CONTAMINATED SOILS, SEDIMENTS, WATER AND ENERGY

Volume 17

CONTAMINATED SOILS, SEDIMENTS, WATER, AND ENERGY
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Heavy Metals
Indoor Air
Remediation
Risk Assessment
Sediments
Site Assessment

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Foreword

Way back in the mid-1980s, a small meeting in the Northeastern US was launched that was intended primarily to highlight issues related to petroleum-contaminated soils. Now known as the Annual International Conference on Soils, Sediments, Water, and Energy, that modest initial scientific forum began a very impressive run, which most recently was represented by the 27th event in October 2011. Hosted by the University of Massachusetts in Amherst, this conference is recognized as being among the most significant and influential environmental conferences in the world, and recently has drawn in the range of 200 presentations/posters, and 600 to 900 participants each year. This has translated to a total of nearly 20,000 attendees from well over 40 countries, and the United States has been represented by nearly all of the 50 states in over a quarter century.

The Conference prides itself on establishing and promoting interactions of all kinds. With important local, regional and global environmental events such as the Gulf Oil Spill, the Japanese earthquake/tsunami, and others occurring worldwide with unfortunate regularity, a conference such as this provides an essential service to the scientific community. That fact is well-illustrated by the array of subjects addressed at the 2011 Conference, which touched on such topics as site investigation approaches, innovative remedial strategies and techniques, vapor intrusion, petroleum, environmental forensics, air quality, military installations, risk assessment, heavy metals, nanotechnology, hydrogeology, manufactured gas plants, and numerous specific workshops, poster sessions and invited addresses. Also well-represented in the presentations and exhibitor booths were many analytical laboratories, technical consultants, regulatory agency personnel, and members of the legal community. This year's Proceedings, which cover indoor air quality, remediation, risk assessment, sediment quality, and heavy metals, are just a snapshot of the broad expanse of technical materials covered by the Conference. The treatment of new ideas and approaches to environmental problems, as well as possible new avenues of research and practical resolution, has always been a hallmark of the Conference, whether in the platform sessions, more informal and discussion-oriented poster sessions, or even during coffee breaks and dinner. It is in those discussions that much of the actual progress occurs and many of the intellectual connections are forged.

It is a personal and professional pleasure to introduce this latest volume in a long-running series that dates back in various forms to 1986. As in past years, the editors, sponsors, conference staff, the Scientific Advisory Boards, and the AEHS Foundation are to be congratulated on the continuation and improvements to a great and influential tradition in our field.

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About the Editors

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.

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

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

Dr. Kostecki is a Professor in the School of Public health & Health Sciences and served as Vice Provost for Research and Vice Chancellor for Research and Engagement at the University of Massachusetts Amherst from September, 2003 to August, 2009. He served as Special Advisor for the Clean Energy China Initiative, Office of the President, University of Massachusetts from 2009 – 2011. He is presently the Director for Online Education at Simmons College.

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

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

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

Christopher Teaf is a Board-certified toxicologist with broad experience in evaluation of potential effects from chemical exposures related to industrial facilities, agriculture, waste management facilities, power generation, educational institutions, and products in general commerce. Dr. Teaf has served on the faculty of the Center for Biomedical & Toxicological Research at Florida State University since 1979, and as Director of Toxicology for Hazardous Substance & Waste Management Research since 1985.

Chris' areas of interest include risk assessments under environmental and occupational elements of federal, state or local regulations, risk communication, and development of risk-based targets to guide remedial actions. He has extensive experience in evaluation of environmental fate and potential health effects from petroleum, solvents, metals, pesticides, pharmaceuticals, biological agents (e.g., mold, microbes) and physical agents (e.g., particulates, asbestos. For over 30 years, he has directed or conducted research in environmental and occupational toxicology for the World Health Organization, NATO, U.S. EPA, U.S. Air Force, U.S. Department of Agriculture (USDA), Florida Department of Environmental Protection, Florida Department of Health, Florida Department of Community Affairs, and Agency for Toxic Substances & Disease Registry (ATSDR), among others. He served as Toxicologist for the Florida Landfill Technical Advisory Group and the state Petroleum Technical Advisory Committee. He served on the Florida Governor's Financial and Technical Advisory Committee and was Chair of the Toxic Substances Advisory Council for the Florida Department of Labor. Chris has organized and taught many graduate and undergraduate courses and technical seminars for presentation to universities as well as international, federal, state and local agencies. He has served as the Chairman of the Dog Island Conservation District since 2004.

Dr. Teaf has served on editorial boards or as peer reviewer for a variety of journals and is Senior Editor for Human Health of the international journal *Human & Ecological Risk Assessment*. In addition to training, research and advisory services to many environmental agencies and private sector firms, he has provided environmental and toxicological services to the U.S. Attorney, Florida State Attorney, and Attorneys General of FL, OK, and WA. Chris has been qualified to testify in federal and state court, as well as administrative proceedings, in a number of states regarding toxicology, health risk assessment, and environmental chemistry.

Dave Ludwig has a Bachelor's of Science from Rutgers University, a master's in Marine Ecology from the Virginia Institute of Marine Sciences, and a doctorate in ecology from the Institute of Ecology at the University of Georgia. He is a systems ecologist by training and an applied environmental scientist and restorationist by trade.

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: Heavy Metals

Chapter 1

CHARACTERISTICS OF SOILS AND HEAVY METAL CONTENT OF VEGETATION IN OIL SPILL IMPACTED LAND IN NIGERIA

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ABSTRACT

This study examined the impact of an oil spill on soil characteristics and heavy metal content of vegetation. Soil and vegetation were sampled using a 1 metre square quadrant at distances of 1 m, 10 m, 20 m and 30 m from the oil spill. After vegetation identification, they were separated into leaves, stems and roots. Analysis of soil characteristics and heavy metals (Pb, Cd and Zn) content of the vegetation was carried out. The data were analyzed using descriptive statistics and ANOVA. *Calopogonium mucunoides, Axonopus compressus and Sida acuta* were identified. Leaves had higher heavy metals content followed by stems and roots. Concentrations of heavy metals in the soils with respect to distances were in the order of 1 m > 10 m > 20 m > 30 m. Soil organic carbon content ranged from 18.75 – 27. 30 g/kg. The soils heavy metal concentrations ranged from 0.10 – 0.18 mgCd/kg, 0.34 – 0.46 mgZn/kg and 0.28 – 0.44 mgPb/kg.

Key words: Soils characteristics; Vegetation; Heavy metals; Oil impacted land

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1. INTRODUCTION

The amount of oil produced and transported between points of production, processing and distribution, or export terminals, has greatly increased as the demand of and dependence on oil has increased. Although this increase in oil production level contributes to Nigeria's economic growth, it also presents increased potential for environmental pollution and degradation. Contamination of soils with crude oil and refinery products is becoming an ever-increasing problem especially in the light of several breakdowns of oil pipelines and wells and distribution of petroleum-based products (Song and Barhta, 1990; Amadi et al., 1996; Jorgensen et al., 2000). Nigerian crude oil is known to have about 0.003 – 42.31 mg/kg of transition metals (V, Cr, Mn, Fe, Co, Ni and Cu) (Nwachukwu et al., 1995); some of which can not be completely removed during the crude refining processes. Once they enter ecosystems, petroleum-based products initiate a series of processes, affecting both biotic and abiotic elements (Malachowska-Jutsz et al., 1997). Oil spills on land may lead to retardation of vegetation growth and causes infertility of soil for a long period of time until natural processes re-establish stability (Sparrow and Sparrow, 1988; Racine, 1993; Wyszkowska et al., 2001). Several studies have shown that metals, such as Pb, Cd, and Ni, are responsible for certain diseases of man and animals (Gustav, 1974). Thus, there is need to clean up oil contaminated soil. Conventional remedial methods include removal of the contaminated soil from the sites, covering the contaminated area with barren soils or impervious cover, remediation in situ to remove contaminants and remediation by reducing bioavailability. (Gleseler, 1987). Remediation by conventional technologies is very expensive (Salt et al., 1995). Therefore, comparatively cheaper and feasible sustainable methods of pollutant removal from soil are necessary. Phytoremediation has emerged as an alternative to the engineering-based methods. In this approach, plants are used to absorb contaminants from the soil and translocate them to the roots, stalk or shoot. The metal-rich plant material may be safely harvested and removed from the site without extensive excavation, disposal cost and loss of top soil associated with traditional remediation practices (Blaylock et al., 1997, Joner et al., 2004). Rock and Sayre (1998) estimated phytoremediation clean up costs of \$ 162 per m^3 compared to \$ 810 per m^3 for excavation and incineration. Identification of plants growing in oil spill impacted land is of prime importance in order to establish suitable plants for the clean up of such oil spills. The objective of this study was to examine the impact of oil spill on soil characteristics and heavy metal content of vegetation growing on the impacted land.

2. MATERIALS AND METHODS

2.1 Study area

This study was carried out at the Atlas Cove-Mosimi Pipeline Right of Way, Mosimi, Sagamu, Ogun State, Nigeria on latitude 6º 45' 18" N, longitude 3º 33' 5" E, at altitude of 77 m.

2.2 Soil and plant sampling

Plants growing along the pipeline were sampled using a 1 m square quadrant at distances of 1 m, 10 m, 20 m and 30 m away from the edge of the pipeline. Vegetation within the quadrant was identified and samples were uprooted for laboratory analysis. Each vegetation sample was replicated three times. The plant samples were kept in labeled polyethylene bags and taken to the laboratory for analysis. Composite soil samples were taken at similar distances (1 m, 10 m, 20 m and 30 m) away from the edge of the pipeline. Ten core samples randomly distributed around the observation points were taken with the aid of stainless steel Dutch auger and bulked. Sampling depths were 0 – 15 cm and 15 – 30 cm, which represent the main feeding zones of the plant roots. Each composite soil sample was replicated three times along each road and the samples were kept in labeled polyethylene bags.

2.3 Chemical analysis

Soil samples were air dried, crushed and passed through a 2 mm sieve. Soil pH was determined using a hand-held HANNA pH meter (Model number HI 98129, Hanna Instruments, California, USA) in distilled water according to Thomas (1996). Soil organic carbon was determined by the chromic acid digestion method of Walkley and Black as reported by Sparks (1996). The total N concentration was determined by the Macro-kjeldahl method according to Bremner (1996). Available P was determined by Bray-I method as described by Kuo (1996). Exchangeable Ca, Mg, K and Na were extracted with neutral normal ammonium acetate buffer according to Helmke and Sparks (1996). K and Na were determined using a Flame Photometer (Jenway, Gransmore Green, Felsted, Dunmow, Essex, CM6 3LB, England) and exchangeable Ca and Mg by Atomic Absorption Spectrophotometer (AAS, Varian SpectrAA-400plus, Varian Techtron Pty limited Mulgrave, Victoria, Australia). Flame Photometer was calibrated for each metal using standard solution of known concentrations (5 ppm, 10 ppm, 15 ppm and 20 ppm of sodium chloride and potassium chloride) while serial standard ranging from 0.03 ppm to 24 ppm were prepared from 1000 ppm industrially prepared standards and used to calibrate the AAS to get line of best fit before analysis. To determine soil heavy metals (Pb, Cd and Zn) content, one gram of the soil sample (< 2 mm fraction) was digested in 1:1 mixture of concentrated nitric and perchloric acids and the mixture was heated over a water bath in a fume cupboard. The solution was heated to dryness and the residue was re-dissolved in 5 ml of 2.0 M HCL as in Ure (1990). The mixture was finally filtered (Whatman No. 40). The resultant extracts were analyzed for the heavy metals using AAS (APHA - AWWA - WPCF, 1980).

The plant samples were placed under running tap to wash off soil particles and oven-dried at 80 ^{0}C for 48 hours. Each sample of the dried plant materials was ground to a fine powder using a laboratory stainless steel hammer mill in order to pass through 1 mm aperture screen. Ground plant samples were collected in polythene bags and kept in desiccator. For the determination of heavy metals, 2 g of each ground sample was accurately weighed into clean platinum crucibles, ashed at 450 °C and then cooled to room temperature in a desiccator. The ash was completely dissolved in 5 ml of 20 % HCl which was then made up to volume (50 ml) while 0.3 g was digested with 4 ml of concentrated sulphuric acid along with drops of hydrogen peroxide for the determination of exchangeable bases (Na, K, Ca and Mg) (Alloway, 1995). Analysis of the digest for the metals content was carried out using AAS.

2.4 Statistical analysis

Data were analyzed using descriptive statistics and Analysis of Variance (ANOVA). Test of significance of the means was by the Least Significant Difference (LSD).

3. RESULTS AND DISCUSSION

3.1 Plant identification at various distances from point of oil spill

Calopogonium mucunoides, *Axonopus compressus* and *Sida acuta* were identified in the oil spill impacted area. *Calopogonium mucunoides* was identified at every distance except 30 m away from the source of pollution (Table 1). These three plant species were able to tolerate the toxicity of oil spill. Prasad and Feitas (2003) identified *Fabaceae*, *Poaceae*, *Euphorbiaceae* and *Flacourtiaceae* as potential hyperaccumulators of heavy metals. Similarly, Bada and Raji (2010) observed that *Malvaceae* absorbed heavy metal from contaminated soil.

Table 1. Plant species encountered on the field

Distance (m)	Family	Plant species	Common name
1	Fabaceae	*Calopogonium mucunoides*	Calopo
	Poaceae	*Axonopus compressus*	Carpet grass
10	Fabaceae	*Calopogonium mucunoides*	Calopo
	Malvaceae	*Sida acuta*	Broom weed
20	Fabaceae	*Calopogonium mucunoides*	Calopo
30	Malvaceae	*Sida acuta*	Broom weed

3.2 Heavy metals and exchangeable cations in plant species

Calopogonium mucunoides at 1 m away from source of oil spill had the highest Cd, Zn and Pb followed by *Axonopus compressus* at 1 m and *Calopogonium mucunoides* at 10 m (Table 2). The levels of heavy metals in the plants decreased with distance away from the point of pollution, as reported by Amusan et al. (2003). This might be due to the proximity of the plants to the source of oil spill. Two basic strategies to explain heavy metal tolerance, metal exclusion and metal accumulator, have been identified (Baker, 1981; Steinborn and Breen, 1999; Yanqun et al., 2004). The excluders prevent metal uptake into roots, avoiding translocation and accumulation in shoots (De Voss et al., 1991). These plants have a low potential for metal extraction but could be used to stabilize the soil. Accumulators concentrate heavy metals in their shoots at both low and high soil metal concentrations and are utilized in extracting heavy metals from contaminated soils (Rotkittikhun et al., 2006). In plants that accumulate heavy metals, shoot/root quotients greater than 1 are commonly reported, while shoot/root quotients less than 1 characterize heavy metal excluders (Ogundiran and Osibanjo, 2008). *Calopogonium mucunoides*, *Axonopus compressus* and *Sida acuta* were potential Zn and Pb accumulators while *Calopogonium mucunoides* and *Axonopus compressus* were Cd accumulators (Table 3); shoot/root quotient greater than 1 (Ogundiran and Osibanjo, 2008). Significantly ($p < 0.05$) higher exchangeable bases (Na, K, Mg and Ca) were observed in the *Sida acuta* at 30 m away from the point of oil spill (Table 2). Significantly ($p < 0.05$) higher Na was observed in the roots, while leaves had higher concentrations of K, Mg and Ca. Contrary to heavy metals, concentration of exchangeable bases increased with distance away from the point of the oil spill. This might result from the degradation of the soil exchangeable bases close to the point of the oil spill. Oil spills on land may lead to infertility of soil for a long period of time until natural processes re-establish stability (Wyszkowska et al., 2001). *Calopogonium mucunoides* and *Axonopus compressus* were exchangeable bases accumulators while Sida *acuta* was a potential Na excluder (Table 3); shoot/root quotient less than 1 (Ogundiran and Osibanjo, 2008)

3.3 Effects of oil spill on soil characteristics

Soil acidity decreased with distance from the point of the oil spill. It also decreased with soil depth except at 30 m away (Table 4). The negative effect of oil on the soil pH can be attributed to the change in soil biochemistry (Atuanya, 1987). Atuanya (1987) confirmed that oil may alter soil biochemistry parameters such as pH, oxygen and nutrient availability. Also, the reduction in the soil pH might be attributed to the production of organic acids by microbial metabolism (Osuji and Nwoye, 2007). However, soil organic carbon content generally increased with distance and it decreased with soil depth (Table 4). Decrease in the organic carbon content close to the point of the oil spill might be due to reduced soil fertility. Oil spills on land may lead to infertility of soil for a long period of time until natural processes re-establish stability (Wyszkowska et al., 2001). Higher heavy metals contents were observed in the soil very close to the source of pollution and this decreased with soil depth (Table 4). The higher metal content might be due to proximity to the source of pollution. Nigerian crude oil contains heavy metals which are not completely removed during refining processes (Nwachukwu et al., 1995). Exchangeable bases increased with distance and decreased with soil depth (Table 4).

5. CONCLUSION

We demonstrate that an oil spill increased acidity and heavy metal content of the soil. It reduced soil organic carbon and exchangeable bases. *Calopogonium mucunoides*, *Axonopus compressus* and *Sida acuta* were identified from oil spill impacted land and contained Pb, Cd, Zn. Phytoremediation of heavy metal contaminated soil can be achieved by the use of these plants.

Table 2. Metals (mg/kg) contents of plant parts collected from oil impacted area

Distance (m)	**Plant species**	**Plant parts**	**Cd**	**Zn**	**Pb**	**Na**	**K**	**Mg**	**Ca**
1	*C. mucunoides*	Root	0.13	0.87	0.30	7.41	2.52	23.96	47.25
		Stem	0.15	1.00	0.37	4.91	2.69	24.30	54.15
		Leaf	0.21	1.44	0.39	4.23	2.69	27.02	56.75
	A. compressus	Root	0.12	0.71	0.28	4.18	1.79	7.80	38.90
		Stem	0.14	0.87	0.35	3.56	2.37	19.82	41.91
		Leaf	0.17	1.29	0.37	7.64	2.51	23.06	43.71
10	*C. mucunoides*	Root	nd	0.62	0.14	7.63	2.97	31.06	56.87
		Stem	0.10	0.63	0.22	5.05	3.00	33.26	61.90
		Leaf	0.12	0.69	0.27	5.44	3.18	33.88	63.44
	S. acuta	Root	nd	0.59	0.09	12.19	3.32	36.51	65.82
		Stem	0.01	0.62	0.22	4.57	3.50	39.07	80.40
		Leaf	0.11	0.63	0.25	4.75	3.77	44.09	82.44
20	*C. mucunoides*	Root	nd	0.44	0.02	9.31	3.94	47.78	84.39
		Stem	nd	0.48	0.05	5.98	4.29	50.10	99.12
		Leaf	nd	0.58	0.05	5.19	4.35	53.83	102.20
30	*S. acuta*	Root	nd	0.33	nd	49.86	6.36	56.71	107.26
		Stem	nd	0.41	0.01	4.41	8.09	69.84	163.08
		Leaf	nd	0.43	0.02	4.59	26.46	72.66	212.36
		LSD	0.05	0.53	0.11	2.68	1.50	22.85	60.26

nd = not detected

Table 3. Shoot/Root quotient of plants collected from oil contaminated area

Distance	**Plant species**	**Cd**	**Zn**	**Pb**	**Na**	**K**	**Mg**	**Ca**
1	*C. mucunoides*	2.79	2.80	2.53	1.23	2.13	2.14	2.35
	A. compressus	2.53	3.04	2.57	2.68	2.73	5.50	2.20
10	*C. mucunoides*	nd	2.13	3.50	1.37	2.08	2.16	2.20
	S. acuta	nd	2.12	5.22	0.76	2.19	2.28	2.47
20	*C. mucunoides*	nd	2.41	5.00	1.20	2.19	2.18	2.39
30	*S. acuta*	nd	2.55	nd	0.18	5.43	2.51	3.50

nd = not determined

Table 4. Selected soil characteristics in the oil impacted area

Distance (m)	**Soil depths (cm)**	**pH**	**Organic carbon (g/kg)**	**Cd (mg/kg)**	**Zn (mg/kg)**	**Pb (mg/kg)**	**Na (cmol/kg)**	**K (cmol/kg)**	**Mg (cmol/kg)**	**Ca (cmol/kg)**
1	0-15	5.38	21.20	0.18	0.46	0.44	2.42	1.22	4.96	13.52
	15-30	5.76	18.75	0.14	0.39	0.34	2.22	1.14	3.57	6.91
10	0-15	5.79	23.80	0.17	0.43	0.40	3.03	1.67	6.36	20.00
	15-30	5.79	23.60	0.13	0.38	0.33	2.73	1.38	5.36	14.10
20	0-15	5.96	25.30	0.16	0.40	0.39	3.06	1.71	6.70	24.76
	15-30	6.07	24.40	0.13	0.38	0.31	2.91	1.41	6.24	18.74
30	0-15	6.51	27.30	0.11	0.36	0.29	9.60	2.26	7.10	27.63
	15-30	6.31	25.90	0.10	0.34	0.28	2.97	1.52	6.28	19.71
	LSD	0.47	2.32	0.09	0.04	0.08	0.90	0.36	0.64	3.10

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Chapter 2

ASSESSING THE BIOAVAILABILITY OF ARSENIC IN SEDIMENTS FOR USE IN HUMAN HEALTH RISK ASSESSMENT

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ABSTRACT

Arsenic concentrations in sediments in a wetlands located downgradient from a landfill in northeastern Massachusetts were found to be over 1,000 mg/kg in several locations with a maximum detected concentration of 4,500 mg/kg. The elevated arsenic in sediment is likely the result of the dissolution of iron and arsenic in the underlying rock under reducing conditions mobilized with the groundwater and co-precipitating out into the sediments when groundwater reaches the oxidizing surface water, producing an iron and arsenic bearing floc. Approximately 15 acres of wetlands appear to be impacted from elevated arsenic concentrations. To assess the potential impacts to human health and to determine the extent of acreage requiring remedial action, a site-specific bioavailability factor was developed using an *in vitro* laboratory assessment. While *in vivo* (live animal) studies are considered to be the most accurate measures of bioavailability for assessing absorption of contaminants by humans, the *in vivo* studies are expensive and lengthy. The *in vitro* approach undertaken for this assessment simulates digestive activity in the stomach, including residence time, pH, temperature, agitation, and solid to liquid ratio. This *in vitro* laboratory approach coupled with an adjustment based on *in vivo* data, along with a mineralogical characterization of the impacted sediments, served to develop a site-specific bioavailability factor that resulted in more accurate human health risk characterization results.

Keywords: arsenic, bioavailability, sediment, risk assessment

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1. INTRODUCTION

Arsenic concentrations in sediments in a wetlands located downgradient from a landfill in northeastern Massachusetts, where arsenic occurs naturally in high concentrations in bedrock were found to be over 1,000 mg/kg in several locations with a maximum detected concentration of 4,500 mg/kg. The elevated arsenic in sediment is likely the result of the dissolution of arsenic and iron in the underlying rock under reducing conditions mobilized with the groundwater and co-precipitating out into the sediments when groundwater reaches the oxidizing surface water, producing an iron and arsenic bearing floc. Approximately 15 acres of wetlands sediments appear to be impacted from elevated arsenic concentrations. To assess the potential impacts to human health, and to determine the extent of acreage requiring remedial action, a site-specific arsenic bioavailability factor was developed using an *in vitro* laboratory assessment supported by other lines of evidence of reduced bioavailability.

2. SITE HISTORY

The landfill began operating shortly after the end of World War II. Historical mapping of the landfill area shows that the site operated as a gravel pit around this same period of time. Dumping was conducted in an "open face" manner by filling in old gravel pits until the early 1960s. Open burning in these pits was the primary method of waste disposal. The landfill was used for disposal of residential, commercial, industrial, and construction demolition wastes. Leachate from the landfill impacted a series of streams in a wetland area adjacent to the landfill. In 1973, an underdrain system was constructed as a pollution control measure to limit the amount of leachate entering the adjacent wetlands, and the landfill was closed to further solid waste disposal. The landfill site continued to be used as a recycling center and for the controlled disposal of leaves, brush and grass cuttings. In the 1980s, soils were used to cover the northern section of the site and ballfields were constructed.

3. CONCEPTUAL SITE MODEL

Typically, organic matter contained within landfills produces a deoxygenated (reducing) environment in groundwater beneath and directly downgradient of the landfill. This removal of oxygen is caused by the degradation of the organic matter by native microorganisms, a process that requires oxygen. Under reducing conditions, metals such as arsenic and iron in the solid phase aquifer materials dissolve into the aqueous phase and become mobilized in groundwater. The source of metals may be natural (i.e., contained within soil and rock formations or as coatings on the surface of aquifer materials), landfilled waste, or some other unknown source. In general, when groundwater conditions become oxidizing, mobilized metals will typically be removed from solution as a solid precipitate.

At this site, reduced groundwater upwells into the wetland located downgradient of the landfill (i.e., the wetland serves as a point of groundwater discharge). When groundwater reaches the oxidizing surface water environment, iron and arsenic in solution precipitate as solid phase iron oxyhydroxides containing arsenic. The presence of iron and arsenic at concentrations below the laboratory method detection limits in downgradient surface water samples appears to indicate that the iron and arsenic are removed from solution via precipitation. Once the iron and arsenic have been removed from solution, the resulting solid phase particles may be transported further downstream via surface water flow. As a result there are depositional locations with elevated concentrations of iron and arsenic, as shown in Figure 1 below.

Figure 1. Example of iron/arsenic floc in sediment streams downgradient of the landfill.

4. DEFINITION OF BIOAVAILABILITY

Bioavailability is the extent to which a substance can be absorbed by a living organism and can cause an adverse physiological or toxicological response. Bioavailability is particularly relevant for metals, which may exist in a variety of chemical and physical forms, not all of which are readily absorbed by the body when ingested. However, most oral reference doses (RfDs) and cancer slope factors (CSF) used in risk assessment are based on studies in which dose is reported as the amount of chemical ingested rather than absorbed (USEPA, 1989).

Such studies make no assumptions concerning bioavailability. If the form of a chemical in the environment is less than that of the form relevant to toxicology or human epidemiological studies, these toxicity criteria may overestimate the risk. An adjustment for reduced bioavailability of some environmental forms of chemicals is needed in such cases to appropriately evaluate risks (USEPA, 2007).

Oral bioavailability of a substance can be expressed as either absolute bioavailability (ABA), or as relative bioavailability (RBA). ABA is the ratio of the amount of chemical absorbed to the amount ingested. RBA is the ratio of the amount of a test material, such as arsenic in soil, that is absorbed to the amount of an appropriate reference material, such as sodium arsenate. Sodium arsenate is considered an appropriate reference material for arsenic because it is a useful surrogate for the form(s) of arsenic on which oral toxicity criteria for arsenic are based. Sodium arsenate is soluble and available information suggests that it is also almost completely absorbed. Typically both ABA and RBA are expressed as a percent. An ABA is useful for characterizing risk when a RfD and/or CSF are based on an absorbed dose. However, since most toxicity criteria are based on an administered dose rather than an absorbed dose, the ABA of a substance is generally not used in the human health risk assessment process. RBA is useful when the bioavailability of a chemical form relative to the form relevant to critical toxicological or epidemiological studies can be estimated (USEPA, 2007).

5. PROCESS FOR DEVELOPING A SITE-SPECIFIC ARSENIC BIOAVAILABILITY FACTOR

5.1 *In Vitro* Analysis for Estimating RBA

Historically the RBA for arsenic has been determined using *in vivo*, (animal-based) studies. Typically the *in vivo* studies for arsenic have utilized young swine or primates, and have determined RBA coefficients through the comparison of the amount of arsenic ingested versus amount of arsenic excreted or retained in the animal. The *in vivo* studies are very expensive and can take many months to complete, but are generally accepted as the best means of assessing bioavailability. Because of the expense and time requirements of the animal-based studies, researchers have developed an *in vitro*, or laboratory-based method to determine RBA coefficients. The efficacy of the method has been tested via comparisons of results with those of animal studies, mainly studies where young swine were fed arsenic containing soil.

Generally, the *in vitro* method consists of placing the sample medium, such as arsenic impacted soil, into a fluid bath that simulates the human stomach. The amount of arsenic in the bulk sample is then compared to the amount of arsenic that has dissolved into solution and an *in vitro* bioavailability (IVBA) coefficient is calculated. The raw results from the *in vitro* tests are then empirically adjusted to an *in vivo* RBA that is used in the risk assessment. In the *in vivo* studies the amount of arsenic excreted in the urine is plotted as a function of the amount of arsenic administered and a best fit linear regression line through the data is determined. Using the regression slope of 0.6966, the following equation is used to calculate the RBA (University of Colorado, 2011):

$$\textit{in vivo}\ \text{RBA} = 0.6966 \text{ x } \textit{in vitro}\ \text{RBA} + 3.2482$$

Several studies, including one on arsenic impacted sediments from the Aberjona River located in northeastern Massachusetts, have been conducted to assess the correlation between *in vivo* and *in vitro* bioavailability results. These studies suggest that the calculated IVBA is an appropriate screening tool for estimating the relative *in vivo* bioavailability (Brattin and Wahlquist, 2002). For the assessment of this site, results from 12 site samples and two reference (background) samples submitted to the University of Colorado Laboratory for Environmental and Geological Studies (LEGS) for *in vitro* analysis indicated low RBA of arsenic in downgradient wetlands sediments, with reported values ranging from 0.02% to 12.35% as presented in Table 1. The regression was applied to the raw *in vitro* results to approximate an equivalent *in vivo* arsenic RBA coefficient. The regression extrapolated *in vivo* RBA ranged from 3.26% to 9.94% with a 95% UCL value of 7.51%. The regression adjusted results, however, were not accepted by MassDEP. Therefore, a maximum value of raw *in vitro* value of 12.35% was selected, adjusted based on the EPA oral cancer slope factor assuming 98% absorption (USEPA, 2011) (0.1235 / 0.98 = 0.126) and a value of 12.6% RBA was selected for the landfill site as recommended by MassDEP.

The correlation between the *in vivo* and *in vitro* studies for arsenic are not strong enough to warrant using the *in vitro* method as a standalone means for the determination of a site-specific arsenic bioavailability coefficient. Therefore, additional information, such as soil mineralogy and forms of arsenic present in this matrix, is required to demonstrate correlations between the samples analyzed via the *in vitro* method and samples previously analyzed via *in vivo* methods. These soil mineralogy and geochemistry characteristics are typically determined using an electron microprobe (EMP) equipped with various spectrophotometers to identify specific elements and mineral forms.

Table 1. In Vitro Arsenic Bioavailability Analysis Results

Sample	Arsenic Concentration in Soil Sample (µg/kg)	*In Vitro* Bioavailability Coefficient (%)	Equivalent *In Vivo* Bioavailability Coefficient (%)
1	271,318	0.02	3.26
2	56,242	0.10	3.32
3	493,450	1.53	4.32
4	764,705	2.09	4.70
5	650,003	2.58	5.05
6	223,853	2.60	5.06
7	85,347	3.51	5.70
8	870,951	4.34	6.27
9	445,282	4.57	6.43
10	1,779,206	6.81	7.99
11	2,573,631	9.61	9.94
12	144,046	12.35	11.85
reference	4,781	53.64	40.61
reference	7,929	54.42	41.16

5.2 Geophysical Data Analysis

The three geochemical properties most commonly considered in relation to metals bioavailability evaluated using EMP are mineral phase, matrix association, and particle size.

- ***Mineral Phase:*** Refers to the chemical form, or species, in which the metal occurs in minerals composing site soil or sediment. Examples for arsenic include iron oxides, iron and zinc sulfates, iron sulfides, and arsenic bearing phosphates. In general, less soluble mineral phases are associated with low RBA values. Results from the EMP work indicated that 100% of the arsenic in all of the samples was present in a low solubility iron oxyhydroxide phase.
- ***Matrix Association:*** Refers to the physical association of the metal bearing grains with other mineral phases or matrices that may limit contact of the metal bearing grain with gastrointestinal fluids. Metal bearing grains that are entirely free in the soil are referred to as "liberated,"

whereas grains that are bound together are referred to as "cemented." Particles that exist in a secondary phase coating are referred to as "rimming." Metal bearing grains that are fully encased or cemented are essentially isolated from gastrointestinal fluid, are not believed to be available for dissolution and adsorption, and thus are typically associated with lower RBA. The most common matrix association of the arsenic containing particles at this site was liberated.

- ***Particle Size:*** Metals bearing particles occur in a large variety of sizes. Because dissolution of the particles in gastrointestinal fluid only occurs on a particle's surface, large particles are more likely associated with lower RBA values than smaller ones, because the ratio of particle surface area to volume tends to decrease as size increases. Average arsenic bearing particle sizes, measured at the longest dimension, ranged from 27.58 microns to 61.51 microns. The average arsenic bearing particle size for all samples was 40.8 microns.

As with any scientific research, not all lines of evidence are going to provide the same level of support. The matrix association indicating that the arsenic containing particles were liberated does not support the findings as strongly as the remaining lines of evidence. While all three of the geochemical properties are considered in the development of a site-specific RBA coefficient, mineral phase shows the strongest correlation to bioavailability, and thus is considered more heavily. Data collected from the Aberjona River study (Brattin and Wahlquist, 2002) suggested that the RBA of the arsenic is likely to be determined primarily by mineral phase and/or particle size rather than by matrix association.

5.3 National Arsenic Bioavailability Library

Dr. Drexler of the University of Colorado LEGS noted that the results of the *in vitro* and EMP analysis for the site sediment samples most closely resembled soil samples collected from Keaau Hawaii as part of an arsenic bioavailability study conducted for the State of Hawaii Department of Health. Similar to the landfill wetland sediment samples, the Keaau samples exhibited high concentrations of iron oxides. The soil samples collected as part of the Keaau study were analyzed for arsenic bioavailability via the *in vitro* and *in vivo* methods. Similar to the landfill samples, the Keaau soils exhibited low arsenic bioavailability (AMEC, 2007). The Keaau study concluded that there was a correlation between decreasing arsenic bioavailability with increasing iron oxide concentrations.

6. CONCLUSION

The cleanup value for arsenic in sediment at this site would be 150 mg/kg if the default value of 100% bioavailability for arsenic was used for a child trespasser scenario. This would result in approximately 15 acres of sediment requiring excavation and removal. Alternatively, a site-specific cleanup value for arsenic in sediment of 900 mg/kg was derived using a 12.6% bioavailability factor using a child trespasser scenario. This results in five hot spot areas requiring excavation and removal totaling approximately one half (0.5) acre of the wetlands area. This results in a considerable reduction in the amount of wetlands that would be disturbed/destroyed if the default value of 100% bioavailabilty was used to assess site health risks and a substantial cost savings to the affected town.

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Chapter 3

MONITORING SOURCES OF MERCURY IN THE ATMOSPHERE

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ABSTRACT

In Virginia and most other states, rain and snow collection stations have been used to determine the concentration of mercury in precipitation. These mercury measurements are distributed by the National Atmospheric Deposition Program through the Illinois State Water Survey (http://nadp.sws.uiuc.edu). Mercury deposition data has been gathered for over a decade and may be compared to the on-line data currently reported from collection sites. Coal-burning power plants are thought to contribute most of the atmospheric mercury, and it was thought that the precipitation collections would prove this hypothesis. In Virginia, this hypothesis is supported. It has been found that the atmospheric content of mercury increases during prolonged intervals without precipitation. In this study, it was found that the atmospheric content of mercury was exceptionally low following an unusually prolonged precipitation event.

Keywords: mercury, pollution, precipitation

1. INTRODUCTION

For many years, the environmental movement has attempted with some success to limit mercury emissions from coal-fired utility power stations. The debate revolves around the cost of dealing with health problems caused by mercury versus the cost limiting mercury emissions. While the actual health costs arr not well defined, there is no doubt that coal combustion contributes to mercury deposition in aquatic ecosystems, and that fish consumption is the primary source of mercury exposure to mankind.

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Coal is the compressed and dehydrated product of plant material that accumulated in an oxygen-poor environment, such as an ancient swamp. To form coal, the plant material must be the dominant part of the accumulating sediment, and must be in an area of geologically slow subsidence, where over time layers of sediment cover the plant debris, and the depth of burial is at least a kilometer. At this depth, the plant debris can be slowly warmed by the radioactivity-generated heat from deep within the planet's crust, and the compressed plant material forms coal.

Oxygen-rich stream and river water that carries sediments into an depositional environment where abundant plant debris accumulates quickly loses its dissolved oxygen content, due to plant decay. Metals in the water, including mercury, precipitate into the plant debris. The metals are not lost as the plant debris is converted into coal. If the coal is burned, as in an electricity generating facility, the metals are vaporized. If the exhaust is not treated properly, mercuty (and other metals) escape into the atmosphere around the facility. The questions raised about this "escaped mercury" include how much mercury escapes, where does it eventually reside, and what is the magnitude of the health problems caused by this mercury.

It is known that when mercury isvaporized and sent into the atmosphere, rain and snowfall wash the mercury into streams and ponds. It is converted into methyl-mercury (and other organic compounds) in the bottom-accumulated plant material that fish consume. Fish enriched in mercury are sometimes eaten by people. It is also known that methyl-mercury causes nervous system and developmental disorders in fetuses and infants (Gobeille et al., 2005). Also, in adults there is evidence that mercury-enriched fish can cause kidney disease, lung cancer, and cardiovascular disease related to chronic mercury exposure through the consumption of fish.

The National Atmospheric Deposition Program (NADP. 1995) of the U.S. Geological Survey and the U.S. Environmental Protection Agency established the Mercury Deposition Network (MDN) in 1995. The MDN consists of several hundred precipitation collection stations designed to accurately measure the concentration of mercury in precipitation in the United States and Canada.

Data from the MDN compilations show that the greatest total amount of mercury in precipitation is in the southeastern United States, probably because this area has a great amount of precipitation (close to the Gulf of Mexico). Conversely, the greatest amount of mercury precipitation during individual precipitation events is in the southwestern United States, probably because this area has small and infrequent precipitation events (Gay et al. 2006).

The national MDN database has been implemented to evaluate potential correlations between sources of mercury emissions into the atmosphere and variations in the amount of mercury in precipitation. It was anticipated that these measurements, plus an understanding of air movement in the atmosphere, could reveal areas where excess amounts of mercury emission and deposition occur.

The central Virginia MDN site is operated in the Center of Basic and Applied Science in Culpeper, Virginia by faculty and students at George Mason University in Fairfax, Virginia. Our site began providing weekly rainfall measurements and mercury collections in the fall of 2002. Culpeper is in the center of Virginia, about 200 kilometers from the nearest coal-fired electrical power stations in eastern Virginia. The other MDN site in Virginia is located in the Shenandoah National Park, west of the Culpeper MDN site and about 230 kilometers from the coal-fired stations. Data now reviewed in the following report were gathered in 2002 through 2005.

Determining if there is a significant correlation between mercury deposition by precipitation and proximity to coal-burning power plants has been a continuing effort among concerned scientists. The processes by which trace elements like mercury are incorporated into cloud droplets, and then rain, sleet, hail or snow, is well known (Walcek, 2003). At least in theory, atmospheric mercury should be deposited quickly and locally in proximity to its emission sources, which in this case are the Virginia coal-burning electrical power plants. Our study began with the anticipation that the Culpeper MDN site, being closer the eastern Virginia coal-fired stations, would regularly reveal large mercury concentrations in precipitation compared to the more distant MDN site in western Virginia.

2. METHODS

At all MDN sites, precipitation is collected over 7 day periods in glass bottles using a motorized collector that opens during intervals of precipitation (Olson and DeWild, 1999). The cumulative weekly total precipitation is recorded and an EPA-approved laboratory determines the mercury concentrations for each water sample. Each month, all the mercury concentrations are and added to the MDN database. During this interval (and today), the mercury deposition data from all the MDN sites are made available on the Internet. (NADP, 2005).

3. RESULTS

The precipitation at the MDN site in Culpeper (MDN Site Number VA-08) had an average annual mercury concentration of about 7.5 ng/L (Table 1). This was about 10% more than the average annual mercury concentration at MDN site in the Shenandoah National Park (MDN Site Number VA-28). Since the Culpeper Site is about 10% closer to the coal-fired power stations and had about 10% more mercury in the precipitation, we regard the data as being evidence that the mercury came, at least in part, fromm the eastern Virginia coal-fired power stations.

The data also show that both the amount of precipitation and the amount of mercury in the precipitation tended to be higher in the summer and fall. We cannot present and explanation. However, it is during these seasons that higher atmospheric temperatures occur, and this could facilitate greater and faster dispersion of mercury across Virginia (Banic et al. 2005).

Fortunately for our study, during the winter quarter of 2003, Hurricane Isabel caused an unusual and brief interval of abundant precipitation and high winds. As shown in Table 1and 2, the average concentration of mercury in the precipitation was very low in this winter quarter. We believe that the brief but heavy precipitation washed most of the mercury out of the atmosphere in Virginia (Kolker et al. 2004).

Table 1. Record of Mercury Deposition at VA-08 in central Virginia

Interval	Hg Concentration (ng/L)	Precipitation Collected (cm)	Total Rain (μg/m^2)
Winter 02-03	5.7	9.2	0.5
Spring 2003	4.6	31.2	1.5
Summer 2003	10.3	42.3	4.3
Fall 2003	10.9	45.6	5.0
Winter 03-04	6.2	31.8	1.9
Spring 2004	8.8	12.0	1.0
Summer 2004	7.9	35.0	2.8
Fall 2004	7.0	37.0	2.6
Winter 04-05	4.3	31.2	1.4
Spring 2005	5.3	21.0	1.2
Summer 2005	7.9	21.9	1.8
Fall 2005	10.2	44.1	4.5
Winter 05-06	3.9	33.3	1.4

Table 2. Record of Mercury Deposition at VA-28 in western Virginia

Interval	Hg Concentration (ng/L)	Precipitation Collected (cm)	Total Rain (μg/m^2)
Winter 02-03	3.6	27.8	1.0
Spring 2003	4.4	47.1	2.0
Summer 2003	16.5	49.2	6.8
Fall 2003	9.9	64.4	4.2
Winter 03-04	4.8	39.0	1.8
Spring 2004	4.9	19.3	0.9
Summer 2004	8.4	37.9	3.2
Fall 2004	5.5	77.9	4.2
Winter 04-05	3.8	31.4	1.2
Spring 2005	4.1	24.3	1.0
Summer 2005	6.9	21.5	1.5
Fall 2005	6.9	41.7	3.1
Winter 05-06	3.4	51.5	1.1

4. CONCLUSIONS

Using the mercury data from MDN sites VA-08 in central Virginia and VA-28 in westernVirginia, it appears that the deposition of mercury in precipitation decreases as the distance to coal-fired electrical generating plants increases. It also appears when a hurricane passed through Virginia during the winter quarter of 2003, a significant amount of mercury was removed from the atmosphere, resulting in a very low precipitation of mercury in central and western Virginia.

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Chapter 4

MERCURY EXPOSURE CONSIDERATIONS: EVALUATING THE CHEMICAL FORM AND ACTIVITIES OF THE INDIVIDUAL

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ABSTRACT

Evaluation of exposure to mercury in an environmental or an occupational context is more complex than that for many other substances, insofar as it requires consideration of a combination of factors including the form of mercury present and the associated toxicology (e.g., elemental vs. organic vs. inorganic), as well as characteristics of the individual/exposure being evaluated (e.g., route, frequency, duration, and magnitude of exposure). Given the major differences in absorption of mercury forms by route, it is not sufficient to discuss simply "mercury exposure", as often occurs in media reports. Methods for addressing each of these characteristics are discussed, and specific case studies are presented to illustrate the practical significance of differences in contact with several common mercury forms that may be encountered under variable exposure circumstances. In addition, a discussion is presented of the variability of responses between adults and children to selected mercury forms, with attention to similarities or differences in observed effects. Finally, common sources of mercury exposure to the general population are discussed, for purposes of comparison with potential exposures in the workplace.

Keywords: Mercury, exposure, environmental, workplace, health, adults, children, toxicology

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1. INTRODUCTION & HISTORICAL PERSPECTIVE

Mercury often is listed as a primary environmental pollutant by the U.S. Environmental Protection Agency (USEPA), as well as other local, state, federal and international entities. Although it is an element found naturally in the earth's crust, an estimated 50-75% of environmental mercury comes from anthropogenic sources (USGS, 2009; Davidson et al., 2004), resulting from increased mercury mobilization and atmospheric release since the 1800s (USEPA, 2001).

Mercury is found in air, water, soil and sediments existing as one of three forms: elemental (metallic) mercury, inorganic mercury compounds, and organic mercury compounds. Elemental mercury is evident as a shiny, silver/white liquid at room temperature, displays some unique properties (e.g., significant vapor pressure, high surface tension, toxic to certain microorganisms, conducts electricity), and in its stable elemental form cannot be destroyed. Mercury cycles between the atmosphere, land, and water while undergoing complex chemical reactions, many of which are not entirely understood (USEPA, 2001; Figure 1). Mercury released to the air may deposit in water or on land where it can be washed into neighboring waterbodies (Zahir et al., 2005). Over 95% of the mercury in the atmosphere exists in the gaseous elemental state, while mercury found in water, sediments and soils is mainly found in the oxidized, divalent state. A small fraction of the divalent form may be converted to methylmercury via microbes in aquatic environments. Methylmercury is the highly toxic form of mercury that can accumulate in fish, shellfish and subsequent elements of the food web.

Ambient air mercury concentrations in the U.S. have been reported to be between 10 and 20 ng/m^3 in nonindustrialized areas (WHO, 2003). Due to industrial activities and other anthropogenic sources, current average levels in the atmosphere are estimated to be on the order of 3 to 6 times greater than preindustrial conditions (WHO, 2003). Because mercury is persistent and travels in the atmosphere for long periods (Zahir et al., 2005), sources of mercury detected in fish in U.S. surface waters are believed to originate from a combination of local, regional and global sources. National Pollutant Discharge Elimination System (NPDES) permits regulate point sources of mercury discharge to waterbodies, while nonpoint sources of mercury contamination are not specifically regulated. However, if shown to cause water quality exceedences, states will be required to develop Total Maximum Daily Load (TMDL) estimates that include potential nonpoint sources. Domestic sources influence mercury deposition in the eastern U.S., while in the West, where fewer domestic sources exist, global sources contribute proportionally more to mercury deposition.

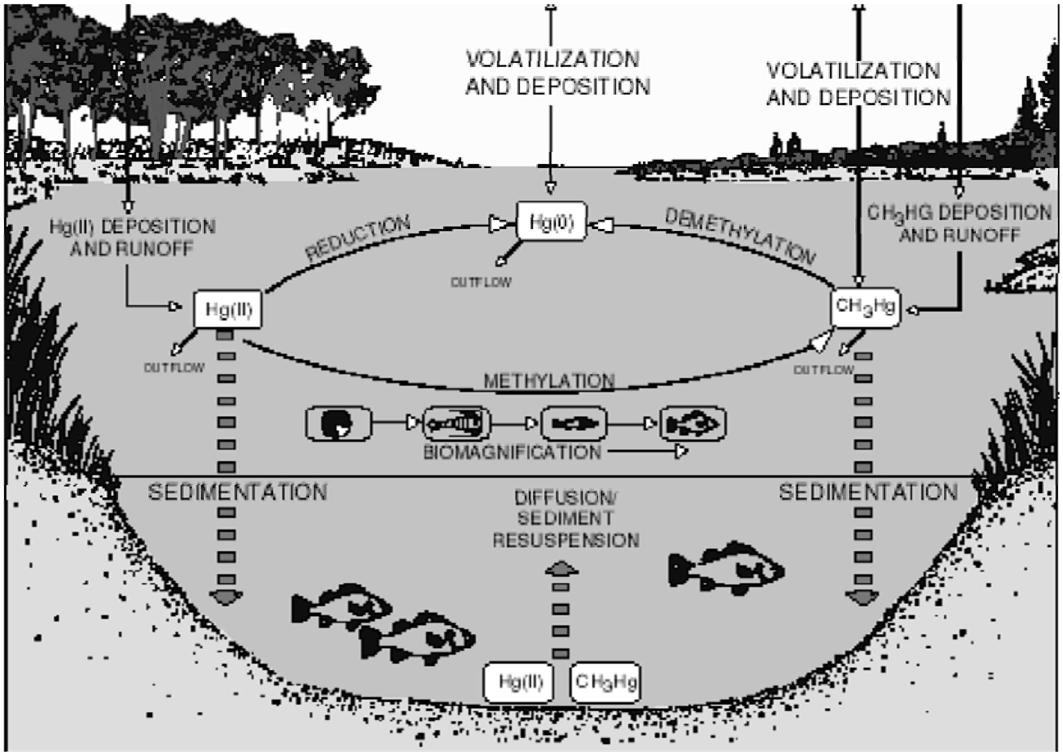

Figure 1. Aquatic mercury cycle. Source: Mercury Pollution: Integration and Synthesis. Copyright Lewis Publishers, an imprint of CRC Press.

Natural sources of mercury include emissions from volcanoes and crystal degassing in the deep ocean (Rasmussen, 1994; UNEP, 2002; Castoldi et al., 2003; Poulin and Gibb, 2008). The largest single U.S. source of airborne anthropogenic mercury is coal-fired power plant emissions (Zahir et al., 2005). Other potential releases from U.S. activities include combustion facilities (e.g., utility boilers, municipal waste combustors, commercial/industrial boilers, hospital incinerators), mining, and manufacturing. There are about 100 facilities in 44 countries that have some mercury cell production capacity (UNEP, 2010). While chloralkali facilities are no longer a major concern in the U.S., problems at former sites in Albania, China and Peru have been identified (Bose-O'Reilly et al., 2010). Over the past decade as international gold prices have risen, more attention has been focused on small-scale gold mining communities, in developing countries such as Ghana (Paruchuri et al., 2010), Mongolia (Steckling et al., 2011), Burkina Faso (Tomicic et al., 2011), Indonesia and Zimbabwe (Bose-O'Reilly et al., 2008), and Tanzania (Spiegel, 2009), where exposure to mercury can occur during traditional extraction operations. At the turn of the 21st century, approximately 13 million people were engaged in small scale mining worldwide, and 80 to 100 million people eventually may depend on the practice for their livelihood (ILO, 1999). Because these often are communities dependent upon fish consumption, they may also be exposed to methylmercury in the diet.

In 2003, the United Nations initiated the Global Mercury Project (GMP), to educate and promote cleaner, more efficient gold mining/extraction technologies for these impoverished communities (Purwana, 2003). The Amazon basin has been extensively studied with regard to miners being exposed to mercury. It was determined that deforestation and erosion that accompanies mining activities were major sources of mercury release to waterways (Passos and Mergler, 2008).

