
**CONTAMINATED SOILS, SEDIMENTS, WATER AND
ENERGY**

Volume 16

CONTAMINATED SOILS, SEDIMENTS, AND WATER
Volume 16

Fate and Transport
Heavy Metals
PBCs
Pesticides
Remediation
Sediments
Vapor Intrusion

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Foreword

2010! For many of us, the Amherst Conference has been a longtime career companion. As we've grown professionally, so has the Conference. It is an interesting exercise to track the proceedings publications through the years. The field of environmental management has matured. We are now working to solve very difficult problems, problems that reflect the complexities of the human and non-human components of the biosphere and especially their interactions.

Before you delve into the technical details of the papers comprising this year's Proceedings, take a moment to reflect on the larger picture, and the kinds of issues these authors have tackled. High-quality, rapid and cost-effective data collection, chemical mixtures, risk assessment and risk management tradeoffs, high-tech remediation methods...we are fighting hard battles. And the Amherst Conference is once again on the front lines. See you here next year!

Dave Ludwig

Kate Sellers

Tim Iannuzzi

ARCADIS US

Annapolis, Maryland

About the Editors

Paul T. Kostecki, Vice Provost for Research Affairs, University of Massachusetts at Amherst and Associate Director, Northeast Regional Environmental Public Health Center, School of Public Health, University of Massachusetts at Amherst, received his Ph.D. from the School of Natural Resources at the University of Michigan in 1980. He has been involved with human and ecological risk assessment and risk management research for the last 13 years. Dr. Kostecki has co-authored and co-edited over 50 articles and 16 books on environmental assessment and cleanup including: Remedial Technologies for Leaking Underground Storage Tanks; Soils Contaminated by Petroleum Products; Petroleum Contaminated Soils, Vols. 1, 2, and 3; Hydrocarbon Contaminated Soils and Groundwater, Vols. 1, 2, 3 and 4; Hydrocarbon Contaminated Soils, Vols. 1, 2, 3, 4 and 5; Principles and Practices for Petroleum Contaminated Soils; Principles and Practices for Diesel Contaminated Soils, Vols. 1, 2, 3, 4 and 5; SESOIL in Environmental Fate and Risk modeling; Contaminated Soils, Vol. 1; and Risk Assessment and Environmental Fate Methodologies. Dr. Kostecki also serves as Associate Editor for the Journal of Soil Contamination, Chairman of the Scientific Advisory Board for Soil and Groundwater Cleanup Magazine, as well as an editorial board member for the journal Human and Ecological Risk Assessment.

Edward J. Calabrese is a board certified toxicologist and professor of toxicology at the University of Massachusetts School of Public Health at Amherst. Dr. Calabrese has researched extensively in the area of host factors affecting susceptibility to pollutants and has authored more than 300 papers in scholarly journals, as well as 24 books, including: Principles of Animal Extrapolation;

Nutrition and Environmental Health, Vols. 1 and 2; Ecogenetic: Safe Drinking Water Act: Amendments, Regulations, and Standards; Soils Contaminated by Petroleum: Environmental and Public Health Effects; Petroleum Contaminated Soils, Vols. 1, 2 and 3; Ozone Risk Communication and Management; Hydrocarbon Contaminated Soils, Vols. 1, 2, 3, 4 and 5; Hydrocarbon Contaminated Soils and Groundwater, Vols. 1, 2, 3, and 4; Multiple Chemical Interactions; Air Toxics and Risk Assessment; Alcohol Interactions with Drugs and Chemicals; Regulating Drinking Water Quality; Biological Effects of Low Level Exposures to Chemicals and Radiation; Contaminated Soils; Diesel Fuel Contamination; Risk Assessment and Environmental Fate Methodologies; Principles and Practices for Petroleum Contaminated Soils, Vols. 1, 2, 3, 4, and 5; Contaminated Soils, Vol. 1; and Performing Ecological Risk Assessments. He has been a member of the U.S. National Academy of Sciences and NATO Countries Safe Drinking Water Committees, and the Board of Scientific Counselors for the Agency for Toxic Substances and Disease Registry (ATSDR). Dr. Calabrese also serves as Director of the Northeast Regional Environmental Public Health Center at the University of Massachusetts, Chairman of the BELLE Advisory Committee and Director of the International Hormesis Society.

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

He founded and built an environmental engineering-science consulting company. For 18 years, he has led a team of specialists in chemical engineering, civil engineering, environmental engineering, geotechnical engineering, mechanical engineering, physics, plant engineering, environmental science, geology, hydrogeology, chemistry, biochemistry, toxicology, and biology. Dr. Dragun and his associates have solved environmental issues for major companies and governments in six continents (Africa, Asia, Australia, Europe, North America, and South America).

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Dr. Ludwig is helping to pioneer AEHS's online learning and training program, building education infrastructure amenable to the interdisciplinary and specialty fields that are difficult for traditional institutions to accommodate. By integrating the Foundation's worldwide reputation and expertise in technical colloquia, environmental planning and policy, and interdisciplinary project leadership, the Education and Training Department is working to meet learning needs critically important for the future of environmental science and management.

PART I: Fate and Transport

Chapter 1

DEVELOPMENT OF A MOBILE LABORATORY SYSTEM FOR SITE CHARACTERIZATION AND ANALYSIS OF SUBSURFACE OIL CONTAMINANTS

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ABSTRACT

A mobile laboratory incorporating the techniques of laser-induced fluorescence (LIF) and cone penetration test (CPT) has been successfully developed and field-tested by members of Kuwait Institute for Scientific Research (KISR).

The LIF/CPT system consists of a custom designed stainless steel probe assembly incorporating a bundle of fiber optics with low absorption in the ultraviolet range. A pulsed 266nm laser source is coupled into one of the optical fibers and is utilized for exciting fluorescence in soil targets. The excitation laser pulse carried through the fiber optics interacts with the soil through a sapphire window placed on the probe head; the emitted fluorescence is collected and channeled back to a detection system through a separate fiber. The probe is capable of reaching a potential maximum depth of 50m. Among the detection systems that have been used for the system were a single and a multi-channel array photomultiplier tube based systems. The entire lab facility is installed inside a CPT 20-ton vehicle.

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The mobile laboratory is referred to as the Environmental Unit for Measuring Subsurface Oil Contaminants (EUMSOC), and it has undergone an extensive series of field tests at different sites in the oil-contaminated areas of north Kuwait.

Keywords: Laser induced fluorescence (LIF), soil, pollution, screening method.

1. INTRODUCTION

In the aftermath of the 1990-1 Gulf War, the environmental status of Kuwait was left in a state of severe damage. Principally, this devastation was due to the destruction of over 700 oil wells by the retreating invading Iraqi military forces. Almost 20 years after the end of the war, signs of the petroleum based environmental damage is seen in many parts of the Kuwaiti deserts. It is estimated that an equivalent of 10% of the country's area (about 18,000 km²) remain under various states of contamination.

A massive series of cleanup operations became imperative to rectify this environmental calamity. Such an endeavor would require measuring types and levels of pollution in the environment and the extent of the damage. Such processes involve the collection of field samples and subsequently subjecting them to a series of lab measurements involving a variety of chemical extractions based on established procedures (e.g.; FTIR, GC/MS, GC/FID).

Given the massive spread of the contamination and the vast scope of the cleanup operations, such methods would pose a prolonged series of time-consuming processes. The need to develop a fast screening; semi-quantitative procedure that may provide in-situ pollutant profiles instantaneously became vital. Such a method should entail an acceptable level of correlation with established traditional lab methods in offering a viable semi-quantitative / qualitative results.

The method of choice that was chosen for this effort is based on prior work conducted at KISR over an extended period that dates back to the early 1980's, and it involves the technique of Laser Induced Fluorescence (LIF). The method involves the measurement and analysis of the optical emission from molecules that have been excited to higher energy levels by the absorption of electromagnetic radiation. The source of this excitation is a monochromatic UV laser source. In conjunction with the stand-alone LIF measurements, it was found that such measurements could be improved upon by augmenting them with diffuse reflectance (DR) measurements from a standard light source (a high pressure xenon lamp).

Over several years, KISR's previous efforts in the LIF field were documented in numerous project reports, as well as several publications. Detailed

comprehensive descriptions of the lab-based LIF system developed by the team at KISR appeared in: (Qabazard et al., 2002), and (Quinn et al., 2002). What follows in this article is a description of the extension of the lab-based assembly and work, which has culminated in the development of a mobile laboratory capable of performing the same types of LIF measurements in-situ, hence providing timely results in the field (KISR, 2008).

2. MATERIALS AND PROCEDURE

2.1 Mobile System Requirements and Development

Leading to the actual construction of the mobile laboratory facility, several steps were taken in order to test the concept. This procedure took the shape of packaging the existing lab-based LIF facility in a sports utility vehicle. With the aid of a custom made probe head and segment; experimental pushes were attempted utilizing the weight of the vehicle to drive down the probe to acquire LIF measurements at subsurface depths. While this procedure failed to drive the probe to any appreciable depths, yet the concept was clearly demonstrated and the decision was made to proceed with the full-scale development of a dedicated mobile system that relied on cone-penetrometer techniques (CPT).

The mobile LIF laboratory system design called for the following main components:

- An optical assembly, incorporating a pulsed Nd/YAG Laser with second and fourth harmonic generating crystals, harmonic separation module, a bundle of fiber optical cables, and fluorescence / diffuse reflectance (DR) detection systems.
- LIF subsurface probe with optics incorporated to direct the excitation light to the soil target through a sapphire window.
- 20-ton truck, equipped with a hydraulic mechanism capable of achieving a force of 200kN.

2.1.1 Optical Assembly

The choice to extend the functionality of the LIF system from the lab to the field entailed the same requirements that were needed in terms of optics and the involved excitation sources. While the lab based system enclosed of two laser sources: a 266 nm and a 366 nm sources (both Nd:YAG laser sources based on the Minilite series from Continuum, Inc.), for the mobile system the choice was made to rely exclusively on the 266nm source, operating at 10Hz to deliver ~1mJ

pulses. Furthermore, while a streak camera was used in the laboratory system as a detector, for the mobile field laboratory two photomultiplier tube (PMT) subsystems are utilized: The first detector consists of a custom-built single channel photomultiplier system for profiling both total integrated fluorescence (300nm to 600nm) and diffuses reflectance (532nm). The second detector is comprised of a 32-channel PMT array (made by Hamamatsu: Model H7260-04) photomultiplier detector for measuring fluorescence spectra at the range spanning: 300 to 600nm. Signals measured by this detector first pass through a polychromator for spectral differentiation (Shamrock 163i, made by Andor Technology). For DR measurements, and rather than only relying on a xenon lamp as a light source, a special setup of optical wedge prism and dichroic mirrors, along with physical blocking apertures are used to separate the second harmonic component of the 266nm laser, equivalent to 532nm. This portion of the pulse is used for DR, and it is delivered ahead of the 266nm pulse by approximately 20ns.

A special bundle of fiber optical cable was utilized to deliver the excitation laser source and to receive the resultant collected fluorescence emissions. The fiber bundle, which was designed by the team and manufactured by Fiberguide Industries Ltd., is comprised of four 600 μ m quartz fibers each with a numerical aperture of 0.22. The 25 meter long bundle is ruggedized with a jacket made of interlocking PVC-covered segments. One fiber is used to channel the 266nm excitation laser pulse to the target. A second fiber is used to channel the 532nm laser pulse for DR measurements purposes. Each one of the remaining two fibers is used for the collection of the emitted responses for LIF and DR measurements, respectively.

2.1.2 The LIF Probe

The conical probe head was designed by the team and fabricated by a specialized precision workshop. The main probe head is 200mm in height and 36mm in diameter. The probe head functions as a conduit for the various pulses from the fiber bundle to the spot of soil under examination behind a synthetic sapphire crystal window, and vice versa for the emissions that are channeled to the detection systems by the fiber bundle. This action would require a 90° diversion in the paths of excitation / emissions from the orientation of the fiber bundle, and this is achieved by an optically coated aluminum finger reflector, situated in front of the sapphire window which is located on the flush surface of the probe. The choice for the sapphire window stems mainly from its extreme hardness (exceeding grade 9 on the Mohs scale), making it extremely rugged and scratch proof in repeated field usage.

The probe head is threaded on its top other end; an arrangement that facilitates the attachment of the conical probe head to the probe segments. Each one of these

hollow segments is 1-meter in length, and the fiber bundle is threaded into each one from the head to the labs optical assembly.

2.1.3 The Vehicle and the Laboratory Compartment

The mobile laboratory utilizes its own weight to drive the probe to subsurface levels. To that end, requirements called for a truck equipped with self-lifting jacks mechanism equipped with a hydraulic pushing device based on cone penetration test (CPT). Once lifted on its own jacks, the truck's CPT press directed the equivalent of 200kN pressure to the LIF/CPT probe and its attached segments through the ground. Operators inside the lab compartment attach the probe segments to one another manually, incrementally adding each one as the need arises to push the probe deeper.

The laboratory's floor plan called for a compartment that is about 4.2 by 1.5 meters. Furthermore, the compartment required a special lift mechanism arrangement to hoist heavy masses (<200kg) such as equipment from the ground up to the labs entrance. The compartment facilitates the three main types of activities encompassed by the relevant nature of the fieldwork activities: the optics (both operating the laser source and the various detectors), the CPT activities and feeding the probe segments. Among the other necessities called for in the design of the compartment was the need to provide measures for environmental control. This was a vital requirement given the often harsh local weather conditions; and not only did it provide for a comfortable working environment for the operators inside the lab, but it also guaranteed a temperature range for the proper operation of the laser sources and optical detectors.

Geomil Equipment, B.V. of the Netherlands, was selected to build the laboratory compartment according to the required specifications. The company also supplied the laboratory's 20-ton MAN truck. Upon its completion the mobile lab became designated as the Environmental Unit for Measuring Subsurface Oil Contaminants (EUMSOC).

2.2 Case Study: Field-Testing the EUMSOC

2.2.1 Analytical Methods

In order to correlate LIF measurements with established laboratory methods, a series of control spiked soil sample were prepared. Various batches of spikes were prepared using a variety of fuels, but mostly concentrating on spikes made with crude oil. The spiking process involves the selection of a representative soil sample from the field, generally from the vicinity of the area under examination. The specimen was chosen to epitomize the type of soil in the area under



Figure 1. The mobile LIF/CPT lab developed at KISR and identified as the Environmental Unit for Measuring Subsurface Oil Contaminants (EUMSOC). In this view the vehicle is raised on the self-lifting jacks, and the lowered LIF probe is seen in between the vehicle's front-rear wheel and the front lifting jack.



Figure 2. View inside of EUMSOC showing the laboratory's main components. From the right: the optical bench incorporating the laser source, detectors and optics. The CPT control, output displays and the main press mechanism are at the center. On the left is the carriage-holder of the probe segments.

observation in terms of the particle size distribution and the amount of background hydrocarbon residue. As such, the representative soil is examined to ascertain the low amount of extractable material within it, as well as establishing particle sand-silt-clay distribution. The physical characteristics of subsurface samples obtained from the test boreholes in that area were equally tested and compared to the representative test soil.

The spikes were then tested both with the LIF process as well as subjected to an extraction laboratory method (e.g., EPA 418.1). Results from the two outcomes are compared and the linearity between the two methods is examined. The LIF results are further refined by applying diffuse reflectance (DR) measurement corrections to account for the variation in the absorbed emissions due to the change in the tested samples opacity with increased levels of contamination. An outline of a typical spiking procedure and the obtained results appeared in (Quinn et al., 2004). For classification purposes, results from the multi-channel detectors are subjected to a series of high-level statistical methods, namely utilizing principal component and discriminant component analysis. The framework of this method in our deployment of LIF measurements appeared in (Alemeddine et al., 2004).

2.2.2 Choice of a Test Location

The laboratory was field-tested at an area in northern Kuwait known as Um Al-Aish. In particular, the spot that was chosen for the field test involved the massive remains of an oil lake that is approximately 0.5km² in area, centered at the geographical location: 29° 48.89' N, 47° 48.02'E. The spot resembles a natural basin in comparison with the adjacent terrain, for the general elevation at the location of interest drops to approximately 30m above sea level, down from a maximum of about 70m in the surrounding location. The aim of the tests centered on the ability of EUMSOCs two detectors: namely the single channel and the 32-channel PMT detectors in identifying traces of pollution at various subsurface levels, and how the results from the two detectors compare to one another.

A series of test boreholes surrounding that location helped to establish the nature of the subsurface soil strata, along with the expected levels of contamination. The area is located inside the compounds of Kuwait Oil Company; it is closed to the public with minimal subsurface infrastructure installations, hence facilitating the subsurface test pushes of the LIF probe.

3. RESULTS AND ANALYSIS

3.1.1 The Nature of Soil at the Test Sites

In comparison with the range of spiking levels applied uniformly for the batches of spiked soil samples (ranging from 250-20,000 ppm) used in the calibration procedures, the amount of total extractable material within the representative test soil selected for the various spiking batches turned out to be low (>56ppm, petroleum hydrocarbons constituted about 70% of that amount). The test soil turned out to be very sandy; it resembled soils extracted at different depths from the test borehole at the site.

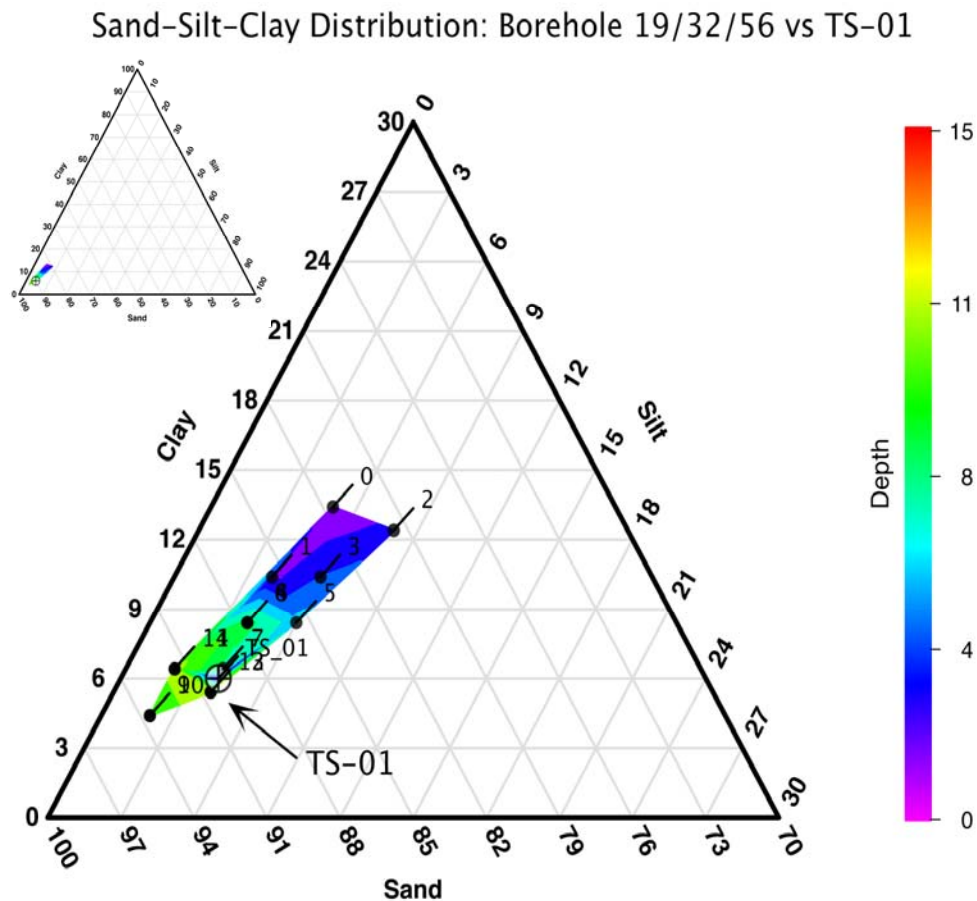


Figure 3. A ternary plot demonstrating a typical sand-silt-clay particle distribution for soil samples obtained from various depths at the site of test borehole: 19/32/56 vs. the test soil (TS-01) used in the various spiking procedures. The inset graph shows the plot in its entirety, with the portion in

the lower left enlarged to show detail. The borehole results verify an increase in the sandy nature of the soil with depth.

3.1.2 Corroborating the LIF Results with Established Techniques

When the batches of laboratory prepared spiked soil samples were tested, the results of the tests (based on the EPA 418.1 method) proved to offer a reasonable linear response when compared with both the single-channel and the multi-channel detectors.

Both the physical nature of the soil used in the spiking procedure, as well as the level of correlation between lab-based and the LIF results led to conclude that EUMSOC could be utilized for field screening purposes. This conclusion stems from the original assumption that LIF measurements conducted on batches of laboratory prepared crude oil-spike soils would constructively correlate with field-based LIF results.

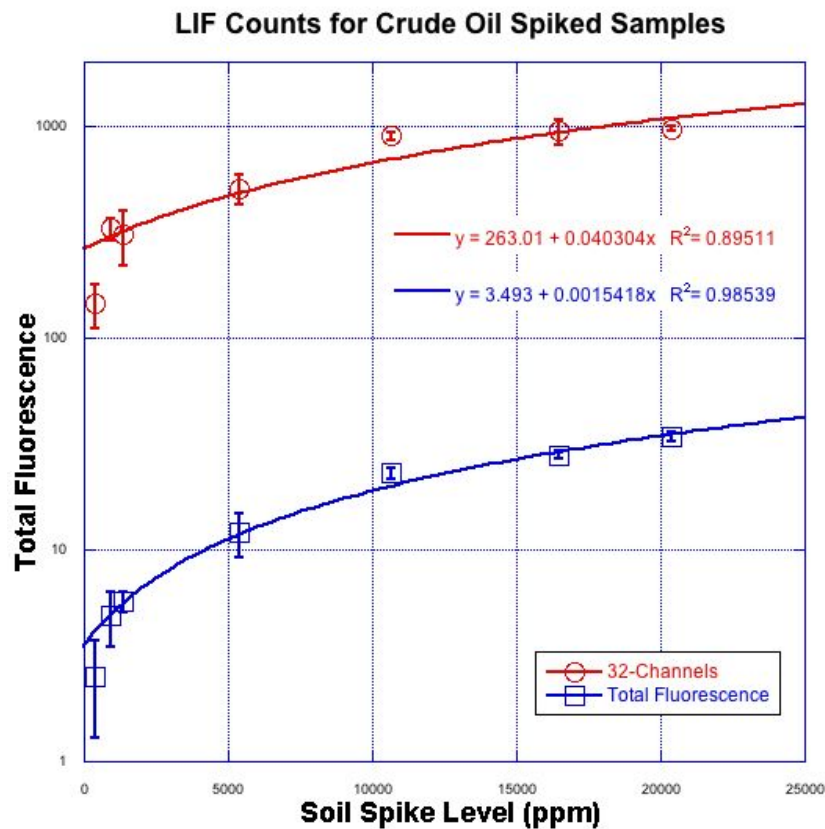


Figure 4. Linearity fits demonstrating high levels of correlation between spiking levels (in part-per-million as verified by EPA 418.1 method) versus the total fluorescence (single channel) and 32-channel LIF detectors used at EUMSOC.

3.2 Probe Tests at Various Depths

The facility was extensively field tested at the oil lake employing the two detectors on board. Tests were conducted over a variety of different terrains, from areas where the topsoil was virtually loose sand, to areas where the ground was covered by a layer of hardened thick dry oil. In general EUMSOC proved to be

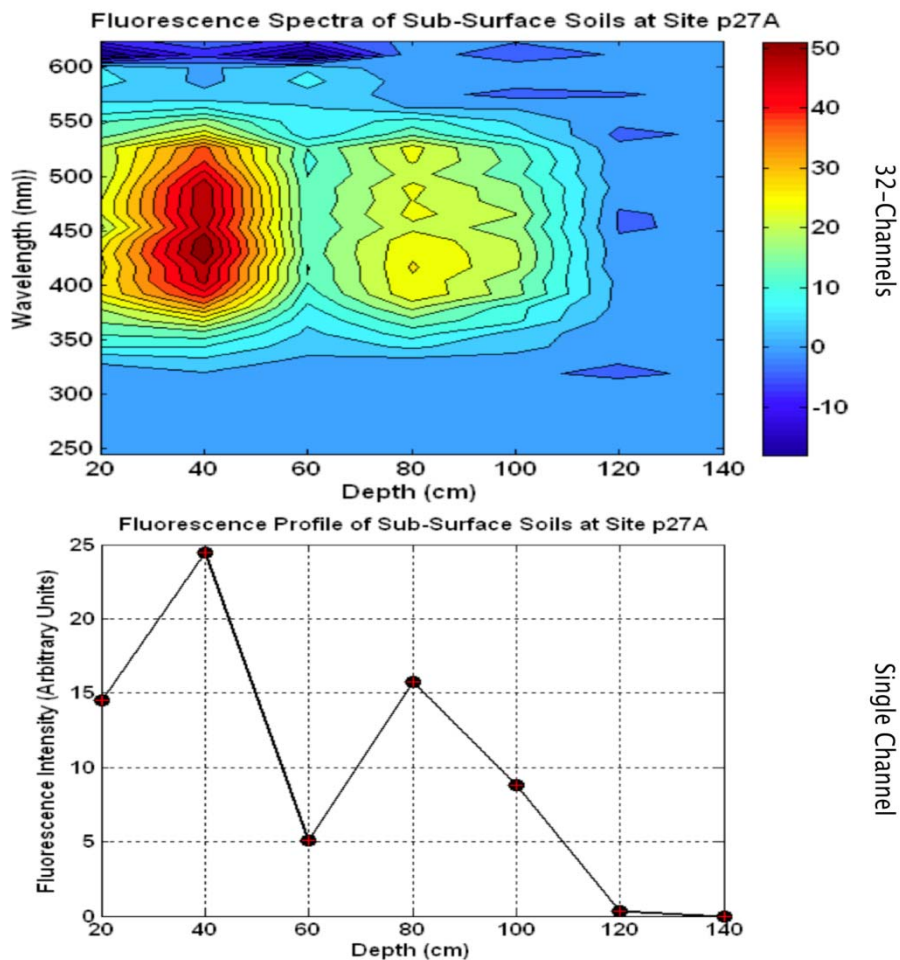


Figure 5. Comparison between the results obtained with the 32-Ch. and single channel PMT detectors at the same test point. The top portion showcases the wavelength vs. depth “fingerprint” obtained with the multi-channel detector. Both results demonstrate that for that particular location there is an increase in responses at a depth of 40-cm, which is followed by a decline in fluorescence at 60-cm. Another, though lower increase is observed at a depth of 80-cm.

both adaptable and highly mobilized. In certain instances, it was required to drive the probe for a test at a confined point. With a combination of hand gestures by members of the team observing from the front and the sides, the driver of the lab managed to precisely position the truck with a minimal amount of effort and time. Once a point is chosen for a subsurface series of measurements, a test – or “dummy” – probe is pushed before using the LIF probe. This practice is employed to guarantee that the actual probe will not be encounter a layer of hardened sand, subjecting it to an aggregated amount of pressure that might damage it. After the push process is completed, the geographic location of each test point was recorded with the aid of a DGPS. The terrain is observed and distinguishing features are noted and recorded. Any holes left from the push were grouted in a separate procedure.

Results from the two detectors generally agreed with one another, with the multi-channel detector yielding an extended insight into the tested spot when the results are combined with the depth to form a “fingerprint” for the range extending from the surface to the furthest point the probe was driven into. In several instances, such fingerprinting provided a perception on the mechanism with which petroleum hydrocarbon based pollutants infiltrated soil layers.

4. CONCLUSIONS

The mobile LIF/CPT laboratory (EUMSOC) was successfully developed and proved to be effective in the fast screening for pollutants in surface and subsurface layers of soil in various areas around Kuwait. It further confirmed the successful demonstration of contaminant classification with the aid of spectral measurement and advanced statistical methods This fast method to screen for the extent of contamination will offer an invaluable service to current and future cleanup operations in the country.

There are other systems built on the concept of LIF/CPT techniques. Chief among such systems is the US Department of Defense Tri-Services “Site Characterization and Analysis Penetrometer System” (SCAPS). The primary difference between these two systems is EUMSOCs implementation of DR corrections. Augmenting LIF results with DR measurements aid with the accuracy of the quantification of contaminant levels.

The lab functionality required supporting data about the nature of the soils being examined, as well as the availability of a database of pre-measured LIF calibration sets of various contaminant sources.

Among the considerations for further system optimization include the augmentation of a full CPT probe head attachment with dedicated strain gauge

sensors. Furthermore, the addition of an optical aid to provide visual feed back to offer a real-time observation of the spot under examination. Such additions will aid in the categorization of soil types and site characteristics with less dependence on extra lab based tests of samples obtained by independent physical collection.

5. ACKNOWLEDGMENTS

The authors would like to recognize the fundamental contributions made by the research assistant of the team, Ms. Lincy Abraham and Mr. Anselm Pereira, the groups technician. We are indebted to their diligent and unremitting efforts. Also, we wish to express the deepest appreciation to the Kuwait Foundation for the Advancement of Sciences (KFAS) for the financial support of the project. In addition, the team would like to thank Kuwait Oil Company (KOC) for their support to implement the field-testing of the system at the company's sites.

