure 1 (Sequino et al, 2011).

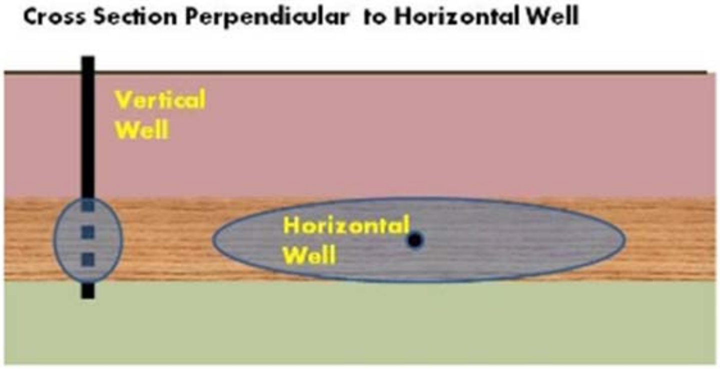

Figure 1.

A horizontal screen delivers oxygen into an LNAPL-impacted soil horizon evenly, as a line source, which is much more effective than the point sources provided by a series of vertical wells. This difference enables HRWs to be successfully used for biosparging.

A retail petroleum site in New England experienced gasoline releases from underground storage tanks (USTs) in the 1990s. The USTs were replaced but only some impacted soil was removed and replaced with clean fill. The remaining impacted soil re-contaminated the clean fill and groundwater. Analysis confirmed that an air sparge/soil vapor extraction (AS/SVE) system using HRWs would be significantly less expensive to install than one using vertical wells. This is because the HRWs avoided costly “soft dig” techniques for trenches required of the vertical system for interconnecting piping installation. In addition, HRW installation avoided the prohibitive cost of interrupting the normal operations of the business.

During preparation of the site’s remediation feasibility study, it was estimated that a vertical well-based AS/SVE system would require 3-5 years of operation and maintenance (O & M) to achieve closure numerical criteria (Raghupathi et al, 2012). The HRW-based AS/SVE system only operated for approximately 1 year when closure criteria were achieved (Raghupathi et al, 2012).

3. DATA AND ANALYSIS

Directional Technologies Inc. installed a network of parallel HRWs (four [4] AS and three [3] SVE) approximately 600 feet long to remediate a large subsurface gasoline release at an international airport in 2011. Horizontal wells were selected because of severe site constraints, the release magnitude and aerial extent—thousands of gallons and multiple acres, respectively and the need to remediate the site quickly. The wells were constructed of four (4)-inch diameter SDR-11 HDPE.

Various tests were performed after well installation and during operation in 2012 to determine HRW performance parameters. Pressure readings were recorded for air pressure exerted on the AS wells and a summary for AS well HAS-2 is presented in Table 1 (Sequino et al, 2011).

The summary shows that air pressure is measured immediately at system start-up along the entire well screen, demonstrating how effective HRWs are compared with vertical wells. This can be attributed to substantially greater screen length and impacted media contact area than a vertical well (as discussed in Section 2.2) and significantly greater ZOI compared with vertical wells. Initially after startup, a horizontal well will have a ZOI that is cigar shaped around the screen (see Figure 2), with a capture zone about as wide as the zone of influence measured in a vertical well test in the same formation (Sequino et al, 2011).

Table 1. HAS-2 Pressure/Air Flow Summary, May-September 2012

Date	Wellhead Pressure (PSI)	Wellhead Pressure (in. WC)	Sparge Well Air Flow (ACFM)	Sparge Well Air Flow (SCFM)
5/17/2012	7	193.9	152.7	216.9
6/1/2012	7	193.9	209.4	303.1
6/15/2012	7.5	207.8	218.2	321.7
6/30/2012	7.25	200.8	218.2	308.8
7/15/2012	7	193.9	218.2	307.6
7/31/2012	7.5	207.8	261.8	376.9
8/15/2012	7	193.9	261.8	371.8
8/31/2012	7	193.9	244.3	344.6
9/13/2012	7.25	200.8	261.8	372.6

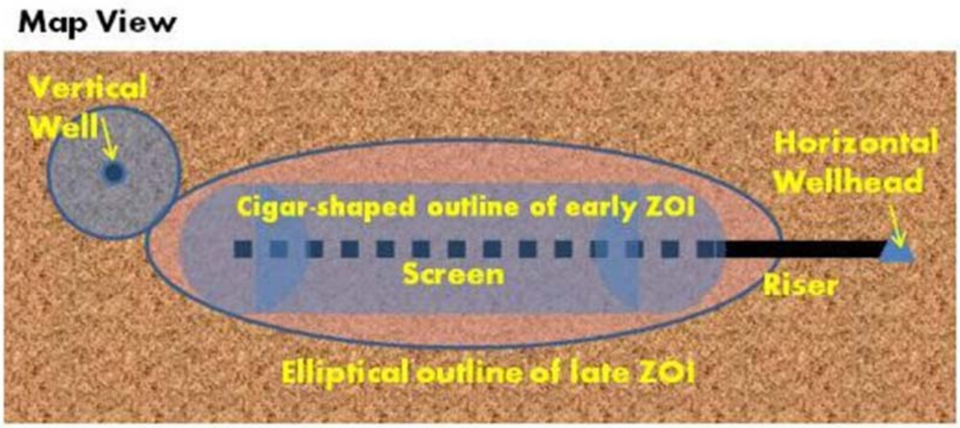

Figure 2.

Unlike the vertical well, which will reach its maximum ZOI relatively quickly, with little variation along its comparatively short screen, the horizontal well's ZOI will gradually develop into an elliptical shape, with the screen endpoints defining the focal points of the ellipse (Sequino et al, 2011). The distance to the edge of the ZOI will be greatest at the well's midpoint (Sequino et al, 2011). Only at the screen endpoints will the horizontal well's ZOI be similar to that of a vertical well in the same formation (Sequino et al, 2011). The HRW's ZOI will typically exceed that of a vertical well along most of the horizontal screen. Our experience shows that the horizontal well screen ZOI is usually many times greater than a corresponding vertical well screen in the same formation. For example, the HRWs installed at the aforementioned airport have a ROI of at least 30 feet on either side of the screen (Sequino et al, 2011). We have HRWs operating in industrial VI mitigation systems with ROI exceeding 200 feet.

This ZOI shape difference is due to two main factors. One is simply the screen length, which is too short in the vertical well for the elliptical shape to present much change in the distance to the edge of the ZOI along the screen (Sequino et al, 2011). The other is the stratified nature of typical target zones of sedimentary origin. Vertical anisotropy resulting from the stratification causes channeling and impedes fluid flow through the porous formation to the vertical screen in the most efficient pattern, producing the greatest rate of pore volume exchange. A horizontal screen placed largely within a single sedimentary unit will develop the most efficient flow pattern within that sedimentary unit (Sequino et al, 2011).

These aforementioned factors explain why HRWs usually significantly outperform vertical wells in the same formation. For example, daily volatile organic compound (VOC) recovery rates (in pounds [lbs.] per day) for SVE well HSVE-2 at the aforementioned airport site for the first six months of 2012 are presented in Table 2 (Sequino et al, 2011).

Table 2. HSVE-2 Vacuum, Air Flow and VOC Recovery Summary January – July 2012

Date	Wellhead Vacuum (in. WC)	Air Flow (SCFM)	VOC Concentration (ppmv)	VOC \Recovery Rate (lbs./day)	Cumulative VOCs Recovered (lbs.)
1/25/2012	14	119	1,256	192	1,041
2/29/2012	32	209	1,300	297	10,665
3/31/2012	24	166	1,270	261	18,339
4/22/2012	52	273	1,197	252	24,080
5/21/2012	56	175	1,197	174	25,154
7/11/2012	20	304	1,173	320	25,291
7/16/2012	40	317	509	235	26,687

The VOC recovery rates range from 174 to 320 lbs. per *day*, with a cumulative VOC recovery of 26,687 lbs. over six months. These performance results were achieved by a single well, indicating that the full-scale horizontal well system will achieve site closure much more rapidly than any equivalent vertical well system.

4. CONCLUSION

Directional Technologies Inc.'s horizontal directional drilling experience coupled with its expertise in engineered well screen design and horizontal well installation technology has a decade-long successful track record. This technology coupling provides unique capabilities related to site/structure access, business disruption avoidance, accelerated site closure and enhanced site safety. Horizontal remediation well technology is proven and has been successfully used for over 20 years. Horizontal remediation wells have consistently outperformed vertical wells because they provide an effective delivery mechanism to reach previously inaccessible remediation targets, enable targets beneath buildings to be remediated without disrupting business operations and usually result in more rapid site closure, providing a superior option for cost-effective site remediation.

5. REFERENCES

Raghupathi N, Finney A.R, Sequino M.J, and Losonsky G, 2012, Rapid Closure of Lingering Off Site Plume Remediation Program in Residential Neighborhood Using Horizontal Air Sparge and Soil Vapor Extraction Wells, Monterey, California, May 21-24, 2012, Battelle, Columbus, Ohio 2012.

Raghupathi, N., Finney, A., and Losonsky, G., 2010, *Site Remediation Using Horizontal Air Sparge/Soil Vapor Extraction and Multi-Phase Extraction Wells,* 16th Annual Florida Remediation Conference [abstracts], Orlando, Florida, October 14-15, 2010.

Sequino, M.J., Losonsky, G., and Oppenheim, J.R., 2011, *Post-Closure Analysis Proves Success of Enhanced Hydrocarbon Bioremediation Using Six Horizontal Sparge Wells at Petroleum Products Bulk Terminal,* Battelle Symposium on Bioremediation and Sustainable Environmental Technologies, Reno, Nevada, June 27-30, 2011.

PART V: Risk Assessment

Chapter 13

DIOXIN IN SOIL: REEXAMINING HOW CLEAN IS CLEAN ENOUGH?

Christopher M. Teaf[1 §] , Douglas J. Covert[2], Gregory Council[3], Talaat Ijaz[4]
[1]*Center for Biomedical & Toxicological Research, Florida State University, 2035 E. Dirac Dr., Tallahassee, FL, 32310,* [2]*Hazardous Substance & Waste Management Research, Inc., 2976 Wellington Circle West, Tallahassee, FL, 32309,* [3]*Tetra Tech GEO, 1165 Sanctuary Parkway, Suite 270, Alpharetta, GA, 30009,* [4]*Tetra Tech GEO, One Salem Square, 295 Route 22 East, Suite 104E, Whitehouse, NJ, 08889*

ABSTRACT

Since 2009, EPA has released several documents related to the toxicity of dioxin and has published (and retracted) draft screening levels for dioxin in soil. These documents have served to raise technical and public awareness about environmental dioxin, particularly at soil contamination sites. Many such U.S. sites, at various stages of what are often contentious and lengthy investigation, remediation, public communication, and site management processes, have highlighted the toxicological issue of "how clean is clean enough". Since the 1980's, USEPA reports that environmental dioxin levels have been reduced more than 90%, and the CDC reports that serum dioxin levels in the U.S. have decreased over 80%. Residential open trash burning now reportedly represents the largest identifiable source of dioxin emissions. Further, the chemical character of recently released dioxin exhibits a greater proportion of congeners of lower toxicity. Thus, in addition to declining overall environmental levels, total risk of dioxin to which humans are exposed is decreasing. Environmental dioxin in soil represents a minor component of aggregate exposure sources, with USEPA estimating that less than 2% of dioxin exposure to Americans occurs through soil contact. Even for residents living on properties with dioxin-impacted soil, recent studies employing fingerprint analyses indicate that observed dioxin body burdens of those individuals do not originate from soil sources. Rather, congener-specific results confirm longstanding observations that diet represents the greatest source

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[§] Corresponding Author: Christopher M. Teaf, 2976 Wellington Circle West, Tallahassee, FL, USA, 32309, Tel: 850- 681-6894, Email: cteaf@hswmr.com

of dioxin exposure. Given the declining body burden of dioxin, lack of evidence suggesting that background levels are a legitimate health concern, impressive reductions in volume and toxicity of dioxin emissions, and the minimal contribution represented by soil dioxin sources, it may be worthwhile to re-evaluate the scientific support for more restrictive health and soil guidelines. Practical examples of alternative protective remedial target levels, approaches, and implemented risk reduction strategies are discussed.