Mercury can be found in common household products such as thermometers, switches, medicines, skin creams and some light bulbs. Disposal of these items is a potential source of environmental impact when placed in landfills or burned in waste combustors, as opposed to recycling (Goldman and Shannon, 2001). There may also be exposures in food products, such as fish, citric acid, sodium benzoate, and high fructose corn syrup (Dufault et al., 2009; Bose-O'Reilly et al., 2010). Use of mercury in fungicides was discontinued in the U.S. in the 1970's based on concern regarding persistence and potential toxicity. Thimerosal, a preservative containing approximately 50% mercury by weight (ethylmercury), has been used since the 1930's as a preservative in vaccines. Apprehensions about the preservative were raised concerning association with autism in children but the American Academy of Pediatrics and the U.S. Public Health Service have concluded that there is insufficient evidence that exposure to these vaccines containing thimerosal could result in developmental neurotoxicity. Both organizations nevertheless recommend use of alternative preservatives (Davidson et al., 2004).

USEPA and other agencies are working to reduce environmental mercury and to limit human exposure. Since the Clean Air Act in 1990, U.S. releases of mercury to the air declined ~58% through 2005 and continue to do so (USEPA, 2009d). Reducing mercury-containing items in trash (e.g., batteries, light bulbs) has resulted in reductions related to waste combustion. The Mercury-Containing and Rechargeable Act (the Battery Act) signed in 1996 was one of the first efforts to reduce mercury containing batteries in landfill and incinerator ash by encouraging recycling (USEPA, 1997).

In March 2005, USEPA issued the Clean Air Mercury Rule (CAMR) which created performance standards and established declining caps for power plant mercury emissions. That rule was vacated in February 2008, causing USEPA to propose the Mercury and Air Toxics Standards (MATS) in March 2011, which is designed to replace CAMR. Comments were accepted on MATS through August 4, 2011 (USEPA, 2011a). The Mercury Export Ban of 2008 prohibits export of mercury beginning in 2013, with the intent to reduce availability of elemental mercury on the global market. The ban does not include mercury compounds (USEPA, 2009a). In 2009, United Nations Environment Programme (UNEP) entered into Global Mercury Partnership program to protect human health and the global environment from release of mercury into the environment (UNEP, 2009).

2. EXPOSURE TO DIFFERENT MERCURY CHEMICAL SPECIES

Mercury can be associated with a variety of effects on health depending on factors such as mercury form, level of exposure, route of exposure, duration/frequency of exposure, and age of the person being exposed. Mercury speciation influences environmental behavior, availability of mercury for possible exposure, transport in the body, as well as the spectrum of toxicity, accumulation, excretion, biomagnification, and ability to transport between environmental compartments (UNEP, 2002; WHO, 2010). Speciation of airborne mercury influences transport and deposition. Most atmospheric mercury is elemental mercury vapor, while mercury in the water, soil, sediments, plants and animals is either inorganic mercury salts or organic mercury (e.g., methylmercury).

Absorption varies among different species of mercury (See Table 1). While the major exposure route to methylmercury typically is ingestion of contaminated fish, the primary exposure route for metallic and inorganic mercury is inhalation. Methylmercury is readily absorbed by the GI tract (~95%), as compared with limited GI absorption of mercury salts (~10 to 30%), and negligible GI absorption of elemental mercury (ATSDR, 1999; WHO, 2010). Various metabolic changes can occur once mercury is absorbed, and it may accumulate in brain or fetal tissues, but subsequently become sequestered as a result of conversion to inorganic divalent cations (ATSDR, 1999). Factors such as nutritional status, drug interactions, temperature, intestinal flora, genetics and age all play a role in metabolic processes following mercury absorption. Mercury elimination is generally slow (Smith et al., 1970; Sallsten et al., 1994). Elimination of elemental mercury occurs primarily via urine and feces, with expired air, sweat, and saliva contributing nominally. Methylmercury is excreted >90% in the feces (ATSDR, 1999; Goldman and Shannon, 2001; Clarkson and Magos, 2006).

Medical monitoring via mercury measurement in hair, blood and urine can be used to provide information regarding chemical form, duration of exposure, and degree of exposure (Mahaffey, 2005; ACGIH, 2001; Risher and De Rosa, 2007).

Table 1. Relative Absorption Efficiencies of Mercury Species.

Route	**Elemental**	**Inorganic***	**Methylmercury**
Inhalation	*High*	*Low*	*Low*
Oral	*Low*	*Low-Moderate*	*High*
Dermal	*Low*	*Low*	*Low*

*Inorganic group includes mercuric chloride, mercurous chloride, mercuric sulfide, mercuric acetate

2.1 Elemental mercury

Elemental mercury vapor is colorless and odorless, and can circulate in the atmosphere for months or years, traveling thousands of miles from a source before settling in water or on land (USEPA, 2001). It is volatile, exhibiting a vapor pressure of 0.2 to 0.3 Pa at 25^{o}C (~0.002 torr; WHO, 2003; ATSDR, 1999). Elemental mercury is lipophilic, can distribute widely in the body and is able to cross blood-brain and placental barriers. About 80% of inhaled elemental mercury is absorbed through the lungs (UNEP, 2002) while only ~0.01% is absorbed via the GI tract after ingestion. The difference is attributed to enterogastric conversion to divalent mercury which binds to sulfhydryl groups, favoring excretion following ingestion (WHO, 2003). Exposure to elemental mercury typically is related to occupational, accidental or self-inflicted events. The brain and kidney are particularly susceptible to effects of metallic mercury poisoning. Elemental mercury is not classifiable as to carcinogenicity in humans [International Agency for Research on Cancer (IARC) Group 3].

Acute, high dose elemental mercury exposure may lead to acute pneumonitis. At lesser exposures, symptoms such as tremor, gingivitis, neurocognitive or behavioral disturbances, irritability, depression, fatigue, memory loss and sleep disturbances may occur, though not always (CDC, 2009). Barboni et al. (2009) reported that chronic low level mercury exposure in workers from mercury recycling plants in San Paulo, Brazil, was associated with visual disturbances but not neuropsychological changes. Although association between exposure of dentists and prevalence of intoxication symptoms has been reported (Neghab et al., 2011), exposure to dental amalgams has not shown consistent association with neurotoxicity. The U.S. Public Health Service concluded that insufficient evidence exists to show that dental amalgams pose a human health threat

(USPHS, 1993; Clarkson and Magos, 2006). Renal dysfunction following elemental mercury exposure has been reported in the workplace. If low level exposure ceases and mercury is excreted, most effects are reversible (ATSDR, 2001).

Occupational guidelines set by Occupational Safety and Health Administration (OSHA), The National Institute for Occupational Safety and Health (NIOSH), American Conference of Governmental Industrial Hygienists (ACGIH) and the Agency for Toxic Substance and Disease Registry (ATSDR) are listed in Table 2. The USEPA has also established a reference concentration (RfC) value of 0.0003 mg/m^3, which is an estimate of continuous inhalation exposure concentration that is likely to be without risk of deleterious effects during a lifetime.

Table 2. Toxicological, Environmental and Occupational Guidelines for Different Mercury Species

Elemental	
OSHA PEL (ceiling)	0.1 mg/m^3
NIOSH REL	0.05 mg/m^3
ACGIH TLV	0.025 mg/m^3
ATSDR MRL	0.0002 mg/m^3
USEPA RfC	0.0003 mg/m^3
Inorganic	
USEPA RfD (mercuric chloride)	0.0003 mg/kg•day
USEPA MCL	0.002 mg/L
Methylmercury	
USEPA RfD	0.0001 mg/kg•day
USEPA Fish Tissue Criterion	0.3 mg MeHg / kg fish tissue

2.2 Inorganic mercury compounds

Examples of inorganic mercury compounds (or salts) include mercuric chloride, mercurous chloride, mercuric sulfide and mercuric acetate. Most inorganic compounds are white powders/crystals, except for red mercuric sulfide which turns black following exposure to light and air (ATSDR, 1999). These compounds are not very lipophilic, but are water soluble and, thus, less easily absorbed through the skin but more readily absorbed after ingestion. Ingestion of one gram of mercuric chloride may cause shock and kidney function collapse, likely due to corrosive damage to the GI tract (Clarkson and Magos, 2006). The dermal route is usually not an issue, although a skin notation often is given, and absorption after inhalation is low. Inorganic mercury compounds can reach most organs, primarily the kidneys, where prominent effects occur (ATSDR, 1999; CDC, 2009). Mercurous chloride use occurred until the mid-1900s in laxatives and teething powder (Clarkson and Magos, 2006). Inorganic mercury compounds are not classifiable by IARC as to human carcinogenicity (IARC Group 3). The RfD for mercuric chloride and maximum contaminant level (MCL) for inorganic mercury are listed in Table 2. The MCL is an enforceable standard, considering health and technical feasibility, and for inorganic mercury the MCL is the same as the maximum contaminant level goal (MCLG), the health-based guideline for drinking water below which there is no expected risk to health.

2.3 Methylmercury

Significant worldwide populations have potential exposure to organic mercury, of which methylmercury is the most common threat to human health, principally through consumption of contaminated fish and shellfish. Widespread historical use of methylmercury for seed dressings and fungicides in paper mills reportedly has caused impacts to global waterways (Grandjean et al., 2010). Methylmercury is absorbed readily via the GI tract (ATSDR, 1999; WHO, 2010). At sufficient dosage, it is a well-known neurotoxin which can pass placental and blood-brain barriers and effect the developing brain (Zahir et al., 2005; WHO, 2010). IARC has classified methylmercury as possibly carcinogenic to humans (Group 2B), though no quantitative potency is available. The National Research Council (NRC) and others (e.g., Mahaffey, 2005) have concluded that the most sensitive endpoint in assessing human exposure to methylmercury is neurodevelopmental effects, and the RfD should be based on that endpoint (NRC, 2000). The RfD for methylmercury is listed in Table 2, along with the fish tissue criterion.

Formation of methylmercury is enhanced at low environmental pH and high sediment mercury levels (WHO, 2003). Methylmercury elimination in fish is slow, and longterm reductions in concentrations are unlikely except for "growth dilution" (e.g., stable mercury mass diluted by increased body size; USEPA, 2001). Size, age, community structure, feeding habits, and food chain position influence fish methylmercury concentration (USGS, 2009). The U.S. Food and Drug Administration (USFDA) and the American Medical Association (AMA) recommend that women who are pregnant, may become pregnant, or nursing mothers and young children should follow local, state and federal fish advisory guidance particularly for swordfish, king mackerel and tilefish, which have been found to contain elevated levels of methylmercury in edible tissues (USFDA, 2001; AMA, 2004; USFDA/USEPA, 2004; Bose-O'Reilly et al., 2010).

Methylmercury is readily absorbed and stored, but inefficiently and slowly demethylated to inorganic mercury in mammalian tissues, yielding a prolonged half-life (WHO, 2010). Following methylmercury exposure, there can be an unexplained long latency period prior to rapid onset of symptoms (USEPA, 2001; Clarkson and Magos, 2006; Grandjean et al., 2010). Selenium is an important micronutrient, deficiency of which can lead to enhanced mercury sensitivity (Clarkson and Magos, 2006; Dufault et al., 2009).

3. VARIABILITY IN RESPONSE

Common recognition of toxic effects from mercury dates to 18th and 19th century England where the phrase "mad as a hatter" was coined. Mercury was used in felt production, and hat factory workers experienced regular mercury exposure, resulting in neurotoxicity (e.g., paraesthesias, slurred speech, anxiety, vision/hearing impairment, hallucinations, depression, lack of coordination, tremors). Other mercury poisoning reports in the early- to mid-1900s included childhood teething powders and ointments. In the 1950s, a well-known chemical plant release of inorganic and methylmercury into Minamata Bay, Japan contaminated fish and shellfish that were consumed by local fishermen and families (Clarkson and Magos, 2006). Devastating health effects were termed Minamata Disease, characterized by infantile cerebral palsy, congenital abnormalities, ataxia, paralysis, hearing/vision loss and other effects of acute and chronic methylmercury toxicity (WHO, 2010). Another famous exposure episode in Iraq in the 1970s involved seed grain coated with a methylmercury fungicide, where the grain subsequently was used in making bread. In that case, official estimates suggested that over 6,500 individuals sustained mercury intoxication, although the actual number may have approached 100,000 (WHO, 2010). Peak methylmercury exposure appears to be the determining factor in assessing response (Clarkson and Magos, 2006).

Signs of mercury toxicity may include tremors, emotional instability, irritability, peripheral neuropathy, gingivitis, vision changes, hearing loss and renal impairment. These effects have been observed in humans exposed to mercury in elemental, inorganic, and organic form (ACGIH, 2001; WHO, 2010). Children are more susceptible to adverse health effects following mercury exposure than adults, and the fetus is particularly vulnerable, due to development of the brain and other systems (WHO, 2010). Differences in metabolic rates, diets, patterns of behavior, growth, and changes of organ systems/functions seen in adults and children, influence the different responses observed (WHO, 2010).

As noted, exposures can occur *in utero* by placental passage of mercury, during early life via breast milk, and during childhood/adolescence via exposure to mercury in the environment, diet and consumer products (WHO, 2010; ATSDR, 1999). In children, toxicity can involve the brain, cardiovascular system, and kidneys, as well as skin (Torres et al., 2000; WHO, 2010). It is important to consider total exposure to different mercury species. Historical home exposures have included teething powders, soaps, medicines, paints (discontinued in the US in 1990), mercury from home coal burning stoves or heaters, fluorescent lightbulbs, antiques, and vintage objects in the home (e.g., thermometers, barometers). Acrodynia, or "pink disease", is a skin condition that can develop in children, but not adults, following exposure to mercury vapor, usually associated with urine mercury levels >100 ug/L (ATSDR, 2001), and characterized by severe pain, swelling and discoloration in the extremities. Beck et al. (2004) presented a case of a three-year old boy who presented with severe hypertension along with other classical mercury signs. Hypertension was found to accompany acrodynia in some case studies (Beck et al., 2004). The rarity and observed wide variability in this skin condition makes a dose-response relationship difficult to develop.

Adequate nutrition is important for maintaining neuronal integrity and learning capacity, and mercury may adversely effect learning if either metallothionein or glutathione metabolic systems are not functioning properly (Dufault et al., 2009). One of the earliest signs of mercury toxicity is “intentional tremor”, indicating cerebellar impairment, the area of the brain involved in coordination and voluntary movements (Wastensson et al., 2008). Motor performance has been described in children following low level mercury exposure.

Complicating diagnosis and assessment processes, clinical signs of mercury intoxication mimic those that can be observed in undiagnosed neurological diseases, pharmacotherapy, vitamin/mineral deficiencies, and psychological stress (Risher and Amler, 2005). Physicians must carefully evaluate relevant biological markers along with symptoms in order to make a complete and accurate diagnosis.

Chelation therapy can be used on patients with evidence of large mercury burden and clinical signs. Agents such as succimer, dimercaptopropanesulfonate, and d-penicillamine have been used to increase mercury elimination, though removal of methylmercury often is difficult (Goldman and Shannon, 2001). Further, chelation can mobilize significant mercury concentrations and can be associated with subsequent renal disease associated with kidney accumulation.

4. COMMON EXPOSURE VS OCCUPATIONAL EXPOSURE

A number or organizations, including USEPA, are involved on national and international fronts to reduce mercury releases to the environment and to limit human exposure (USEPA, 2009a). The World Health Organization (WHO) also is working with national, regional and global health partners to reduce mercury exposure in children by eliminating uses of mercury products where alternatives are available in industrial, medical and occupational sectors (WHO, 2010). As noted, the most important source of mercury exposure in the general U.S. population is consumption of contaminated fish (USEPA, 2008). Occupational exposure is much less common in recent years. Humans also can be exposed to elemental mercury vapors through inhalation and eye/skin contact following breakage of products in poorly-ventilated indoor spaces. Other non-occupational exposures include contaminated soils, as well as playing with liquid mercury from broken electrical switches, thermometers and barometers. Mercury vapors are heavier than air so at significant concentrations they may remain near the floor and may get into ventilation systems where they can spread through the house (ATSDR, 2001). Exposures from ambient air and drinking water typically are minor. Fish consumption advisories involving mercury accounted for 80% of all such advisories in 2008, involving nearly 17 million lake acres (USEPA, 2009b).

In 2001, instead of a water concentration-based criterion, USEPA developed a fish tissue-based criterion for methylmercury of 0.3 mg per kg (0.3 parts per million, ppm) of wet weight fish tissue (USEPA, 2001). This value was obtained by assuming a 17.5 gram/day fish ingestion rate, a 70 kg body weight, and a target reference dose (RfD) of 0.0001 mg/kg•day (= 0.1 ug/kg•day). The RfD is the level of exposure without expectation of adverse effects when exposure is encountered daily for a lifetime. The derivation of the reference dose by USEPA is explained in detail elsewhere (Rice et al., 2003; USEPA, 2011c). While neurotoxicity to the developing fetus was used to calculate the RfD, it is not specific to children and often is used for the general population, though quite conservative for adults. Equivalent guidelines set by USFDA and ATSDR are 0.5

ug/kg•day and 0.3 ug/kg•day, respectively (Clarkson, 2002). If additional states, tribes and territories adopt EPA's recommended fish tissue criterion, the number of water bodies listed under Section 303(d) of the Clean Water Act as "impaired" will increase (USEPA, 2010). Nearly 2,100 U.S. waterbodies are listed as impaired for mercury (USEPA, 2011b). A National Study of Chemical Residues in Lake Fish Tissue found that mercury concentrations in predators exceeded the human health screening value (0.3 ppm) in 36,422 U.S. lakes (USEPA, 2009c).

In occupational settings, elemental mercury typically is the primary source of exposure. Historical occupations of interest include workers in lightbulb manufacturing, chemical laboratories, mines, industrial manufacturing, and thermometer production (Mahaffey, 2005; UNEP, 2010). In some instances, as with other chemicals, workers may bring mercury home with them on clothing and shoes.

Medical monitoring (e.g., baseline and periodic exams) is common in the workplace where mercury exposure may occur. Routine air and biological monitoring are available to assess exposure levels in comparison to those tied to adverse effects (NJDOH, 2004). Measurements typically should be carried out several times per year in potentially exposed workers and evaluated on individual and group bases. Early nonspecific signs of mercury exposure may, but not always, include personality changes, weight loss, irritability, nervousness, memory loss, tremor, coordination loss, indecision and intellectual decline (NJDOH, 2004). Potential sensitive target organs for workplace mercury exposure are CNS and kidneys (Holmes et al., 2009). Cardiovascular effects of low level methylmercury exposure are uncertain (Holmes et al., 2009; Lim et al., 2010; Mozaffarian et al., 2011).

Neurobehavioral tests are available to detect early changes in nervous system effects of mercury exposure. A 24-hour urine collection to evaluate mercury in urine is ideal, but is often not feasible. In other cases, a regular sample should be taken at the same time of day near the end of the work week after several months of steady exposure. The results should be corrected for grams of creatinine in the urine (ug Hg/gm creatinine). Many reports dealing with exposure to mercury have not accounted for the creatinine level, rendering it difficult to compare results across studies.

The most reliable biomarker for longterm mercury exposure is considered to be urine samples (Holmes et al., 2009). The urine mercury levels are also a good indicator of kidney load because the kidneys tend to be the main site of mercury deposition, and this may also be a rough indicator of total body burden (Clarkson and Magos, 2006). Blood samples can be utilized for shortterm high level exposures but do not reflect body burden over long periods of time because mercury has a relatively short blood half-life. Blood concentrations decline with a half-life of 1 to 3 weeks (CDC, 2009). Inorganic forms of mercury are not excreted in significant amounts in hair, making it an unreliable biomarker for occupational exposure, though it has been used to assess methylmercury exposure.

The toxicological literature is not conclusive in determining a relationship between urinary levels of mercury, airborne levels of mercury and observed symptoms (Tsuji et al., 2003; WHO, 2003). The variability in each of these measurements presents a challenge for epidemiologic studies (Symanski et al., 2000). Several studies concur that average exposure to elemental mercury at a concentration of 20 ug/m^3 may yield subtle CNS effects in occupationally exposed workers (WHO, 2003). A meta-analysis performed by Meyer-Baron et al. (2002) reported evidence for neurobehavioral impairments associated with urinary concentrations at or below 100 ug Hg/g creatinine, while older work (e.g., Mattiusssi et al., 1982) was focused on correlations between mercury air concentrations and urine concentrations of exposed workers. Concentrations of urinary mercury over 10 ug/L suggest that a person has some exposure (ATSDR, 2001), while neurological signs may be evident at levels greater than 100 ug/L (Goldman and Shannon, 2001). However, "Finding a measureable amount of mercury in blood or urine does not mean that the level of mercury causes an adverse health effect." (CDC, 2009).

WHO concluded a high probability of developing tremor, erethism, and proteinuria at urinary mercury levels $\geq$100 ug/g creatinine (Poulin and Gibb, 2008). Mercury blood levels reflect exposure to organic mercury, inorganic mercury and the metallic form thus the blood test is not recommended for assessing exposure to occupational mercury. Urinary mercury consists primarily of inorganic mercury, though if not specified in testing, it cannot be segregated from the other possible forms. Laboratory analytical practices typically will reduce all of the mercury present in a biological sample to its elemental state prior to analysis, although this is not acceptable when speciation is desired (Holmes et al., 2009). Being relatively volatile, mercury can be lost during sample preparation, requiring precautions.

5. SELECTED CASE EXAMPLES

5.1 Fish Consumption

Results of three large epidemiologic cohort studies from Seychelles, Faroe Islands, and New Zealand, have enhanced our level of knowledge, but have also increased the ambiguity associated with mercury exposure and the potential for adverse health effects. Studies conducted in the Faroe Islands and New Zealand reported associations between mercury in maternal hair and several neurotoxic endpoints, whereas work conducted in the Seychelles did not show an association.

Myers et al. (2003a) investigated 779 mother-infant pairs living in the Seychelles in which the mother consumed large amounts of fish per week. Prenatal exposure was determined by maternal hair concentration during pregnancy. The authors in that study did not detect an association between neurodevelopmental risk and prenatal methylmercury exposure from fish consumption. This conclusion was controversial, as illustrated by author exchanges in scientific journals (Myers et al., 2003b; Lyketsos, 2003; Keiding, 2003; Stern, 2004). Several years later the same authors (Myers et al., 2009) reiterated that there was no consistent association.

In contrast, a cohort study of 1,022 single births in the Faroe Islands reported that several aspects of brain function may be affected by prenatal mercury exposure and that study, coupled with an integrative analysis of all three mentioned epidemiologic studies, was used by USEPA as rationale for keeping the RfD derived in 1995 the same in 2001 (Grandjean et al., 1997; Rice et al., 2003). Qualitatively similar results were reported in earlier studies by Kjellstrom et al. in 1986 and 1989 (as cited in Rice et al., 2003) from New Zealand.

A current detailed review of the three principal cohorts is found elsewhere (Bose-O'Reilly et al., 2010).

5.2 Chloralkali facilities

A Canadian cross-sectional study of 241 people living near a closed chloralkali facility found that 33.8 % of the participants had blood mercury levels above Health Canada's 20 ug/L guideline. Significantly higher blood mercury levels in participants with elevated local fish and seafood consumption, showing that dietary intake, not air, was the major exposure route (Chang et al., 2008).

Another cross-sectional study carried out in Sweden, Italy and Poland followed subjects living near chloralkali plants, as well as occupationally exposed men, to biomarkers of early kidney damage (Jarosinska et al., 2008). Limited statistical associations were found, although there were limitations to the study.

Wastensson et al. (2008) studied 43 mercury-exposed workers from two different chloralkali plants located in similar regions of Sweden. Only 12 exposed subjects showed any deviations in neurological testing, 10 of which presented with tremor. Overall, the study did not show any significant adverse health effects associated with low level exposure to mercury in that circumstance.

5.3 Other cases

One unusual case study involved a pregnant women with extremely elevated levels of blood mercury and urinary mercury who was able to deliver a healthy infant with no early signs of adverse health effects noted up through 8 months (Pugach and Clarkson, 2009). The mercury levels detected in the infant fell from 190 ng Hg/mL in the cord blood to 17 ng Hg/mL in infant blood at 4 months of age. The child continues to be monitored for signs of developmental delays.

Accidental household poisonings have been reported from mercury being brought home from school. Tezer et al. (2011) described a six-member family being exposed to mercury brought home by an elder child. Symptoms originally were diagnosed as a *Brucella* infection. It later was learned that the children played with the mercury and actually spilled some on the carpet and surrounding furniture. The 12 year old presented with the classic signs of acrodynia ("pink disease") following approximately two months of exposure, including joint and muscle pain, tremors, chills, weight loss and fever with dark pink appearance of the hands. Six weeks later her urine mercury was elevated at 73 ug/L and succimer treatment (chelation) was given, resulting in decreased urine mercury levels. The other two children (11 year old boy, 16 year old girl) presented with symptoms a little over a week after her first sign, while the other brother and parents, who slept in different rooms, were not affected. The 11 year old brother had initial urine mercury of 74 ug/L and following chelation therapy his complaints decreased yet his urine mercury increased to 118 ug/L. Following a second course of treatment urine levels returned to normal and the patient's complaints resolved. A 16 year old sister had initial urine mercury of 573 ug/L. Following first round of chelation, this remained high at 210 ug/L. She then consulted with the psychiatric department with complaints of behavior problems.

Home mercury poisoning occurred when a 36-year old woman became ill and her 14-month old child died as a result of inhalation and skin exposure to elemental mercury brought home and heated by an older child (Sarikaya et al., 2010). The child had fever and died before hospital admission. The autopsy listed possible mercury poisoning leading to likely cardiorespiratory death. The woman complained of abdominal pain, diarrhea and fever on admission to the emergency department. Neurological exam did not show tremor, paresthesia, ataxia, spasticity, hearing or vision loss and no other laboratory findings of disease were found. On the seventh day of admission the patient had a blood mercury level of 30 ug/dL. At follow-up two weeks later, the patient was asymptomatic.

6. CONCLUSION

There are many pieces to the puzzle that are essential when evaluating mercury exposure and potential risk to human health. Not only must the species of mercury be known, but the route of exposure, age of person at exposure, and the length of exposure are critical. The three major areas of interest related to mercury exposure are contaminated fish consumption, accidental or intentional exposure, and occupational exposures. Children generally are much more susceptible to effects of all mercury forms, though the precise extent and nature of sensitivities are poorly understood. Several studies have shown pregnant women exposed to methylmercury exhibit few or no symptoms, yet their offspring showed neurotoxic effects. Other studies have shown similar impacts to mothers and children. Fish are a lean low-calorie source of protein, with many benefits balancing risks, causing USEPA to develop a fish advisories website and other sources to help consumers to select fish that are low in mercury and to limit intake of fish known to be high in mercury. Caution should be taken at home to avoid accidental exposure to elemental or inorganic mercury in both adults and children.

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PART II: Indoor Air

Chapter 5

HOW OVERLY CAUTIOUS RISK ASSESSMENT METHODS OVERSTATE RISK FROM PCBS IN INDOOR AIR

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ABSTRACT

The past use of building materials that contained polychlorinated biphenyls (PCBs) is prompting public concern and expensive PCB removal projects. Building materials that may contain PCBs include paint, caulk, floor finishes and many other interior and exterior construction components manufactured before 1972. While initial concern about PCBs in buildings has focused on schools, it is likely that PCB-containing materials will also be found in many residential, commercial, and industrial structures.

In buildings, the primary route of human exposure is the inhalation of PCBs that volatilize out of building materials. The USEPA has indicated that inhalation of airborne PCBs may pose a significant human exposure pathway in schools. EPA's approach to PCBs in schools is evolving quickly. Initial estimates of health risk from indoor PCBs were calculated using risk assessment methods and EPA published toxicity factors. Recently, EPA established guidance titled "Public Health Levels for PCBs in Indoor School Air" to assist school systems in remediation efforts. These criteria are intended to be "prudent public health levels that maintain PCB exposures below the 'reference dose' – the amount of PCB exposure that EPA does not believe will cause harm."

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This article considers two factors central to the accurate assessment of PCB indoor air risk: 1) the difference in the chemical make up of PCBs in air compared to the chemical make up of the PCBs in the building materials they originated from; and 2) how the variability in certain commercial lots of PCBs (Aroclors) can result in different degrees of toxicity. Each of these factors may act to significantly modify the level of risk associated with the inhalation of PCBs in buildings. At the present time, EPA has not incorporated these factors into its calculation of its Public Health Levels.

Keywords: PCBs, PCBs in building materials, PCBs in schools, PCBs in indoor air, Aroclor 1254.

1. INTRODUCTION

The work described in this article began as research to better understand how the chemical makeup of PCB mixtures change as they volatilize out of a solid matrix and into air. This topic is of interest because the inhalation of PCBs in indoor air is increasingly seen as a significant exposure pathway for building users. Commercially manufactured PCBs were mixtures of many different but similar chemicals with varying degrees of chlorination. The volatility of different PCBs is generally correlated with their degree of chlorination, such that PCBs with more chlorine substitutions are less volatile than those with fewer chlorine substitutions (Fiedler, 2002; Foreman and Bidleman, 1985). Available research supports the notion that PCBs with less chlorination preferentially volatilize out of solid and/or liquid media (Casey et al, 1999).

There is also a general correlation between the degree of a PCB mixture's chlorination and its level of toxicity (USEPA, 1996). It has been observed that PCB mixtures with lower average molecular weights (and thus a lower degree of chlorination) are less toxic than those with higher average molecular weights (and thus a higher degree of chlorination). Therefore, the partitioning process that occurs when PCBs volatilize into air may result in the airborne PCBs having a lower degree of chlorination and a lower degree of toxicity than the parent PCB mixture in the solid source materials.

Based on the review of almost 300 indoor air sample PCB test results considered in the present study, Aroclor 1254 was the most frequently detected commercial PCB product among the samples. Further research into the chemical makeup of Aroclor 1254 revealed that, while there is batch to batch variability, there were also two broadly different 1254 products with different chemical and likely toxicological characteristics. These two Aroclor 1254 types appear to have arisen from different manufacturing processes and are likely have different toxicological properties.

1.1 PCBs in Building Materials and Their Initial Regulation

There has been growing attention to the past use of PCBs in building materials because of their ability to volatilize from these materials into indoor air (Herrick at al. 2004; MIT, 2007; and MADPH, 2009). Prior to 1971, PCBs were used as ingredients in paints, caulk and adhesives to impart plasticity and extend the useful life of the materials to which they were added. Sometime in the 1970-1971 period, Monsanto Company, the sole US PCB manufacturer, stopped the sale of PCBs for uses that were not considered “totally enclosed”. Since the use of PCBs in building materials was not considered totally enclosed, it is likely that the manufacture of PCB containing building materials stopped after this time. The concept of limiting future uses of PCBs to those that were “totally enclosed” was carried through to the 1976 Toxic Substances Control Act (TSCA, 1976) and from there to the 1978 PCB regulations promulgated pursuant to TSCA.

The 1978 PCB regulations (40 CFR 761) brought a legal end to use of PCBs in new building products, but did not place limitations on the continued use of existing PCB containing building materials. EPA’s initial PCB enforcement activity focused on: 1) stopping the production and continued distribution of new PCBs in commerce; and 2) taking steps to identify and regulate the remaining stock of liquid PCBs and PCB electrical equipment. The bulk of PCB liquids were in electrical equipment such as transformers and capacitors, and EPA believed the greatest PCB risks arose from the potential mismanagement of these PCB liquids.

With the promulgation of 1978 PCB regulations, the continued legal use of existing PCBs could only occur when permitted by specific “use authorizations” described in the regulations. While different from "use authorizations", the 1978 regulations also contained a *de facto* exemption for PCBs that were defined as being “in service”. The “in service” category was a regulatory catch-all that lumped together a variety of PCBs whose continued use was considered outside of the intended scope of the PCB regulations.

The “in service” category included the continued use of existing, in-place PCB-containing building materials. However, the “in service” category also included PCBs that had been released to the environment prior to the effective date of the regulations; this was because the TSCA regulations were not intended to be used to enforce the cleanup of pre-1978 PCB releases. In 1978 this was not seen as a regulatory deficiency because the agency had other legal tools to force cleanups of spilled PCBs.

When the 1978 PCB regulations were adopted, there were few health or environmental concerns being expressed about PCBs in building materials. This reflected the view that the PCBs in building materials were effectively "locked in" to the materials and, thus, did not pose an exposure risk.

1.2 The 1998 Mega-Rule and Increased Regulation of PCB Containing Building Materials

In 1998, EPA promulgated sweeping revisions to the PCB regulations; so many changes were made that the new regulations were referred to as the "1998 PCB Mega-Rule". The preamble to the Mega-Rule explains that EPA had decided to eliminate the concept of PCBs being "in-service" because the agency wanted the ability to regulate pre-1978 PCB cleanups under the PCB regulations. The Mega-Rule contained no explanation or analysis of the fact that by eliminating the "in-service" category the agency was, with the same stroke, making the continued use of PCBs in existing building materials a TSCA violation.

Following the 1998 PCB Mega-Rule changes, EPA seemed slow to recognize that it had adopted the responsibility for regulating in-place PCB-containing building materials. This slow recognition could be seen in the absence of EPA's program planning and inconsistent regional responses to PCBs in building materials. Recently, national guidance on the management of PCB-containing building materials has begun to appear on EPA's web site.

1.3 PCBs in Indoor Air from Building Materials

By the early 1990s, reports of PCBs in indoor air were appearing in research journals. Much of the early work was conducted in Germany (Benthe et al, 1992; Balfanz et al, 1993). A survey article on indoor air PCB testing appears in *Spengler's Indoor Air Quality Handbook* (Spengler et al, 2000). In the subsequent eleven years, there have been a growing number of articles describing PCBs in building materials and their potential to enter indoor air, particularly in schools (Daley, 2009; Egbert, 2008). The greater frequency of PCB detections in schools is in part the result of schools being the most common location for investigators to examine.

Initial estimates of health risks from PCBs in indoor air were based on the use of standard EPA exposure and risk assessment models. These assessments considered carcinogenic and non-carcinogenic risk. More recently, EPA has published "Public Health Levels for PCBs in Indoor School Air" that are based on the Aroclor 1254 PCB reference dose (RfD) that uses solely a non-cancer toxicological endpoint (USEPA, 2009).

2. MATERIALS AND PROCEDURES

The term PCB does not refer to single chemical, but rather to a group of chemicals with between one and ten chlorine substitutions that all have the biphenyl 12-carbon aromatic chemical structure in common. There are 209 different chemical arrangements of chlorine atoms that can occur on biphenyl; each of these different chlorinated biphenyl arrangements is referred to as a "congener", and there are 209 different congeners in the PCB group. Different congeners that have the same number of chlorine substitutions are referred to as "homologs"; there are ten different homolog subgroups ranging from the monochloro homolog (with one chlorine substitution) to the decachloro homolog (with ten chlorine substitutions).

The goal of commercial PCB manufacturing was the production of congener mixtures rather than making any single congener. The sole US producer of PCBs was the Monsanto Chemical Company and its PCB products were sold under the trade name "Aroclor". Each Aroclor PCB mixture contained many different congeners. There were several different formulations of Aroclors that were differentiated based on the percent chlorine in the mixture (e.g. Aroclor 1242 would have 42% chlorine and Aroclor 1254 possessed 54% chlorine). Of the 209 different PCB congeners, a number of them occur rarely or not at all in Aroclors mixtures; these rare or absent congeners are referred to as non-Aroclor PCBs.

2.1 Measurement of PCBs in Media

Most analyses of PCBs employ: 1) an extraction step where PCBs are transferred from the sample to an organic solvent; 2) a separation step where the sample extract is introduced on to a gas chromatograph; and 3) a detection step where the presence of the PCBs is identified and recorded, a variety of detectors may be used for this step. Depending upon the specific project requirements, the results of PCB analysis may be quantified as Aroclors, as homologs, or as individual congeners (in increasing order of analytical difficulty).

When there is little likelihood of change in the makeup of a PCB mixture in a sample matrix due to environmental weathering or other influences, analysis of samples for Aroclors often proves adequate. However, if there is reason to suspect that the PCB composition has changed, or if the goal of the project is to assess possible changes in PCB makeup, then analysis for PCB homologs or congeners will produce more useful results (Prignamo et al, 2006). Quantification of PCBs as Aroclors presumes that the different PCB components (congeners and homologs) are present in fixed ratios to each other, whereas analysis for homologs and congeners does not require this assumption.

Since the objective of the present investigation was to assess whether the composition of PCBs changed as they volatilized out of the solid phase (building materials) into the gaseous phase (indoor air), it was necessary to compare the results of congener and homolog data for the solid phase to that of the air phase.

2.2 Measurement of PCBs in Air

To conduct a meaningful comparison of indoor air PCB composition to the PCB composition in building materials, it was necessary to acquire a PCB in air data set that represented a variety of different settings. Two of this article's authors (Rezendes and Occhialini) are engaged in the day to day analysis of air samples for PCBs and they provided the results of approximately 300 indoor air samples for PCBs quantified as either congeners or homologs. Air samples were collected in accordance with EPA Method TO-4/TO-10 and were analyzed in accordance with EPA Method 680/8270-SIM (USEPA – SW846, 2011).

There were two limitations inherent to this indoor air data set: 1) because of the need to maintain confidentiality regarding the sampled location, the only information that could be made available for this work was the mass of each congener or homolog measured on the sample cartridge; and, 2) it was not possible to directly compare the indoor air PCB result with a known solid phase PCB source.

2.2.1 Sample Result Limitations

Because the mass of each congener or homolog retained on the sample cartridge was the only information available for each sample, it was not known what the actual concentration of each PCB was in air. In other words, the sample volume was not known. This was not a serious shortcoming because the current study was concerned with the relative abundance of each congener or homolog as a fraction of the total mass of PCBs in the sample. Not knowing the volume of air collected for the sample did not limit the usability of the data for assessing the composition of PCBs in the sample.

2.2.2 Limitations Due to Inability to Compare Air Data with a Known PCB Source Material

The inability to compare air data with a known PCB solid phase source was potentially a more serious limitation. The overall study objective was to assess whether there were changes in the mixture composition as the PCBs volatilized out of the solid phase source and into indoor air. Not knowing the composition of the starting material was an obstacle. However, in most cases it was possible to identify the parent Aroclor (that is the Aroclor present in the solid phase) based on the congeners/homologs detected in the air samples. Knowledge of the Aroclor type was generally sufficient to develop an approximation of the starting material PCB composition.

In fact, there is documentation in the literature supporting the general uniformity of homolog distribution in the Aroclors. There is more batch to batch variability in the congener makeup of the Aroclors than there is homolog variability. Therefore, PCB homolog distribution results were chosen as the comparative parameter that would be used in this study. For the purpose of this work, the Aroclor homolog distributions published by Frame (Frame et al, 1996) were adopted as the basis for comparison to the air samples.

3. DATA, ANALYSIS AND DISCUSSION

To permit a comparison of air sample PCB homolog results to the results for Aroclors, three indicators were used along with a more general evaluation of the homolog pattern for the samples and Aroclors.

3.1 Homolog Data for Aroclors

The PCB Aroclors have distinctive homolog profiles that make identifying them from homolog data straightforward (see Table 1). As a primary identifying characteristic, each Aroclor has a different dominant homolog (except for Aroclors 1242 and 1016) and a second identifying characteristic is the relative concentration of the next heaviest homolog. These two characteristics are generally adequate for identifying an Aroclor from homolog data. A variation of a few percent in Aroclor homologs from batch to batch is not uncommon.

Another indicator that is a useful characteristic of a PCB mixture is the average number of chlorine substitutions per PCB molecule (last column in Table 1). This value is calculated with the following formula:

Cl/PCB = 1* (percent mono) + 2*(percent di) + 3*(percent tri) . . . . + 10*(percent deca)

The Cl/PCB indicator can be helpful for comparing homolog data from environmental samples to parent Aroclors. Changes in the degree of chlorination of a mixture can be tracked using this statistic.

Table 1. Homolog Content and Average Chlorine Substitutions per PCB molecule for Aroclors

	mono	di	tri	tetra	penta	hexa	hepta	octa	nona	deca	Totals	Cl/PCB
1221	**60.05%**	33.27%	4.20%	1.89%	0.48%	0.00%	0.00%	0.00%	0.00%	0.00%	99.89%	1.49
1232	**27.98%**	**26.84%**	21.09%	16.80%	2.90%	0.19%	0.00%	0.00%	0.00%	0.00%	95.80%	2.28
1016	0.73%	17.74%	**54.61%**	26.50%	0.57%	0.00%	0.00%	0.00%	0.00%	0.00%	100.15%	3.09
1242	0.47%	13.86%	**48.02%**	32.76%	5.48%	0.18%	0.00%	0.00%	0.00%	0.00%	100.77%	3.32
1248	0.02%	0.32%	22.00%	**56.49%**	17.55%	1.95%	0.57%	0.00%	0.00%	0.00%	98.91%	3.96
1254	0.02%	0.18%	1.24%	16.38%	**52.95%**	26.75%	2.65%	0.04%	0.04%	0.00%	100.25%	5.14
1260	0.01%	0.00%	0.00%	0.38%	8.07%	**41.15%**	**39.72%**	7.94%	0.40%	0.00%	97.67%	6.34
1262	0.04%	0.16%	0.47%	0.43%	3.08%	26.60%	**47.34%**	19.51%	1.77%	0.00%	99.40%	6.82

* Adapted from Frame et al, 1996; **Bolded** values indicate dominant homologs.

3.2 Homolog Data for Air Samples

The volume of data involved precludes the presentation of the PCB in air data set used for this article. However, some summary statistics are described. Detected PCBs ranged from 2.7 to 6,836 nanograms per sample. Figure 1 shows the distribution of total PCB mass per indoor air sample. In general, where the total mass of PCBs detected in a sample was less than 10 nanograms, reliable homolog information could not be discerned. The most frequently detected homolog (at highest percent concentration) was the penta-chloro homolog, with the tetra-chloro homolog second.

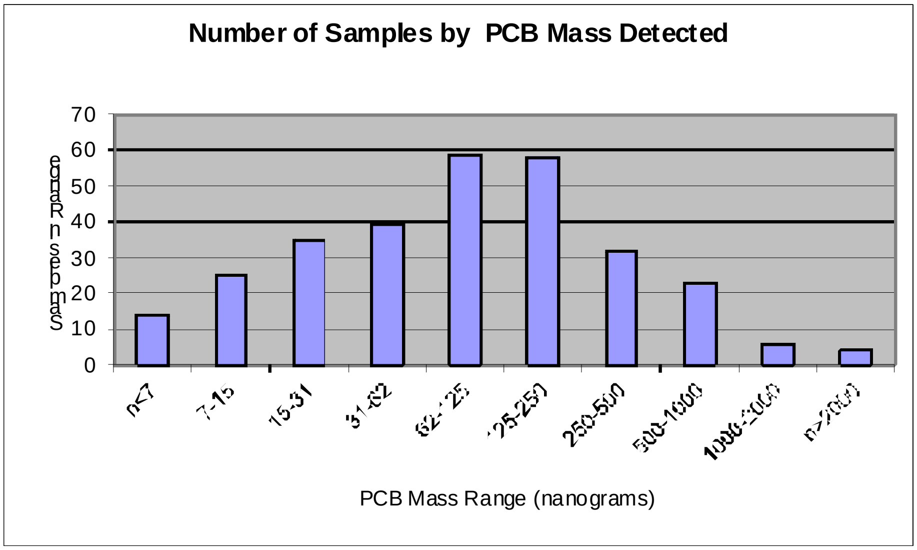

Figure 1. This bar chart shows the distribution of PCB masses detected on air sample cartridges used in the study. PCB air concentrations could not be calculated because the sample volumes were unknown.

The mean Cl/PCB ratio was 4.35 and the median value was 4.41. Approximately 20 air samples appeared dominated by an Aroclor 1260 source; these had Cl/PCB ratios of between 4.98 and 5.94. Approximately 180 samples appeared dominated by an Aroclor 1254 source; these had Cl/PCB ratios of between 4.00 and 5.27. Fewer than 10 air samples are dominated by Aroclors 1221 or 1232. The remaining air samples appear to be a combination of Aroclor mixtures containing 1016/1242, 1248 and/or 1254; the Cl/PCB ratio for these samples range from 4.20 to 2.46. The last column in Table 1 shows the Cl/PCB ratios for the common Aroclor PCB mixtures and Figure 2 shows the distribution of CL/PCB ratios for the study samples.

Few samples contained octa-chloro, nona-chloro or deca-chloro homologs. For those that did, it is suspected that particulate matter in the sample may have contributed to the PCB load.

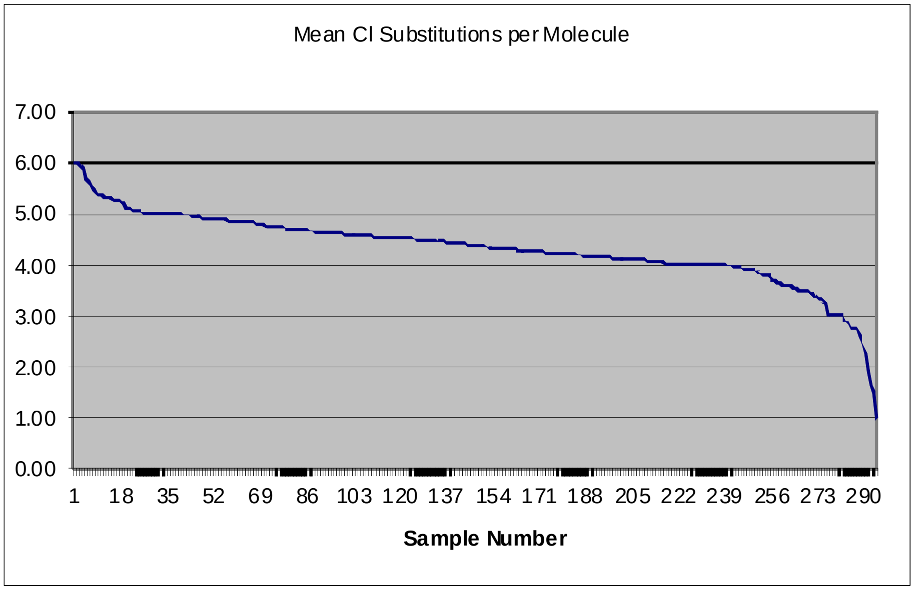

Figure 2. This chart shows the average chlorine substitutions per PCB molecule (along the y-axis) for the study sample set in descending order. Note one sample contained solely decachloro-biphenyl and that sample is not represented on the chart.

3.3 Comparison of Air Sample Homologs to Aroclors

For approximately two-thirds of the air samples, the Aroclor source of the PCBs was readily apparent from the homolog distribution in the air sample. However, even in these samples the homolog distribution was clearly shifted towards a greater proportion of lower chlorinated homologs relative to the parent Aroclor formulations. This shift towards lower chlorinated homologs is believed to be attributable to their overall greater volatility.

3.4 Variability of Aroclor 1254

Among the air sample set used in this study, Aroclor 1254 was by far the most frequently identified PCB mixture. In the course of identifying typical congener and homolog distribution patterns for the Aroclors, 1254 proved to be the most variable one in the literature. In his 1996 work, Frame discussed the variability he observed in Aroclor 1254 and noted that he had not observed nearly as much variability in the other Aroclor mixtures he analyzed.

Frame described chemical profiles for two different lots of Aroclor 1254. One lot he referred to as “A4”, obtained from AccuStandard of New Haven, CT. A second lot was referred to as “G4” was obtained from an old General Electric source. Frame concluded that the A4 material contained much higher concentrations of the coplanar PCB congeners than did the G4 material. Later reports by other researchers referred to an Aroclor 1254 mixture with properties similar to Frame’s A4 as either “Aroclor 1254 (Late)” or as “Type 2 Aroclor 1254” (AccuStandard, 2011). The more common Aroclor 1254 (Frame’s G4) is often referred to as “Type 1 Aroclor 1254”.

3.4.1 Type 1 Aroclor 1254

It is now believed that Type 1 Aroclor 1254 represents approximately 99% of the total Aroclor 1254 production, Type 2 made up the rest. Type 1 is believed to have been manufactured by a one-step chlorination process where biphenyl was chlorinated over a metal catalyst until it has achieved the desired degree of chlorination (54%). Type 1 Aroclor 1254 has generally been shown to have low concentrations of polychlorinated dibenzofurans (PCDFs) and coplanar PCBs (PCB 77, 126 and 169).

3.4.2 Type 2 Aroclor 1254

Type 2 Aroclor 1254 has a more complex and interesting history. It has its origins in Monsanto’s reaction to the 1968 mass poisoning incident in Japan, where PCB-containing heat transfer fluid leaked into rice bran oil intended for human consumption (Kuratsune et al, 2007). Thousands of people were seriously sickened in what became internationally known as the Yusho rice oil poisoning. The Yusho incident dramatically heightened concerns about the safety of PCBs (although subsequent studies found that it was actually other contaminants in the heat exchange fluid that caused the poisoning).

Monsanto decided to seek a safer alternative to the PCB formulations then on the market and in 1970-1971 they started selling Aroclor 1016. In its physical properties, Aroclor 1016 was equivalent to Aroclor 1242 (with 42% chlorine content), but it had much lower concentrations of the tetra-chloro and higher chlorinated homologs. Toxicity studies subsequently confirmed that Aroclor 1016 was less toxic than the other PCB formulations.

However, the process used to manufacture Aroclor 1016 resulted in a chlorinated biphenyl by-product that did not meet the Aroclor 1016 specification. These off-specification chlorinated biphenyls were subjected to a second chlorination step to bring that brought them up to 54% chlorine content. This “Type 2” Aroclor 1254 had the same physical properties and uses as Type 1, but it had some distinctive chemical differences, including a significantly higher content of PCDFs and coplanar PCBs.

As sales of Aroclor 1016 increased, so did the production of Type 2 Aroclor 1254. It is not known whether the production of Type 2 Aroclor 1254 included the addition of "virgin" biphenyl being added to the Aroclor 1016 off-specification by-product. Sales and manufacturing of Aroclor 1254 ceased by 1977, but just prior to that time it is believed that Type 2 was the dominant Aroclor 1254 mixture being sold.

3.5 Aroclor 1254 Types in Building Materials

Since Type 2 Aroclor 1254 has a significantly higher content of the most toxic PCB constituents (the coplanar PCBs) in addition to higher concentrations of the highly toxic PCDFs, it is important to consider which type of Aroclor 1254 was used in building materials. At about the same time that Monsanto was developing Aroclor 1016, the company adopted its voluntary policy of not selling PCBs for uses that were not deemed to be "totally enclosed". This was at about the same time that the first lots of Type 2 Aroclor 1254 were being produced. Therefore, it is likely that little if any Type 2 Aroclor 1254 was ever used in building materials, a use that is not "totally enclosed".