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Chapter 2

GREENHOUSE GAS EMISSIONS MODELING: A TOOL FOR FEDERAL FACILITY DECOMMISSIONING

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ABSTRACT

The Federal Aviation Administration (FAA) facility inventory is constantly changing as newer systems supplant older infrastructure in response to technological advances. Transformational change embodied by the FAA's Next Generation Air Transportation System (NextGen) will affect the replacement of thousands of ground-based air traffic control systems with satellite-based systems by 2025. NextGen alone will drive a massive facility decommissioning effort with the potential for major environmental impacts from demolition and disposal activities, including emissions of greenhouse gases (GHGs), criteria pollutants, and air toxics, erosion, runoff, noise, generation of solid waste, and the migration of contamination associated with historic releases of hazardous waste, fuel constituents, and hazardous building materials. The FAA and other federal agencies need effective environmental impact assessment tools to design mitigation strategies and ensure compliance with regulatory and policy drivers, including Executive Order (EO) 13514 Federal Leadership in Environmental, Energy, and Economic Performance, which establishes integrated strategies towards sustainability and greenhouse gas emissions reductions in the Federal Government. In this study we develop a model to facilitate the quantitative analysis of comprehensive GHG emissions inventories from demolition debris reuse, recycling, and disposal activities that accounts for scope 1, scope 2, and scope 3 emissions as defined by EO 13514. The results of the model are used to inform a trade-off analysis that compares the relative impacts of debris management alternatives. Data from the decommissioning of an air traffic control tower and an air route surveillance radar facility are used as case studies to refine and validate the model, which could be used as a tool to guide future

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decommissioning efforts at Federal facilities and to provide input to FAA's agency-wide GHG emissions inventory.

Keywords: greenhouse gas emissions, green house inventory, federal facilities, decommissioning, disposal, demolition

1. INTRODUCTION

The Federal Aviation Administration (FAA) facility inventory is constantly changing as newer systems supplant older infrastructure in response to technological advances. Transformational change embodied by the FAA's Next Generation Air Transportation System (NextGen) will necessitate the replacement of thousands of ground-based air traffic control systems with satellite-based systems by 2025. NextGen alone will drive a massive facility decommissioning effort with the potential for major environmental impacts from demolition and disposal activities, including emissions of greenhouse gases (GHGs), criteria pollutants, and air toxics, erosion, runoff, noise, generation of solid waste, and the migration of contamination associated with historic releases of hazardous waste, fuel constituents, and hazardous building materials.

In the United States, the federal government has focused considerable recent attention towards addressing GHG emissions. On December 7, 2009, the United States Environmental Protection Agency (EPA) Administrator Lisa Jackson signed a final action, under Section 202(a) of the Clean Air Act, finding that greenhouse gases constitute a threat to public health and welfare, and that the combined emissions cause and contribute to the climate change problem. If greenhouse gases continue to increase, climate models predict that the average temperature at the Earth's surface could increase from 3.2 to 7.2 °F (1.8 to 4.0 C) above 1990 levels by the end of this century (EPA, 2010) with negative impacts to the biosphere. President Barack Obama signed Executive Order (EO) 13514, also in 2009, mandating federal agencies inventory and establish reduction goals for GHG. EO 13514 requires the federal government to report on GHG emissions directly linked to facility and vehicle fleet operation in what are known as scope 1 (direct fossil fuel combustion) and scope 2 (facility energy consumption via off-site fossil fuel combustion, e.g. electricity) sources. In addition, the executive order creates the first requirement in any nation to account for and set reduction targets for all other indirect sources of GHG, known as scope 3 emissions.

Currently, only scope 3 emissions related to Federal employee commuting, business travel, energy transmission and distribution losses, waste water, and solid waste are included in the federal inventory. Section 2(b)(i) of EO 13514 states that federal agencies shall consider reductions associated with "pursuing

opportunities with vendors and contractors to address and incorporate incentives to reduce GHG...” It is anticipated, that remediation and deconstruction projects will fall under this requirement as GHG related regulatory updates are promulgated. The research team retro-actively calculated GHG emissions as a potential guidance approach for future scope 3 accounting and reduction opportunities related to site demolition projects.

In this study we develop a model to facilitate the quantitative analysis of comprehensive GHG emissions inventories from demolition debris reuse, recycling, and disposal activities that accounts for scope 1, scope 2, and scope 3 emissions as defined by EO 13514. The model is used to inform a trade-off analysis that compares the relative impacts of debris management alternatives using data from the decommissioning of two FAA facilities as case studies to refine and validate the model: the St. Albans Air Route Surveillance Radar (ARSR) facility (St. Albans, Vermont) and the former North Las Vegas Airport Air Traffic Control Tower (ATCT) located in Las Vegas, Nevada.

1.1 St. Albans ARSR Site

In 1951, the United States Air Force (USAF) constructed the St. Albans Air Force Station as part of the Defense Early Warning System. During early operations, the USAF maintained an array of radar towers and extensive support facilities. With gradual improvements in radar technology and the Department of Defense (DoD) movement towards satellite-based tracking systems, radar operations were consolidated into smaller facilities and transitioned to the FAA in 1976 for use in tracking commercial aircraft within the National Airspace System (NAS). In 1979, the USAF departed from the installation, which was subdivided and transferred to the FAA and other parties. Beginning in 1991, the USAF, FAA, and others have been actively engaged in a variety of decommissioning-related activities, including site investigation and remediation to address legacy environmental contamination, removal and closure of fuel storage tanks, abatement of hazardous building materials, and the demolition and disposition of abandoned buildings and other infrastructure. In 2001, the FAA completed extensive decommissioning actions on its property (now known as the St. Albans ARSR site), including the demolition and disposal of a 16,159 ft² (1,500 m²) concrete, steel-reinforced former Operations Building and two abandoned concrete radome foundations; data from this effort serve as our first case study. Demolition debris generated from this action included concrete and masonry that was crushed and reused onsite, asphalt, steel scrap, and non-ferrous metal shipped offsite for recycling, and construction debris, including wood, drywall, fasteners, lighting fixtures, fiberglass insulation, and other building materials disposed of at

an offsite landfill. The duration of the demolition activities at the site was approximately 61 work days.

1.2 Former North Las Vegas Airport ATCT

In 2000, the FAA constructed a new ATCT at the North Las Vegas Airport, abandoning the original tower that was built in 1976 on land leased from the Clark County Department of Aviation (DOA). The FAA relinquished use of the property back to the DOA, but was required to remove, demolish and dispose of the ATCT and other onsite infrastructure. The abandoned ATCT site was approximately 6,000 ft² (557 m²) in size and included an eight story steel-frame control tower, an airport vault building, a pad-mounted transformer, and a paved parking area. Intermediate floors within the ATCT included offices and equipment rooms, with the 8th floor being the tower cab. The ATCT also included an elevator, with its motor and associated equipment located on the 1st floor. Following the abatement of asbestos and other hazardous materials and removal and disposal of building contents and furnishings, the abandoned ATCT was demolished and the concrete slab removed. Demolition debris included scrap metal and steel that was recycled offsite and construction debris that was disposed of at an offsite landfill. The demolition activities were completed in 2007 and the total duration of the effort was approximately 20 work days.

2. METHODS

Where possible, the model input data for the case studies were obtained directly from project record documents prepared by the vendors who performed the demolition work at each site. As discussed below, where data were not available, reasonable estimates were made to facilitate the GHG emissions analysis based on information from project planning documents, photographic records, interviews and the professional judgment of two of the coauthors who oversaw the demolition work in the field. Input data incorporated into the model was organized under scopes 1, 2, and 3 as shown in Table 1 and includes the following:

- Scope 1: Equipment used onsite, estimated percent equipment operating time, and its estimated average fuel consumption per hour.
- Scope 2: The area of facilities undergoing demolition
- Scope 3: The type and mass of demolition debris generated and its method of disposal and estimates of the distance traveled (business travel) in support to support the project.

Table 1. GHG Model Input Data

St. Albans ARSR			N. Las Vegas ATCT		
Scope 1			Scope 1		
Equipment (fuel type), Operating Time	Average Fuel Combustion/hour		Equipment (fuel type), Operating Time	Average Fuel Combustion/hour	
	(gallons)	(liters)		(gallons)	(liters)
Concrete Crushing (Diesel), 20%	9.91	37.51	120-Ton Crane (Diesel), 10%	12	45.42
Excavator / shear (Diesel), 20%	9.45	35.77	Front loader/Backhoe John Deere 710 (Diesel), 25%	2.65	10.03
Excavator / universal processor(Diesel), 80%	9.45	35.77	2 Small bobcat loaders (Diesel), 100%	5.31	20.1
Dozer D4 (Diesel), 100%	4.83	18.28	Cat 966F (Diesel), 5%	3.55	13.44
Excavator with bucket (Diesel), 100%	9.45	35.77	Ten-wheeled truck (Diesel) 10%	1.7	6.44
Loader track 2.5 (Diesel), 100%	2.66	10.05	2 JLG Variable reach Man-lift (diesel), 100%	1.96	7.42
Pick up 100% (Gas), 100%	1.23	4.66			
Generator 100% (Gas), 100%	0.75	2.84			
Scope 2			Scope 2		
Facilities	Area		Facilities	Area	
	ft ²	m ²		ft ²	m ²
1020, 935, 925	16159	1501.22	ATCT	6000	557.42
Scope 3			Scope 3		
Demolition Debris Type	Quantity (Metric Tons)	Disposal Method	Demolition Debris	Quantity (Metric Tons)	Disposal Method
Concrete	9183.67	On Site	Scrap Metal (mixed)	15.81	Recycled
Asphalt	56.7	Recycle	Scrap Steel	24.49	Recycled
Lumber	65.05	Landfill	Lumber	1.72	Landfill
Clay	7.53	Landfill	Fiberboard	2.3	Landfill
Fiber Board	48.08	Landfill	Paper	0.57	Landfill
Glass	35.47	Landfill	Glass	2.3	Landfill
Paper	24.77	Landfill	Mixed MSW	16.03	Landfill
Steel (landfill)	18.23	Landfill	Refrigerant	0.02	Recycled
Metal (recycled)	113.4	Recycle			
Business Travel	miles	km	Business Travel	miles	km
Air transport	3504	5639.14	Air transport	9756	15700.76
Ground Transport	4544	7312.86	Ground transport	3180	5117.7

To estimate scope 1 emissions we used an EPA method for calculating carbon dioxide (CO₂) emissions per volume of fuel consumed by the construction equipment used during demolition activities at each site (EPA Office of Transportation and Air Quality, 2005). The EPA method incorporates an oxidation factor of 0.99 as recommended by the Intergovernmental Panel on Climate Change (IPCC) in its guidelines for calculating emissions inventories (i.e., 99 percent of the carbon in the fuel is eventually oxidized, while 1 percent remains un-oxidized). Two separate CO₂ emissions values are given in the EPA method based on whether the fuel source is diesel or gasoline, with the combustion of diesel fuel generating greater CO₂ emissions than an equivalent volume of gasoline based on the higher carbon content of diesel (2,778 grams) compared to gasoline (2,421 grams) used by EPA (US Government Printing Office, 2007). The CO₂ emissions calculations also incorporate a multiplier (ratio of the molecular weight of CO₂ to the molecular weight of carbon (44/12)) to convert carbon to CO₂ equivalent.

CO₂ emissions from a gallon of gasoline:

$$\begin{aligned} &= 2,421 \text{ grams carbon/gallon gasoline} \times 0.99 \times (44/12) \\ &= 8.8 \text{ kg CO}_2/\text{gallon gasoline} \\ &= 19.4 \text{ pounds CO}_2/\text{gallon gasoline} \end{aligned}$$

CO₂ emissions from a gallon of diesel:

$$\begin{aligned} &= 2,778 \text{ grams carbon/gallon diesel} \times 0.99 \times (44/12) \\ &= 10.1 \text{ kg CO}_2/\text{gallon diesel} \\ &= 22.2 \text{ pounds CO}_2/\text{gallon diesel} \end{aligned}$$

The actual volume of fuel used during the execution of each project was not recorded and had to be estimated. Since an inventory of equipment actually used during the demolition work at each site was not available, the equipment included in Table 1 was estimated from cost estimates and project work plans that were prepared in advance of the work, which identified proposed construction equipment (Marcor Remediation Inc, 2000, 2001, MWH Americas Inc 2006). The percentage of the time each piece of equipment was in operation at each site was also estimated and is included in Table 1 to the right of the equipment description. The type of fuel (diesel or gasoline) and an average volume of fuel consumption per hour of operating time were determined or estimated based on equipment manufacturer's published data. An eight hour work day was assumed for each site for the duration of each project: 61 work days for the St. Albans ARSR site and 20 work days for the N. Las Vegas ATCT site.

Scope 2 emissions were estimated using EPA's Emissions & Generation Resource Integrated Database (eGRID), a comprehensive inventory of environmental attributes of electric power systems. eGRID is based on available

plant-specific data for all U.S. electricity generating plants that provide power to the electric grid and report data to the U.S. government and integrates many different federal data sources on power plants and power companies, from three different federal agencies: EPA, the Energy Information Administration (EIA), and the Federal Energy Regulatory Commission (FERC). Emissions data from EPA are carefully integrated with generation data from EIA to produce useful values such as mass of CO₂ emissions per megawatt-hour of electricity usage. Each region and sub-region has a corresponding mix of GHG emissions based on the range of different types of power plants (e.g. nuclear, coal-fired, hydro-power, etc.). For this study, we used the EPA's web-based eGRID interface to tailor the electricity-related GHG emissions to each project's geographic region. Project total building area and/or project area, area code, and total project duration were inputted into eGRID and the tool calculated the regional GHGs associated with each project. The total area of buildings undergoing demolition was used for the St. Albans site, while the total project site area was used at the N. Las Vegas site (because it was a very compact site and the total building area was not available). eGRID estimates electricity generation based on an average commercial building of the size entered into the tool. It is recognized that the ARSR and ATCT facilities are not average commercial buildings and the overall approach is expected to overestimate the electricity usage at both sites neither facility was fully active for the project duration.

Scope 3 GHG emissions estimates incorporate the embodied energy in the waste generated from demolition activities as well as business travel to and from the project sites. EPA has derived GHG emissions factors for a variety of waste materials from life-cycle analysis work, which can be applied as multipliers to estimate GHG emissions based on metric tons of waste generated and the method of disposal (EPA, 2006, EPA, 2003). Our case study source data included project close-out reports that documented types and quantities (either volume of mass) of demolition debris that was generated at each site and whether that debris was reused, recycled, or disposed of at an offsite landfill (Marcor Remediation Inc, 2002, MWH Americas Inc, 2007). Conversion of waste volumes to mass was based on average density factors found in common estimating guides (Spradlin, 1986). For the St. Albans ARSR site, four general categories of demolition debris were reported: concrete and masonry (reused onsite), asphalt (offsite recycle), construction debris (offsite landfill), and scrap metal (offsite recycle). Four general categories of demolition debris were also reported for the N. Las Vegas ATCT site and included refrigerants (offsite recycle), scrap tin (offsite recycle), scrap steel (offsite recycle), and other inert construction and demolition waste (offsite landfill). Where necessary to facilitate use of EPA's GHG emissions factors, which are listed for more specific categories of waste, the general categories of debris generated at each site were further subdivided into more

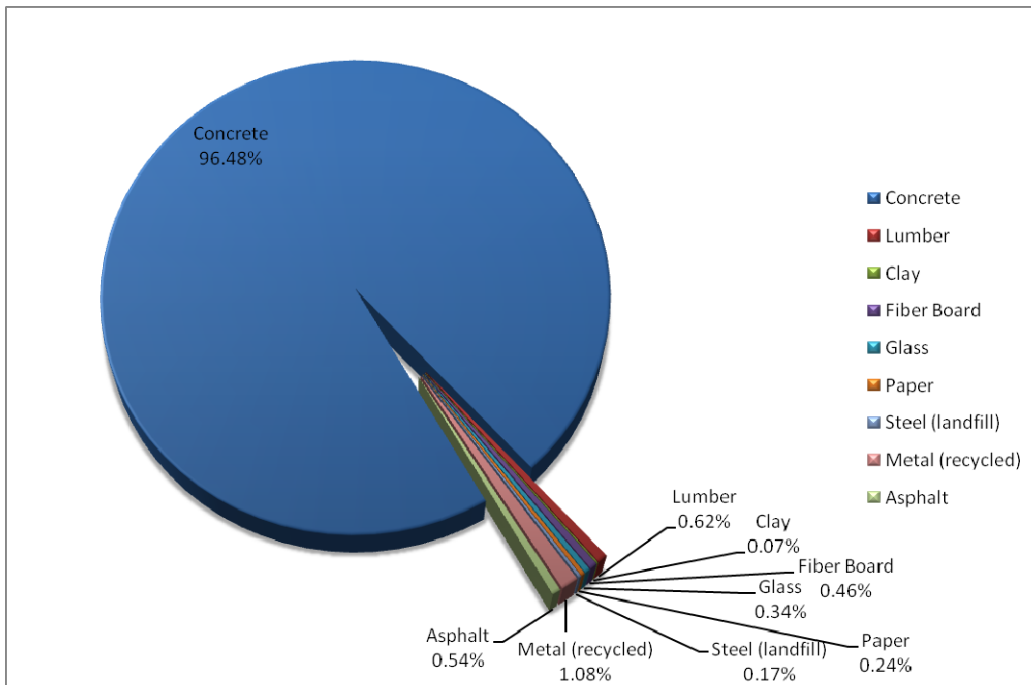


Figure 1a. Waste composition at the St. Albans ARSR site

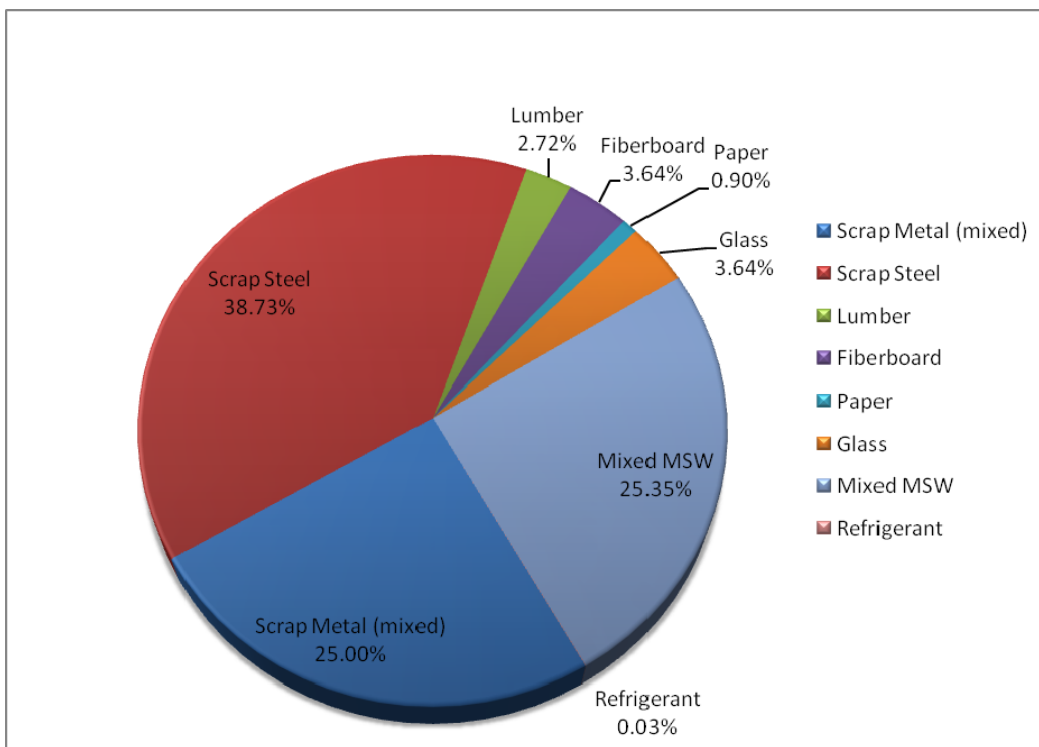


Figure 1b. Waste composition at the N. Las Vegas site

specific categories listed in Table 1 (and shown graphically in figures 1a and 1b) based on percentage distributions deemed reasonable for the purpose of this exercise.

GHG emissions for business travel were estimated using the Greenhouse Gas Protocol Initiative's Mobile Combustion GHG Emissions Calculation Tool, which calculates metric tons of CO₂ equivalent GHG emissions from distance traveled (Greenhouse Gas Protocol Institute, 2010). Since business travel data were not available, the distance traveled to and from the site by air or ground transport was estimated based on estimates of the composition and location of the work crews and work schedules based on input from the coauthors who oversaw field work at the sites (Table 1).

To help understand the relative impacts on GHG emissions of reuse and recycling that was performed at each site (the *actual scenario*), we evaluated an *alternate scenario*, under which all of the demolition debris generated at each site was assumed to have been landfilled. As such, the two scenarios differed only in the scope 3 emissions relating to the embodied energy in the waste generated, and the quantity of GHG related to waste transport avoided through reuse and/or recycling.

3. RESULTS AND DISCUSSION

Total GHG emissions estimates and the distribution among scopes 1, 2, and 3 for each case study are shown in Table 2 and displayed in Figure 2. The total estimated GHG emissions calculated for the St. Albans ARSR site (actual scenario) was 720.02 metric tons (MT), with the largest share 529.73 MT (73.6 %) of the total emissions attributable to scope 3, 175.73 MT (24.4 %) for scope 1, and 14.56 MT (2.0 %) for scope 2. The total estimated GHG emissions for the St. Albans alternate scenario (all demolition-generated debris landfilled) was 2,510.74 MT, 1,790.62 MT greater than the estimated GHG emissions for the actual scenario. This difference represents the estimated GHG emissions avoided by incorporating reuse and recycling into the project. For the alternate St. Albans scenario, the magnitudes of the scope 1 and scope 2 emissions are the same as the actual scenario, but their share of the total emissions is less; 175.73 MT (7.0 %) for scope 1 and 14.56 (0.6 %), with scope 3 emissions under the alternate scenario responsible for 2,320.44 MT (92.4 %).

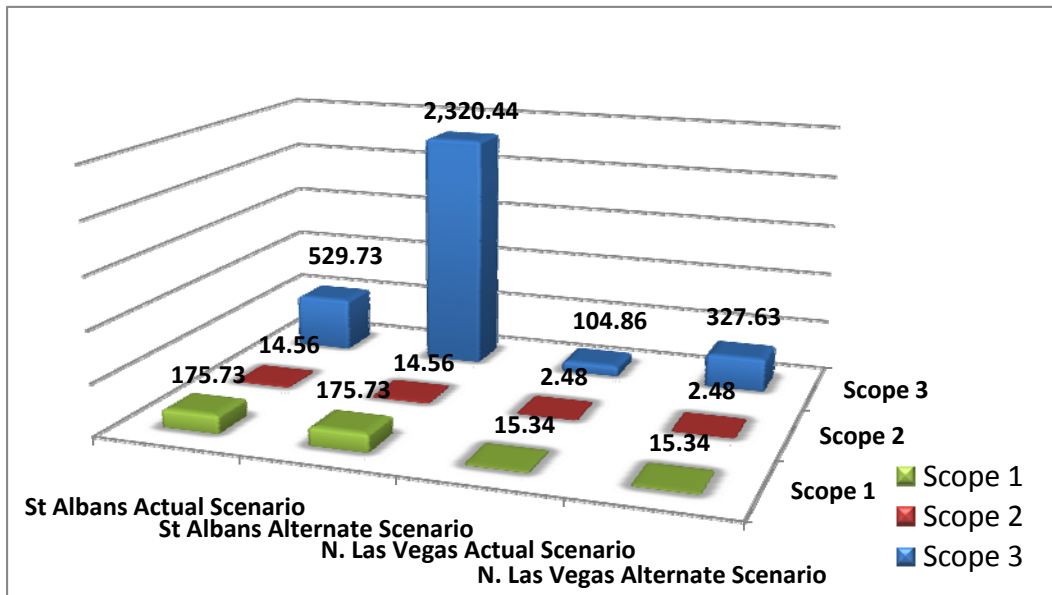


Figure 2. Comparison of greenhouse gas emissions estimates (metric tons)

The total estimated GHG emissions calculated for the N. Las Vegas ATCT (actual scenario) was 122.68 MT; 15.34 MT (12.5 %) for scope 1, 2.48 MT (2.0 %) for scope 2, and 104.86 MT (85.5 %) for scope 3. The total estimated GHG emissions for the N. Las Vegas alternate scenario was 345.45 MT, representing 222.77 MT GHG emissions avoided by incorporating reuse and recycling. Similarly, under the alternate N. Las Vegas scenario, the magnitudes of the scope 1 and scope 2 emissions are the same as the actual scenario and their share of the total emissions is also less; 15.34 MT (4.4 %) for scope 1 and 2.48 (0.72 %) for scope 2, with scope 3 emissions under the alternate scenario responsible for 327.63 MT (94.8 %).

The percent contribution of each type of demolition debris to the total GHG emissions for the actual and alternate scenarios for the St. Albans ARSR site and the N. Las Vegas ATCT site are shown in Figures 3a and 3b, respectively. These figures show the relative importance debris reuse and recycling efforts, especially concrete reuse at the St. Albans site and refrigerant recycling at the N. Las Vegas site. Under the St. Albans actual scenario, the top contributors to GHG emissions are metals (recycled offsite, 46.7 %), lumber (landfilled, 26.8 %), and steel (landfilled, 13.9 %), while the GHG emissions under its alternate scenario (all demolition debris landfilled) is attributable to concrete and asphalt disposal (70.4 %) and metals (18.3 %) (figures 3a and 3b). And, under the actual scenario at N. Las Vegas, the top contributors to GHG emissions are scrap steel (38.7 %), scrap metal (25.0 %), and mixed municipal solid waste (MSW) (25.4 %), while the

Table 2. GHG Emissions Inventory

St. Albans ARSR						
	Actual Scenario - Direct Fossil Fuel Combustion			Alternate Scenario - Direct Fossil Fuel Combustion		
Scope 1	Fuel burned per day (diesel)	272.30 gallons	1030.75 liters	Fuel burned Per day (diesel)	272.30 gallons	1030.75 liters
	Fuel burned Per day (gas)	15.84 gallons	59.96 liters	Fuel burned Per day (gas)	15.84 gallons	59.96 liters
	Total GHG emissions per day	6352.27 lbs.		Total GHG emissions daily	6352.27 lbs.	
	Total Scope 1 GHG Emissions (20 days)	175.73 MT		Total Scope 1 GHG Emissions (20 days)	175.73 MT	
	Actual Scenario - Energy Consumption Via Off-Site Fossil Fuel Combustion			Alternate Scenario - Energy Consumption Via Off-Site Fossil Fuel Combustion		
Scope 2	NO emitted	29.58 lbs.	13.42 kg	NO emitted	29.58 lbs.	13.42 kg
	SO2 emitted	81.39 lbs.	36.92 kg	SO2 emitted	81.39 lbs.	36.92 kg
	CO2 emitted	32000.93 lbs.	14515.38 kg	CO2 emitted	32000.93 lbs.	14515.38 kg
	Total Scope 2 GHG Emissions	14.56 MT		Total Scope 2 GHG Emissions	14.56 MT	
	Actual Scenario - Embodied Energy in Waste			Alternate Scenario - Embodied Energy in Waste		
Scope 3	Total MTCE	143.29		Total MTCE	631.62	
	Total MTCO2E	525.43		Total in MTCO2E	2316.14	
	Total GHG Lbs. for Waste	148,131.31		Total GHG Lbs. for Waste	192559.78	
	Actual Scenario - Bussiness Travel			Alternate Scenario - Bussiness Travel		
	Total GHG Emission MTCO2E	4.35		Total GHG Emission MTCO2E	4.35	
	Total Scope 3 GHG Emissions	529.73 MT		Total Scope 3 GHG Emissions	2320.44 MT	
	Total GHG Emissions Actual Scenario	720.02 MT		Total GHG Emissions Alternate Scenario (metric tons)	2510.74 MT	
Total	Scope 1 %:	24.41		Scope 1 %:	7.00	
	Scope 2 %:	2.02		Scope 2 %:	0.58	
	Scope 3 %:	73.57		Scope 3 %:	92.42	

Table 2. GHG Emissions Inventory (con't)

N. Las Vegas ATCT						
	Actual Scenario - Direct Fossil Fuel Combustion			Alternate Scenario - Direct Fossil Fuel Combustion		
Scope 1	Fuel burned per day (diesel)	76.18 gallons	288.37 liters	Fuel burned Per day (diesel)	76.18 gallons	288.37 liters
	Fuel burned Per day (gas)	0 gallons	0 liters	Fuel burned Per day (gas)	0 gallons	0 liters
	Total GHG emissions per day	1691.20 lbs.		Total GHG emissions daily	1691.20 lbs.	
	Total Scope 1 GHG Emissions (20 days)	15.34 MT		Total Scope 1 GHG Emissions (20 days)	15.34 MT	
	Actual Scenario - Energy Consumption Via Off-Site Fossil Fuel Combustion			Alternate Scenario - Energy Consumption Via Off-Site Fossil Fuel Combustion		
Scope 2	NO emitted	8.77 lbs.	3.98 kg	NO emitted	8.77 lbs.	3.98 kg
	SO2 emitted	4.49 lbs.	2.04 kg	SO2 emitted	4.49 lbs.	2.04 kg
	CO2 emitted	5447.84 lbs.	2471.1 kg	CO2 emitted	5447.84 lbs.	2471.1 kg
	Total Scope 2 GHG Emissions	2.48 MT		Total Scope 2 GHG Emissions	2.48 MT	
	Actual Scenario - Embodied Energy in Waste			Alternate Scenario - Embodied Energy in Waste		
Scope 3	Total MTCE	67.18		Total MTCE	631.62	
	Total MTCO2E	246.35		Total in MTCO2E	2316.14	
	Total GHG Lbs. for Waste	148,131.31		Total GHG Lbs. for Waste	192559.78	
	Actual Scenario - Business Travel			Alternate Scenario - Business Travel		
	Total GHG Emission MTCO2E	7.40		Total GHG Emission MTCO2E	7.40	
	Total Scope 3 GHG Emissions	104.86 MT		Total Scope 3 GHG Emissions	327.63 MT	
	Total GHG Emissions Actual Scenario	122.68 MT		Total GHG Emissions Alternate Scenario	345.45 MT	
Total	Scope 1 %:	12.50		Scope 1 %:	4.44	
	Scope 2 %:	2.02		Scope 2 %:	0.72	
	Scope 3 %:	85.48		Scope 3 %:	94.84	