Keywords: dioxin, soil, screening, cleanup guidelines, risk, human exposure

1. INTRODUCTION

Nearly thirty years have passed since the Centers for Disease Control (CDC) produced a dioxin risk assessment for residential soils (Kimbrough et al., 1984), which subsequently led to EPA recommending a 1 part per billion (ppb; 1,000 parts per trillion or ppt) Action Level (USEPA, 1998). That Action Level, as originally published, represented a concentration in residential soil at CERCLA and RCRA sites above which some form of corrective action was judged to be appropriate. As derived, the 1 ppb level was estimated to represent an upper bound cancer risk level of 2.5×10^{-4} (USEPA, 1998), which is near the upper end of EPA's acceptable risk range. In the intervening years, federal and state agencies, university researchers, industry investigators, and independent consumer advocacy groups have attempted to come to consensus on defining the true toxic potential of dioxin to humans. In this review and analysis, we focus on human exposure to dioxin in soil under unrestricted residential circumstances, with particular emphasis on the establishment of appropriate protective remedial target concentrations. Through the use of the term "dioxin" we refer to the group of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/Fs). When specificity is needed, we refer explicitly to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), or TCDD-TEQ (Toxic Equivalent).

2. HISTORICAL ENVIRONMENTAL SOURCES AND BODY BURDENS

According to the most recent comprehensive evaluation of dioxin sources to the environment, emissions from municipal waste combustion dropped from being the number one source to number four on the list between 1987 and 2000 (USEPA, 2006). As of 2000, backyard burning of domestic refuse represented the primary source of airborne dioxin emissions in the United States. The document also reported that, in that timespan of 1987 to 2000, dioxin releases to the circulating environment of the United States from all known sources saw a reduction of approximately 90% (USEPA, 2006).

In parallel fashion, human blood serum levels in the U.S. population have dropped by approximately 80% in the intervening decades (based on NHANES 2003-2004 data; CDC, 2009a; CDC, 2009b). Although low levels of dioxin continue to be detectable in human blood serum and other tissues, the CDC (2009b), in discussing human dioxin concentrations, notes that "There are no firmly established relationships between concentrations (mainly considering TCDD) and health effects in people."

It is likely that environmental levels, and to a similar extent, body burdens have continued to decrease since the early 2000's, based on the scientific and regulatory scrutiny that dioxin has received.

3. HUMAN INTAKE OF DIOXIN

It is widely accepted that current human dioxin intake for the general population is dominated by dietary sources (ATSDR, 1998; NAS, 2006; USEPA, 2006), with USEPA (2006) stating that diet typically accounts for more than 95% of human exposure. It has been estimated that soil dioxin may contribute significantly to human intakes in an indirect manner through the food chain (e.g., soil ingestion by cattle, and via runoff to water bodies that may be resources of food fish and other seafood species; USEPA, 2006). However, direct human intake of impacted soil through ingestion, dermal contact and inhalation of particulates, even in areas of high concentration, is expected to result in less than 2% of total dioxin intake (Pohl et al., 1995; DeRosa et al., 1997). Further, it has been reported in some studies that people who live in homes that have high soil or indoor dust levels do NOT exhibit elevated serum levels (Aberg et al., 2009; Tohyama et al., 2011; UM, 2011). Specifically, Aberg et al. (2009) concluded that:

> "For most residents living at or near PCDD/F contaminated sites… it is likely that their dietary habits and food preparation routines are more important for the internal body burden of PCDD/F rather than the magnitude of the measured soil concentrations at the site."

Similarly, Tohyama et al. (2011) concluded that "…people living around the dioxin-contaminated area did not take in and accumulate an excess amount of dioxins from the soil of the playground and residential areas…" This conclusion was reached even though soil concentrations in play areas were up to 6.8 times greater than the Japanese environmental standard of 1,000 ppt (1 ppb), and the study population included children from 3 to 15 years of age. In that age group of the study, blood dioxin levels were most significantly correlated with previous breast feeding duration (Tohyama et al., 2011).

Conventional theoretical considerations aside, if relatively highly contaminated soils on which children are actively playing do not appear to result in increased human intake, it seems unlikely that low concentrations approaching common background levels of dioxin, such as the same available screening levels that would result from use of the recently proposed toxicological guidance levels, would be of any toxicological significance. Background soil levels of dioxin and dioxin-like compounds in rural areas with no known local or specific sources of dioxin have been estimated to range from 0.2 to 11.4 ppt dioxin TEQ, with an average of 1.69 ppt (USEPA, 2007). These values are within the range of and somewhat consistent with earlier USEPA (2003) estimates of 2.8 ppt in rural soils and 9.4 ppt in urban soils. Somewhat disturbingly, these are also in the range of default residential guidance concentrations of dioxin from some agency sources, often in the 4 to 10 ng/kg (= ppt) range for soils (USEPA, 2009b).

4. SOIL SCREENING, REMEDIATION AND RISK MANAGEMENT

4.1 Soil Screening

Soil screening activities typically involve the practice of initially evaluating site soil concentrations against default guidelines based on conservative unrestricted exposure assumptions. Depending on the particular state or federal agency from which they come, these screening guidelines are termed Regional Screening Levels, Preliminary Remediation Goals, Tier 1 Levels, Soil Cleanup Target Levels, etc. Irrespective of the name, they generally may be thought of as default, lifetime exposure “safe” levels, below which no significant risk from exposure to soil chemicals is anticipated. They are not intended for use as *de facto* cleanup levels for environmental investigation sites and should not be used as such (USEPA, 2012a).

Throughout the 1990s to the early 2000s, federal soil screening levels for dioxin (as 2,3,7,8-TCDD equivalents) were set at approximately 4 parts per trillion (ppt), and were available from EPA Regions 3, 6 and 9 in summary risk tables that had different names and slightly different derivations. In 2004, the various USEPA screening levels were consolidated into a single set of values termed the Regional Screening Levels (RSLs). The current USEPA (2012a) RSL for 2,3,7,8-TCDD is 4.5 ppt, based on potential for carcinogenic effects at a risk level of 10^{-6}.

In 2008, the CDC, via the Agency for Toxic Substances and Disease Registry (ATSDR), clarified their previous dioxin evaluation policy to establish a single comparison value for evaluation of residential soil at 50 ppt TCDD equivalents (ATSDR, 2008). The 50 ppt comparison value was the existing ATSDR screening level (Tier 1) in their former three tiered approach to evaluation, with the 1 ppb USEPA Action Level being their Tier 3 level. The 2008 clarification did not reflect new science, it did not impact ATSDR's published Minimal Risk Level (MRL; 1 pg/kg•day; comparable to the more commonly seen term "reference dose" or RfD), and it did not replace EPA's 1 ppb dioxin Action Level.

Upon the release of its Draft Interim PRG document in 2009, EPA proposed a change to the PRG for dioxin in residential soils to 72 ppt (0.072 ppb; USEPA, 2009a). That proposed interim PRG was based on non-cancer effects, but was noted as being protective of cancer effects at approximately the 1×10^{-5} risk level. The Draft PRG document also included an alternative PRG of 3.7 ppt, based on potential cancer risks at 10^{-6}. As with the ATSDR/CDC updated guidance, the potential new PRG was not based on any new scientific studies. For potential cancer risks, the calculated interim PRG was based on a 1985 oral cancer slope factor derived by EPA's Office of Health and Environmental Assessment, and for the proposed interim PRG of 72 ppt for non-cancer effects, the PRG was based on ATSDR's 1998 MRL of 1 pg/kg•day. The interim proposed PRG, as well as the entire Draft document, were withdrawn as of October 2010, when the EPA dioxin reanalysis process was bifurcated into a dose-response/RfD evaluation (Volume 1) and a cancer risk evaluation (Volume 2; pending).

Prior to the October 2010 decision to separate the process, EPA released the Draft Reanalysis of Key Issues Related to Dioxin Toxicity (USEPA, 2010) in May of 2010. In that document, candidate non-cancer and cancer toxicity factors were offered (oral RfD of 0.7 pg/kg•day; oral CSF of $1X10^6$ $(mg/kg•day)^{-1}$). Although no soil screening levels were included in the draft reanalysis, the identified RfD value is consistent with the former interim PRG document and would result in a screening level of approximately 70 ppt for non-cancer effects using the same exposure assumptions. As with the 2009 Draft Interim PRG document, the 2010 Draft Reanalysis document was withdrawn as of October 2010.

In addition to the USEPA and CDC/ATSDR federal risk-based screening levels, many state environmental agencies have adopted their own dioxin soil screening levels and cleanup targets. As shown in Table 1 (adapted from USEPA, 2009b), the risk-based targets range from 3.9 ppt to 1,000 ppt (the latter value is implemented by Alabama and Texas as discussed in the footnote of the original USEPA (2009b) table), depending primarily on the chosen cancer risk level, oral CSF, and soil ingestion rate.

Table 1. From USEPA, 2009b. State residential default dioxin in soil target levels.

State / US Territory	Default Soil Target (ppt)	Oral Slope Factor $(mg/kg\bullet day)^{-1}$	Target Cancer Risk	Soil Ingestion Factor (mg•yr/kg•day)
New England	3.9	1.50E+05	1.0E-06	114
Delaware	4	1.50E+05	1.0E-06	114
Mississippi	4.26	1.50E+05	1.0E-06	114
Arizona	4.5	1.30E+05	1.0E-06	114
Maryland	4.5	1.30E+05	1.0E-06	114
Oregon	4.5	1.30E+05	1.0E-06	114
Wyoming	4.5	1.30E+05	1.0E-06	114
Florida	7	1.50E+05	1.0E-06	69
New Hampshire	9	1.50E+05	1.0E-06	105
Maine	10	1.30E+05	1.0E-06	120
Washington	11	1.50E+05	1.0E-06	75
Iowa	19	1.50E+05	5.0E-06	114
Minnesota	20	1.40E+06	1.0E-05	45
Ohio	35.8	1.50E+05	1.0E-05	114
Alaska	38	1.50E+05	1.0E-05	114
Indiana	45	1.50E+05	1.0E-05	114
Kansas	60	1.50E+05	1.0E-05	42
Georgia	80	Not Specified	1.0E-05	48
Michigan	90	7.50E+04	1.0E-05	114
Pennsylvania	120	1.50E+05	1.0E-05	57
Hawaii	390	1.50E+05	1.0E-04	114
American Samoa	450	1.30E+05	1.0E-04	114
Guam	450	1.30E+05	1.0E-04	114
Northern Mariana Islands	450	1.30E+05	1.0E-04	114
Alabama	1000	OSWER Directive for residential soil		
Texas	1000	OSWER Directive for residential soil		

In their state cleanup guidance summary document, USEPA (2009b) provided the following cautionary language:

> "…a number of states have essentially adopted values developed for screening purposes (rather than cleanup decisions) as their cleanup level. These low levels match the U.S. EPA Regional Screening Level for unrestricted use. The scientific basis, external peer review, and transparency of these adopted

> values do not appear to be well documented for such an application, i.e., for other than the screening purpose for which they were designed."

4.2 Remediation

In addition to the default screening levels, Action Levels (ALs) and other cleanup levels, also called "target levels", represent values above which some remedial action or exposure limitation is recommended for site rehabilitation. Much like screening levels, target levels are default, generic guidelines that do not typically take into account potential site-specific features and risk management options. In order to include site-specific considerations, cleanup target levels may be adjusted for use as remediation levels, which represent the ultimate levels to which a site cleanup should conform. If risk managers for a site conclude that site-specific considerations are not necessary, the cleanup target levels may be accepted as remediation levels.

The only published cleanup level that is widely used on a federal basis is the USEPA Action Level of 1,000 parts per trillion (ppt; 1 part per billion; 1 ppb). As discussed above, many state environmental agencies have established screening and cleanup levels for dioxin in soil, but the somewhat ambiguous application of those values at times makes it difficult to identify any specific value as a cleanup value versus a screening level. Some states (e.g. TX, AL) have adopted the USEPA Action Level as state guidance.

With respect to refinement of cleanup levels for use as remediation levels, a review of more than 170 soil/sediment Records of Decision (RODs) for dioxin based on current or future residential exposures revealed that the vast majority of sites ultimately used the AL of 1 ppb as the final remedial target level (ACC, 2010).

4.3 Risk Management

When confronted with dioxin and dioxin-like compounds in soil at a site for which unrestricted residential exposures need to be assumed, project managers and risk assessors may consider multiple risk management options. Public acceptance is an important consideration; however, in this review we comment on the technical aspects of risk management. While there is a substantial body of literature for various technical considerations relevant to dioxin risk assessment, there is not scientific consensus on the best assumptions and methods to use. For instance, the following factors are still the subject of some scientific debate:

- ***Toxicological basis for evaluation.*** Which category of effects is more relevant to human health, systemic toxicity or carcinogenic effects? Does dioxin have a linear nonthreshold mode of action, or, as many studies suggest, is it a threshold carcinogen having a floor level below which adverse impacts do not occur?;

- ***Toxicological guidance values.*** After several decades of intense study, no consensus cancer slope factor is available with which to evaluate potential carcinogenic effects from exposure to dioxin, and only recently has EPA offered final toxicological guidance for systemic effects;

- ***Relative bioavailability.*** SRC (2010) and others (e.g., WHO, 2005) conclude that relative bioavailability for dioxin in soils is likely to be substantially less than 100%. However, due to uncertain effects of congener chlorination, and due to significant differences between results among different test species, it has not been possible to identify a representative range or upper bound level for use in human estimates; and,

- ***Appropriate cancer risk level.*** In general, the classic 10^{-4} to 10^{-6} acceptable risk range still is widely cited, though some states use 10^{-5} as a dioxin-specific default and some states use 10^{-6}.