As a consequence of the general absence of Type 2 Aroclor 1254 from building materials it is reasonable to assume that the PCBs present in indoor air derived from building materials would be not be Type 2 Aroclor 1254.

3.6 Aroclor 1254 Types Used in Toxicological Studies

While there have been numerous toxicological studies conducted to assess the toxicity of PCBs, there are two principal studies that underpin EPA's selection of the PCB toxicity factors (USEPA – IRIS, 2011). For the cancer slope factor (CSF), the 1998 Mayes et al (1998) (also cited as Brunner et al (1996)) was used. For the reference dose (RfD), the 1993 work by Arnold et al (1993) was the principal study.

The Mayes et al (1998) paper evaluated the toxicity of four different Aroclors in Sprague-Dawley rats. Among the four Aroclors studied, the Aroclor 1254 contained the highest concentrations of polychlorinated dibenzo-dioxins (PCDDs), PCDFs, and coplanar PCBs. This was identified by the authors as Type 2 Aroclor 1254. Prior to conducting the animal feeding study, the Aroclor 1254 was treated to eliminate the PCDFs, which also reduced the concentration of PCB 126 (the most toxic coplanar PCB) by 35%. The concentration of PCB 126 in the treated Aroclor 1254 was estimated to be 3 to 5 times greater than would be expected in typical Aroclor 1254 (Type 1). The authors estimated that the toxicity equivalent factor (TEF) for their Aroclor 1254 was about twice the TEF for typical Aroclor 1254.

The Arnold et al (1993) work, which was used by the EPA to establish the PCB RfD, also included the results of Aroclor 1254 analysis for the lot used in his monkey feeding study. Citing the results of an unpublished memo, this lot of Aroclor 1254 was reported to contain no PCDD (<0.1 ppm); 5.2 ppm total PCDF; 0.05% PCB 77; 0.01% PCB 126; and 1 ppm PCB 169. It is not apparent from this information whether Arnold's lot of Aroclor 1254 is Type 1 or Type 2. The PCDF and coplanar PCB contents are elevated above the levels expected for Type 1, but not sufficiently elevated to permit easy classification as Type 2.

4. CONCLUSIONS

From the results of indoor air PCB homolog testing, the characteristics of the parent Aroclor mixture could be readily discerned approximately two-thirds of the time, even though the air samples displayed significant deviations from the parent Aroclor homolog distributions. In most air samples (>80%) there was a strong shift towards lower chlorinated homologs relative to the parent Aroclor formulation. The Aroclor identified most frequently in the air samples (in approximately 65% of the samples) was Aroclor 1254.

Aroclor 1254 is known to have a higher degree of chemical variation from lot to lot than other Aroclors. This is due in part to the two-step manufacturing method used by Monsanto in the last years of its production (between 1971-1977). This two-step method resulted in significantly higher concentrations of PCDFs and coplanar PCBs in the Type 2 Aroclor 1254 than occur in the more Typical Type 1 material. As a consequence of the higher concentrations of toxic PCDFs and coplanar PCBs, there is a reasonable likelihood that Type 2 Aroclor 1254 is more toxic than Type 1 Aroclor 1254. The authors are not aware of comparative animal studies having been conducted to test this hypothesis.

Because of Monsanto's voluntary ban on the use of PCBs in other than totally enclosed applications (beginning in 1970-1971), it is unlikely that Type 2 Aroclor 1254 was used in building materials. As a result, indoor air containing Aroclor 1254 from building materials is likely to be Type 1.

At the time researchers began conducting toxicological studies on PCBs, much or all of the Aroclor 1254 being produced was the potentially more toxic Type 2, as this was what was generally available to researchers. In evaluating the potential risks from exposures to the much more abundant Type 1 Aroclor 1254, toxicity studies conducted using Type 2 Aroclor 1254 may significantly overestimate actual risk.

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Chapter 6

INTERPRETATION OF BIOLOGICAL DATA ON INDOOR AIR QUALITY: PRESENCE DOESN'T EQUATE TO SIGNIFICANCE

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ABSTRACT

Based on results of residential air tests, homeowners may be advised that a significant mold problem exists in their home, and that extensive cleanup or remediation is required. Those living in such homes may attribute perceived or actual health conditions to reported levels of, or exposure to, molds. Consensus numerical guidelines or agency standards for evaluation of mold exposure do not exist. Toxicological evidence does not support a contention that healthy individuals are at significant health risk from common mold levels. Putative sensitive populations are not well-documented, and the literature is controversial or inconsistent. Factors influencing likelihood that indoor mold exposure contributes to adverse health effects include indoor vs. outdoor mold levels, concentration/types of mold species indoors vs. outdoors, number of samples collected indoors vs. outdoors, and number of sample events. For situations in which prevalence and speciation of indoor mold is indistinguishable from or less than outdoors, adverse health effects cannot be solely or predominantly a result of indoor exposures. Mold concentration data are reviewed from several residences where mold test results were presented as indicating a "mold problem". We conclude, despite the fact that extensive and expensive remediation efforts and protracted litigation occurred, these data do not support allegations of adverse health effects from potential exposure to indoor mold in the observed homes.

Keywords: Mold, air, exposure, home, toxicology, health, litigation

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1. INTRODUCTION

There are numerous human conditions that have been associated with mold and these manifest specific signs, symptoms, and established etiologies. There are, however, many who believe that exposure to mold can also cause multiple, poorly defined syndromes, and these weakly supported beliefs have proven profitable for some (Pettigrew et al., 2010). "Mold related illness" is a highly controversial condition consisting primarily of nonspecific symptoms such as headache, rhinorrhea, fatigue, memory loss, and eye irritation. Although inhalation of high concentrations of mold spores in special cases has been reported to cause respiratory distress such as hypersensitivity pneumonitis, allergic rhinitis, and asthma exacerbation, the relationship between mold exposure and clinical outcomes remains unclear (Edmondson et al., 2009).

Litigation related to mold typically involves bold assertions that exposure to indoor molds has caused a variety of ill-defined illnesses (Bush et al., 2006). The current literature does not provide compelling evidence that exposure at levels expected in most indoor environments where mold is detectable are likely to result in measurable health effects (Gots and Pirages, 2002). Simply stated, the fact that mold is detectably present does not constitute evidence of meaningful exposure. For example, detection of toxigenic fungi in indoor environments does not necessarily indicate the presence of mycotoxins, unless those substances actually are measured (Khalili and Bardana, 2005).

An understanding of the capabilities and limitations of fungal air data is of great importance, given the role that it plays in supporting the opinions of experts who may be involved in claims of environmental damage or health effects (Spicer et al., 2005). Consensus numerical guidelines or agency standards for evaluation of mold exposures with regard to effects on human health do not exist (Srikanth et al., 2008; Storey et al., 2004), although numerous suggested recommendations have been proposed (Rao et al., 1996). Without an established numerical standard which defines “clean”, “acceptable”, or “contaminated”, the characterization of a building with respect to fungi must be conducted on a relative basis. That is, data from a reference environment that an investigator has good reason to believe is “acceptable” can be compared to a building that is suspected of being problematic. For air samples, the comparison most often used is that of outdoor air, under the paradigm that a building is performing adequately if the indoor environment is not significantly different from the general ambient environment in terms of microbiota.

Certain types of fungi have been associated with various health effects in some circumstances. Because of the problem in defining a “significant” difference between a suspect indoor environment and the reference environment, any detection of air-borne fungal types associated with potential health effects often results in the subjective statement that an indoor environment is “contaminated”. As a result, the normal rules of scientific evidence which demand an objective and quantifiable treatment of data often are overlooked (Spicer et al., 2005).

2. OBSERVED RESIDENTIAL MOLD CONCENTRATIONS

Indoor and outdoor mold spore concentration data for five residential buildings (single family houses or apartments) were available for evaluation. Three of the buildings had reported evidence of water intrusion or a plumbing leak and water damage, as determined by a “mold inspector” hired by the building occupants or their representatives. Two of the buildings had evidence of exterior water damage, but no reported evidence of interior water damage (Table 1).

Table 1. Water Damage/Elevated Mold Matrix

Residence	Evidence of Interior Water Damage (Y/N)	Evidence of Exterior Water Damage (Y/N)	Heath Effects Reported (Y/N)	Elevated Aspergillus/ Penicillium (Y/N)
1	Y	Y	Y	Y
2	N	Y	Y	Y
3	Y	N	Y	Y
4	N	Y	Y	Y
5	Y	Y	Y	N

A number of air samples for mold analysis were collected from each building, and from outside locations in each instance, for comparison purposes. The results of the mold sampling results for each building are presented in Table 2 through Table 6. Sampling locations indoors included bedrooms, dining rooms, kitchens, living/family rooms, bathrooms, closets, and hallways.

The mold sampling data do not indicate that any significant difference exists between the concentrations in indoor air compared to those in outdoor air. In fact, the geometric means of the total mold spore concentrations in the outdoor air exceed those of the indoor air in Residences 1-5 (Tables 2-6) by two to four-fold (Table 7).

Table 2. Residence 1: Outside/Inside Mold Spore Concentrations

Sample Name	Outside	Outside	Outside	Outside	Kitchen	Kitchen	Dining Room
Date	5/29/08	5/29/08	7/18/08	7/18/08	7/18/08	5/29/08	5/29/08
Organism	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3
Alternaria		40					
Ascospores	2720	2160	640	427	27	440	520
Aspergillus/Penicillium	640	720			507	1080	2120
Basidiospores	840	640	3413	2560	67	40	80
Bipolaris/Drechslera	40	40			27		
Chaetomium						80	
Cladosporium	520	360	13	893	80	160	120
Curvularia			13		27	40	
Epicoccum		40			27		40
Myxomycetes	40			133	133		
Nigrospora							
Pithomyces							
Total	4800	4000	4079	4013	895	1840	2880

Sample Name	Family Room	Upstairs Hall	Master Bedroom	Master Bedroom	Master Bathroom	Living Room	Bedroom
Date	5/29/08	5/29/08	5/29/08	7/18/08	5/29/08	7/18/08	7/18/08
Organism	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3
Alternaria	40						40
Ascospores	440	560	360	27	320	13	13
Aspergillus/Penicillium	1680	1280	1560	293	2720	533	480
Basidiospores	40	40			80	27	13
Bipolaris/Drechslera				40		27	93
Chaetomium							
Cladosporium	360	160	200	13	480	40	320
Curvularia				93		67	120
Epicoccum	40	40				27	53
Myxomycetes				80		53	67
Nigrospora							13
Pithomyces							13
Total	2600	2080	2120	546	3600	787	1225

Table 3. Residence 2: Outside/Inside Mold Spore Concentrations

Sample Name	Outside	Outside	Outside	Dining Room	Family Room	Bedroom	Bedroom	Bedroom	Bedroom	Front Room
Date	7/25/08	7/25/08	3/18/09	7/25/08	7/25/08	7/25/08	3/18/09	7/25/08	3/18/09	3/18/09
Organism	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3
Alternaria	80		53				80		173	40
Ascospores	3120	2880	40	320	480	680	293	600	333	93
Aspergillus/Penicillium	680	840		4280	3080	1640	640	2760	213	880
Basidiospores	840	640	27	80	80	40	93	80	53	27
Bipolaris/Drechslera									147	13
Chaetomium							13			
Cladosporium	680	1120	3627	320	240	440	867	360	267	173
Curvularia	40	80	27	40		240	240	200	213	27
Epicoccum			693				80	40	267	107
Myxomycetes	80	160		40				80	133	67
Nigrospora			27						13	
Pithomyces							13		133	13
Total	5520	5720	4494	5080	3880	3040	2319	4120	1945	1440

Sample Name	Kitchen	Kitchen	Laundry Room	Master B/R	Master Bath	MBR-2nd Floor	Rear Room	Study	Upstairs Bath
Date	3/18/09	7/25/08	7/25/08	7/25/08	7/25/08	3/18/09	3/18/09	7/25/08	7/25/08
Organism	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3
Alternaria	27					147	120		
Ascospores	107	320	360	360	280	373	67	360	240
Aspergillus/Penicillium	453	640	520	3000	1120	280	613	3640	2080
Basidiospores	13	40	120		40	27		40	
Bipolaris/Drechslera	27					53	40		
Chaetomium					40				
Cladosporium	160	200	320	280	160	307	360	160	280
Curvularia	40	40	120	160		213	67	40	
Epicoccum	93					107	240		
Myxomycetes	80	40		40		133	27		40
Nigrospora	27					27	40		
Pithomyces	27					107			
Total	1054	1280	1440	3840	1640	1774	1574	4240	2640

Table 4. Residence 3: Outside/Inside Mold Spore Concentrations

Sample Name	Outside	Outside	Outside	Master Bath	Master BR	Master BR	Master BR
Date	6/9/08	11/ 11/ 08	6/9/08	6/9/08	11/ 11/ 08	6/9/08	6/9/08
Organism	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3
Alternaria	40	13					40
Ascospores		120	120			40	40
Aspergillus/Penicillium	240	40	40		507	120	960
Basidiospores	760	733	440	80	53		
Bipolaris/Drechslera					13		40
Chaetomium							
Cladosporium	200	213	880	40	13	120	40
Curvularia							
Epicoccum					40		
Myxomycetes/Smuts		13					40
Nigrospora							
Pithomyces					13		
Total	1240	1132	1480	120	639	280	1160

Sample Name	Master BR	Guest BR	Kitchen	Corridor Bath	2nd BR	Living Room
Date	6/9/08	6/9/08	6/9/08	6/9/08	11/ 11/ 08	11/ 11/ 08
Organism	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3
Alternaria						13
Ascospores		40			40	27
Aspergillus/Penicillium					4320	440
Basidiospores				40	40	13
Bipolaris/Drechslera					13	
Chaetomium						13
Cladosporium	80	40	120	40	27	120
Curvularia						27
Epicoccum						
Myxomycetes/Smuts			120			13
Nigrospora						
Pithomyces						
Total	80	80	240	80	4440	666

Table 5. Residence 4: Outside/Inside Mold Spore Concentrations

Sample Name	Outside	Outside	Outside	Outside	Den	Den	Kitchen
Date	7/1/08	7/1/08	7/19/08	7/19/08	7/1/08	7/19/08	7/1/08
Organism	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3
Alternaria		40	27		40	93	
Ascospores	3680	3120	1120	560	840	133	520
Aspergillus/Penicillium	320	520		53	240	520	760
Basidiospores	480	920	1840	893	120	107	80
Bipolaris/Drechslera						27	
Chaetomium							
Cladosporium	1280	1080	120	200	320	120	200
Curvularia	160	40				147	
Epicoccum				13		93	
Myxomycetes	120	80	67	80		413	40
Nigrospora							
Pithomyces							
Total	6040	5800	3174	1799	1560	1653	1600

Sample Name	Kitchen	Front BR	Master BR	Front BR	Front BR	Garage BR
Date	7/19/08	7/1/08	7/19/08	7/1/08	7/19/08	7/19/08
Organism	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3
Alternaria	13		13			
Ascospores	107	960	133	600	53	267
Aspergillus/Penicillium	1187	1240	333	720	320	93
Basidiospores	133	160	53		27	173
Bipolaris/Drechslera		40	53	40	120	107
Chaetomium						
Cladosporium	13	280	27	160	53	67
Curvularia	53	40	27		27	80
Epicoccum	13				13	13
Myxomycetes	93		93	40	27	80
Nigrospora						13
Pithomyces					13	13
Total	1612	2720	732	1560	653	906

Table 6. Residence 5: Outside/Inside Mold Spore Concentrations

Sample ID	Outdoor	Outdoor	Outdoor	Outdoor	Outdoor	Outdoor	Outdoor	Outdoor	Outdoor	Outdoor	Outdoor	Outdoor	Outdoor	Outdoor	Outdoor
Date	8/15/03	10/22/03	2/3/05	2/3/05	9/17/03	9/25/03	9/30/03	10/6/03	8/9/04	8/9/04	8/9/04	12/3/03	12/3/03	12/3/03	2/15/07
Organisms	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3
Alternaria								46	26	13	34	7			
Ascospores	53	213			91		46		1322	2737	863	27		60	173
Aspergillus/Penicillium	2773	213		53	46	46			1293	501	324	20			
Basidiospores			107	67		46	91		3140	3456	1745	7		140	640
Bipolaris									7		27				
Chaetomium											7				
Cladosporium				53		91	46	46	475	587	148	107	337610	67	493
Curvularia									92	132	27		19581		107
Epicoccum															27
Myxomycetes		53			91	46	46		145	66	40	7		20	27
Nigrospora						46			20	26	34	7	39163		13
Pithomyces											7				
Total	2826	479	107	173	228	275	229	92	6520	7518	3256	182	396354	287	1480

Sample ID	Den	Dining Rm	Dining Rm	Dining Rm	Dining Rm	Dining Rm	East BR	Guest BR	Guest BR	Hall	Kitchen	Kitchen	Kitchen	Kitchen	Kitchen
Date	11/19/04	10/22/03	9/2/03	12/3/03	11/19/04	2/15/07	9/2/03	2/3/05	12/3/03	8/9/04	10/22/03	2/3/05	9/25/03	9/30/03	10/6/03
Organisms	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3
Alternaria										47					
Ascospores	13	213				53		27	41		107	40			
Aspergillus/Penicillium	67	373		54	53	13		53	61	27	213	53		46	
Basidiospores	13			34		213		387	74	94		80			
Bipolaris				7					14						
Chaetomium															
Cladosporium				34		680		53	108	47		53			46
Curvularia	13	53	46	14	13		46	13		40	53	27	46		
Epicoccum															
Myxomycetes				27	53			13	7						
Nigrospora				7				13		7	53				
Pithomyces									7						
Total	106	639	46	177	119	959	46	559	312	262	426	253	46	46	46

Sample ID	Kitchen	Living Rm	Living Rm	Living Rm	Living Rm	Living Rm	LR Chase	Master Bath	Master BR	Master BR	Master BR	Master BR	Master BR	Master BR	Master BR
Date	11/19/04	10/22/03	2/3/05	9/25/03	12/3/03	11/19/04	8/9/04	11/19/04	10/22/03	2/3/05	9/17/03	8/9/04	8/9/04	12/3/03	11/19/04
Organisms	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3
Alternaria												7			
Ascospores		160			74	13			107		46	40	59	14	
Aspergillus/Penicillium	627	213	53	46	209	307		120	160	53		34	40	14	573
Basidiospores	27		107		88		101		53	160		81	53	47	
Bipolaris															
Chaetomium					7										
Cladosporium			53	46	74				267	160		67	165	20	80
Curvularia		53			7				53			20	46	14	
Epicoccum															
Myxomycetes	13	53			27	13			53				7	20	
Nigrospora														7	
Pithomyces	13				7							7		7	
Total	680	479	213	92	493	333	101	120	693	373	46	256	370	143	653

Table 7. Mold Measurement Summary

	Residence 1		Residence 2		Residence 3		Residence 4		Residence 5	
	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outdoor	Indoor
	Geometric Mean	Geometric Mean	Geometric Mean	Geometric Mean	Geometric Mean	Geometric Mean	Geometric Mean	Geometric Mean	Geometric Mean	Geometric Mean
Organism	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3	Spores/m3
Alternaria	40	40	65	80	23	23	33	28	21	18
Ascospores	1,126	123	711	281	120	37	1,638	266	183	48
Aspergillus/Penicillium	679	977	756	1,102	73	644	207	464	187	82
Basidiospores	1,472	42	244	48	626	39	923	93	227	74
Bipolaris/Drechslera	40	41	NA	41	NA	19	NA	56	14	10
Chaetomium	NA	80	NA	23	NA	13	NA	NA	7	7
Cladosporium	216	130	1,403	276	335	51	427	91	268	78
Curvularia	13	60	44	94	NA	27	80	51	233	27
Epicoccum	40	37	693	112	NA	40	13	21	27	NA
Myxomycetes	73	78	113	59	13	40	85	74	41	20
Nigrospora	NA	13	27	25	NA	NA	NA	13	60	12
Pithomyces	NA	13	NA	37	NA	13	NA	13	7	8
Total	4,210	1,590	5,216	2,300	1,276	313	3,761	1,321	886	204

The geometric means for a number of common indoor mold genera such as *Ascospores*, *Basidiospores*, *Cladosporium*, *Epicoccum*, and *Myxomycetes* are typically less than the concentrations detected in outdoor air. Indeed, the only mold type for which the indoor air concentrations were regularly greater than the outdoor concentrations was the *Aspergillus/Penicillium* category. *Aspergillu*s and *Penicillium* grow mainly indoors (Ren et al., 2001) so their presence at a higher indoor concentration is not unexpected. Even for these molds, however, the indoor concentration was less than the outdoor concentration in one residence that had clear evidence of water intrusion and visible mold (Table 1).

Among the plaintiffs occupying each of the buildings a wide variety of adverse health effects were alleged to have been caused by exposure to molds in the indoor environment. These effects included multiple sclerosis, asthma, brain lesions, immune effects, celiac disease, ear infections, and lung cancer. Litigation regarding these health effects was initiated by occupants of each of these buildings, or their representatives. Although exposure to mold has been reported to be associated with exacerbations of some of these health effects (e.g., asthma), none of these have been demonstrated to be caused by indoor air mold exposure.

3. DISCUSSION

Although exposure to mold has been reported to be associated with a variety of health effects in humans, whether these effects can be attributed solely or even to a greater degree from indoor exposures depends on the relative magnitude of the potential exposures between indoor air and outdoor air. In the cases presented here, it is apparent that the potential risks for adverse health effects from exposure to mold indoors are not significantly different than those from mold exposure in outdoor air.

Although consensus numerical guidelines or agency standards for evaluation of mold exposures with regard to effects on human health are not available (Srikanth et al., 2008; Storey et al., 2004), there have been suggestions for “acceptance” or "post-remedial clearance" criteria for Aspergillus/Penicillium spore concentrations at less than 750 counts/m^3 (Baxter et al., 2005) or less than 666 counts/m^3 (Robertson and Horner, 2004). Highly sensitive individuals would be expected to react to relatively low concentrations regardless of whether these are present indoors or in the outside air. The point at which mold contamination becomes a threat to health is not known with precision (Robbins et al., 2000). From the perspective of reports of health effects caused by indoor mold exposure, the question is whether the indoor air concentration of mold spores represents a significantly elevated risk above that of concomitant outdoor environments so that any suggested health effects can be clearly attributed to those indoor exposures.

To support an allegation of adverse health effects, the indoor mold air concentrations must exceed those found outdoors and the concentrations of individual mold species or genera found indoors should also exceed those found outdoors. Typical clean building total mold spore concentrations have been reported to be less than 4,000 spores/m^3 in approximately 90% of buildings sampled. Even so, results of airborne fungal analyses alone may not be sufficient to classify a building as "clean" or "moldy" without a thorough evaluation (Baxter et al., 2005).

Concentrations of *Aspergillus/Penicillium* in "clean" buildings have been reported in a number of instances. Codina et al. (2008) reported an indoor concentration range for *Aspergillus/Penicillium* of 0-656 spores/m^3 compared to an outdoor range of 0-3,250 spores/m^3. Barnes et al. (2007) reported a maximum post-remediation *Aspergillus/Penicillium* concentration of 10,912 spores/m^3. MacIntosh et al. (2006) reported a maximum indoor *Aspergillus/Penicillium* concentration of 667 spores/m^3 compared to a maximum outdoor concentration of 5,200 spores/m^3. Finally, Kozak et al. (1985) reported an indoor concentration range for *Penicillium* species of 0-4,737 spores/m^3 and a concentration range for *Aspergillus* species of 0-306 spores/m^3 in Southern California homes. The ranges of *Aspergillus/Penicillium* concentrations measured in the evaluated residences are well within those reported in the literature.

4. CONCLUSION

For each of the residences that have been evaluated, the building occupants or their representatives have alleged a variety of adverse health effects and have initiated litigation on the basis of health concerns and building damage. In each instance, the mold air concentrations were represented to the building occupants as elevated, although for two of the buildings, competing "experts" disagreed regarding whether the mold concentrations were, in fact, elevated sufficiently to represent a "mold problem".

In four of the five buildings, remediation to reduce mold concentrations was recommended. In the fifth building, there was a recommendation to dispose of porous household items even though there was no evidence of water intrusion or inside water leakage.

Despite reports of adverse health effects, the concentrations of mold spores detected in the indoor air samples in each of these residences do not support a conclusion that indoor mold exposure would have contributed to any health effects to a greater extent than that from outdoor exposures.

The subjective judgments of mold experts must be addressed by an objective evaluation of the mold data. For instances where litigation has alleged that adverse health effects resulted from exposure to mold, a demonstration that indoor mold concentrations significantly exceed those outdoors can provide essential support. Careful evaluation of the data in cases such as those presented here can indicate that there is little, if any, support for the common suggestion that the presence of mold in the indoor environment is the cause of adverse health effects. The first step in countering the subjective claims of some mold evaluators regarding the presence of a “mold problem” and the subsequent recommendation for expensive remediation, therefore, is a rigorous evaluation of the mold concentration data.

Comparison of mold spores in indoor vs. outdoor air is the first, limited, step in a rigorous evaluation. More detailed analysis of other airborne components (e.g., volatiles, mycotoxins) is essential if their presence is being included in suggestions concerning adverse health effects.

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PART III: Remediation

Chapter 7

DECHLORINATION OF PENTACHLOROPHENOL BY ZERO VALENT IRON AND BIMETALS: EFFECT OF SURFACE CHARACTERISTICS AND BIMETAL PREPARATION PROCEDURE

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ABSTRACT

Treatment of Pentachlorophenol (PCP) is challenging due to its hydrophobic nature and the stability of the carbon-chlorine bond, particularly in aromatic molecules. Zero Valent Iron (ZVI) has been used as an effective in situ passive treatment process for PCP contaminated groundwater. However, ZVI applications can experience a decrease in degradation rates over time due to: ZVI surface passivation, the formation of non-conducting iron oxides on the ZVI surface, and the accumulation of less chlorinated intermediates. In this study, ZVI modification by acid washing and formation of bimetallic systems by the incorporation of Nickel (Ni) was explored to overcome these limitations.

PCP degradation was investigated in batch tests using ZVI as received (unwashed or UW) and acid washed (AW) ZVI. Two forms of bimetals were tested - one in which the Ni powder and ZVI (UW or AW) were physically mixed (Ni_S/Fe) and the other in which the Ni was coated onto acid washed ZVI (Ni_C/Fe) by reacting ZVI with $NiSO_4$ solutions. PCP dechlorination was confirmed by gas chromatography quantifying PCP and all intermediates formed. Raman spectroscopy was used to characterise the ZVI surfaces.

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The effectiveness of dechlorination was largely dependent on the composition of the iron oxides on the particle surface. The presence of magnetite was associated with an enhancement in PCP dechlorination while the presence of wustite, maghemite, lepidocrocite or hematite resulted in surface passivation. Complete PCP dechlorination was achieved using the Ni_S/Fe system. After 7 days, Ni_S/Fe with ZVI (AW) completely dechlorinated PCP forming phenol and cyclohexanol (96% and 3% respectively) as the major products. ZVI (UW and AW) and Ni_C/Fe bimetal showed partial PCP degradation with accumulation of less chlorinated phenols. The Ni_S/Fe system offers a simple way of effectively treating PCP without the limitations of other ZVI based procedures currently used.

Keywords: Catalyst, Dechlorination, Iron oxides, Passivation, Pentachlorophenol, Zero Valent Iron

1. INTRODUCTION

Chlorinated phenols (CPs) have been widely used as disinfectants, biocides, wood preservative and pesticides and are byproducts of industrial processing such as the bleaching of pulp using chlorine or chlorine dioxide and during the production of higher chlorinated phenols. CPs have been detected in groundwater, surface water, wastewater, air and soils as a result of improper disposal, leaching from landfills, and incineration of chlorinated wastes (ATSDR 1999). Among all CPs, pentachlorophenol (PCP) has been identified as the most toxic (Tanjore and Viraraghavan 1994) and is considered a possible human carcinogen from exposure via inhalation and dermal contact (USEPA 2010). PCP has a solubility of 14 mg/L in water (Arcand et al., 1995) and tends to bind to organic matter in soil further reducing its water availability and subsequent mobility. It has been identified as a contaminant in New Zealand soils, especially around industries where sawmilling and logging operations were conducted. PCP is listed as a priority pollutant by the United States Environmental Protection Agency (USEPA) and the maximum PCP level in drinking water is defined as 1 ppb (USEPA 2011). PCP is difficult to degrade due to its low water solubility, high degree of chlorination and the chemical stability of chlorinated aromatic compounds.

The use of zero valent iron (ZVI) is a practical effective treatment technology for dechlorination of many organic chlorinated contaminants due to ZVI's relatively high reactivity, inexpensiveness and low environmental impact (Choi et al., 2008). However, only a few studies have focused on PCP degradation by ZVI (Cheng et al., 2010, Kim and Carraway 2000, Marshall et al., 2002, Morales et al., 2002). PCP degradation by ZVI occurs through reductive dechlorination, though loss of PCP from solution involves a combination of dechlorination and sorption onto ZVI surface (Kim and Carraway 2000). The application of ZVI is limited by several factors (Kim et al., 2007) including (i) decrease in rate of PCP degradation over time due to increase in solution pH and ZVI surface passivation from iron oxide formation on reactive sites and (ii) accumulation of lower chlorinated compounds over time. Furthermore, the rate of dechlorination is highly influenced by ZVI surface characteristics such as morphology, the presence of impurities and oxides, specific surface area and crystallinity (Su and Puls 1999). Low rates of dechlorination by ZVI have also been partly attributed to excessive sorption of the contaminant to nonreactive sites and the impeding of electron transfer by oxide layers (Gotpagar et al., 1999). The reactivity of ZVI surface can be sustained in the presence of oxides such as magnetite (Fe_3O_4) and green rust (Fe [II]/Fe [III] hydroxide), while the presence of goethite (α-FeOOH) and hematite (α-Fe_2O_3) decrease the reactivity (Farrell et al., 2000, Huang et al., 2003, Satapanajaru et al., 2003). Magnetite is a semiconductor with a small band gap of 0.1 eV and has the highest conductivity of all iron oxides (Cornell and Schwertmann 2003). Iron oxides such as hematite, goethite, maghemite and wustite have higher band gaps compared to magnetite (2.2 eV, 2.10 eV, 2.03 eV and 2.3 eV, respectively) and have very low conductivities at room temperature (Cornell and Schwertmann 2003).

The use of modified iron particles is being explored as a means to overcome the above limitations. Acid pretreatment of ZVI has been shown to increase the specific surface area of ZVI (Agrawal and Tratnyek 1996, Lin and Lo 2005) affecting the dechlorination rates. In addition, acid washing of ZVI can remove the oxides present on the surface and also cause the formation of different oxides resulting in a change of surface reactivity and leading to either higher or lower dechlorination rates depending on the conditions (Liu et al., 2006). The introduction of a hydrogenation catalyst such as Nickel (Ni) can enhance the PCP dechlorination efficiency by ZVI. Physically mixing nano-scale Ni and ZVI increased the PCP dechlorination rates (Cheng et al., 2010), whereas some studies have reported that bimetals prepared by coating a catalytic metal on ZVI were poorer at PCP dechlorination than unmodified iron (Kim and Carraway 2000).

In this study, PCP dechlorination was investigated using ZVI with and without its modification as a means to overcome the limitations to using ZVI as a reductant. Unwashed (UW) and acid washed (AW) ZVI were tested under anoxic conditions to study the effect of acid washing and various iron oxides on PCP dechlorination by ZVI. Bimetals of ZVI were tested for enhanced PCP dechlorination with Ni used as the catalyst. Bimetallic systems with either physically mixing Ni and ZVI (Ni_S/Fe) or Ni coated ZVI (Ni_C/Fe) were tested to investigate their potential for enhanced PCP dechlorination and the effect of bimetal preparation procedures.

2. MATERIALS AND METHODS

2.1 Materials

The zero valent iron (ZVI) used was electrolytic iron powder with particle size 100 mesh and smaller. ZVI powder was sourced from two suppliers: ACROS, Thermo Fisher Scientific (ZVI-T) and North American Höganäs (ZVI-H). Analytical grade solvents (ethyl acetate and acetone), sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) were obtained from Ajax Finechem. Nickel powder (<150 µm, 99.99%), PCP powder (ACS grade, 98%), standard solutions of PCP, phenol, cyclohexanol and chlorophenol isomers in methanol and $NiSO_4.6H_2O$ (>98%) were purchased from Sigma-Aldrich. Deionised (DI) water (resistivity of 18.20 MΩcm, Millipore-Q system) was used in the experiments. Deoxygenated DI water was prepared by degassing DI water at 80^0C and 100 kPa for 1 hour and then sparging with nitrogen gas for half an hour. A 5000 ppm PCP stock solution was prepared in ethyl acetate.

2.2 ZVI modifications

ZVI particles were acid washed in 1N H_2SO_4 solution using the method described by Liu et al (2006). The Ni coated iron particles (Ni_C/Fe) were prepared using a reductive adsorption process involving acid washed ZVI-T and ZVI-H and a stock solution of 2.4% Ni (as $NiSO_4$) in 10% H_2SO_4. An aqueous solution of $NiSO_4$ (2 mL of Ni stock solution in 200 mL of degassed DI water) was prepared and added to a container with 100 g of acid washed ZVI. The contents were mixed at room temperature for 1 hour at 100 rpm on a rotary shaker. All modified ZVI particles were rinsed with deoxygenated DI water and acetone, dried in air at room temperature and stored in an anaerobic chamber under nitrogen until use. Analysis of solutions (using atomic absorption spectrophotometer, AAS) before and after Ni coating showed 92% and 85% removal of Ni from solutions with acid washed ZVI-T and ZVI-H respectively.

2.3 Iron surface characterization

The surface area of iron, nickel and Ni_C/Fe bimetallic particles was measured using BET N_2 adsorption analysis with the Micromeritic Tristar 3000 surface area analyzer. Specific surface area of ZVI, Ni, and Ni_C/Fe bimetallic particles are presented in Table 1. Environmental Scanning Electron Microscopy (ESEM- FEI

Quanta 200 F) coupled with SiLi (Lithium drifted) Energy Dispersive Spectroscopy (EDS) was used to obtain surface topography, characteristics and elemental information of selected regions of each material's surface. Images were collected using the back-scattered detector at a beam potential of 20 kV.

Table 1. Specific surface area of metal particles

Material	**Specific surface area (m^2/g)**
ZVI-T (UW)	0.2505 ± 0.0037
ZVI-T (AW)	2.3182 ± 0.0122
ZVI-H (UW)	0.2117 ± 0.0018
ZVI-H (AW)	0.9104 ± 0.0033
Nickel powder	0.3854 ± 0.0035
Ni_C/Fe (with acid washed ZVI-T)	4.4668 ± 0.0209
Ni_C/Fe (with acid washed ZVI-H)	2.6957 ± 0.0108

The iron oxides present on ZVI (unwashed and acid washed) and Ni_C/Fe bimetallic particles before and after exposure to PCP solution were identified using Raman spectroscopy (Renishaw Raman system 1000 spectrometer). Nine oxides commonly found on iron surfaces (akaganeite, maghemite, hematite, magnetite, wustite, lepidocrocite, goethite, feroxyhyte and ferrihydrite) were used as the reference iron oxides in Raman analysis (Cornell and Schwertmann 2003). Quantification of iron oxides was performed using Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) within MATLAB (Mathworks®) (Jaumot et al., 2005).

2.4 Experimental procedure

Experiments were carried out in batch reactors using Wheaton amber vials (30 mL). To each reactor 1.00 (±0.01) g of unwashed or acid washed ZVI or 1.00 (±0.01) g of Ni_C/Fe bimetal or 1.00 (±0.01) g of Ni powder was added. For the experiments with Ni_S/Fe bimetal, 1.00 (±0.01) g or 0.10 (±0.01) g of Ni powder was mixed with 1.00 (±0.01) g of unwashed or acid washed ZVI-H. Mixture of 1 g of ZVI and 1 g of Ni is referred to as Ni_S (1.0)/Fe and the mixture of 1 g of ZVI and 0.1 g of Ni is referred to as Ni_S (0.1)/Fe. Then the reactors were filled with 10 mL of deoxygentated DI water and spiked with 10 µL of PCP stock solution (5000 ppm) prepared in ethyl acetate. Immediately after spiking with PCP stock solution, reactors were sealed with aluminum caps and PTFE/silicone septa and agitated on a rotary shaker at 100 rpm at 23 (±1)°C until sampled. Control vials were prepared similarly, except that no solid was added. Four reaction vials and two controls were sacrificed for analysis at each sampling time. The pH of the reaction solutions was measured in situ in all reactors.

2.5 Analysis

An acid modified liquid-liquid extraction procedure was followed to determine the total (dissolved + sorbed) concentration of PCP and degradation products (Kim and Carraway 2000). For this, 5 mL of ethyl acetate was added to each reactor, which were then placed on a rotary shaker for 30 minutes followed by addition of 1 mL of concentrated HCl and mixing for an additional 10 minutes. The ethyl acetate phase (1.5 mL) was collected using a glass syringe and filtered using 0.2 µm RC (Regenerated Cellulose) membrane filters for analysis. The PCP and degradation products' concentrations were measured with gas chromatography-mass spectrometry analysis (GC/MS-Shimadzu model GCMS-QP2010S) with ZEBRON ZB5-msi capillary column (30 m L x 0.25 mm ID x 0.25 µm thickness) using the Selected Ion Monitoring (SIM) analysis method. Hydrogen gas was analysed using SRI 8610C gas chromatograph with Thermal Conductivity Detector (TCD). A HayeSep Q 80/100 column (Alltech, 6' x 1/8" x 0.085" SS) was used at a temperature of 24 ^{0}C. Nitrogen was used as the carrier gas at a flow rate of 10 mL/min.

3. RESULTS AND DISCUSSION

3.1 Effect of surface characteristics on PCP degradation by ZVI and bimetals

Figure 1 presents the PCP degradation by ZVI-T and ZVI-H (unwashed and acid washed) and Nickel coated iron (Ni_C/Fe) prepared using acid washed ZVI-T and ZVI-H. The two ZVI samples behave surprisingly differently. With no Ni, ZVI-H (UW) showed the highest PCP degradation with 79% PCP degraded after 25 days. In contrast, ZVI-T (UW) showed the least PCP degradation with 34% PCP degraded after 25 days. Acid washing enhanced the PCP degradation by ZVI-T achieving 62% PCP degraded by ZVI-T (AW) after 25 days. Acid washed ZVI-H showed a decrease in the performance with 74% PCP degraded after 25 days (Figure 1). PCP dechlorination was confirmed by quantifying the less chlorinated compounds produced during each treatment using GC/MS analysis and mass balance recoveries were all within 92% to 96% (data not shown). Previous studies showed enhanced trichloroethylene (TCE) dechlorination with acid washed ZVI (Lin and Lo 2005, Liu et al., 2006).

Nickel coated acid washed ZVI-T (Ni_C/Fe (ZVI-T)) showed the highest efficiency among all treatments tested (Figure 1). After 25 days, Ni_C/Fe (ZVI-T) resulted in 97% PCP degradation; phenol was the major degradation product (69% of the end products) while trace amount of tetra-, tri-, di- and mono-CPs were measured (data not shown). Nickel coating on acid washed ZVI-H (Ni_C/Fe (ZVI-H)) did not increase the performance of ZVI-H; in fact, a decrease in PCP degradation (Figure 1) and accumulation of tetra-, tri- and di-CPs were observed. It is interesting to observe that a deposited Ni coating enhanced PCP dechlorination by ZVI-T, but inhibited dechlorination by ZVI-H. Similarly coating ZVI with Pd or Ni has been reported to enhance dechlorination of TCE (Kim 1999), though Kim and Carraway (2000) reported slower PCP degradation rates with Ni/Fe bimetallic particles in comparison to unamended iron.

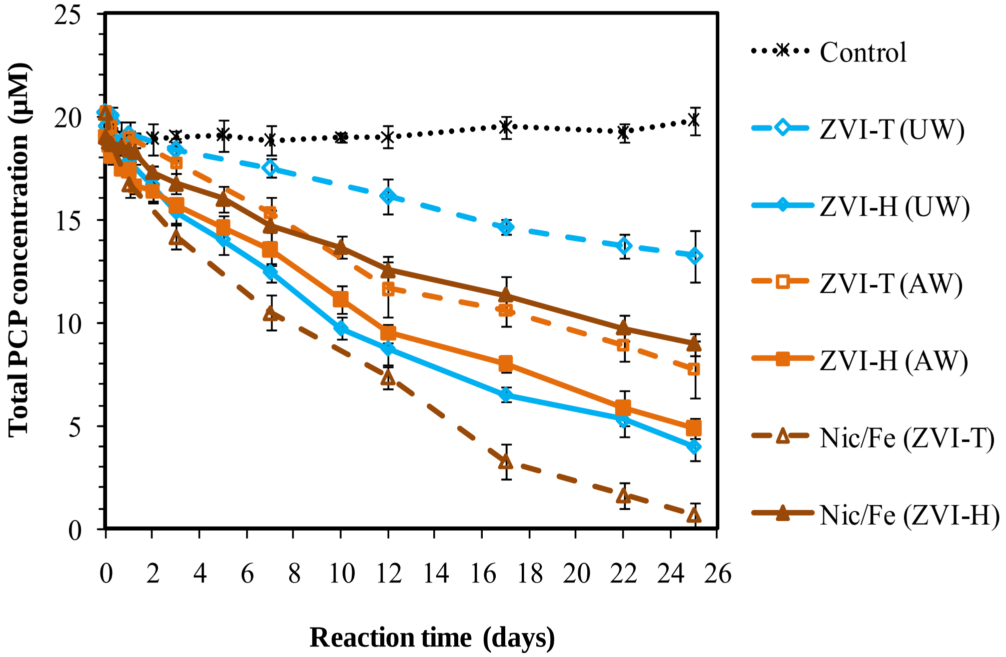

Figure 1. PCP degradation by ZVI and Ni_C/Fe bimetals

Raman spectra were measured to characterize the iron oxides present on the ZVI surfaces for all samples before and after reaction with PCP. For almost all samples, a mixture of iron oxide phases were observed and MCR-ALS was used to determine the sample composition. Figure 2 shows the Raman spectra for the pure oxides and typical sample spectra ranging from before reaction to after 25 days of reaction. A mixture of oxides (wustite, magnetite and ferrihydrite) was observed on unwashed ZVI surfaces. While ZVI-H (UW) was predominantly covered with magnetite, wustite was observed as the major oxide on ZVI-T (UW). Both wustite and magnetite are semiconductors. The magnetite band gap is only

0.1 eV and it is almost metallic with the highest conductivity of all iron oxides. The wustite band gap is 2.3 eV and wustite has a much lower conductivity than magnetite (Cornell and Schwertmann 2003). Hence, the lower reactivity of ZVI-T (UW) was attributed to the presence of wustite on the surface hindering electron transfer process. Acid washing of ZVI-T removed wustite while increasing the amount of magnetite on the surface. Magnetite is electrically conductive and allows electron transfer facilitating the dechlorination reaction (Ritter et al., 2002). Therefore, higher reactivity of ZVI-H (UW) as well as ZVI-T (AW) was attributed mainly to the presence of magnetite. For the ZVI-H PCP degradation was almost unchanged before and after acid washing. This observation is consistent with the Raman spectra showing the ZVI-H having a magnetite oxide layer both before and after acid washing.

A definitive explanation for the different effect of Ni coating on the two ZVI materials is not clear from the work; however, some possibilities are noted. In the present study, AAS analysis of the solutions as well as the ESEM/EDS analysis of Ni_C/Fe particles showed less Ni deposition on ZVI-H (AW) surface compared to ZVI-T (AW) surface (data not shown). Moreover, the specific surface area of Ni_C/Fe (ZVI-H) was smaller than the surface area of Ni_C/Fe (ZVI-T) (Table 1).

Hydrogen gas (H_2 (g)) production was seen in all treatments with the exception of ZVI-T (UW) (data not shown). It was observed that H_2 (g) production in Ni_C/Fe (ZVI-H) system was lower than the H_2 (g) measured in Ni_C/Fe (ZVI-T), indicating lower reactivity or inhibition of hydrogen production due to Ni deposition on reactive sites of ZVI-H (AW). Therefore, the lower PCP degradation by Ni_C/Fe (ZVI-H) could be a result of lower Ni deposition and specific surface area, inhibition of hydrogen production and excessive formation of iron oxides (predominantly magnetite) on the Ni/Fe surface interfering with the Fe^{2+} movement.

3.2 Effect of bimetallic preparation procedure on PCP degradation

Bimetallic systems prepared by physically mixing Ni with ZVI were compared with the Ni coated ZVI described in Section 3.1 to investigate the effect of bimetallic preparation procedure on PCP dechlorination. Physical mixing used Ni powder (Ni_S) with ZVI in either a 1:1 or a 0.1:1 Ni_S/Fe ratio (w/w). Figure 3 presents the PCP degradation by just ZVI and both different bimetallic systems. The Ni particles, when used without ZVI, showed the least PCP degradation (Figure 3). The standard reduction potential of Ni is higher than that of Fe, meaning that Ni is a poorer electron donor for PCP dechlorination, as indicated by the lower PCP degradation.

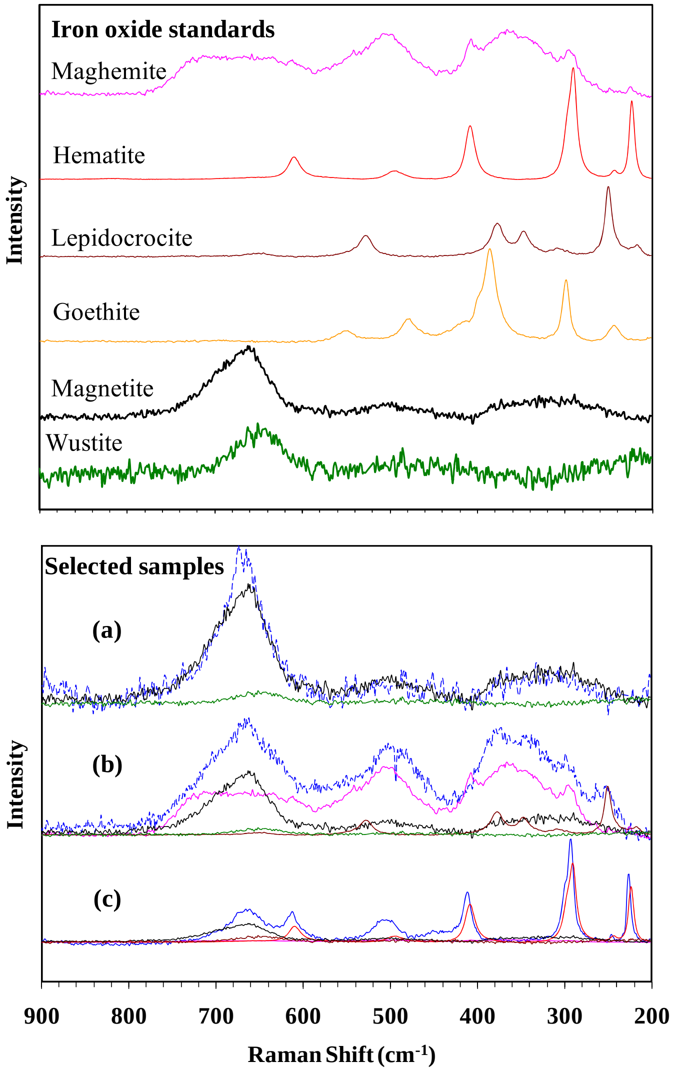

Figure 2. Raman spectra of pure iron oxides and typical sample spectra (ZVI-T AW) that was (a) unreacted (b) after 1 day and (c) after 25 days reaction. Sample Raman spectra are shown in blue with their fitted components in colours as per the oxide standards.

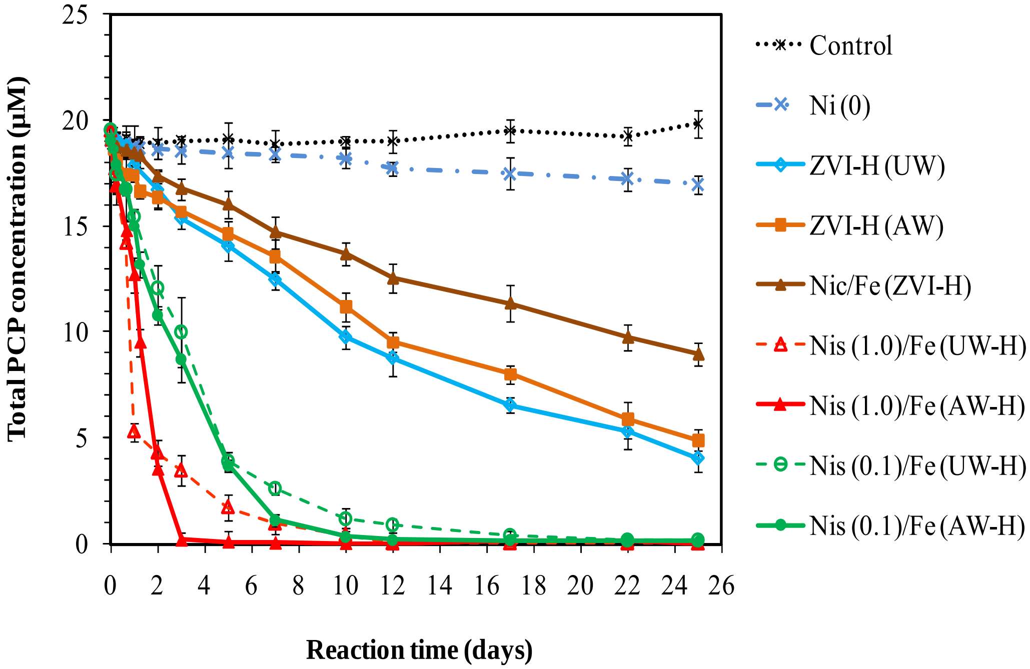

Figure 3. PCP degradation by ZVI and different Ni-ZVI bimetallic systems

Physically mixing Ni and ZVI (Ni_S/Fe) significantly enhanced the PCP dechlorination compared to ZVI (UW and AW) and Ni_C/Fe treatments. For example, with Ni_S/Fe using ZVI-H (AW) and a 1:1 w/w Ni_S/Fe, complete dechlorination of PCP to phenol and cyclohexanol (96% and 3% of the end products, respectively) was observed after 7 days. In comparison, after 7 days, the nickel coated ZVI treatment (Ni_C/Fe) resulted in only 27% PCP degradation while accumulating tetra-, tri- and di-CPs as degradation products in the solution. Similarly, ZVI-H (UW and AW) treatments resulted in partial PCP degradation (Figure 3) and accumulation of tetrachlorophenols in the solution. The Ni_S/Fe system resulted in complete PCP dechlorination and also in complete degradation of intermediate CP's such that after 25 days' reaction in all Ni_S/Fe systems, the final degradation products were either just phenol or were phenol and cyclohexanol. In addition, the rate of dechlorination was substantially faster with the Ni_S/Fe than with the Ni coated ZVI. The amount of Ni added to the system affected the rate of PCP dechlorination and the intermediate byproducts distribution with higher PCP degradation rates being observed by mixing 1 g of Ni compared to 0.1 g of Ni (Figure 3).