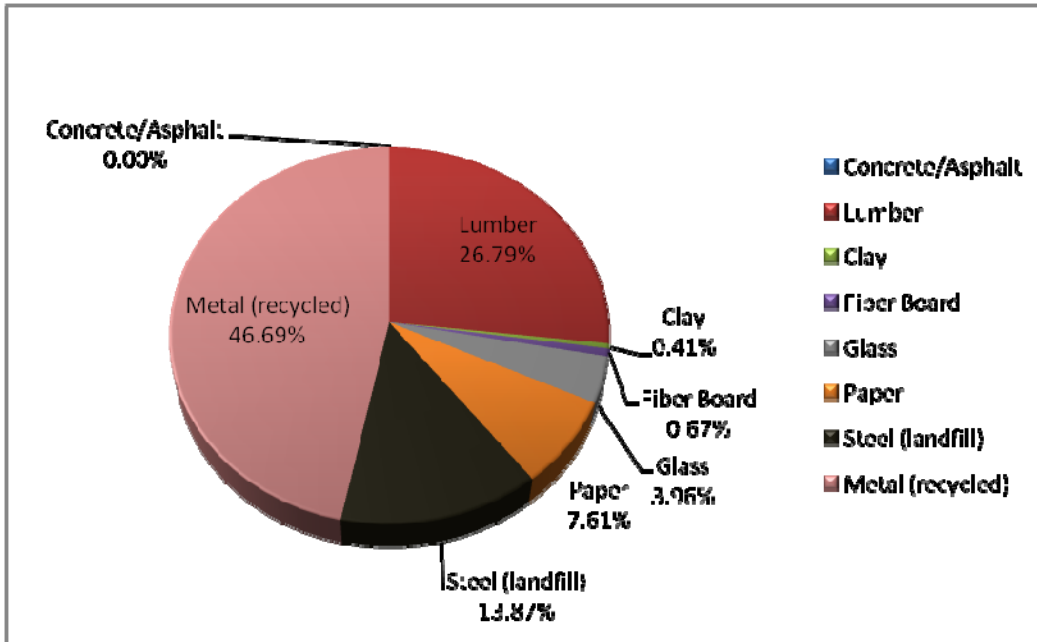


Figure 3a. Percent contribution to total GHG emissions by waste type– St. Albans actual scenario

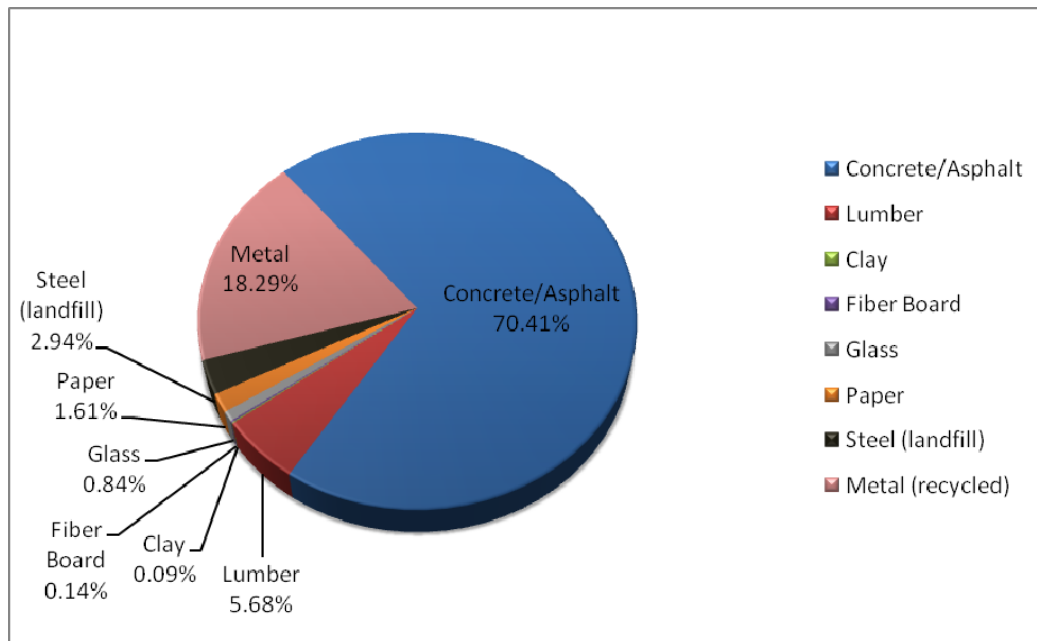


Figure 3b. Percent contribution to total GHG emissions by waste type– St. Albans alternate scenario

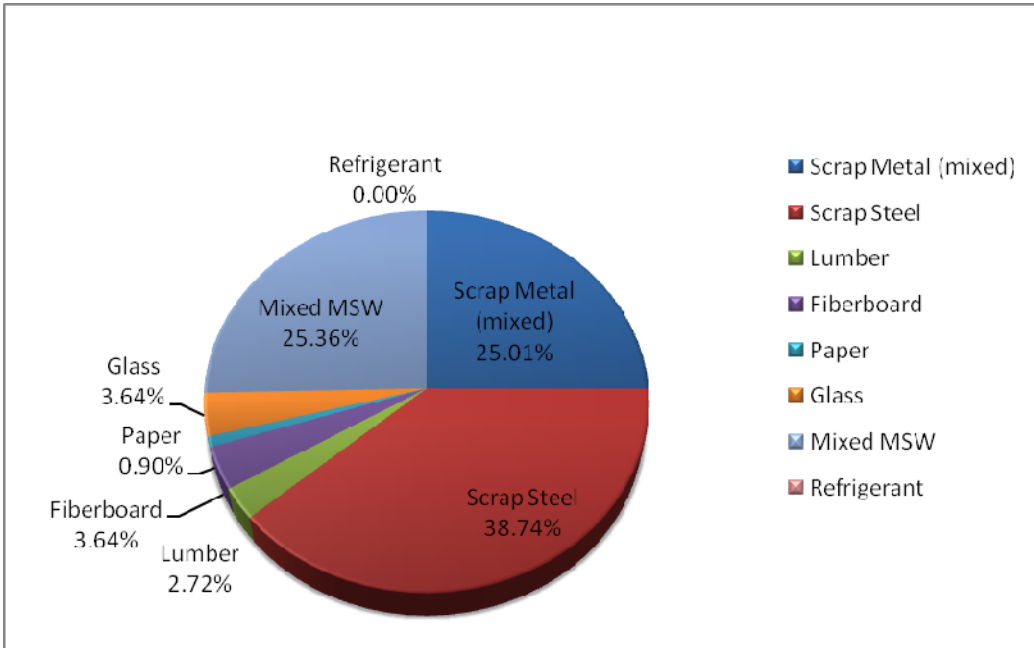


Figure 4a. Percent contribution to total GHG emissions by waste type– N. Las Vegas actual scenario

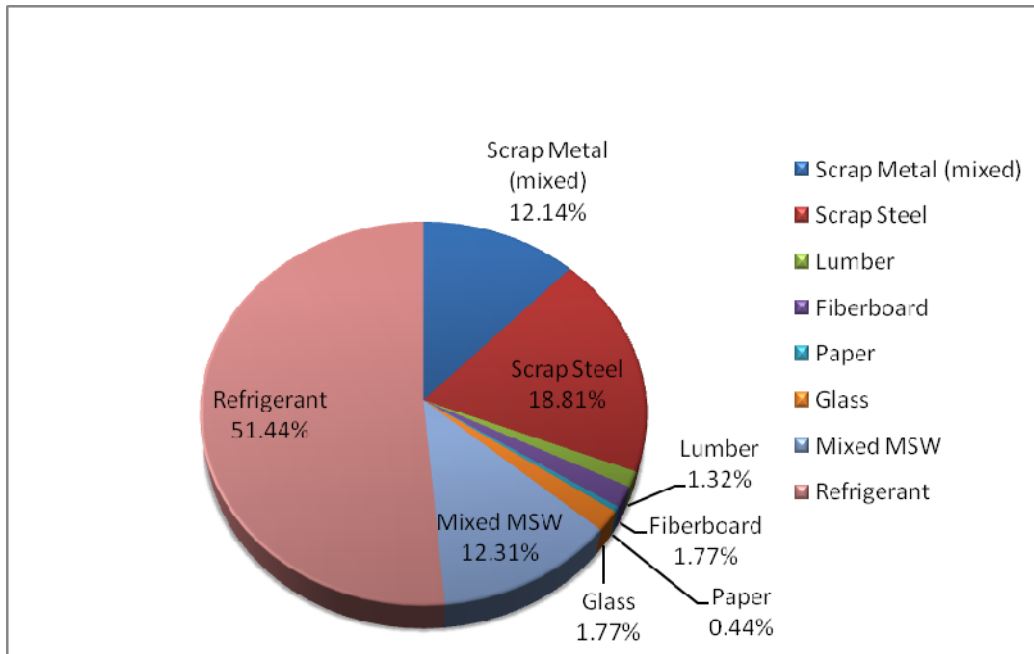


Figure 4b. Percent contribution to total GHG emissions by waste type– N. Las Vegas alternate scenario

GHG emissions under the N. Las Vegas alternate scenario, is dominated by refrigerant (51.4 %) followed by scrap steel (18.8 %), mixed MSW (12.3 %), and scrap metal (12.1 %) (figures 4a and 4b). The significance of the impact of refrigerant recycling was surprising given that it comprises just 0.03 % of the total quantity of demolition debris generated.

4. CONCLUSIONS AND RECOMMENDATIONS

The largest share by far of the total GHG emissions estimates under all scenarios we evaluated was attributable to scope 3 emissions and driven primarily by the embodied energy in the waste generated from demolition activities. This suggests that for decommissioning projects involving demolition activities, a more comprehensive accounting of scope 3 GHG emissions may be warranted under future reporting updates that could be issued in association with EO 13514 mandates and could improve the ability of federal agencies such as the FAA to assess and mitigate the environmental impacts of major initiatives such as NextGen.

The comparison of actual scenarios to an alternate (all demolition debris landfilled) scenario suggests that there are significant opportunities for reducing GHG emissions through reuse and recycling. For many materials such as metals, recycling is commonplace due to market forces or is governed by regulation (e.g., refrigerants). However, we can see from our analysis that the consequences of overlooking such opportunities or requirements can be significant, even for a relatively small amount of material as would have been the case had refrigerants not been recovered at one of our case studies. For other materials, such as concrete and masonry debris, our analysis showed that there are tremendous additional opportunities for reducing GHG emissions through onsite reuse.

The accuracy of our analysis was limited by our reliance on a number of assumptions as discussed above where actual data was not available. However, as a first order approximation to understand the general impacts facility disposition activities could have on GHG emissions in the federal sector and to prepare agencies for more comprehensive GHG emissions accounting mandates that may arise in the future, the results of this study are instructive. For more accurate accounting, it is recommended that agencies maintain logs of onsite fuel consumption (scope 1), meter electrical usage (scope 2), and provide detailed accounting of commuting and business travel (scope 3) during project execution. Since the federal government typically hires contractors to perform demolition work, it is recommended that a GHG emissions analysis be incorporated as a technical evaluation factor when selecting contractors for award. Contractors would ideally provide both their GHG estimate and their calculation

methodology. Fostering competition to minimize GHG emissions would likely help to accelerate the development of new and innovative emissions reduction strategies.

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Part II: Heavy Metals

Chapter 3

NICKEL DERMAL BIOAVAILABILITY IN PIG SKIN INCREASED BY A CHEMICAL MIXTURE: ROLE OF GENDER

Nickel Dermal Bioavailability Increased by a Chemical Mixture

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ABSTRACT

Exposure to chemical mixtures is more common than exposure to a single chemical. Skin is the largest tissue in the human body and is an important route of exposure to chemical mixtures. The aim of this study was to assess the effect of toluene, trichloroethylene (TCE) and phenol on the dermal bioavailability of nickel. All four compounds are prevalent in the environment, at industrial facilities, and at hazardous waste sites. An *in vitro* approach was employed which utilized radiotracer methodology and a modified Teflon flow-through diffusion cell system to measure the amount of chemical which penetrated through or became bound to dermatomed male or female pig skin. In males, there was almost a 2-fold increase in the total cumulative percentage of radioactivity in the receptor fluid after treatment with the mixture compared to nickel alone. In females, significantly more radioactivity (2-fold) penetrated into receptor fluid when skin was treated with the chemical mixture of nickel versus nickel alone. The chemical mixture produced a significant increase in the total penetration and the amount of nickel that became bound to skin relative to nickel alone in both sexes. Also, more radioactivity remained loosely adsorbed to skin and could be easily washed off of

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the skin surface when nickel was applied alone rather than in combination to male or female skin. However, the total penetration and the radioactivity in the skin matrix were significantly higher in females than in males treated with the nickel mixture. This study revealed that the bioavailability of nickel to skin is significantly higher when administered in the chemical mixture compared to nickel alone. Furthermore, females are at greater risk than males from dermal exposure to the nickel mixture.

Keywords: nickel bioavailability, dermal exposure, mixture effects, gender differences

1. INTRODUCTION

Occupational and environmental exposures to chemicals occur more often to mixtures rather than to a single compound (Ogata *et al.*, 1993) Because of its extensive surface area, skin is a major route of exposure to chemical mixtures. When dermal exposure occurs simultaneously to two or more chemicals, the bioavailability of the mixture can be altered relative to that predicted by the separate components of the mixture. In order to accurately assess the human health risks from dermal exposure to chemical mixtures, data on the bioavailability of the mixtures is needed. The purpose of this research was to utilize an *in vitro* approach consisting of Teflon flow-through diffusion cell methodology and radiotracer techniques to determine the effects of a mixture of toluene, TCE and phenol on the *in vitro* dermal bioavailability of nickel. Each of the chemicals in the mixture is prevalent in hazardous waste sites as well as at industrial facilities, and in the environment. Several million workers worldwide are exposed to nickel resulting in excess incidences of cancer of the nasal cavity and the lungs. However, the most frequent health effect from chronic exposure to nickel in humans is allergic contact dermatitis (ATSDR, 1993a). Although the best *in vitro* model for human risk assessment is human skin, the source of human skin is limited and, for comparison purposes, it is difficult to control the gender, race, anatomical site, age and condition of the donor skin. Pig skin, having many morphological and functional characteristics similar to human skin, is considered one of the best animal models for penetration studies and was used in the investigation (Meyer *et al.*, 1978).

2. MATERIALS AND METHODS

2.1 Chemicals

⁶³Nickel chloride, having a specific activity of 12.63 mCi/mg and radiochemical purity of 99.9%, was obtained from E.I. Dupont de Nemours and Co., Inc., New England Nuclear (NEN) Research Products, Boston, MA.

2.2 Animal Model

Whole pig skin was obtained from the costo-abdominal areas of euthanized (40-60 lb) 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). 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).

2.3 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 mounted into Teflon flow-through diffusion cells (Crown Bio Scientific Inc., Clinton, NJ). The exposed skin surface area was 0.64 cm^2 and was maintained at a temperature of 32°C. The dermal side of each skin sample was bathed with HHBSS receptor fluid containing 10% fetal bovine serum (Sigma Chemical Co., St Louis, MO) at a flow rate of 5 ml/h by a multichannel peristaltic cassette pump (Manostat, NY) and aerated continuously with 99.9% oxygen (Collier *et al.* 1989). ⁶³Nickel chloride was administered either individually or in the mixture to the stratum corneum surface of the epidermis in a total volume of 10 μL . The chemical dose of nickel chloride was 100 ng/cm^2 containing 0.92 μCi of radioisotope. The chemical doses of the non-labeled chemicals were 5.8 mg TCE, 3.4 mg toluene, and 6.8 μg phenol/ cm^2 . Perfusate was collected at 15 minute intervals up to 1 h, at 1.5 and 2 h, then at 2 h intervals up to 16 h postdosing.

At the conclusion of the 16 h study, a gentle stream of air was allowed to flow over the skin surface for 1 h. Any of the radioactive compound which volatilized

from the surface could be extracted with hydrochloric acid from charcoal tubes (SKC Inc., Eighty-Four, PA) attached to the upper chambers of the diffusion cells. Unabsorbed chemical was washed off of the skin surface with 1% aqueous soap solution followed by distilled water. Skin samples were completely solubilized in Solvable (NEN) to determine the binding capacity of the skin. Radioactivity was counted in Formula 989 liquid scintillation cocktail (NEN) by a Beckman LS-7500 spectrometer. Sample quench was corrected using the H-ratio method.

2.4 Statistical Analysis

All data were reported as the mean \pm standard error of the mean (SEM). Statistical differences between treatment groups were determined by Student's independent t-test. The level of significance was $p < 0.05$.

3. RESULTS AND DISCUSSION

The cumulative penetration of nickel was used to describe the total amount as percent of initial nickel dose which permeated skin and appeared in receptor fluid within a designated time interval. In males, the total cumulative percentage of radioactivity in receptor fluid at 16 h was increased almost 2-fold in the mixture compared to nickel alone (Table 1).

Table 1. Cumulative penetration of ⁶³nickel alone or in a chemical mixture through male pig skin into receptor fluid

Time (h)	Nickel Alone	Nickel Mixture ^a
0-4	0.1 \pm 0.0 ^b	0.3 \pm 0.1 ^c
0-8	0.2 \pm 0.0	0.5 \pm 0.1 ^c
0-12	0.3 \pm 0.1	0.6 \pm 0.1 ^c
0-16	0.4 \pm 0.1	0.7 \pm 0.1

^a Mixture consists of ⁶³nickel, toluene, TCE and phenol.

^b Values (mean \pm S.E.M.) represent the percentage of the initial dose collected in the receptor fluid at the indicated time, from 12-17 replicates per treatment *in vitro*.

^c Significantly different from nickel alone, t-test ($p < 0.05$).

In females, there was a significant increase in the dermal bioavailability of nickel when exposure occurred in the presence of toluene, TCE and phenol (Table 2). This was supported by the significantly higher cumulative percentage of nickel in a mixture penetrating skin into receptor fluid throughout the study. At the end of the 16 h study, the total cumulative percentage of the nickel mixture was 2-fold higher than nickel alone.

A summary of the amount of nickel-derived radioactivity that penetrated pig skin into receptor fluid as well as the binding capacity of nickel to pig skin is shown in Tables 3 and 4. In males treated with the mixture, significantly more

Table 2. Cumulative penetration of ⁶³nickel alone or in a chemical mixture through female pig skin into receptor fluid

Time (h)	Nickel Alone	Nickel Mixture ^a
0-4	0.1 ± 0.0 ^b	0.3 ± 0.1 ^c
0-8	0.2 ± 0.0	0.6 ± 0.1 ^c
0-12	0.3 ± 0.0	0.8 ± 0.1 ^c
0-16	0.5 ± 0.1	1.0 ± 0.1 ^c

^a Mixture consists of ⁶³nickel, toluene, TCE and phenol.

^b Values (mean ± S.E.M.) represent the percentage of the initial dose collected in the receptor fluid at the indicated time, from 12-16 replicates per treatment *in vitro*.

^c Significantly different from nickel alone, t-test (p < 0.05).

radioactivity remained bound to skin (68.9% of the initial dose) compared to nickel alone (57.6%) (Table 3). The total amount of absorbed nickel that is available for distribution to the body (total penetration) is the sum of the total dose in the receptor fluid and bound to skin. Total penetration of nickel was significantly increased in males when nickel was applied as a mixture to skin (69.5%) versus nickel alone (57.9%). At the same time, significantly less radioactivity was found in the skin wash of the mixture (26.5%) than nickel alone (34.3%).

Table 3. Summary of the penetration of ⁶⁵nickel alone or in a chemical mixture through male pig skin

	Nickel Alone	Nickel Mixture ^a
Receptor Fluid	0.4 ± 0.1 ^b	0.7 ± 0.1 ^c
Skin Digest	57.6 ± 2.2	68.9 ± 3.6 ^c
Total Penetration	57.9 ± 2.2	69.5 ± 3.6 ^c
Skin Wash	34.3 ± 2.0	26.5 ± 3.4 ^c

^a Mixture consists of ⁶⁵nickel, toluene, TCE and phenol.

^b Values (mean ± S.E.M.) represent the percentage of the initial dose recovered at the end of the 16 h study (n = 12-17 replicates per treatment) *in vitro*. Total penetration is the sum of radioactivity in the receptor fluid and bound to skin. There was no volatilization from the skin surface.

^c Significantly different from nickel alone, t-test (p < 0.05).

Similar results were observed in females (Table 4). The amount of radioactivity bound to skin after treatment with the nickel mixture (79.3% of the initial dose) and the total penetration (80%) were significantly higher than nickel by itself (57.7% and 58.1%, respectively). Females also showed a significant decrease in radioactivity when skin was washed with soap and water after treatment with the mixture (26.3%) versus nickel alone (41.5%).

Table 4. Summary of the penetration of ⁶³nickel alone or in a chemical mixture through female pig skin

	Nickel Alone	Nickel Mixture ^a
Receptor Fluid	0.5 ± 0.1 ^b	1.0 ± 0.1 ^c
Skin Digest	57.7 ± 2.3	79.3 ± 2.9 ^c
Total Penetration	58.1 ± 2.3	80.0 ± 2.8 ^c
Skin Wash	41.5 ± 2.2	26.3 ± 2.4 ^c

^a Mixture consists of ⁶³nickel, toluene, TCE and phenol.

^b Values (mean ± S.E.M.) represent the percentage of the initial dose recovered at the end of the 16 h study (n = 12-16 replicates per treatment) *in vitro*. Total penetration is the sum of radioactivity in the receptor fluid and bound to skin. There was no volatilization from the skin surface.

^c Significantly different from nickel alone, t-test (p < 0.05).

When a comparison was made between males and females to assess the penetration of nickel from the mixture, the total penetration of radioactivity and the amount bound to the skin matrix were significantly higher in females than in males (Table 5).

Table 5. Comparison of the penetration of ⁶³nickel in a chemical mixture through male and female pig skin ^a

	Male	Female
Receptor Fluid	0.7 ± 0.1 ^b	1.0 ± 0.1
Skin Digest	68.9 ± 3.6	79.3 ± 2.9 ^c
Total Penetration	69.5 ± 3.6	80.0 ± 2.6 ^c
Skin Wash	26.5 ± 3.4	26.3 ± 2.3

^a Mixture consists of ⁶³nickel, toluene, TCE and phenol.

^b Values (mean ± S.E.M.) represent the percentage of the initial dose collected in the receptor fluid at the indicated time, from 12-17 or 12-16 replicates per treatment *in vitro*, for males and females, respectively.

^c Significantly different from male, t-test (p < 0.05).

4. CONCLUSIONS

This study demonstrates that ionic nickel binds to and can penetrate pig skin, as has been shown previously in human skin (Larese *et al.*, 2007). These results support the dermal bioavailability of nickel and are consistent with the metal's ability to produce allergic contact dermatitis, a serious health hazard resulting from the exposure to nickel in the environment due to pollution, in the workplace, and during daily contact with items such as coins, jewelry, and stainless steel products (Gazel, *et al.*, 2008). Moreover, the effect of the phenol-toluene-TCE mixture was to significantly increase the dermal penetration as well as skin binding of nickel in both male and female skin. This finding supports increased

nickel bioavailability resulting from dermal exposure to the mixture and, thus, increased health risk particularly in females whose results were significantly higher than males.

The protein denaturing action of phenol together with the defatting action of toluene and TCE (Roberts *et al.*, 1977, ATSDR, 1992, ATSDR, 1993b) on skin may be contributing factors to increased penetration of nickel in the mixture. Alterations in skin integrity induced by the chemical mixture in this study are consistent with increased penetration of nickel in human skin that had been physically abraded (Larese-Filon, F, *et al.*, 2009). These findings underscore the need for workers exposed to nickel under similar mixture conditions to use protective clothing, such as gloves.

The gender differences revealed in this study are the first to be reported for nickel. The mechanisms by which these differences arise are not completely understood. However, a previous *in vitro* study in our laboratory (McCormick and Abdel-Rahman, 1991) showed similar results, with TCE dermal penetration greater in the skin of female than male rats. The maintenance of skin moisture and thickness and enhancement of keratinocyte proliferation by estrogen (Kanda and Watanabe, 2005) may also play a role in greater nickel penetration and binding in females. Further studies are required to explore these possibilities.

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PART III: PCBs

Chapter 4

RELATIONSHIP BETWEEN SEDIMENT MORPHOLOGY AND PCB CONTAMINATION IN THE ACUSHNET RIVER, NEW BEDFORD, MASSACHUSETTS

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ABSTRACT

The New Bedford Harbor Superfund Site in southeastern Massachusetts includes the shallow northern reaches of the Acushnet River estuary through the commercial port of New Bedford and adjacent areas of Buzzards Bay. The sediments in the harbor are contaminated with high levels of polychlorinated biphenyls (PCBs) and heavy metals from the industrial development surrounding the harbor. From the 1940s through the 1970s, electrical capacitor manufacturing plants discharged PCBs into New Bedford Harbor and its estuaries. In the mid-1970s US Environmental Protection Agency (EPA) sampling identified PCBs in the river and harbor sediments greater than 100,000 mg/kg. In 1979, the Massachusetts Department of Public Health prohibited fishing and shell-fishing from the river and harbor due to the high levels of PCB contamination found in the harbor and in the seafood from the area. The site was included on the National Priorities List (NPL) in September 1983 as one of the most contaminated PCB sites in the United States. In September 1998, after years of study and public debate, EPA selected a cleanup remedy that involved the dredging and containment of approximately 170 acres of PCB-contaminated sediment. The principal goals of the project were the reduction in health risks from consumption of PCB-contaminated local seafood and from exposure to contaminated shoreline sediments, and the improvement of water quality in the marine ecosystem. The

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prescribed PCB cleanup standards for the sediment ranged from 1 mg/kg in shoreline areas immediately adjacent to residential properties up to 50 mg/kg in sediment in remote salt marshes not readily accessible to the public. Removal of sediments to achieve the cleanup standards requires mechanical or hydraulic dredging of more than 800,000 cubic yards of material. Correlation of analytical data and sediment cores shows a relationship between the presence of PCB contamination and distribution of the organic layer in the river. This relationship exists because of the chemical nature of PCBs and their affinity for partitioning into organic material. Sediment cores have been collected to define and refine the modeled sediment removal maps and determine target depths for dredging.

Keywords: compliance depth, Z^* , polychlorinated biphenyls, soil morphology, organic matter, partitioning, precision dredging

1. INTRODUCTION

Previous studies at the New Bedford Harbor Superfund Site have found the OL (organic-low plasticity)/non-OL interface to be the same as the boundary of polychlorinated biphenyl (PCB) contamination and have used this interface in the development of site remediation limits (Foster Wheeler, 2002). The site remediation limits in the context of dredging are referred to as the compliance depth, and have been given the name Z^* . The Z^* value is assigned to every 25-foot-by-25-foot block in the remediation area and is the depth below the mud line where the sediment PCB levels are below the specified target clean-up level.

Prior to dredging a particular section of the remediation area called a Dredge Management Unit (DMU), dredge plans are produced using information from the Z^* database and pre-dredge cores. The information from the Z^* database and pre-dredge cores include target elevations based on field observations and geostatistical modeling results. Pre-dredge cores are used to refine the Z^* depths using the visually observed OL/non-OL interface. Post-dredge cores in some dredged areas have shown OL existing below the Z^* depth which indicates that Z^* is no longer an accurate compliance depth, either due to inaccuracies in the initial development of Z^* or due to the redistribution of sediment from the tidal and flow movement of the river that has naturally occurred since the development of Z^* . Dredging to a Z^* depth that is no longer accurate has resulted in over-dredging or under-dredging which necessitates re-mobilization and re-dredging in some DMUs to remove remaining contaminated sediment.

The purpose of this investigation was to confirm that the sediment morphology collected in “real-time” ahead of the dredge provides a more precise

dredging strategy. Precision dredging further refines the dredge plans and guides the dredge operation to completely remove the contaminated material while the dredge is in place, maximizes the removal of PCBs in the DMUs, and eliminates the need for improper set-up of the dredge areas or re-positioning the dredge either in the current dredge season or in subsequent dredge seasons. Hydraulic dredging in New Bedford Harbor consists of establishing a perimeter of sheet piles around the dredge area, extending cables between the sheet piles to which the hydraulic dredge is winched, measuring the sediment-water interface during dredging, and adjusting the cutter head during the dredging process. These steps are time-consuming, and accurate characterization of contaminated sediment is crucial to cost-effective remediation.

This study examined the relationship between PCB concentration and Unified Soil Classification System (USCS) (ASTM, 1985) soil classification and looked at the following relationships:

- PCB concentration and USCS soil classification
- PCB concentration and soil color
- PCB concentration and soil consistence

This investigation applied these relationships to sediment cores taken during the 2010 dredging season and implemented precision dredging in the five DMUs that were active during the season.

2. SITE SETTING

The New Bedford Harbor Superfund Site in southeastern Massachusetts includes the shallow northern reaches of the Acushnet River estuary south through the commercial port of New Bedford (Figure 1) and adjacent areas of Buzzards Bay. The sediments in the Harbor are contaminated with high levels of PCBs and heavy metals from the industrial development surrounding the Harbor. From the 1940s through the 1970s, electrical capacitor manufacturing plants discharged PCB waste into New Bedford Harbor both directly and indirectly via New Bedford's sewerage system.



Figure 1. Aerial View of New Bedford Harbor, Facing South.

In the mid-1970s, U.S. Environmental Protection Agency (EPA) investigations identified PCBs in both the Harbor sediments and the seafood harvested from the New Bedford area. In 1979, the Massachusetts Department of Public Health prohibited fishing and lobstering from the Harbor due to extremely high levels of PCB contamination, which were found to be greater than 100,000 mg/kg in parts of the Upper Harbor. The site was included on the Superfund National Priorities List (NPL) in September 1983 as one of the most contaminated PCB sites in the United States.

The three areas of the site – Upper, Lower, and Outer Harbor – have been divided based on geographical features and levels of contamination (Figure 2). Remedial action efforts have initially focused on the most contaminated Upper Harbor area.

In September 1998, after years of study and public debate, EPA selected a cleanup remedy that involved the dredging and containment of approximately 170 acres of PCB contaminated sediment. The principal goals of the project were the reduction in health risks from consumption of PCB-contaminated local seafood and from exposure to contaminated shoreline sediments, and the improvement of water quality in the marine ecosystem in the Harbor.