Putting all of this into perspective for exposure to dioxin and dioxin-like compounds in residential soil, the lowest presently acceptable soil concentration below which no significant risk is assumed to occur currently is approximately 4 ng/kg or 4 ppt (see RSL of 4.5 ppt for residential exposure; USEPA, 2012a), and the highest Action Level above which some form of cleanup action is advised is 1,000 ppt (1 part per billion, 1 ppb; the USEPA (1998) Action Level). The following section presents information for going forward with evaluations of soil dioxin based on the traditional approach as envisioned by the ongoing reanalysis process, as compared with alternative approaches that are scientifically valid and that have been accepted by various regulatory agencies.

5. RISK MANAGEMENT APPROACHES

5.1 Traditional Approach

As noted, current screening levels and remediation levels based on traditional, deterministic, point estimate methods for specific exposure assumptions, and based on the standard acceptable risk level range of 10^{-6} to 10^{-4}, span from approximately 4 ppt to 1,000 ppt. Maintaining the traditional approach, but incorporating more recent toxicological guidance from the USEPA (2012b) Volume 1 Reanalysis document, an oral Reference Dose (RfD) was proposed and now is published in the Integrated Risk Information System (IRIS; USEPA, 2012c). As such, that RfD (0.7 pg/kg•day; $7X10^{-10}$ mg/kg•day) now represents the preferred value with which to develop site-specific dioxin screening levels

(USEPA, 2012d). According to USEPA (2012d), use of the newly promulgated IRIS RfD for dioxin, along with default exposure factors, would result in a screening level of 50 ppt. This level, as well as remediation levels derived using the non-cancer IRIS RfD, are expected to fall within the acceptable cancer risk range currently used by USEPA. Thus, the 50 ppt screening level and any associated remediation levels based on the IRIS RfD are judged to be protective of potential cancer effects as well (USEPA, 2012d).

5.2 Alternative Approach 1 – Probabilistic Risk Assessment

Although considerably more common in present-day risk assessments over the past 20 years (e.g., Burmaster and von Stackelberg, 1991; USEPA, 1997; USEPA, 2009c), Probabilistic Risk Assessment (PRA) techniques have been used infrequently in "backward" calculations of screening levels and target levels. Of the federal and state screening and cleanup values presented in this review, all were prepared using deterministic or point estimate methods. The well-documented concern for both risk assessment and cleanup level development under a deterministic scheme is the compounding of individual conservative estimates or assumptions, which can lead to unreasonably high risk estimates and unreasonably low cleanup levels when combined. With the PRA approach, rather than selecting a single conservative point estimate for each of the several input parameters needed for estimating risk or calculating a cleanup level, an appropriate statistical distribution of values for each parameter is used. Modern readily available desktop computing power, a wide and growing range of population exposure data, and refined PRA techniques, make it possible to confidently apply PRA to the development of screening levels and cleanup targets.

The probabilistic approach mathematically accounts for variability and uncertainty in a robust manner. Inputs that have known (or assumed) variability or uncertainty are defined in terms of likelihood (e.g., by percentiles or as a normal distribution with specified mean and standard deviation). The key is to define probability distributions for the risk-assessment input variables on the basis of sound scientific studies that are based on reasonable and defensible assumptions. Rather than yielding a single-value (deterministic) result for a cleanup level, the probabilistic method results in cleanup level probability distributions, with reasonable ranges and confidence intervals, from which a single cleanup level can be chosen to meet the desired target risk requirement and degree of certainty. Knowledge of the full distribution provides a sense of the significance that receptor variability and input uncertainty have in defining these risk-based cleanup standards.

The major distinction of the PRA approach as compared to the deterministic approach is the description of the input parameters as statistical distributions, as opposed to a single point estimate value, that would be used in a traditional, deterministic approach. These statistical distributions are integrated into the risk calculation, and through the process of Monte Carlo (random) sampling, they provide a statistical distribution of risks.

In each of the examples below, cleanup levels were developed based on multiple routes of exposure (e.g., oral, dermal and inhalation). For ease of presentation, and because the calculation for dioxin is dominated by the ingestion route, we will discuss only the assumptions used for that route. The inhalation and dermal pathways contribute no more than 10% of the overall risk.

5.2.1 Florida-specific Example with Fixed Toxicity Guidelines

In this example, only protection from potential cancer effects was considered, and the Florida-mandated risk level of 10^{-6} was used as a default target risk level. Other key point estimates that were assumed included an Averaging Time of 25,500 days and an oral cancer potency factor (CPF; or cancer slope factor, CSF) for 2,3,7,8-TCDD of $1.5X10^{5}$ $(mg/kg•day)^{-1}$, as required by the State of Florida Department of Environmental Protection for evaluation of dioxin. Exposure factors that were given probabilistic treatment included body weight, exposure duration, exposure frequency, fraction contacted from contaminated source, soil ingestion rate, and relative bioavailability. The algorithm defining the Soil Cleanup Target Level (SCTL) for cancer effects is as follows:

$$SCTL = \frac{TR \times BW \times AT}{EF \times ED \times FC \times [(IR_o \times CSF_o \times RBA_o) + (SA \times AF \times DA \times CSF_d \times RBA_d) + (IR_i / PEF \times CSF_i \times RBA_i)]}$$

where,

TR=Target Risk
BW=Body Weight
AT=Averaging Time
EF=Exposure Frequency
ED=Exposure Duration
FC=Fraction Contacted from contaminated source
IR=Intake Rate; oral or inhalation
CSF=Cancer Slope Factor; oral, dermal or inhalation
RBA=Relative Bioavailability; oral, dermal or inhalation
SA=Skin Surface Area
DA=Dermal Absorption
PEF=Particlate Emission Factor

Depending on the particular exposure parameter of interest, specific distributions were developed based on review of the scientific literature, government databases (e.g., National Health and Nutrition Examination Surveys

(NHANES)), other authoritative documentation (e.g., USEPA's Exposure Factors Handbook), as well as professional judgment.

The 90th percentile cleanup target level for 2,3,7,8-TCDD, assuming an oral CPF of $1.5X10^5$ (mg/kg•day)$^{-1}$ and a risk level of 10^{-6}, was calculated to be 50 parts per trillion (ppt).

5.2.2 Generic PRA Example with Uniform Distribution of Toxicity Guidelines

Paustenbach et al. (2006) developed extensive PRA-based soil cleanup level tables based on both potential cancer effects at a 10^{-5} risk level and based on noncancer toxicity criteria at a Hazard Index of 1. For both the cancer and noncancer evaluations, of the parameters included in the typical target level calculation, the authors used probabilistic distributions for soil ingestion rate, exposure duration, body weight, and relative bioavailability. In this evaluation, a distribution of cancer potency was added to the probabilistic approach, as was the reference dose for the noncancer evaluation. Because the authors wanted to compare their results with other available soil target levels, they held exposure frequency (350 d/yr), averaging time (25,550 days), target risk level (10^{-5}), and target hazard index (1) steady at typical deterministic values.

Paustenbach et al. (2006) presents calculated cleanup levels based on a wide array of desired distributions and protection level percentiles. Table 2 summarizes the 90th, 95th, and 99th percentile cleanup levels at a cancer risk level of 10^{-5}, and presents various point estimate deterministic results versus probabilistic results under assumptions of three different uniform distributions of cancer potency factors.

Looking at the most comprehensive distribution of potency factors, the resulting 90th to 99th percentile probabilistic cleanup levels range from 120 ppt to 50 ppt. Compared with the deterministic values at the most restrictive point estimates (70 to 30 ppt), the probabilistic values all are nearly twice the deterministic values.

With respect to the noncancer cleanup levels, Paustenbach et al. (2006) identified an extensive list of potential reference dose (RfD) or RfD-equivalent values (e.g., MRLs and Tolerable Daily Intakes; TDIs) to use in calculating the point estimate comparison values. The range of RfD-equivalent values were then grouped into three uniform distributions for use in the probabilistic approach. Table 3 presents the 90th, 95th and 99th percentile cleanup levels at a noncancer Hazard Index of 1 and RfD-equivalent values ranging from $5X10^{-10}$ to $1X10^{-8}$

mg/kg•day. The recently released USEPA IRIS RfD ($7X10^{-10}$ mg/kg•day) falls near the conservative end of the range considered by Paustenbach et al. (2006).

Table 2. From Paustenbach et al. (2006). Probabilistic cleanup levels at 10^{-5} cancer risk level.

Cancer Potency	**90th Percentile Cleanup Level (ppt)**	**95th Percentile Cleanup Level (ppt)**	**99th Percentile Cleanup Level (ppt)**
Deterministic Estimates with noted Potency Factors			
Potency Factors			
$9.6X10^{4}$	7,100	5,500	3,400
$1.56X10^{5}$	440	380	210
$1.0X10^{6}$	70	50	30
Probabilistic Estimates with noted Potency Factor uniform distributions			
Potency Factors			
$9.6X10^{4}$ to $1.56X10^{5}$	750	540	320
$9.6X10^{4}$ to $2.5X10^{5}$	480	350	200
$9.6X10^{4}$ to $1.0X10^{6}$	120	90	50

Table 3. From Paustenbach et al. (2006). Probabilistic cleanup levels at Hazard Index 1.

Noncancer Toxicity RfD equivalent	**90th Percentile Cleanup Level (ppt)**	**95th Percentile Cleanup Level (ppt)**	**99th Percentile Cleanup Level (ppt)**
Deterministic Estimates with noted RfD equivalent			
RfD equivalent			
$1.0X10^{-9}$	600	460	300
$4.0X10^{-9}$	2,400	1,800	1,200
$1.0X10^{-8}$	6,000	4,600	3,000
Probabilistic Estimates with noted RfD equivalent uniform distributions			
RfD equivalent			
$5.0X10^{-10}$ to $5.0X10^{-9}$	1,000	720	370
$1.0X10^{-9}$ to $4.0X10^{-9}$	1,200	920	520
$1.0X10^{-9}$ to $2.0X10^{-8}$	3,200	2,100	1,000

As with the cancer-based cleanup level comparisons, the most restrictive range of probabilistic cleanup levels (1,000 to 370 ppt) were notably higher than those calculated using deterministic, point estimates (600 to 300 ppt).

Paustenbach et al. (2006) concluded in part that EPA's historical guidance of 1 ppb remains a reasonable and protective screening level for most residential soil exposure circumstances.

> "Our analysis supports the historical position of the U.S. EPA and ATSDR that a 1 ppb dioxin TEQ soil cleanup criterion is almost certainly adequately protective for most urban residential locations for both possible cancer and non-cancer health effects associated with exposure to PCDD/Fs."

5.3 Alternative Approach 2 – Site-Specific

Whether deterministic or probabilistic, the most logical and most defensible approach to establishing cleanup levels at a site is through the use of site-specific information regarding as many exposure variables as possible. Each environmental dioxin site will have a different makeup of PCDD/F congeners, with each congener having a different toxicity guideline and different relative bioavailability. Those important assumptions to the calculation, as well as the significant assumptions of fraction contacted from contaminated source and natural or anthropogenic background dioxin levels, can have significant impact on the ultimate cleanup level.

6. DISCUSSION

So, from all of this falls the critical question: How Clean is Clean Enough? with regard to dioxin in soil. Studies showing high soil and indoor dust levels of dioxin in residential circumstances suggest no elevated serum levels in the occupants. Environmental levels and body burdens have decreased dramatically over the past few decades, with no reason to suspect a reversal of the trend, given the intense scrutiny and regulatory pressure currently directed at dioxin and related compounds. Published default "safe" screening levels and available action levels for dioxin in soils for unrestricted, residential use range from a few parts per trillion up to a thousand parts per trillion. Reported background soil dioxin levels are similar to the lower screening levels. Broad variability and little or no scientific consensus exists related to the fundamental components required to establish health-based cleanup levels (e.g., toxicological guidance values, relative bioavailability estimates, and acceptable risk levels). The most promising of the alternative approaches is that of probabilistic risk assessment (PRA), which provides a quantitative treatment of the uncertainty associated with residential exposure assumptions. PRA presents a reasonable and readily applied alternative approach to the traditional risk assessment approach.