Figure 4 presents an example of the PCP degradation products from a Ni_S/Fe treatment. This illustrates the rapid production of phenol through the less chlorinated phenol intermediates. The concentrations of intermediates indicate their relative rates of production and destruction, and the most prominent intermediates were the CP's with 4 chlorines followed by those with 3 then 2 and lastly 1 chlorine. The mass balance achieved in these Ni_S/Fe systems was consistently ≈ 90 %, which could be due to (1) incomplete recovery of non-chlorinated compounds (that are formed during rapid dechlorination of PCP) during chemical extraction and/or (2) possible loss of the more volatile non-chlorinated compounds during sample handling.

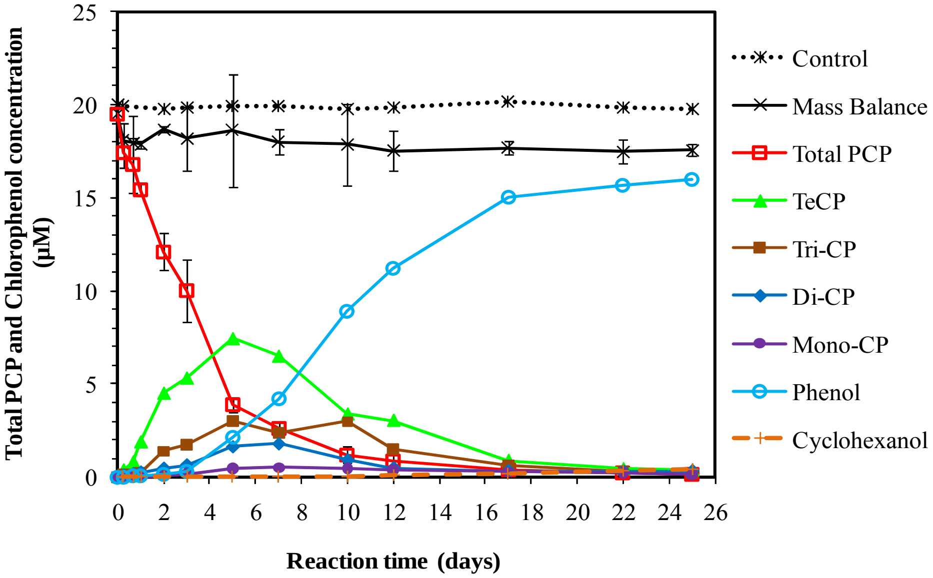

Figure 4. PCP degradation by Ni_S/Fe bimetal (physical mix of 1 g ZVI (UW) + 0.1 g Ni powder) and intermediate products distribution

Hydrogen gas production was seen in treatments with ZVI-H (UW and AW), Ni coated ZVI-H and physical mix of Ni and ZVI-H, but not when Ni powder was used without ZVI (data not shown). The highest H_2 (g) production was observed with the Ni_S/Fe systems and more H_2 (g) was produced with 1 g Ni than with 0.1 g Ni. For example, after 25 days reaction, Ni_S/Fe systems with ZVI-H (AW) produced 201% (i.e. the H_2 partial pressure in the vessel was 2.01 atm) and 106% H_2 (g) with 1 g Ni and 0.1 g Ni, respectively. The lowest H_2 (g) production (45% after 25 days reaction) was seen with the Ni_C/Fe (ZVI-H) treatment.

Another important difference between the Ni_S/Fe samples and Ni_C/Fe samples was the iron oxide phases formed on the surface after reaction with PCP as determined by Raman spectroscopy. Prior to reaction with PCP, a mixture of magnetite and/or wustite was observed on ZVI (UW) while only magnetite was present on the ZVI (AW) and Ni_C/Fe surfaces. After 25 days reaction with PCP several iron oxides, including lepidocrocite, magnetite, hematite, wustite and ferrihydrite, were found on the Ni_C/Fe bimetallic particles. Oxides such as lepidocrocite, hematite, wustite and ferrihydrite have low conductivity at room temperature (Cornell and Schwertmann 2003). Formation of these oxides can decrease the number of reactive sites on the ZVI surface and electron transfer process hindering PCP dechlorination. However, in the treatments with physically mixing Ni particles and ZVI, only magnetite was present on ZVI (UW) and ZVI (AW) consistent with an increase in PCP dechlorination compared to Ni coated Fe system.

In a ZVI/H_2O system, although ZVI acts as the main reductant, there are also other reducing agents, Fe^{+2} and H_2, which were produced during iron corrosion, and are available for PCP reduction. However, the reaction of Fe^{+2} with the chlorinated compound is known to be a slow process, and H_2, in the absence of a catalyst, is not an effective reductant (Matheson and Tratnyek 1994). When Ni particles are physically mixed with ZVI, Ni acts as an effective catalyst, resulting in higher H_2 (g) production, and potentially increasing the ratio of indirect reduction of PCP by H_2. Feng and Lim (2005) reported enhanced reduction of chlorinated compounds by nano-scale Nickel-iron bimetal as compared to unmodified ZVI, and the effect was attributed to indirect reduction by H_2 in the presence of nickel.

This study explores some of the complexities involved in the dechlorination of chlorinated organics using bimetallic systems. There are several apparently contradictory studies in the literature, which may result from differences in the methods of producing the bimetallic phase. For example, previous studies have reported enhanced PCP dechlorination with physically mixed nano-scale Ni and ZVI (Cheng et al., 2010). On the other hand, a comparison of isolated ZVI, with physical mix of nano-scale Pd-ZVI, and Pd coated on ZVI, showed enhanced TCE dechlorination rates only in the Pd coated system (Zhang et al., 1998). Therefore, the catalytic reactivity of bimetals and the dechlorination rate depends on, (1) the properties of target chlorinated compounds, (2) properties and surface characteristics of ZVI used and (3) method of bimetallic preparation.

4. CONCLUSIONS

PCP degradation was studied using different ZVI materials (with and without acid pretreatment) and bimetallic systems with ZVI and Ni. The performance of ZVI and the effect of acid washing were dependent on the surface characteristics of ZVI particles. Acid pretreatment of ZVI removed wustite while increasing magnetite on the surface. In general, the presence of magnetite increased the PCP degradation. Nickel coated ZVI (Ni_C/Fe) prepared with acid washed ZVI-T showed complete PCP degradation. However, the catalytic effect of Ni was dependent on the surface characteristics of ZVI used. The presence of oxides such as wustite, lepidocrocite, hematite and ferrihydrite was consistent with lower PCP degradation by Ni_C/Fe prepared with ZVI-H (AW). A physical mix of Ni powder with ZVI (Ni_S/Fe) dramatically increased the PCP dechlorination and achieved complete degradation of PCP and intermediate CPs. The amount of Ni added to the system affected the rate of PCP dechlorination and the distribution of intermediate products. Rapid and complete PCP degradation can be achieved by following physical mixing of Ni and ZVI as a method of bimetallic preparation. This can minimize the limitations of ZVI use such as accumulation of less chlorinated byproducts and slower dechlorination rates due to oxide formation and ZVI surface passivation.

5. ACKNOWLEDGEMENTS

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Chapter 8

REMEDIATION OF A FORMER MGP SITE IN NORWICH NEW YORK: A CASE STUDY

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ABSTRACT

Former Manufactured Gas Plant (MGP) production from circa 1860s through the 1950s at a site in Norwich, New York, resulted in impacts to both on-site and off-site soils and groundwater. Site remediation includes four phases of treatment: in situ solidification (ISS) of on-site source materials; recovery of NAPL from off-site; in-situ chemical oxidation (ISCO) of off-site areas; and enhanced bioremediation of off-site groundwater.

Approximately 52,103 cubic yards (39,835 cubic meters) of impacted sand and gravel were solidified in-situ using auger mixing technology, and over 54,000 gallons (210,000 liters) of NAPL have been recovered to date. An ISCO bench-scale study revealed that four applications of hydrogen peroxide will reduce BTEX and naphthalene by 99% and TPH by 50%. Full-scale ISCO application will occur upon completion of NAPL recovery, followed by enhanced bioremediation of dissolved phase contamination (benzene and naphthalene).

1. INTRODUCTION

A Manufactured Gas Plant (MGP) is a facility that produced gas for lighting and heating homes and businesses. The Norwich former MGP, Norwich, Chenango County, New York, USA, produced gas using the coal gasification and carbureted water gas processes. Coal gas was produced by heating coal in retorts or beehive ovens, carbonizing the coal in the absence of air. The carbureted water gas process involved the passage of steam through burning coal, forming a gaseous mixture (water gas or blue gas) that was sprayed with oil as it then passed through a super heater. The oil spray would generate additional gas, enhancing the heat and light capacity of the overall gas mixture.

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In each process, the gas was cooled and purified prior to distribution. During cooling, an oily liquid known as coal tar would condense from the hot gas and settle in the bottom of gas holders, pipes and other structures. These structures were typically built below ground, using groundwater as a bottom seal. Therefore, they posed significant potential to introduce coal gas byproducts directly into the ground. The gas was purified using wood chips treated with iron oxide to remove hydrogen sulfide from the gas.

Coal tar is typically a reddish-brown oily liquid, which does not readily dissolve in water. It is commonly categorized as a non-aqueous phase liquid (NAPL). Although most coal tars are slightly denser than water, the difference is slight. Consequently, the coal tar can either float or sink when in contact with water. The coal tar is evident as sheen on a water surface or as NAPL in soil or water. At the Norwich MGP site, coal tar was found in the subsurface surrounding former MGP structures, and in downgradient areas.

The Norwich former MPG site is located in a residential and commercial area. The former MGP operations previously occupied approximately 1 acre (0.4 ha). It is believed that plant operations began sometime between 1863 and 1887. Gas production ceased in 1953. Little is known of the generation and disposal practices of the residues from the Norwich MGP, except that two subsurface tar storage vessels existed until they were removed in 1997 as part of an Interim Remedial Measure (IRM). The IRM also included removal of a relief holder, related piping, and surrounding soil.

Specific volatile organic compounds (VOCs) of concern include benzene, toluene, ethylbenzene, and xylenes (collectively, BTEX). Semivolatile organic compounds (SVOCs) of concern are polycyclic aromatic hydrocarbons (PAHs).

2. RECORD OF DECISION

The presence of hazardous wastes at the Norwich site, including MGP tars and purifier waste (i.e., spent wood chips), created significant threats to human health and the environment. To eliminate or mitigate these threats, the New York State Department of Environmental Conservation (NYSDEC) selected a remedy with these components:

- In-situ solidification (ISS) of impacted on-site source area
- Removal of free-phase NAPL from select off-site areas
- In-situ chemical oxidation (ISCO) treatment of off-site source material
- Bioremediation of dissolved phase contamination

Performance goals for ISS treatment included:

- Unconfined compressive strength (UCS) greater than 50 pounds per square inch (psi) (345 kPa) at 28 days
- Hydraulic conductivity less than 1×10^{-6} cm/s at 28 days

Note that solidification refers to the process of encapsulating a waste to form a solid material and to restrict contaminant migration by decreasing the surface area exposed to leaching (USEPA, 2010). As such, the focus should be to divert groundwater flow around the low-permeability monolith to minimize contaminant leaching. The strength criterion should be secondary (in the authors' opinion.)

The ISS phase of the remediation was completed spring of 2011. Off-site NAPL recovery operations began in 2009 and are ongoing. ISCO treatment is in the planning stages, and will be implemented when the rate of NAPL recovery tapers off.

In general, the local community is supportive of the selected remedy, particularly the creation of developable property.

3. SITE GEOLOGY AND HYDROGEOLOGY

The site is underlain by four stratigraphic units, in order of increasing depth:

- Fill: Loose to compact sand and gravel with concrete fragments, coal, and asphalt, extending to depths up to 7 ft (2 m).
- Sand and Silt: Loose to medium compact fine sand and silt, generally extending to depths of about 5 ft (1.5 m). (It is absent in areas where fill is deep). This stratum is interpreted to be alluvium.
- Gravel: Loose to medium compact gravel and sand, extending to depths of 17 to 22 ft (5 to 7 m). This stratum is interpreted to be glacial outwash.
- Clay: Medium to stiff clay. This stratum serves as a continuous confining layer beneath the Gravel.

Index testing of representative samples indicates that the gravel stratum contains 8 to 26 percent fines passing the No. 200 sieve size. The fines content in this stratum tended to decrease with depth, being least at the bottom. Atterberg limits tests indicate that the Gravel fines have some plasticity, with Plasticity Indices ranging from 0 to 9 percent.

Geotechnical test borings were made using hollow stem augers and split spoon sampling. Based on consistent Standard Penetration Test blow counts and the judgment of the driller, it was inferred that the natural soils at this site did not contain significant cobbles and boulders.

Groundwater at the site was typically at a depth of about 6 ft (1.8 m).

4. ISS BENCH STUDIES

ISS bench scale studies were performed by Kemron Environmental Services, Inc., (Kemron), Atlanta, GA. The primary goals of the bench scale treatability studies were to confirm the feasibility of ISS as a remedial remedy at this site and to provide guidance for selection of ISS reagents to achieve required performance criteria in the field. The bench studies focused primarily on reducing the hydraulic conductivity of the gravel soil layer. This was considered key to success of this project. The following reagents were evaluated in the treatability study:

- Portland Cement (PC). This is the primary reagent. PC additions of 5 to 15 percent by weight were evaluated.
- Bentonite (B). Bentonite was intended to reduce hydraulic conductivity. Bentonite additions of 1 to 2 percent were evaluated.
- Cement Kiln Dust (CKD). CKD was evaluated for potential beneficial reduction in hydraulic conductivity, primarily by introducing fines to fill void spaces within the gravel soil. CKD was obtained from the Lafarge Cement Plant, Ravena, NY.

Kemron proportioned the reagents, and then added water to create a slurry. Sufficient water was added to produce a slurry that was visually judged to be pumpable (no slurry testing was performed). The reagent slurry was then mixed with representative soil samples and allowed to cure.

Analytical testing of the soil samples indicated that contaminant concentrations were representative of average or typical conditions. Bench testing was not performed on heavily contaminated soils (which would represent worst case conditions) because it was assumed that heavily contaminated zones within the soil profile would be intermixed and “diluted” during ISS operations. General conclusions derived from the bench studies include:

- As expected, unconfined compressive strength increases with increasing cement content. Addition of CKD typically resulted in only minor strength improvement. Addition of bentonite typically resulted in minor strength reduction.

- Hydraulic conductivity decreases with increasing cement content. Adequate reduction of the hydraulic conductivity of the gravel soil was more difficult to achieve and controlled the design.
- Addition of 1 percent bentonite decreased the hydraulic conductivity of the gravel stratum by about an order of magnitude. Additional bentonite (i.e., > 1%) resulted in negligible further improvement in hydraulic conductivity.
- Addition of CKD resulted in only small decrease in hydraulic conductivity. Reduction was greatest when the cement content was low.

The treatability study indicated that two mix designs: (1) 8% Portland Cement and 1% bentonite or (2) 11% Portland Cement (no bentonite), would meet the stipulated performance criteria, with a predicted hydraulic conductivity on the order of 5×10^{-7} cm/s at 28 days, providing a reasonable safety factor.

5. REMEDIAL DESIGN

Closely spaced test borings were made within the ISS area during final design to establish the elevation of the top of the clay barrier layer across the ISS footprint. These data were used to develop a detailed top of clay surface to define the required depth of ISS treatment at any location. The ISS footprint was subdivided using a 25 by 25 ft (7.6 by 7.6 m) grid, and the required depth of treatment was defined by the deepest clay elevation within each grid box. ISS treatment generally extended 2 ft (0.6 m) into the clay except along the ISS treatment area perimeter, where the toe was increased to 4 ft (1.2 m). The intent was to afford greater certainty that the ISS treatment would extend completely through the impacted soils along the treatment area boundary, providing a continuous cutoff. A smaller toe was considered appropriate within the interior of the treatment area because any minor untreated zones above the clay surface would be isolated and completely confined. Because the design borings were closely spaced and provided reliable data regarding depth to the clay barrier layer, no confirmation borings were required during construction. The specifications also required that the perimeter of the treatment area be completed first, to confine the MGP impacted area and minimize risk of MGP NAPL migrating outward beyond the treatment area boundary.

The ISS grout mix was specified to be 8% Portland cement and 1% bentonite. Although bench studies indicated that an alternative mix with 11% Portland cement without bentonite would also meet design performance requirements, but was not considered because the resulting high strength could potentially impede effective column overlap. The contractor was also allowed to develop alternative grout mix designs. The initial water:reagent ratio was specified to be 1:1 by weight, but higher water to solids ratios could be used, if necessary. Auger mixing was specified; bucket mixing was not permitted.

The design required pre-excavation to a depth of 4 ft (1.2 m) prior to ISS treatment, corresponding to local frost depth. This pre-excavation would subsequently be backfilled with clean soil, protecting the top of the ISS monolith from degradation by freeze-thaw action. The precut also served to contain spoils during the work.

5.1 Means and Methods

Remedial ISS was performed by WRScompass, Windsor, NJ, between December 2010 and April 2011. ISS was performed using a 10-ft (3.0 m) diameter mixing auger powered by a crane mounted Diesel-Hain drill platform having 400,000 foot-pounds (540 kJ) of torque. Type I Portland cement was delivered to the site in pneumatic trucks and offloaded into storage pigs. Bentonite was delivered in 50-lb (220 N) bags. Grout was prepared using a high-shear mixer. The batch tank had a working volume of approximately 5 cubic yards (3.8 m^3).

Required reagent quantities were calculated for each column considered its required depth and overlap with adjacent columns. The predetermined grout volume was pumped to injection ports located along the arms of the mixing tool and blended with the impacted soils. The 10-ft (3.0 m) diameter columns were positioned in a triangular pattern with nominal spacing of 8.67 ft (2.64 m), providing full coverage without gaps. Three vertical mixing passes were typically used, resulting in a homogeneous mixture of the impacted granular soils.

Initial trials indicated that the 8% Portland cement plus 1% bentonite grout mix was not pumpable when mixed at the initial 1:1 water:reagent ratio. To create a pumpable mix, the water to solids ratio was increased to 1.85:1. Since this would significantly increase the quantity of spoils (i.e., swell), the Contractor constructed several test columns to evaluate the feasibility of reducing the quantity of bentonite and water in the grout mix. These test columns indicated that the quantity of bentonite could be reduced to 0.75% (and possibly 0.5%), without significant increase in hydraulic conductivity and a substantial reduction of water. Based on these tests, the grout mix was modified to 8% Portland cement plus 0.75% bentonite, mixed at a 1.23:1 water to reagent ratio. The modification reduced the required quantity of reagents somewhat, but more importantly, reduced the required volume of water and resulting volume of ISS spoils, which required costly off-site disposal for this project.

ISS treatment (Figure 1) totaled 52,103 cubic yards (39,835 m3). Spoils (swell) amounted to approximately 21,180 tons (19,215 tonnes). This equates to approximately 25 percent spoils, assuming 1.6 tons per cubic yard.

Figure 1. ISS mixing operations

5.2 Quality Control

Treated material was sampled using a sampling tool with a hydraulically operated lid (Figure 2). The lid is opened after the sampler is lowered to the desired sampling depth, allowing the treated soil to flow into the sampling device. Representative samples were typically obtained at two or three depths within an ISS column, and these were subsequently blended to create a single composite sample for the column. Test cylinders were created from the composite sample after screening out larger sized particles. The test cylinders were stored and cured in a water bath in a heated room. At the end of the cure period, the samples were delivered to the test laboratory by courier. Laboratory testing was performed by Atlantic Testing Laboratories, Ltd., Canton, NY.

Figure 2. ISS sampling operations

A total of 113 Quality Control samples (Figure 3) were obtained by the design engineer (AECOM). Unconfined compression strength testing was performed at 7 days to provide an early indication of ISS performance. Unconfined compression strengths ranged from 39 to 351 psi (270 to 2,420 kPa), averaging approximately 180 psi (1,240 kPa) at 7 days. The standard deviation of the sample pool was 70 psi (480 kPa). Only one sample had strength less than the required 50 psi (345 kPa); however, its strength increased to 69 psi (475 kPa) at 28 days.

Hydraulic conductivity tests were performed at 28 days. Measured hydraulic conductivities ranged from 5×10^{-8} to 3×10^{-6} cm/s, averaging about 6×10^{-7} cm/s. The standard deviation of the sample pool was 5×10^{-7} cm/s. Ten samples failed to achieve the specified criterion of 1×10^{-6} cm/s at 28 days. Subsequent testing, however, demonstrated that the specified hydraulic conductivity was achieved with additional curing at 56 days. The data show that it would be necessary to target a design hydraulic conductivity of about 1×10^{-7} cm/s to ensure that practically all samples will achieve the required maximum allowable value of 1×10^{-6} cm/s at 28 days.

Figure 3. ISS sample (note gravelly nature of the sample)

6. NAPL RECOVERY

NAPL recovery activities began in 2009 with the installation of three recovery wells located on an off-site property downgradient to the former MGP property. These wells produced NAPL from a pooled depression in the clay confining layer. Four additional recovery wells were subsequently installed to tap the NAPL pool, and a recovery test using mechanical rotary pumps produced a total of approximately 19,000 gallons of NAPL/water mixture over a 9-day period. Several samples of the collected NAPL/water mixture were analyzed to determine their approximate water content. Each sample was weighed, placed in a dry oven for 24 hours, and subsequently weighed again. The results indicated that the collected NAPL/water mixture contained between 50% and 95% NAPL by mass.

Following the recovery test a recovery system was installed in 2010, including a series of bladder pumps controlled by an electronic controller connected to a compressor. The bladder pumps did not emulsify the NAPL with water as the mechanical rotary pumps had done, allowing the system to more efficiently collect NAPL while minimizing inclusion of water. The resulting NAPL/water mixture is believed to contain about 95% NAPL by mass. Three additional recovery wells were also installed within a second depression identified in the confining clay layer during pre-design investigations in 2010. Current NAPL recovery is ongoing with a total of over 60,000 gallons (225,000 liters) recovered to date.

7. ISCO TREATMENT

Two vendors (VeruTEK, Bloomfield, CT, and XDD, Stratham, NH) were selected to perform ISCO treatability studies. XDD evaluated commercially available oxidants: activated persulfate and catalyzed hydrogen peroxide (CHP). VeruTEK evaluated proprietary surfactant-enhanced ISCO technology, Fe-EDTA activated persulfate, green synthesized zero valent iron (G-nZVI) catalyzed hydrogen peroxide, VeruSOL-3, and VeruSOL-11.

Based on the results of the XDD treatability study, a 12.5 percent solution of CHP with 20 mM citric acid and 3.5 g/kg acid was the most effective and reliable ISCO chemical for the Site. The treatability study indicated preferential treatment of BTEX (99%) and to a lesser extent PAHs and TPH (approximately 50%) after four applications of ISCO on moderately impacted soils. Approximately 20 lbs of oxidant is expected to be used per lb of contaminant treatment of moderately impacted soils. The XDD study also indicated that more applications will be required to treat the heavily impacted soils, and NAPL may smear from the contaminated intervals into less or non-contaminated intervals.

The VeruTEK treatability study indicated that VeruSOL-3 solubilized TPH more effectively than VeruSOL-11 and that S-ISCO efficiently oxidized COCs in the emulsion. Overall, G-nZVI CHP was the best performing oxidant/activator with reductions of 99% in VOCs, 96% in SVOCs, and greater than 66% reduction in TPH (DRO and GRO) concentrations relative to the control. The concentration reduction percentage can be misleading since VeruTEK failed to provide overall contaminant mass balance (i.e., contaminant concentration reduction due to treatment of the contaminants or flushing through the treatment cell could not be determined).

Based on the treatability study results, CHP will be used for full-scale ISCO injection for the treatment of off-site NAPL impacted area, upon completion of the NAPL recovery. Continued NAPL monitoring and recovery will be conducted during and following the ISCO injection. Follow-up soil and groundwater monitoring will be conducted for a period of up to 6 months to evaluate the effectiveness of ISCO.

8. CONCLUSIONS

a. ISS successfully treated MGP impacted soil at the Norwich former MGP site, achieving the required unconfined compressive strength of 50 psi (345 kPa) at 28 days and maximum hydraulic conductivity of 1×10^{-6} cm/s at 28 to 56 days.

b. Unconfined compression strengths ranged from 39 to 351 psi (270 to 2,420 kPa), averaging approximately 180 psi (1,240 kPa) at 7 days. The standard deviation of the sample group was 70 psi (480 kPa). All test results exceeding the specified minimum of 50 psi at 28 days.

c. Measured hydraulic conductivities at 28 days ranged from 5×10^{-8} to 3×10^{-6} cm/s, averaging about 6×10^{-7} cm/s. The standard deviation of the sample group was 5×10^{-7} cm/s. Ten samples failed to achieve the specified criterion of 1×10^{-6} cm/s at 28 days. However, subsequent testing demonstrated that the specified hydraulic conductivity was achieved after 56 days curing.

d. The volume of spoils (swell) was approximately 25 percent. This exceeded initial estimates, the increase largely caused by the need for additional water to improve grout pumpability. The greater volume of spoils resulted in cost overruns, as excess spoils required off-site disposal for this project.

e. Selection of the design grout mix focused on achieving the required hydraulic conductivity in the gravel soils at this site, while also controlling strength gain so that column overlap could readily be achieved. This was accomplished by using bentonite in the grout mix. Although bentonite was clearly beneficial in reducing hydraulic conductivity and controlling strength, its use required increased water content, which increased the volume of swell and spoils. Effort should be made during bench studies and field trials to minimize the quantity of bentonite to control the volume of spoils.

f. Consideration should be given to other potential reagents that may achieve suitable results, while reducing the required quantity of water (e.g., granulated blast furnace slag (GBFS)). Use of GBFS has successfully been used on other ISS projects with little or no bentonite addition (personal communication, WRS Compass). GBFS has also been used for other grouting applications, such as hydraulic cutoffs in bedrock (Weaver and Bruce, 2007).

g. Significant NAPL recovery is potentially achievable. Detailed modeling of the surface of confining layers is useful to identify potential NAPL pools.

9. REFERENCES

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PART IV: Risk Assessment

Chapter 9

SAMPLING STRATEGY AND RISK EVALUATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL NEAR A FORMER PIPELINE IN MAINE

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ABSTRACT

In 1952 a 7.25-mile long jet propulsion fuel (JP-5) supply pipeline was built within a 30-foot wide easement from the fuel farm at Defense Fuel Support Point, Casco Bay to Naval Air Station Brunswick, Maine. This subterranean pipeline, which spanned 115 private properties in Harpswell, Maine, was in operation until 1991 when it was decommissioned and abandoned in place. During construction, the pipeline was wrapped with an asbestos covering and, to eliminate any potential threat to humans from exposure to this covering, a decision was made to remove the pipeline. The pipeline remained in place until the Maine Congressional delegation acquired funding in 2007 for the removal. Pipeline removal began on February 8, 2010 and was completed by May 18, 2010.

Polycyclic aromatic hydrocarbons (PAHs) were detected in soil during routine monitoring associated with pipeline removal. Whereas the source of PAHs was originally thought to have been JP-5 fuel oil releases, the project team determined that this was not the case and searched for another source of PAHs. This paper describes the planning and conduct of an environmental investigation that was necessary to evaluate the nature and extent of pipeline-related PAH contamination and potential human health risks from exposure to PAHs in easement soil. Collaboration between Maine Department of Environmental Protection (MEDEP)

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and the Navy was a key component in minimizing investigative costs while ensuring that the health of local residents was protected. A statistically based sampling design and statistical data analyses supported the project.

Keywords: soil, pipeline, Maine, polycyclic aromatic compounds, PAHs, statistical sampling, risk assessment, background estimates.

1. INTRODUCTION

The soil investigation described herein was performed to determine an effective sampling strategy for contaminant delineation and risk characterization for residential properties located along the former Casco Bay Pipeline, and to obtain initial estimates of residential health risks, including risks from soils in the pipeline easement area. Results of the pilot soil investigation were used to determine the extent of soil containing polycyclic aromatic hydrocarbons (PAHs) and if PAH concentrations in soil pose a potential unacceptable risk to exposed receptors in compliance with the Maine Department of Environmental Protection "Remediation Guidelines for Petroleum Contaminated Sites in Maine" (MEDEP 2009). It was the Navy's intent to return the easement property back to the original property owners without encumbrances.

1.1 Site Location and Description

The Casco Bay Pipeline was an underground pipeline that extended approximately 7.25-miles from the northern boundary of Mitchell Field in the town of Harpswell, Maine to the southern boundary of the former Naval Air Station Brunswick (NASB) located in the town of Brunswick, Maine. Property use surrounding the former Casco Bay Pipeline is residential and located in a rural area characterized by woodlands and wetlands. The pipeline was situated within a 30-foot wide easement that crossed 115 private properties. The pipeline system consisted of two separate underground pipes that were used to transfer jet propulsion (JP) fuel, primarily JP-5, from about 1952 until 1991 when the pipeline was taken out of service. The two pipes were constructed of carbon steel with welded joints of 8-inch, and 10-inch diameter and were set approximately three feet apart. The pipes were wrapped in asbestos and covered in an asphalt exterior coating, and placed on approximately 6 to 8 inches of bedding materials (either imported sand or native materials) in a narrow trench and covered with up to 5 feet of native materials that were excavated during construction of the trench.

In 1991, the pipeline was drained, cleaned and taken out of service. At this time, the pipes were also pressurized with nitrogen. This treatment persisted until 1995 when the NASB fuel tank-farm located in Mitchell Field was dismantled.

1.2 Previous Sampling Activities

The Navy's pipeline removal contractor began pipeline removal on February 8, 2010 and completed removal on or before May 18, 2010. Surficial materials above the pipeline were removed and placed to the sides of the excavation to enable removal of the pipeline. Sections of the pipeline were removed, placed on polyethylene sheeting, and transferred to roll-off containers. Excavated soils were used as backfill, with MEDEP approval.

The contractor collected soil samples at 20-foot intervals for MEDEP bag-headspace field-screening with a photo-ionization detector (PID). Soil samples were also collected a few inches beneath the pipeline at locations spaced 100-feet apart. These sampling locations were called "stations." These sub-pipeline samples were analyzed for volatile petroleum hydrocarbons (VPH) and extractable petroleum hydrocarbons (EPH). Naphthalene (a PAH) is the only VPH target analyte for which detected concentrations exceeded the MEDEP "Soil Remediation Guidelines" (MEDEP, 2009) leaching-to-groundwater criterion (1,700 micrograms per kilogram [µg/kg]). This criterion was exceeded at nine of the 375 locations, two of which were co-located with relatively high concentrations of other PAHs, and the remaining seven locations were associated with low or non-detectable concentrations of other PAHs.

It is well known that PAHs are common constituents of charcoal, ash, and asphalt products (e.g., shingles, paving, sealers), are produced from burning wood (e.g., in fire places, wood stoves, and forest fires), and can be distributed over long distances by atmospheric deposition (ATSDR, 1996). Therefore, PAHs are ubiquitous in the environment and can have various anthropogenic sources. Wetland sediments, which contain abundant organic matter, tend to accumulate PAHs, especially if they receive runoff from asphalt-paved areas (ATSDR, 1996). In both terrestrial and aquatic depositional areas, various processes, such as photo-oxidation and microbial action, can break down PAHs (ATSDR, 1996). This would result in PAH concentrations eventually decreasing to natural or anthropogenic levels over a sufficient period of time. Degradation of PAHs is expected to occur more rapidly in surface soil than in subsurface soil and the degradation times are anticipated to be on the order of weeks to months (ATSDR, 1996).

2. MATERIALS AND METHODS

2.1 Sampling Design

Soil sampling was conducted at Stations 18+00, 23+00, and 170+00 where previous sampling by another Navy contractor in March-April 2010 indicated the presence of elevated PAH concentrations that may have been derived from the former pipeline. Two sampling strategies were used at each Station:

- A large area grid representing the 30-foot wide pipeline easement spanning the width of an individual property to 10-feet below ground surface (bgs) or to refusal/bedrock, whichever was shallower. Each large grid was designed to emulate as closely as possible the volume of soil that a resident could get exposed, i.e., and exposure unit (EU).
- A small area grid representing approximately 100 square feet and a soil depth spanning the range of 1-foot above the former pipeline bottom to 1-foot below the pipeline bottom (or top of bedrock, whichever was shallower). The small area grid was required by MEDEP to determine the extent of the PAHs in the vicinity of the PAH “hotspot”. MEDEP required that the data sets generated from both the small-area and large-area sampling approaches be compared to determine which sampling approach could be used to estimate human health risk at the remainder of the pipeline, if necessary.

For each soil boring location, soil samples were selected from upper, middle, and lower depth intervals. In the small area grids, sample depth intervals were based on the depths of the previous contractor’s soil sample. These samples constituted available soil from the previous sample depth and depth intervals immediately above and below the previous depth. In the EU-based grids, sample intervals were selected based on risk characterization’s “surface soil” vs. “subsurface soil” to support the risk characterization. Surface soil is between 0 and 2-feet bgs; subsurface soil is between 2-feet and bedrock.

The small and large sampling grids for each Station were centered on the location of PAH contamination detected previously at each of the properties. Nine borings were randomly located within the small grid, 14 were located randomly within the large grid, and both grids shared a boring at the center of the grids. The boring locations at Stations 18+00, 23+00, and 170+00 are depicted on Figures 1, 2 and 3, respectively, in Section 3.

The intent of the resampling was to compare the small and large grid subsurface soil concentrations and other characteristics (e.g., spatial coverage) to determine which grid best represented PAH exposure. The small grid was designed to delineate the previously identified contamination within a small area. The large grid was designed to represent a scenario in which a resident is exposed to soil in the entire easement. The small area sampling focused on subsurface soil characterization whereas the large grid incorporated surface and subsurface soil sampling because residents are exposed to surface soil as well as subsurface soil. This sampling design yielded the following nine sets of samples and corresponding PAH concentrations:

- Station 18+00 small area sampling subsurface soil only;
- Station 18+00 large area sampling surface soil;
- Station 18+00 large area subsurface soil;
- Station 23+00 small area sampling subsurface soil only;
- Station 23+00 large area sampling surface soil;
- Station 23+00 large area subsurface soil;
- Station 170+00 small area sampling subsurface soil only;
- Station 170+00 large area sampling surface soil; and,
- Station 170+00 large area subsurface soil.

2.2 Soil Sampling and Analysis

Soil cores were collected continuously from each borehole using an all-terrain vehicle-mounted direct push rig equipped with a dual-tube soil sampling system. The dual-tube sampler consisted of a 1-inch inside diameter, 3-foot-long core barrel equipped with a new acetate liner. A total of 72 soil borings were advanced and 178 soil samples were collected for chemical analysis.

Soil cores from each of the three depth intervals were mixed in separate, steam-cleaned aluminum pans, and a sample of this soil was collected for EPH analysis following the Massachusetts Department of Environmental Protection method (MADEP, 2004a). Also, because naphthalene was elevated when compared to MEDEP Petroleum Remediation Guidelines (MEDEP, 2009) at Station 23+00, sub-cores were collected for VPH method for naphthalene analysis following the MADEP method (MADEP, 2004b) in both the small area and EU-based area. Each sub-core was collected using a new sub-coring device provided by the laboratory. The sub-coring device was used to collect three 5-gram samples, approximately equally spaced over the length of each soil interval. After collection of the sub-cores, the remainder of the soil in each interval was thoroughly mixed in separate, steam-cleaned aluminum pans, and approximately 30-grams of soil was collected for EPH analysis.

2.3 Statistical Analysis Methods

A dataset to dataset comparison was required in order to evaluate the most effective sampling strategy for use on the remainder of the pipeline. For statistical and mathematical manipulations, non-detect values were represented by one-half the reported non-detect value. Duplicate results (original and duplicate) were averaged to represent the concentration at the sample location for statistical evaluations. The statistical package R version 2.9.2 (R Development Core Team, 2011) was used to conduct the statistical evaluations. Statistical methods utilized can be found in statistical references (Moore, 1995).

The small area data were compared to large area data assuming the two datasets were similar, against the alternative that the two datasets were different. The comparisons were performed using side-by-side boxplots, normal Quantile-Quantile (Q-Q) plots, histograms, summary statistics, and hypothesis tests. The contractor soil samples (3 samples total or 1 sample per Station) were excluded from this analysis because they were present in both the small area and large area data sets.

2.4 Risk Evaluation Methods

PAH concentrations were used to estimate cancer and non-cancer risks for residents whose properties include portions of the 7.25-mile long pipeline easement. A risk ratio calculation method based on default exposure assumptions (USEPA, 1989) were used as the starting point for these calculations. That method is introduced in Sections 2.4 and 2.4.1, and its adaptation to account for site-specific conditions is described in Section 2.4.2.

Carcinogenic risks are expressed in the form of dimensionless probabilities referred to as incremental lifetime cancer risks (ILCRs). The ILCR per sampled location was derived by dividing the detected concentration at each sampling location by the risk-based concentration (RBC) equivalent to 1 x 10^{-6} ILCR. The MEDEP Petroleum Remediation Guidelines (MEDEP, 2009) risk-based residential screening values (ILCR = 10^{-6}) were used as the RBCs. The following equation shows how this calculation was carried out:

$$\mathrm{ILCR} = \sum_{i=1}^{n} \left(\frac{C_i}{\mathrm{RBC}_i} \times 10^{-6} \right)$$

where: ILCR = Incremental lifetime cancer risk.

C_i = Detected concentration for compound i.

RBC = 1 x 10^{-6} ILCR equivalent concentration for compound i.

The exposure assumptions used as the basis for the ILCRs computed in this manner are conservative and are considered to represent an overestimate of actual risks. For this project 1 x 10^{-5} ILCR or more was considered to be unacceptable.

Non-carcinogenic risk estimates are presented in the form of hazard quotients (HQs) and Hazard Indices (HIs). The HQ for each sampled location was derived by dividing the detected concentration for each chemical by the non-carcinogenic RBC. Compounds potentially resulting in non-carcinogenic (systemic) effects were evaluated using the following equations:

$$HQ_i = \frac{C_i}{RBC} \qquad HI = \sum_{i=1}^{n} HQ_i$$

where: HQ_i = Hazard quotient for compound i.
C_i = Detected concentration for compound i.
RBC = HQ=1 concentration equivalent for compound i.

For this project a HI greater than 1 was considered to be unacceptable. Sixteen PAH concentrations (excluding naphthalene) were measured in each sample from the three Stations. Naphthalene was also analyzed using the EPH method at Stations 18+00 and 170+00 but it was analyzed using the VPH method at Station 23+00. Naphthalene concentrations at Station 23+00 were shown through previous sampling by the contactor to be relatively high when compared to MEDEP Petroleum Remediation Guidelines (MEDEP, 2009) including risk-based residential soil guidelines and Leaching to Groundwater guidelines. Naphthalene has a low enough boiling point that it behaves as a volatile petroleum hydrocarbon as well as a semivolatile hydrocarbon. A list of the PAHs and whether they are considered to be carcinogenic or non-carcinogenic is presented in Table 1.

The toxicity equivalency factor (TEF) indicates its carcinogenic toxicity relative to benzo(a)pyrene carcinogenic toxicity as well as the MEDEP risk-based residential screening values for carcinogens and non-carcinogens. The measured PAH concentrations were used to estimate human health risks from exposure to PAHs in soil for each of these data sets.

2.4.1 Initial Risk Estimation Methodology

To compute carcinogenic and non-carcinogenic risks, the first step was to compute the exposure point concentration (EPC) for each PAH. The EPC is the concentration that represents the level of PAHs to which a hypothetical receptor is exposed within an exposure unit. The soil exposure unit, in this case, is the volume of soil to which the hypothetical resident is exposed through various pathways, such as dermal contact, incidental ingestion, and inhalation. To estimate the EPC, data from all samples within the exposure unit were used. Instead of computing ILCRs directly, however, an upper bound on the range of concentrations for each chemical in each exposure unit (EU) was computed as described below and this value was used to compute the ILCR. The project team recognized that sampling provides only an estimate of the true EPC and that repeating the sampling event would almost certainly yield a different estimate every time it was repeated.

Table 1. Targeted PAHs and their carcinogenicities.

PAH	**Carcinogenicity**	**Toxicity Equivalency Factor, TEF**	**MEDEP RAGS Residential Values**	
			ILCR = 1E-6, mg/kg	**HI=1, mg/kg**
2-Methylnaphthalene	Non-carcinogenic	Not applicable	NA	4.7E+02
Acenaphthene	Non-carcinogenic	Not applicable	NA	4.8E+03
Acenaphthylene	Non-carcinogenic	Not applicable	NA	5.1E+03
Anthracene	Non-carcinogenic	Not applicable	NA	2.2E+04
Benzo(a)anthracene	Carcinogenic	0.1	2.6E-01	NA
Benzo(a)pyrene	Carcinogenic	1	2.6E-02	NA
Benzo(b)fluoranthene	Carcinogenic	0.1	2.6E-01	NA
Benzo(g,h,i)perylene	Non-carcinogenic	Not applicable	NA	3.7E+03
Benzo(k)fluoranthene	Carcinogenic	0.01	2.6E+00	NA
Chrysene	Carcinogenic	0.001	2.6E+01	NA
Dibenzo(a,h)anthracen	Carcinogenic	1	2.6E-02	NA
Fluoranthene	Non-carcinogenic	Not applicable	NA	5.0E+03
Fluorene	Non-carcinogenic	Not applicable	NA	4.1E+03
Indeno(1,2,3-	Carcinogenic	0.1	2.6E-01	NA
Naphthalene	Non-carcinogenic	Not applicable	2.0E+02	1.9E+03
Phenanthrene	Non-carcinogenic	Not applicable	NA	3.5E+03
Pyrene	Non-carcinogenic	Not applicable	NA	3.7E+03

Therefore, the initial approach was to place an upper bound (i.e., a 95 percent upper confidence limit [UCL]) on the range of EPCs that would be obtained if multiple sampling events occurred within the EU. This approach is a standard approach that uses statistics to estimate the EPC for each chemical within each of the nine data sets. ProUCL software, version 4.00.05 (USEPA, 2010), was used for these calculations.

Some complicating factors were encountered when using ProUCL. One factor was the dearth of detectable PAH concentrations. Approximately 75 percent of all measured PAH concentrations based on 178 samples collected for this investigation were less than detectable levels. The ProUCL calculations generally require at least five detectable results in each data set before a statistically based EPC can be computed. There were not enough PAH detections to support the calculation for all PAHs when the total number of data points was divided by station, depth (i.e., surface or subsurface), and sampling grid (i.e., large or small). In samples for which PAHs are not detectable, it is possible that PAHs are present at low, unquantifiable concentrations. Therefore, the project team considered the EPCs computed by ProUCL to be non-representative of an actual EPC and decided to abandon the EPCs computed by ProUCL for a different approach as described below.

2.4.2 Risk Management Methodology

The following text describes the rationale to estimate a realistic EPC for each of the data sets. PAHs are produced during many different combustion processes, such as internal combustion engine operations, backyard burning, building fires, and forest fires, that tend to deposit PAHs onto surface soil. PAHs as a group are relatively immobile in soil and all of these potential activities can explain why surface soil PAH concentrations were generally greater than subsurface concentrations. Therefore, it was concluded that low concentrations of PAHs outside the easement represent background PAH concentrations. Access to the property outside of the easement, however, was not available for sampling because of access constraints on private property. Therefore, to determine what the level of background PAH benzo(a)pyrene equivalents (BAPEs) might be, the PAH concentrations were ranked by their BAPEs by substituting one-half the detection limit for non-detected carcinogenic PAH values. By doing so, it became evident that most carcinogenic BAPEs on a sample-by-sample basis were less than 1×10^{-5} and would be considered to represent an acceptable level of risk if they were equal to the actual EPC. Therefore, the mean concentration of all BAPEs representing cancer risk less than 1×10^{-5} was computed and to this mean was added 2.6 (the approximate 95 percent Student's t-factor) times the standard deviation of the individual concentrations. The resulting value, 110 μg/kg, represents an upper end of the distribution of the individual concentrations. Most PAH concentrations within the easement were less than 110 μg/kg regardless of whether they represented surface or subsurface soil. This was an additional indication that BAPEs less than 110 μg/kg (equating to a cancer risk of approximately 4×10^{-6}) represent a general low level of PAHs not related to pipeline operations. Additional data to support this assertion are in a compilation of soil data from a related investigation (Tetra Tech, 2012) in which soil samples were collected for PAH analysis in areas known to be uncontaminated outside the pipeline easement. For these additional data the BAPEs were well below 110 μg/kg, indicating that 110 μg/kg is a conservatively high upper estimate of BAPE concentrations in an uncontaminated area such as the property outside the easement.

By estimating the general, low level of risk from soil PAH exposure that is not related to pipeline operations, it was possible to compute a realistic risk estimate for a resident exposed to soil over the entire property. If one assumes that a resident has equal probability of being exposed to soil from any particular portion of the residential property, then the actual risk incurred from living on the property is an average of risks associated with all soil within the property boundaries. This means that the risk from exposure to soil in the easement and risk from exposure to soil throughout the rest of the property can be combined using a simple area-weighted average representing the relative sizes of the two areas. The soil depth to which a resident could be exposed is assumed to be the same across the entire property. The only missing information was an estimate of the relative sizes of the easement and the rest of the property at each of the sampled stations. A review of town records indicate that all residential properties along the pipeline are about 2-acres or larger with some of the properties being on the order of 20-acres or more. Using the conservative value of 2-acres, the proportion of the area associated with the easement would be 0.5-acres divided by 2-acres, or 0.25 of the total area.

A simple arithmetic average of all data points within each large sampled area was computed. It was assumed that each data point from the large samples area carried equal weight in representing the easement portion of the EPC. The average PAH concentrations (i.e., the EPC) were computed for each PAH and the BAPEs for each sampled area. These BAPEs were converted to the equivalent ILCR for the sampled area and also for the overall residential property. This is described in more detail in Section 3.4.

3. RESULTS AND DISCUSSION

3.1 Soil Analytical Results

The following 17 PAHs were detected: 2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene (see Table 2).

Five PAHs, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, dibenzo(a,h)anthacene, and indeno(1,2,3-cd)pyrene exceeded Maine screening values for residential soil using an Incremental Lifetime Cancer Risk (ILCR) equal to 1 x 10^{-6}. The five PAHs exceeded these criteria in eight out of a total of 178 pilot soil samples, which represents approximately 4.5 percent of the samples. The eight samples that exceeded residential criteria were located at the following pilot soil sample locations:

- Station 18+00: two borings - SB10 (1.3-2.3 feet bgs), and SB20 (0-2 feet bgs)
- Station 23+00: four borings - SB06 (1.3-2.3 feet bgs), SB11 (0-2 feet bgs), SB15 (2 samples – 1-2 ft bgs, 2-3 feet bgs), and SB17 (0-2 feet bgs)
- Station 170+00: one boring - SB21 (0-2 feet bgs)

Benzo(a)pyrene was detected in a total of 15 other soil samples at concentrations ranging from 37 to 158 µg/kg. These values do not exceed the 260 µg/kg benzo(a)pyrene criterion (MEDEP, 2010) for a single contaminant (ILCR equal to 1 x 10^{-5}).

PAH concentrations did not exceed MEDEP Leaching-to-Groundwater criteria in any of the soil samples except one of the contractor's soil samples located at Station 23+00 where naphthalene was detected at 6,440 µg/kg. Naphthalene's criterion is 1,700 µg/kg.

The concentrations of carcinogenic PAHs exceeding the residential soil guidelines (ILCR equal to 1 x 10^{-5}) were normalized to benzo(a)pyrene equivalent (BAPE) concentrations. This normalization facilitates a spatial comparison of the eight samples where multiple PAHs exceeded residential guidelines of ILCR equal to 1 x 10^{-6} (exceedances) at the three stations. The following seven PAHs are used to calculate the BAPE concentration: benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo (a,h)anthracene, and indeno(1,2,3-cd)pyrene.

The locations of the eight exceedances from the pilot soil investigation and the contractor's original "hot spot" sample are depicted on Figures 1 through 3. A description of the exceedance locations at each of the three pilot study areas follows:

- At the Station 18+00 study area (Figure 1), BAPE exceedances were measured at two samples within five feet of the former pipeline. One of the samples is located within the small area grid at boring SB10 and the remaining sample is located within the large area grid at boring SB20. Both samples were collected from surface soils (0 to 2.3 feet bgs).
- At the Station 23+00 study area (Figure 2), BAPE exceedances were measured in five samples within the large area grid. Four were within five feet of the former pipeline and the one was located between five and 10

feet from the former pipeline. Two of the five exceedances were from surface soil.

- At the Station 170+00 study area (Figure 3), BAPE exceedances were measured at one sample at boring SB21 located in the large area grid approximately six feet of the former pipeline. This sample was from surface soil.

These results indicated that most (5 out of 8) exceedances were from surface soils. The highest BAPE concentrations at each of the three stations were in the contractor's samples. These samples were collected within a few inches of the pipeline during the excavation process. In comparison, the soil investigation samples were collected at the three stations after pipeline removal and restoration of the easement area.

3.2 Statistical Analysis Results

The data were analyzed to determine whether they are similar or different. The percentage of non-detected concentrations for all the chemicals at each of the three stations was greater than 50 percent; therefore, the two-proportion test was used to determine whether there was a difference between the percentage of samples above the action level. A cancer risk action level of 10^{-5} (incremental lifetime cancer risk [ILCR]) was used for carcinogens and a non-cancer risk action level equal to 1 (hazard index [HI]) was used. The ILCR is the incremental probability of an individual developing cancer over a lifetime, as a result of exposure to a contaminant (MEDEP, 2009). The HI is the sum of hazard quotients (HQs) for substances that affect the same target organ or organ system. The HQ is the ratio of the potential exposure to the substance and the level at which no adverse effects are expected. If the HQ is calculated to be equal to or less than 1, then no adverse health effects are expected as a result of exposure. If the HQ is greater than 1, then adverse health effects are possible.