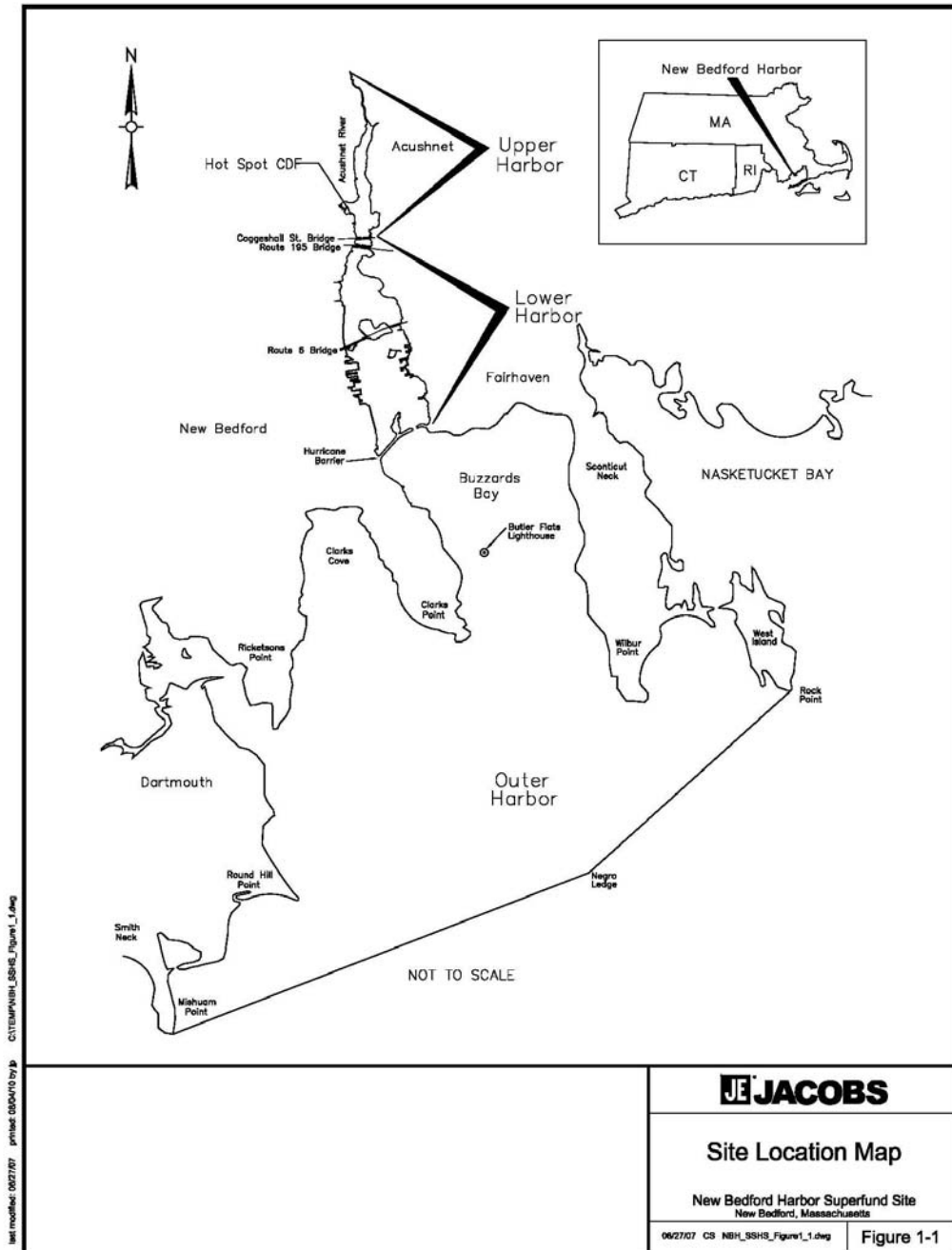


Figure 2. New Bedford Harbor Superfund Site Location Map.

The prescribed PCB cleanup standards for the sediment were 1 mg/kg in shoreline areas immediately adjacent to residential properties, 25 mg/kg in marsh areas subject to beach-combing activities, 10 mg/kg shoreline to shoreline (subtidal area) in the Upper Harbor with the exception of beneficial salt marsh and wetland areas, and 50 mg/kg both in remote salt marshes not readily accessible to the public and in the subtidal areas of the Lower Harbor.

Removal of sediment to achieve the cleanup standards requires mechanical or hydraulic dredging (Figure 3) of more than 800,000 cubic yards of material. As of September 2010, approximately 185,000 cubic yards of sediment/material has been removed.



Figure 3. Dredging New Bedford Harbor.

3. BACKGROUND

The New Bedford Superfund project team used sediment morphology as a means of defining the extent of PCB-contaminated sediment in the Harbor. Sediment likely containing higher concentrations of PCBs is distinctive compared to the underlying, clean sediment. In general, the contaminated sediment is darker,

looser, and more organic than the underlying sediment, which is lighter in color, more consolidated, and lower in organic matter content. By identifying the sediments that met these characteristics, the New Bedford Harbor Superfund project team was able to more precisely identify the contaminated sediment with reduced analytical costs, develop Z^* , and focus its dredging efforts.

Correlation of analytical data and sediment cores shows a relationship between the presence of PCB contamination and distribution of the OL in the Harbor sediment. The differences between the organic horizon and the underlying mineral horizons are very distinctive. The OL horizon is generally dark (5Y 2.5/1 – [black]), has a loose consistence, and has visible organic fibers in the matrix. The underlying horizons (ML/CL) are generally coarser, have a friable to firm consistence, and a lighter color (5Y 4/3 – [olive]). In the desanding facility, this distinction between horizons is recognized by increased sand content on the separator, which indicates that dredging depths have been exceeded. This information is then communicated to the dredge operator from the desanding facility. Sediment cores taken ahead of the dredge lanes help to refine the location of the OL and provide a guide to the dredge operator to avoid over-dredging (Figure 4).

Organic matter affects the morphology of a soil or sediment matrix and the upper sediments in New Bedford Harbor contain significant amounts of organic matter. This organic matter originates from plant material within and outside the Harbor as well as organisms residing within the harbor that settle to the bottom as organic detritus. The accumulation of organic matter or humus tends to give the matrix dark brown to black colors. Granulation and stability of soil aggregates are enhanced because the organics can coat the soil or mineral particles, isolate them from the matrix and, in turn, increase the relative porosity within the matrix. Clayey soils or sediments show reduced plasticity, cohesion, and stickiness with the addition of organic matter. Water retention is increased and thereby addition of organic matter content can increase both infiltration rate and water-holding capacity. Because the organic fraction of a soil has a higher cation exchange capacity than the mineral fraction, soils with high organic matter retain and make available nutrient cations (potassium, calcium, magnesium, etc.). This effect also allows the organic fraction to immobilize and retain heavy metals such as cadmium and lead. Also, nutrients such as nitrogen, phosphorus, and sulfur are stored as constituents in organic matter until released by mineralization (Brady and Weil, 1996).



Figure 4. Collecting a Sediment Core from New Bedford Harbor.

PCBs are man-made organic compounds that are not found in the natural environment prior to the 1900s. PCBs are chlorinated oils that have a low degree of reactivity, are not flammable, have high electrical resistance, and are stable when exposed to heat. PCBs are well suited for use in dielectric fluids, insulators for transformers and capacitors. Because of these properties, PCBs are difficult to break down in the natural environment. The basic structure of a PCB consists of two aromatic rings with a carbon-to-carbon bond. PCBs vary by the number of chlorines substituted in the available sites around the aromatic rings (209 possible combinations) (Barbalace, 2003). Because of the non-polar nature of PCBs, they tend to partition into non-polar materials (Poerschmann et al., 2000; Xing and Pignatello, 1997). Organic matter provides a suitable medium for this partitioning, and PCBs are generally found in the natural environment in association with soil or sediment media with high organic matter contents (Chiou et al., 1983, 1986; Boyd and Sun, 1990; Castro and Vale, 1995; Brannon et al., 1998; Schorer, 1999; Jönsson and Carman, 2000; Durjava et al., 2007; Fairey et al., 2010).

This investigation was developed to identify the morphological characteristics of New Bedford Harbor sediments containing high contents of organic matter.

These properties include the color, consistence, and classification of the sediment as a means of identifying sediments with variable organic matter contents. In addition, the PCB concentrations in these sediments are used to show that morphological properties of the sediment can be used to identify those with a high affinity for partitioning of PCBs.

4. METHODS AND MATERIALS

Three field events were used for this investigation. These investigations included sampling of sediments in New Bedford Harbor with detailed descriptions of the sediment column and analysis of total PCBs. Studies used in the analysis included 43 samples collected by Battelle in 2005 (Battelle, 2007), 12 samples collected by Jacobs in 2009 (Jacobs, 2010), and 49 samples collected by Woods Hole Group in 2009 (Woods Hole Group, 2010). Because of variability in PCB concentration in the Harbor, particularly in the near-shore areas, the samples used in this investigation were collected in areas where PCB concentrations were known to be elevated. All samples were classified according the Unified Soil Classification System (ASTM, 1985). The soils were described according to color, texture, consistence, amount of coarse fragments, and other observations (such as odors or sheen). Total PCBs were analyzed for each sample using EPA method SW8082 (EPA, 2007).

The PCB concentrations in the New Bedford Harbor sediments were analyzed using a One-Way Analysis of Variance (ANOVA) procedure. Categories included color, consistence, and soil type. Each of the categories was divided into two groups. For color, those that were considered “black” (ranging from 2.5Y 2.5/1 [black] to 5Y 2.5/1 [black] on *Munsell Soil Color Charts* [Munsell Color, 1994]) were placed into one group and those considered “gray” (ranging from 2.5Y 3/1 [very dark gray] to 5Y 3/2 [dark olive gray] were placed into a second group. For consistence, any description of loose or soft was placed into one group, and any description that stated consolidated, firm, or stiff was placed into the second category. For the soil type, any USCS classification that was considered “organic” (OL or OH [organic – high plasticity]) was placed in one category and all other mineral horizons (ranging from CL [lean clay] to SP [poorly-graded sand]) were placed in the second category. The ANOVA test was performed to determine if the two groups in each category were different at the $\alpha = 0.05$ significance level. If the results were significant, it was then determined that each group represented two different populations.

5. RESULTS

There was generally good agreement between high PCB concentrations and sediment morphology based on organic matter content. A comparison of mean PCB concentrations between the different groups shows that there is evidence of PCB partitioning into the organic fraction of the sediments in New Bedford Harbor. The matrix in which the PCBs are partitioned is distinguished by its morphological properties.

5.1 Soil Type

Soil type (USCS classification) was an adequate predictor of sediments with high PCB concentrations. Sediment that was defined as organic had a mean PCB concentration of 725 mg/kg in comparison to all other soil types (mean of 39.3 mg/kg) (Table 1). Figure 5 shows that there is a visual difference in the means and the medians, however, the ANOVA (Table 2) had an F-ratio probability of 0.058, which is not significant at the $\alpha = 0.05$ probability level. This is likely due to some classification errors based on a subjective assessment of soil type. The maximum PCB concentration in the non-organic soil category is 780 mg/kg whereas the median value is 2.63, indicating that the mean may be influenced by outliers due to misclassification. The three highest values of the non-organic material were 780, 680, and 134 mg/kg with a 95 percent confidence interval of 6.76 to 71.9 mg/kg, showing that some outliers may be impacting the results of the ANOVA. A non-parametric Wilcoxon Rank-Sum Test for soil type shows that the median values (182 mg/kg-OL, 2.63 mg/kg-ML) were significantly different. In general, there is relatively good agreement with identification of OL soil type and elevated concentration of PCBs.

5.2 Color

Sediment color was the best indicator of high PCB concentrations with the darker colors exhibiting higher concentrations. The sediments identified as “black” had a mean PCB concentration of 306 mg/kg compared to those of a “gray” or “olive gray” color (54.0 mg/kg) (Table 1 and Figure 6). The ANOVA shows that these two means are significantly different at the $\alpha = 0.05$ probability level (Table 2). Therefore, color is a good predictor of high PCB concentrations in sediments.

Table 1. New Bedford Harbor Sediment Descriptive Statistics for PCB Concentrations.

Soil Type					
Source	n	Mean (mg/kg)	Median (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)
OL	40	725	182	3.62	18200
ML	64	39.3	2.63	ND	780
Soil Color					
Source	n	Mean (mg/kg)	Median (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)
black	18	306	215	5.36	2150
gray	41	54.0	8.2	ND	780
Soil Consistence					
Source	n	Mean (mg/kg)	Median (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)
loose	26	220	89.0	1.42	2150
firm	34	54.8	2.46	ND	780

mg/kg = milligrams per kilogram

n = number of observations

ND = nondetect

Table 2. Analysis of Variance of New Bedford Harbor Sediments.

Soil Type					
Source Term	df	Sum of Squares	Mean Square	F-Ratio	Probability Level
Model	1	1.16E+07	1.16E+07	3.68	0.058
Error	102	3.21E+08	3.14E+06		
Total (Adjusted)	103	3.32E+08			
Total	104				
Soil Color					
Source Term	df	Sum of Squares	Mean Square	F-Ratio	Probability Level
Model	1	7.92E+05	7.92E+05	9.16	0.0037
Error	57	4.93E+06	8.65E+04		
Total (Adjusted)	58	5.72E+06			
Total	59				
Soil Consistence					
Source Term	df	Sum of Squares	Mean Square	F-Ratio	Probability Level
Model	1	4.04E+05	4.04E+05	4.37	0.0409
Error	58	5.35E+06	9.23E+04		
Total (Adjusted)	59	5.76E+06			
Total	60				

df = degrees of freedom

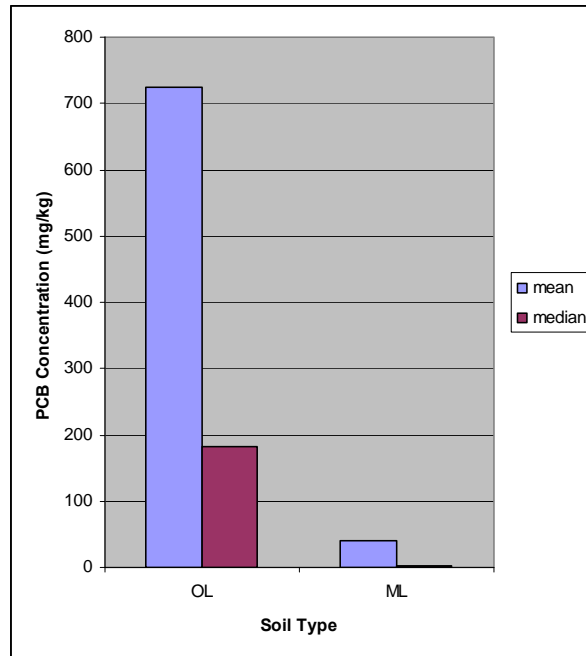


Figure 5. Mean and Median of PCB Concentrations in Sediment Classification Groups for New Bedford Harbor Sediments.

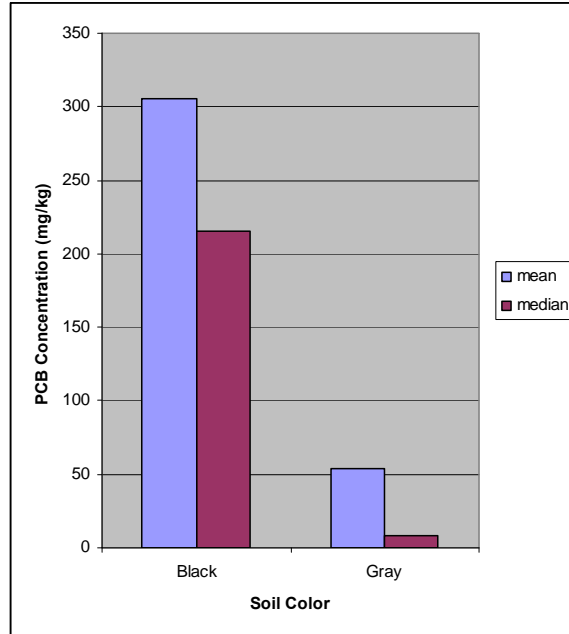


Figure 6. Mean and Median of PCB Concentrations in Sediment Color Groups for New Bedford Harbor Sediments.

5.3 Consistence

Sediment consistence was also a reliable indicator of high PCB concentration. Sediments that were described as “loose” or “soft” had a mean PCB concentration of 220 mg/kg whereas sediments described as “firm” or “stiff” had a mean PCB concentration of 54.8 mg/kg. (Table 1 and Figure 6). An ANOVA on these data show that the means of these two groups are significantly different at the $\alpha = 0.05$ probability level (Table 2). Therefore, consistence can be used to predict high concentrations of PCBs in New Bedford Harbor sediments.

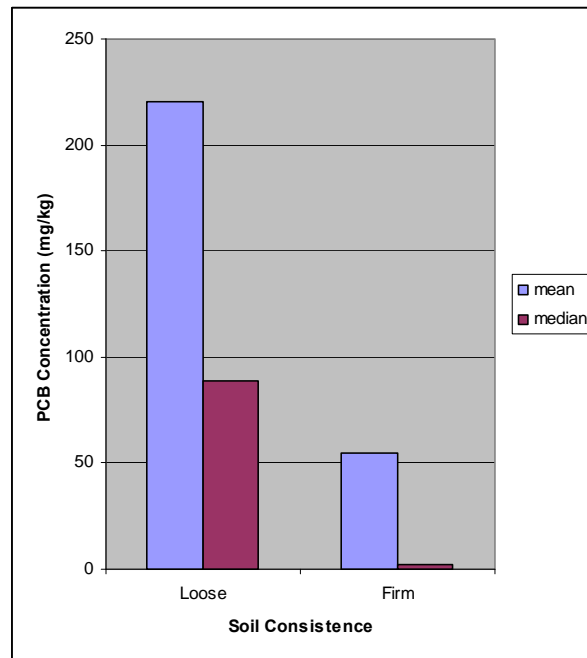


Figure 7. Mean and Median PCB Concentrations for Sediment Consistence Groups for New Bedford Harbor Sediments.

6. DISCUSSION

PCB-contaminated sediments in New Bedford Harbor comprise more than 800,000 cubic yards that require remediation (less 185,000 cubic yards removed by September 2010). The costs for dredging, processing, and transporting these sediments for disposal are significant. Therefore, finding a method that differentiates the contaminated sediment from the uncontaminated sediment is crucial to managing effort and maintaining costs throughout the execution of the project. For New Bedford Harbor, the morphological differences are distinct.

The PCB-bearing sediments are darker, looser, and in some cases, finer than the underlying clean sediment.

Mapping these sediments has been a critical part of managing PCB-contaminated deposits. Prior to commencing dredging each year, the areas for dredging are identified based on the previous years' progress, the PCB concentrations in remaining DMUs, and estimated volume of material to be dredged. The site remediation limits start with the modeled Z^* value. The Z^* value was assigned to every 25-foot-by-25-foot block in the remediation area (Figure 8) and defines the modeled depth below the mud line where the sediment PCB levels are supposed to be below the specified target clean-up level for a given area (Foster Wheeler, 2002).

Techniques such as coring and bathymetric surveys have been used to refine the compliance depth in the planning stages. An example of using coring to refine the compliance depth would be if the Z^* depth was 2 feet, but pre-dredge core analytical results indicated PCBs greater than the target clean-up level at 2.5 feet; thus, the Z^* would be increased. Visual interpretations of the pre-dredge cores were generally not used to refine Z^* . Core analytical results were a reliable but costly way to determine whether Z^* needed refinement. Therefore, cores were taken and analyzed in only select areas of the DMUs. An example of using bathymetric surveys to refine the compliance depth would be examining a pre-dredge bathymetric survey for drastic changes in sediment contours, interpreting whether the contours indicated recent deposition or removal of sediment, and applying that addition or absence of sediment to the original Z^* .

Prior to the 2010 dredging season, the final dredge plan was generated using Z^* , core analytical results, and bathymetric survey results, and was not modified once the dredge season started. In 2010, real-time cores were collected ahead of the dredge using a piston interface corer. Visual interpretations of the cores were used to verify or modify the compliance depth. The statistical analysis of this study supports the use of visual interpretations for refinement of the dredge plans. For each core collected, the visually-observed OL/non-OL interface depth was compared to the Z^* in the dredge plan. As a result, the dredge plan could be modified throughout the dredge season.

After the 2010 dredge season, post-dredge cores will be collected. Those results will indicate whether the real-time cores and modified dredge plans were beneficial in precision dredging of the DMU.

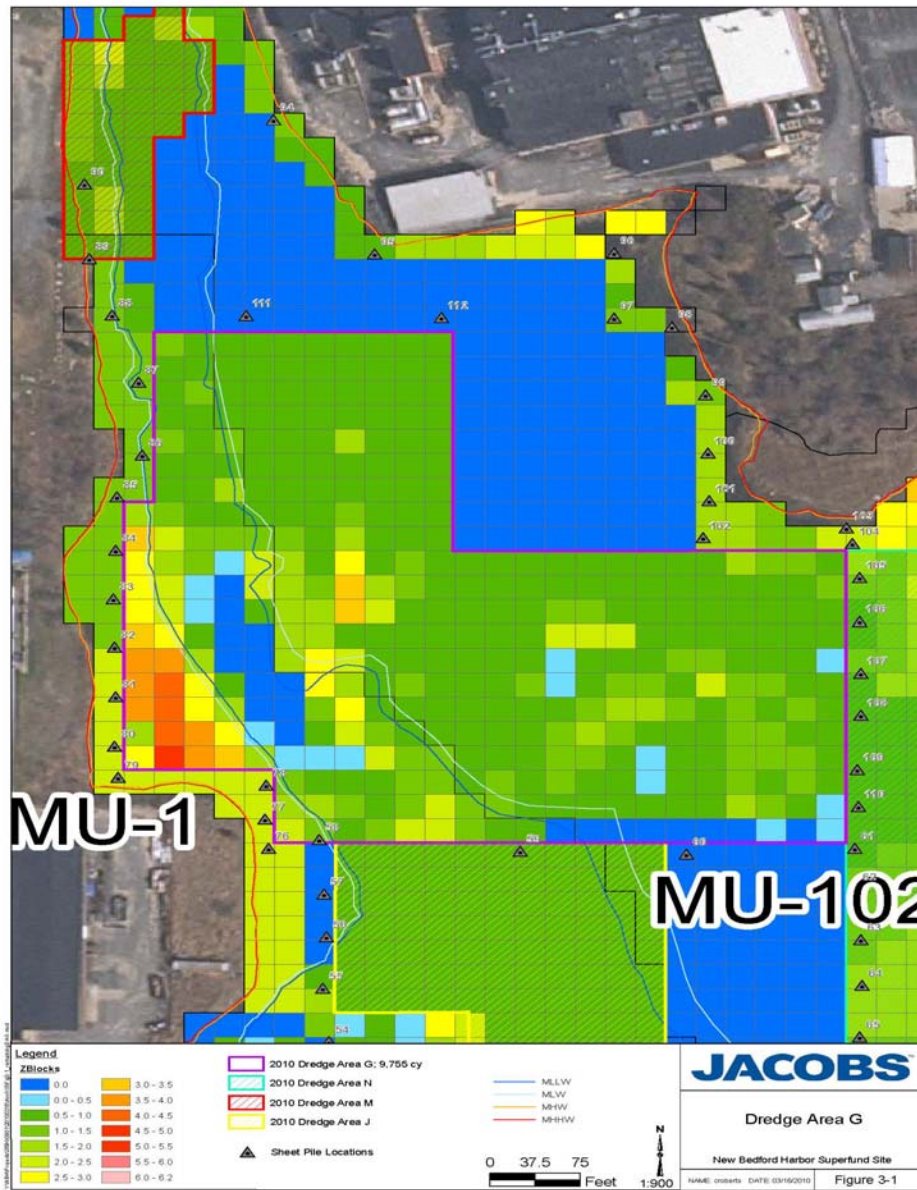


Figure 8. Example Dredge Plan.

In terms of the three criteria examined in this investigation, soil type, color, and consistence all were effective at distinguishing the high PCB concentration sediments from the low. Based on probabilities, the rankings of effectiveness for these criteria are, in order, color, consistence, and soil type. The color of the sediment was determined by *Munsell Soil Color Charts* (Munsell Color, 1994) and provided a consistent measure among investigators. The soil type, as

determined in the field, is the most subjective and least effective of the three criteria. This would indicate that there is significant investigator variability distinguishing these characteristics in the field.

7. CONCLUSIONS

Three criteria – soil type, color, and consistence – provided a reliable field measure for predicting the occurrence of sediments with high PCB concentrations. The more contaminated sediment had black colors, loose or soft consistence, and organic soil types. The partitioning of the non-polar PCB molecules into the non-polar portions of the organic matrix is the likely cause for this distinction. Sediments with lower PCB concentrations were lighter in color, more firm in consistence, and classified as a mineral soil (ML, CL). The lack of organic matter in these lower sediments (that generally underlie the upper OL sediments) is the most likely reason PCB concentrations are lower in these sediments.

The investigation and characterization of these sediment criteria have provided a tool for helping with cost-effective management of dredge areas. Using sediment cores in a dredge area, the remediation team can enhance the precision of dredging by refining Z^* and dredge plans. By identifying the high PCB concentration sediment and focusing on dredging only to those depths where high organic matter sediment occurs, the dredging operation can more precisely focus on the contaminated sediment. This, in turn, helps reduce costs that would be incurred from under- or over-dredging. These costs include time of dredging, separation of sand and oversize, added weight in shipment of filter cake to the disposal site, and remobilization. The use of precision dredging can help maximize the efficiency by dredging only those areas that are truly contaminated.

8. ACKNOWLEDGMENTS

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Chapter 5

PCBS IN BUILDING CAULK: HEALTH HAZARD OR REGULATORY OVERREACTION?

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ABSTRACT

Growing public concern about the past use of polychlorinated biphenyl (PCB) containing building caulk in schools has prompted expensive caulk removal projects at a time of limited public resources. Building caulk, used during construction to fill narrow gaps around windows and door frames, was often formulated with PCBs to increase its plasticity and durability. This PCB use was banned in 1978, but even three or more decades later, schools with PCB containing caulk may still have detectable levels of PCBs in indoor air. The USEPA (2010a) has expressed concern that the inhalation of these airborne PCBs may be a significant exposure pathway for children.

Despite their presence in buildings for more than 30 years, there have been no reported adverse health effects attributable to PCBs in building caulk or other building materials. Health concerns about PCBs in schools are based on results of risk assessment models that rely on toxicity factors derived from animal studies. The USEPA has opted to use animal studies for estimating PCB risk to people even though there is abundant evidence that PCBs are significantly less toxic to people than they are to animal test species. PCB numerical risk modeling for schools appears to be an instance where there has been a significant overestimation of the actual risk posed to children.

There is a considerable body of human health data derived from occupational and non-occupational settings that supports the view that human PCB toxicity is not accurately represented by the USEPA toxicity factors, particularly the cancer slope factors. This article explores human PCB toxicity by reviewing three lines of scientific evidence: 1) a closer look at the actual causes of the Yusho and Yu-Cheng rice oil poisonings; 2) a comparison of the human health effects from

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PCBs to those caused by three other common environmental contaminants; and 3) a brief review of the arguments used to support the claim of PCB carcinogenicity.

If PCBs are significantly less toxic than represented by the USEPA cancer slope factor, then expensive efforts to remove building caulk and other PCB containing materials from schools may provide no health benefit. At a time of contracting school system budgets, avoiding unnecessary expenses is an obvious priority.

Keywords: PCBs, building caulk, schools

1. INTRODUCTION

There has been growing attention to the past use of PCBs (polychlorinated biphenyls) in building materials (Herrick et al., 2004; MIT, 2007; and MADPH, 2009). Prior to 1978, PCBs were often used as an ingredient in paints, caulks and adhesives to impart plasticity and extend the anticipated useful life of the materials. Analytical laboratory chemists (ConTest, 2010) have reported they can often identify whether a sample of building caulk contains PCBs based on whether it is soft and pliable; if so, it likely contains PCBs. A caulk sample that is brittle and dry is less likely to contain PCBs. Despite concerns about their health effects, PCBs remain faithful to their original function.

In 1978, the USEPA promulgated new regulations (40 CFR 761) banning the continued use of PCBs in many products, including building materials. As described in the introduction to the regulations, EPA scientists understood that PCBs had been used in building materials; but the agency chose not to focus further regulatory attention on this issue. Instead, EPA focused their regulatory efforts on: 1) stopping the production and continued distribution of PCBs in commerce; and 2) taking steps to identify and regulate the remaining stock of liquid PCBs. Then, as now, the bulk of liquid PCBs are found in electrical equipment such as transformers and capacitors. EPA identified the greatest risks as those arising from the mismanagement of liquid PCBs, particularly in electrical equipment.

By the early 1990s, environmental scientists were publishing accounts of PCBs being detected in indoor air, with much this early work taking place in Germany (Benthe et al., 1992; Balfanz et al., 1993). Since PCBs are a mixture of chemicals with similar structure, there is no single indicator parameter that accurately communicates their degree of volatility. There are however significant trends: overall PCBs have low volatility and the lower chlorinated species, or congeners, are considerably more volatile than the higher chlorinated congeners (Foreman and Bidleman, 1985). Although their vapor pressure is quite low, it was shown that low concentrations of PCBs could volatilize out of building materials

and into indoor air. A survey article on the state of PCB testing in indoor air appears in Spengler et al.'s 2000 Indoor Air Quality Handbook.

In the ten years since 2000, there have been increasing reports of PCBs in building materials and indoor air, particularly in schools (Daley, 2009; Egbert, 2008). It is likely that PCBs are being found in schools with a high frequency because investigators have focused more effort looking for them there. At this time there is no reason to suppose that PCBs occur with greater frequency in schools than they do in other buildings.