Given these facts, particularly the lack of clear scientific consensus on even the most fundamental aspects of dioxin exposure and toxicity, it is appropriate to reexamine the traditional approach, and to offer alternatives that maintain the ultimate goal of protecting public health, but to balance that goal with the realities that have become evident over the years (e.g., cost vs technical feasibility of cleanup; health benefits at very low concentrations). Figure 1 presents the range of existing and potentially applicable dioxin screening levels for residential soils.

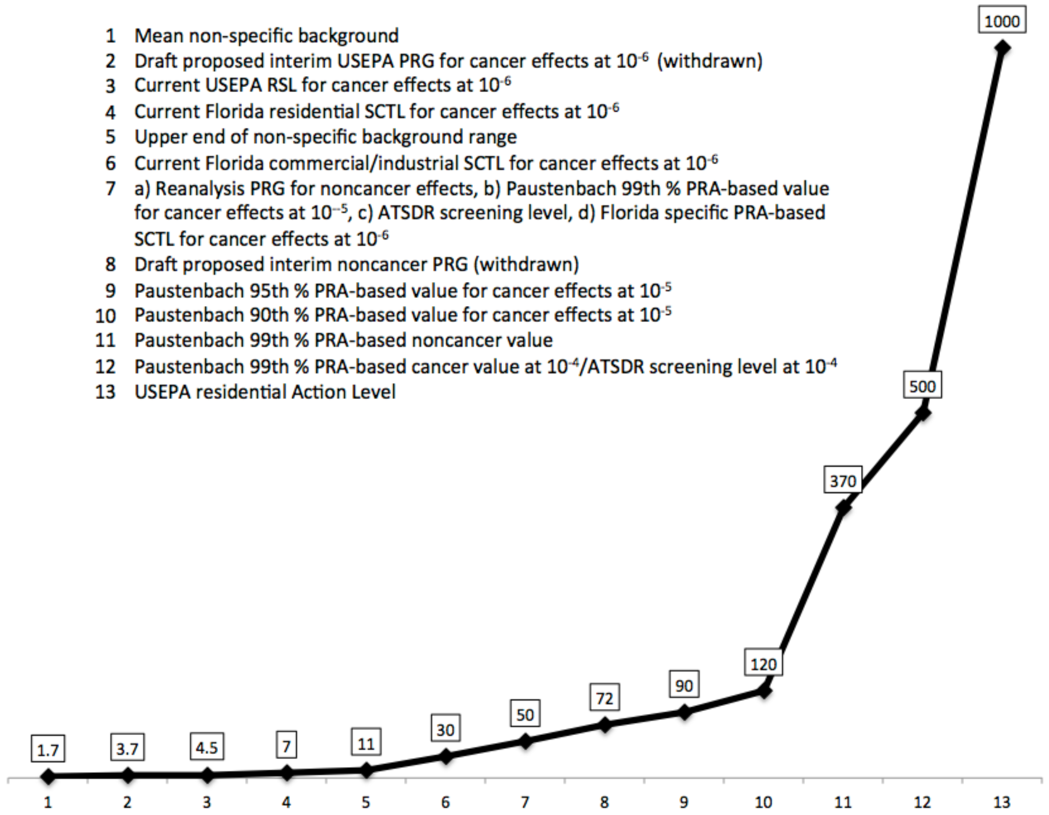


Figure 1. Existing and potentially applicable soil dioxin evaluation target levels. All concentrations in parts per trillion (ppt; ng/kg).

7. CONCLUSION

As discussed in this review, the toxicity factors applicable to evaluation of potential carcinogenic effects of exposure to dioxin remain highly uncertain. The same is true for dioxin exposure factors as well (e.g., relative bioavailability). These observations suggest either the use of a traditional noncancer approach with updated toxicity guidance, as described in Section 5.1, or the use of a probabilistic approach to the cancer based evaluation to appropriately account for the range of proposed cancer potency factors that are available, as described in Section 5.2. The traditional approach results in a Preliminary Remediation Goal (PRG) of 50 parts per trillion (ppt). Remember that a PRG is a screening level that should not be used as a *de facto* cleanup level or remediation level. The probabilistic approach yields potential cleanup levels that range from 50 ppt to 500 ppt or more, depending on the assumed acceptable risk level. It should not be overlooked that a 50 ppt conservative, safe level for exposure to dioxin has been calculated by multiple agencies and scientists using divergent techniques and considerably different input assumptions.

As probabilistic approaches mature even further, and as scientific consensus is established on the several uncertain exposure factors, it will become more reasonable and defensible to always undertake a site-specific approach to cleanup and even to initial screening of a site.

8. REFERENCES

ACC (American Chemistry Council). 2010. Comments of the Chlorine Chemistry Division of the American Chemistry Council in Response to EPA's Draft Recommended Interim Preliminary Remediation Goals for Dioxin in Soil at CERCLA and RCRA Sites. Before the United States Environmental Protection Agency. EPA-HQ-SFUND-2009-0907. April 2, 2010.

ATSDR (Agency for Toxic Substances and Disease Registry). 1998. Toxicological Profile for Chlorinated Dibenzo-p-Dioxins: Update. U.S. Department of Health and Human Services. December 1998.

ATSDR (Agency for Toxic Substances and Disease Registry). 2008. Update to the ATSDR Policy Guideline for Dioxins and Dioxin-Like Compounds in Residential Soil. November 2008.

Aberg, A., M. Tysklind, T. Milsson, M. MacLeod, A. Hanberg, R. Andersson, S. Bergek, R. Lindberg, and K. Wilberg. 2009. Exposure assessment at a PCDD/F contaminated site in Sweden – field measurements of exposure media and blood serum analysis. Environ Sci Pollut Res (2010) 17:26-39.

Burmaster, D.E. and K. von Stackelberg. 1991. Using Monte Carlo simulations in public health risk assessments: estimating and presenting full distributions of risk. J Exposure Anal Environ Epidemiol (1991) 1(4): 491-512.

CDC (Centers for Disease Control and Prevention). 2009a. Fourth National Report on Human Exposure to Environmental Chemicals. CDC Department of Health and Human Services.

CDC (Centers for Disease Control and Prevention). 2009b. Dioxins, Furans and Dioxin-like Polychlorinated Biphenyls. CDC Fact Sheet. November 2009.

DeRosa, C.T., D. Brown, R. Dhara, W. Garrett, H. Hansen, J. Holler, D. Jones, D. Jordan-Izaguirre, R. O'Connor, H. Pohl, and C. Xintaras. 1997. Dioxin and Dioxin-like Compounds in Soil, Part II: Technical Support Document for ATSDR Interim Policy Guideline. Toxicol Indust Health Vol 13 No 6.

Kimbrough, R.D., H. Falk, and P. Stehr. 1984. Health Implications of 2,3,7,8-Tetrachlorodibenzodioxin (TCDD) Contamination of Residential Soil. J Toxicol Env Health, 14:47-93.

NAS (National Academy of Sciences). 2006. Health Risks from Dioxin and Related Compounds: Evaluation of the EPA Reassessment. Public Summary. July 2006.

Paustenbach, D.J., K. Fehling, P. Scott, M. Harris, and B. Kerger. 2006. Identifying Soil Cleanup Criteria for Dioxins in Urban Residential Soils: How Have 20 Years of Research and Risk Assessment Experience Affected the Analysis? J Toxicol Environ Health, Part B. 2006 (9)87-145.

Pohl, H., C. DeRosa, and J. Holler. 1995. Public Health Assessment for Dioxins Exposure from Soil. Chemosphere 1995 Jul; 31(1)2437-2454.

SRC (SRC, Inc.). 2010. Final Report: Bioavailability of Dioxins and Dioxin-Like Compounds in Soil. Prepared for USEPA Office of Superfund Remediation and Technology Innovation, Environmental Response Team – West. December 20, 2010.

Tohyama, C., I. Uchiyama, S. Hoshi, M. Hijiya, H. Miyata, M. Nagai, S. Nakai, M. Yauchi, and S. Ohkubo. 2011. Polychlorinated dioxins, furans, and biphenyls in blood of children and adults living in a dioxin-contaminated area in Tokyo. Environ Health Prev Med (2011) 16:6-15.

UM (University of Michigan). 2011. Measuring People's Exposure to Dioxins: Along the Tittabawassee River and Surrounding Areas. Findings from the University of Michigan Dioxin Exposure Study. 2011 Updated.

USEPA 1997. Guiding Principles for Monte Carlo Analysis. Risk Assessment Forum. Washington, D.C. EPA/630/R-97/001. March 1997.

USEPA 1998. OSWER Directive 9200.4-26. Approach for Addressing Dioxin in Soil at CERCLA and RCRA Sites. April 13, 1998.

USEPA 2003. Exposure and Human Health Reassessment of 2,3,7,8-Tetra-Chlorodibenzo-p-Dioxin (TCDD) and Related Compounds. NAS Review Draft. December 2003.

USEPA 2006. An inventory of sources and environmental releases of dioxin-like compounds in the United States for the years 1987, 1995, and 2000. NCEA, Washington, D.C.

USEPA 2007. Pilot Survey of Levels of Polychlorinated Dibenzo-p-dioxins, Polychlorinated Dibenzofurans, Polychlorinated Biphenyls, and Mercury in Rural Soils of the United States. NCEA, Washington, D.C. EPA/600/R-05/048F. April 2007.

USEPA 2009a. Public Review Draft, Draft Recommended Interim Preliminary Remediation Goals for Dioxin in Soil at CERCLA and RCRA Sites. OSWER 9200.3-56. December 30, 2009.

USEPA 2009b. Review of State Soil Cleanup Levels for Dioxin. December 2009. NCEA, Washington, D.C.

USEPA 2009c. Using Probabilistic Methods to Enhance the Role of Risk Analysis in Decision-Making with Case Study Examples. External Review Draft. Risk Assessment Forum. EPA/100/R-09/001.

USEPA 2010. EPA's Reanalysis of Key Issues Related to Dioxin Toxicity and Response to NAS Comments. EPA/600/R-10/038A.

USEPA 2012a. Regional Screening Levels website, reviewed online in September 2012 at www.epa.gov/region9/superfund/prg/.

USEPA 2012b. EPA's Reanalysis of Key Issues Related to Dioxin Toxicity and Response to NAS Comments, Volume 1. EPA/600/R-10/038F. February 2012.

USEPA 2012c. Integrated Risk Information System (IRIS) online database reviewed in September 2012 at www.epa.gov/iris/.

USEPA 2012d. EPA Non-Cancer Toxicity Value for Dioxin and CERCLA/RCRA Cleanups: Questions and Answers. Superfund website reviewed September 2012 at epa.gov/superfund/policy/remedy/sfremedy/remedies/dioxinsoil.html. Last updated May 9, 2012.

WHO (World Health Organization). 2005. The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds. Toxicol Sci 93(2): 223-241.

PART VI: Sediments

Chapter 14

HETEROGENEITY OF PHOSPHORUS IN AQUATIC SEDIMENT

Jonathan B. Higgins[§]
Higgins Environmental Associates, Inc., 19 Elizabeth Street, Amesbury, MA 01913

ABSTRACT

Conventional thinking of phosphorus in aquatic sediments considers phosphorus, an internal loading nutrient most often responsible for harmful algae bloom formation in freshwater, as concentrating within the deepest part of a water body only to be released under summer, anoxic conditions. The author's field testing, laboratory results, and published literature findings by other authors document that phosphorus occurrence in and release from aquatic sediments can be spatially and temporally highly variable over a given water body. Areas of elevated phosphorus in sediment can be concentrated in shallow aerobic parts of a water body at the end of one year then released and taken up by algae or nuisance plants the following year, only to be deposited again at the end of the growing season at altogether separate and concentrated area(s) of the same water body, with the process repeating each year.

Field and laboratory analysis of surface water, sediment and algae collected from a lake between June 2010 and September 2012 documented the spatial and temporal heterogeneity of phosphorus in the lake, its release from sediment, and patterns of harmful algae blooms in the lake as a whole. By understanding the heterogeneity of phosphorus in aquatic sediment, areas of elevated phosphorus can be identified and efficiently removed in a controlled manner to reduce the magnitude of future harmful algae blooms or nuisance plant growth.

[§] Corresponding Author: Jonathan B. Higgins, CPG, LSP, Higgins Environmental Associates, Inc. Amesbury, MA, Tel: 978-834-9000, Email: higginsenv@comcast.net

Keywords: phosphorus, fixed phosphorus pools, mobile phosphorus pools, sediment, heterogeneity, cyanobacteria, harmful algae blooms, nuisance plant growth, internal loading nutrient.