The actual numerical comparisons were based on chemical-specific concentrations equivalent to these action levels. The assumed null hypothesis for the two-proportion test was that the proportion of samples greater than the action level in the small area dataset is statistically similar to the proportion of samples greater than the action level in the large area dataset. The alternative hypothesis was that the proportion of non-detected concentrations in the small area dataset is statistically different than the proportion of non-detected concentrations in the large area dataset. If the probability value (p-value) associated with the proportion test was less than 0.05, it was concluded that the proportion of samples greater than the action level in the small area dataset is different than the

Table 2. Data Summary Table, Pilot Soil Investigation, Casco Bay Pipeline, Harpswell, Maine

Parameter(1,2)	**Frequency of Detects**	**Minimum Detection (µg/kg)**	**Maximum Detection (µg/kg)**	**Average (µg/kg)**	**Sample Max. Detected**	**Residential(3) (ILCR=10-6, HQ=0.2)**		**Residential(3) (ILCR=10-5, HQ=1)**	
						(µg/kg)	**No. >**	**(µg/kg)**	**No. >**
2-METHYLNAPHTHALENE	7/178	15	54	8.74	CBP-23-SB15-2-3	94000	0	470000	0
ACENAPHTHENE	37/178	2.4	595	16.7	CBP-170-SB21-0-2	970000	0	4800000	0
ACENAPHTHYLENE	16/178	2.7	113	8.63	CBP-23-SB15-0-2	1000000	0	5100000	0
ANTHRACENE	56/178	2.9	1260	33.9	CBP-170-SB21-0-2	4300000	0	22000000	0
BENZO(A)ANTHRACENE	46/178	7.4	3810	82.5	CBP-18-SB20-0-2	260	8	2600	1
BENZO(A)PYRENE	50/178	3.7	2610	67.4	CBP-18-SB20-0-2	26	23	260	8
BENZO(B)FLUORANTHENE	77/178	6.85	4120	89.3	CBP-18-SB20-0-2	260	8	2600	1
BENZO(G,H,I)PERYLENE	51/178	3.3	1260	36	CBP-18-SB20-0-2	750000	0	3700000	0
BENZO(K)FLUORANTHENE	60/178	2.5	1250	34.3	CBP-18-SB20-0-2	2600	0	26000	0
CHRYSENE	45/178	5.8	2660	68.2	CBP-18-SB20-0-2	26000	0	260000	0
DIBENZO(A,H)ANTHRACENE	32/178	2.4	309	13.6	CBP-18-SB20-0-2	26	8	260	1
FLUORANTHENE	45/178	14	5190	147	CBP-170-SB21-0-2	1000000	0	5000000	0
FLUORENE	34/178	3.5	579	16.8	CBP-170-SB21-0-2	830000	0	4100000	0
INDENO(1,2,3-CD)PYRENE	75/178	3.6	1430	40.2	CBP-18-SB20-0-2	260	8	2600	0
NAPHTHALENE	13/118	11.2	102	10.1	CBP-170-SB21-0-2	200000	0	1900000	0
PHENANTHRENE	47/178	6.6	4770	104	CBP-170-SB21-0-2	700000	0	3500000	0
PYRENE	46/178	11	4080	122	CBP-170-SB21-0-2	750000	0	3700000	0
NAPHTHALENE(4)	4/60	536	1330	96.5	CBP-23-SB15-2-3	200000	0	1900000	0

Notes/Abbreviations: (1) - Sample and sample duplicate values averaged. (2) EPH analyte except as noted (see note 4). (3) - Criteria Reference: Maine Remedial Action Guidelines, January 13, 2010. (4) VPH analyte. No.> - No. of samples exceed criterion. µg/kg – micrograms per kilogram.

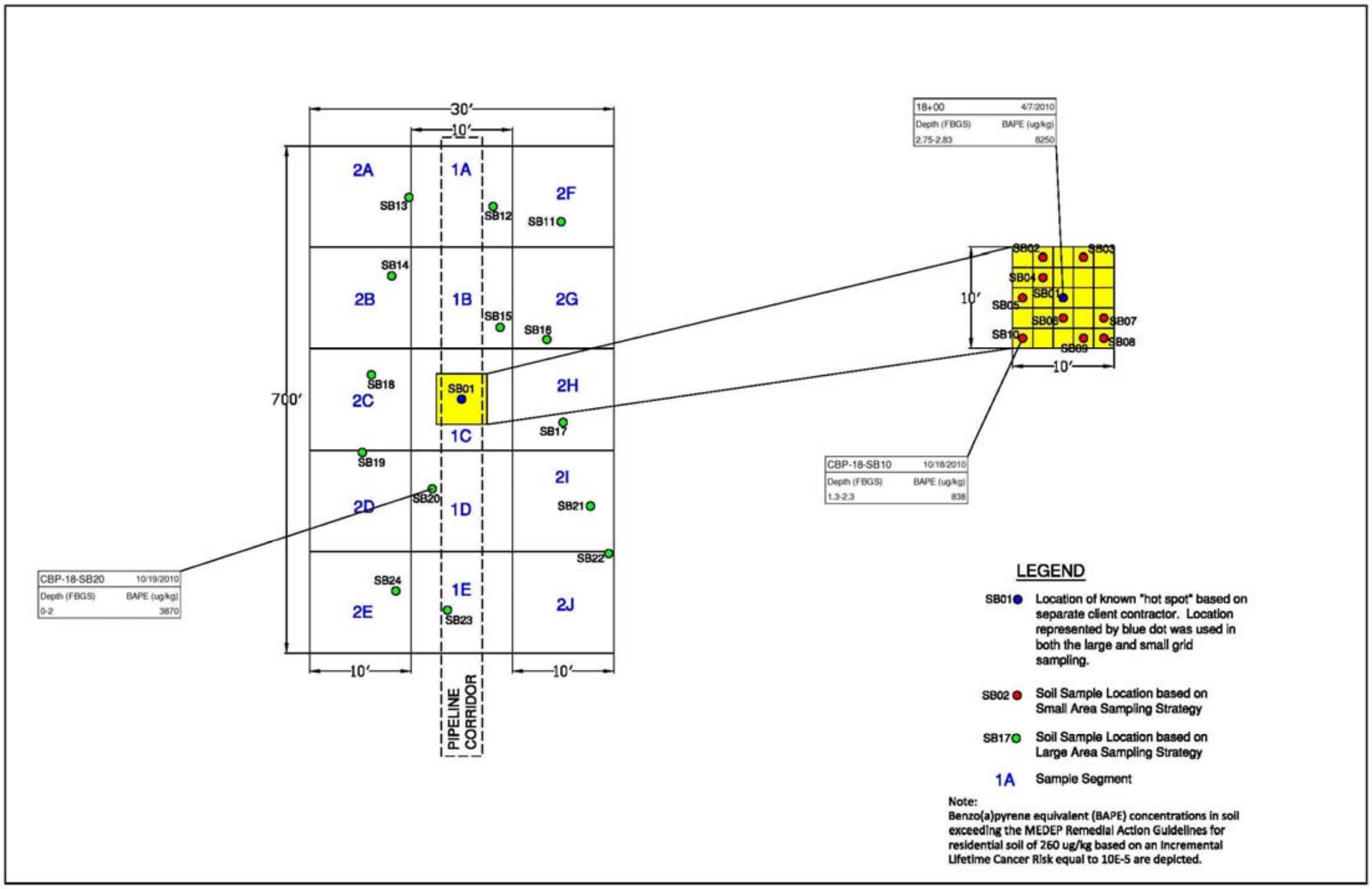


Figure 1. BAP Equivalents Exceeding 260 µg/kg MEDEP Residential Soil Guideline at Station 18+00 Pilot Soil Study Area.

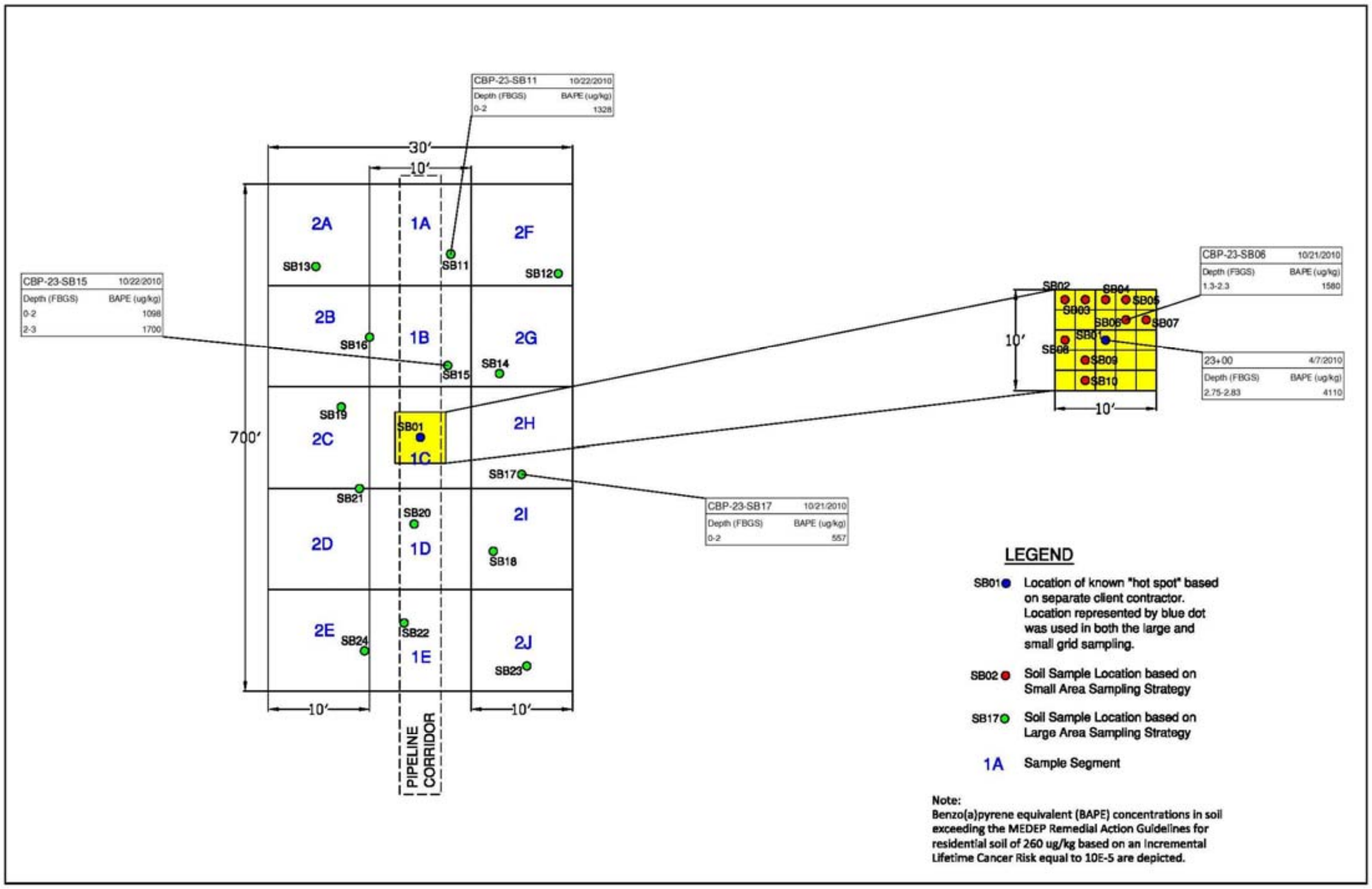
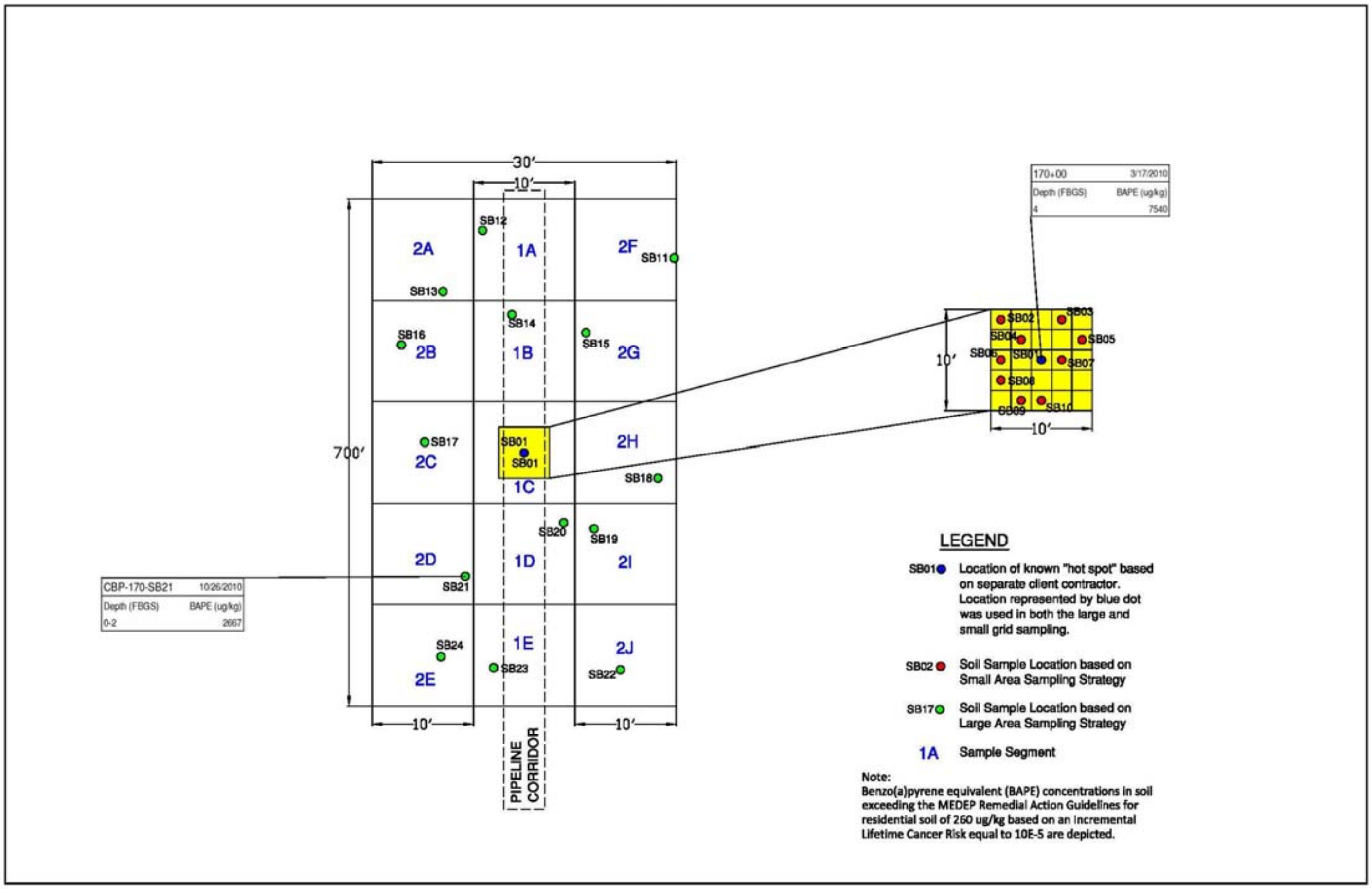


Figure 2. BAP Equivalents Exceeding 260 μg/kg MEDEP Residential Soil Guideline at Station 23+00 Study Area.



170+00	3/17/2010
Depth (FBGS)	BAPE (ug/kg)
4	7540

CBP-170-SB21	10/26/2010
Depth (FBGS)	BAPE (ug/kg)
0-2	2667

Note:
Benzo(a)pyrene equivalent (BAPE) concentrations in soil exceeding the MEDEP Remedial Action Guidelines for residential soil of 260 ug/kg based on an Incremental Lifetime Cancer Risk equal to 10E-5 are depicted.

Figure 3. BAP Equivalents Exceeding 260 µg/kg MEDEP Residential Soil Guideline at Station 170+00 Pilot Study Area.

proportion of samples greater than the action level in the large area dataset. If the p-value associated with the two proportions test was greater than 0.05, it wasconcluded that the proportion of samples greater than the action level in the small area dataset is similar to the proportion of samples greater than the action level in the large area dataset. Fisher's Exact Test was computed if the normal approximation two proportion test assumptions were not valid. The normal approximation assumptions are that the proportion of samples greater than action level times sample size, and one minus the proportion of samples greater than the action level times the sample size, are greater than or equal to five for each dataset.

The results of the two-sample proportion test show that the proportion of samples greater than the action level for the small delineation area are statistically similar to the proportion of samples greater than the action level for the larger "EU-based" area for many parameters in the small area and large area datasets. This suggests the spatial representation is not a significant factor: one represents an area of 100 square feet, and the other represents approximately one-half acre including the 30-foot wide easement.

3.3 Human Health Risk Results

The initial analysis of human health risk using the risk-ratio method indicated that cancer risk estimates exceeded the ILCR equal to 1×10^{-5} in all surface and subsurface soils. Initial non-cancer risk estimates were acceptable in all surface and subsurface soils.

Some of the "95 percent Upper Concentration Limits (UCLs)" were set to be equal to the maximum observed PAH concentrations, according to ProUCL software, and because many of the PAH concentrations were less than detectable limits in many samples of an EU-based area, valid statistical calculations were not possible. In these cases, the true EPC would be less than the maximum detected PAH concentrations, even if the receptor was only exposed to easement soils. Therefore, an attempt was made to compute a more realistic estimate of human health risk.

3.4 Risk Management Results

The human health risks calculated for each of the three stations assume human receptors will be exposed only to soil within the easement. This assumption is unlikely to be true because residents would not be physically restricted to this small area, such as a 30-foot-wide area of a residential parcel. Furthermore, it is evident that PAH contamination is heterogeneously distributed within the easements.

To calculate a more realistic estimate of true cancer and non-cancer health risks, the EPC was estimated for the portion of the property outside the easement. This was done by first observing that most PAH concentrations within the sampled EU-based areas were less than 110 µg/kg. Next, it was assumed that PAH concentrations outside the easement are no greater than those inside the easement. This seemed reasonable because the distance from the assumed PAH contamination source (the former pipeline) is greater for locations outside the easement, and contaminant concentrations commonly decrease with distance from a contaminant source. The value of 110 µg/kg was conservatively assumed to represent the average PAH concentrations outside the easement; this equates to a cancer risk of 4×10^{-6} and appeared to be an upper limit to background PAH concentrations.

In the next step, some assumptions were made about the total area over which a resident is exposed and the amount of that area represented by the easement. Although some of the residential lots are much more than four times the size of the easements on the lots, the sampled EU-based areas were assumed to represent 25 percent of the total residential property. The average cancer risk for a land parcel comprised of 25 percent easement and 75 percent uncontaminated property would then be the sum of 0.25 times the average EU cancer risk and 0.75 times 4×10^{-6}. This area-weighted risk was computed for each station. When this was done, the results listed in Table 3 were obtained. The column labeled, "Overall Cancer Risk" is the area-weighted risk that was computed as described here. In the same table, the "Average Cancer Risk" represents a simple average of the cancer risk equivalent of the BAPE at each sample location within the EU.

Table 3. Average BAPE Concentrations and Calculated Cancer Risk for Surface and Subsurface Soil at the three Pilot Study Areas.

Station	**Depth**	**Average of BAPE HalfND**	**Average of Cancer Risk**	**Overall Cancer Risk**
18+00	subsurface	528	2×10^{-6}	8×10^{-6}
18+00	surface	303	12×10^{-5}	6×10^{-6}
23+00	subsurface	404	2×10^{-6}	7×10^{-6}
23+00	surface	243	9×10^{-6}	5×10^{-6}
170+00	subsurface	594	2×10^{-6}	9×10^{-6}
170+00	surface	227	9×10^{-6}	5×10^{-6}

Note: BAPE HalfND means BAPE is calculated substituting ½ the detection limit for non-detected analytes.

All of these results are less than the cancer risk threshold of 1 x 10^{-5}. This occurs because the larger proportion of the residential property to which a resident is exposed has a lower soil PAH concentration than the easement soil PAH concentration, and because even the easement soil PAH concentrations are heterogeneously distributed, with very localized areas of contamination dispersed among generally uncontaminated or slightly contaminated soil. Although the overall cancer risks computed in this manner are less than the MEDEP threshold of unacceptable risk, these risks are believed to be exaggerated, compared to what is anticipated to be the true cancer risks. When these calculations were repeated for non-cancer risks, all non-cancer risks for the sampled residential properties were less then HI equal to 1.

These calculations were not performed for the small area sampling because:

- The results would be similar, because the EPCs for the small area sampling were similar to the EU-based area sampling; and,
- The small area sampling represents a much smaller area than an actual residential soil exposure unit

4. CONCLUSIONS

Five PAHs, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, dibenzo(a,h)anthacene, and indeno(1,2,3-cd)pyrene exceeded Maine screening values for residential soil. This is based on an Incremental Lifetime Cancer Risk (ILCR) equal to 1 x 10^{-6}. Only eight out of a total of 178 pilot soil samples, which represents approximately 4.5 percent of the samples, exceeded this ILCR value. The exceedances were primarily detected in surface soils, rather than in subsurface soils.

The statistical analysis results show that the proportion of samples greater than the action level for the small delineation area are statistically similar to the proportion of samples greater than the action level for the larger “EU-based” area for many parameters in both the small area and large area datasets.

The human health risks calculated for each of the three stations assume human receptors will incur contact only with soil within the easement. This assumption is unlikely because residents would not be physically restricted to a small area, such as a 30-foot-wide portion of a residential parcel. Therefore, a more realistic estimate of human health risk took into account the area of two-acre land parcel and the fact that few samples had PAH concentrations greater than what appears to be general background concentrations. The results of the revised risk analysis indicate the overall health risks to a resident are less than both the MEDEP ILCR equal to 1 x 10^{-5} and HI equal to 1.

5. ACKNOWLEDGMENTS

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Chapter 10

RISK CONSIDERATIONS RELATED TO ARSENIC EXPOSURE: DRINKING WATER INGESTION VERSUS DIETARY INTAKE OR SOIL EXPOSURE

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ABSTRACT

The February 2010 release of the Draft Toxicological Review of Inorganic Arsenic by the U.S. Environmental Protection Agency provoked discussion of a potential significant downward revision of the arsenic cancer slope factor (CSF), which would be applicable to many oral exposure evaluations. Given the extreme variability in soil cleanup guidelines that are in use throughout the United States and internationally for arsenic, it may be appropriate to more seriously consider bifurcating the manner in which arsenic is evaluated in environmental media. In much the same fashion by which manganese and cadmium presently are evaluated from a risk perspective, arsenic may lend itself to similar evaluation from a drinking water exposure standpoint separately from a dietary or an environmental soil route of exposure. This paper examines the basis for the current oral toxicological guidance with respect to specific exposure route and environmental medium of exposure, and addresses possible means for alternative toxicity guidance related to arsenic, based on differences in exposure through soil or the diet.

Keywords: arsenic, soil, organic, inorganic, drinking water, cleanup guidelines, risk, relative bioavailability

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1. INTRODUCTION

Arsenic is the perennial number one entry in the CERCLA Priority List of Hazardous Substances (ATSDR, 2007a), and is listed as a constituent of concern at more than 40% of NPL sites (ATSDR, 2007b). Although the CERCLA list is not based solely on toxicity, and the NPL occurrence is based primarily on exceedance of often artificially low cleanup guidelines, the perception is such that arsenic, no matter the medium, accessibility, or concentration, is a serious human health concern. As with most meaningful health questions that are posed, the true answer to the question of whether arsenic is a concern is "It depends". It depends on the arsenic form (inorganic, organic). It depends on the exposure medium (soil, food, air, water). It depends on the intake route (oral, dermal, inhalation). It depends on the exposure magnitude (concentration, duration). Any one of these factors, or more likely, a combination of them all, determines whether arsenic can exert its ability to cause toxic effects.

In the case of arsenic toxicity, particularly from exposure to soils, health-based screening levels and some cleanup guidelines are derived using conclusions largely based upon long term, high concentration drinking water studies, resulting in sub part per million protective soil targets. Human exposures to soil arsenic at concentrations far in excess of these health-based screening levels occur frequently in all parts of the U.S. and worldwide. However, reports conclusively connecting exposures to arsenic in soil with adverse health effects are not readily found in the toxicological literature.

2. NATURAL OCCURENCE

Many, if not a substantial majority of, areas in the U.S. contain soils that have measurable levels of arsenic. Often, these detectable levels are referred to as "elevated." Of course, elevated is the operative word defining the discussion. Depending on the screening level that is considered, even naturally occurring background concentrations of arsenic in surface soil may be viewed as "elevated." By way of example, a 2009 study by Vosnakis, et al. evaluated more than 1,600 samples from 189 sites in seven states in the northeastern U.S. (KY, MD, NY, OH, PA, VA, WV). The authors found that, following data validation and site screening, the retained arsenic in soil results ranged from 1.1 mg/kg to 89 mg/kg (Vosnakis, et al., 2009; see Table 1). When compared with each state's soil screening level for arsenic, the reported background concentrations were from 2x to 40x greater than the respective screening levels, and the highest background level was approximately 60x the lowest screening level.

Table 1. Arsenic Background vs Soil Screening Levels for 7 States

State	Frequency of Detection	95th Percentile Surface Soil As (mg/kg)	Risk Based Screening Level (mg/kg)
Kentucky	57 of 57	15.6	0.39
Maryland	28 of 32	10.1	0.39
New York	42 of 50	22.8	13
Ohio	94 of 143	21.7	6.8
Pennsylvania	219 of 220	23.7	12
Virginia	91 of 98	13.6	0.39
W Virginia	314 of 316	15	8.64

Each of these states allows for some consideration of background in their cleanup guidance, and a few incorporate background directly into the screening levels. However, the fact remains that large areas of soil in the U.S. exceed health-based screening levels for arsenic.

3. HEALTH EFFECTS

Given the intrinsic toxicity of arsenic, the very low soil screening levels theoretically required to protect human health, and the presence in most soil of arsenic far exceeding health-based guidelines, where are all of the reports of arsenic-related illness, disease and death? Going briefly back to the Vosnakis, et al. (2009) study of elevated background arsenic, we can look at selected state soil concentrations and compare those with reported cancer incidences. As shown on Table 2, even though statewide soil arsenic concentrations are twice or three times the national average, and up to 60-times greater than the lowest RBSL, cancer incidence rates for bladder, liver and skin cancer are not significantly different from national rates.

Clearly, establishing a causal link between *any* factor and the development of cancer is a highly complex undertaking, but at the theoretical doses (and the associated grossly elevated risk levels) suggested by the above soil concentrations, the logical conclusion would be that rates broadly elevated beyond screening levels would be associated with noticeably elevated cancer incidences. In further attempts to support that hypothesis, Hinwood et al. (1999), in an Australian study of residential areas having soil arsenic concentrations greater than 100 mg/kg, did not show a statistically significant increase in relevant cancer incidences.

Table 2. Selected State Cancer Incidence Rates (NCI, 2010)
(cases per 100,000 population per year, 2004-2008)

Location (background As)	**Bladder Cancer Incidence**	**Liver Cancer Incidence**	**Skin Cancer Incidence**
U.S. (7.2 mg/kg; ATSDR, 2007b)	21.2	6.2	18.8
Kentucky (15.6 mg/kg)	22.6	5.1	22.3
New York (22.8 mg/kg)	23.9	7.6	15.8
Pennsylvania (23.7 mg/kg)	25.2	6.1	17.7

The above observation is consistent with the opinion of multiple authors who have proposed a sublinear or threshold basis for arsenic carcinogenicity, irrespective of medium of exposure (Rudel, et al., 1996; ERG, 1997; ATSDR, 2007b).

Consistent with the lack of evidence supporting cancers resulting from common soil arsenic exposures, no articles or studies were found citing systemic effects following human exposure to arsenic in soil under normal circumstances. In a German study of the potential transfer of arsenic from the environment to humans, it was observed that hair and urine arsenic levels actually were lower in the study area of elevated arsenic than in the reference area of low arsenic concentrations (Gebel, et al, 1998). Soil levels in the former mining region ranged from 2 to 605 mg/kg, but drinking water had low arsenic, and no occupational exposure was noted. Although a slight increase in hair and urine levels was associated with increasing soil levels, the most significant factor contributing to the observed levels was seafood consumption.

4. WHY THE DISCONNECT?

So, it is clear that arsenic occurs naturally and frequently in soils at levels much greater than health-based regulatory guidelines. There also is some evidence that cancer incidence is not elevated in areas of elevated soil arsenic, and there is a notable lack of evidence that elevated soil arsenic results in adverse systemic effects.

Many authors have reported on the various aspects that are involved in arsenic occurrence in soil, exposure, toxicokinetics, and toxicity, but very little consensus has developed at this point. Over the past several years, even the recognized certainty that arsenic methylation in the human body is a key detoxification step has been shown to be less than reliable (Thomas, et al., 2001; 2007; Hughes, et al., 2011; Steinmaus, et al., 2000). Other key areas of debate include whether arsenic is indeed a linear, nonthreshold carcinogen, or, as offered by many authors, a threshold carcinogen, or at the least a sublinear carcinogen (ERG, 1997; Abernathy, et al., 1996; Carlson-Lynch, et al., 1994; Lamm, et al., 2004). Separate from further refinement of the fundamental question of carcinogenicity from drinking water exposure, this paper pursues a solution to the disparity between the observed drinking water toxicity and the lack of reported health effects from exposure to elevated soil arsenic.

The list of possible explanations for the disconnect is long, and includes at least the following:

- arsenic form (inorganic, organic);
- exposure medium (soil, food, air, water);
- methylation and other toxicokinetic processes (absorption, detoxification or activation);
- intake route (oral, dermal, inhalation); and,
- exposure magnitude (concentration, duration).

Any one of these factors, or more likely, a combination of them all, determines whether arsenic can exert its potential to cause toxic effects.

5. POSSIBLE SOLUTIONS

In order to resolve the inconsistency observed between the adverse effects from exposure to arsenic in drinking water and the lack of actual or reported harm from elevated soil arsenic, three of the most readily quantifiable influences were evaluated: 1) relative bioavailability, to address intake route and exposure medium; 2) analogy to cadmium and manganese, to address absorption and exposure medium; and, 3) inorganic versus organic form of exposure.

5.1 Relative bioavailability adjustment

As noted earlier, a few state environmental agencies (e.g., Florida Department of Environmental Protection) explicitly acknowledge the oft-reported reduced relative oral bioavailability of arsenic in soil within their cleanup guidelines development process (FDEP, 2005). The most frequently reported range for relative bioavailability adjustment (RBA) is on the order of 20 to 60 percent (ATSDR, 2007b; Roberts, et al., 2002; Bradham, et al., 2011; Freeman, et al., 1993; 1995), while ranges from 5 to 75 percent are not unheard of. Thus, taking 30 percent as the midrange estimate, and 5 and 75 percent as the low and high estimates, respectively, Table 3 presents plausible risk based screening levels (RBSLs) for arsenic that would be calculated using procedures consistent with development of the USEPA regional screening levels (RSLs; USEPA, 2011a).

Table 3. Arsenic RBSLs based on estimated RBA

Reported RBA Estimates	**Default EPA RBSL mg/kg**	**RBA-Based RBSL mg/kg**
Default (100%)	0.39	0.39
Upper (75%)	0.39	0.52
Mid (30%)	0.39	1.3
Lower (5%)	0.39	7.8

As shown on Table 3, the midrange RBA estimate results in a possible RBSL of 1.3 mg/kg. While this value is scientifically defensible, health-based, and it provides considerable relief from default guidelines, it does not remotely approach naturally occurring arsenic levels in most soils in the U.S. Thus, adjustments for RBA are appropriate, based on a multitude of studies, but RBA adjustment is likely only a piece of the puzzle.

5.2 Exposure medium/route adjustment

In the case of cadmium and, to a lesser extent, manganese, the route of exposure dictates the applicable toxicological guidance that is recommended for use in risk assessment and cleanup activities. The oral RfD for cadmium when the exposure medium is water is 5E-4 mg/kg•day, and the oral RfD for cadmium in food is 1E-3 mg/kg•day (IRIS; USEPA, 2011b), or twice that for water. The IRIS profile for cadmium reports that the difference in RfD values is based on observed differences in absorption (i.e., 2.5% absorption of Cd from food or 5% from water; USEPA, 2011b). Specifically, it states “Since the fraction of ingested Cd that is absorbed appears to vary with the source (e.g., food vs. drinking water), it is necessary to allow for this difference in absorption when using the toxicokinetic model to determine an RfD.” For cadmium, the differences in toxicological guidance typically are reflected in differential media screening levels through use of the water RfD when calculating the tapwater level and through use of the food RfD when calculating the soil level (FDEP, 2005; USEPA, 2011a).

With respect to human absorption of arsenic, very little consensus is available, but there does appear to be a reduced absorption rate in animal studies when comparing insoluble, bound arsenic forms (i.e., those most often found in soil) with soluble, unbound arsenic forms (i.e., those most often found in drinking water; ATSDR, 2007b; NRC, 1999). Freeman et al. (1993) reported that, in rabbits, approximately 80% of the arsenic from an ingested soil bolus (primarily smelting soil in the form of sulfides) was eliminated (i.e., approximately 20% absorption). In contrast, 50% of a soluble oral dose and 10% of an injected dose were eliminated (i.e., 50% and 90% absorption, respectively). Thus, arsenic absorption from soil may range from 30-70% less than absorption from more soluble forms. This conclusion is consistent with results from

Roberts et al. (2002) who reported that between 60% and 80% of an ingested arsenic dose in soil was eliminated by *Cebus apella* monkeys, suggesting absorption of 20% to 40%.

Although much work is needed to refine knowledge regarding human absorption differences based on medium of exposure, the likely impact would be in the same general magnitude as that presented for adjustments based on relative bioavailability (e.g., 1.5 to 20 fold; see Table 3).

5.3 Form of arsenic adjustment

One promising potential solution to the presence/significance conundrum may lie in being able decisively to identify the form of arsenic, inorganic or organic, to which an individual is exposed. Determining which form is present in the soil, and, more importantly, identifying which form ultimately is present in the body following human exposure, is a subject of considerable debate. However, as presented by ATSDR (2007b), distinct chronic human oral minimal risk levels (MRLs) are available for inorganic and organic forms of arsenic, thus providing a potential mechanism for development of screening levels, if consensus on typical exposure forms in specific media can be reached.

The inorganic MRL is 3E-4 mg/kg•day and that value was derived from a human drinking water study. For the organic arsenic compounds monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA), the chronic human oral MRLs are 1E-2 mg/kg•day and 2E-2 mg/kg•day, respectively (ATSDR, 2007b), and both of these values are based on feeding studies in mice. The MRL development process is conceptually similar to that which is used to produce Reference Doses, including the application of uncertainty and modifying factors. Thus, analogous to the development of USEPA default RSLs, risk based screening levels (RBSLs) may be developed for arsenic in soil using the MRLs for inorganic arsenic and organic arsenic compounds. As shown on Table 4, the proposed RBSLs for organic arsenic in soil range from nearly 30 times greater to more than 50 times greater than the RBSL for inorganic arsenic in soil.

Table 4. Arsenic RBSLs based on form-specific toxicological guidance

As Form	**Chronic Oral MRL mg/kg•day**	**Default EPA RSL mg/kg**	**MRL-Based RBSL mg/kg**
Inorganic	0.0003	0.39	22
Organic (MMA)	0.01	NA	~600
Organic (DMA)	0.02	NA	~1,200

6. DISCUSSION

Significant monetary and human resources are expended on the characterization and mitigation of arsenic in soil, based primarily on the fundamental assumption that its potential toxicity following soil exposure is consistent with its potential toxicity following drinking water exposure. No conclusive reports were found to support that position, and an increasing body of evidence is available to undermine the conclusion. While the exact mechanisms and processes that result in the disparity remain unclear, it is time to begin refining an approach to the multiple potential solutions to the problem. As presented in this paper, the most promising and straightforward solutions lie in adjustments to the numerical toxicological guidance based on several factors including: 1) relative bioavailability; 2) differences in absorption between the water and soil matrices; and/or, 3) differences in the toxicity between inorganic and organic forms of arsenic.

Possible recommendations for future health investigations, as well as a few critical areas for continued toxicological study include the following:

- inorganic vs organic determination whenever soil investigations take place;
- refined toxicokinetics to conclusively identify methylation or other relevant processes and their importance;
- inexpensive, rapid *in vitro* methods for site-specific determinations of relative bioavailability; and,
- more conclusive determination of the mode of action for arsenic carcinogenicity.

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PART V: Sediments

Chapter 11

SOUTHERN CASPIAN SEA COASTS, MORPHOLOGY, SEDIMENT CHARACTERISTICS, AND SEA LEVEL CHANGE

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ABSTRACT

As the world's largest closed body of water, considerable changes in the Caspian Sea water level make it an unique laboratory to study all aspects of coastal zones. This research was aimed at evaluating the linkage between sea level changes and sediment characteristics of the south Caspian Sea coast. Initially, three field surveys were made along 700 km of the southern Caspian Sea coast. In addition to nearshore sampling, land forms were mapped. On the basis of the field reconnaissance, eight principal sampling stations were chosen. Sediments were sampled by divers along profiles at right angles to the coast at 5 depths (2, 4, 6, 8,10 meters). Hydrographic profiles also were surveyed. Laboratory tests on the sediment samples were made, and the sediment characteristics and morphological features were divided into distinct zones based on their response to sea level changes.

Keywords: Caspian Sea, water level changes, sediment characteristics, sampling, morphology

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1. INTRODUCTION

The Caspian Sea is the largest closed body of water on Earth with a surface area of around 380,000 km^2 and a volume of about 78,000 km^3. This volume accounts for approximately 40% of the world's lake waters (Kaplin and Selivanov, 1995). It is believed to be a remnant of the Tethys Ocean that became landlocked about 5.5 million (MM) years ago due to plate tectonics (Kroonenberg et al., 2007). Five different countries border this sea, namely Iran, Turkmenistan, Kazakhstan, Azerbaijan and Russia (Fig. 1). This sea measures around 1,180 km North-South (between latitudes 36° and 47°) and as much as 480 km East-West (between longitudes 49° and 54°). It has no tides, and its salinity (5 to 13 gr/ litre) is only approximately one third of that of the open oceans, increasing from the north, where the Volga River flows into the sea, to the south (Peeters et al., 2000).

The Caspian Sea can be considered as having three parts (Froehlich et al., 1999; Kaplin and Selivanov, 1995): a northern part, with a mean water depth of only 10 m; a central part, where the water depth increases up to 788 m; and a southern part, wherein the water depth increases up to 1025 m.

A range of small and large rivers feed the Caspian Sea mostly from the south, west, and north and variations in their discharge can significantly affect the water volume and therefore the water level.

The considerable drop in the Caspian Sea level began in 1930. Prior to that the observed water level had been more constant, fluctuating around -26 m for about eight decades. In 1929, the water level stood at 26.1 m below open oceanic levels. This level dropped rapidly by around 1.6 m and reached -27.7 m by 1940. After that the Caspian's sea level continued to decline but at a slower rate, falling by around 1.4 m within 37 years and reaching -29.1 m by 1977. After 1977, the sea level suddenly began to rise such that a water level of about -26.7 was recorded in 1995 showing an increase of 2.6 m over the period 1977 to 1995. Since 1995, a slow rate of decline has occurred.

Historical repeated water level oscillations in the Caspian Sea, mostly interpreted from sedimentary deposits, have been the subject of several research studies. For example, biostratigraphical and radiometric investigations of the Kura Delta and its Holocene deposits show a repeated alternation between deltaic and marine environments. The changes resulting from high frequency changes in the Caspian Sea surface level representing four episodes of delta progradation followed by erosional transgressive surfaces (Hoogendoorn et al., 2005). The Volga Delta was also surveyed by Kroonenberg et al. (1997) and five magnitudes (phases?) were recognized through stratigraphical studies for the Quaternary Caspian Sea water level variations. The authors found that a highstand (Caspian Sea level reached 50 m above global sea level) in the early Pleistocene linked the Caspian Sea and the Black Sea. As another example, lagoonal deposits and barrier-lagoon systems, as well as deltaic deposits, suggest past oscillations in the Caspian Sea. Kroonenberg et al. (2007) studied the Holocene barrier along the Dagestan coast and found that the last notable highstands took place around 2600 BP.

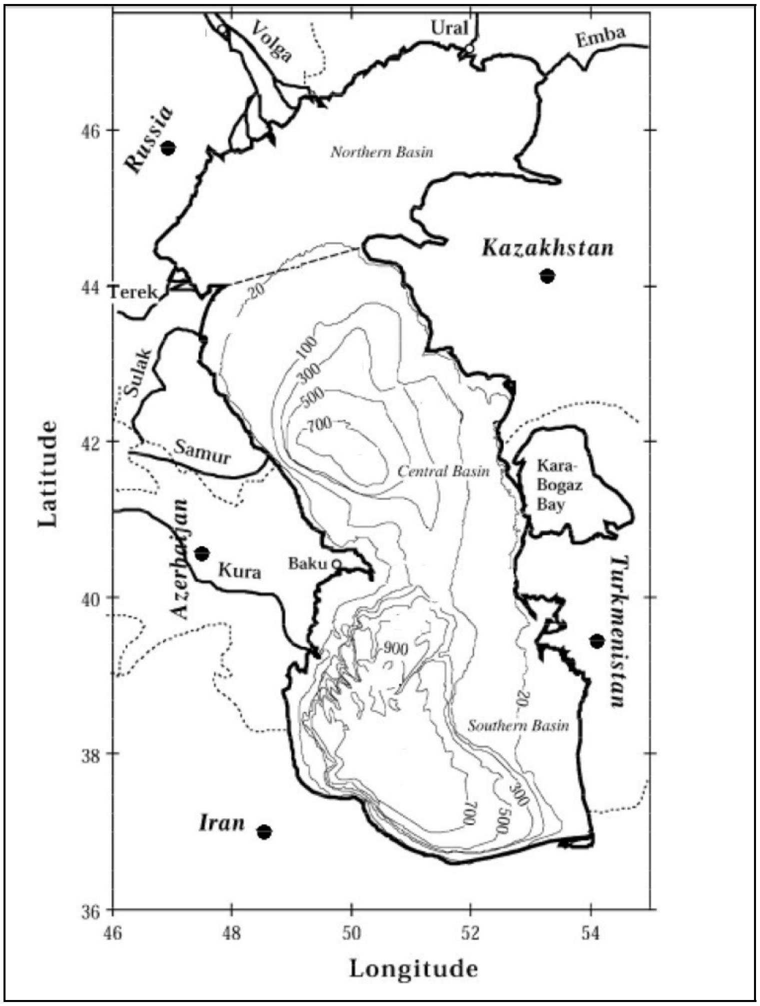

Figure 1. The Caspian Sea bathymetry, bordering countries, subbasins, and major rivers (After Peeters et al., 2000).

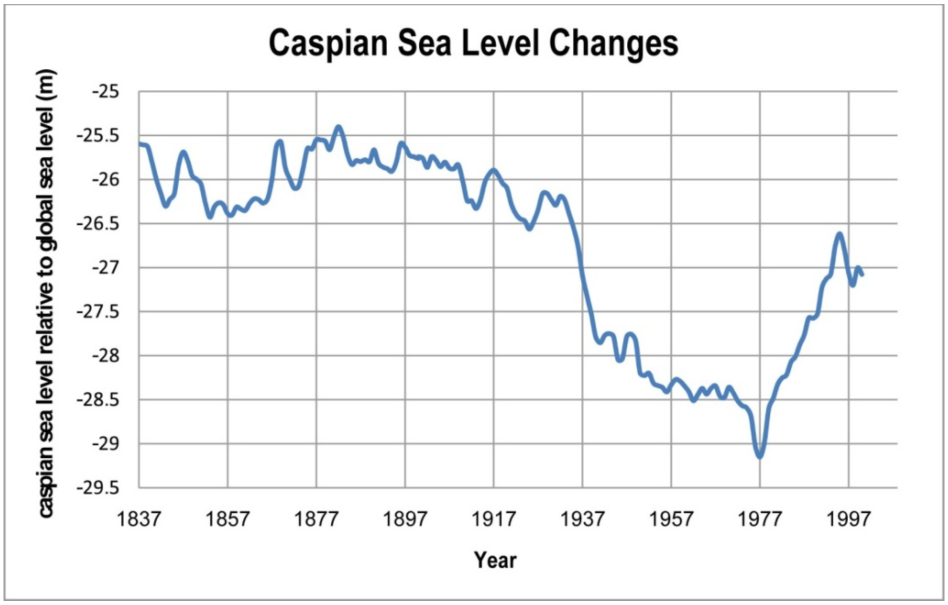

Figure 2. The Caspian Sea level fluctuations during the 20th century (Data based on Baltic Sea level).

The causes of fluctuations in Caspian Sea level are not yet entirely clear (Kroonenberg et al., 2007; Boomer et al., 2005). Most studies, however, emphasize climate change and anthropogenic factors (Shiklomanov *et al*., 1995), rather than geological and tectonical effects (e.g., Rychagov, 1997; Golitsyn, 1995). Aspects of Caspian Sea level change have been the subject of various research studies related to hydrology, geomorphology, and biology, but the effect of these changes on the seismic regime in the Caspian Sea region has not been studied in detail. The recent Caspian Sea level changes have created a new system of beach deposits and profiles. While these coastal evolutions under conditions of sea level change have been studied on the northern and western Caspian Sea coastline (Kaplin and Selivanov, 1995; Kroonenberg et al., 2007; Kroonenberg et al., 2000), the southern Iranian Caspian Sea coast has not been adequately explored. The present research investigated the impact of the 20th century changes in Caspian Sea level on the Iranian Coast of the Caspian Sea.

2. SEA LEVEL VARIATION AND COASTLINE CHANGES

Prediction of coastal changes related to sea level changes is fraught with difficulties. Predictive models are not being reliably generated due to a lack of knowledge of the interaction between coasts and energy sources. On the other hand, a model which is developed to forecast the behaviour of a particular coast cannot be applied to another because natural processes depend on coastal features which differ from one coast to another. Bruun (1962) proposed that the equilibrium beach profile does not change in response to sea level variations (Bruun Rule), and in the case of sea level changes only a given volume of sand will move from the upper part of the profile. This volume of sand will lie over the lower part of the profile, and the accumulated volume is equal to the eroded volume (Fig. 3).

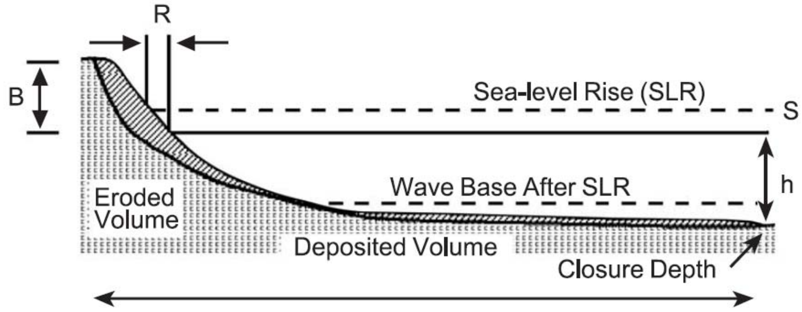

Figure 3. Shoreline erosion under rising sea level conditions, the Bruun Rule (Cooper and Pilkey, 2004).

Based on the Bruun Rule, since the shore-normal geometry of beaches remains unchanged under sea level rise conditions, the amount of shoreline retreat can be calculated if the amplitude of sea level rise and the form of the original profile are known. This geometric model can be applied if assumed geometric rules are valid. Cooper and Pilkey (2004) concluded that the Bruun Rule does not work and should be abandoned for three reasons.

First, there are some assumptions which cannot be found in nature. For example, longshore transport is omitted in this two dimensional model. Second, this rule ignores some main variables such as particle sizes existing on beaches, bottom currents, and bedforms. Finally, the concepts providing the foundation for the Bruun Rule are known to be outdated.

Leatherman et al. (2000) confirmed the Bruun Rule by modelling a number of coasts, for example the New Jersey coast in the United States. However, their claim was very soon rejected by Sallenger et al. (2000) and Pilkey et al. (2000) who claimed that the data had been selected with a view to validating the Bruun Rule.

The aforementioned critical study of Cooper and Pilkey (2004) is convincing because they evaluated almost all studies conducted on the Bruun Rule. Furthermore, Kaplin and Selivanov (1995) estimated shoreline retreat for three depositional coasts of the Caspian Sea over the period of the Caspian Sea level rise. Their study showed overestimations of up to 600 percent by the Bruun Rule.

For instance, field data showed a 20-25 m shoreline retreat on the Lenkoran coast of Azerbaijan, but the Bruun Rule estimated it at around 130-150 m. Even with some modification, this estimation only decreased to around 90-105 m.

The effect of sea level change on coastal morphology is based on reconstructions, not on real time observations. These are troublesome because the rate of present sea level change is so slight (about 10-20 cm per century, the present sea level has an upward trend, and the last lowstand deposits can only be investigated by drilling or deep sounding and other similar methods. It is necessary to validate numerical models using real time data, and laboratory simulations are hindered by drawbacks such as downscaling (Kroonenberg et al, 2000). While the linkage between sea level changes and coastal landforms has not yet been completely understood (Cooper and Pilkey, 2004) the Caspian Sea can play an important role in enhancing our knowledge of coastal behaviours in response to sea level variations. This is because of its significant water level changes and approximately 7,000 km of coastline are available for investigation.

The Caspian Sea as the best natural laboratory for studies related to coastal response to sea level changes. Present coasts of the Caspian Sea were formed in response to its repetitive level variations during the New Caspian transgression which began 8,000 yrs B.P. These coasts can be classified into four categories (Kaplin and Selivanov, 1995): mud flats; depositional coasts composed of bars, spits, etc.; erosional coasts; and deltaic coasts. The Caspian Sea possesses all of the different coastal types which can be found along the world's coastlines and these coasts show different behaviour in response to sea level changes.

3. THE CASPIAN SEA COAST UNDER RECENT WATER LEVEL VARIATIONS

The Caspian’s various coastal types were introduced in the previous section. Their responses to Caspian Sea level changes are discussed in this section.

3.1 Mud flats

Mud flats tend to lie beside the lowland areas, stretched along the northeastern, southeastern corner, and northwestern coasts of the Caspian Sea during the period of Caspian Sea level fall from 1930 to 1977. Also, in this period, mud flats surrounded all bays of the Caspian Sea including Kirov Bay, Krasnovodsk Bay, Kizlyar Bay, and Komsomoletz Bay, though the rate of shoreline migration differed. For example, the shoreline of Kizlyar Bay advanced by 150-200 m/yr while the rate of shoreline migration in Komsomoletz Bay was 700-800 m/yr (Kaplin and Selivanov, 1995).