To date there have been no studies linking the presence of building material derived PCBs to actual adverse human health effects. Concerns about possible health effects arise from numerical models that use as inputs values for PCB concentration, exposure assumptions and toxicity factors to predict carcinogenic risk. As discussed in the present article, this approach to PCB risk prediction is problematic and prone to overestimating actual risk. The primary sources of modeling error are: 1) the presumption that the congener mixture present in indoor air is of similar chemical make-up as the one used to derive the cancer slope factors (Prignamo et al., 2006); and 2) that humans respond physiologically to PCBs in a manner similar to the test species (rats) used to derive the cancer slope factors (Johnson, 2006).

It is the thesis of this article that numerical risk assessment, as used to characterize cancer risk to people from PCB exposures to indoor air, significantly overestimates that risk. The extent of the overestimation is so large that it prompts the misallocation of resources towards unnecessary remedial action.

2. MATERIALS AND PROCEDURE

It is a fundamental tenet of toxicology (Menzel and Smolko, 1984) that the data used to predict toxic effects in a species of interest should be developed using a test species that is as biochemically and physiologically close to the species of interest as possible. Humans are most often the species of interest and it is usually unethical to use humans as the test species in toxicological studies. However, in the case of PCBs, there are tens of thousands of well documented human exposures described in the literature that often include thorough long term medical follow-up (Swanson et al., 1995). This human data is from occupational and environmental exposures. This human data should be of obvious importance in evaluating possible human health effects.

To assess carcinogenic risk from PCBs, the typically requires the use of the IRIS web site as the source for cancer slope factors (USEPA, 2010b). The IRIS database includes a presentation on carcinogenicity that discusses a few studies

involving human exposures, but concludes that the results of these studies are “inconclusive” and “inadequate”. IRIS therefore relies entirely on the results of animal studies that use rats as the basis for deriving cancer slope factors. IRIS does not explain that the liver tumors seen in rats following exposure to PCBs do not have human physiological counterparts. The rat liver (and rodent hepatic system more generally) is physiologically different from the human (and primate) liver (Johnson, 2006), and rats appear to be more susceptible to PCB toxicity than are humans.

This article considers three lines of human based toxicological evidence that support the thesis that PCBs are less toxic than is represented in the IRIS database. The first line of evidence is from a re-examination of the Yusho and Yu-Cheng rice oil poisonings; the second line of evidence is a comparison of the known toxic effects of PCBs to those arising from asbestos, lead and radon; and the third line of evidence is to review the human data for indications of whether exposures to PCBs have resulted in human cancers.

3. INFORMATION AND DISCUSSION

The information presented in this section is divided into three subsections, each representing a line of human evidence concerning the toxicity of PCBs.

3.1 Yusho and Yu-Cheng Rice Bran Oil Poisonings

The signal event that brought PCBs to world attention was the 1968 Yusho mass poisoning incident in Japan (Pfafflin and Ziegler, 2006). This tragic incident occurred when a brand of cooking oil became contaminated by heat exchange fluid. While little known in North America, rice bran oil is a popular type of cooking oil in Asia, valued for its healthful properties. The toxic rice bran oil was prepared by a process that included the use of an industrial heat exchanger containing PCB heat transfer fluid. The heat exchanger leaked and the PCB heat transfer fluid contaminated the rice bran oil. The contaminated oil was sold to consumers who used it in food preparation. The oil’s consumers experienced health symptoms that began as skin lesions and spread across physiological systems resulting in pronounced and horrific toxicity. The results were effectively irreversible.

Ten years later in 1978 an eerily similar poisoning with rice bran oil occurred in Taiwan. The circumstances and particulars of the two poisonings were nearly identical.

The initial assessment of the Yusho poisonings concluded that the PCBs from the heat exchange fluid had caused the toxic effects. However, as analytical

chemists began to test the fluid, a much more complex story emerged (Kuratsune et al., 2007). A test of the rice oil based on the analysis of total organic chlorine indicated that 3,000 mg/kg of PCBs should have been in the oil; but when the same sample was analyzed by gas chromatography, there were only 1,000 mg/kg of PCBs. What could explain the presence of the remaining organic chlorine?

More testing found the rice oil contained a range of chlorinated organic chemicals, most notably polychlorinated dibenzofurans (PCDFs) and polychlorinated quaterphenyls (PCQs). PCDFs are chemically similar to PCBs, but contain a single oxygen atom bridge between carbons 2 and 2' that replaces either the hydrogen or chlorine substitution. PCQs are dimers of PCBs. Testing showed that neither PCDFs nor PCQs would have been present in significant concentrations in the original PCB heat transfer fluid.

Where did the PCQs and PCDFs come from? It turned out that when PCBs were heated above 250°C (about 450°F) they reacted chemically with each other and with any oxygen that was present. This reaction was catalyzed by the presence of metals (including iron) and was greatly accelerated by the presence of even small amounts of water.

To this day there has been little if any toxicity testing on the PCQs, although it is believed that they have a low order of toxicity. By contrast, PCDFs have been very well characterized and are generally considered to be among the most toxic chemicals ever discovered. PCDFs are structurally similar to the highly toxic polychlorinated dibenzodioxins (PCDDs). PCDFs are often cited as being between 10,000 to 100,000 times more potent than PCBs on a mass-to-mass basis.

To aid in evaluating the relative toxic potency of chemical mixtures containing PCDDs, PCDFs and/or PCBs, toxicity equivalence factors (TEF) have been developed for each of the individual congeners. The relative toxicity of a mixture may be estimated by multiplying the concentration of each congener times its TEF and then summing these products. When the TEF calculation was made for the Yusho rice oil, it was demonstrated that the vast majority of the oil's toxicity can be explained by the presence of just two chemicals in the oil: 2, 3, 7, 8-tetrachlorodibenzofuran and 2, 3, 4, 7, 8-pentachlorodibenzofuran. While present at much higher concentrations, it was concluded that the PCB congeners played no or almost no role in causing the poisonings (Dyke and Stratford, 2002).

Another observation from the Yusho and Yu-Cheng incidences that was inconsistent with known cases of occupational PCB poisoning was the severity and persistence of the symptoms. The symptoms of occupationally-induced PCB toxicity were generally reversed once the continuing exposure was curtailed. However, the victims of the Yusho and Yu-Cheng poisonings did not experience relief after the exposure was stopped. The symptoms of Yusho/Yu-Cheng

poisoning were significantly more extensive, severe and persistent than had previously been seen with human PCB toxicity. Clearly the toxicology was different at biochemical and physiological levels.

3.1.1 Could a Yusho-type Poisoning Occur due to Exposure to PCB Building Materials?

The Yusho and Yu-Cheng poisonings have been shown to have been caused by the consumption of rice bran oil that contained toxicologically high concentrations of PCDFs. While the oil also contained PCBs, we now know that they were not the significant causative agents. The commercial mixtures of PCBs manufactured in the US have been tested and found not to contain toxicologically significant concentrations of PCDFs. The temperature required to initiate the conversion of PCBs to PCDFs (250°C and higher) can occur in a burning building, but do not occur in a building under normal operating conditions, even when materials are exposed to direct sunlight in a tropical setting. Therefore, under normal building conditions, there is no realistic possibility of building occupants being exposed to PCDFs from building materials. Without PCDF exposure, a Yusho type poisoning is not likely.

3.1.2 How are Exposures to PCBs in Building Materials Different?

Most of the PCB dose a person receives from building materials comes by way of inhalation. Some additional dose may be due to direct contact with dust and some may result from incidental ingestion of dust, but these contributions are relatively minor (Herrick et al., 2004). The distribution of PCB congeners in air is decidedly different from the congener mixture in the building material itself. This is because the vapor pressure of the congeners decreases with increasing chlorination (Annema et al., 1995). Congener studies of indoor air generally show that greater than 85% of the PCBs in indoor air are the mono-, di-, and tri-chloro congeners. These are generally considered the least toxic of the many PCBs.

However, in a numerical risk assessment performed in accordance with USEPA methods (USEPA Risk, 2010), these less-chlorinated PCBs are considered to have the same level of toxicity as the higher-chlorinated congeners. The partitioning of the congeners that occurs when PCBs volatilize from building materials has the effect of lessening the toxicity of the material people are exposed to, further reducing any likelihood that a Yusho-type poisoning incident could occur.

3.2 Comparison to Other Toxic Materials in Buildings

To provide the perspective from which it is easier to rationally evaluate health risk from PCB-containing building materials, it is useful to consider some of the other toxic materials frequently encountered in buildings. For this purpose it is useful to consider asbestos, lead and radon.

3.2.1 Asbestos

Asbestos may well be the most dangerous building material people have ever used (NIH, 2010). Sickness and fatalities from asbestos have been known since early times. To this day between 10,000 and 20,000 Americans die each year from asbestos-related disease and that number is still going up.

Asbestos disease is documented to have occurred from as little as a single inhalation exposure, but more commonly occurs following multiple exposures. The onset of disease is usually slow, sometimes taking decades to be identified. Asbestos-related disease is generally progressive and irreversible. Fortunately federal law requires the identification and control of asbestos building materials in schools and worker protection laws are enforced.

Unlike asbestos in building materials, disease from PCBs in building materials is unknown. There are no recorded incidents of poisoning or other adverse health effects from PCBs in building materials, despite their presence in buildings for more than half a century. Unlike asbestos disease, PCB toxicity is generally reversible.

3.2.2 Lead

This year (2010) in Nigeria more than 300 children (and many adults) were killed by lead poisoning when their drinking water supply was contaminated with mining waste water containing lead (NYT, 2010). In addition to the fatalities, many suffered from poisoning, but did not die from it.

In the United States it is estimated by the Centers for Disease Control (CDC, 2007) that 1% of all children in the nation have blood levels high enough to reduce their ability to learn. In Massachusetts, a state with strictly enforced lead laws, that number is 0.69%. Like asbestos, the toxic properties of lead have been known for some time. Benjamin Franklin wrote about the toxic effects experienced by those who drank whiskey from stills made of lead.

What is the number of children in the United States whose learning has been impaired by PCBs? There have been no reported cases.

3.2.3 Radon

Radon is a naturally occurring gas that is constantly produced in the earth as a result of the radioactive decay of uranium (ATSDR, 2010). While chemically inert, radon is radioactive and produces ionizing radiation. Radon continuously migrates out of the earth's crust and into the atmosphere. Radon's short half-life prevents it from accumulating in high concentrations, but it can be very hazardous even at low concentrations. There is no question that when inhaled, the ionizing radiation released by radon can and does result in increased lung cancer risk to people.

The USEPA estimates that between 8,000 and 45,000 lung cancer deaths per year are caused by radon gas that seeps into indoor air from the ground; the risk is generally considered to be ten times higher for smokers (USEPA, 2010c). Radon is the number one cause of lung cancer for non-smokers. The "acceptable level" of radon in indoor air is considered to be 4.0 pCi/l (pico-curies of radon per liter of air). The USEPA estimated that the increased risk for a non-smoker exposed to 4.0 pCi/l for a lifetime is 7×10^{-3} ; that's 7 extra lung cancer cases per thousand people exposed. This is a very large risk by environmental standards. There is no national program to test schools for radon or to correct high radon levels if they are detected.

What is the number of lung cancer deaths caused by PCBs in building materials? There have been no reported cases.

3.2.4 Getting Perspective on Toxic Risks

The point of this comparison is to provide perspective on the differences between relatively small and large toxic risks. Asbestos, lead and radon kill and cause irreversible injuries to hundreds of thousands of people each year and the scientific literature is replete with case studies and unambiguous documentation of the harm caused. No such scientific literature exists to support the supposition that PCBs in building materials are dangerous to people. When PCB toxicity has occurred in people, it has been the result of doses thousands of times larger than could be received from exposures to PCBs in building materials. Also important is the fact that adverse health effects from PCBs are generally reversible. Health effects from asbestos and radon are generally irreversible; lead exposure in children may result in irreversible effects.

3.2.5 PCBs and Human Cancer

There is a widely held belief, frequently expressed in the popular environmental media (CWAC, 2010), that PCBs have been scientifically demonstrated to cause

cancer in people, but this is actually not true (Golden et al., 2004). PCBs have been shown to cause cancer in rodents, particularly rats. Rats metabolize PCBs in the liver in a manner that has no parallel in humans or other primates. PCBs can cause cancer in rats, not because they are geno-toxic (or mutagenic), but because they interfere with the particular functioning of the rat liver physiology. Humans have no comparable physiology and are not subject to the same type of cancer. PCB feeding studies in monkeys have failed to show a link between PCBs and cancer.

There are many well-documented epidemiological studies of tens of thousands of people (Golden et al., 2004) who have been exposed to PCBs in occupational and non-occupational settings. The PCB doses these people received were frequently thousands of times higher than would be likely to occur for a student attending a school with PCB-containing building materials. Many of the subjects of these studies have been followed throughout their lives with regular medical checkups to determine whether they were more prone to a variety of illnesses, including cancer. No pattern of increased cancer incidence or other illnesses has been reported from these studies (Shields, 2006). There is no scientific literature that supports a causal link between human cancer and PCBs.

4. CONCLUSIONS

This article has provided a preliminary examination of the hazard posed by PCBs in building caulk and other in-place PCB containing building materials. The USEPA has adopted a PCB risk assessment approach that relies largely on the results of cancer slope factors derived from studies with rats, a species known to be particularly sensitive to PCBs. In contrast, and in keeping with the fundamentals of toxicology, this article has reviewed some of the considerable data available on the health effects of PCBs on humans.

The article considers three lines of human-based toxicological evidence: 1) a reconsideration of the Yusho and Yu-Cheng poisoning incidents; 2) a comparison of the reported adverse health effects from asbestos, lead and radon to those reported from PCBs; and 3) a review of the epidemiological literature concerning the occurrence of cancer in people known to have been exposed to PCBs.

Consideration of the three lines of human PCB exposure studies did not identify a causal link between exposure to PCBs and any form of human cancer. The data available regarding human exposures to PCBs is extensive and robust. Given the divergent results from studies with rats and studies with people, good toxicological practice would place greater emphasis on the results of human studies.

Health concerns about the occurrence of PCBs in building materials are based on the assumption that PCBs do cause human cancer; yet there is no scientific evidence to support this contention. It is the opinion of the author that decisions to undertake expensive interior PCB abatement projects with the objective of reducing possible adverse health effects be carefully evaluated to assess whether they are truly cost-effective.

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PART IV: Remediation

Chapter 6

THE TREATMENT OF “MGP” GROUNDWATER CONTAMINATED WITH COMPLEXED CYANIDES, HEAVY METALS AND VARIOUS ORGANICS USING A THREE STAGE ADVANCED OXIDATION PROCESS

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Keywords: MGP, Heavy Metals, Groundwater, Oxidation Process

1. INTRODUCTION

This paper covers the results of a bench-scale pilot study carried out in order to develop a remediation technology that could be capable of treating contaminated groundwater commonly found at former manufactured gas plants (MGP) sites. These groundwaters are contaminated with complexed cyanide, heavy metals, polynuclear aromatics hydrocarbons (PAHs), and volatile organic compounds (VOCs), and are usually found at MGP sites across the US. The complexed cyanide compounds were commonly produced by the purification process of the gas. The process used for the gas purification involved a treatment with iron oxide impregnated onto solid materials (e.g. wood chips). Thus cyanide complexes of iron were also produced. The data generated by this subject bench-scale pilot test program originates from a pilot study treating groundwater from an MGP site in the Pacific Northwest. The groundwater at the site has elevated levels of contamination with complexed cyanide, iron, PAHs and VOCs and is hydraulically connected to a nearby surface water body. As such, the site is under order to restrict any untreated discharges of contaminated groundwater into the nearby surface water body and require the treatment of any permitted discharges.

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In order to meet these requirements, a groundwater extraction system has been proposed to carefully control any discharges into the surface water body. To meet the stringent discharge limitations proposed by the regulatory agency, a series of bench-scale semi-batch or semi-continuous flow treatment tests were conducted on the groundwater collected from the site. The bench-scale pilot plant testing was performed in order to evaluate and determine the capabilities of a proposed three stage advanced oxidation processes (AOP) to treat the contaminated "MGP" groundwater. The groundwater collected from the site was shipped overnight to the laboratory-pilot plant in Stamford, CT and was treated with a combination of treatment processes including ozone, hydrogen peroxide, and ultra violet (UV) light treatments and filtration for the removal of heavy metal oxides. The bench scale tests were carried out in two sequential treatment process steps; Pre-treatment Process and Main Treatment Process. The Main Treatment Process involved two steps: iron removal by ozone oxidation and filtration followed by final oxidation for the removal of organics.

2. RESULTS AND DISCUSSION

2.1 Pretreatment

In one area of the site the groundwater was found to have extremely high levels of dissolved iron (> 400 mg/L) and complexed cyanide. Based on the assumption that this area of the site would only make up a small portion of the total pumping volume of the contaminated groundwater, an oxidation pretreatment process step was selected and evaluated in order to control and minimize the need for groundwater movement. This area of the site had historically contained the wood chips impregnated with iron oxide. The pre-treatment experiments were carried out to assess and to compare the effects of three oxidant feed gases; air, oxygen, and ozone to be used for the treatment and removal primarily of iron and heavy metals, but also total cyanide, free cyanide, amenable cyanide, VOCs and PAHs from the water treated. The treatment was followed by filtration for the removal of iron oxides. Experiment 1 consisted of oxidation of the pretreatment water with an air feed for a 20 minute reaction periods. The iron oxide produced was removed by filtration. Experiments 2 and 3 were similar to Experiment 1 except oxygen gas or ozone was used for the oxidation. For Experiment 3 a 20 mg/l dosage of ozone was used. Based on the results it was determined that the ozone treatment had the highest level of oxidation and removal of iron and complexed cyanide (Figure 1).

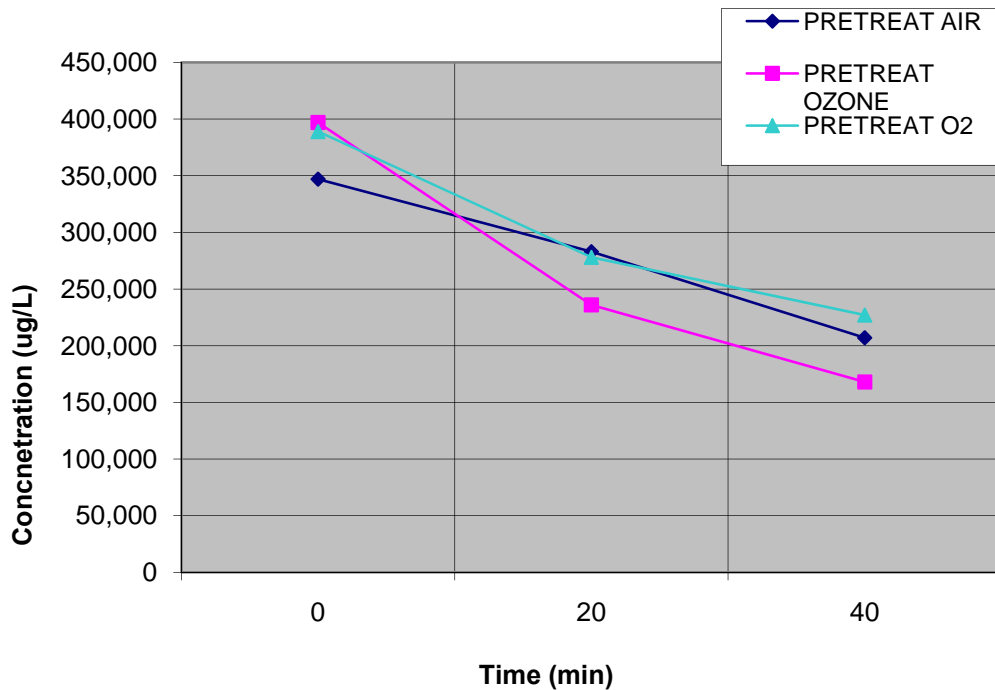


Figure 1. Pretreatment for iron removal

2.2 Main Treatment

Based on the Pretreatment Process test results, ozonation the most effective pretreatment method was selected for use in the area of extremely high concentrations of iron and complexed cyanide. Next the Main Treatment Process, described below, was used for the complete treatment of a mixture of the a pretreated water in combination with the remaining yet untreated contaminated groundwater from the site for a complete treatment of the entire groundwater flow. Within this stage of the bench-scale testing, an additional six experiments were carried out. During this Main Treatment Process treatability study the experiments were carried out to evaluate and study further the most promising treatment process parameters that are known to influence the ozone-H₂O₂-UV light reactions. For each experiment the water to be treated was made up from a mixture of a 20% aliquot of pretreated water and an 80% aliquot of untreated groundwater. Thus the total treated flow represented 80% of the flow necessary for groundwater control at the site. Groundwater that represented 80% of the total flow volume treated was collected from existing monitoring wells at the site that contained extremely high concentrations of VOCs and PAHs. These wells also

contained dense non-aqueous phase liquid (DNAPL) and elevated levels of iron and complexed cyanide. The Main Treatment experiments were carried out for a maximum reaction time of 90 minutes. Sampling was conducted at 0, 20, 60, and 90 minutes reaction time to evaluate treatment and dosage effectiveness. The first step of the Main Treatment Process is a treatment with ozone. Approximately 60 mg/L ozone dosage was added during the first 20 minutes of the reaction time to complete the oxidation of iron. Then the iron oxide was removed by filtration. Thereafter the filtered water was treated in a final polishing step with a combination of ozone, UV light, and H₂O₂ in an AOP process for the removal of residual organics. The process parameters were varied throughout each experiment as shown in Figure 2.

2.3 Main Treatment Experiments

2.3.1 Experiment 5

The pretreated aliquot, 20% of the total, was mixed with groundwater representing the 80% of volume flow and subjected to further treatment with approximately 100 mg/L ozone and UV light during a 90 minutes reaction time.

2.3.2 Experiment 6

As with Experiment 5, the pretreatment aliquot was mixed with groundwater representing the 80% volume flow. Then the water was treated with 5.0 mg/L H₂O₂ and with approximately 100 mg/L ozone and UV light simultaneously during 90 minutes.

2.3.3 Experiment 7

This experiment was carried out similarly to Experiment-6 except the H₂O₂ dosage was 10.0 mg/L.

2.3.4 Experiment 8

This experiment was carried out similarly to Experiment-7 except there was no H₂O₂ dosage.

2.3.5 Experiment 9

This experiment was carried out similarly to Experiment-7 except the H₂O₂ dosage was 15.0 mg/L.

2.3.6 Experiment 10

This experiment was carried out similarly to Experiment-7 the H₂O₂ dosage was 10.0 mg/L, but the water sample was treated with lime to a pH of 8.5 for the removal of carbonates and hydro carbonates and possibly other free radical inhibitors.

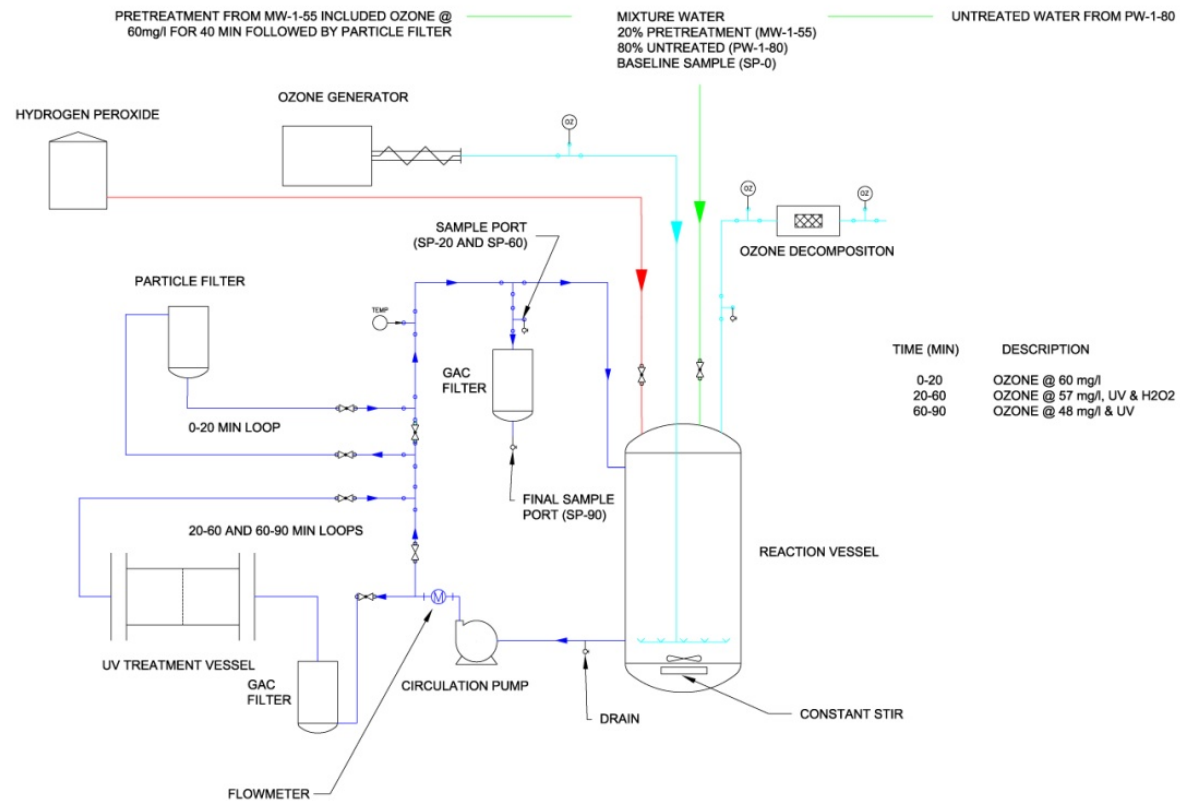


Figure 2. Main Treatment Process

Table 1. DEQ Proposed Discharge Limits

Parameter	units	Limit
Arsenic	ug/L	0.14
Cadmium	ug/L	0.094
Chromium (VI)	ug/L	11
Chromium (III)	ug/L	67
Copper ug/L	ug/L	2.7
Lead ug/L	ug/L	0.54
Mercury ug/L	ug/L	0.012
Nickel ug/L	ug/L	49
Selenium ug/L	ug/L	35
Silver ug/L	ug/L	0.12
Zinc ug/L	ug/L	33
Iron	ug/L	1,000
Manganese	ug/L	100
Free Cyanide	ug/L	5.2
Total Cyanide	ug/L	140
TPH	mg/L	1
Oil & Grease	mg/L	10 & 15
pH		6.5-8.5
Temperature	F	68
Benzene	ug/L	25
Total BTEX	ug/L	250
Trichloroethene	ug/L	30
Tetrachloroethene	ug/L	3.3
Vinyl Chloride	ug/L	2.4
Benzo(a)anthracene	ug/L	0.032
Benzo(b)Fluoranthene	ug/L	0.032
Benzo(k)Fluoranthene	ug/L	0.032
Benzo(a)pyrene	ug/L	0.032
Chrysene	ug/L	0.032
Dibenzo(a,h)anthracene	ug/L	0.032
Indeno(1,2,3-cd)pyrene	ug/L	0.032
Total PAHs	ug/L	250
Total Phenols	mg/L	0.5/0.7

Results from the experiments (Figures 3 – 6) indicated that all advanced oxidation processes proved effective in reducing the target compounds to below regulatory discharge limits. However, the most effective treatment process involved the treatment with ozone plus hydrogen peroxide and plus UV light. No pH adjustment was necessary.