1. INTRODUCTION

Phosphorus availability is regarded as the most important factor for determining the water quality of freshwater bodies (Søndergaard, Jensen and Jeppesen, 2003). For many years, it has been recognized that existing and historical external sources of phosphorus to water bodies often led to degradation of water quality, loss of aquatic habitat function, and impacts to human health and environmental receptors. In addition to health effects, all of these impacts can have a negative economic influence on real estate prices, fisheries, and ecotourism (Carpenter et al., 1998, and others). The growth potential of algae is also directly proportional to the available phosphorus concentration (Schindler, 1977; Carpenter et al., 1992; Stumm and Morgan, 1996; and others). Appropriately enough, much of the initial focus on reducing phosphorus-related impacts such as algae blooms, nuisance densities of plants, anoxic conditions and fish kills was directed at removing or controlling external sources of phosphorus loading (inflows) to water bodies. External control methods commonly included improvements to: storm water conveyance and treatment; land use practices; sanitary waste handling; and point source discharges. Once existing external sources of phosphorus were addressed, it was possible in some instances that internal sources may diminish over time due primarily to hydraulic flushing of a water body. Flushing of a water body is where the body of water volume is subject to loss over time through a stream or river (outflow); however, depending upon the characteristics of each water body, flushing may not occur or be minimal or restricted. In these high retention, low flushing rate situations, problems related to internal sources of phosphorus can persist for many years.

External loads to water bodies have been estimated by a combination of modeling and assigning loads to various watershed contributing land uses by identification of point sources, and to varying degrees, by using laboratory analysis of water quality within the receiving water body and its surface water inflows and outflows. When combined, this approach helped to identify existing areas of high nutrient external loading sources, and these external sources could then be targeted for improvement. Under this external input-output evaluation of phosphorus loading, the internal loading within the water body itself is often treated as a well-mixed receiving pool with a determined output flushing rate. If measured inflows in a particular contaminant like phosphorus exceeded the measured or estimated outflow volume, the difference was assigned as an internal loading gain. High output concentrations relative to input would be assigned as a loss from a water body. With an initial focus on controlling external sources, there was little consideration given to defining the internal loading cycle itself. If completed at all, sediment sampling and laboratory analysis to evaluate internal loading was often limited to deeper parts of the receiving water body.

While researching the historical background regarding this deep water sediment sampling rationale, it seems that the origin of this approach was based on the assumption that the deepest portion would provide results representative of: 1) changes in nutrients/phosphorus over time as a whole within the receiving water body; 2) release of phosphorus under anoxic conditions; and, 3) to minimize the year to year variance posed by shallower water column sediment quality.

The input-output external loading assessment approach worked well enough for existing external loading but less so for: 1) historical external loading sources; 2) water bodies with minimal to no surface water inflows and outflows (high retention, low flushing); and, 3) for water bodies that already contained excess phosphorus.

Once excess phosphorus is present in a water body, it can be reused or recycled by aquatic biota (including harmful algae blooms and nuisance plant growth) for many years; this is the internal load. Recycling and reuse of phosphorus originates primarily from the microbial degradation and recycling of biogenic and particle-sorbed phosphorus when deposited onto aquatic sediment (Hallberg et al, 1973; Kamp-Nielsen, 1975; Gächter and Meyer, 1993; and others). As documented by this study and by others, phosphorus can also be released from sediment under either aerobic or anoxic conditions.

Now that the focus is turning towards addressing internal sources of phosphorus, it is important to recognize that phosphorus occurrence in water bodies can be both spatially and temporally variable, and not necessarily well mixed and uniformly distributed as often assumed under the earlier external loading assessment approach. When found, areas where phosphorus concentrates can be targeted to more efficiently remove excess phosphorus from a water body. There are also three primary, physical forms of available phosphorus in a water body: soluble reactive, colloidal or suspended, and fixed (either bound in sediment or within aquatic biota). Once the phosphorus is taken up by algae and plants, its distribution in the water body is directly related to where these algae and plants are located at the end of each growing season. When water temperatures in New England drop below about 12 degrees Celsius (about 50 degrees Fahrenheit) and sunlight radiance diminishes, the planktonic algae are less able to control their buoyancy, they drop out of the water column, and aquatic plants begin to die back. Some forms of harmful algae bloom species also form the equivalent of seeds (akinetes and heterocysts) with sufficient carbohydrates and phosphorus to hatch when light radiance and water temperatures increase in the spring (Brunberg and Boström, 1992; Pettersson et al., 1993; Brunberg and Blomquist, 2003). Some algae species simply rest until water temperatures increase above 10 to 12 degrees Celsius in the spring.

Soluble reactive forms of phosphorus can be released from sediment when bottom waters of the hypolimnion become anoxic (Selig, 2003; Kleeberg and Kozerski, 1997; Gächter and Meyer, 1993; Cyr et al, 2009; and others). In New England, anoxic conditions can occur from late May through early September when water temperatures increase, the solubility of oxygen in water decreases, and aerobic bacterial degradation of biogenic detritus increases. Under common pH ranges in fresh water bodies, anoxic conditions favor the geochemical release of labile and redox sensitive forms of phosphorus from the sediment surface and into the overlying water column by diffusion of soluble reactive phosphorus (SRP).

As documented in this study, a large portion of the sediment-recycled internal phosphorus load also originates from aerobic portions of water bodies. Sediment phosphorus content and release in aerobic portions of the water body are not uniformly distributed, and release mechanisms are more difficult to characterize than the diffusive release of SRP under anoxic conditions.

Mechanisms of phosphorus release from sediment within aerobic portions of a water body include: diffusion of interstitial sediment pore water through the commonly oxic sediment-water interface; decomposition of biogenic seston; bioturbation; ebulation; physical forcing of sediment and pore water release by wave action and convection currents; boat motor turbulence; or sediment resuspension (Holdren and Armstrong, 1980; Søndergaard et al, 2001; Eckert et al, 2003; Cyr et al, 2009; and others). The hydrologic interaction of ground water with surface water and sediment pore water would also contribute (positively or negatively) to phosphorus flux at the sediment-water interface. Another important, but less frequently referenced source of phosphorus release is directly related to recruitment {return of living and newly formed algal cells (germlings) to the water column} (Brunberg and Blomquist, 2003; Karlsson Elfgren, 2003).

Phosphorus is a particle-reactive element that rapidly binds or adsorbs to suspended and particulate matter, including to algae cells and plant surfaces. Once released to aerobic portions of the water column, SRP is commonly only soluble for a very brief time period, approximately 15 minutes. As such, once phosphorus is released into the water column it either remains in anoxic bottom waters, can be transported in aerobic waters as a particle or colloid, or bound to larger solid surfaces such as plants, debris and algae cells.

In any case, it is important to recognize that the majority of phosphorus returns to the sediment surface as organic phosphorus bound within biotic cells and seston, a very loose, predominantly organic material containing detritus from bacteria, plants and animals. Some of the settled seston algae matter remains viable to produce algae blooms when the sunlight increases and water warms in early to late spring. Other biologically-formed molecules containing phosphorus need to be broken down by bacterial action before the phosphorus can be recycled and made available for uptake by aquatic biota (Hallberg et al, 1973; Kamp-Nielsen, 1975; Gächter and Meyer, 1993; and others).

Treatment of harmful algae blooms or nuisance concentrations of plant life without actually removing the phosphorus, can lead to repeat or new occurrences of algae blooms and nuisance plant growth in the future. If excess phosphorus remains in a water body, algae and plants can continue to use any “recycled phosphorus” to proliferate at concentrations that may be harmful to humans and other environmental receptors/users.

Most of the phosphorus that leads to nuisance concentrations of algae and plants is then at some point organically-bound phosphorus. This is the phosphorus that is taken up and bound to other elements like carbon and nitrogen to help form algae and plant cell materials. When the algae and plant material die, or get eaten and excreted by aquatic fauna like zooplankton, shellfish and fish, the detrital matter falls to the bottom of the water body where ever the algae or plant material life cycle ended. These detrital or organic phosphorus accumulation areas can be in deep or shallow areas of the water body. For gas vacuolate algae, like some types of cyanobacteria, their seasonal life cycle essentially ends when the water temperature drops to below approximately 12 degrees Celsius, at which point they are no longer able to regulate their buoyancy and will sink to the bottom. Pelagic algae blooms are not always uniformly distributed within a water body, so depending upon water basin characteristics such as current, bathymetry, littoral characteristics, wind fetch, and water temperature dropping below the gas vacuolate critical temperature of 12 degrees Celsius, high volumes of algae bloom cells, detritus, and organic bound phosphorus can be concentrated in specific areas of a water body.

2. STUDY AREA, SAMPLING AND ANALYTICAL METHODS

From June 2010 until September 2012, the author has evaluated the spatial and temporal variability of phosphorus in the top five centimeters of sediment within littoral and profundal portions of Lake Attitash in Amesbury, Massachusetts, USA. The Lake Attitash study location is depicted on Figure 1.

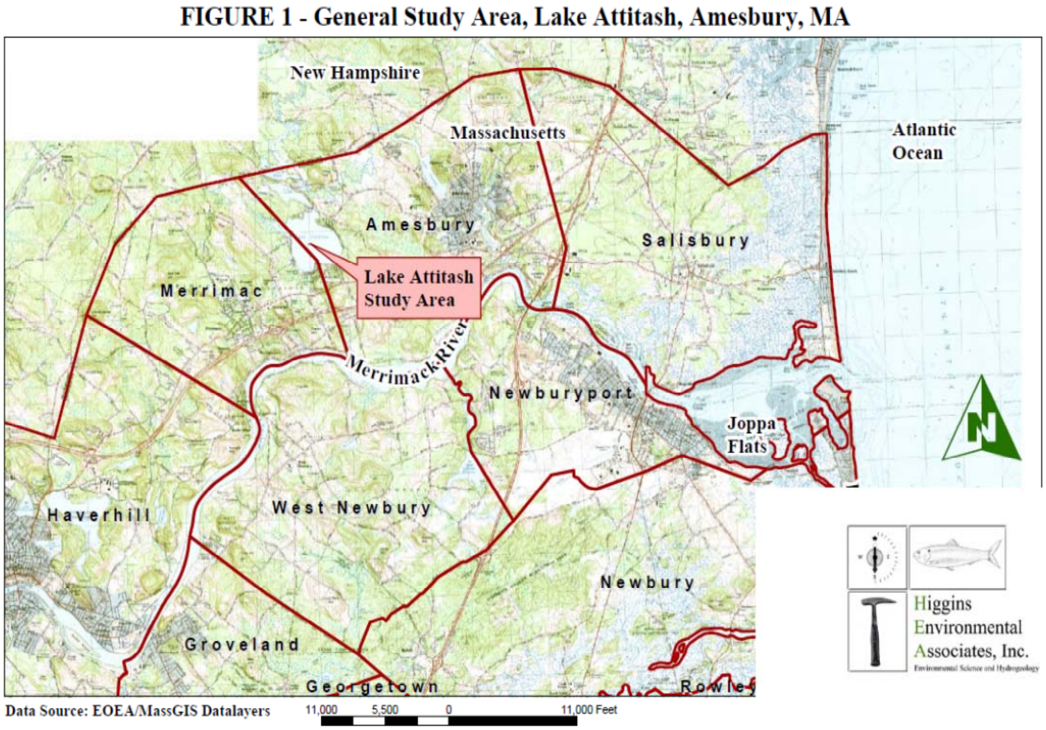


Figure 1. General Study Area, Lake Attitash, Amesbury, Massachusetts

Lake Attitash is an approximately 400 acre eutrophic water body in northeastern Massachusetts. The lake and its water quality have been extensively studied by the Massachusetts Department of Environmental Protection, the U.S. Environmental Protection Agency, the University of New Hampshire and others since the 1970s. Initial efforts to control external sources of phosphorus loading were formally implemented decades ago (connection of homes to public sewer in the 1980s), and efforts to assess and control other potential external sources have been ongoing since the 1980s. Yet, impacts from the internal recycling of phosphorus already in the lake remain in the form of recurring harmful algae blooms, water contact health-related restrictions, and nuisance densities of aquatic plant growth, and as such, the lake was well suited to evaluate the spatial and temporal heterogeneity of phosphorus in aquatic sediment.

The mean depth of the lake is between 2 to 3 meters with two deep basins approaching 6 to 10 meters in depth, respectively. As confirmed by the author and by hydroacoustic surveys of the U.S. EPA, littoral shallow water areas extend up to approximately 100 feet from the shoreline around the majority of Lake Attitash with a larger, littoral area located within the northern portion of the lake. Profundal areas, deeper water areas where light penetration is minimal and seasonally anoxic conditions occur, as confirmed by SCUBA diving, U.S. EPA's hydroacoustic surveys, and long term field chemistry and Secchi disk readings since the 1970s, are located in areas of the lake where the depth of the water column exceeds 3 meters. Figure 2 depicts the relative extent of littoral and profundal areas by plant coverage. Based on the author's SCUBA diving surveys, mapped areas on Figure 2 with less than 40 percent plant coverage can be considered profundal.