3.2 Depositional coasts

The period during which the Caspian Sea level showed a decreasing trend is marked by an increase in the size and volume of depositional bodies such as dunes, barriers, and spits, except those which were being supplied by cliff erosion. In this period cliffs were inactive resulting in a decrease in longshore drift causing erosion to spits. On the coasts where nearshore slope was relatively gentle (tangent slope 0.0005-0.005), landward migration of these bodies occurred while their geometry remained almost unchanged (Kaplin and Selivanov, 1995). Moderate nearshore bottom slopes (tangent 0.005-0.01) usually mark barrier coasts (Roy et al., 1994) and under the Caspian Sea level fall its barriers increased their width and volume. Under rising sea level conditions however, sand ridges emerged on the coasts and a rise in the groundwater table formed a lagoon behind the ridges. On the coasts with a steep backshore (tangent slope over 0.03-0.05) lagoons did not form. Steep nearshore bottom slopes (tangent slope over 0.01) caused intensive erosion to beaches leading to the formation of scarps of up to 1-1.5 m (Kaplin and Selivanov, 1995). Barrier coasts were comprehensively studied by Kroonenberg et al. (2000), who investigated the barrier coast of Kaspiisk in Russia at the western Caspian Sea coast which had been monitored during the period of recent Caspian Sea level changes.

3.3 Deltaic coasts

When the sea level began to decrease a passive emergence occurred on the deltaic coasts. The Kura delta and the Sulak delta expanded up to 50-60 and 100-200 m/yr, respectively. The Volga delta together with the Ural delta located on the northern Caspian Sea coasts experienced a considerable expansion and caused the shoreline to move ahead by hundreds of kilometres. When the trend reversed and the Caspian Sea level started to increase, the deltaic shorelines retreated. The rate of the shoreline retreat was not as much as the shorelines' advance in some deltas. While some areas were completely inundated the Volga delta retreated by only 2-4 m/yr. A main reason for this was the increase in sediment discharge. It is suggested that Volga sediment discharge increased by 33 percent due to an increase in its water discharge during the 1980s (Kaplin and Selvianov, 1995). Volga sediment discharge is composed of silt, clay, and very fine sand forming a gently sloping coast. Sea level rise and increasing Volga discharge worked together to vertically grow sediment bodies while sea level fall increased channel erosion leading to fast shoreline advances (Kroonenberg et al., 1997). The maximum level that the Caspian Sea experienced during the past century was 25 m below global sea level and it has been suggested that it may increase to near the original level again, in which case a wide area will be inundated (Li et al., 2004). The present day Kura delta is composed of sandy and clayey bodies. The aggradation process, during the period of water level increase in the Caspian Sea resulting from flooding of the Kura River delta, and progradation over the period of sea level fall, both control the Kura River delta as much as do river dynamics (Hoogendroon, 2005).

3.4 Erosional coasts

Erosional coasts can be observed in the coasts of Azerbaijan, Russia, Kazakhstan, and Turkmenistan. During the period of sea level fall the cliffs were left behind and cliff erosion ceased because the causative waves broke over the newly emerged area. When this area was submerged again by an increasing sea level, erosive waves attacked the cliffs and the result was an increase in the length of the erosional coasts of the Caspian Sea such that, for example, in Azerbaijan there was an increase from 20 to 55 percent in length along the whole coastline (Kaplin and Selvianov, 1995).

4. SOUTHERN COASTS OF THE CASPIAN SEA UNDER WATER LEVEL VARIATIONS

These segments of coastline, similar to other coasts, had appropriate responses to the sea level changes but published data is in relatively short supply (Kazanci et al., 2004). These coasts can be morphologically categorized into five zones. The morphodynamics of each zone were characterized to evaluate vulnerability of beaches and for hazard assessment by Khoshravan (2007) and hazardous areas were marked. His study showed that nearshore slope, shore morphology, and sediment characteristics vary along the southern Caspian Sea coastline. There exist several lagoons and bays along the Southern Caspian coast the most important ones being Anzali lagoon in the west and Gorgan Bay in the east (Fig. 4). The recent Caspian Sea level rise, which occurred between 1977 and 1995, doubled the Anzali lagoon surface from 80 to 160 km2 (Kazanci et al., 2004). The Alborz mountain range governs the shore width throughout the coastline and the rivers feeding the Caspian Sea from the south contribute great amounts of sediment to the shores to expand their width.

In the east, where the coast is composed of fine grain sediment, waves are prevented from reaching the shore due to the gentle slope of the nearshore zone. Sandy beaches stretch along the hundreds of kilometers of the southern Caspian Sea coastline and coarse grain beaches can be observed in some segments. These coasts were affected by the Caspian Sea level rise in accordance with their offshore and onshore slopes (Lahijani et al., 2007).

Fig. 4 illustrates the formation of southern Caspian Sea coasts under conditions of rising sea level. The variety of behaviours is due to the differences between offshore and shore gradients (Lahijani, 2009, Pers. Comm.).

Studies related to the sea level rise conducted on the southern coasts of the Caspian Sea are limited and there is a gap in the information available for this area. Although Fig. 4 is a schematic representation of the behaviours prevailing on some coasts it is not sufficient for a coastline of 700 km in length which has a wide variety of features.

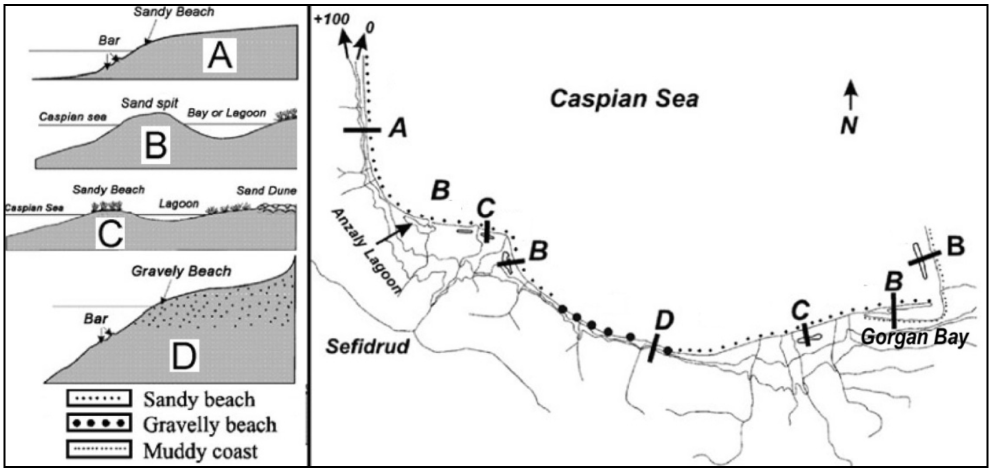

Figure 4. Southern Caspian Sea coasts' behaviour in response to sea level rise (After Lahijani et al., 2007).

5. METHODOLOGY

The goal of this research is to investigate the effects of the Caspian Sea water level variations on the Iranian Coast. Factors determining the coastal response to sea level changes include nearshore gradient, sediment supply, wave regime, and sea level rate (Roy et al. 1994), together with shore slope are discussed for the southern Caspian Sea coasts. Response of the southern coast to the water level variations is discussed.

The flowchart illustrated in Fig. 5 shows the process applied in this researcht in four main steps: the first, the second, and the third field surveys together with the final data analysis. Factors affecting the Caspian Sea coasts were identified by reviewing the literature and background of the subject. On the basis of that knowledge, the first field survey was conducted.

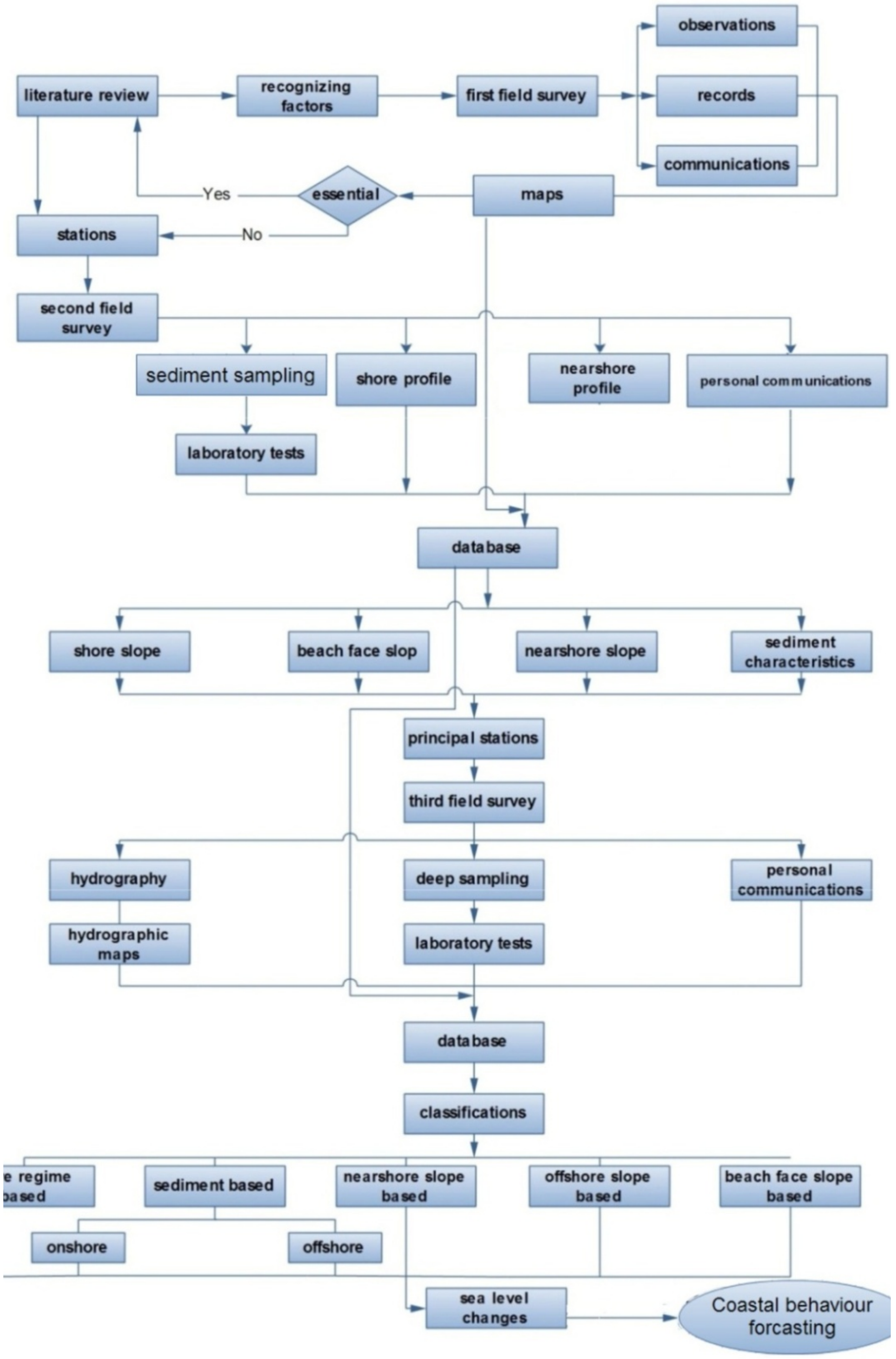

Figure 5. Applied process to examine the impacts of the Caspian Sea level changes on Iran's Caspian Sea coast.

The major objective of initial field work was to gather appropriate information about the study area. For this reason, all observations were documented and locations taken. Also, interviews with coastal residents were performed throughout the survey. Information was compared with the available maps. Finally, the stations of the second survey were chosen.

During second survey the information came from nearshore sediment sampling, offshore hydrography, onshore topography, and personal communications, providing a database for the whole coastline consisting of sediment characteristics, beach profiles, and a general view of each segment of the coastline. Beach profiles provide shore slopes, beach face slopes, and nearshore slopes. A suite of laboratory tests on sediment samples yielded a database of the results. On the basis of the field reconnaissance, principal sampling stations of the third survey were chosen.

The third survey aimed to evaluate deep sediment characteristics of the southern Caspian Sea coast. At this stage hydrographic profiles were surveyed from the shoreline to a depth of 10 m. These profiles were compared with the available hydrographic maps and a set of laboratory tests were conducted on the sediments sampled by divers along profiles at specific depths. The results emerging from this step along with the information obtained from the previous stages created a comprehensive database.

In the final stage, data was analyzed. Several classifications were developed based on wave regime, shore slope, beach face slope, nearshore slope, offshore slope, and sediment characteristics. Finally, the effect of Caspian Sea level changes on Iran's Caspian Sea coasts was evaluated for use in forecasting the behaviour of these coasts in response to future sea level changes.

6. THE FIRST SURVEY

Since field observations play an important role in comprehending the problem, it was decided to study all of the available information, morphological, hydrographic and topographic maps on the scale of 1/100000.These pieces of information were provided by the Iranian Caspian Sea National Research Centre, Iran's National Cartographic Centre, the Geological Survey of Iran, and the Iranian National Institute for Oceanography.

With regard to Fig. 6, the northern part of Iran, where the Southern Caspian Sea coast lies, is divided into three provinces; Guilan, Mazandaran, and Golestan. Guilan province extends from Astara, northeast of Iran where it has a common border with Azerbaijan, to Ramsar, which marks Mazandaran province’s border.

Guilan is home to cities such as, Astara and Talesh in the west, Anzali, Dastak and Kiashahr in the centre, and Kelachay in the east.

Figure 6. Three of Iran's provinces bordering the Caspian Sea, 1: Azerbaijan; 2: Astara; 3: Talesh 4: Anzali; 5: Kiashahr; 6: Dastak; 7: Kelachay; 8: Ramsar; 9: Nashtarood; 10: Noor; 11: Babolsar; 12: Gorgan; 13: Bandar Torkaman; 14: Gorganrood; 15: Gomishan.

Mazandaran province is bounded by Ramsar in the west and to the east it shares its border with Golestan province. The western coasts of Mazandaran are home to cities such as Nashtarood and Ramsar, while Noor is situated in the centre; Eastern Mazandaran is famous for cities such as Babolsar.

Golestan province, the most important city of which is Gorgan, lies on the south eastern coast of the Caspian Sea; its Bandar Torkaman, Gorganrood and Gomishan coasts are amongst those which are important to this study.

The reason why the northern regions of Iran have been described is that the rest of this study and the classifications of coasts use these proper names. Moreover, most of the stations selected in this research are introduced by the names of the cities in which they are situated.

This field survey began in Astara in the west. In almost every region, where even the slightest possibility of access to the coast existed, a survey was carried out. All the observations were documented, and the coordinates of the spots which seemed to be important in later stages were recorded by a hand GPS. For consequent stages of research, some pictures were taken, while other places where mere pictures could not explain the overall situation were filmed.

Communications with local people were important and helpful in understanding the region. For instance, locals, especially fishermen, had a working knowledge of sandy bars on the nearshore bottom. This survey began on 1st May 2009 and finished on 11th May 2009 in Gomishan on the east of Iran's northern coast. It covered almost all of the 700 km length of the southern coast of the Caspian Sea. The following are the results of the observations:

1. The morphological phenomena mentioned in section 8.2 are rarely seen all together in one region;
2. Shore sediments and nearshore sediments vary along the coast based on their type, and where the overall width of the coast (the distance between mountain and sea) lessens, the sediments grow coarser.
3. Shore slope varies from place to place;
4. In some parts, the beach face slope is different from the general beach face slope observed along these coasts; that is, the coarser the sediments around the shoreline, the steeper the beach face slope;
5. With attention to the way onshore bars have been formed, one can identify the dominant direction of the sediment transport in some regions;
6. Waves reach the coast at an angle to a line perpendicular to the coastline. This angle varies at different points, lessening as one moves towards the central areas of the coastline;
7. Observations on landforms from sea to mountain, as well as the information obtained from coastal residents about offshore slope, along with previous information obtained from hydrographical and topographic maps, show that both the offshore slope and shore slope are changing along the coast, and these two slopes are substantially different in most regions.

During this survey, the overall morphology of the region was evaluated, and the most outstanding tectonic phenomenon of the region is the Alborz mountain range, by which the whole length of Iran's northern coast is southerly bounded (see Chapter 5, section 5). Also, on the western coastline the Talesh mountain range is oriented in a south-north direction. The distance of these mountain ranges from the sea in different areas of the coastline determines the width of the shore. At some points, the shore width is very narrow, nearly 1 km (for example western Mazandaran, around Ramsar), while in other places such as the eastern parts it exceeds 60 km.

Shore width is one of the factors determining the shore slope, and therefore, it should be paid an appropriate level of attention in this study. In some regions great rivers (for example the Sefid-Rud in central Guilan) which flow into the Caspian Sea expand the shore width. More than 50 rivers flow into the Caspian

Sea from the south, the sediments of which have affected the morphology of the shore and in some cases posed problems for the locals. At a certain point in Kelachay, the local fishermen talked about an obstacle at a depth of around 2.5 m that would tear their fishing nets. Later, in the third field survey, this problem was investigated. On this shore, fishermen would cast their fishing nets in 3–5 m depths of water and after a specified time would drag them out with tractors to gather in the fish. By diving, it was proved that this was a very thin, locally created layer of cohesive clay, probably formed by sediments transported by several small rivers running close to each other. While being dragged along the seabed, the fishing nets must have been torn by this layer.

Onshore sandy bars are mostly seen at the coast at Guilan and eastern Mazandaran, while nearshore sandy bars are formed in most regions, except Golestan (Pers. Comm. with local people, 2009). Small and relatively big lagoons can be seen in eastern Mazandaran and central Guilan. Coastal sediments are mainly sand, except for at the western Mazandaran coast in some segments where gravelly beaches can be seen, and on the Golestan coast where coastal sediments are mostly clay.

After obtaining a general view of the region, it was necessary to match the acquired information with the available maps and studies previously conducted on similar coasts, so that the methodology could be refined.

7. THE SECOND SURVEY

This survey was conducted in order to acquire the information necessary for evaluating Iran’s coast. Based on the first survey and supplementary studies, 24 stations were selected along the coast. In Fig. 7 the locations of these stations have been specified. This field work started on 4th June 2009 in Astara in the west and finished on 15th June 2009 on the Gorganrood coast. During this survey foreshore profiles were mapped, beach sediments were sampled, and observations of shore features were documented. Past information about the Caspian Sea level changes and impacts on coastal geomorphology were collected by personal communications with southern Caspian Sea coast residents.

Figure 7. Twenty-four stations selected during the second survey, 1: Astara; 2: Landvil; 3: Talesh; 4: Parrehsar(1); 5: Parrehsar(2); 6: Kapourchal; 7: Anzali (Bashman); 8: Golshan(1); 9: Golshan(2); 10: Golshan(3); 11: Kiashahr(1); 12: Kiashahr(2); 13: Kiashahr (3); 14: Dastak; 15: Kelachay; 16: Ramsar; 17: Nashtarood; 18: Chalus; 19: Noshahr; 20: Noor; 21: Mahmood Abad; 22: Babolsar; 23: Larim; 24: Gorganrood.

Sediments were sampled along profiles at backshore and surf zone locations in each station. In this research no undisturbed samples were required because the main goal was to determine the grading of the sediments. Cross shore profiles were surveyed within a distance of 150–300 m from the shoreline, dependent on shore slope and landforms. Also, the nearshore profile up to a depth of 1.5 m was mapped by wading.

Selecting 24 stations along 700 km of coastline helped the researchers to gather more complete information about the coast. The high number of selected stations and prolonged timeframe of the whole operation brought about some problems. For example, by taking sediment samples in each station, and each sample weighing about 1 kg, at the end of the operation about 70 kg of theses samples was being transported. In some places, access to the shore was problematic, as some parts of the southern coast of the Caspian Sea are owned by private companies or governmental institutes. In some other places, vehicles could not access the points which were considered important for this research, so the equipment had to be carried by survey personnel (e.g., estuary of the Sefirud River near Kiashahr).

The selected station locations were representative of the general situation. A series of laboratory experiments were carried out, as described in the following sections. Finally, comprehensive information about sediments, shore slope, nearshore slope, and beach face slope was acquired. Only information about deep sediments and overall slope of the seabed was missing. It was decided that in the next survey the hydrography of the seabed should also be carried out.

8. THE THIRD SURVEY

Given that information about the shore and nearshore shallow depths had been acquired, it seemed that with some information about great depths offshore, the information necessary for conducting this research would be complete. On that basis the third survey was planned, the aim of which was to sample sea bottom sediments up to a depth of 10 m and to acquire information concerning the hydrography. For the following reasons, this task was in some respects more difficult than the previous two:

1. The need for boats at specified stations along 700 km of the coast;
2. The need to dive to a depth of up to 10 m;
3. Essential need for the sea to be calm both for diving and for hydrography;
4. The need to obtain required permits for diving and offshore hydrography from local authorities;
5. Identification of more suitable stations which, although fewer in number, would be representative of the whole region;
6. The air capsules needed to be filled with compressed air at each station because the divers were using the air not only for breathing but also to fill their specialist diving suits to help them rise to the surface after sampling.

After reviewing previous data and studies conducted by Iran's Caspian Sea National Research Centre and the Iranian National Institute for Oceanography, eight principal sampling stations were chosen (Fig. 8). The required permits were obtained from local authorities, and two divers were hired for sampling operations. After the climatic status of the two provinces of Mazandaran and Guilan as forecast by weather forecasting centre was reviewed, the 20th December 2010 was chosen for the beginning of this survey.

Locals provided useful information about boats for hire at the stations or nearby.

In each station, sediments were sampled by divers along profiles at right angles to the coast at five depths (2, 4, 6, 8, and 10 m). Hydrographic profiles were surveyed by sounding up to a depth of 10 m.

After five days five stations (Astara, Anzali, Dastak, Kelachay, and Nashtarood) had been surveyed. The survey team arrived at Chalus, a city near to Noor which was the sixth station. At this stage a typhoon began to blow and work stopped and started again after the storm. The survey finished at the last station, on the Gorganrood coast. On this coast, sediments were sampled only at depths of 2 and 4 m. The beach profile was also surveyed to a depth of 4 m because of the very gentle slope of the shore and offshore. To reach a depth of 10 m in this area, a distance of at least 30 km must be navigated (according to the available hydrographic maps) which was not possible because of the lack of available facilities. The sediment samples were carried to a laboratory for testing. Samples were washed with fresh water to remove the salts. Since some sediment samples had a portion of very fine grained particles, the first experiment damaged one sample by removing the finer particles, so this approach was abandoned. Because the Caspian Sea salinity is not as great as that of the oceans, existing salts should not have a serious effect on the result. With the information acquired from this field survey, the required research database was completed.

Figure 8. Principal stations, 1: Astara; 2: Anzali; 3: Dastak; 4: Kelachay; 5: Nashtarood; 6: Noor; 7: Babolsar; 8: Gorganrood.

9. THE COAST CATEGORIZATION

Based on the observations, measurements, and information obtained from reviewing the available maps the southern Caspian Sea coast was divided into 5 distinct areas (Fig. 9):

1. West of Guilan Province, from Astara to around Anzali (West Guilan);
2. From Anzali to around Kelachay (Central Guilan);

3. Eastern Guilan and western Mazandaran have common features and were merged to create a zone known as West Mazandaran. Thus, West Mazandaran includes areas from around Kelachay to Noor;
4. From Noor to Gorgan Bay a wide coast can be seen (East Mazandaran);
5. Eastern coasts situated in Golestan Province (Golestan).

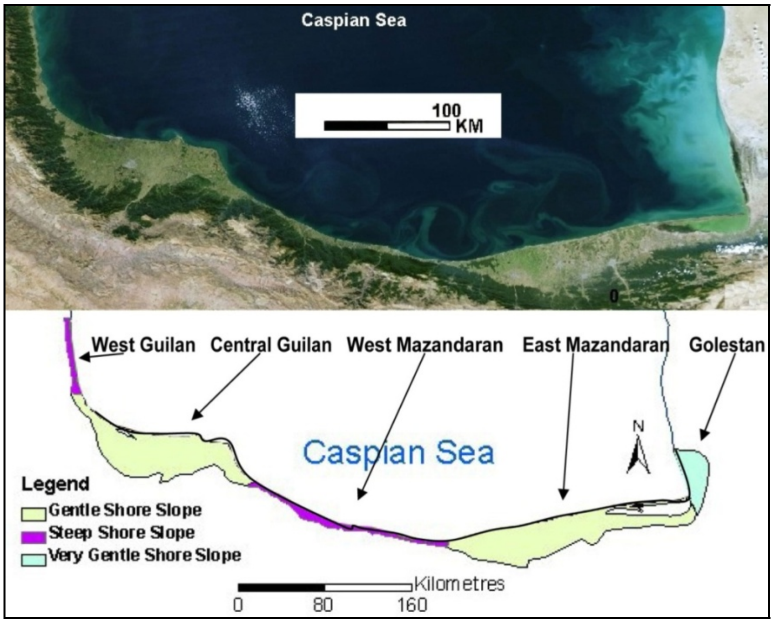

Figure 9. Iran's Caspian Sea coast classification into five areas based on shore slope. Correlation between shore width and shore slope (Data from observations, measurements, and available maps provided by the Geological Survey of Iran, and the Iranian National Institute for Oceanography).

Nearshore gradient, sediment supply, wave regime, and sea level change rate introduced by Roy *et al*. (1994), together with shore slope factors are discussed for these coasts.

10. SHORE SLOPE

The database of information obtained from the three surveys and available maps shows that Iran's Caspian Sea Coast can be subdivided into three groups of areas on the basis of the shore gradient (tangent of the shore slope angle):

a) Areas with a steep gradient (0.01 to 0.07) including West Guilan and West Mazandaran,
b) Areas with a gentle gradient (0.003 to 0.009) including Central Guilan and East Mazandaran,

c) Areas with a very gentle gradient (less than 0.001) which can be observed on the Golestan coasts.

Fig. 9 shows a narrow coastline in the western shoreline. Due to a short distance between the mountains and the Caspian Sea in the West Guilan, the shore slope in this zone is steep. In contrast, gently sloping coasts mark Central Guilan. The steep slope of the coast of West Guilan can be observed in West Mazandaran, reaching 1 km at some points. While a gently sloping coast can be found in East Mazandaran, in some parts the shore width exceeds 60 km; Golestan is marked by its very gently sloping coasts. Fig. 9 shows a classification of coastal areas according to their slopes. This figure was produced by combining two maps to show the relation between the location of the mountains, shore width and shore slope. It is believed that the shore slope plays an important role in determining the coastal behaviour in response to sea level changes, a factor rarely taken into consideration in other published studies.

11. NEARSHORE BOTTOM SLOPE

Kaplin (1989) suggested that nearshore bottom slope is the factor which most substantially affects coastal behaviour in response to sea level rise. Later, this idea was confirmed by other researchers such as Ignatov *et al*. (1993), Roy *et al*. (1994), Kaplin and Selivanov (1995), and Kroonenberg *et al*. (2000). Nearshore bottom slope determines not only the location of the wave breaking zone and the nature of the breaking process, but the patterns of coastal evolution (Bauch *et al*., 2005).

Considering Fig. 10 sediment movements are affected by nearshore slope. It shows that under sea level rise, a passive inundation occurs on very gently sloping coasts (a). On coasts with a gentle nearshore slope the dominant direction of sediment transport is landward (b and c), while on the steeper coasts sediments tend to move seaward (d and e).

Kaplin and Selivanov (1995) suggested four patterns for natural evolution of the Caspian Sea coasts under conditions of rising sea level (Fig. 11). Their study revealed that a passive shoreline retreat was marked by a very gently sloping coast (tangent nearshore slope $(\propto)$ < 0.0005) as sea levels rose. On the relatively steep coasts ($tan \propto \cong 0.0005$ to 0.005), however, depositional submarine bodies (sandy bars) moved landward. Coasts with a steeper nearshore zone ($tan \propto \cong 0.005$ to 0.01) showed another type of response. On these coasts, lagoons were formed as a result of both the landward movement of the beach ridge and the rising groundwater table, while on the very steep coasts

($\tan \propto > 0.01$) the dominant direction of the sediment movement was seaward, causing the beach face to erode.

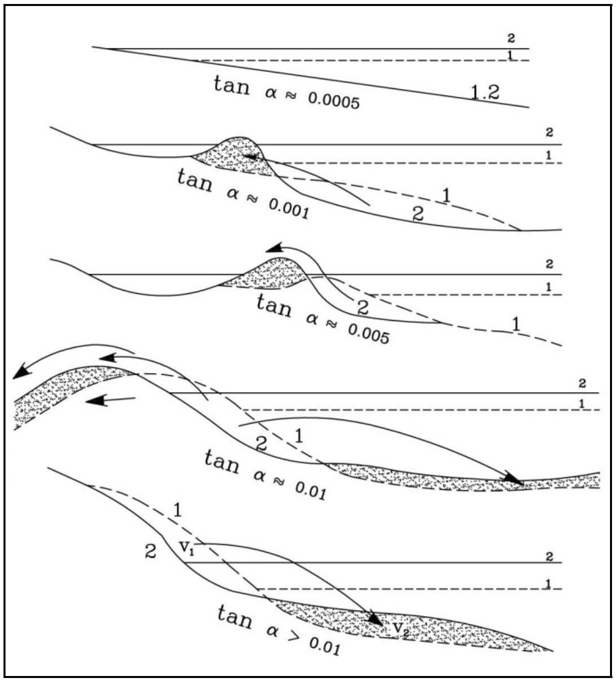

Figure 10. The dominant direction of sediment transport determined by nearshore bottom slope when the sea level rises from the dotted line to the solid line (1 to 2). Dashed areas indicate deposited parts and arrows show the dominant direction of sediment movement (Redrawn after Bauch et al., 2005).

Iran's Caspian Sea displayed specific behaviours, mostly due to the considerable differences between shore slope and nearshore slope on these coasts. In west Guilan around Astara, based on Fig. 11, onshore depositional bodies and lagoons are expected due to the gentle slope of the nearshore zone ($\tan \propto \cong 0.001$ to 0.005, based on field data) but during three field surveys, mostly erosional scarps were observed because of the steep slope of the shore.

Iran's Caspian Sea coast can be divided into three areas based on the nearshore slope. Fig. 12 shows the classification of the southern Caspian Sea coasts according to their nearshore slope. A gently sloping nearshore zone marks West Guilan. Coasts with a steep nearshore slope stretched along Central Guilan, West Mazandaran, and East Mazandaran. Low-lying lands of the Golestan coasts are

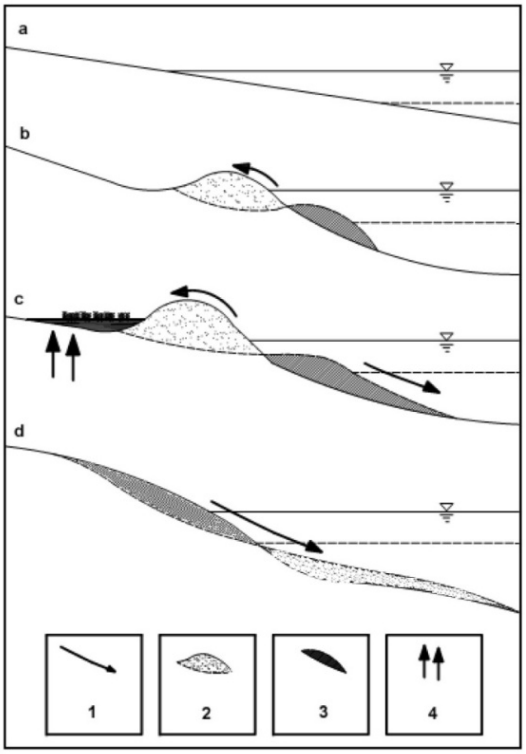

Figure 11. Different types of coastal response to the Caspian Sea level rise, a: passive shoreline retreat on very gentle coasts ($\tan \propto$, < 0.0005); b: landward movement of sediments and sandy bars on relatively steep coasts ($\tan \propto \cong 0.0005$ to 0.005); c: formation of barrier-lagoon system on the steeper coasts ($\tan \propto \cong 0.005$ to 0.01); d: seaward movement of sediments on very steep coasts ($\tan \propto > 0.01$); 1: dominant direction of the sediment movement; 2: eroding parts; 3: depositional parts; 4: groundwater table rise (modified after Kaplin and Selivanov, 1995).

marked by very gentle nearshore slopes. Fig. 12 shows an obvious difference between the nearshore slope and shore slope throughout Iran's Caspian Sea coastline. Based on this figure the areas defined in section 9 can be characterized as follows:

a) West Guilan: gentle nearshore slope (tangent slope ~ 0.001 to 0.005) and steep shore slope;
b) Central Guilan and East Mazandran: steep nearshore slope (tangent slope ~ 0.005 to 0.009) and gentle shore slope;
c) West Mazandaran: steep nearshore slope (tangent slope angle ~ 0.008 to 0.02) and steep shore slope; and
d) Golestan: very gentle nearshore slope (tangent slope less than ~ 0.0009) and very gentle shore slope.

Fig. 13 shows a classification based on three zones of offshore gradients. Coasts with a gentle offshore gradient are exemplified by West Guilan, where the point at which water depth reaches 100 m is approximately 20-40 km from the shore. This distance decreases to around 6-13 km in Central Guilan, West Mazandaran, and East Mazandaran which have steep offshore gradients, and increases dramatically to around 65-75 km in Golestan which is marked by very gentle offshore gradients. Figs. 12 and 13 show that offshore gradient in each region governs nearshore gradient.

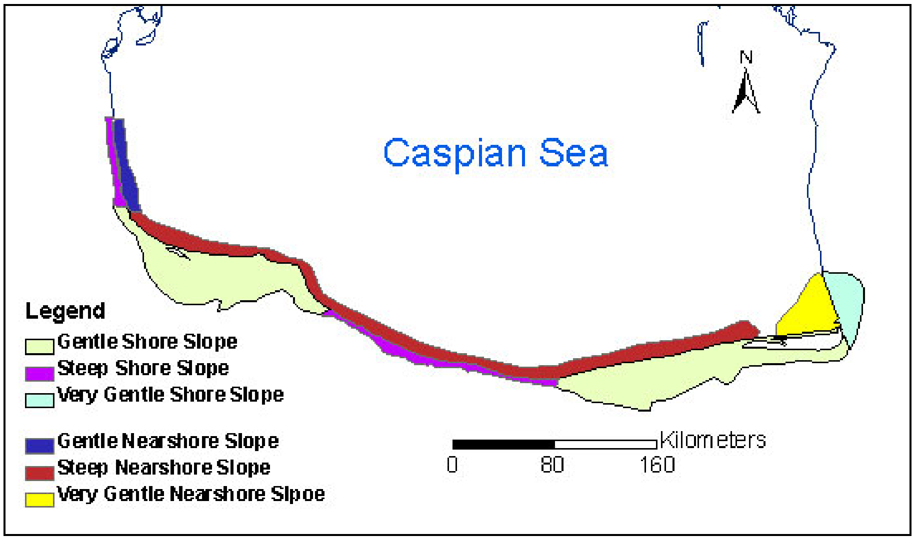

Figure 12. Coastal classification based on nearshore bottom slope, the width of the nearshore zone is not drawn to scale (data from field surveys and available maps).

12. WAVE REGIME AND CURRENTS

Waves and currents are driving forces behind many of the coastal processes by which coastal areas are formed. These energy sources are important parameters in the Caspian Sea which influence the morphology of its coasts. The relief of the Caspian Sea bottom isolates three sub-basins from each other which may be one of the causes of water circulation. Rivers feeding the sea are another cause among which the Volga has the most important role because of its considerable discharge (Fig. 14).

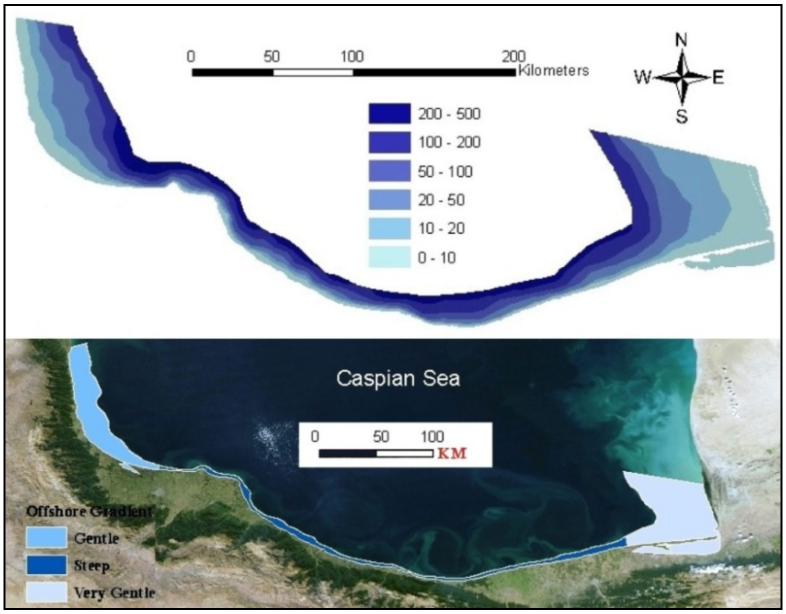

Figure 13. Caspian Sea bathymetry (data from Iran's Caspian Sea National Research Centre) (top). Coastal classification based on offshore gradient along Iran's Caspian Sea coast (bottom).

The North basin is marked by low energy waves and the South basin is characterized by moderate waves. In the Middle Caspian basin however waves have higher energy. Generally, the southern Caspian Sea coasts are exposed to waves which come from the north, northeast and the northwest. The waves coming from the north and northeast reach the western part of the coastline, namely West Guilan, Central Guilan, and West Mazandaran, while the waves reaching the eastern part including East Mazandaran and Golestan come from the North and Northwest (Lahijani *et al*., 2007). As a result of these waves longshore currents can be observed in a North-South direction along the western and eastern coasts of the south basin and along Iran's Caspian Sea coast a prevailing eastward longshore current flows, the effects of which can be observed in the formation of Gorgan Bay (Fig. 4 and 14).

The southern Caspian Sea coast is mostly dominated by spilling breakers especially in Central Guilan, West Mazandaran, and East Mazandaran. In Golestan the closure depth point is far from the shore, as is the wave breaking point, due to the low beach gradient. As a result, the waves are prevented from approaching the shoreline and do not have a significant impact on the coasts. In West Guilan, nearshore zone is steeper than that of Golestan and waves lose a portion of their energy before reaching the shore, while waves are breaking close to the shore in the other segments of the southern Caspian Sea coastline as a result of the steep gradient of the nearshore zone (Fig. 12).

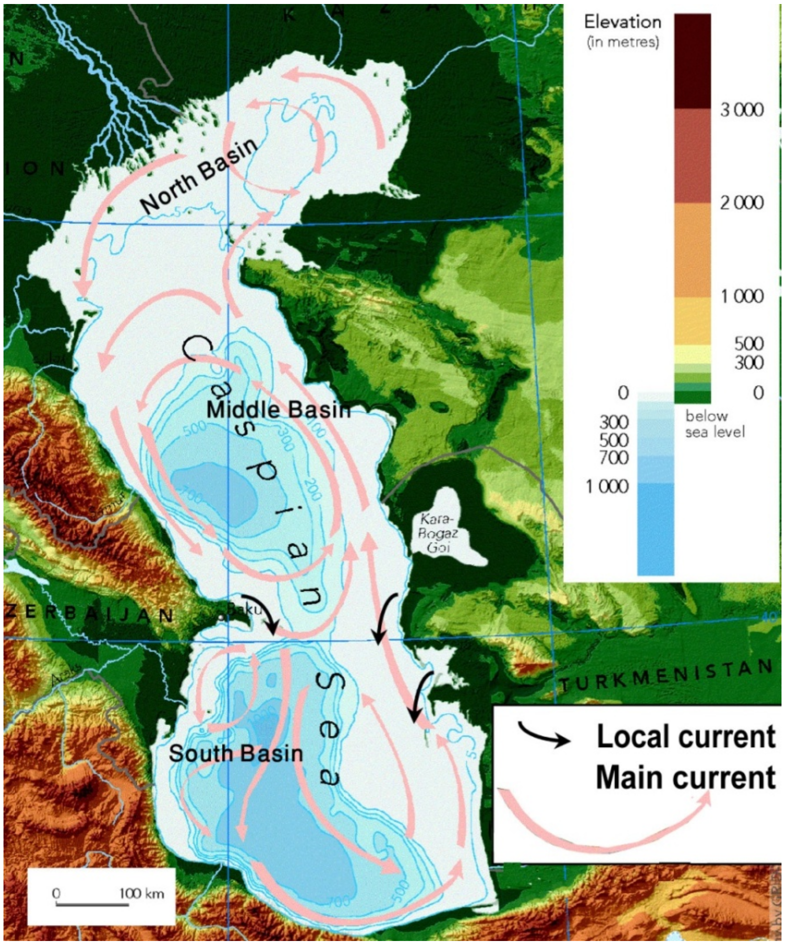

Figure 14. Caspian Sea basins including bathymetry, relief of the surrounding areas, and currents. Local currents are interpreted from headlands (After European Environment Agency).

13. SEDIMENT CHARACTERISTICS OF IRAN'S CASPIAN SEA COAST

A necessary part of any coastal investigation is the analysis of sediments sampled from both the shore and offshore. This analysis helps the researchers not only to forecast the future movements and coastal evolution but also to interpret past processes. For this reason all the sediment samples taken from the shore and offshore during the surveys were carried to a laboratory where sieving tests were performed (Guilan University for the second survey's samples and Azad University of Zanjan for the third survey's samples). Sieve analyses were performed in accordance with ASTM C136.

Generally Iran's Caspian Sea coast can be classified into three areas based on onshore sediments:

1. Sandy beaches: West Guilan, Central Guilan, and East Mazandaran;
2. Gravelly beaches: West Mazandaran (in some segments; not the whole coastline); and
3. Muddy beaches: Golestan.

Nearshore sediment is mostly sand throughout the Caspian Sea coast of Iran except that of Golestan which is clay and silt dominated. Also, in some segments of West Mazandaran gravelly particles are seen even at depths of up to 4 m. Moreover, clay and silt particles can be observed at depths along the profiles. In West Guilan clay and silt are observed at depths of over 2 m with the percentage of silt and clay along the profile of the first station of the third survey (Astara) being 38%, 36%, 40%, 25%, and 15% at depths of 10, 8, 6, 4, and 2 m, respectively. In the other stations the presence of silt and clay along the profiles surveyed during the third period of field work were as follows:

- Anzali (Central Guilan): after a depth of 6m (around 2.5% at 6 m, 13% at 8 m, and 18% at 10 m);
- Dastak (Central Guilan): after a depth of 4 m (around 5% at 4 m, increasing seaward);
- Kelachay (Central Guilan): after a depth of 2 m (around 3% at 2 m, 11% for 4 m, and 15% for 6 m, increasing seaward);
- Nashtarood (West Mazandaran): after a depth of 6 m (around 9% at 6 m, increasing seaward);
- Noor (West Mazandaran): no clay and silt observed until a depth of 10 m;
- Babolsar (East Mazandaran): after a depth of 6 m (around 25% at 6 m, increasing seaward)

Generally, silt and clay along the Caspian Sea coast of Iran can be observed from a depth of 2 m seaward in West Guilan. In Central Guilan and East Mazandaran the depth at which clay and silt exists is 6 m while for West Mazandarn usually there is no clay and silt in the samples taken from depths up to 10 m. In Golestan both shore and nearshore sediments are dominated by clay and silt.

14. ANALYSIS OF THE IRANIAN CASPIAN SEA COAST AND FUTURE FORCASTING

This study classifies the southern Caspian Sea coast into four groups - West Guilan, Central Guilan-East Mazandaran, West Mazandaran, and Golestan - each of which will be discussed here to characterize its nature and to forecast its evolution under conditions of probable future sea level change, as discussed inprevious sections.

West Guilan: generally this coastal zone has a steep shore slope (tangent slope angle ~ 0.01 to 0.05) and gentle nearshore slope (tangent slope angle ~ 0.001 to 0.005) which follows the gentle offshore gradient in this area (Fig. 13). Based on Fig. 11, this zone falls into group b of Kaplin and Selivanov's (1995) classification but the steep slope of the shore forms erosional scarps on the beach face. It is suggested that, given future sea level rise in this zone, erosional scarps and submarine sandy bars will be formed, specifically from Astara to around Talesh, and in some areas, specifically from Talesh to Anzali, small lagoon-barrier systems will be created around the mouths of the small rivers entering the Caspian Sea where the shore slope is becoming relatively lower and coarse grained material is provided by rivers. Under conditions of falling sea level however, the shore would widen and consequently onshore sandy bars would form. No lagoon is expected to form except for a few very small lagoons around the river mouths.

Central Guilan-East Mazandaran: since gently sloping shores (tangent slope angle ~ 0.003 to 0.009) but steep nearshore slopes (tangent slope angle ~ 0.005 to 0.009) mark this zone, this group of areas mostly fall into group c of Kaplin and Selivanov's (1995) classification. On shore and submarine sandy bars together with sandy dunes are seen in these areas. As a result of formation and landward movement of barriers, several big lagoons and a notable number of small lagoons were formed during the recent sea level rise. With future rises in sea level these conditions are expected to continue and lagoons may increase in size due to the gentle shore slope of this area and the existence of a wide shore. When the sea level falls, no big lagoons are formed and existing lagoons lose their size (personal communication with East Mazandaran residents). Submarine depositional bars emerge and other bars are formed by storms.

West Mazandaran: having both steep shore and nearshore gradients (tangent shore slope angle ~ 0.01 to 0.07 and tangent nearshore slope angle ~ 0.008 to 0.02) this coastal zone mostly falls into group d of Kaplin and Selivanov's (1995) classification and, in a few segments, into group c. Hence, in this zone the steep gradient of the nearshore zone prevents the sediment from moving shoreward and onshore bars are very rare (observations agree with this). As a result of seaward movements of the sediments multiple bars are formed on the nearshore bottom. Given a future rise in sea level more sediments can be expected to move seaward and under an accelerated sea level fall depositional submarine bars may emerge without losing their size.

Golestan: in this zone both the nearshore and shore slopes are very gentle (tangent nearshore slope angle less than ~ 0.0009 and tangent shore slope angle less than ~ 0.001) and a passive shoreline regression and transgression occurs under sea level changes.

15. CONCLUSION

Recent Caspian Sea level changes make this sea a unique natural laboratory for studies related to coastal response patterns. This research examined the Iranian coast of the Caspian Sea to introduce its behaviour in response to sea level changes which can be applied to predict future evolutions. All available maps were reviewed and three field surveys were performed: the first survey provided useful information and gave a general insight into the study area; the second survey was aimed at nearshore sediment sampling, nearshore hydrography, and shore topography; and the third survey evaluated deep sediment characteristics and provided hydrographic profiles surveyed from the shoreline to a depth of 10 m. A database was created including information about: shore slopes, nearshore bottom slopes, sediment characteristics, and longshore current regime. This research classified the southern Caspian Sea coast into four categories with respect to their response to sea level change: West Guilan with gentle nearshore slope and steep shore slope; Central Guilan and East Mazandaran with steep nearshore slope and gentle shore slope; West Mazandaran with steep nearshore slope and steep shore slope; and Golestan with very gentle nearshore slope and very gentle shore slope.

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PART VI: Site Assessment

Chapter 12

PCDDS/PCDFS IN SOILS AT A FORMER TANNERY SITE - PROFILES AS EVIDENCE OF PCP CONTAMINATION

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ABSTRACT

PCDDs/PCDFs contamination in soils at a former tannery site in Eastern Massachusetts was found to be widespread. PCDDs/PCDFs concentrations (the sum as (Cl_4 – Cl_8); tetra-octachloro totals) in the majority of the soil samples (17/32) far exceeded concentrations (10-1000 times) typically found in soils in industrial/urban settings worldwide (1-10 ppb). The distribution pattern of PCDDs/PCDFs in site soils in combination with highly elevated concentrations did not indicate significant influences from off-site sources (e.g. aerial distribution pattern). Widespread chromium contamination in soils often collocated with elevated concentrations of OCDD suggested that both contaminants could be attributed to a common industrial source: the former tannery operations. (total chromium concentrations in the soil samples ranged from 22.2 – 3,457 mg/kg).

Elevated PCDDs/PCDFs concentrations predominated by OCDD were most likely attributable to the historical use of pentachlorophenol (PCP) and/or products containing PCP. PCP was likely used as a fungicide/biocide in tannery processes that took place at the site. PCP origins were established through comparison of PCDDs/PCDFs profiles found in soils to those characteristic of PCP products as reported in the open literature (PCDDs/PCDFs profiles found in PCP products are predominated by hexa, hepta and octa congeners). Elevated OCDD concentrations present in site soils may not be solely attributable to historical use of PCP. OCDD, which is the most common PCDDs/PCDFs

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congener present as a contaminant (artifact of PCP production chemistry) in PCP may also be formed photochemically. The latter reaction takes place over time in surface soils with PCP serving as the precursor compound. The extent to which this reaction has contributed to OCDD levels found in soils has been estimated by comparison of profiles found in site soils to those characteristic of commercial PCP products.