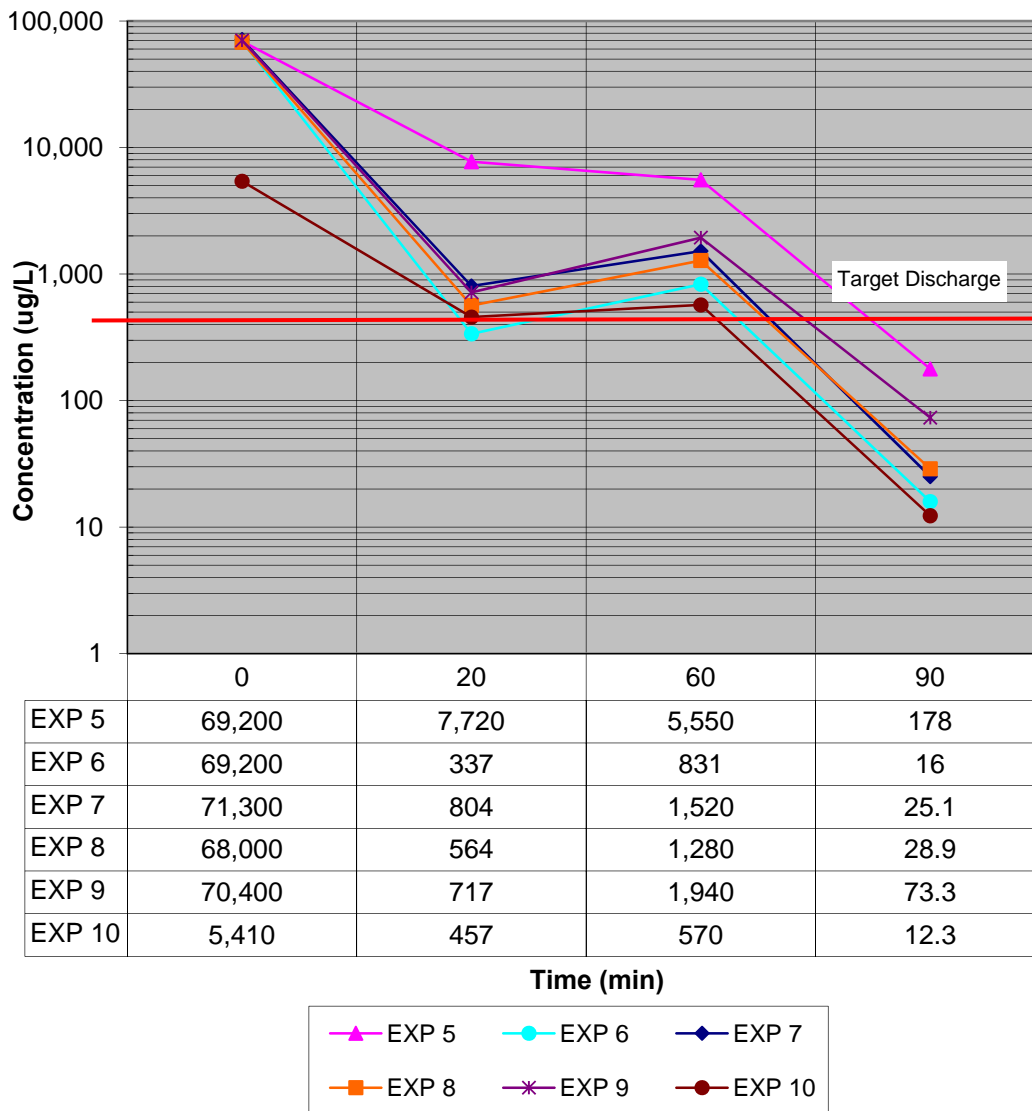


Figure 3. Results of Main Stream AOP: Iron Removal

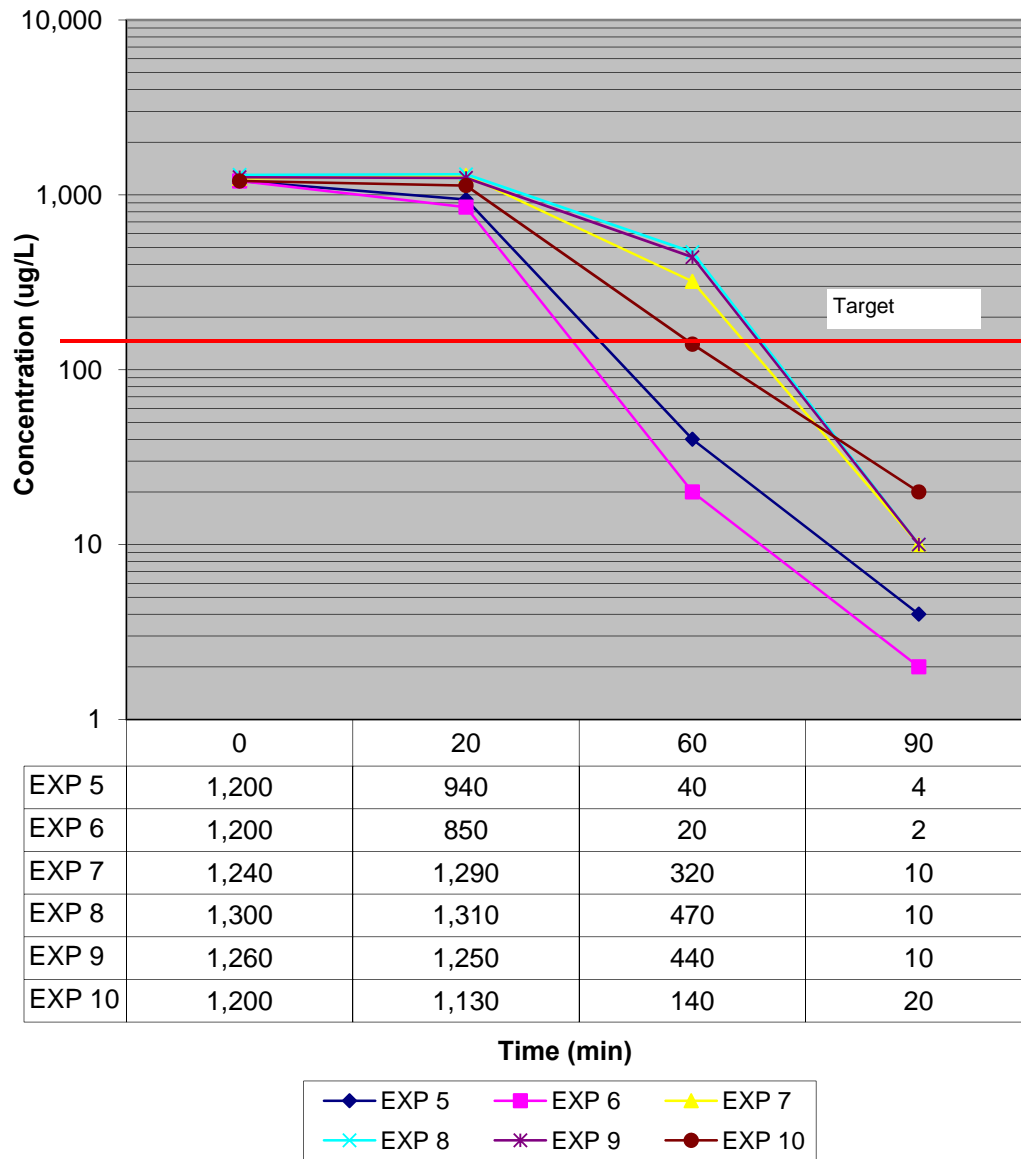


Figure 4. Total CN Removal

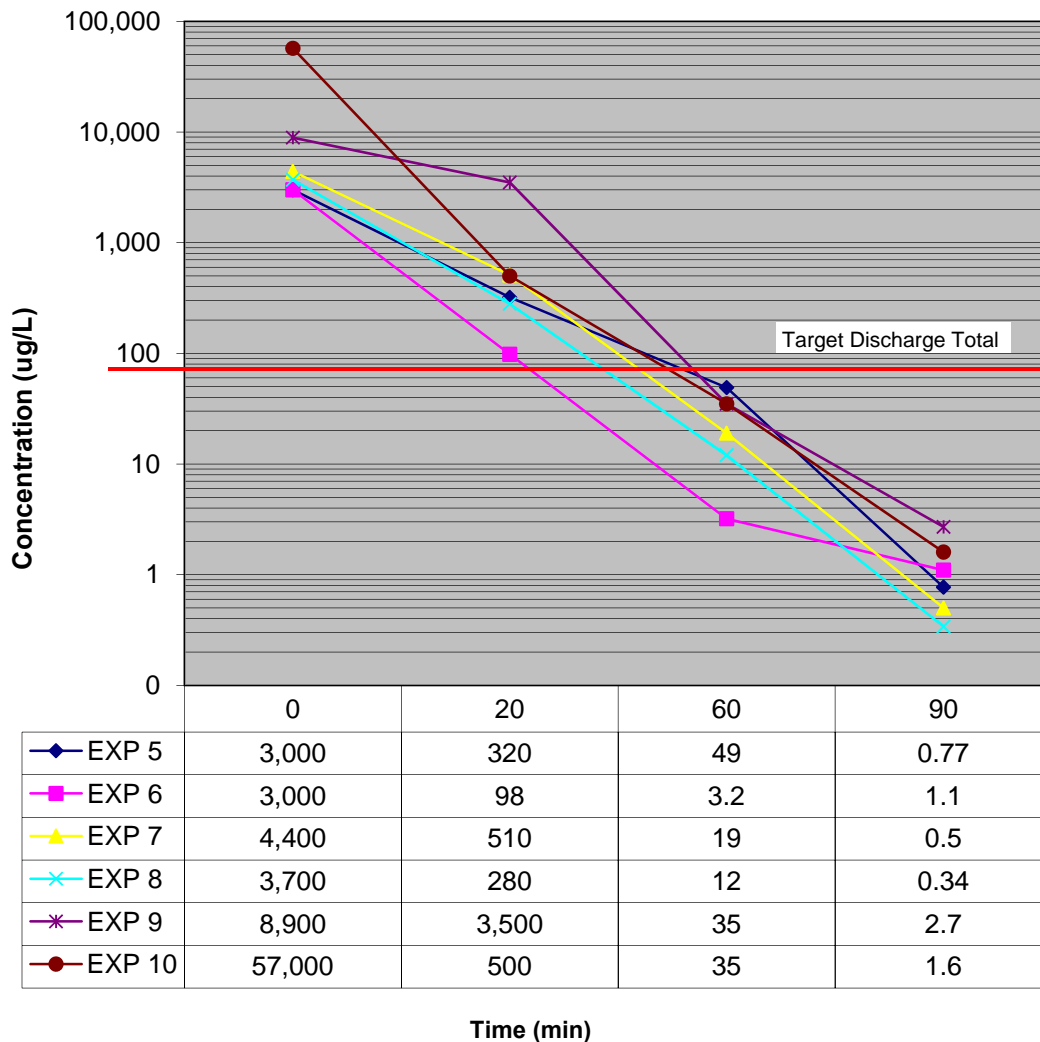


Figure 5. Naphthalene Removal

3. CONCLUSION AND RECOMMENDATIONS

Based on the results of these AOP treatment experiments, it appears that the contaminated groundwater from this MGP site can be readily treated to achieve the surface water discharge limits as required by the governing regulatory agency. In order to further refine the treatment process and to determine the minimum required dosages of ozone, H₂O₂ and UV light intensity, further experiments could be carried out in a full-scale plant or a pilot plant could be constructed on site and operated to test the process under actual larger continuous

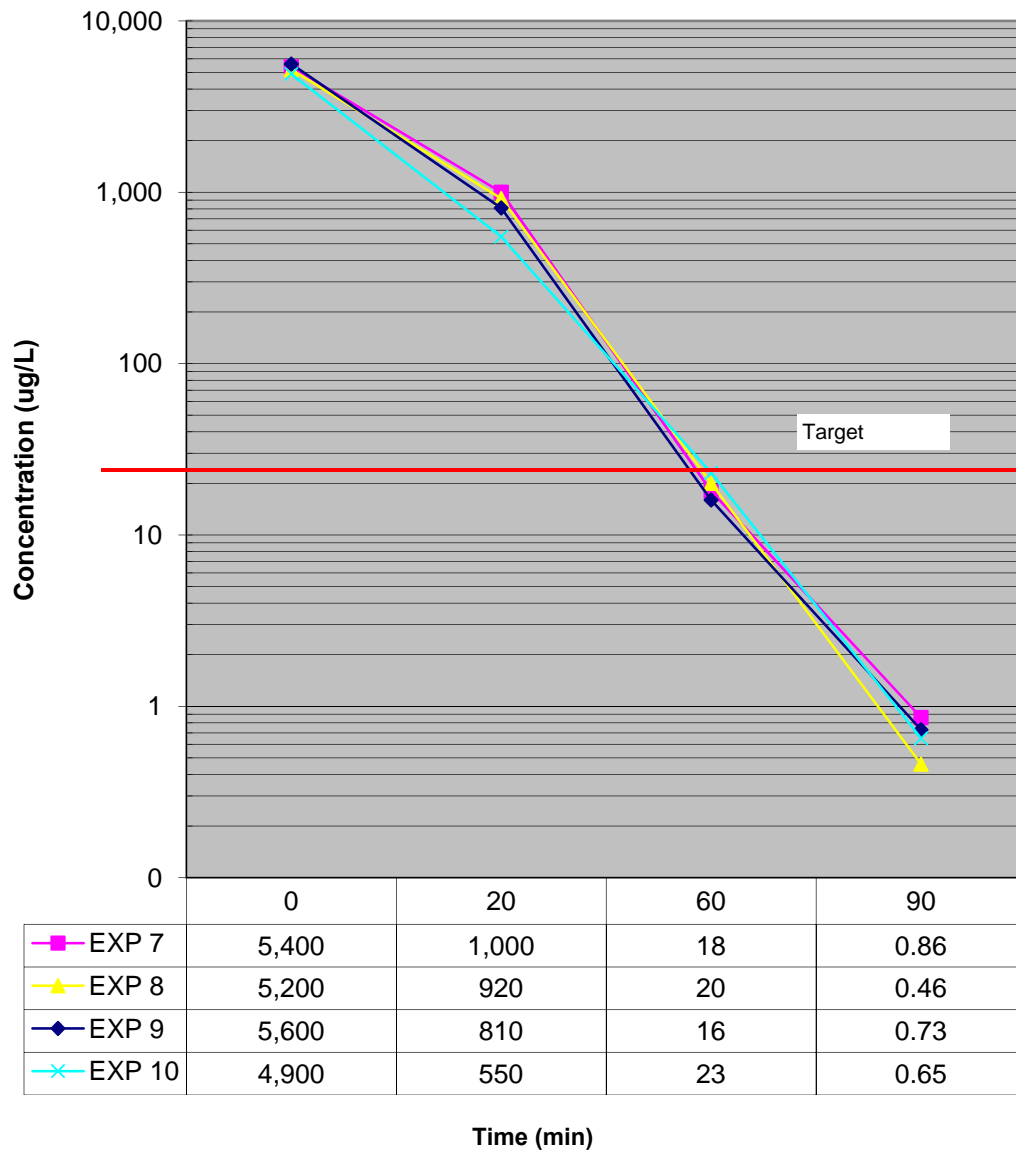


Figure 6. Benzene Removal

flow conditions. The full scale plant or pilot plant could be run under continuous flow conditions while varying the dosages. For the treatment process experiments described herein there was no need for pH adjustment or the addition of other chemicals to treat the groundwater under continuous flow conditions. The full-scale pilot system would also allow for the gathering of additional information for solids handling and optimize filter design requirements. Shown

below is a conceptual full-scale process design based on the bench-scale results (Figure 7). It is sized for the treatment of a continuous flow of groundwater at the rate of up to 400 gpm.

The groundwater samples collected from the site for the subject study were analyzed and found to contain among others the following contaminants: Total Cyanide = 1,300 – 950ppb,, Benzene = 5,600 – 1,400 ppb, Naphthalene = 57,000 – 3,700 ppb, Iron = 452,000 – 69,200 ppb. The test results indicate that the subject “Pump and Treat” ozone process is superior to GAC (granular activated carbon) filtration in three respects: 1) It removes the contaminants by complete oxidation and does not transfer them from the water to another location such as to the GAC for further treatment. 2) The carbon footprint is at the theoretical minimum. No other materials than the contaminants are oxidized. 3) The estimated cost of treating a groundwater flow of 400 GPM with the subject three stage ozone process indicates that it is less than half of the estimated cost of GAC treatment.

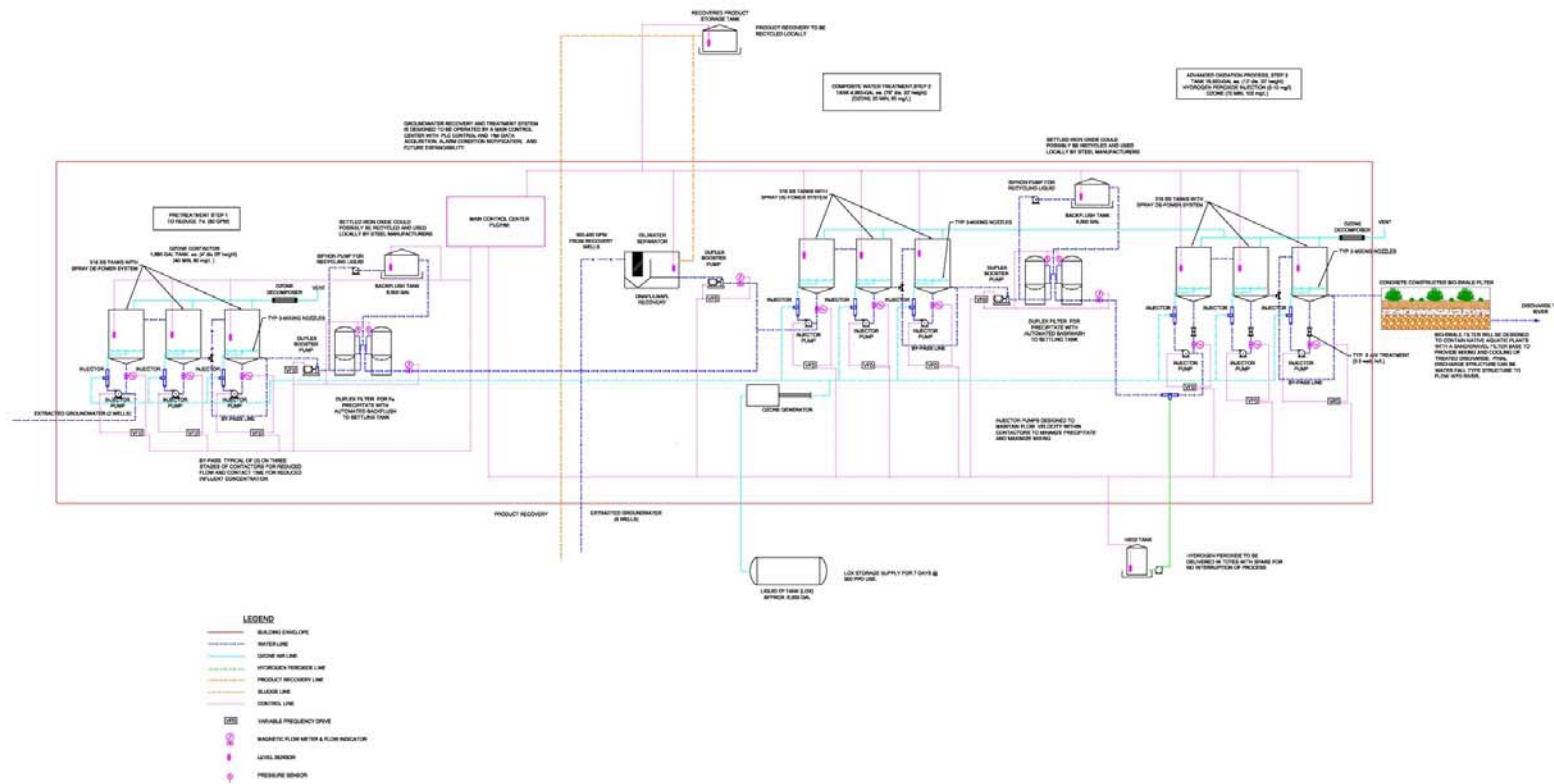


Figure 7. Conceptual full-scale process design based on the bench-scale results.

Chapter 7

APPLICATIONS AND BENEFITS OF GROUNDWATER RECIRCULATION FOR ELECTRON DONOR DELIVERY AND PH-ADJUSTMENT DURING ENHANCED ANAEROBIC DECHLORINATION

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ABSTRACT

The enhanced anaerobic dechlorination (EAD) process is used for in-situ degradation of various chlorinated organic compounds. Electron donors must be delivered to the targeted treatment area and anaerobic subsurface conditions must be maintained for a period of time to degrade both the soluble and adsorbed contaminants. The most common EAD approaches use batch addition of either small volumes of high strength electron donors such as emulsified oil or solid phase hydrogen release compounds, or large volumes of diluted dissolved donors such as molasses or other carbohydrates. Both approaches typically rely on groundwater transport to carry the additives across the entire EAD targeted area. However, groundwater flow is generally laminar, predominantly horizontal, and soluble electron donors added in batch mode can only be adequately distributed in the subsurface with either high-density point installation or large volume addition, or some balanced combination of both. In addition, both batch approaches often require relatively high groundwater flow velocity to distribute the additives down gradient in reasonable time frames and before the electron donor is fully degraded. These difficult requirements for proper batch donor addition often cause dechlorination to stall midway through the process or have a limited treatment area due to a lack of donor distribution. Proper maintenance of neutral pH is a second important requirement for EAD, and is often not controlled adequately during batch addition approaches. Dehalococcoides, the organisms responsible for breakdown of cis-dichloroethene to vinyl chloride and ethene, are not active at a pH below 6.0-6.3. Batch addition methods provide little recourse to

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adjust pH without excessively raising pH in the area immediately surrounding the injection location. Continuous groundwater extraction and recirculation approaches to electron donor and pH buffer addition, however, address these issues and can provide faster and more thorough remediation than the batch processes. Groundwater recirculation provides greater donor distribution through increased injection volumes and hydraulic gradients. Alkalinity can be added as needed to counter decreases in pH and conducted in the form of a large scale titration. Bioaugmentation cultures, when needed, can also be added and quickly dispersed throughout the area. Groundwater recirculation systems for EAD typically divide the treatment area into sections and recirculate and amend groundwater as needed within each section depending on the size of the target area and the aquifer conditions. The proper design and implementation of groundwater recirculation for EAD will be presented and concepts reviewed.

Keywords: anaerobic dechlorination, groundwater remediation

1. INTRODUCTION

There has been an increasing awareness and application of enhanced anaerobic dechlorination (EAD) process for in-situ biodegradation of chlorinated aliphatic hydrocarbons (CAH) in groundwater such as tetrachloroethene (PCE), trichloroethene (TCE), and trichloroethane (TCA) (USEPA, 2000). Anaerobic dechlorination occurs when bacteria utilize CAHs for respiration as alternate electron acceptors under anaerobic conditions in place of oxygen, a process called halorespiration. This dechlorination process occurs naturally if anaerobic conditions are present in the subsurface, or it can be enhanced in the subsurface with the introduction of biologically degradable substrates such as molasses, corn syrup, lactate, whey, oil, or ethanol. These substrates act as electron donors, and biological degradation of these substrates requires electron acceptors. Electron acceptors are typically utilized sequentially based on the energy they yield to the microbe as follows: oxygen, nitrate, manganese, iron, sulfate, and carbon dioxide (CO₂) until methanogenic conditions are established. Dechlorination typically occurs under sulfate reducing and methanogenic conditions, when other electron acceptors are scarce and the energy yielded by halorespiration of CAHs is more favorable.

In these reactions, hydrogen (H₂) is produced from the fermentation of the organic substrate by a mixed microbial community and then hydrogen serves as the direct electron donor for the reduction of the chlorinated compound. The degradation of the substrate and the production of hydrogen occur with a mixed microbial culture that take the primary substrates and produce a variety of secondary substrates such as ethanol, lactate, propionate, and butyrate, which in

turn are degraded and produce acetate, CO₂ and H₂. The hydrogen utilization rate for dechlorination is very small, however, due to often significant hydrogen demands from other electron acceptors, including methanogens. Therefore, enough organic substrate must be added to produce hydrogen in quantities sufficient to satisfy all electron acceptor demand and then be able to maintain hydrogen concentrations for the time required to complete dechlorination of the CAHs present.

Dechlorination occurs first for the most heavily chlorinated CAHs, with PCE being degraded with the substitution of one chloride ion with one hydrogen ion to form TCE. Dechlorination proceeds sequentially in the same manner through TCE to cis-1,2-dichloroethene (DCE), to vinyl chloride (VC), and then to ethene. Each step in the dechlorination process requires one mole of hydrogen per mole of CAH and yields one mole of hydrochloric acid (HCl), such that one mole of PCE yields four moles of HCl with complete dechlorination. Dechlorination of high concentrations of CAH can cause significant alkalinity demand or a sharp drop in pH if sufficient buffering capacity is not present.

Dechlorination can often be accomplished with mixed microbial cultures, with a wide variety of microbes capable of dechlorinating PCE and TCE to DCE; many of these are also sulfate reducers. Less common are microbes that are able to dechlorinate DCE completely to ethene; *Dehalococoides Ethanogenes*, (DE) is the only species that has shown the ability to completely degrade PCE to ethene. EAD performance will be optimized if the proper conditions for viability of DE are maintained. Viability of DE and related mixed cultures is very pH-dependent, and complete dechlorination has been shown to slow significantly at a pH below 6.0-6.3.

The conditions required for complete dechlorination to occur in the subsurface with the EAD process are:

- strongly anaerobic conditions (sulfate reducing to methanogenic);
- presence of a microbial community (DE) capable of complete dechlorination; and,
- buffering capacity sufficient to maintain a near-neutral pH.

The proper design of an EAD system provides processes to achieve and maintain these conditions.

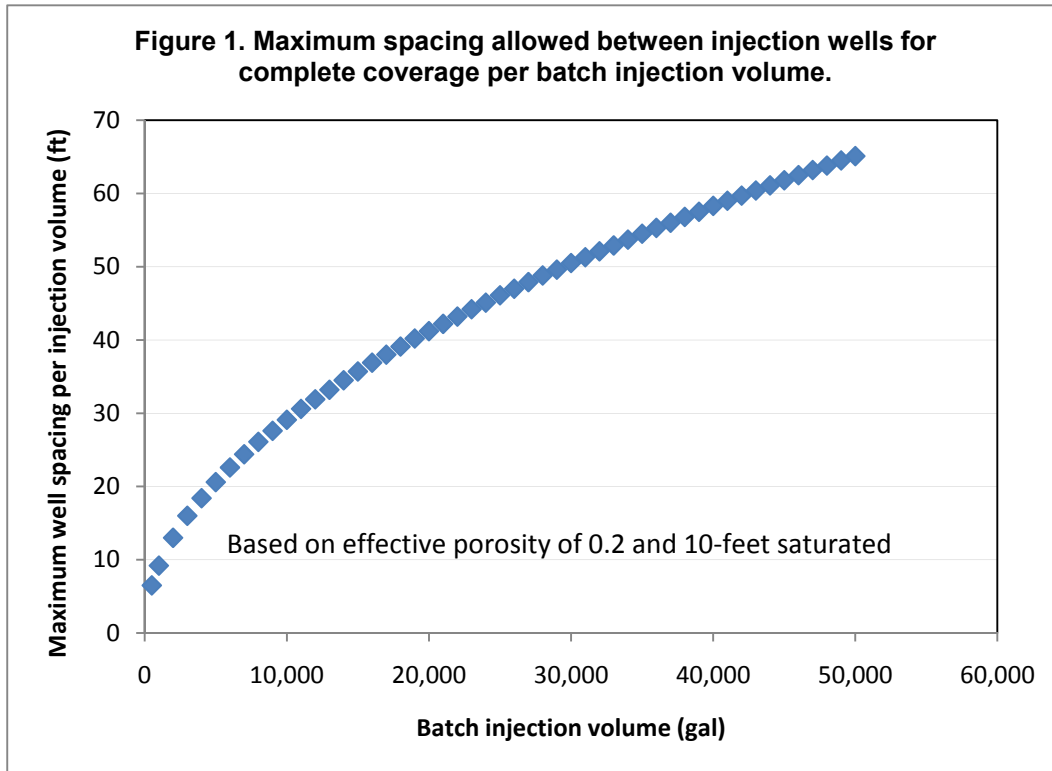
2. SUBSTRATE AND ADDITIVE DELIVERY APPROACHES

The methods utilized for delivery of degradable organic substrates and other additives can be grouped into three primary approaches: stationary or solid phase substrate addition, batch liquid phase substrate addition, and continuous recirculation with liquid substrate. The different approaches all have to be able to distribute the substrate evenly across the width of the targeted treatment area, and provide substrate concentrations sufficient to distribute substrate throughout the entire targeted area.

Stationary or solid phase addition generally uses substrates such as high viscosity lactate, vegetable oil (either straight or emulsified), or materials such as chitin or mulch. Liquid phase batch substrate addition typically uses soluble substrates such as molasses, corn syrup, whey, alcohol, or emulsified oil, diluted slightly or significantly prior to injection. In both of these approaches, the substrate is placed in the ground and is dissolved and degraded as groundwater flows across and through it under existing site gradients. The major limitation of these two approaches is that they rely on groundwater velocity and dispersion to distribute substrate. Groundwater velocity can be easily calculated from site data, but often plumes have been established over long periods of time, so it is difficult to place enough substrate in batches to cover the entire area over reasonable time frames. Dispersion effects have been shown to be limited also, with standard estimates of longitudinal dispersion at a maximum of approximately ten percent of plume length (EPA 1992). Transverse dispersivity has also been shown to be very low and is essentially negligible for design purposes (Grathwohl and Klenk, 2000).

Large volume batch substrate addition can address these limitations somewhat if the target treatment area is completely covered with transects of injection wells and the wells are closely spaced such that the outer limits of injection volumes meet midway between adjacent injection wells. Spacing of the injection wells is a balance between number of wells and the time/effort required to inject enough liquid substrate volume to reach the midpoint between the next adjacent injection well. For example, with an aquifer with a saturated thickness of ten-feet, effective porosity of 0.2, and well spacing of 30-feet, it takes approximately 10,000 gallons of liquid substrate injected into each well in the transect to push substrate midway to the next adjacent well and provide complete coverage. Figure 1 illustrates this issue and shows the substrate injection volumes required for coverage under various well spacing distances. Large volumes of injected batch substrate can also displace the dissolved phase contamination since the groundwater is not immediately biologically active, and as such, plume spreading is likely with tap

water batch addition approaches unless site groundwater is utilized as make-up water to dilute the substrate. In a practical field application of this batch approach, injection of these large volumes into the aquifer simultaneously can become very difficult when applied to several wells and transects across a plume.



Even with sufficient coverage between batch injection wells, distribution of substrate down gradient is still dependent on groundwater velocity to carry substrate across the targeted area at least to the next down gradient transect of batch injection wells. Multiple transects of batch injection wells are therefore typically used to provide sufficient coverage over large plumes which developed over many years. Design of spacing between transects is a balance of the substrate concentration in the diluted batch volume, the half-life of the substrate in groundwater, and the groundwater velocity between transects. Groundwater substrate concentrations need to be sufficient to sustain biological growth and maintain anaerobic conditions for an extended time period. Empirical data from industry practice has indicated that at least 50 mg/l of total organic carbon (TOC) needs to be maintained for a minimum of 100 days time from the point of substrate addition (AFCEE et al, 2004). Initial batch substrate concentrations in the injected volume need to be sufficiently high such that residual TOC concentrations remain within these guidance values after groundwater has

traveled through the batch injection area. Selecting the right substrate with a long half-life and at a sufficiently high initial concentration to last between injection transects is therefore required. Experience has shown that initially starting at a high concentration of TOC at the injection wells can cause a drop in pH due to excessive production of organics acids and generated carbon dioxide gas, therefore the TOC concentration of an injected substrate solution should be less than 3,000 mg/l. Figure 2 shows the residual TOC concentrations for various substrates with time after subsurface injection based on their estimated half-lives.