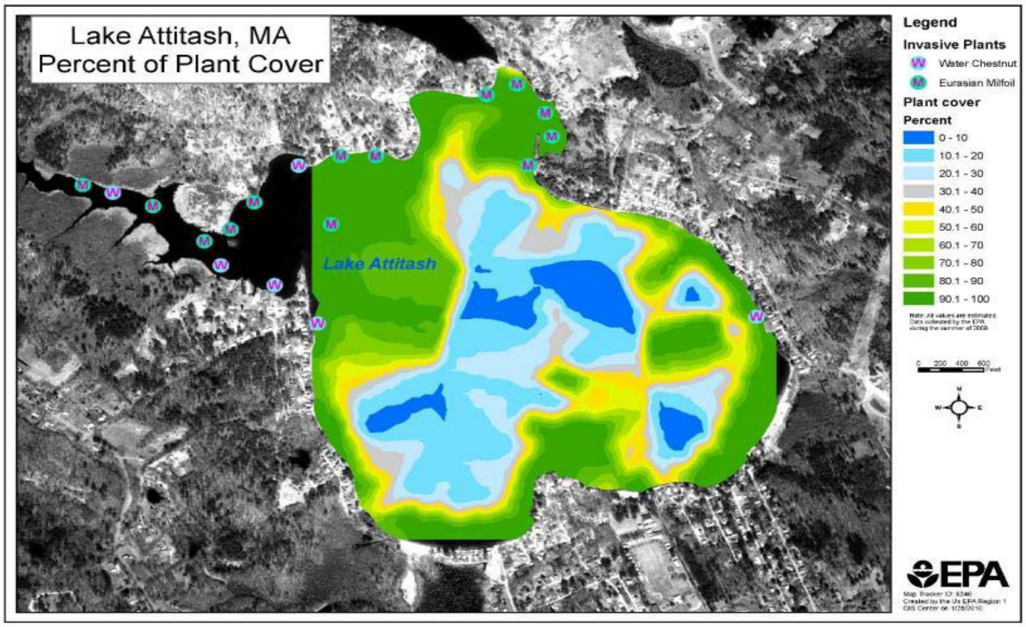


Figure 2. Percent Plant Coverage, Lake Attitash hydroacoustic survey, U.S. EPA, 2010.

In 2010-2011, the author initially completed a pilot study in Lake Attitash for an innovative phosphorus removal system, called the P-Pod^{TM}. As part of the pilot study, sediment samples were collected by SCUBA diving from the top five centimeters of sediment in this portion of the lake from June through December 2011. Water samples from the same portion of the lake were collected by either direct immersion of laboratory glassware, or through the use of a small peristaltic pump and a fixed-in-place, dedicated, polyethylene tubing.

In 2012, to expand upon information gained by the 2010-2011 pilot study, the author completed four (January, June, August and September) rounds of sediment sampling (between 15 to 20 discrete samples per round) within littoral (less than 3 meters) and profundal (greater than 3 meters) areas of the lake. Sampling stations are depicted on Figure 3.

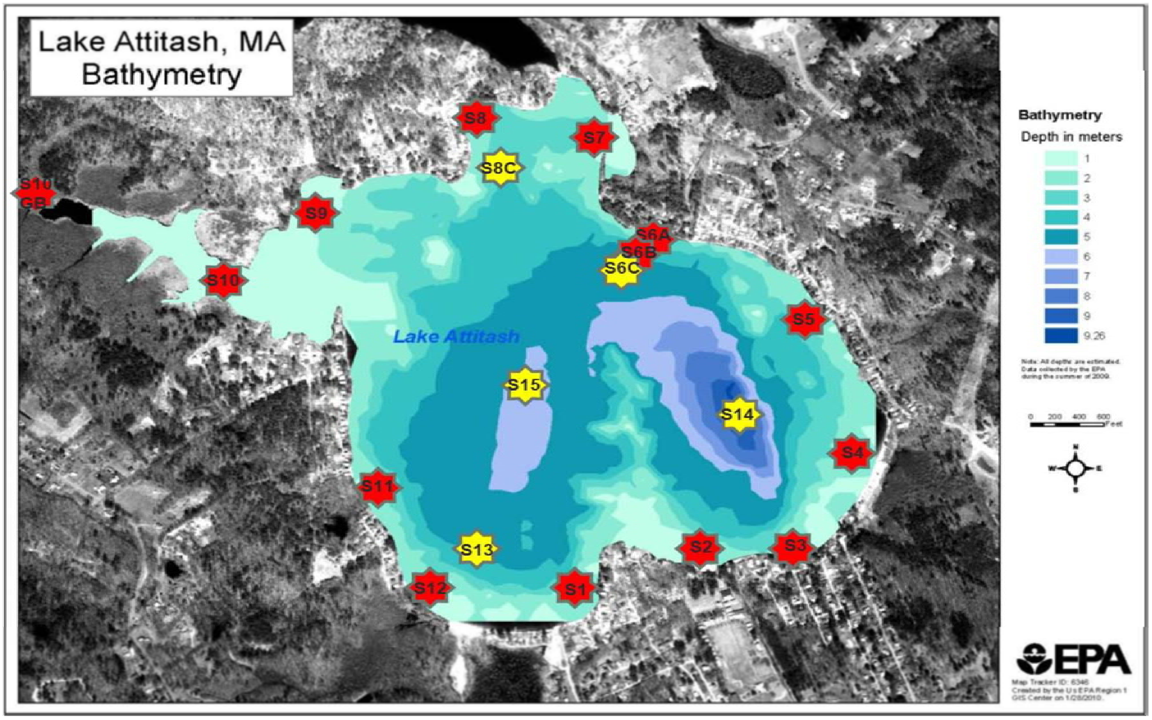


Figure 3. Sediment Sampling Locations, Lake Attitash (red symbols are littoral stations, yellow are profundal). Source of base map: U.S. EPA 2010 Assessment.

In 2012, sediment samples were collected through the use of a scoop and an impermeable bag attached to an extendable and graduated pole, as developed by the author for this sampling program. A string and weight system was used to open and close the bag at the desired sampling interval. Sediment samples were collected from approximately the top five centimeters of sediment at each location.

Each round of sediment sampling from Lake Attitash included one duplicate sample. The relative percent difference (RPD) between duplicate sample results for each sampling round was within acceptable limits (less than 25 percent). All samples were analyzed for total phosphorus content by U.S. Environmental Protection Agency (US EPA) Method 6010C (inductively coupled plasma- atomic emission spectrometry). Additionally, the June, August, and September 2012 sediment samples were also initially ashed by the ignition method described by Andersen (1976) at 550 degrees Celsius for one hour prior to laboratory extraction and analysis. The acid digestion of the ashed samples used a combination of nitric and hydrochloric acid, and hydrogen peroxide. All results were reported on a dry weight basis.

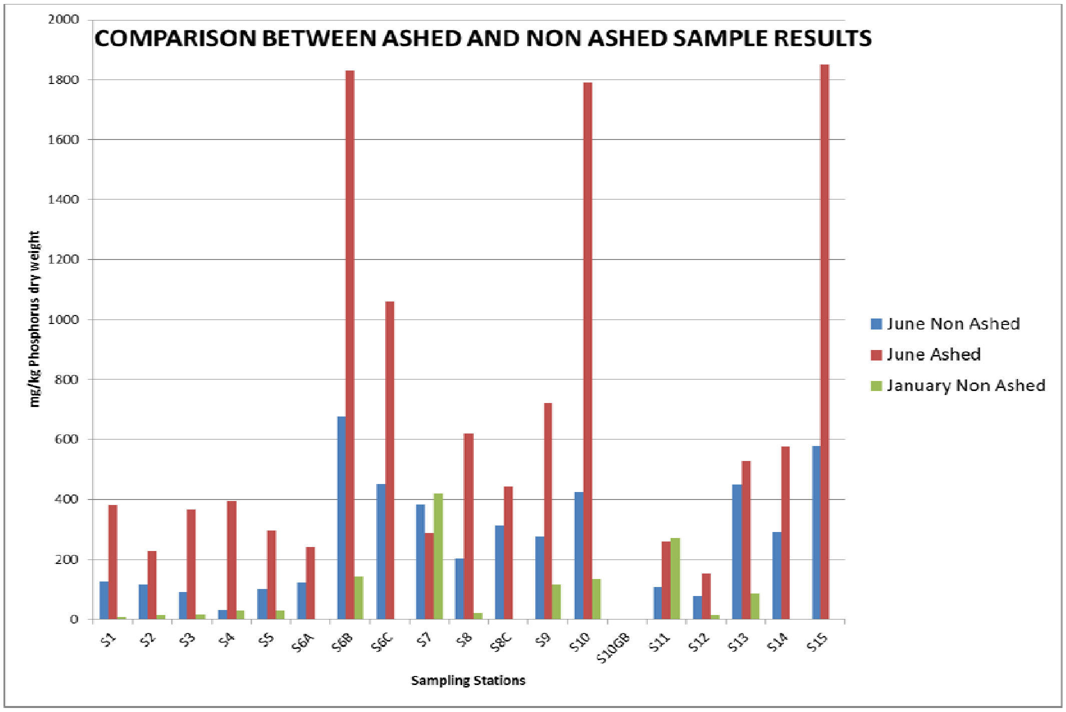
During each sampling round from June to September 2012, water column measurements for pH, temperature, dissolved oxygen, conductivity, and oxidation reduction potential were collected at regular depth intervals at the deepest water column sampling station (S14) and at one or more littoral sediment sampling locations. Measurements were collected directly through the use of a Yellow Springs Institute (YSI) 650 MDS data logger and a 600XL multiparameter sonde on an eight meter cable. As such, the full depth of the water column at the deepest station (S14) of approximately 10 meters could not be assessed. The YSI was calibrated at the start and end of each field day using standard calibration solutions and a two point calibration curve for pH of between 7 and 10 pH units, the expected range for pH within the water column. Dissolved oxygen was calibrated at ambient, moist air conditions assumed to be representative of 100 percent dissolved oxygen in water.

In September 2012, when present at sampling locations, samples of benthic algae (Nitella or filamentous algae, depending upon location) were collected using a small rake and submitted for the same analysis by ashing and acid extraction as the sediment samples. Benthic algae was not present at each sampling station and when present, degrees of coverage varied. Benthic algae were not visibly present at profundal sampling locations (water column depth of greater than 3 meters).

3. RESULTS

For Lake Attitash sediment samples, total phosphorus concentrations at all stations varied from 30 to 2,370 milligrams per kilogram (mg/kg) dry weight for ashed samples. Non-ashed samples typically had much lower total phosphorus results for the same sampling locations. Non-ashed total phosphorus concentrations ranged from 8.69 mg/kg to 667 mg/kg dry weight for all stations. A sediment sampling round collected in January 2012 was not ashed. In June 2012, each sediment sample was analyzed separately by both non-ashing and ashing the sample prior to acid digestion and extraction in accordance with U.S. EPA Method 6010C. Figure 4 depicts a comparison between ashed and non-ashed sediment samples from January 2012 to June 2012. As a trial run, ashing was also completed at a lower temperature (330 degrees Celsius) for one hour and compared to a duplicate run at 550 degrees Celsius for the same sample. Total phosphorus results for the lower temperature were less than that obtained at 550 degrees Celsius. This was an important evaluation as phosphorus can be lost to sublimation at temperatures greater than approximately 525 degrees Celsius; depending primarily upon calcium content (Andersen, 1976).

Figure 4. Variance between Total Phosphorus for ashed and non ashed sediment samples.



All subsequent sampling rounds in August and September were also ashed at 550 degrees Celsius following the method by Andersen (1976) prior to analysis by U.S. EPA Method 6010C for total phosphorus. Laboratory results for each sampling round from June through September 2012 are summarized in Figure 5.