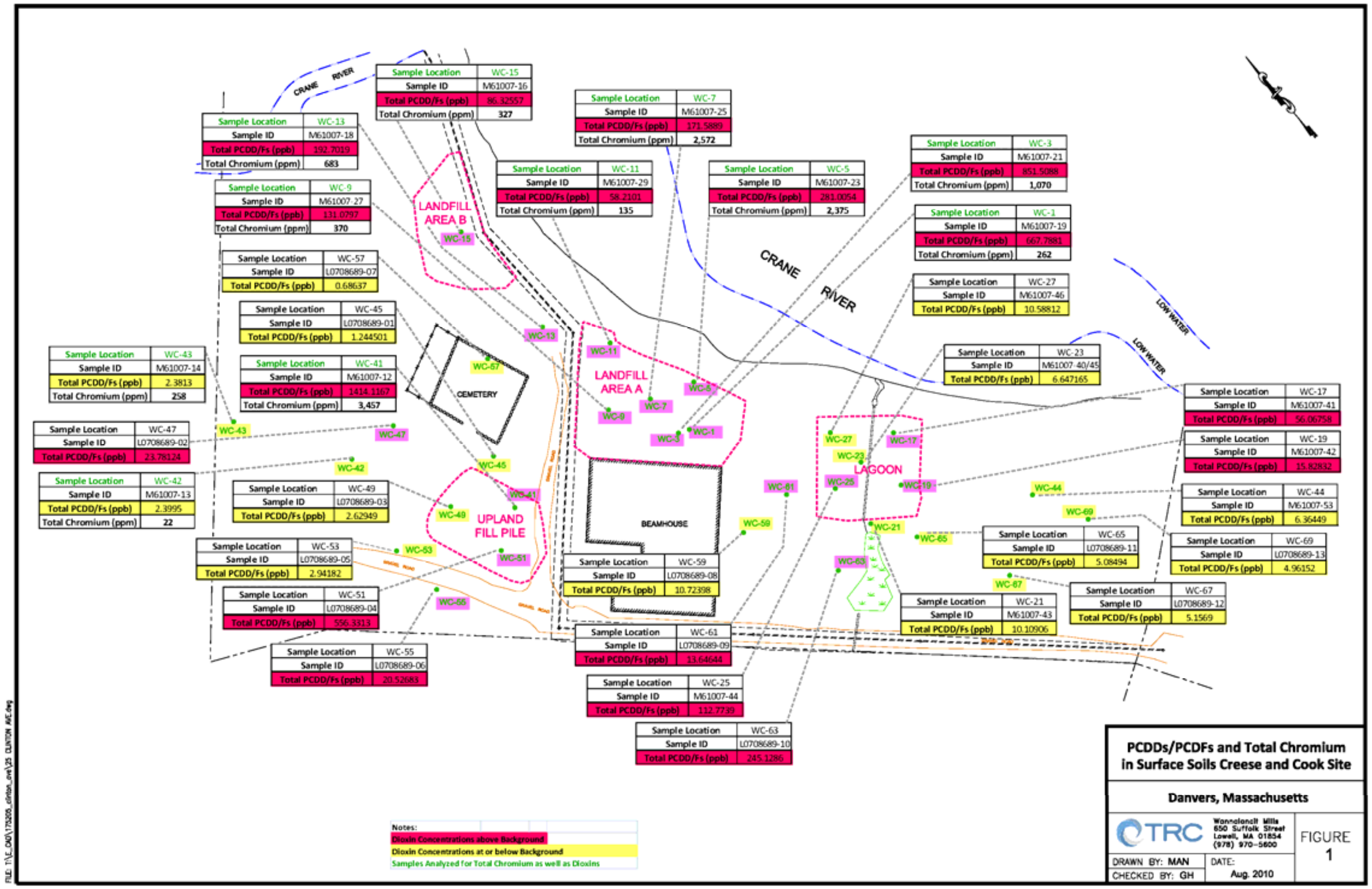
Keywords: PCDDs, PCDFs, tannery site, soil

1. INTRODUCTION

PCDDs/PCDFs contamination in soils at a former tannery site in Eastern Massachusetts was found to be widespread. PCDDs/PCDFs concentrations in the majority of the soil samples far exceeded concentrations typically found in soils in industrial/urban settings worldwide. Widespread chromium contamination in these same soils collocated with elevated concentrations of OCDD suggested that both contaminants could be attributed to the former tannery operations. PCP was likely used as a fungicide/biocide in tannery processes that took place at the site. Historically, pentachlorophenol was often used to prevent growth of bacteria on the animal skin prior to mineral tanning, using chromium sulfate. PCDDs profiles in these highly contaminated soils were compared to profiles characteristic of commercial pentachlorophenol (PCP) and PCP containing products. Results of these analyses provide evidence for the presence of PCP in soils on site. OCDD formation via photochemical reactions from precursor PCP is also suggested.

2. MATERIALS AND PROCEDURE

Surficial soils were sampled across the property of the former tannery site. Refer to Figure 1 for the actual locations of sampling sites. Analyses were performed using high-resolution gas chromatography in combination with high resolution mass spectrometry. Details of the sample collection and laboratory analyses are described in Orchard Farm Trust (2007). PCDDs/PCDFs profiles were examined in soil samples with elevated concentrations of both chromium and PCDDs/PCDFs. These profiles were compared to PCDDs/PCDFs profiles found in a number of PCP products as reported in the open literature.



Sample Location	WC-15
Sample ID	M61007-16
Total PCDD/Fs (ppb)	86.32557
Total Chromium (ppm)	327

Sample Location	WC-13
Sample ID	M61007-18
Total PCDD/Fs (ppb)	192.7019
Total Chromium (ppm)	683

Sample Location	WC-9
Sample ID	M61007-27
Total PCDD/Fs (ppb)	131.0797
Total Chromium (ppm)	370

Sample Location	WC-57
Sample ID	L0708689-07
Total PCDD/Fs (ppb)	0.68637

Sample Location	WC-45
Sample ID	L0708689-01
Total PCDD/Fs (ppb)	1.244501

Sample Location	WC-43
Sample ID	M61007-14
Total PCDD/Fs (ppb)	2.3813
Total Chromium (ppm)	258

Sample Location	WC-41
Sample ID	M61007-12
Total PCDD/Fs (ppb)	1414.1167
Total Chromium (ppm)	3,457

Sample Location	WC-47
Sample ID	L0708689-02
Total PCDD/Fs (ppb)	23.78124

Sample Location	WC-42
Sample ID	M61007-13
Total PCDD/Fs (ppb)	2.3995
Total Chromium (ppm)	22

Sample Location	WC-49
Sample ID	L0708689-03
Total PCDD/Fs (ppb)	2.62949

Sample Location	WC-53
Sample ID	L0708689-05
Total PCDD/Fs (ppb)	2.94182

Sample Location	WC-51
Sample ID	L0708689-04
Total PCDD/Fs (ppb)	556.3313

Sample Location	WC-55
Sample ID	L0708689-06
Total PCDD/Fs (ppb)	20.52683

Sample Location	WC-7
Sample ID	M61007-25
Total PCDD/Fs (ppb)	171.5889
Total Chromium (ppm)	2,572

Sample Location	WC-11
Sample ID	M61007-29
Total PCDD/Fs (ppb)	58.2101
Total Chromium (ppm)	135

Sample Location	WC-5
Sample ID	M61007-23
Total PCDD/Fs (ppb)	281.0054
Total Chromium (ppm)	2,375

Sample Location	WC-3
Sample ID	M61007-21
Total PCDD/Fs (ppb)	851.5088
Total Chromium (ppm)	1,070

Sample Location	WC-1
Sample ID	M61007-19
Total PCDD/Fs (ppb)	667.7881
Total Chromium (ppm)	262

Sample Location	WC-27
Sample ID	M61007-46
Total PCDD/Fs (ppb)	10.58812

Sample Location	WC-23
Sample ID	M61007-40/45
Total PCDD/Fs (ppb)	6.647165

Sample Location	WC-17
Sample ID	M61007-41
Total PCDD/Fs (ppb)	56.06758

Sample Location	WC-19
Sample ID	M61007-42
Total PCDD/Fs (ppb)	15.82832

Sample Location	WC-44
Sample ID	M61007-53
Total PCDD/Fs (ppb)	6.36449

Sample Location	WC-65
Sample ID	L0708689-11
Total PCDD/Fs (ppb)	5.08494

Sample Location	WC-69
Sample ID	L0708689-13
Total PCDD/Fs (ppb)	4.96152

Sample Location	WC-59
Sample ID	L0708689-08
Total PCDD/Fs (ppb)	10.72398

Sample Location	WC-21
Sample ID	M61007-43
Total PCDD/Fs (ppb)	10.10906

Sample Location	WC-67
Sample ID	L0708689-12
Total PCDD/Fs (ppb)	5.1569

Sample Location	WC-61
Sample ID	L0708689-09
Total PCDD/Fs (ppb)	13.64644

Sample Location	WC-25
Sample ID	M61007-44
Total PCDD/Fs (ppb)	112.7739

Sample Location	WC-63
Sample ID	L0708689-10
Total PCDD/Fs (ppb)	245.1286

Notes:
- 🟥 Dioxin Concentrations above Background
- 🟨 Dioxin Concentrations at or below Background
- Samples Analyzed for Total Chromium as well as Dioxins

PCDDs/PCDFs and Total Chromium in Surface Soils Creese and Cook Site

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DRAWN BY: MAN
CHECKED BY: GH
DATE: Aug. 2010

FIGURE 1

3. DATA AND ANALYSIS

Results for the thirty-two soil samples expressed as total PCDDs/PCDFs (the sum of Cl_4 – Cl_8) in units of ppb are shown in Figure 1. The majority of the soil samples (17/32) far exceeded concentrations (10-1000 times) typically found in soils in industrial/urban settings worldwide (1-10 ppb) (Jones and Duarte-Davidson, 1997, Im et al, 2002, Birmingham, 1990, Creaser et al, 1990, Pearson et al, 1990). The distribution pattern of PCDDs/PCDFs in site soils in combination with highly elevated concentrations did not indicate significant influences from off-site sources (e.g. aerial distribution pattern). Twelve (12) of the seventeen (17) soil samples showing the highest dioxin levels were concentrated in areas identified as the locations of former tannery operations (see Figure 1). Widespread chromium contamination in these same soils often collocated with elevated concentrations of OCDD suggested that both contaminants could be attributed to the former tannery operations. Total chromium concentrations in the soil samples as shown in Figure 1 ranged from 22.2 – 3,457 mg/kg. Results for the most highly contaminated soil samples are shown in Table 1 on a congener sum specific basis (Cl_4-Cl_8PCDDs/PCDFs). The profiles shown are dominated by heptaCDDs and OCDD. Profiles for seven (7) of these soils samples expressed on a % basis (% contribution of concentration of each congener to the total concentration of Cl_6-Cl_8PCDDs) are shown in Figure 2.

All seven (7) of these soil samples also contained total chromium at concentrations > 260 ppm (mg/kg) and represent locations used for former tannery processes (Orchard Farm Trust, 2007). Profiles representing three (3) commercial PCP containing products expressed on a % basis (% contribution of concentration of each congener to the total concentration of Cl_6-Cl_8PCDDs) are shown in Figure 3. The profiles shown in Figure 3 represent actual results from analyses of thirty-four (34) individual batches of technical PCP produced by three (3) separate manufacturers (Singh et al, 1985).

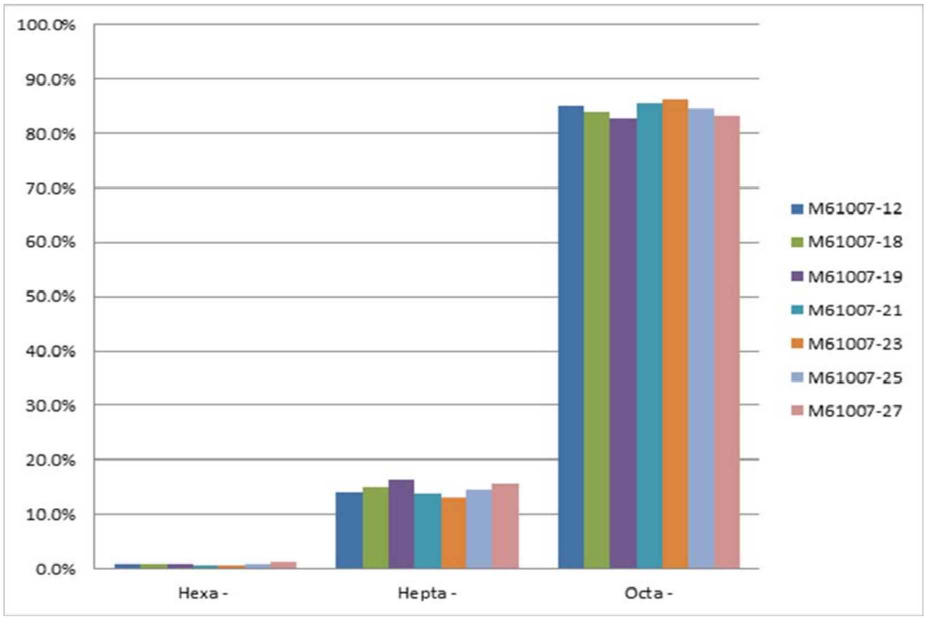

Figure 2: PCDD (Cl_6- Cl_8) Profile of Soil Samples with High Chromium (>260ppm)

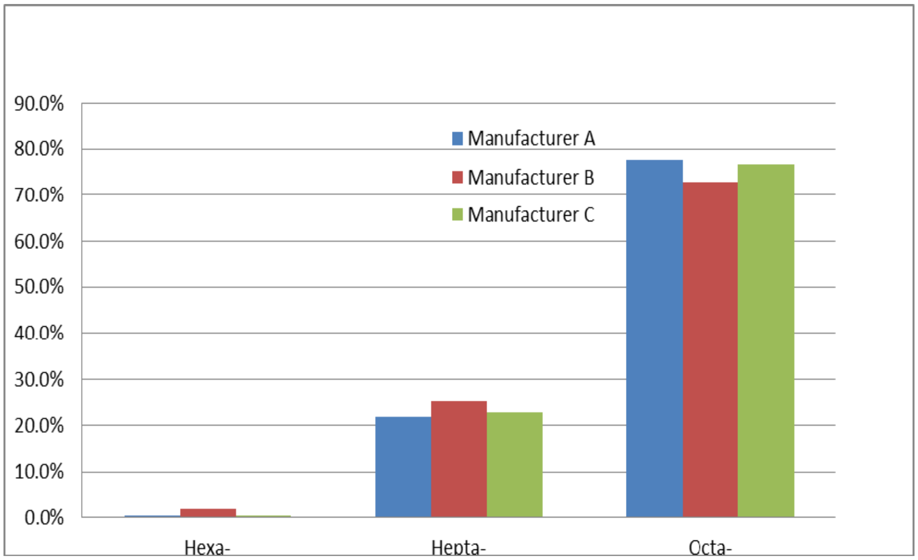

Figure 3. PCDD (Cl_6- Cl_8) Profile of Technical Grade PCP Products

Table 1: Summary of Results – Soil Samples

Concentrations ranging from 91 ppb to 300 ppb

Sample ID	L0708689-10	M61007-18	M61007-23	M61007-25	M61007-27	M61007-44	**AVERAGE**
Sample Collection Date	6/18/2007	11/21/2006	11/21/2006	11/21/2006	11/21/2006	11/22/2006	**Concentration**
Analyte							
OCDD	**182**	**158**	**218**	**136**	**98.9**	**94.4**	147.883
OCDF	**16.1**	**1.1**	**11.8**	**4.23**	**4.4**	**0.826**	6.409
Total TCDDs	**0.0278**	**0.0211**	**0.116**	**0.032**	**0.0524**	**0.0165**	0.044
Total PeCDDs	**0.14**	**0.115**	**0.12**	**0.128**	**0.168**	**0.119**	0.132
Total HxCDDs	**1.9**	**1.69**	**1.8**	**1.4**	**1.37**	**1.06**	1.537
Total HpCDDs	**29.2**	**28.5**	**32.9**	**23.3**	**18.5**	**13.9**	24.383
Total TCDFs	**0.0668**	**0.0118**	**0.0334**	**0.015**	**0.0273**	**0.0149**	0.028
Total PeCDFs	**0.194**	**0.04**	**0.126**	**0.0939**	**0.102**	**0.0305**	0.098
Total HxCDFs	**2.3**	**0.794**	**2.41**	**1.08**	**1.28**	**0.407**	1.379
Total HPCDFs	**13.2**	**2.43**	**13.7**	**5.31**	**6.28**	**2**	7.153
Total PCDDs	213.2678	188.3261	252.936	160.86	118.9904	109.4955	173.979
Total PCDFs	31.8608	4.3758	28.0694	10.7289	12.0893	3.2784	15.067
Total Dioxins and Furans	245.1286	192.7019	281.0054	171.5889	131.0797	112.7739	189.046

Concentrations greater than 500 ppb

Sample ID	L0708689-04	M61007-12	M61007-19	M61007-21	**AVERAGE**
Sample Collection Date	6/18/2007	11/22/2006	11/21/2006	11/21/2006	**Concentration**
Analyte					
OCDD	**458**	**1180**	**502**	**683**	705.750
OCDF	**3.13**	**9.89**	**30.4**	**24.3**	16.930
Total TCDDs	**0.0388**	**0.0956**	**1.08**	**0.747**	0.490
Total PeCDDs	**0.247**	**0.454**	**0.54**	**0.437**	0.420
Total HxCDDs	**6.48**	**12.5**	**6.24**	**5.8**	7.755
Total HpCDDs	**80.1**	**195**	**98.7**	**110**	120.950
Total TCDFs	**0.0255**	**0.0391**	**0.0871**	**0.0638**	0.054
Total PeCDFs	**0.18**	**0.288**	**0.301**	**0.261**	0.258
Total HxCDFs	**2.8**	**4.85**	**7.34**	**5.6**	5.148
Total HPCDFs	**5.33**	**11**	**21.1**	**21.3**	14.683
Total PCDDs	544.8658	1388.0496	608.56	799.984	835.365
Total PCDFs	11.4655	26.0671	59.2381	51.5248	37.074
Total Dioxins and Furans	556.3313	1414.1167	667.7981	851.5088	872.439

4. CONCLUSION

The most dominant congeners in all of the batch samples of PCP analyzed were Cl_6-Cl_8PCDDs. The predominance of these congeners in both PCP products and site soils in combination with the profiles shown in Figures 2 and 3 strongly suggests PCDD contamination in soils at the former tannery site is attributable to PCP containing products.

Elevated PCDDs/PCDFs concentrations were dominated by OCDD likely attributable to the historical use of pentachlorophenol (PCP) and/or products containing PCP. Elevated OCDD concentrations present in site soils are likely not solely attributable to historical use of PCP. OCDD, which is the most common PCDDs/PCDFs congener present as a contaminant (artifact of PCP production chemistry), in PCP may also be formed photochemically in soils , with PCP serving as the precursor compound (Holt et al, 2008, Liu et al, 2002, Lampariski et al, 1980).

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Chapter 13

NEW CONTINUOUS MONITORING TECHNOLOGIES FOR VAPOR INTRUSION, REMEDIATION AND SITE ASSESSMENT

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ABSTRACT

Typically, site investigation is carried out by using handheld or transportable field instruments coupled with offsite lab analyses. When using field instruments, the data generated represents a snapshot in time and space. Often, as with a PID or FID, data is presented as a total of contaminates present at that time and place. More sophisticated field equipment such as GC/MS can provide speciation, but still suffer from poor spatial and temporal resolution.

As an alternative, investigators can choose methods such as Summa canisters that sample for a fixed period, say 24 hours, followed by lab analysis. The data generated provides speciation but the concentrations represent an average for the sampling period.

Investigators are aware that environmental conditions such as pressure, temperature, water level and air movement substantially affect concentrations on a range of timescales, therefore uncertainty will always exist when using methods that lack temporal resolution.

The presentation describes instrumentation that provides real time continuous data both down hole and ambient for multiple parameters such as VOCs, methane, oxygen, carbon dioxide, hydrogen sulfide and carbon monoxide together with atmospheric and borehole pressure. Data is presented from field work carried out by, among other, the Maine DEP, for applications such as vapor intrusion, recovery well monitoring and landfill gas migration.

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A comparison between spot sampling and continuous monitoring raises questions about the value of limited spot sampling.

Keywords: GasClam, vapor, soil gas, monitoring

1. INTRODUCTION

The Maine Department of Environmental Protection (MEDEP), Division of Response Services provides initial response actions for oil and hazardous materials releases. Air monitoring is an important component for both the initial response and follow on work at the site particularly for residential petroleum releases from home heating oil tanks.

Conditions in a home or occupied building can change considerably over the course of a day and certainly over longer periods of time because of human activity (doors opening), number of people in the house, weather, household chemicals and smoking. Spot sampling with a handheld instrument (PID or FID for example) does not give a good representation of the overall condition/progress of the site. With the GasClam, we can also observe data from times when residents have complained that the vapors were elevated but MEDEP was not there to observe reported vapor conditions. We can look back at the GasClam data and quiz owners, residents, contractors etc with more specific questions concerning certain times which the gas clam data had abnormalities or spikes.

Air testing with canisters cannot provide time stamped data; even a 24 hour summa test only gives one result, averaged over the collection period, for each parameter analyzed. This is not to say that air testing with canisters does not have a place, it does, especially when there are unidentified contaminants. The GasClam can give us real time data or numerous data points over time at sites with known contaminants more effectively than many other methods.

We also use the GasClam to monitor recovery wells where contaminated soil cannot be excavation due to structures, piping or other physical limitations. The data from recovery wells indicates hydrocarbon degradation/attenuation probably due to microbiological activity consuming the hydrocarbons. (Discussion of microbiological activity is beyond the scope of this paper.) We have been using the GasClam for nine months at numerous sites both short and long term; some of the sites are outlined in the Data section.

2. MATERIALS AND METHODS

The GasClam was designed to operate remotely, specifically in monitoring wells. The GasClam purchased monitors and records the following: CH_4, O_2, CO, CO_2, H_2S, VOCs, atmospheric pressure, borehole pressure, pressure difference, temperature and water level. The instrument is intrinsically safe and operates on two D-cell batteries for a month or longer (dependent upon sampling rate). The case (housing) is constructed of high quality stainless steel and fits into a 2 inch borehole. In addition to petroleum sites, the GasClam is designed to monitor landfill gases, brownfields, coal mines and carbon capture and storage.

Some technical info on the GasClam includes a memory able to record 65,000 time/date stamped readings. It weighs 13.2 lbs or 7 kg. The overall length is 33.5 inches (85 cm), with the borehole tube length of 30.75 inches (78 cm). The borehole tube diameter is 1.75 inches and the head diameter is 4.25 inches. We have no problems locating a place for it at sites for collection of data.

3. CASES AND DATA

3.1 Calais, Maine

An apartment complex had a 1,000 gallon underground storage tank (UST) supplying #2 fuel to two furnaces in the basement of the apartment building. The 1,000 gallon UST was 33 years old and 13 years out of compliance; it was discovered leaking when the building owner smelled petroleum vapors in the basement and then observed free product in the basement drain which runs under the center of the building longitudinally. Liquid from this drain ultimately ends up in the city wastewater facility. The leak was discovered in the middle of the winter; the apartment building is supplied with public water and sewer making vapor intrusion into the occupied spaces the primary concern.

The UST was located on the exterior side of the foundation wall where the communal laundry room is located. An inlet to the building's drainage system was located in the middle of the laundry room allowing petroleum vapors to enter the room. A total of five connected drains were spaced approximately 25 feet apart within the basement were observed; free product was found throughout the basement drain system. During the initial MEDEP's visit the PID results were mostly in the 1-3 part-per-million (ppm) in the breathing zone (approximately 4-5 feet above the floor). PID readings just above the drains were between 80-120 ppm.

Initial actions included removing the remaining product from the UST and taking it out of service. Two 275 gallon above ground tanks (ASTs) were installed inside the basement to supply the furnaces. The owner then agreed to have the drain pipe cleaned. We installed the GasClam to get a better understanding of vapors in the basement especially before and after the drain cleaning. The removal of the UST was going to occur after the ground thawed. The drains could not be sealed due to groundwater seeping through cracks in the foundation walls and floor. Water was flowing even during MEDEP's initial visit.

The GasClam was installed in a secured room adjacent to the laundry room. It was placed in this room mostly due to security concern. The GasClam was placed 5.5 feet above the floor and it was programmed to sample once every 60 minutes (Figure 1).

Initial readings for the first 24 hours indicated VOC readings between 1-4 ppm, with an average of 2 ppm. On the second day at the 1400 hrs sampling time the VOC reading jumped to 10 ppm and gradually subsided to 2 ppm over the next four hours. After discussions with the owner we were able to determine this peak in VOC's was when the owner performed cleaning of the building's drains. Communication between the owner and MEDEP were difficult at best.

We had asked the owner to call the MEDEP a day or two prior to the cleaning so that we could observe and oversee the drain cleaning, that did not occur. Nonetheless, GasClam allowed MEDEP to observe the effects of the drain cleaning in the data; it also showed that VOCs declined within a few hours to pre cleaning levels. Within three days of the drain cleaning VOC levels dropped to zero and remained zero for the following month, at this point the GasClam was removed from this site.

3.2 Orono, Maine

An AST developed a small pinhole leak in the bottom of the tank. It appeared to have leaked slowly (drips) over a year or so and then finally gave way, discharging approximately 25 gallons onto the dirt cellar. The house is large, greater than 5,000 square feet, and is greater than 100 years old. The foundation is fieldstone with a small amount of concrete/mortar. The house is on public water and sewer.

The AST was located next to the fieldstone foundation wall. One of the rental's kitchens is directly overhead on first floor and a sunken living room (compared to kitchen) is approximately 20 feet away with a french door separating the basement from living room. Vapors were noticed in the kitchen and living room shortly after the spill by the owner.

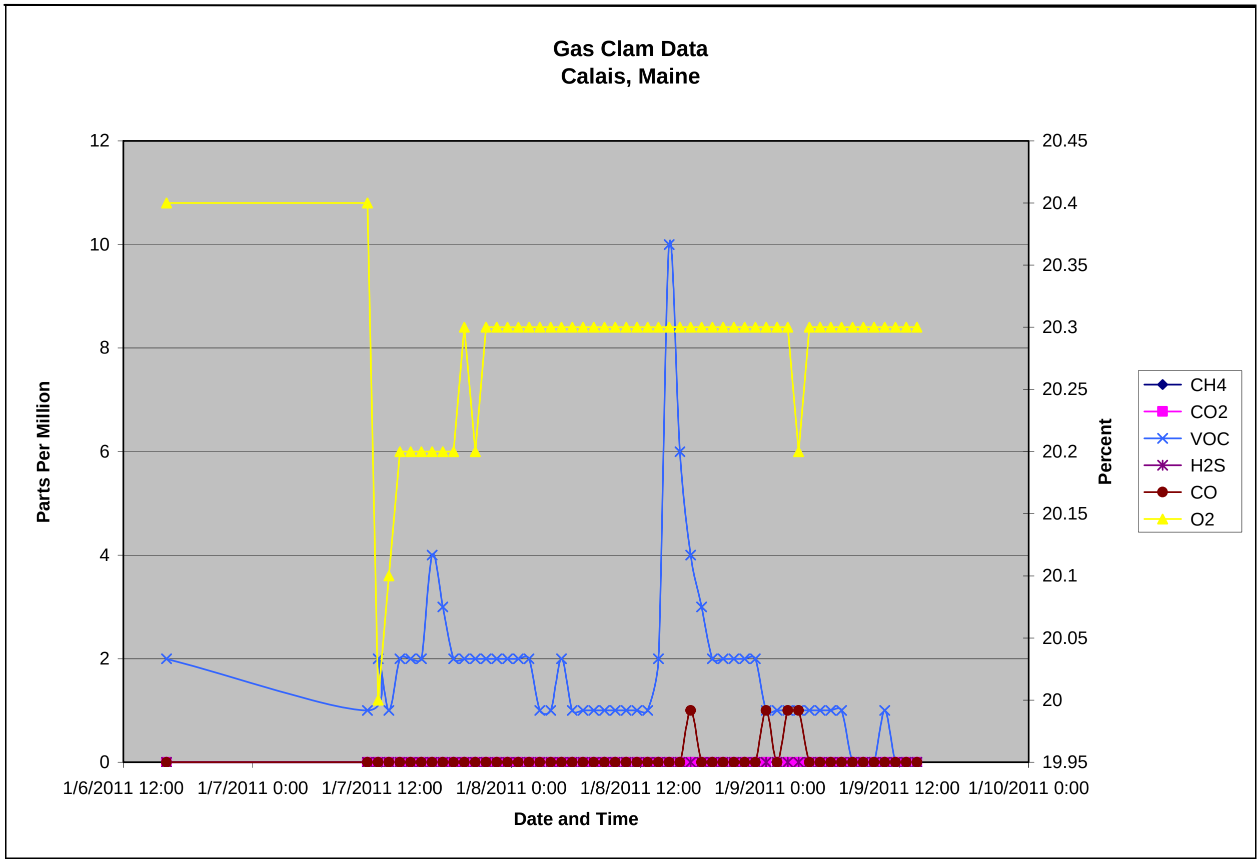

Figure 1. GasClam Data, Specifically O2, CO and VOC recorded at the Calais Maine site

Soil was impacted underneath the tank and around the tank, including under the fieldstone basement wall. Clay was found approximately 2-4 inches beneath surface layer of dirt/organic debris, oil also soaked into wood and debris in the cellar.

A wood floor area, approximately 5 feet by 5 feet, was impacted by the oil. Additional debris and materials in the basement were also contaminated and the majority of them were removed for proper disposal. Some debris impacted by oil was bagged and left for the owner to sort through, prior to removal. After the AST was removed, a small amount of soil, approximately 800 pounds, was removed from beneath the AST. It appeared that oil migrated towards the fieldstone basement wall. Due to the condition of the foundation wall contaminated soil was left undisturbed near and under the fieldstone foundation wall.

After removal of most of the contaminated material, 6 mil plastic was laid over the contaminated soil and up against the fieldstone wall and secured in place. Venting to the outside with a fan was an option but the owner was not 100% in line with approval with the installation of a fan and it would have required some creative pipe work since the closest window was almost into the living room. It was agreed to see if the poly would keep vapors suppressed until summer when windows could be opened.

Initially PID readings with Ion Science Phocheck 3000 were in the 9-15 ppm range next to the AST in the basement. PID readings on the first floor were below 3 ppm. Subsequent visits with Phocheck indicated readings below 1 ppm on the first floor and 4-7 ppm in basement until plastic on floor was disturbed or work was performed. Readings would then escalated back into the 9-15 ppm range.

Even though the owner insisted there were no issues in the house, PID readings indicated a potential for indoor vapor issues. The GasClam was installed approximately 7 feet from the AST and approximately 5.5 feet above the floor and programmed to sample every 60 minutes.

The GasClam showed a slow decline in VOC's, although when there were disturbances in the basement it caused elevated VOC readings for many hours afterward (Figure 2). Site visits generally resulted in higher VOC reading which was observed on the PID. Just walking on the poly caused an elevated reading on the PID and readings would stay at those levels for several hours. The GasClam data gave a better representation of the conditions of the basement over the long term, highlighting short term changes.

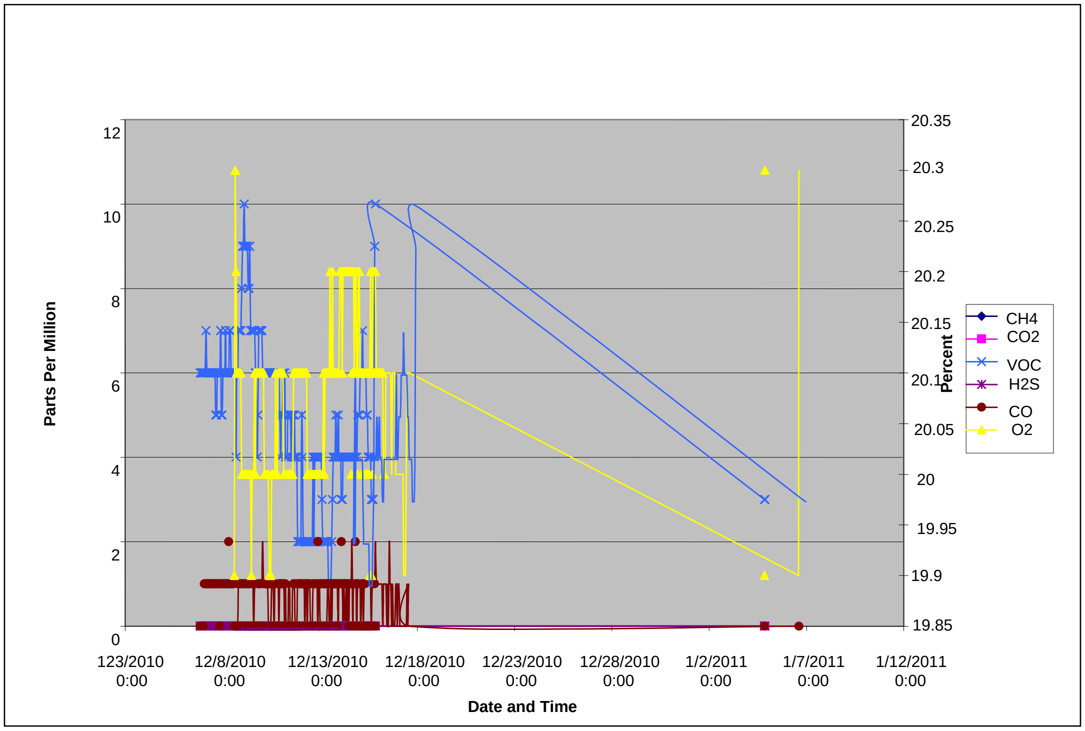

Figure 2. GasClam Data, specifically O2, CO and VOC, recorded at the Orono Maine Site

3.3 Bangor Gardens

The house was built in the 1950s or early 1960s as military base housing. The house is a single level on a concrete slab with neither a crawl space nor a basement. When the house was built a 275 gallon fuel oil tank was buried approximately 6 feet below grade. The UST was removed in late 1980s and a 275 gallon above ground oil storage tank (AST) was installed in the garage. The old UST supply line was connected to the new AST supply line approximately halfway between the garage and house. The entire supply line was buried with no secondary containment. The house is supplied by public water and sewer.

In early fall, approximately 250 gallons of #2 heating fuel leaked over a couple days. A patch of dead grass was observed in the back yard and was above the fitting connecting the old UST supply line and the newer AST supply line. It appears this connection had been leaking for some time and finally failed completely discharging the tank's contents.

MEDEP excavated approximately 3 cubic yards of contaminated soil to a depth of 6 feet. The concrete pad/bollard for the former UST was found at this depth. Free product was found collecting in the bottom of the excavation. A recovery well was installed and the excavation was backfilled. The recovery well is a 15 inch black culvert pipe installed vertically into the excavation. Numerous ½ inch holes were drilled into the culvert and erosion fabric was wrapped around the exterior. A loose culvert cap was installed on top of the recovery well. Stone, 1.5 inch, was backfilled around the culvert until approximately 1 foot below grade. Soil was then placed and the area was seeded.

A shed, attached garage and house were all within 5 feet of the excavation. Soils were highly contaminated at a depth of 6 feet below the surface. Free product flowed in from the direction of the house at the 6 foot depth. Vapors entering the house were the main concern at this site. The old supply line was located under the house from the excavation, a potential pathway. The owner already had existing health issues, specifically respiratory problems. No vapor issues from the spilled oil were observed in the house and a request to place the GasClam inside the house for a few weeks was denied by the owner. An initial PID sweep of the living area nearest to the spill indicated no vapor issues at that time. According to the owner there have been no vapor issues since.

Approximately 25-30 gallons of free product has been collected in the past year, mostly through the use of absorbent pads from the recovery well. Collection of free product is still ongoing, albeit at a much lower collection rate. The oil collected currently is weathered, has a faded yellow appearance compared the initial dark red appearance. The GasClam has been installed at various times of the past year to record conditions within the recovery well. The GasClam was programmed to sample every 60 minutes.

Interesting data has been recorded with the GasClam at this site (Figure 3). Data from the GasClam has shown O_2 declining; lowest recorded data point was 10.1%. O_2 levels stayed above 16% consistently during cool or cold periods. During warmer periods, generally when temperatures are greater than 19 degrees Celsius, O_2 levels would drop below 16%. When O_2 levels dropped below 15% it was usually for less than 5 hours. In general, the lowest O_2 readings were observed during daylight hours.

There was one period, June 9th, 2011, where O_2 levels dropped below 15% for approximately 12 hours and included the 10.1% data point. The highest Methane, 1.8 ppm, and highest CO_2, 8.7 ppm, reading occurred at that same hour reading as the 10.1% O_2 reading. The recorded temperature was 21 degrees Celsius at that data point. VOC's also had one of the highest readings at 114 ppm. VOC readings were initially recorded between 437 and 565 ppm for a 26 hour period in mid October, 2010. They have dropped off substantially since and are usually under 100 ppm.

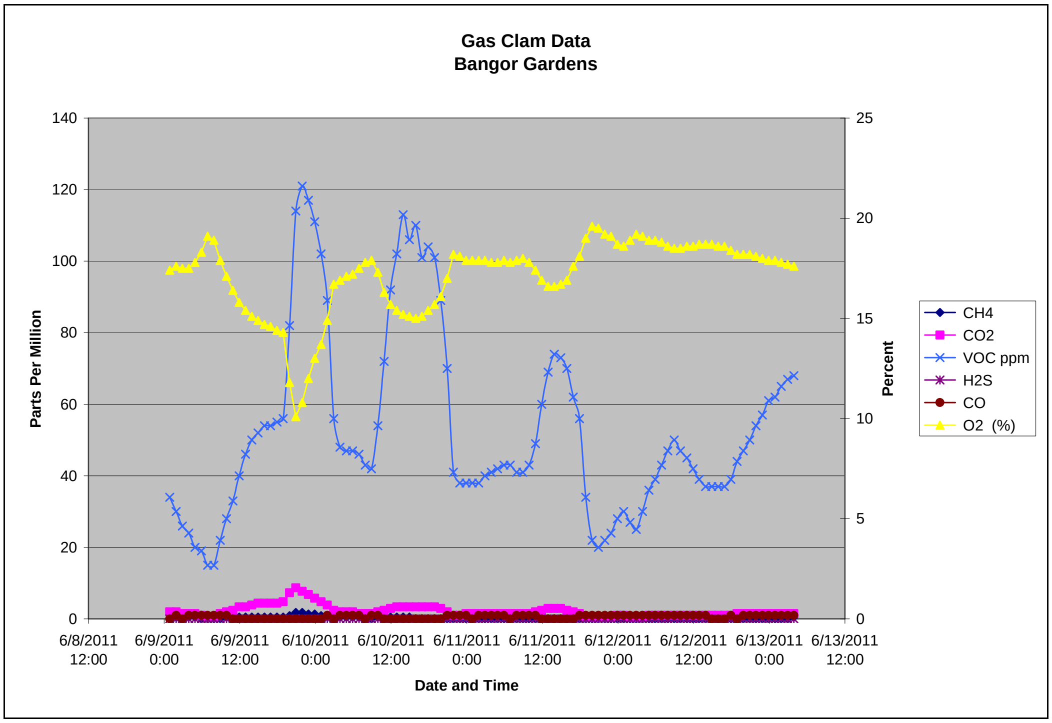

Figure 3. GasClam Data, specifically O2, CO2, CH4, and VOC, recorded at the Bangor Gardens Site

CO_2 levels overall would generally increase as O_2 levels declined and also hits of methane were recorded at these low O_2 periods. Carbon Monoxide (CO) consistently stayed between 0-2 ppm, with an average of less than 1 ppm. H_2S was detected three times (1 ppm) by the GasClam over the entire dataset.

During the most recent installation of the GasClam at this site it was observed that there were no hits of methane and VOCs were low, under 76 ppm with many readings in the 10-20 ppm range over a two week period. CO_2 levels fluctuated between 0-7.8 ppm; in general, the highest and lowest CO_2 readings occurred in the afternoon or evening. This was an unexpected observation considering the prior data. It was discovered through talking with the owner that she had just had a water leak fixed under her house. This would explain why there was water in the bottom of the well when in the past it was usually dry during times of minor precipitation. Public water draining into this area in a steady flow may have also caused some mortality of the petroleum eating bacteria. The water may have transported free product away from the well also since VOC data has been at the all time low since data collected started at this site and has been lower than spring and early summer readings.

With the current data from the GasClam, large decline of free product recovered from recovery well and oil recovered currently being very weathered, this site will be closed.

4. DISCUSSION

Maine DEP has been undergoing a major revision of the petroleum cleanup guidelines. The changes are broad and include sampling, field instrument use and bases cleanup decisions, after free product cleanup, on risk assessments, including risks to human health. Using the GasClam for continuous monitoring and data collection at petroleum sites has proved to be useful in making decisions about the risk of vapor intrusion and future cleanup actions.

5. APPENDIX I

Table 1. GasClam Raw Data Collected at the Calais Maine Site

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole	Atmospheric	Different Pressure	Temperature (celsius)
01/06/2011 16:01	0	0	20.4	2	0	0	993	996	-3	22.3
01/07/2011 10:39	0	0	20.4	1	0	0	996	999	-3	13.2
01/07/2011 11:39	0	0	20	2	0	0	995	998	-3	14.8
01/07/2011 12:39	0	0	20.1	1	0	0	993	997	-4	15.6
01/07/2011 13:39	0	0	20.2	2	0	0	993	997	-4	15.8
01/07/2011 14:39	0	0	20.2	2	0	0	993	997	-4	15.9
01/07/2011 15:39	0	0	20.2	2	0	0	993	997	-4	15.9
01/07/2011 16:39	0	0	20.2	4	0	0	993	996	-3	15.8
01/07/2011 17:39	0	0	20.2	3	0	0	992	996	-4	15.9
01/07/2011 18:39	0	0	20.2	2	0	0	992	996	-4	16.1

Table 1. GasClam Raw Data Collected at the Calais Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole	Atmospheric	Different Pressure	Temperature (celsius)
01/07/2011 19:39	0	0	20.3	2	0	0	992	995	-3	16.1
01/07/2011 20:39	0	0	20.2	2	0	0	991	995	-4	16.3
01/07/2011 22:39	0	0	20.3	2	0	0	991	994	-3	16.3
01/07/2011 23:39	0	0	20.3	2	0	0	990	994	-4	16.3
01/08/2011 0:39	0	0	20.3	2	0	0	990	994	-4	16.2
01/08/2011 1:39	0	0	20.3	2	0	0	990	993	-3	16.4
01/08/2011 2:39	0	0	20.3	1	0	0	989	993	-4	16.3
01/08/2011 3:39	0	0	20.3	1	0	0	990	993	-3	16.2
01/08/2011 4:39	0	0	20.3	2	0	0	989	993	-4	16.3
01/08/2011 5:39	0	0	20.3	1	0	0	990	993	-3	16.3
01/08/2011 6:39	0	0	20.3	1	0	0	990	994	-4	16.4
01/08/2011 7:39	0	0	20.3	1	0	0	990	994	-4	16.4

Table 1. GasClam Raw Data Collected at the Calais Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole	Atmospheric	Different Pressure	Temperature (celsius)
01/08/2011 8:39	0	0	20.3	1	0	0	991	994	-3	16.3
01/08/2011 9:39	0	0	20.3	1	0	0	991	995	-4	16.1
01/08/2011 11:39	0	0	20.3	1	0	0	990	994	-4	16.3
01/08/2011 12:39	0	0	20.3	1	0	0	991	994	-3	16.3
01/08/2011 13:39	0	0	20.3	2	0	0	991	994	-3	16.3
01/08/2011 14:39	0	0	20.3	10	0	0	990	994	-4	16.4
01/08/2011 15:39	0	0	20.3	6	0	0	991	995	-4	16.2
01/08/2011 16:39	0	0	20.3	4	0	1	991	995	-4	16
01/08/2011 17:39	0	0	20.3	3	0	0	991	995	-4	16.3
01/08/2011 18:39	0	0	20.3	2	0	0	990	994	-4	16.3
01/08/2011 19:39	0	0	20.3	2	0	0	990	994	-4	16.4
01/08/2011 20:39	0	0	20.3	2	0	0	989	993	-4	16.1

Table 1. GasClam Raw Data Collected at the Calais Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole	Atmospheric	Different Pressure	Temperature (celsius)
01/08/2011 21:39	0	0	20.3	2	0	0	989	992	-3	16.1
01/08/2011 22:39	0	0	20.3	2	0	0	988	992	-4	16.2
01/08/2011 23:39	0	0	20.3	1	0	1	988	992	-4	16.1
01/09/2011 1:39	0	0	20.3	1	0	1	986	991	-5	16.2
01/09/2011 2:39	0	0	20.2	1	0	1	985	989	-4	16.1
01/09/2011 3:39	0	0	20.3	1	0	0	985	990	-5	16.2
01/09/2011 4:39	0	0	20.3	1	0	0	985	990	-5	16.1
01/09/2011 5:39	0	0	20.3	1	0	0	985	989	-4	16.2
01/09/2011 6:39	0	0	20.3	1	0	0	985	990	-5	16.2
01/09/2011 7:39	0	0	20.3	0	0	0	985	989	-4	16.2
01/09/2011 8:39	0	0	20.3	0	0	0	985	989	-4	16.2
01/09/2011 9:39	0	0	20.3	0	0	0	985	989	-4	16.1

Table 1. GasClam Raw Data Collected at the Calais Maine Site (continued)

Date and Time	**CH_4**	**CO_2**	**O_2**	**VOC**	**H_2S**	**CO**	**Borehole**	**Atmospheric**	**Different Pressure**	**Temperature (celsius)**
01/09/2011 10:39	0	0	20.3	1	0	0	984	989	-5	16.4
01/09/2011 11:39	0	0	20.3	0	0	0	984	989	-5	16.4
01/09/2011 12:39	0	0	20.3	0	0	0	985	989	-4	16.3
01/09/2011 13:39	0	0	20.3	0	0	0	986	990	-4	16.4

Table 2. GasClam Raw Data Collected at the Orono Maine Site

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/8/2010 14:33	0	0	19.9	6	0	0	987	991	-4	18.3
12/8/2010 15:33	0	0	20.3	6	0	0	988	992	-4	14
12/8/2010 16:33	0	0	20.2	6	0	0	989	994	-5	12.4
12/8/2010 17:33	0	0	20.1	6	0	0	990	995	-5	11.8
12/8/2010 18:33	0	0	20.1	6	0	0	991	996	-5	11.6
12/8/2010 19:33	0	0	20.1	6	0	1	992	997	-5	11.3
12/8/2010 20:33	0	0	20.1	6	0	1	993	997	-4	11.1
12/8/2010 21:33	0	0	20.1	7	0	1	994	998	-4	10.8
12/8/2010 22:33	0	0	20.1	6	0	1	995	998	-3	10.6
12/8/2010 23:33	0	0	20	6	0	1	995	999	-4	10.4
12/9/2010 0:33	0	0	20	6	0	1	996	999	-3	10.2
12/9/2010 1:33	0	0	20	6	0	1	996	1	0	-4

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/9/2010 2:33	0	0	20	6	0	1	997	1	0	-3
12/9/2010 3:33	0	0	20	6	0	1	997	1	0	-3
12/9/2010 4:33	0	0	20	6	0	1	998	1	1	-3
12/9/2010 5:33	0	0	20	6	0	1	998	1	2	-4
12/9/2010 6:33	0	0	20	6	0	1	999	1	2	-3
12/9/2010 7:33	0	0	20	6	0	1	1	0	1	3
12/9/2010 8:33	0	0	20	6	0	1	1	1	1	4
12/9/2010 9:33	0	0	20	5	0	1	1	1	1	5
12/9/2010 10:33	0	0	20	5	0	1	1	1	1	4
12/9/2010 11:33	0	0	19.9	6	0	1	1	1	1	4
12/9/2010 12:33	0	0	20	6	0	1	1	1	1	4
12/9/2010 13:33	0	0	20	6	0	1	1	2	1	5

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature ($^oCelsius$)
12/9/2010 14:33	0	0	20	6	0	0	1	3	1	5
12/9/2010 16:33	0	0	20	5	0	1	1	5	1	7
12/9/2010 17:33	0	0	20.1	5	0	1	1	6	1	9
12/9/2010 18:33	0	0	20.1	6	0	1	1	8	1	10
12/9/2010 19:33	0	0	20.1	6	0	1	1	8	1	10
12/9/2010 20:33	0	0	20.1	6	0	1	1	9	1	11
12/9/2010 21:33	0	0	20.1	7	0	1	1	10	1	12
12/9/2010 22:33	0	0	20.1	6	0	1	1	11	1	13
12/9/2010 23:33	0	0	20.1	6	0	1	1	11	1	13
12/10/2010 0:33	0	0	20.1	6	0	1	1	12	1	14
12/10/2010 1:33	0	0	20.1	6	0	2	1	13	1	14
12/10/2010 2:33	0	0	20.1	7	0	1	1	14	1	15

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/10/2010 3:33	0	0	20	7	0	1	1	15	1	16
12/10/2010 4:33	0	0	20	6	0	1	1	15	1	16
12/10/2010 5:33	0	0	20	6	0	1	1	15	1	16
12/10/2010 6:33	0	0	20	6	0	1	1	16	1	17
12/10/2010 7:33	0	0	20	6	0	1	1	16	1	17
12/10/2010 8:33	0	0	20	6	0	0	1	17	1	18
12/10/2010 9:33	0	0	19.9	6	0	0	1	17	1	18
12/10/2010 10:33	0	0	19.9	4	0	0	1	16	1	18
12/10/2010 11:33	0	0	19.9	6	0	0	1	16	1	17
12/10/2010 12:33	0	0	20	6	0	1	1	15	1	16
12/10/2010 13:33	0	0	20	7	0	1	1	15	1	16
12/10/2010 14:33	0	0	20	7	0	1	1	15	1	16

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	**CH_4**	**CO_2**	**O_2**	**VOC**	**H_2S**	**CO**	**Borehole Pressure**	**Atmospheric Pressure**	**Differential pressure**	**Temperature (^{o}Celsius)**
12/10/2010 15:33	0	0	20	7	0	0	1	15	1	16
12/10/2010 16:33	0	0	20	7	0	1	1	15	1	16
12/10/2010 17:33	0	0	20.1	8	0	1	1	15	1	16
12/10/2010 18:33	0	0	20	9	0	1	1	15	1	16
12/10/2010 19:33	0	0	20	9	0	1	1	14	1	15
12/10/2010 20:33	0	0	20.1	10	0	1	1	13	1	14
12/10/2010 21:33	0	0	20.1	9	0	0	1	12	1	14
12/10/2010 22:33	0	0	20.1	9	0	1	1	12	1	13
12/10/2010 23:33	0	0	20.1	9	0	1	1	11	1	13
12/11/2010 0:33	0	0	20.1	9	0	1	1	11	1	12
12/11/2010 1:33	0	0	20.1	8	0	1	1	10	1	12
12/11/2010 2:33	0	0	20.1	8	0	1	1	10	1	12

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/11/2010 3:33	0	0	20	9	0	1	1	9	1	11
12/11/2010 4:33	0	0	20	7	0	0	1	8	1	10
12/11/2010 5:33	0	0	20	7	0	1	1	8	1	10
12/11/2010 6:33	0	0	20	7	0	0	1	8	1	10
12/11/2010 7:33	0	0	20	7	0	0	1	8	1	10
12/11/2010 8:33	0	0	20	7	0	0	1	8	1	10
12/11/2010 9:33	0	0	20	7	0	1	1	8	1	10
12/11/2010 10:33	0	0	20	6	0	1	1	8	1	10
12/11/2010 11:33	0	0	20	6	0	0	1	7	1	9
12/11/2010 12:33	0	0	20	4	0	0	1	7	1	9
12/11/2010 13:33	0	0	20	5	0	0	1	7	1	9
12/11/2010 14:33	0	0	20	7	0	1	1	8	1	9

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/11/2010 15:33	0	0	20.1	7	0	1	1	8	1	10
12/11/2010 16:33	0	0	20.1	7	0	1	1	8	1	10
12/11/2010 17:33	0	0	20.1	7	0	0	1	9	1	10
12/11/2010 19:33	0	0	20.1	6	0	0	1	10	1	12
12/11/2010 20:33	0	0	20.1	6	0	1	1	10	1	12
12/11/2010 21:33	0	0	20.1	6	0	1	1	11	1	12
12/11/2010 22:33	0	0	20.1	6	0	1	1	10	1	12
12/11/2010 23:33	0	0	20.1	6	0	1	1	11	1	12
12/12/2010 0:33	0	0	20.1	6	0	1	1	11	1	13
12/12/2010 1:33	0	0	20.1	6	0	1	1	11	1	13
12/12/2010 2:33	0	0	20.1	6	0	1	1	11	1	13
12/12/2010 3:33	0	0	20.1	6	0	1	1	11	1	13