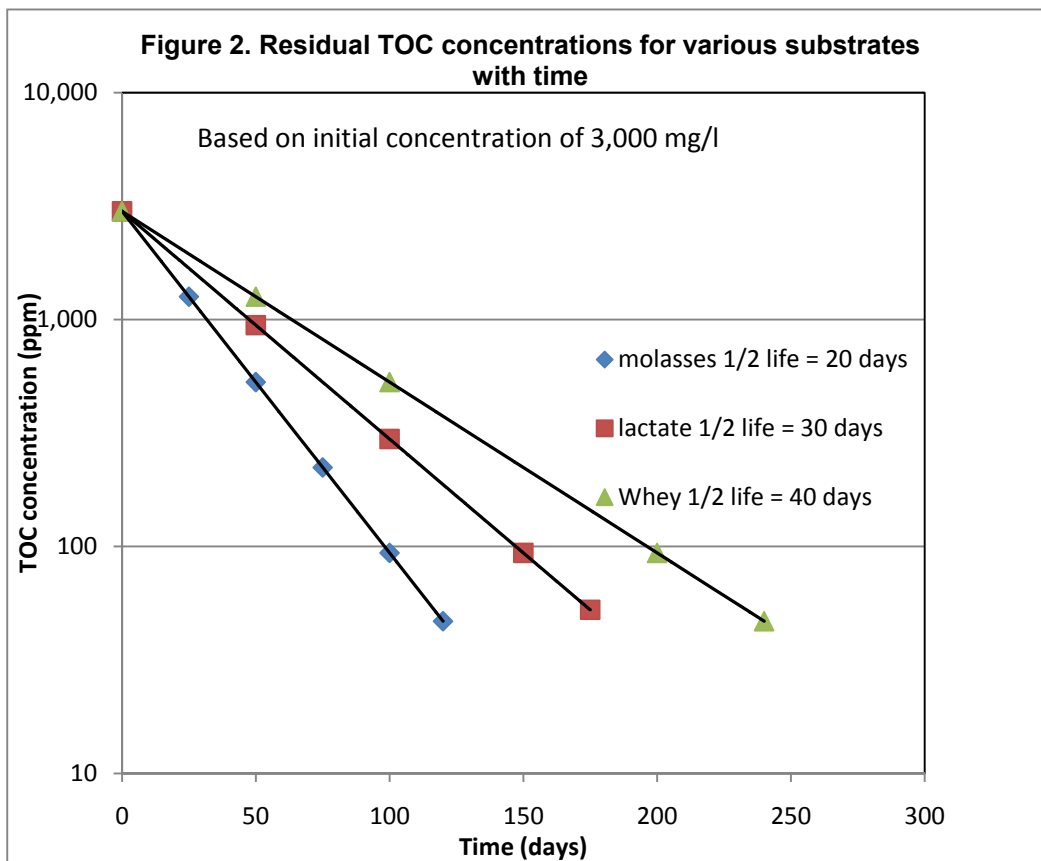


Figure 2 can be used to estimate treatment distance down gradient from the injection transect. As an example, at a groundwater velocity of 1 foot/day, a substrate solution with a half-life of 20 days (such as molasses) added at an initial concentration of 3,000 mg/l TOC would provide effective treatment 120-feet down gradient from the point of addition. More complex substrates (such as whey) with longer half-lives (40+ days) would provide coverage further down gradient (250 feet). Increasing the initial substrate concentration also can provide

coverage further down gradient up to a point, but risks causing a pH drop and stalling the EAD process. The upper limit of acceptable substrate concentration combined with the substrate degradation half-life constants indicate that the maximum period of time in which substrate added to groundwater can exist above 50 mg/l TOC varies from approximately 120 days for molasses up 250 days for whey. Spacing of batch injection well transects therefore have to be designed such that the travel time between transects is short enough that there will still be effective concentrations of substrate present by the time the injected water reaches the next down gradient transect; i.e., 120 to 250 days travel time, depending on the substrate used. Ideally, large batch volumes of dilute substrate should be injected frequently, but often in practice, small volumes of highly concentrated substrates are injected infrequently due to the cost and difficulty in handling and injecting large volumes. The result is that the performances of many EAD batch injection systems suffer because of inadequate substrate distribution and low pH issues. A proper EAD design needs to consider a combination of groundwater velocity, substrate half-life, and initial and residual TOC concentrations to determine injection well transect spacing.

Control of pH within the EAD treatment zone also needs to be monitored and controlled to stay near neutral (greater than 6.0-6.3) order for the DE microbe to complete dechlorination. The dechlorination process produces hydrochloric acid in a molar ratio of four moles of HCL per mole of PCE, with lesser chlorinated compounds producing correspondingly less acid. For each mg/l of PCE, 1.2 mg/l of alkalinity is required to neutralize the acid formed, and this affect is more pronounced when high concentrations of PCE are encountered (McCarty et al, 2007). Significant alkalinity is also needed to neutralize the carbon dioxide and acetic acid and other organic acids produced from the fermentation of the different substrates used as electron donors. Glucose generally requires the most alkalinity to maintain neutral pH levels, and formate and lactate require the least. Batch substrate addition systems often need at least some inherent pH buffering capacity added with the substrate in order to counter the acid generating effects of dechlorination, organic acid production, and production of carbon dioxide in the aquifer. In practice, it is very difficult to provide sufficient buffer in a batch process such that the pH starts and remains near neutral during biological degradation of the substrate and chlorinated solvents. For this reason, many EAD systems suffer from low pH conditions and dechlorination stalls at DCE and VC since the DE microbe is inhibited at low pH. Adjusting pH in groundwater after a batch addition is also very difficult, and there can be a significant time delay since delivery of alkalinity is also dependent on groundwater velocity.

Recirculation systems can overcome many of the limitations of batch injection systems since they can manipulate groundwater flow velocity and travel times,

move and inject large volumes of substrate-amended groundwater, and can be operated to provide pH buffering by adding small amounts of alkalinity continuously to the recirculated groundwater. Recirculation EAD systems use similar substrates as liquid phase batch systems, but with the addition of extraction and injection wells to increase gradients and move substrate faster than under existing conditions. Substrate addition can occur either continuously with the liquid substrate added to the extracted groundwater and re-injected, or batch added to the subsurface and the groundwater recirculated through the area of substrate addition. The design approach of EAD systems with groundwater recirculation is presented in the following sections.

3. DESIGN OF EAD RECIRCULATION SYSTEMS

The design of an EAD recirculation system evaluates and considers the following variables:

- Evaluate existing biogeochemical conditions and assess need for bioaugmentation;
- Identify targeted treatment area/volume, aquifer parameters, and existing groundwater velocity;
- Estimate substrate demand from electron acceptors;
- Assess alkalinity demands and need for additional buffering capacity; and,
- Design of extraction and injection system pumps, piping, and controls.

3.1 Evaluate Existing Biogeochemical Conditions

The existing site biogeochemical conditions should be evaluated to assess the extent to which the EAD process is occurring naturally, and the degree to which it may need to be enhanced for it to completely degrade the target contaminants. Electron donors which can biologically degrade and create anaerobic conditions should be measured and may include non-chlorinated VOCs, petroleum hydrocarbons, and other forms of degradable organic carbon collectively measured as TOC. Electron acceptors such as oxygen, nitrate, iron and manganese (as oxides in the aquifer matrix), and sulfate should be measured or estimated, and provide an indication of competing electron donor demands that must be met before anaerobic conditions are fully established. The presence/absence of electron acceptors and the presence/absence of reduced end products such as ferrous iron, sulfide, and methane can indicate the degree to which anaerobic conditions have been established. Water quality parameters such as pH and alkalinity should be measured and assessed for the potential buffering capacity of the groundwater and aquifer matrix materials.

Evidence of anaerobic conditions leading to anaerobic dechlorination would include a lack of oxygen, nitrate, and sulfate, and the presence of reduced iron and manganese, sulfide, carbon dioxide, methane, and suitable electron donors (summarized as TOC). Evidence of on-going dechlorination with anaerobic conditions would include the presence of degradation by-products such as DCE, VC, and ethene. Conversely, the presence of oxygen, nitrate, and sulfate, and a lack of electron donors and reduced end products or dechlorination by-products indicate that anaerobic conditions are not present and dechlorination is not proceeding. The degree to which the site is more aerobic or anaerobic may vary between these two extremes and will influence the ease of establishing the EAD process.

The potential need for bioaugmentation can also be assessed at this time based on the site evidence for existing dechlorination, the results of treatability testing, or polymerase chain reaction testing (PCR). Current practice indicates that all three should be considered (Environmental Security Technology Certification Program, 2005), but bioaugmentation may not be warranted if there is existing evidence of complete dechlorination to final end-products. Bioaugmentation will likely be needed if there is no evidence of dechlorination, particularly if anaerobic conditions are not yet established.

3.2 Identify Targeted Treatment Area and Parameters

The area targeted for treatment with EAD should be determined from the lateral and vertical extent of impacts to determine total groundwater volume to be treated. In addition, the aquifer hydraulic conductivity and the hydraulic gradient need to be determined to assess groundwater velocity, associated travel times across the target area, and expected yield of extraction and injection wells. The targeted area volume and the aquifer parameters are then used to determine the recirculation system parameters based with the half-life of the substrate to be used. As noted previously, empirical evidence indicates that electron donor concentrations need to be maintained at levels above 50 mg/l as TOC in the aquifer to establish effective EAD conditions. Limitations in the maximum substrate concentration combined with the substrate degradation half-life constants indicate that substrate concentration can only effectively be maintained for between 120 and 250 days (depends on substrate), and this holds true for both batch injection and recirculation systems. A recirculation system should therefore be designed to turn over the targeted treated volume in a period of time that is less than the time it takes the substrate to degrade from its initial injected concentration to a residual concentration of 50 mg/l TOC.

The rate at which groundwater can be extracted, amended with substrate and re-injected, and the increased hydraulic gradients which can be established at a

site will vary based on the site conditions. These recirculation parameters can be adjusted by the designer to allow controlled substrate addition and recirculation flow rates and predictable treatment times, which results in better distribution and therefore better treatment. This is in contrast to waiting for existing groundwater flow to distribute substrate throughout a plume than likely took many years to develop under static hydraulic gradients.

3.3 Estimate Substrate Demands

The total substrate demand in terms of hydrogen utilized should be estimated based on the potential electron acceptors, the levels of chlorinated compounds present in dissolved and adsorbed phases, and a safety factor to account for unknown demands and competing processes. Guidelines for completing this estimate are available (AFCEE et al, 2004), but require collection of the field data described previously in the biogeochemical evaluation. The greatest demand for electron acceptors does not typically come from the contaminants, but from the inorganic species that act as electron acceptors and must be reduced prior to establishing anaerobic conditions suitable for the EAD process. These inorganic species primarily include iron and sulfate, and to a lesser extent manganese, nitrate and oxygen. Sulfate does not have to be completely reduced to sulfide across the site, but sulfate reducing conditions have to at least be established. Competing reactions include the production of methane from carbon dioxide, which acts to increase the amount of substrate required to maintain the anaerobic conditions. A safety factor, often in the range of five to ten times the calculated demand is also incorporated at the end to account for unknowns and inefficiencies in the EAD process.

3.4 Assess Alkalinity Demands

The alkalinity demands of the aquifer in the EAD treatment area will be affected by the initial pH and alkalinity, the acidity generated by the mass of chlorinated compounds to be degraded, and the pH effects of the substrates used in the process. The initial pH can be easily measured and the amount of alkalinity needed to adjust the pH determined by traditional methods. The amount of alkalinity needed for neutralization of the acid generated during the dechlorination process can be determined from the total mass and type of chlorinated compounds present in the dissolved and adsorbed phases as discussed previously. The amount of alkalinity needed for these demands should be added at the beginning of substrate addition as a preventative measure. Lastly, the amount of alkalinity needed to control the acid generated from substrate degradation and maintain pH near neutral is hard to predict and should be tracked during the initial operational period. After a maximum operating period of three months, the extracted

groundwater pH and alkalinity should be measured and the need for additional alkalinity considered if pH levels have decreased and are approaching 6.0-6.3. A recirculation system for EAD has a significant advantage over a batch injection system in terms of maintaining pH and adding alkalinity: alkalinity can be added in small quantities in the recirculated water on an as-needed basis to maintain pH levels. In a batch injection EAD system it is very difficult to adjust pH without having significant increases in pH at the point of substrate addition. The recirculation system can be used like a large scale titration to measure in small amounts of alkalinity as needed at any time during the process.

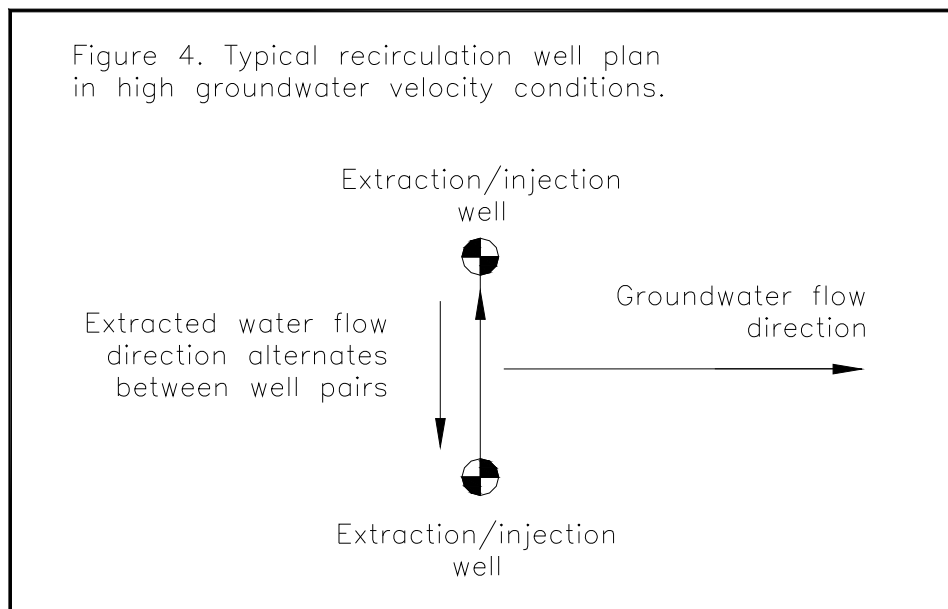
3.5 Design of Extraction, Amendment, and Injection System

The design of the EAD recirculation system can be configured simply with three main components: the extraction wells and pumps, the amendment system, and the injection wells. The extraction wells are typically located down gradient of the injection wells, at a distance determined from the allowable travel time as discussed previously. The extraction wells can be operated with simple electrical or pneumatic recovery pumps. The amendment system should consist of a feed tank to hold several week's worth of amendment, and a feed system to add the substrate and alkalinity to the extracted and recirculated groundwater. The injection wells can be constructed in the same manner as the extraction wells but without the internals.

There are many patterns of extraction and injection well plans, but they are typically based on two approaches. In the first, most common approach, groundwater is recirculated between extraction and injection wells in a pattern that is parallel to the normal direction of groundwater flow, as shown in Figure 3. This is used to facilitate rapid delivery and distribution of substrate by increasing gradients between extraction and injection wells at a low to moderate groundwater velocity site.

Extraction wells are placed down gradient from the injection wells, at a distance based on the travel time between the extraction and injection wells and substrate half-life. The number of wells and lines of extraction and injection wells will vary based on site conditions. In the second approach, groundwater is extracted, amended with substrate, and then re-injection within a well pair orientated perpendicular to groundwater flow. This approach is used where the groundwater velocity is high to mix substrate within the groundwater as it flow through an area. In this case, groundwater velocity is sufficiently high to allow for distribution to down gradient locations and the recirculation system simply ensures it is well mixed within the groundwater. The extraction and injection directions within a well pair are alternated on a regular basis to ensure even substrate distribution within the aquifer; this approach is shown in Figure 4.

The locations of the extraction and injection wells typically focus on the source area, and groups of extraction/injection wells may be formed based on contaminant concentrations in groundwater. Recirculating substrate across source areas can add substrate and promote degradation where it is needed most, but can also dilute high concentrations to levels acceptable for biodegradation. Desorption and associated flushing of contaminants from source areas allows for a larger treatment zone and can significantly increase the overall remediation rate.



4. CONCLUSIONS

There are several benefits of groundwater recirculation for implementation of the EAD process including:

- Rapid and complete distribution of substrate and amendments to targeted areas;
- Distribution of amendments before they are consumed;
- Rapid distribution of bioaugmentation cultures when needed;
- Ability to add alkalinity as needed to maintain neutral pH;

- Promotes desorption and flushing of contaminants for subsequent degradation; and,
- Allows for manipulation of groundwater flow conditions to complete site remediation in reasonable time frames.

The benefits of recirculation systems for EAD far outweigh alternate approaches that use batch injection and should be considered for all EAD systems. The basic design approach outlined previously provides the methods to account for the aquifer characteristics and implement EAD remediation in reasonable timeframes. The increased capital costs and associated complexity of EAD recirculation systems is justified in that it provides faster and more complete remediation and an overall lower project cost by shortening the duration of remediation, monitoring, and associated project management.

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PART V: Sediments

Chapter 8

REVIEW OF MECHANICAL AND HYDRAULIC DREDGING AT TWO SEDIMENT REMEDIATION SITES

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ABSTRACT

Tetra Tech assists the U.S. EPA Great Lakes National Program Office (GLNPO) with design and construction management of sediment remediation projects in the Great Lakes region. Tetra Tech is currently managing two sediment remediation projects for GLNPO: the West Branch of the Grand Calumet River (WBGCR) in Hammond, Indiana, and the Ottawa River in Toledo, Ohio.

The WBGCR flows through an industrialized area in northwest Indiana. Mechanical excavation of 32,000 cubic yards of sediment was completed in August 2010. The design for additional sections of the river is underway with construction planned for December 2010.

The Ottawa River is part of the Maumee River Area of Concern in northwest Ohio. Hydraulic dredging of about 250,000 yards of sediment from the Ottawa River commenced in May 2010 and is scheduled to be completed in November 2010. The principal contaminant of concern is polychlorinated biphenyls at concentrations both above and below 50 ppm.

This paper will compare and contrast the methods for sediment dredging, focusing on the specific site conditions that influenced selection of each approach as well as lessons learned during construction activities at both locations. Factors influencing remedy selection include sediment physical and chemical characteristics, site hydraulics, and site access.

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Key Words: sediment, Grand Calumet, Ottawa, mechanical, hydraulic, dredging

1. INTRODUCTION

Tetra Tech, as part of the joint venture SulTRAC, provides support to the U. S. Environmental Protection Agency (USEPA) Great Lakes National Program Office (GLNPO) for design and construction management at sediment remediation sites. The sediment projects are part of the Great Lakes Legacy Act funding program. The Act provides funding to take the necessary steps to clean up contaminated sediment in "Areas of Concern located wholly or partially in the United States," including specific funding designated for public outreach and research components. The GLNPO provides between 50 and 65 percent matching funds with non-federal public or private partners to facilitate remediation of contaminated sites.

Tetra Tech performed design and/or construction management at two contaminated sediment sites in 2010: the West Branch of the Grand Calumet River (WBGCR) in Indiana and the Ottawa River in Ohio. The principal partners on the WBGCR are the Indiana Departments of Environmental Management and Natural Resources. The non-federal partner funding sources are a trust fund established after settlement of natural resource damage claims and in-kind services, which is funding 35% of the construction cost. The principal partners on the Ottawa River are the Ottawa River Group (ORG), composed of several manufacturing firms with operations along the Ottawa River, and the City of Toledo, Ohio. The non-federal partners are providing 50% of the funding for the project design and construction cost.

1.1 WBGCR

The WBGCR flows through a heavily industrialized area in northwest Indiana with municipal and industrial influent accounting for 90% of the river's flow. The project area is divided into 7 reaches between Indianapolis Boulevard and the Indiana/Illinois State line with poly-aromatic hydrocarbons (PAHs) and metals the principal contaminants of concern. Mechanical excavation of 32,000 cubic yards of sediment from Reach 3 was completed in August 2010. The design for Reaches 4 and 5 is underway with construction start planned for December 2010, using mechanical excavation in the dry and mechanical dredging of submerged areas of the channel.

Reach 3 of the WBGCR lies within the corporate boundary of Hammond, Indiana. The reach is bounded on the east by Columbia Avenue and on the west by Calumet Avenue. Small commercial and residential properties line the south

bank while the north bank is occupied by Hammond Sanitary District (HSD) support facilities and baseball fields managed by the City of Hammond.

The HSD waste water treatment plant discharges an average of 50 million gallons per day approximately 2000 feet east of Reach 3. Five to ten percent of the HSD daily discharge flows west through Reach 3 with the remaining volume flowing east into the Indiana Harbor Canal. An additional source of water into Reach 3 is the Howard Avenue outfall, which is located on the south bank at the midpoint of Reach 3. During storm events the Howard Avenue outfall can discharge a flow of 50 cubic feet per second into the channel.

Prior to remediation, Reach 3 of the WBGCR was a shallow, meandering creek approximately 50 feet wide and 1-2 feet deep during most of the year. The remaining surface area within the 150-wide channel had been overgrown with vegetation, primarily invasive species including the common reed. During heavy rains water depth would rise to several feet, covering the vegetation from bank to bank.

Within the center of the WBGCR the soft sediment is about 10 feet deep. Vegetation along the sides of the river provides enough support for personnel, but can not support equipment without the use of composite mats or similar material. Because of the private property along the south bank, the river could only be accessed from the north bank.

1.2 Ottawa River

The Ottawa River is part of the Maumee River Area of Concern in northwest Ohio. Sediment remediation is focused on three sections of the lower 8.8 miles of the river, which have been impacted by historical municipal and industrial uses including several landfills within the project area. The project area is divided onto three reaches:

- Reach 2: River Mile (RM) 3.2 to RM 4.9
- Reach 3: RM 4.9 to RM 6.5
- Reach 4: RM 6.5 to RM 8.8

The river generally flows in a northeasterly direction through the project area. The banks are developed with structural material to form stable embankments for highways, and abutted by waste disposal sites and industrial properties throughout the project area. The banks throughout the targeted remediation area are often defined by concrete, riprap and sheet piling.

The lower Ottawa River is a lacustrary system in the area of RM 0.0 to approximately RM 6. This means that this section of the river is subject to a temporary change in flow direction resulting from the movement of water from

Lake Erie during wind-aided seiche events. In general, the river widens and lowers its gradient as it moves downstream, with the steepest and narrowest section being Reach 4, Reach 3 a transitional zone and Reach 2 being broad and flat.

In Reach 4, the river is narrow (average of 75 feet in width) and steep and has a deep channel where velocities and morphology tends to create erosive conditions. Water depths range from about 1 to 4 feet in mid channel. Reach 4 is recognized as a true riverine environment due to the lack of a lacustrary effect and consequently flows in one direction. In Reach 4, the presence of at least 14 major road and one rail crossings spanning the river and extensive sections of the shoreline has modified its form, and the river channel has been dredged, channelized and moved in places to accommodate road construction. The impact of these road crossings can create erosive conditions in this section of the river, especially in the lower portion of the reach.

Hydraulic dredging of about 250,000 yards of sediment from the Ottawa River commenced in May 2010 and is scheduled to be completed in November 2010. The principal contaminant of concern is polychlorinated biphenyls (PCBs) at concentrations both above and below 50 ppm, with lead, PAHs, and oil and grease also present within the sediment (Design Report, 2009).

2. MEANS AND METHODS

Several types of equipment have been developed for environmental dredging projects. Environmental dredging typically deals with smaller volumes and shallower cuts than navigational dredging projects. Environmental dredge projects may also have other operational constraints such as dewatering operations and contaminant re-suspension. (Palermo 2008). Site conditions and project partner requirements dictated the means and methods selected for the two sediment remediation projects. On the WBGCR mechanical excavation was selected while on the Ottawa River hydraulic dredging was the option agreed upon by the project partners. A more thorough review of dredge equipment and methods can be found in USEPA or US Army Corps of Engineer guidance documents.

2.1 WBGCR

Because of the limited amount of water flowing through the channel at most times during the year, mechanical excavation of the contaminated sediment in dry conditions was selected as the remedial option for Reach 3. Support facilities, to include project trailers, a dewatering pad, and waste water treatment plant, were

located in an upland area on HSD property. Access routes on the north bank were identified on the design drawings. Where possible, access routes used gaps in the tree line to minimize tree removal.

Sheet pile was initially installed at the east limit of the project area to reduce the inflow of water from the HSD. Additional sheet pile was installed at the Howard Avenue outfall to separate Reach 3 into an east and west segment. Initially the sheet pile at Howard Avenue directed storm water flows to the west, leaving the east dry for remediation. Once the east segment was complete, an additional sheet was installed at Howard Avenue to direct water east so that the west segment could be completed in the dry.

Although contaminated sediment within the channel is over 10 feet thick, only 3 feet were to be removed. The remaining sediment was covered by an engineered cap to isolate the contaminants of concern. The designed cap consisted of an activated carbon mat covered by 2 feet of granular material.

Bidders proposed several means and methods to remove sediment. The selected contractor proposed installing temporary sheeting at 200-foot intervals to provide additional stability during sediment removal and cap placement. Surface water within the excavation area would be pumped downstream from one section to the next to allow for sediment removal, cap placement, and restoration. Composite mats placed over the vegetated areas of the excavation area allowed a long stick excavator to reach the south bank. Excavated material was stockpiled within the excavation area and allowed to gravity drain prior to transfer to the sediment dewatering area.

Sediment was transferred to the sediment dewatering area by articulated dump trucks. The dewatering pad was approximately 20,000 square feet and consisted of the following layers from bottom to top: two inches of sand, a 40-mil liner, four inches of crushed stone, geo grid, six inches of crushed stone, and a perimeter earthen berm. Lime, polymer, or other agents could be mixed into the sediment so that the material passed the Paint Filter Test. Waste water elutriated from the sediment was treated at an on-site treatment plant prior to discharge into the HSD treatment system. Dewatered sediment was sent by truck to the Newton County landfill in Newton County, Indiana.

Engineered cap placement consisted of a geo grid, granulated activated carbon mat, and 2 feet of granular material. Once a section was excavated and surveyed, the geo grid and then the activated carbon mat were rolled across the river perpendicular to the direction of flow. Adjacent mat panels were overlapped by 12 inches. After mat placement, the granular cover was placed over the geosynthetic layers. Initially the 24-inch cover was placed in a single 24-inch lift, pushed out from the north bank. This placement method was unsuccessful. A

telescoping belt conveyor was then used to distribute the granular cover in thinner layers over the geosynthetic material (Figure 1).

After cap placement, areas of the north and south bank disturbed by the remediation were seeded and replanted with trees and shrubs. The sheet pile installed at the east and west project limits was retained to support remediation at other sections of the WBGCR.



Figure 1. Granular cap placement by belt conveyor

2.2 Ottawa River

Hydraulic dredging was selected by the project partners for removal of 235,000 yards of sediment with PCBs under 50 ppm and 14,000 yards of greater than 50 ppm PCB sediment. SulTRAC managed procurement and construction oversight of the dredge and sediment delivery operation. SulTRAC also managed construction of two sediment dewatering facilities. The non-federal partner was responsible for land-side management, to include operation of the geotextile tube dewatering facilities and construction and management of the waste water treatment plant.

Sediment dewatering operations are sited on the Hoffman Road Landfill, owned by the City of Toledo. The sediment with PCB concentrations lower the 50 ppm will be dewatered and left in place within the landfill waste limit. Sediment exceeding 50 ppm and the waste water treatment plant are located outside the permitted solid waste footprint. Access to the Hoffman Road landfill was secured by the non-federal partner in December 2009, allowing construction of the waste water treatment plant and dewatering pads to commence in early 2010.

The landside facilities were substantially complete in April 2010. Upon completion of the pre-dredge survey, dredging operations began May 3, 2010. The contractor mobilized two 8-inch dredges and one 10-inch dredge. One 8-inch dredge and the 10-inch dredge would normally operate 24 hours per day, six days per week, with the second 8-inch dredge on standby in case one of the operating dredges needed to be taken off line (Figure 2).



Figure 2. Ten-inch hydraulic dredge working area in Reach 2

The clean up goals were established on the basis of Surface Weighted Area Concentrations (SWACs) for PCBs, PAH, and lead. The post-cleanup SWAC goals for all reaches are:

- 1.5 mg/kg for total PCBs
- 30 mg/kg for total PAHs
- 180 mg/kg for lead

The design process evaluated the distribution of concentrations of the constituents of concern to identify how to delineate areas for remedial action. The evaluation entailed the testing of several "cut line" options, to demonstrate the resulting volume of sediment removed, mass of contaminants removed, and resulting SWACs generated when different concentration limits were applied to dredging. This process determined that "cut lines" set to remove sediment observed, or projected to contain, greater than or equal to 5 mg/kg total PCB, 30 mg/kg PAH, and 200 mg/kg lead would be sufficient to attain SWAC concentrations at or below the post-cleanup goals.

The dredge limits for the project were established by delineating areas of sediment exceeding these concentrations, using physical limits of the sediment body as established by the river banks and the base of unconsolidated sediment. These delineated areas were designated as Dredge Management Units (DMUs), defined as running along certain lengths and widths of the river to a defined depth in the sediment body. There are seven DMUs in Reach 2, eighteen DMUs in Reach 3 and six DMUs in Reach 4.

Dredging began on DMUs with PCB concentrations lower than 50 ppm with one 8-inch dredge operating in Reach 4 and the 10-inch and standby 8-inch dredges working Reach 3. Once Reach 4 was complete, the 8-inch dredge would switch to sediment greater than 50 ppm in Reach 3. Sampling completed by USEPA identified additional areas of contamination within Reach 4 DMUs after the start of dredging operations. A fourth 8-inch dredge was mobilized to the site in August to remove the impacted sediment from three new DMUs.

3. RESULTS AND DISCUSSION

3.1 WBGCR

The final volume of sediment removed from the WBGCR was 32,142 cubic yards. Unusually heavy rains in the spring and through the summer delayed completion beyond the original schedule by three months. The sheet pile diversion structures were successful in directing most storm water flows away

from the open excavation area. The project specifications allowed for most storm water in the excavation zone to be pumped downstream after a 24-hour settling period. Water within one foot of the sediment surface was pumped into tanks, treated if necessary, and discharged to the HSD. Approximately 4.5 million gallons of water was sent to the HSD over the 9 month project.

Although the contractor planned to install temporary sheet pile at 200-foot intervals to provide additional stability during excavation and cap placement, this process was abandoned after the first two iterations. The sediment was generally firmer than the contractor anticipated. Temporary silt fence was installed below the excavation areas to minimize loss of contaminated sediment during storm events.