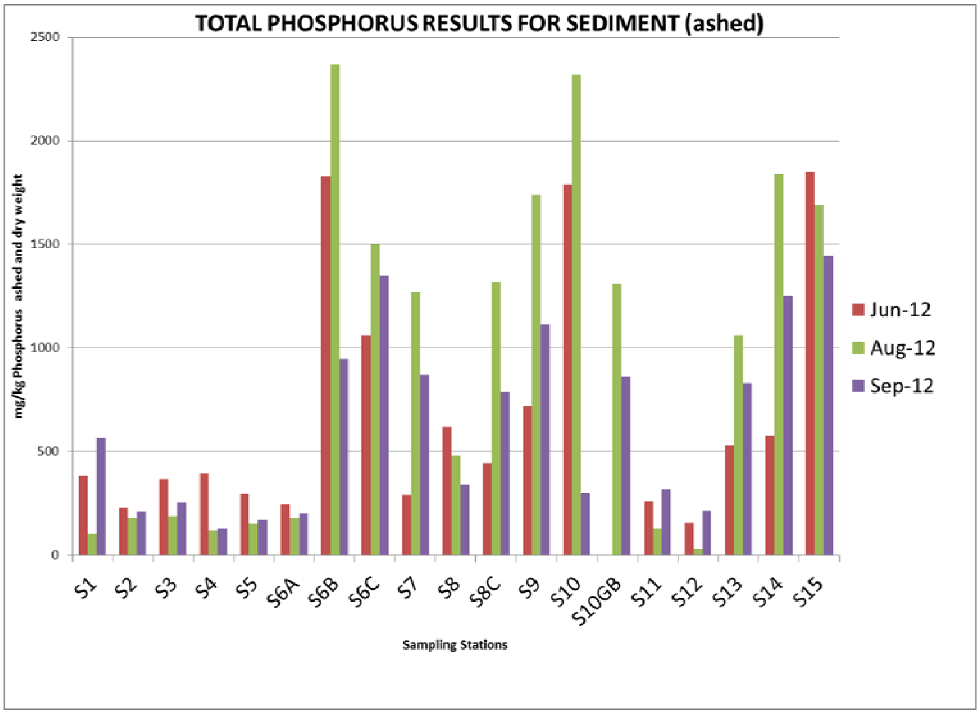


Figure 5. Summary of Total Phosphorus Results for Sediment June to September 2012, Lake Attitash. Results are ashed, extracted and reported as dry weight.

To summarize water column field geochemical parameters for the deep station (S14) from June through September 2012 (by minimum and maximum dissolved oxygen depths):

June 2012 Field Parameters Deep Station (S14)

D.O. (mg/l)	**Depth (ft)**	**ORP (mV)**	**pH (s.u.)**
2.65 (minimum)	14	-9.9	7.46
4.19 (maximum	4.5	5.6	8.14

August 2012 Field Parameters Deep Station (S14)

D.O. (mg/l)	**Depth (ft)**	**ORP (mV)**	**pH (s.u.)**
0.58 (minimum)	23.6	-204	7.55
8.96 (maximum	10.7	2.2	7.7

September 2012 Field Parameters Deep Station (S14)

D.O. (mg/l)	**Depth (ft)**	**ORP (mV)**	**pH (s.u.)**
1.24 (minimum)	20.5	-205.4	7.16
9.21 (maximum	5.2	44.4	7.68

During June, we were unable to identify an anoxic layer (dissolved oxygen less than 2 mg/l) in the water column for a maximum depth of monitoring of 19 feet on that day. Near anoxic conditions were noted in June at the 14 foot sampling interval, but dissolved oxygen content increased above and below 14 feet. However, during an initial monitoring event on May 20, 2012 we confirmed anoxic conditions at the deep station (S14) at a depth of 18.1 feet with a corresponding oxidation reduction potential of -116 millivolts and a pH of 8.83 units. In August and September 2012, anoxic conditions (<2 mg/l DO) in the water column were noted at depths greater than 11 and 20 feet, respectively.

So based on field data collected by this study, as summarized in the preceding tables and text, from May to September 2012 the lake was anoxic at depths greater than 18 feet (6 meters). Monitoring at littoral stations (< 3 meters) during all sampling rounds and within one foot of the sediment surface noted dissolved oxygen concentrations at or near saturation, oxidation reduction potentials between 5 to 182 millivolts, and a range of pH between 7.66 to 8.25 units. Historically, the author has obtained elevated pH readings throughout the water column (surface to 19 feet) of up to 10.35 units, with dissolved oxygen concentrations in excess of 100 percent saturation (October 2009 sampling at deep station S14). During the author's 2011 pilot test for the P-Pod^{TM}, used in this case to capture phosphorus released from sediment, pH in this littoral area ranged between 4.97 to 10.84 units from June to December 2011.

The P-Pod^{TM} is a new and innovative device and process (patent pending) developed by the author to remove excess nutrients/contaminants from water bodies. Using the present study findings on phosphorus heterogeneity in sediment as a potential P-Pod^{TM} application example, the author has documented that there are relatively mobile and fixed pools (concentrated areas) of phosphorus in aquatic sediment. The primary purpose of the P-Pods would then be to remove selected areas of concentrated phosphorus from sediment before the phosphorus (or phosphorus containing biotic cells) could be released back into the water column and used by future harmful algae blooms or nuisance/invasive plant species.

The year 2012 was an unusually warm period with record breaking and consistently elevated air temperatures from March through July. Lake Attitash did not completely freeze over during the winter of 2011-2012. Water temperatures during 2012 ranged from 14.75 degrees Celsius (18.1 feet at the deep station S14) in May to 28.5 degrees Celsius (83 degrees Fahrenheit) in August (at 1.3 feet from the deep station). Field chemistry and water temperatures were not recorded during the January 2012 sampling round. From June through September 2012, the littoral stations (even those with full southerly exposure) were up to 5 degrees Celsius cooler than the shallow water at the deep station (S14). This temperature difference may be related to ground water baseflow contribution into the lake and amelioration of water temperatures within thinner water column littoral areas of the lake.

Of the approximately fifteen sampling stations sampled in June, August and September 2012, three sampling locations routinely contained the highest concentrations of total phosphorus in sediment: samples S6B, S10 and S15. The first two sampling locations are located within littoral areas of the lake at water column depths of 3 meters or less. These areas have been documented as consistently being within aerobic portions of the lake's water column. The last sampling location, S15, is located within a profundal area of the lake at a depth of approximately 5 meters within one of the two deepest basins. This deeper area is commonly subject to anoxic (<2 mg/l dissolved oxygen) conditions for part of each summer (May through early September). Total phosphorus results for ashed sediment samples from June to September 2012 are depicted on Figure 5. Samples collected at depths of 3 meters or less (littoral areas) include samples: S1, S2, S3, S4, S5, S6A, S6B, S7, S8, S9, S10, S10GB, S11, and S12. Profundal sediment samples collected at depths greater than 3 meters include: S6C, S8C, S13, S14 and S15.

Total phosphorus results varied significantly throughout lake sediment stations, and between littoral and profundal areas. From June to September, total phosphorus results by station showed a general decrease (release of phosphorus) in littoral stations. Total phosphorus in sediment at littoral stations S1 and S7 increased slightly (gained phosphorus) from June to September. In contrast to littoral sampling areas, with the slight exception at station S15, profundal and anoxic, deep sampling stations generally increased (gained) in total phosphorus content from June to September.

For the three stations with the highest concentrations of total phosphorus in June (Stations S6B, S10 and S15), by September two of these continued to have high concentrations of total phosphorus in sediment (S6B and S15), but the total phosphorus concentration at S10 had a significant decrease (release) of total phosphorus. Figure 6 depicts the concentration of total phosphorus released (+) or gained (-) at each station from June to September 2012.

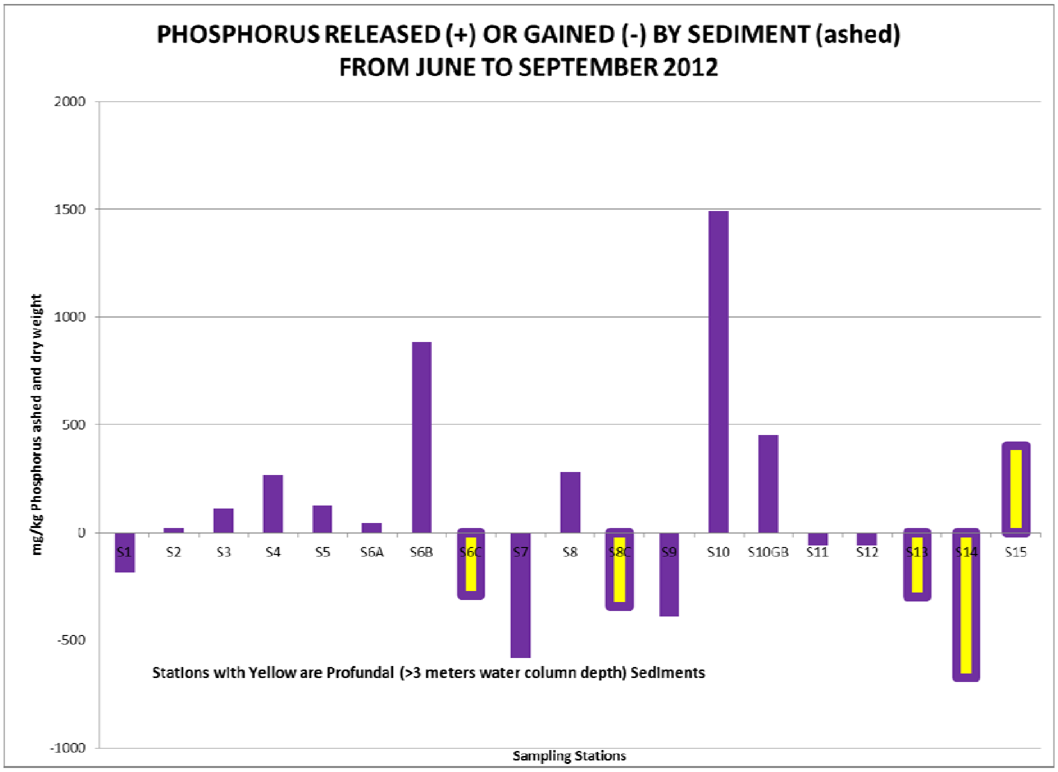


Figure 6. Total Phosphorus Released (+) or Gained (-) at each sample station. Stations with yellow inserts are profundal, all others are littoral.

Littoral sampling stations included sediment types ranging from a coarse to fine sand and fine gravel to a thin layer of very fine silt and detritus. Higher concentrations of total phosphorus were noted within areas of very fine sediment or detritus. Based on SCUBA diving visual observations, areas of very fine sediment in littoral and profundal areas were easily disturbed and almost smokelike. A wave of the hand would cause the upper layer of sediment to be resuspended. In littoral areas, the very fine silt layer was typically only a few centimeters thick. The thickness of very fine silt in profundal areas increased with water column depth (greater than three feet near stations S14 and S15).

By September 2012, benthic coverage of submerged algae and macrophytes at some stations became readily apparent. Coverage by benthic algae approached 100 percent at Stations S1, S6B, S7, S8, S9, S10, S10GB, and S12. Other stations contained pockets of near complete benthic algae coverage or less with approximately 40 percent coverage overall within 10 feet of the sampling stations. Laboratory results for samples of benthic algae collected in September 2012 are summarized on Figure 7. Results for total phosphorus in all algae samples were elevated and in part likely included particulate total phosphorus settling or attaching to benthic algae. During sampling, care was taken to keep fine sediments on algae intact.

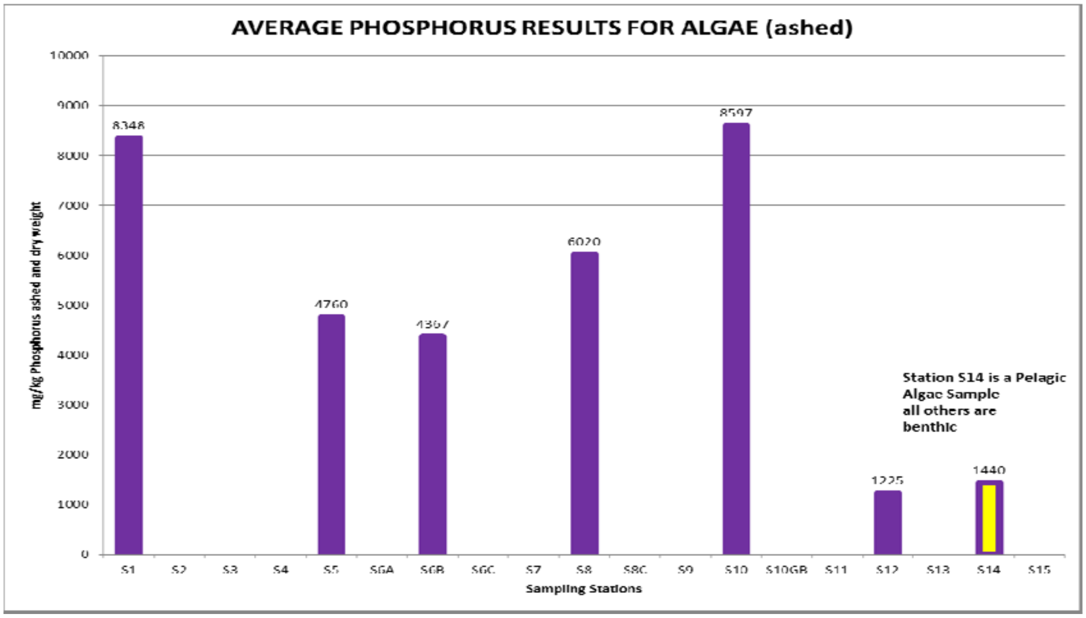


Figure 7. Total Phosphorus Results for Algae. Algae samples were ashed, extracted and reported as dry weight. The yellow insert designates a pelagic (suspended) algae sample collected from the deep station. All others are littoral, benthic algae samples.

By comparing total phosphorus in sediment results to total phosphorus in algae at the same locations where sufficient benthic algae was present for sampling, it is apparent that some portions of the lake have relatively stationary (or fixed) pools of phosphorus that may be exchanged primarily between sediment and overlying benthic algae and plants (Stations S6B and S10), whereas other areas such as at stations S1, S5 and S8 have gained phosphorus (mobile phosphorus pools) during the 2012 monitoring event.

From June through September 2012, a dense layer of suspended (pelagic) algae (cyanobacteria species) was present at approximately 5 to 6 meters within the deepest portion of Lake Attitash at Station S14. The deep algae layer was apparent by echo sounding from the sampling boat, and also confirmed by discrete water column sampling by the author and by the University of New Hampshire during class field trips (personal communication with Lake Attitash Association representatives). Based on the author's assessments, the deep suspended algae layer was not present within the second deep basin at Station S15. Laboratory results of the suspended algae collected at Station S14 (deepest area of the lake) by the author in September 2012 are summarized on Figure 7. Total phosphorus content of the suspended algae was similar to the level of total phosphorus in sediment at this same location.

From 2009 to present, the Massachusetts Department of Public Health (MassDPH), and to varying degrees others including the U.S. EPA and University of New Hampshire (UNH), have sampled primarily water within Lake Attitash to evaluate the nature and occurrence of nutrients, the phytoplankton cyanobacteria, and in part to test for the presence of the cyanobacteria-related toxin microcystin. During weekly monitoring events from June through September 2012, MassDPH frequently detected algae cell counts greater their 70,000 cells per milliliter (cells/ml) guideline and/or confirmed the presence of algae scums in excess of their guidelines for water contact. In 2009, a maximum algal cell count of 350,000 cells/ml was detected by MassDPH in Lake Attitash. The 2009 harmful algae bloom persisted for eight weeks and a fish kill was confirmed by MassDPH during the bloom event and reported to the Center for Disease Control. Fish kills were observed by the author in 2009 through 2012, and have been reported by lake front property owners in the past. In 2010, UNH completed an algae survey of the lake and confirmed that algae cell counts (density) varied throughout the lake surface (top 3 feet). The spatial distribution of cyanobacteria detected in lake water and documented in the 2010 survey report is depicted on Figure 8. Algae cell counts in lake water reported earlier by UNH in October 2009 were 200 times greater in concentrated (algae bloom) areas near the shoreline than in the deepest portion of Lake Attitash (S14).

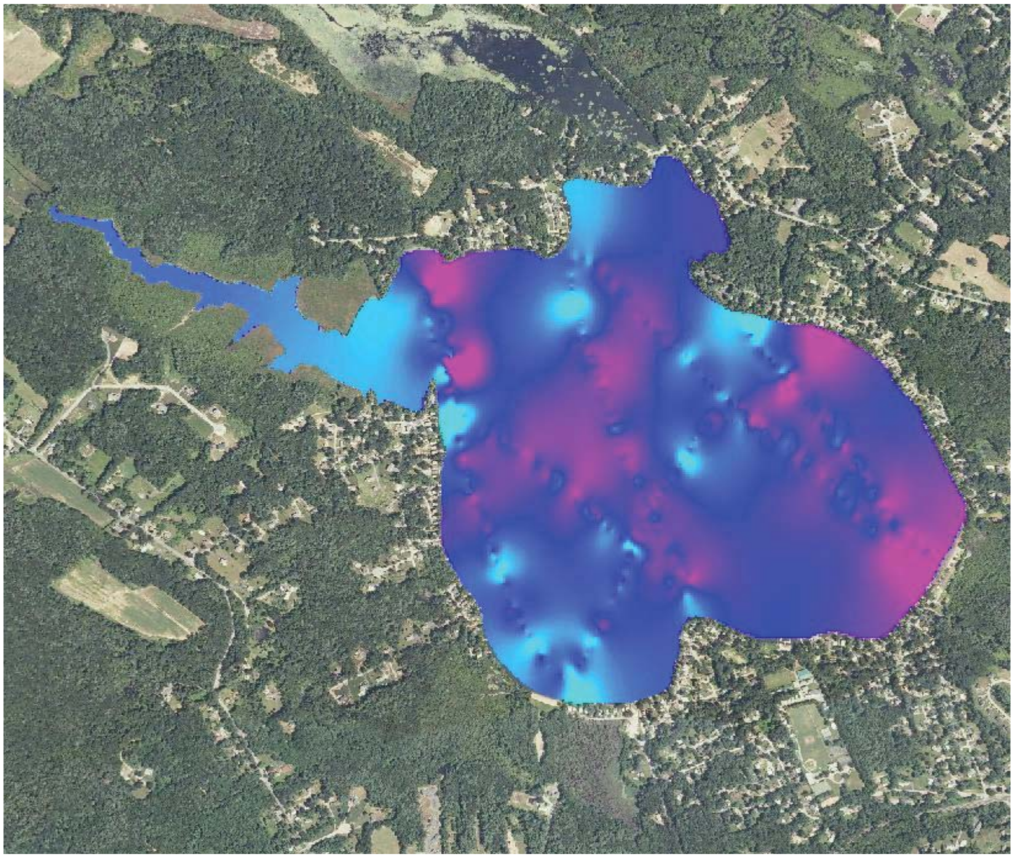


Figure 8. Spatial Distribution of Cyanobacteria in lake water, 2010. Source: University of New Hampshire, Citizens Cyanobacteria Monitoring Program Report for Lake Attitash, Amesbury, Massachusetts. 2010. Areas in "red" color are concentrated algae cell areas.

4. DISCUSSION AND CONCLUSIONS

Study results of aquatic sediment and algae monitoring from 2010 through 2012 in Lake Attitash have documented that phosphorus in aquatic sediment and harmful algae blooms in lake water are spatially and temporally variable throughout the lake. The majority of total phosphorus in sediment released from June through September 2012 occurred within aerobic, littoral areas whereas deeper, seasonally anoxic areas were typically net gainers for total phosphorus. While these results contradict the general convention that phosphorus release is greatest under anoxic conditions, it is important to note that anoxic conditions were present in deeper portions of the lake prior to the June 2012 sampling round and to some undetermined extent in this study, some more labile, redox-sensitive portions of the total phosphorus content in sediment within the deeper basins may have already been released under anoxic conditions present before sampling of sediment in June 2012. 2012 was an unseasonably warm year and anoxic conditions within deeper basins occurred earlier than in most prior monitored years since the 1970s.

We interpret the variance in total phosphorus results between ashed and non-ashed analytical methods for the same sediment sample set as attributable to some combination of high moisture content, low percent solids, and an organic fraction of total phosphorus that without ashing may not be readily amenable to acid digestion by common laboratory methods. As phosphorus is the primary limiting nutrient in fresh water systems, once present, it would be readily taken up by the biotic community and bound, often strongly, within living and dead cells, akinetes and heterocysts, and to some extent used again by the same biotic communities when growth conditions (temperature and light radiance) are favorable.

Although classifying the actual modes of phosphorus release from sediment in aerobic, littoral or anoxic, profundal areas of the lake was not the objective of this study, it is important to note that in addition to well documented and conventionally prescribed diffusive release of redox sensitive forms of phosphorus under anoxic conditions, other mechanisms of phosphorus release contribute to internal loading including: resuspension of sediments; release of phosphorus from sediment pore water; temperature sensitive release mechanisms associated with increased biological activity; and direct transport of phosphorus from sediment to the water column by algae cells. Cyanobacteria, other forms of benthic and suspended algae, and macrophytes have evolved over millions of years, competing with each other in varied environments to acquire the nutrients they need to proliferate. In freshwater, the limiting nutrient is usually phosphorus. As the concentration of phosphorus increases, so do the algae and plant communities that are best able to thrive in a particular environment. This creates a dynamic environment where the spatial and temporal concentrations of phosphorus, algae, and plant communities tend to vary within each water body. Some water bodies may have very limited littoral zones, or have dominance by one or several algae or plant species that may lead to more uniform distributions of phosphorus in water or sediment.

The findings of this study have documented the importance of taking into account the spatial and temporal heterogeneity of phosphorus content in aquatic sediment. By understanding the spatial and temporal changes for phosphorus in a water body, areas of excess phosphorus can be efficiently captured and removed. As the overall volume of internal loading phosphorus is reduced, the occurrence and density of harmful algae blooms and nuisance plants would diminish.

5. REFERENCES

Andersen J.M. 1976. An ignition method for determination of total phosphorus in lake sediments. Water Research 10:329-331.

Brunberg A-K and Boström B. 1992. Coupling between benthic biomass of Microcystis and phosphorus release from the sediments of a highly eutrophic lake, Hydrobiologia 235/236:375-385.

Brunberg A-K. and Blomquist P. 2003. Recruitment of Microcystis (Cyanophyceae) from lake sediments: the importance of littoral inocula. Journal of Phycol. 39:58-63.

Carpenter S.R., Bolgrien D., Lathrop R.C., Stow, C.A., Reed T., and Wilson, MA. 1992. Ecological and economic analysis of lake eutrophication by nonpoint pollution. Australian Journal of Ecology 23:68-79.

Cyr H., McCabe S.K., and Nürnberg G.K. 2009. Phosphorus sorption experiments and the potential for internal phosphorus loading in littoral areas of a stratified lake. Water Research 43:1654-1666.

Eckert W., Didenko J., Uri E., and Eldar D. 2003. Spatial and temporal variability of particulate phosphorus fractions in seston and sediments of Lake Kinneret under changing loading scenario. Hydrobiologia 494:223–229.

Gächter R., and Meyer J. 1993. The role of microorganisms in mobilization and fixation of phosphorus. Hydrobiologia 253:103-121.

Hallberg, R.O., Bagander, L.E., Engwall, A.G., Lindstrom, M., Oden, S., and Schippel F.A. 1973. The chemical microbiological dynamics of the sediment-water interface. Contrib. Asko Lab., 2 (1): 1--117.

Holdren G.C., and Armstrong D.E. 1980. Factors affecting phosphorus release from intact lake sediment cores. American Chemical Society Journal 14(1):79-87.

Kamp-Nielson L. 1975. A kinetic approach to the aerobic sediment-water exchange of phosphorus in Lake Esrom. Ecological Modelling 1:153-160.

Karlsson Elfgren I. 2003. Studies on the Life Cycles of Akinete Forming Cyanobacteria. Acta Universitatis Upsaliensis. Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 856.

Kleeberg, A. and Kozerski H.P. 1997. Phosphorus release in Lake Großer Müggelsee and its implications for lake restoration. Hydrobiologia 342/343:9–26.

Lake Attitash Association, Publically-available records including field chemistry and Secchi disk measurements and personal communications.

Massachusetts Department of Public Health, Publically-available records for Lake Attitash through present.

Pettersson K., Herlitz E., and Istvánovics V. 1993. The role of *Gloeotrichia echinulata* in the transfer of phosphorus from sediments to water in Lake Erken. Hydrobiologia 253:123-129.

Schindler, D.W. 1977. Evolution of phosphorus limitation in lakes. Science 195:260-262.

Selig, U. 2003. Particle size-related phosphate binding and P-release at the sediment–water interface in a shallow German lake. Hydrobiologia 492: 107–118.

Søndergaard, M., Jensen, J.P., and Jeppesen E. 2003. Role of sediment and internal loading of phosphorus in shallow lakes. Hydrobiologia 506–509:135–145.

Søndergaard, M., Jensen, J.P., and Jeppesen E. 2001. Retention and internal loading of phosphorus in shallow, eutrophic lakes. The Scientific World 1:427–442.

Stumm W., and Morgan J.J. 1996. Aquatic Chemistry. Wiley, New York.

University of New Hampshire. 2010. Citizens Cyanobacteria Monitoring Program Report, Lake Attitash.

United States Environmental Protection Agency. 2010-2011. Assessment of nutrient loading and Lake Attitash conditions data, draft results and personal communications.

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