The design for the engineered cap consisted of an activated carbon mat covered by two feet of granular material. More than one bidder suggested a geo grid between the sediment and activated carbon mat. The addition of the geogrid provided some additional stability during cap placement. After unrolling the geo grid and activated carbon mat, the contractor initially attempted to spread the granular cap over the mat in a single 2 foot lift. Uncontrolled movement of the underlying sediment created small mud waves that disrupted the mat placement and final excavation elevation. Placement of the granular cover was modified by using a telescoping belt conveyor to distribute the granular cover in thinner layers over the geosynthetic material.

3.2 Ottawa River

Hydraulic dredging of the Ottawa River met project expectations through the summer of 2010 and is on schedule for a November 2010 completion. Dredge performance typically exceeded 90% efficiency. Landside operations also performed well with only minor issues at the geotextile bag dewatering pads and the water treatment plant. Dredging of sediment with PCB concentrations over 50 ppm was completed in September with 13,954 cubic yards removed. Once the greater than 50 ppm sediment is dewatered, the material will be loaded on trucks and sent to a licensed disposal facility in Michigan before the end of 2010.

Dredging of sediment below 50 ppm will continue until November 2010. Although placement of sand cover was anticipated for some areas, dredging has proven sufficient to meet the clean up objectives. Additional dredging below the original design elevation as well as dredging near some underground pipelines that cross the project area was required to meet these objectives.

Independent sampling of the project area by USEPA identified additional areas of contamination in Reach 4. Three additional DMUs, beyond the original six in this area, were established to manage removal of the new sediment

excavation zones. Since the dredge that had completed work in this area had already moved downstream into Reach 3, a third 8-inch dredge was mobilized to the site. Two of the three new DMUs were upstream of the original project limit in very shallow water. A Portadam[®] system was installed downstream of the dredge areas to increase the water depth and allow placement and operation of the new dredge.

Seiche effect would periodically push most of the water out of the Ottawa River creating an expansive mud flat. During these events dredging operations were halted. These periods seldom lasted more than one day.

4. CONCLUSION

Several remedial methods are available to address contaminated sediment sites. Mechanical excavation and hydraulic dredging are two methods shown to be effective on the WBGCR and Ottawa River, respectively.

Additional sections of the WBGCR are in various stages of design or construction, with both mechanical excavation and mechanical dredging planned for different sections of the river.

Completion of dredging on the Ottawa River is planned for November 2010. Sediment with PCB concentration of 50 ppm will be disposed at a licensed landfill in Michigan. Sediment with lower concentrations will remain within the dewatering pad limit and incorporated into the Hoffman Road landfill.

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Part VI: Vapor Intrusion

Chapter 9

VAPOR INTRUSION ASSESSMENT – A COMPARATIVE ANALYSIS OF SUBSURFACE VAPOR SAMPLING METHODS

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ABSTRACT

The paper and presentation focus on subsurface vapor data collected as part of a vapor intrusion assessment where tetrachloroethene (PCE) is the principal volatile organic compound of interest. In support of this assessment, we have conducted soil gas sampling and analysis to aid in identifying and delineating the presence of PCE in soil fill and residual silt-clay saprolite soils derived from in-place weathering of siltstone bedrock.

During the assessment, we collected soil gas samples from temporary points, which were advanced using hand-operated Geoprobe® direct push rods to depths ranging from 2 to 7 feet below ground surface. Grab samples were collected using the Geoprobe® post-run tubing (PRT) system into evacuated glass vials, which were later analyzed off-site.

Following vial collection and retrieval of the Geoprobe® rods, several sampling locations were completed with permanent soil gas monitoring implants constructed using stainless steel screen and tubing, and backfilled using a glass bead pack overlaid by bentonite chips. Several weeks later, we collected soil gas samples from the monitoring implants using Summa canisters.

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Despite the differences between sampling techniques, time and duration of sampling, and volume of the samples, PCE concentrations measured in vial and canister samples are remarkably comparable, generally exhibiting order of magnitude agreement. With some limitations, the results suggest that vial sampling can be used as a complementary method to conduct subsurface vapor surveys.

Canister samples collected from the vapor implants on a bimonthly basis illustrate the effects of seasonal variability and underline the importance of monitoring over a period of time under different seasonal conditions to support a rigorous assessment of vapor intrusion potential.

Keywords: vapor intrusion, soil gas, tetrachloroethene, sampling, canister, vial, implant

1. INTRODUCTION

In this paper, we compare results from soil gas samples collected as part of a vapor intrusion assessment where tetrachloroethene (PCE) is the principal volatile organic compound (VOC) of interest. In support of this assessment, we collected soil gas samples from temporary probes using pre-evacuated glass vials; and from permanent implants, which were constructed following retrieval of the temporary probes and sampled using 1-liter Summa canisters. For perspective, we also review vapor concentration changes over time at the permanent implants, as well as the precision of data associated with each sampling method through the collection of field replicate samples. We show that despite their limited sensitivity relative to canister samples, vial samples can be a cost effective and reliable method to obtain subsurface survey data.

2. MATERIALS AND METHODS

2.1 Sampling from Temporary Probes Using Glass Vials

Temporary probes were driven into the saprolite at multiple locations to depths ranging from 2 to 7 feet (ft) below ground surface and sampled using a Geoprobe® post run tubing (PRT) system (Geoprobe® Systems, 2010). The probe installation procedure, which is shown on Figure 1, consisted of breaking the asphalt (where present) using a hammer drill; and manually driving a series of 1-inch (in) diameter Geoprobe® direct-push stainless steel hollow rods fitted with an expendable stainless steel drive point. Upon reaching sampling depth, field personnel inserted Teflon® tubing and a PRT adapter into the rods and threaded

the adapter to the PRT point holder (see Figure 1). The rods were then retracted by approximately 6 inches to expose a sampling window between the drive point and the PRT point holder. To limit potential for ground surface leakage during vapor sampling, the annular space around the rods was sealed at ground surface with hydrated bentonite. Between sampling locations, the probe's stainless steel parts were cleaned using Liquinox® detergent and potable water. Teflon® tubing was discarded after one use.

Soil gas samples were collected from the temporary probes into 22-milliliter (ml) pre-evacuated glass vials provided by Microseeps, Inc. of Pittsburgh, Pennsylvania. The soil gas sampling procedure consisted of first purging the equivalent of one volume of Teflon® sampling line using a disposable syringe fitted with two stopcock valves. Following purge, about 40 ml of sample was withdrawn from the probe and injected into a vial by piercing its septum with a needle and pressurizing the vial with the sample. The procedure was repeated on a second vial. Between sampling locations, syringes, needles, and stopcock valves were discarded.

The vials were shipped to Microseeps for analysis of PCE and its common breakdown compounds by gas chromatography/electron capture detector (GC/ECD). For quality control purposes, we also prepared blind duplicate samples, which were obtained by collecting a second pair of vials at selected sampling locations; and equipment blanks, which were prepared by collecting and injecting ambient air into a pair of vials using a single-use syringe, stopcock valve, and needle.

2.2 Sampling from Permanent Probes Using Canisters

Following vial collection and retrieval of the stainless steel rods, twelve of the temporary probes (with depths ranging from 3.4 to 5 ft) were finished with permanent probes (referred to as soil gas monitoring implants) by lowering a 6-in long, 1/4-in diameter stainless steel screen connected to 1/4-in diameter stainless steel tubing in each exploration and threading the screen to the remaining drive point at the bottom of the exploration (see Figure 2). Glass beads were poured around the screen as filter pack to approximately 6 in above the top of the screen. The remainder of each borehole was filled with hydrated bentonite chips to within approximately 6 inches of the ground surface where a road box was installed and set in concrete. Leak testing was later conducted with helium tracer gas to confirm the integrity of the installation.

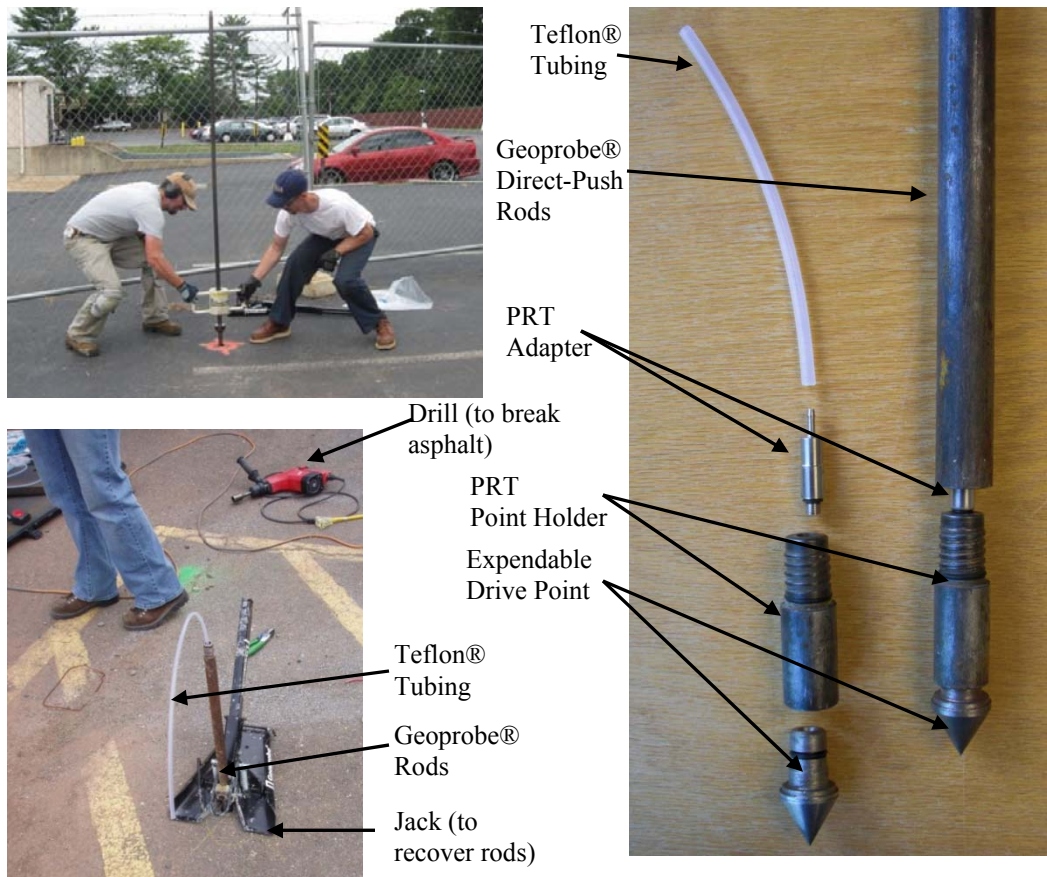


Figure 1. Installation of temporary soil gas sampling probe.

About a month following implant installation, we collected soil gas samples using 1-liter, stainless-steel, pre-evacuated Summa canisters and 1-hour capillary column flow controllers (Air Toxics Ltd., 2010) provided by Air Toxics Ltd. of Folsom, California ATL. The canisters were individually certified clean for the list of target compounds. The typical sampling procedure consisted of connecting a short section of Teflon® tubing to the implant using Swagelok® stainless steel compression fittings (see Figure 2); purging the implant of the equivalent of one volume (corresponding to the length of the implant and attached tubing) using a disposable syringe; connecting the canister and collecting the sample over an hour during which the canister vacuum dropped from about 30 inches of mercury (in Hg) to about 5 in Hg. The canisters were submitted for analysis of PCE and its common breakdown products by gas chromatography/mass spectrometry (GC/MS) (USEPA, 1999).

Between sampling locations, reusable sampling equipment, such as Swagelok® fittings and valves were cleaned using Liquinox® detergent and potable water. Teflon® tubing and Swagelok® ferrules were discarded after use. Flow controllers were used only once before being returned to the laboratory.

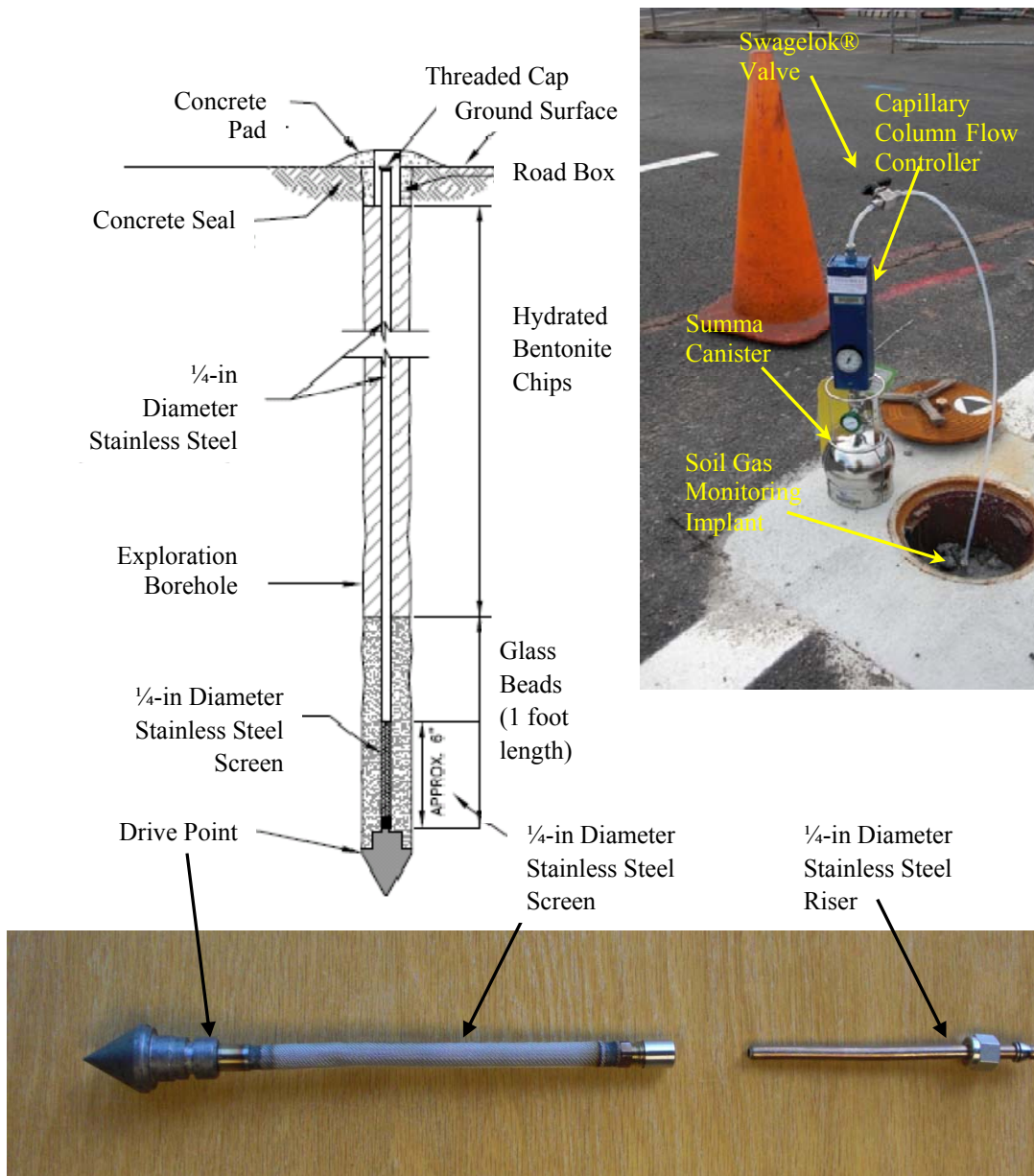


Figure 2. Installation and sampling of soil gas monitoring implant.

Blind duplicate samples were collected using pairs of canisters and flow controllers connected in parallel with a Swagelok® “T” fitting. Two-hour flow controllers were used to maintain a sample collection rate similar to that of a single canister equipped with a 1-hour flow controller. We also collected equipment blanks, which were prepared in the field by connecting a laboratory-provided canister filled with nitrogen to a regular sample canister and flow controller. The equipment blank was submitted for analysis along with the other canisters.

3. RESULTS AND DISCUSSION

3.1 Comparison of Vial and Canister Data

To compare sampling methods, we evaluated the relative percent difference (RPD) between results for a given sample analyte using the following equation:

$$RPD = \frac{|c_1 - c_2|}{(c_1 + c_2)/2} \times 100\% , \quad (1)$$

where *RPD* is the relative percent difference and c_1 and c_2 indicate the analyte concentration in the vial sample and canister sample, respectively.

Figure 3 presents a graphic comparison of PCE analytical results associated with canister samples (along the y-axis) and vial samples (along the x-axis). As illustrated by the figure, PCE concentrations in canister samples are comparable to those obtained using vial samples. Where PCE was detected in both the vial and canister samples, agreement is typically within the same order of magnitude, as delimited by the band representing the 100% *RPD* between sample pairs. In most instances where PCE is below the detection limit in a sample obtained using vials (about half of the 12 samples), PCE is either below detection limit in the companion canister sample or detected at a concentration comprised between the canister detection limit and the vial detection limit.

While most concentrations fall within the same order of magnitude, differences in concentration are to be expected. The samples were collected at different times and using different means. They were analyzed by two different labs using different analytical methods. The samples are also different in volume. For perspective, the vial sample contains approximately 40 ml of gas and is collected in a few seconds as a grab sample. In contrast, the canister sample is equivalent to about 800 ml of gas and is collected over an hour (flow rate of 13.3 ml per minute). Assuming that the gas comes from air-filled porosity associated

with fracturing, and considering site subsurface conditions, a canister sample may draw gas from a subsurface volume equivalent to a sphere with a radius on the order of 1 foot, while the sphere of influence of the vial sample will only extend to about a third of that radius. In practice, the gross volume of subsurface is unlikely to be spherical or regularly shaped.

3.2 Observed Seasonal Variations

In Figures 4 and 5, we present PCE concentrations recorded in bimonthly sampling of soil gas monitoring implants. Each of the selected implants was sampled 4 to 6 times over the course of about one year using the canister sampling method summarized in Section 2.2.

Figure 4 shows the range of PCE concentrations obtained for six selected implants. Each vertical bar represents the minimum, maximum and median PCE concentrations measured in canister samples during the one-year period. For perspective, the figure also shows the vial-canister data pairs presented in Figure 3. Figure 5 shows changes in PCE concentration as a function of time for three implants selected from Figure 4.

The analytical results show changes in PCE concentration by about one half to two orders of magnitude over the course of one year. Of particular interest, PCE concentrations at implant A reach several hundreds of micrograms per cubic meter ($\mu\text{g}/\text{m}^3$), even though PCE was initially below detection limits in both the vial sample and the first canister sample.

Collectively, the data presented herein suggest that one sampling event may be insufficient to properly assess VOC vapor conditions. The results also show that the difference in PCE concentrations measured in the vial sample and the initial canister sample is small relative to the change in PCE concentration observed over time at a given location.

Seasonal variations in soil gas concentrations, especially at depths close to the surface, have been reported previously (ITRC, 2007) and are attributed to changes in temperature, precipitation, and soil moisture cycling in the vadose zone. For the subject site, we believe that soil gas concentration variations in excess of one order of magnitude can be further attributed to the heterogeneous nature and low effective porosity of the fractured sedimentary rock and saprolite soil.

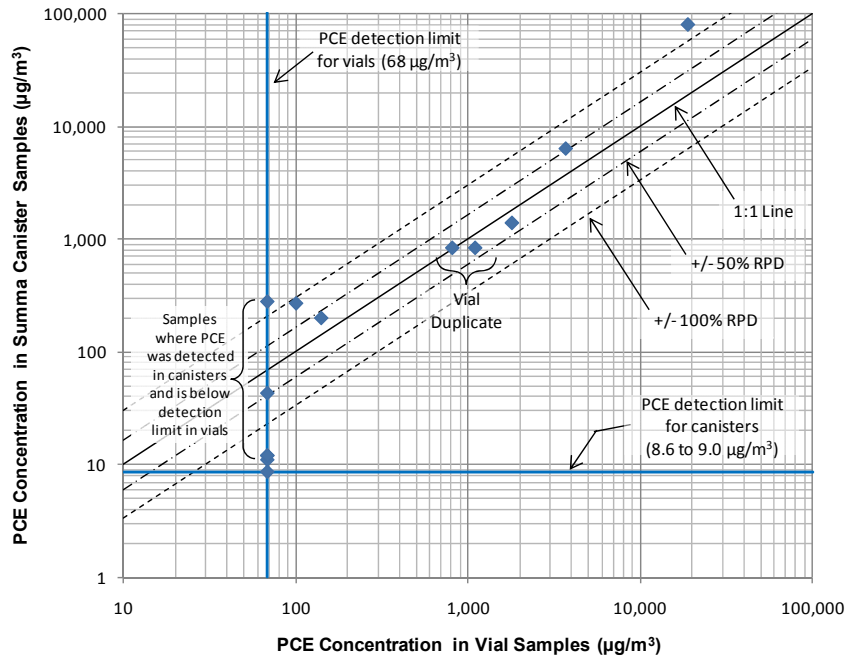


Figure 3. Comparison of PCE concentrations from vial and canister samples.

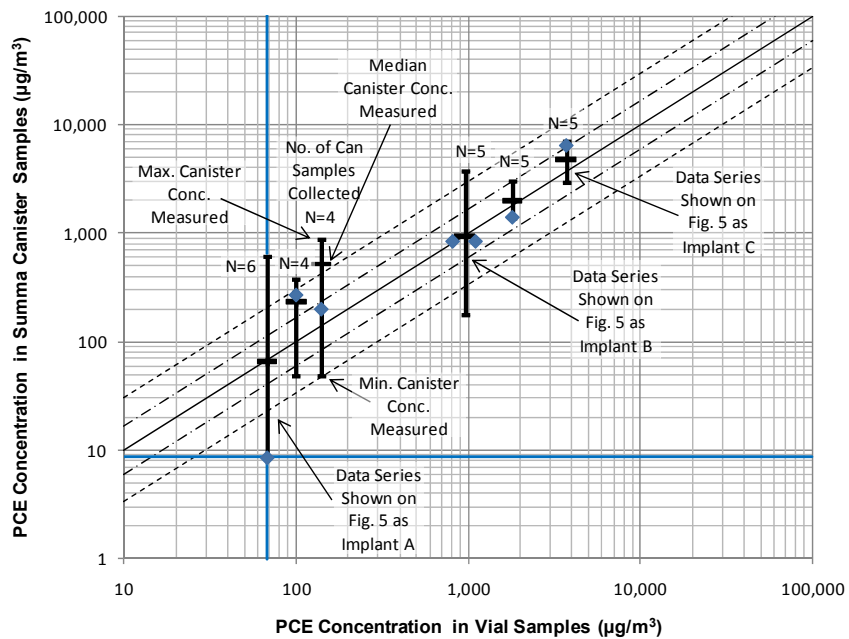


Figure 4. Range of PCE concentrations in samples collected bimonthly at selected soil gas monitoring implants.

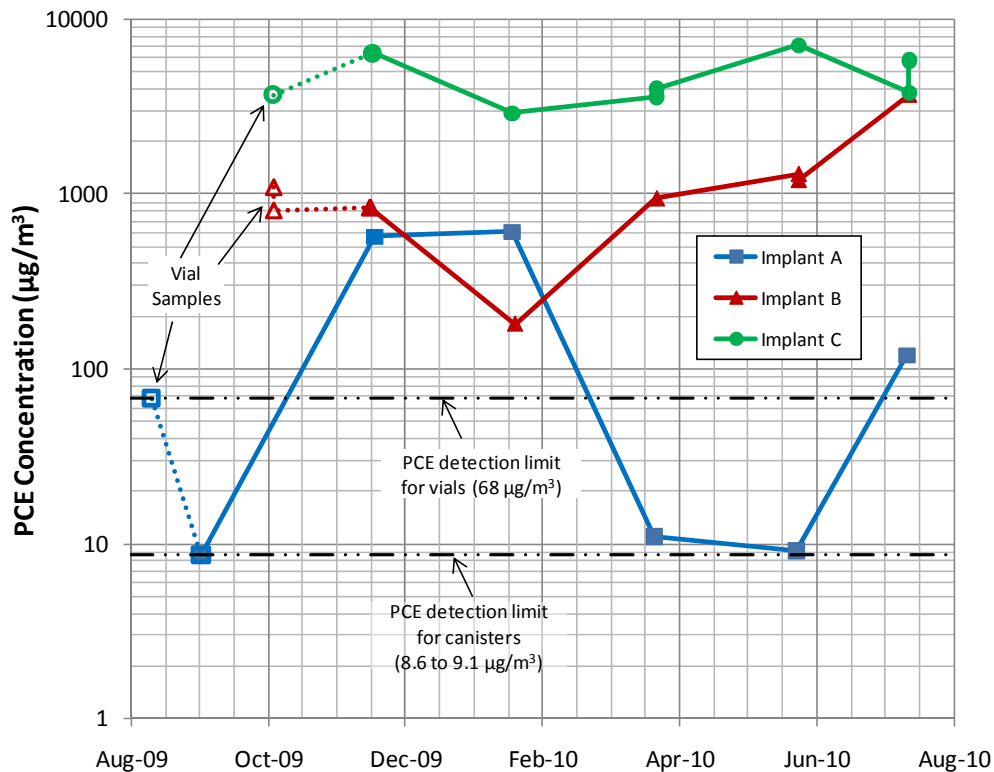


Figure 5. PCE concentration recorded in bimonthly sampling of selected soil gas monitoring implants.

3.3 Comparison of Method Precision

Precision is the degree of agreement among repeated measurements of the same characteristic (e.g. analyte concentration) under the same or similar conditions. Precision data provide an indication of the consistency and reproducibility of field sampling and analytical procedures. For canister sampling, precision is assessed by analyzing blind duplicate samples collected in the field using two canisters connected in parallel (see Section 2.2). For vial sampling, the duplicate soil gas sample is collected into a second pair of vials.

To evaluate sampling method precision, we calculated the *RPD* for the duplicate sampling results using equation (1) where c_1 and c_2 now refer to the original and duplicate sample concentrations, respectively.

Figure 6 provides a graphical comparison of blind duplicate samples collected into vials and canisters. The canister dataset includes 21 soil gas sample pairs for which one to three analytes were detected, including PCE, trichloroethene (TCE)

and cis-1,2-dichloroethene (35 data points). The vial dataset includes 4 soil gas sample pairs for which one to three analytes were detected (9 data points).

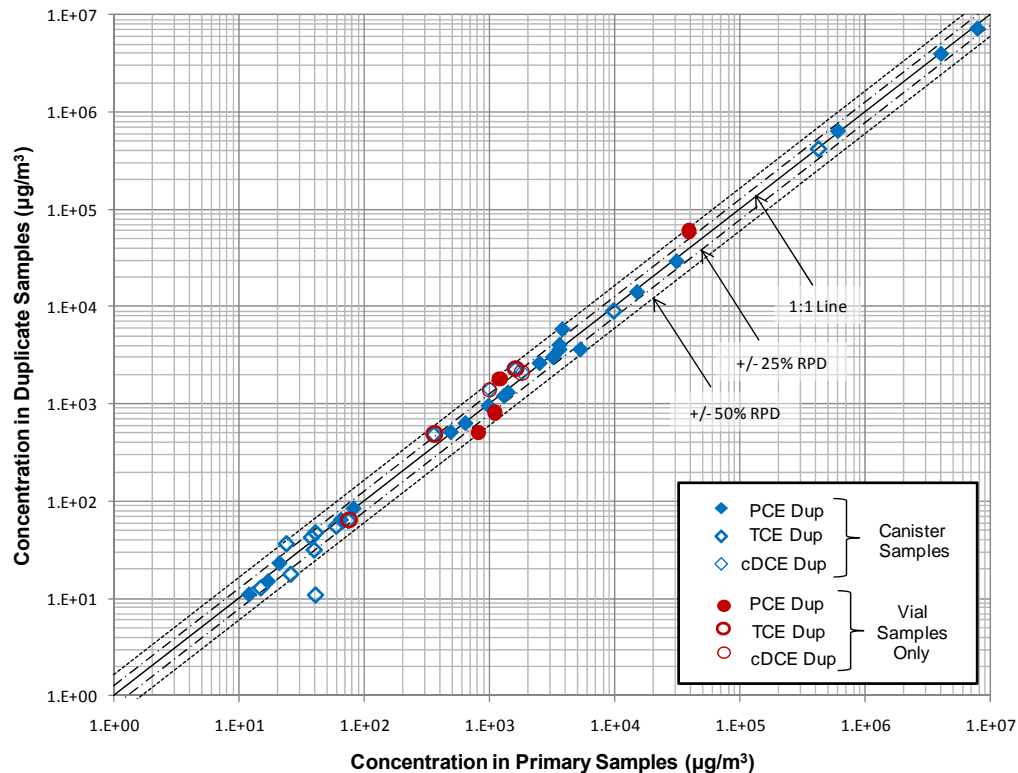


Figure 6. Comparison of blind duplicates samples collected with vials and canisters.

Overall, most duplicate pairs fall within an RPD of 50%. The RPD associated with vial duplicate pairs range from 15% to 45% (average 32% and median 34%). The range of RPDs associated with canister duplicate samples is larger with RPDs from 0 to 115% (average 16% and median 7%).

4. CONCLUSION

Comparison of soil gas data obtained as part of a vial and canister sampling program suggest that vial samples can provide a cost effective and relatively reliable way of gathering subsurface survey data:

- Despite the lesser sensitivity (i.e., higher detection limit) achieved in this case by vial sampling relative to canister sampling, concentrations of PCE from

vial samples, where detected, were found to be in generally good agreement with canister sampling results.

- Where long-term soil gas monitoring was conducted, changes in PCE concentration in canister samples collected at different times were found to be greater than differences in results that may initially exist between canisters and vials. This result suggests that one canister sampling event alone may not be sufficient to assess subsurface conditions and that multiple instances of vial sampling may prove a cost effective way of assessing subsurface conditions over different seasonal conditions.

5. ACKNOWLEDGMENTS

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