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	**CH_4**	**CO_2**	**O_2**	**VOC**	**H_2S**	**CO**	**Borehole Pressure**	**Atmospheric Pressure**	**Differential pressure**	**Temperature (^{o}Celsius)**
12/12/2010 4:33	0	0	20.1	6	0	1	1	10	1	12
12/12/2010 5:33	0	0	20.1	6	0	0	1	10	1	12
12/12/2010 6:33	0	0	20.1	6	0	1	1	10	1	12
12/12/2010 7:33	0	0	20.1	6	0	1	1	11	1	13
12/12/2010 8:33	0	0	20	6	0	0	1	10	1	11
12/12/2010 9:33	0	0	20	6	0	1	1	9	1	11
12/12/2010 10:33	0	0	20	6	0	1	1	8	1	9
12/12/2010 11:33	0	0	20	6	0	1	1	5	1	7
12/12/2010 12:33	0	0	20	6	0	0	1	3	1	5
12/12/2010 13:33	0	0	20	6	0	0	1	1	1	4
12/12/2010 14:33	0	0	20	6	0	0	1	0	1	3
12/12/2010 15:33	0	0	20	6	0	1	998	1	2	-4

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/12/2010 16:33	0	0	20	5	0	1	996	1	0	-4
12/12/2010 17:33	0	0	20	4	0	1	995	999	-4	11.5
12/12/2010 18:33	0	0	20	5	0	1	993	997	-4	11.7
12/12/2010 19:33	0	0	20	5	0	1	991	995	-4	11.8
12/12/2010 20:33	0	0	20	6	0	1	989	993	-4	11.8
12/12/2010 21:33	0	0	20	5	0	0	986	991	-5	11.9
12/12/2010 22:33	0	0	20	6	0	1	985	990	-5	11.9
12/12/2010 23:33	0	0	20	4	0	1	983	988	-5	12.2
12/13/2010 0:33	0	0	20	4	0	0	980	986	-6	12.4
12/13/2010 1:33	0	0	20	4	0	0	978	984	-6	12.5
12/13/2010 2:33	0	0	20	5	0	0	976	982	-6	12.6
12/13/2010 3:33	0	0	20	5	0	0	974	980	-6	12.6

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/13/2010 4:33	0	0	20.1	5	0	0	973	979	-6	12.8
12/13/2010 5:33	0	0	20	5	0	0	972	979	-7	12.9
12/13/2010 6:33	0	0	20.1	4	0	0	972	979	-7	13.2
12/13/2010 7:33	0	0	20.1	5	0	0	972	979	-7	13.4
12/13/2010 8:33	0	0	20.1	5	0	0	972	979	-7	13.6
12/13/2010 9:33	0	0	20.1	4	0	1	972	978	-6	13.8
12/13/2010 10:33	0	0	20.1	5	0	1	972	979	-7	14
12/13/2010 11:33	0	0	20.1	4	0	0	970	976	-6	14.3
12/13/2010 12:33	0	0	20.2	4	0	0	970	977	-7	13.9
12/13/2010 13:33	0	0	20.1	4	0	1	969	976	-7	13.9
12/13/2010 14:33	0	0	20.1	2	0	0	969	976	-7	14.3
12/13/2010 15:33	0	0	20.2	2	0	1	969	976	-7	13.2

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/13/2010 16:33	0	0	20.1	2	0	1	968	975	-7	13.6
12/13/2010 17:33	0	0	20.1	2	0	1	969	976	-7	13.9
12/13/2010 18:33	0	0	20.1	2	0	1	967	974	-7	14.1
12/13/2010 19:33	0	0	20.1	5	0	1	965	972	-7	14.3
12/13/2010 20:33	0	0	20.1	4	0	1	965	973	-8	14.4
12/13/2010 21:33	0	0	20.1	2	0	1	964	972	-8	14.6
12/13/2010 22:33	0	0	20.1	2	0	0	964	972	-8	14.6
12/13/2010 23:33	0	0	20.1	2	0	1	963	971	-8	14.5
12/14/2010 0:33	0	0	20.2	2	0	1	965	972	-7	14.4
12/14/2010 1:33	0	0	20.2	2	0	1	966	973	-7	14.4
12/14/2010 2:33	0	0	20.2	2	0	1	967	974	-7	14.3
12/14/2010 3:33	0	0	20.1	2	0	1	967	974	-7	14.2

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/14/2010 4:33	0	0	20.2	2	0	0	967	975	-8	14.2
12/14/2010 5:33	0	0	20.2	2	0	1	968	975	-7	14.1
12/14/2010 6:33	0	0	20.2	2	0	0	969	976	-7	14.1
12/14/2010 7:33	0	0	20.2	2	0	0	970	977	-7	13.9
12/14/2010 8:33	0	0	20.2	2	0	1	971	978	-7	13.9
12/14/2010 9:33	0	0	20.2	4	0	0	972	979	-7	13.9
12/14/2010 10:33	0	0	20.2	2	0	1	973	979	-6	13.9
12/14/2010 11:33	0	0	20.2	4	0	0	973	980	-7	13.8
12/14/2010 12:33	0	0	20.2	4	0	1	974	980	-6	13.6
12/14/2010 13:33	0	0	20.2	4	0	1	974	981	-7	13.6
12/14/2010 14:33	0	0	20.2	4	0	1	975	982	-7	13.8
12/14/2010 15:33	0	0	20.2	4	0	2	976	982	-6	13.7

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	**CH_4**	**CO_2**	**O_2**	**VOC**	**H_2S**	**CO**	**Borehole Pressure**	**Atmospheric Pressure**	**Differential pressure**	**Temperature (^{o}Celsius)**
12/14/2010 16:33	0	0	20.2	4	0	0	977	983	-6	13.8
12/14/2010 17:33	0	0	20.2	4	0	1	978	984	-6	13.9
12/14/2010 18:33	0	0	20.1	4	0	1	978	984	-6	13.9
12/14/2010 19:33	0	0	20.2	4	0	1	978	984	-6	13.8
12/14/2010 20:33	0	0	20.2	3	0	1	978	984	-6	13.8
12/14/2010 21:33	0	0	20.1	2	0	0	978	983	-5	13.6
12/14/2010 22:33	0	0	20.1	2	0	1	976	983	-7	13.5
12/14/2010 23:33	0	0	20.2	2	0	1	976	983	-7	13.3
12/15/2010 0:33	0	0	20.2	2	0	1	978	983	-5	13.1
12/15/2010 1:33	0	0	20.1	2	0	1	978	984	-6	12.8
12/15/2010 2:33	0	0	20.1	2	0	0	976	982	-6	12.6
12/15/2010 3:33	0	0	20.1	2	0	1	976	982	-6	12.4

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/15/2010 4:33	0	0	20.1	1	0	1	976	982	-6	12.3
12/15/2010 5:33	0	0	20.1	1	0	0	976	982	-6	12.1
12/15/2010 6:33	0	0	20.1	1	0	1	977	983	-6	11.9
12/15/2010 7:33	0	0	20.1	1	0	1	977	983	-6	11.8
12/15/2010 8:33	0	0	20.1	2	0	1	978	984	-6	11.8
12/15/2010 9:33	0	0	20.1	3	0	1	979	985	-6	12.3
12/15/2010 10:33	0	0	20.1	4	0	1	979	985	-6	13.3
12/15/2010 11:33	0	0	20.1	4	0	1	980	985	-5	13.6
12/15/2010 12:33	0	0	20.1	4	0	1	979	985	-6	13.4
12/15/2010 13:33	0	0	20.1	5	0	1	980	986	-6	13.4
12/15/2010 14:33	0	0	20.2	4	0	1	980	986	-6	13.3
12/15/2010 15:33	0	0	20.1	4	0	0	981	987	-6	13.5

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/15/2010 16:33	0	0	20.1	5	0	1	981	987	-6	14.4
12/15/2010 17:33	0	0	20.2	4	0	1	982	987	-5	14.3
12/15/2010 18:33	0	0	20.2	4	0	1	982	988	-6	13.8
12/15/2010 19:33	0	0	20.2	4	0	1	984	988	-4	13.3
12/15/2010 20:33	0	0	20.2	3	0	2	984	989	-5	12.9
12/15/2010 21:33	0	0	20.1	3	0	1	984	989	-5	12.4
12/15/2010 22:33	0	0	20.1	4	0	1	984	989	-5	12.1
12/15/2010 23:33	0	0	20.1	4	0	1	984	989	-5	11.9
12/16/2010 0:33	0	0	20.1	4	0	1	984	989	-5	11.7
12/16/2010 1:33	0	0	20.1	4	0	1	985	990	-5	11.3
12/16/2010 2:33	0	0	20.1	4	0	1	985	990	-5	10.9
12/16/2010 3:33	0	0	20.1	4	0	1	986	991	-5	10.7

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/16/2010 4:33	0	0	20.1	4	0	1	987	992	-5	10.4
12/16/2010 5:33	0	0	20.1	4	0	0	987	992	-5	10.2
12/16/2010 6:33	0	0	20	4	0	1	988	993	-5	9.9
12/16/2010 7:33	0	0	20	4	0	1	989	993	-4	9.9
12/16/2010 8:33	0	0	20	4	0	1	989	994	-5	11.1
12/16/2010 9:33	0	0	20.1	4	0	1	990	995	-5	11.9
12/16/2010 10:33	0	0	20.1	4	0	0	990	994	-4	11.9
12/16/2010 11:33	0	0	20.1	4	0	1	990	994	-4	12.1
12/16/2010 12:33	0	0	20.1	4	0	0	990	994	-4	12.2
12/16/2010 13:33	0	0	20.1	6	0	2	990	994	-4	11.2
12/16/2010 14:33	0	0	20.1	4	0	1	991	995	-4	10.7
12/16/2010 15:33	0	0	20.1	4	0	1	992	996	-4	10.7

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/16/2010 16:33	0	0	20	5	0	0	992	997	-5	11.3
12/16/2010 17:33	0	0	20.1	5	0	1	993	997	-4	11.6
12/16/2010 18:33	0	0	20.1	5	0	0	993	997	-4	11.4
12/16/2010 19:33	0	0	20.1	6	0	0	993	997	-4	11
12/16/2010 20:33	0	0	20.1	6	0	0	993	997	-4	10.5
12/16/2010 21:33	0	0	20	6	0	1	992	997	-5	10.2
12/16/2010 22:33	0	0	20	7	0	1	992	997	-5	10
12/16/2010 23:33	0	0	20	6	0	0	992	997	-5	9.8
12/17/2010 0:33	0	0	20	6	0	1	992	996	-4	9.6
12/17/2010 1:33	0	0	20	6	0	1	992	997	-5	9.4
12/17/2010 2:33	0	0	20	6	0	0	992	997	-5	9.3
12/17/2010 3:33	0	0	20	5	0	0	992	996	-4	9.2

Table 2. GasClam Raw Data Collected at the Orono Maine Site (continued)

Date and Time	CH_4	CO_2	O_2	VOC	H_2S	CO	Borehole Pressure	Atmospheric Pressure	Differential pressure	Temperature (^{o}Celsius)
12/17/2010 4:33	0	0	20	5	0	0	991	996	-5	9.1
12/17/2010 5:33	0	0	20	4	0	0	991	996	-5	8.9
12/17/2010 6:33	0	0	20	4	0	0	991	996	-5	8.8
12/17/2010 7:33	0	0	19.9	4	0	0	992	996	-4	8.8
12/17/2010 8:33	0	0	19.9	4	0	0	992	997	-5	9.3
12/17/2010 9:33	0	0	19.9	3	0	0	992	997	-5	10.4
12/17/2010 10:33	0	0	20	3	0	0	992	997	-5	12.5
12/17/2010 11:33	0	0	20.1	3	0	1	992	996	-4	12.8
12/17/2010 12:33	0	0	20.1	4	0	0	992	996	-4	12.9
12/17/2010 13:33	0	0	20.1	9	0	1	992	997	-5	12.8
12/17/2010 14:33	0	0	20.1	10	0	0	993	997	-4	12.5
1/6/2011 14:16	0	0	19.9	3	0	0	993	996	-3	22.5
1/6/2011 14:51	0	0	20.3	3	0	0	993	996	-3	23

Table 3. GasClam Raw Data Collected at the Bangor Gardens Site

Date and Time	**CH_4**	**CO_2**	**O_2 (%)**	**VOC ppm**	**H_2S**	**CO**	**Atmospheric Pressure**	**Temp (°F)**	**Precip**	**Sea Level Pressure**
06/09/2011 0:54	0	2	17.4	34	0	0	999	62.1	0.04	29.71
06/09/2011 1:54	0.5	2	17.6	30	0	1	999	62.1	0	29.72
06/09/2011 2:54	0.5	1.5	17.5	26	0	0	998	62.1	0	29.69
06/09/2011 3:54	0.5	1.5	17.5	24	0	1	999	62.1	0	29.7
06/09/2011 4:54	0.5	1.5	17.8	20	0	1	999	61	0	29.72
06/09/2011 5:54	0	1	18.3	19	0	1	1	61	0	29.75
06/09/2011 6:54	0	0.5	19.1	15	0	1	1	60.1	0.13	29.77
06/09/2011 7:54	0	0.5	18.9	15	0	1	1	61	0.64	29.78
06/09/2011 8:54	0	1.5	17.9	22	0	1	1	64	0	29.75
06/09/2011 9:54	0.5	2	17.1	28	0	1	1	68	0	29.74
06/09/2011 10:54	0.5	2.4	16.4	33	0	0	999	75	0	29.71
06/09/2011 11:54	0.5	3.4	15.8	40	0	0	999	80.1	0	29.72

Table 3. GasClam Raw Data Collected at the Bangor Gardens Site

Date and Time	CH_4	CO_2	O_2 (%)	VOC ppm	H_2S	CO	Atmospheric Pressure	Temp (°F)	Precip	Sea Level Pressure
06/09/2011 12:54	0.5	3.4	15.4	46	0	0	998	84	0	29.69
06/09/2011 13:54	0.5	3.9	15.1	50	0	0	998	84	0	29.68
06/09/2011 14:54	0.5	4.4	14.9	52	0	0	999	86	0	29.7
06/09/2011 15:54	0.5	4.4	14.7	54	0	0	998	82	0	29.69
06/09/2011 16:54	0.5	4.4	14.6	54	0	0	997	82.9	0	29.66
06/09/2011 17:54	0.5	4.4	14.4	55	0	0	998	75.9	0	29.67
06/09/2011 18:54	0.5	4.8	14.3	56	0	0	998	73.9	0	29.68
06/09/2011 19:54	0.9	7.3	11.8	82	0	0	1	66	0	29.77
06/09/2011 20:54	1.8	8.7	10.1	114	0	0	1	68	0	29.75
06/09/2011 21:54	1.8	7.7	10.8	121	0	0	1	68	0	29.76
06/09/2011 22:54	1.4	6.8	12	117	0	0	1	66.9	0	29.76
06/09/2011 23:54	1.4	5.8	13	111	0	0	1	66.9	0	29.76

Table 3. GasClam Raw Data Collected at the Bangor Gardens Site

Date and Time	CH_4	CO_2	O_2 (%)	VOC ppm	H_2S	CO	Atmospheric Pressure	Temp (°F)	Precip	Sea Level Pressure
06/10/2011 0:54	0.9	4.8	13.7	102	0	0	1	66.9	0	29.78
06/10/2011 1:54	0.9	3.9	14.9	89	0	1	1	64.9	0	29.79
06/10/2011 2:54	0.5	2.4	16.7	56	0	0	1	62.1	0.06	29.81
06/10/2011 3:54	0.5	2	16.9	48	0	1	1	63	0.02	29.83
06/10/2011 4:54	0.5	2	17.1	47	0	1	2	62.1	0	29.85
06/10/2011 5:54	0.5	2	17.2	47	0	1	3	62.1	0	29.89
06/10/2011 6:54	0.5	1.5	17.5	46	0	1	4	62.1	0	29.91
06/10/2011 7:54	0.5	1.5	17.8	43	0	0	5	62.1	0	29.94
06/10/2011 8:54	0	1.5	17.9	42	0	1	5	64	0	29.95
06/10/2011 9:54	0.5	2	17.3	54	0	1	6	66	0	29.96
06/10/2011 10:54	0.5	2.4	16.3	72	0	0	7	68	0	29.98
06/10/2011 11:54	0.5	2.9	15.7	92	0	0	7	70	0	29.98

Table 3. GasClam Raw Data Collected at the Bangor Gardens Site

Date and Time	CH_4	CO_2	O_2 (%)	VOC ppm	H_2S	CO	Atmospheric Pressure	Temp (°F)	Precip	Sea Level Pressure
06/10/2011 12:54	0.5	3.4	15.4	102	0	0	7	71.1	0	29.97
06/10/2011 13:54	0.5	3.4	15.2	113	0	0	7	73	0	29.97
06/10/2011 14:54	0.5	3.4	15.1	106	0	0	7	73	0	29.97
06/10/2011 15:54	0	3.4	15	110	0	0	7	73.9	0	29.98
06/10/2011 16:54	0	3.4	15.1	101	0	0	7	73	0	29.98
06/10/2011 17:54	0	3.4	15.4	104	0	0	8	73.9	0	30
06/10/2011 18:54	0	3.4	15.7	101	0	0	8	72	0	30
06/10/2011 19:54	0	2.9	16.1	89	0	0	9	68	0	30.03
06/10/2011 20:54	0	2	17	70	0	1	9	64.9	0	30.06
06/10/2011 21:54	0	1	18.2	41	0	1	10	63	0	30.08
06/10/2011 22:54	0	1	18.1	38	0	1	10	60.1	0	30.08
06/10/2011 23:54	0	1.5	17.9	38	0	1	11	60.1	0	30.1

Table 3. GasClam Raw Data Collected at the Bangor Gardens Site

Date and Time	CH_4	CO_2	O_2 (%)	VOC ppm	H_2S	CO	Atmospheric Pressure	Temp (°F)	Precip	Sea Level Pressure
06/11/2011 0:54	0	1.5	17.9	38	0	0	12	55.9	0	30.12
06/11/2011 1:54	0	1.5	17.9	38	0	1	12	53.1	0	30.13
06/11/2011 2:54	0	1.5	17.9	40	0	1	13	55	0	30.14
06/11/2011 3:54	0	1.5	17.8	41	0	1	13	54	0	30.14
06/11/2011 4:54	0	1.5	17.8	42	0	1	13	54	0	30.14
06/11/2011 5:54	0	1.5	17.9	43	0	1	14	55	0	30.17
06/11/2011 6:54	0	1.5	17.8	43	0	0	14	57.9	0	30.17
06/11/2011 7:54	0	1.5	17.9	41	0	1	14	60.1	0	30.17
06/11/2011 8:54	0	1.5	18	41	0	1	14	64	0	30.19
06/11/2011 9:54	0	1.5	17.8	43	0	1	14	66.9	0	30.18
06/11/2011 10:54	0	2	17.4	49	0	1	14	68	0	30.17
06/11/2011 11:54	0	2.4	16.9	60	0	0	13	69.1	0	30.15

Table 3. GasClam Raw Data Collected at the Bangor Gardens Site

Date and Time	CH_4	CO_2	O_2 (%)	VOC ppm	H_2S	CO	Atmospheric Pressure	Temp (°F)	Precip	Sea Level Pressure
06/11/2011 12:54	0	2.9	16.6	69	0	0	13	71.1	0	30.14
06/11/2011 13:54	0	2.9	16.6	74	0	0	13	70	0	30.13
06/11/2011 14:54	0	2.9	16.7	73	0	0	13	69.1	0	30.13
06/11/2011 15:54	0	2.4	16.9	70	0	0	13	64.9	0	30.13
06/11/2011 16:54	0	2	17.6	62	0	0	13	61	0	30.14
06/11/2011 17:54	0	1.5	18.1	56	0	1	13	60.1	0	30.14
06/11/2011 18:54	0	0.5	19	34	0	1	13	59	0	30.13
06/11/2011 19:54	0	0.5	19.6	22	0	1	13	57.9	0	30.14
06/11/2011 20:54	0	0.5	19.5	20	0	1	13	57	0	30.14
06/11/2011 21:54	0	0.5	19.2	22	0	1	13	57	0	30.14
06/11/2011 22:54	0	0.5	19.1	24	0	1	12	55	0	30.12
06/11/2011 23:54	0	1	18.7	28	0	1	11	55	0	30.12

Table 3. GasClam Raw Data Collected at the Bangor Gardens Site

Date and Time	CH_4	CO_2	O_2 (%)	VOC ppm	H_2S	CO	Atmospheric Pressure	Temp (°F)	Precip	Sea Level Pressure
06/12/2011 0:54	0	1	18.6	30	0	1	11			
06/12/2011 1:54	0	0.5	18.9	27	0	1	11	53	0.41	30.02
06/12/2011 2:54	0	0.5	19.2	25	0	1	11	AVG	Total	AVG
06/12/2011 3:54	0	0.5	19.1	30	0	1	10			
06/12/2011 4:54	0	1	18.9	36	0	1	10			
06/12/2011 5:54	0	1	18.9	39	0	1	10			
06/12/2011 6:54	0	1	18.8	43	0	1	10			
06/12/2011 7:54	0	1	18.6	47	0	1	10			
06/12/2011 8:54	0	1	18.5	50	0	1	10			
06/12/2011 9:54	0	1	18.5	47	0	1	9			
06/12/2011 10:54	0	1	18.6	45	0	1	9			
06/12/2011 11:54	0	1	18.6	42	0	1	9			

Table 3. GasClam Raw Data Collected at the Bangor Gardens Site (continued)

Date and Time	CH_4	CO_2	O_2 (%)	VOC ppm	H_2S	CO	Atmospheric Pressure	Temp (°F)	Precip	Sea Level Pressure
06/12/2011 12:54	0	1	18.7	39	0	1	8			
06/12/2011 13:54	0	1	18.7	37	0	1	7			
06/12/2011 14:54	0	1	18.7	37	0	0	7			
06/12/2011 15:54	0	1	18.6	37	0	0	7			
06/12/2011 16:54	0	1	18.6	37	0	0	6			
06/12/2011 17:54	0	1	18.4	39	0	1	5			
06/12/2011 18:54	0	1.5	18.2	44	0	0	5			
06/12/2011 19:54	0	1.5	18.2	47	0	1	4			
06/12/2011 20:54	0	1.5	18.2	50	0	1	4			
06/12/2011 21:54	0	1.5	18.1	54	0	1	3			
06/12/2011 22:54	0	1.5	18	57	0	1	4			
06/12/2011 23:54	0	1.5	17.9	61	0	1	3			

Table 3. GasClam Raw Data Collected at the Bangor Gardens Site

Date and Time	CH_4	CO_2	O_2 (%)	VOC ppm	H_2S	CO	Atmospheric Pressure	Temp (°F)	Precip	Sea Level Pressure
06/13/2011 0:54	0	1.5	17.9	62	0	1	2	57	0.02	29.96
06/13/2011 1:54	0	1.5	17.8	65	0	1	2	AVG	Total	AVG
06/13/2011 2:54	0	1.5	17.7	67	0	1	2			
06/13/2011 3:54	0.5	1.5	17.6	68	0	1	1			

Chapter 14

THE INFLUENCE OF GROUNDWATER SAMPLE FLOW RATE ON SUSPENDED SOLIDS, GEOCHEMICAL AND CONTAMINANT CONCENTRATIONS AND ITS EFFECT ON TREND ANALYSIS

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ABSTRACT

Adherence to a standard groundwater sampling method is a fundamental requirement for the accurate assessment of contaminated sites. Confidence in expensive analytical results relied upon to evaluate contaminant fate, transport and risk potential is lost when possible sampling error is suspected. A correlation between suspended solids content and elevated fuel oil hydrocarbon concentrations was observed at sites where aggressive groundwater sampling methods were employed. This relationship was not observed when suspended solids were removed via filtration or at gasoline release sites, independent of filtration. The higher octanol-water coefficient of middle distillate petroleum compounds was attributed to the additive effect imparted by suspended solid-bound contaminants on dissolved phase concentrations. To further explore potential groundwater sampling induced error associated with aggressive purge and sample collection flow rates independent of turbidity, a controlled experiment was conducted over a range of groundwater flow rates at a gasoline impacted site. Volatile petroleum hydrocarbon (VPH) and geochemical parameter levels varied substantially between sampling treatments that ranged from 50 to 1,000 ml/min (including hand bailing) despite achieving stabilization of the geochemical parameters during each treatment. Sample precision was greatest for the 100 ml/min purge and sample flow rate. Possible sources of VPH concentration variability among the various treatments are discussed along with the importance of developing and adhering to site-specific sampling protocols, and the challenge of not doing so to trend analysis.

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Keywords: low-flow method, mobile-phase groundwater, trend analysis

1.0 INTRODUCTION

The collection of representative samples and an understanding of site-specific conditions are prerequisites for an accurate characterization of contaminated groundwater at release sites. Inconsistency in the development or adherence to an appropriate groundwater sampling program creates uncertainty in expensive analytical results used to support contaminant trends and direct response actions. Unless the sampler or data analyst take notice of the inherent variability that exists between sample locations and/or events, false assumptions in data interpretation can lead to erroneous conclusions and/or prolonged site closure strategies.

In an effort to standardize the collection of mobile dissolved phase groundwater, the United States Environmental Protection Agency (US EPA) developed a sampling method predicated on the purging and collection of groundwater from monitoring wells at recommended flow rates of 10 to 100 milliliters per minute (ml/min) in an effort to minimize the introduction of suspended solids that can contribute target analytes of interest. Emphasis is placed on limiting groundwater table drawdown to below 0.3 foot with sample collection occurring upon stabilization of monitored geochemical parameters (i.e. temperature, pH, conductivity, dissolved oxygen, redox potential and turbidity). Provided the monitoring well maintains sufficient hydraulic connection with the surrounding formation, the groundwater samples collected are considered to be representative of mobile dissolved phase constituents (US EPA, 1996, 2010).

Unfortunately, site conditions conducive to meeting the US EPA low flow method criteria are not always present. In practice, considerable variability in soil type, zone of contamination and groundwater flow can exist from well to well and between sampling events. Experience also demonstrates that the groundwater purge and sampling flow rates recommended by the US EPA (10-100 ml/min) may not be readily performed due to field technicians being unfamiliar with the method, equipment limitation or perceived inability to achieve well stabilization under low flow rates.

Analytical data obtained from numerous sites impacted with fuel oil or gasoline were compared to the groundwater sampling methods employed to assess the degree to which mobile, dissolved phase contaminant concentrations may be influenced by variations in sampling protocol. As expected, contaminant concentrations were directly related to groundwater purge flow rates and suspended solid content where solid-bound contaminants contributed falsely to mobile dissolved phase concentrations. This effect was most pronounced at fuel oil-impacted sites with little to no correlation at gasoline impacted sites. In order to evaluate the influence of groundwater purge rates on contaminant concentrations, independent of suspended solids, a field experiment was performed that monitored groundwater conditions at a gasoline-impacted site employing five sampling treatments, inclusive of the use of the hand bailer method.

2. MATERIALS AND METHODS

2.1 Analysis of Site Specific Data

Analytical results were obtained from sites where groundwater was impacted from releases of fuel oil/diesel fuel or gasoline, where groundwater sampling methods evolved from hand bailing to active groundwater purging at relatively high rates (500 to 3,000 ml/min), to the lower rates recommended by the low flow sampling protocol (100 ml/min). The filtering of groundwater samples were performed at gasoline- and fuel-oil impacted sites to evaluate the potential for suspended solid-bound analytes to have an additive effect on dissolved phase concentrations. Field filtered and unfiltered groundwater samples were submitted for laboratory analysis according to the Massachusetts Department of Environmental Protection (MassDEP) volatile petroleum hydrocarbon (VPH) and_extractable petroleum hydrocarbon (EPH) Methods (MassDEP, 2002 and 2004 Revision 1.1).

Turbidity was measured as an indicator of the relative amount of suspended solids present in groundwater that could contribute solid-bound analytes to dissolved phase concentrations. While turbidity is readily accepted as a relative measure of the suspended solids content of a water sample, the degree to which suspended solids affect light scatter is dependent upon the type of material suspended. A comparison of suspended solid content in milligram per liter (mg/l) and turbidity measurements (NTUs) demonstrated relatively consistent results at turbidity levels at or below 5 NTUs, whereas results varied substantially at turbidity levels of 10 to 30 NTUs (B. Tease, unpublished data). Groundwater was collected in a clean spectrophotometric cuvette at the discharge end of the flow-through chamber for turbidity screening once stabilization of the geochemical parameters (e.g., temperature, pH, conductivity, dissolved oxygen, and oxidation-reduction (redox) potential) occurred in accordance with US EPA criteria. Continuous monitoring of turbidity was not instituted due to the inherent uncertainty introduced by the frequent fouling of turbidity meter probes. Groundwater samples collected at diesel/fuel oil sites for the analysis of dissolved phase concentrations were field filtered using in-line Waterra 0.45 micron disposable filters. Turbidity was also measured in the field filtered samples as a means to assess filter failure.

2.2 Design and Evaluation of Field Experiment

An experiment was designed to evaluate the effect of different groundwater purge and sampling flow rates on total VPH fraction concentrations at a gasoline impacted site. Groundwater samples were collected in triplicate from a two-inch diameter, 20-foot deep PVC groundwater monitoring well. The well consisted of 15 feet of PVC schedule 20 well screen, standard well grade sand backfilled to two feet above the top of the well screen, a two-foot bentonite seal, schedule 40 PVC riser pipe to 6 inches below grade backfilled with clean native fill material, and completed with a well head protective box cemented flush to grade. The inlet of the sample tubing was positioned at the midpoint of the water column within the screened portion of the well (i.e. 13.3 feet below ground surface), approximately 3 feet below the contaminant smear zone. The smear zone is demonstrated by the elevated concentrations of total organic vapors (TOVs) detected by photoionization detector field screening of split spoon soil samples collected during well installation, which ranged from 190 parts per million (ppm) to 600 ppm across the 6 to 10 foot depth range. A peristaltic pump capable of achieving a sufficient range in flow rate was used to collect groundwater samples.

The desired flow rate was confirmed by measuring the rate at which groundwater filled a graduated cylinder. An electronic groundwater meter probe was used to measure the groundwater table elevation in feet at the start of each sampling treatment and at five minute intervals to monitor groundwater table drawdown. Geochemical parameters (temperature in degrees Celsius (^{0}C), pH, conductivity in microSiemens per centimeter (μS·cm-1), dissolved oxygen in milligrams per liter (mg/l), and redox potential in electron volts (eV) were also recorded in five-minute intervals. Upon stabilization of the geochemical parameters, as determined through observation of repetitive measurements consistent with the US EPA low flow method, groundwater samples were collected for field turbidity screening in Nephelometric Turbidity Units (NTU) and laboratory analysis of VPH fractions in milligrams per liter (mg/l) and target analytes in micrograms per liter (ug/l). All samples were stored on ice at 4 +/- 2 ^{0}C until delivery occurred to Spectrum Analytical, Inc. of Agawam, MA. Sample collection and parameter measurements began at the 50 ml/min flow rate and proceeded sequentially to 100 ml/min, 500 ml/min, and 1,000 ml/min. At the completion of the low flow sampling series, three well volumes of groundwater were removed from the well using a 1 ¼ inch diameter disposable plastic bailer. The groundwater table elevation was measured before and after well purging via hand bailer and immediately prior to sample collection for field turbidity measurement and submittal for laboratory analysis. Filtration was not performed to eliminate uncertainty associated with potential volatilization of gasoline related hydrocarbons.

3. RESULTS

3.1 Petroleum Release Sites

Analytical results depicting three representative disposal sites located in Massachusetts are summarized in Tables 1, 2 and 3. Table 1 presents analytical results for groundwater samples collected over a 12 year period where the hand bailing method was used during the 1998 and 2002 sampling events, high volume groundwater purging by peristaltic pump was implemented in 2003, and the low flow sampling method was employed in 2009 and 2010. Filtered and unfiltered samples were submitted in November 2009 for laboratory analysis of dissolved phase and total EPH fractions, respectively.

Total EPH fraction concentrations fluctuated erratically without any clear trend between sampling events, suggesting the potential for inconsistent sample collection. A review of groundwater sampling logs revealed that changes in groundwater table elevation, soil type or smear zone influences were not sufficient enough to account for the variations observed in contaminant concentrations. Variations in sampling methods, however, suggested that elevated levels of suspended solids were introduced into the samples as a result of aggressive well purging, which resulted in the fluctuations observed in EPH fraction concentrations. A decrease in low flow sampling flow rate from 444 ml/min to 100 ml/min resulted in a four-fold decrease in turbidity, and a 10-20 fold decrease in total EPH concentrations. Sample filtration conducted during the November 2009 sampling event resulted in a substantial reduction in turbidity and the absence of EPH fraction concentrations above the minimum laboratory reportable detection limits.

Table 2 summarizes analytical results from a gasoline release site where reductions in groundwater purge rate and turbidity had minimal effects on total VPH fraction and the target analytes ethylbenzene and xylene. Naphthalene concentration appeared to be affected by the reduction in suspended solids where decreased turbidity correlated with decreased concentration, albeit at low levels.

Table 1. Summary of Total EPH Fraction Concentrations, Turbidity andGroundwater Purge Rates at a Diesel Fuel Impacted Site

Parameter	Units	Sample Date								
		11/98	7/02	3/03	8/03	6/04	10/08	5/09	11/09	5/10
Depth to GW	feet	12.35	NM	11.93	10.24	10.60	9.98	9.96	9.05	10.31
Flow Rate	ml/min	HB	HB	GP	GP	GP	GP	444	444	100
Turbidity (filtered)	NTU	NT	NT	NT	NT	NT	NT	89	97 (5)	24
Total EPH (filtered)	mg/l	279	379	4.45	25	3.7	130	23.4	13.5 (<DL)	1.5

HB = hand bailed NT = not tested
GP = Groundwater purge at high flow rate <DL = less than minimum reportable detection limit

Table 2. Summary of Total VPH Fraction and VOC Target Analyte Concentrations, Turbidity and Groundwater Purge Flow Rate at a Gasoline Release Site

Parameter	Units	Date		
		11/06	8/09	5/10
Purge Flow Rate	ml/min	NT*	444	150
Turbidity	NTU	NT*	41	1
Total VPH	ug/l	3,177	2,620	2,300
Benzene	ug/l	<5	<5	<5
Toluene	ug/l	10	13	<5
Ethylbenzene	ug/l	139	<5	56
Xylene	ug/l	166	<10	58
Naphthalene	ug/l	56	40	29

NT = not tested
* = Purge rate and turbidity levels likely similar to that recorded 8/09
<5 = less than minimum reportable detection limit

Table 3 represents analytical results for groundwater samples collected at a #2 fuel oil release site where changes in purge flow rate were directly related to turbidity and total EPH fraction concentrations. A decrease in groundwater sampling flow rate from 444 ml/min to 100 ml/min resulted in a four-fold decrease in turbidity, and a 10-20 fold decrease in total EPH concentration. Changes in flow rate, turbidity and concentrations were of the same degree as the results presented in Table 1. While these results suggest a possible close relationship between turbidity and total EPH fraction concentration, the data sets where such relationships were observed are insufficient to make any general conclusions. Sample filtration conducted during the November 2009 sampling event resulted in the absence of total EPH fraction concentration above the minimum laboratory detection limit.

Table 3. Summary of Total EPH Fraction Concentrations, Turbidity and Groundwater Sampling Flow Rate at a #2 Fuel Oil Release Site

Parameter	Units	Date		
		5/09	11/09	5/10
Flow Rate	ml/min	440	444	100
Turbidity	NTU	89	97	24
Total VPH (filtered)	ug/l	23	13 (<DL)	1.5
Date for unfiltered samples except where noted <DL = less than minimum reportable detection limit				

3.2 Field Experiment

Analytical results depicting VPH fraction concentrations in replicate samples collected and geochemical parameter trends measured during the various groundwater purge treatments are summarized in the figures presented below. The analytical and field measured parameter results are summarized in Tables 4 and 5, respectively. VPH target analytes were not detected above the minimum laboratory reportable detection limit in any of the samples analyzed. The average concentrations of the individual VPH fractions for the various purge treatment sample replicates are depicted in Figure 1, along with turbidity measurements.

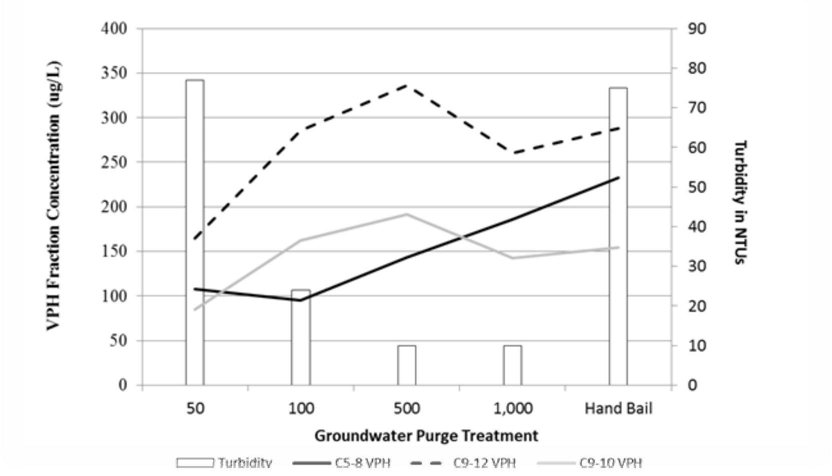

Figure 1. Average VPH Fraction Concentrations and Turbidity per Purge Treatment

In general, the lowest VPH fraction concentrations were detected in the 50 ml/min and 100 ml/min treatment samples. The highest VPH fraction concentrations were detected in the 500 ml/min sample set. Sample turbidity was greatest for the 50ml/min and hand bailer treatments, and least for the 500 ml/min and 1,000 ml/min treatments. No correlation was observed between VPH concentrations and turbidity. The variability in VPH concentrations among the sample replicates is presented in Figure 2 along with Total VPH fraction concentration trends.

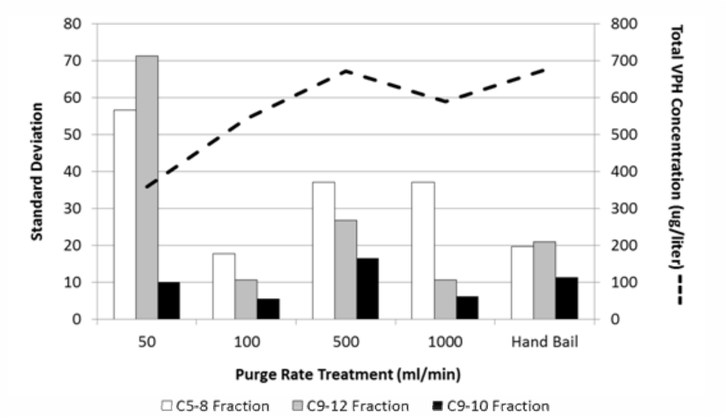

Figure 2. Standard Deviation of Individual and Total VPH Fraction Concentrations per Groundwater Purge Treatment

The VPH fraction concentrations for the 100 ml/min purge treatment replicates exhibited the greatest precision of all treatments, while the samples collected at the 50 ml/min purge rate varied the most, particularly for the C5-8 VPH and C9-12 VPH fractions. The C9-10 VPH fraction concentrations were the most reproducible across all five purge treatments. Figures 3, 4, and 5 depict stabilization trends for the geochemical parameters, dissolved oxygen, redox potential, and conductivity, respectively.

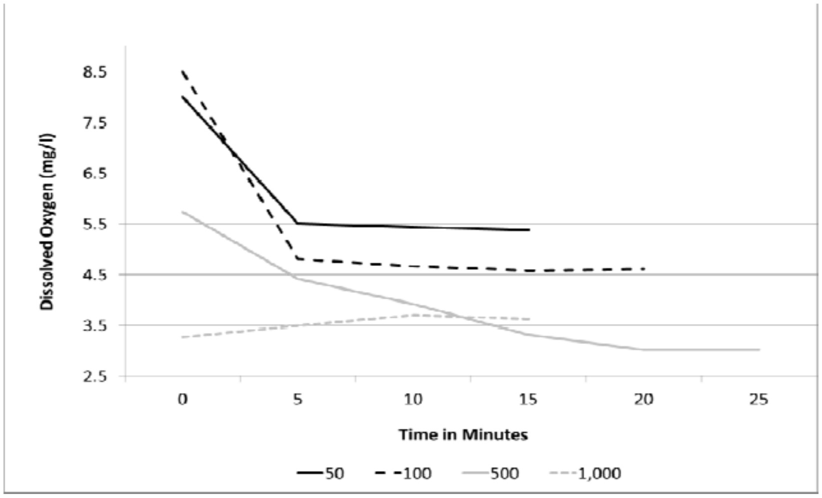

Figure 3. Dissolved Oxygen Concentration Trends per Groundwater Purge Rate

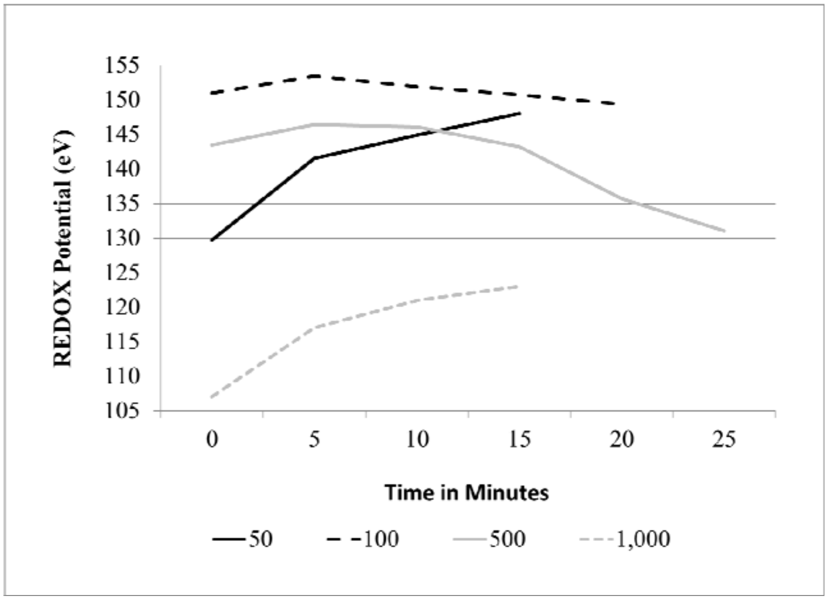

Figure 4. REDOX Potential Trends per Groundwater Purge Rate

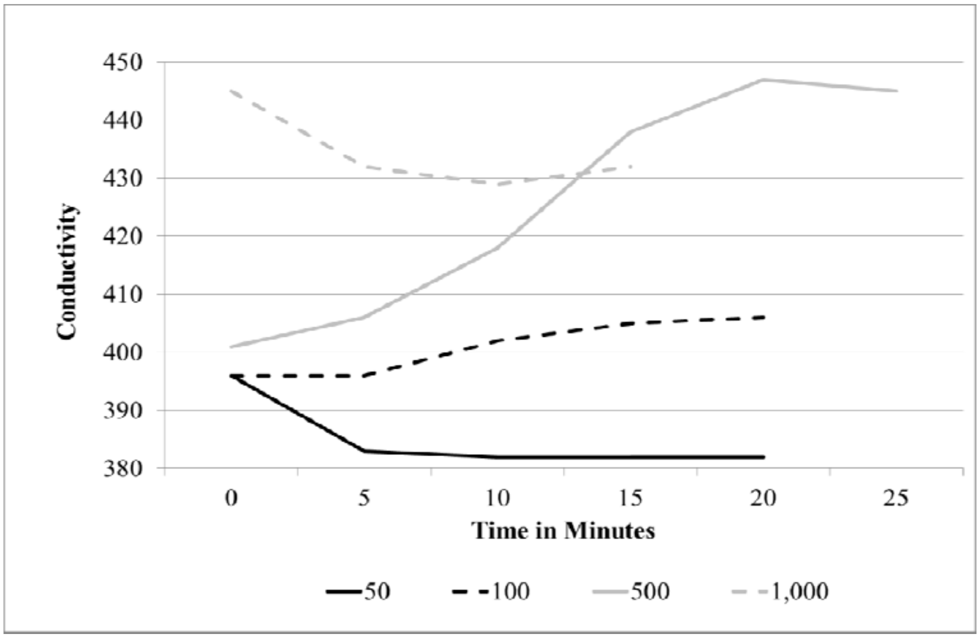

Figure 5. Conductivity Trends per Groundwater Purge Rate

Trends in pH and temperature were similar to the other geochemical parameters as seen in Table 5. Regardless of flow rate, stabilization of the geochemical parameters was achieved within 20 minutes of groundwater purging. Groundwater elevation trends are plotted against purge treatment in Figure 6.

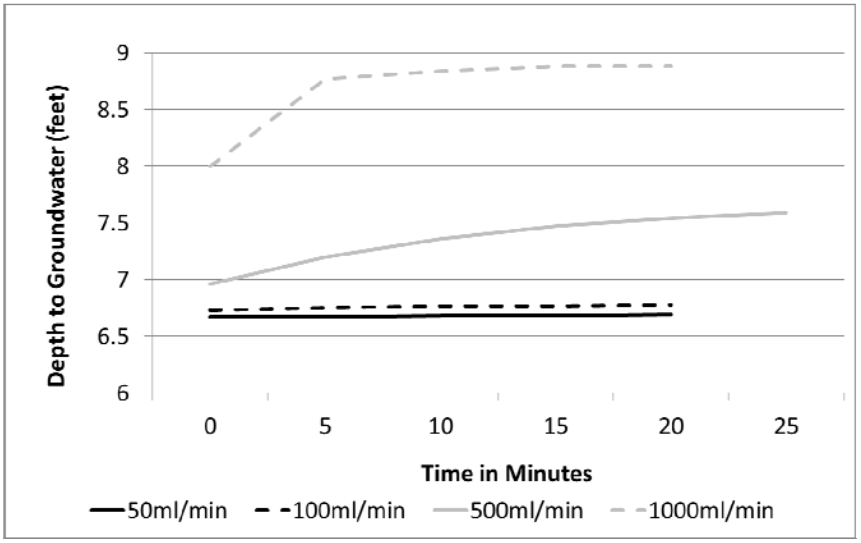

Figure 6. Groundwater Elevation Trends per Groundwater Purge Rate

The groundwater table elevation dropped 0.02 foot and 0.05 foot, respectively, during groundwater purging at the 50 ml/min and 100 ml/min flow rates, whereas the 500 ml/min, 1,000 ml/min, and hand bailer treatments induced a drop in groundwater table elevation of 0.63 foot, 0.88 foot, and 3.54 feet, respectively.

Table 4. Summary of VPH Concentrations (ug/l) and Statistical Parameters per Purge Treatment

Treatment	Replicate	C5-8	C9-12	C9-10	Total VPH
50 ml/min	A	**75**	158	86	319
	B	**75**	239	95	409
	C	173	97	**75**	345
Mean		108	165	85	358
Std Deviation		56.6	71.2	6.4	46.6
t value		3.3	4.0	14.76	13.37
Pr > [t]		0.081	0.057	0.0056	0.0055
Significant Difference		no	no	yes	yes
100 ml/min	A	**75**	295	168	538
	B	106	287	162	555
	C	105	274	157	536
Mean		95	285	162	543
Std Deviation		0.7	10.6	5.5	10.4
t value		9.4	46.6	51.1	90.08
Pr > [t]		0.011	0.0005	0.0004	0.0001
Significant Difference		yes	yes	yes	yes
500 ml/min	A	138	324	185	647
	B	154	318	179	651
	C	138	367	210	715
Mean		143	336	191	671
Std Deviation		37.1	26.7	16.4	38.2
t value		26.9	21.8	20.2	30.46
Pr > [t]		0.001	0.0021	0.0025	0.0011
Significant Difference		yes	yes	yes	yes

Table 4. Summary of VPH Concentrations (ug/l) and Statistical Parameters per Purge Treatment (continued)

Treatment	Replicate	C5-8	C9-12	C9-10	Total VPH
1,000 ml/min	A	143	250	137	530
	B	204	271	149	624
	C	210	260	141	611
	Mean	186	260	142	588
	Std Deviation	37.1	10.5	6.1	50.9
	t Value	8.7	42.9	40.4	20.01
	Pr > [t]	0.013	0.0005	0.0006	0.0025
	Significant Difference	yes	yes	yes	yes
Hand Bailer	A	249	298	160	707
	B	238	302	161	701
	C	211	264	141	616
	Mean	233	288	154	675
	Std Deviation	19.6	20.9	11.3	50.9
	t Value	20.6	23.9	23.67	22.46
	Pr > [t]	0.002	0.0017	0.0018	0.0019
	Significant Difference	yes	yes	yes	yes

4. DISCUSSION

4.1 Petroleum Release Sites

While the unexpected increases in contaminant concentrations may be indicative of a new release, migrating groundwater plume, or seasonal fluctuations in groundwater table elevation, such increases are not expected at sites where stable concentration trends have been documented over time, or where the above conditions can be ruled out. Spikes in contaminant concentrations can prolong response actions if the unexpected results can not be explained.

The review of the groundwater sampling and analytical data from several fuel oil sites revealed the additive effect contaminant-bound suspended solids have on dissolved phase groundwater concentrations as a result of aggressive well purging methods. The US EPA low flow method recommends limiting purge and sampling flow rates in the range of 10 to 100 ml/min in an effort to minimize the collection of suspended solids, as measured by turbidity levels (ideally less than 5 NTUs), and to maximize the recovery of mobile dissolved-phase groundwater. Since it is mobile groundwater that poses the greatest risk potential to

Table 5. Summary of Geochemical Parameters and Turbidity Levels per Purge Treatment

Treatment	Time	Temp	pH	Cond.	D.O.	Redox	Turbidity
50 ml/min	0	9.15	5.89	396	8.00	130	
	5	8.81	5.82	383	5.51	142	
	10	8.84	5.81	382	5.44	145	
	15	8.86	5.80	382	5.38	148	
	20	-	-	382	-	-	77
100 ml/min	0	8.08	5.89	396	8.50	151	
	5	8.50	5.76	396	4.81	153	
	10	8.04	5.75	402	4.67	152	
	15	8.43	5.74	405	4.59	151	
	20	8.44	5.74	406	4.61	149	24
500 ml/min	0	7.32	5.92	401	5.74	144	
	5	7.11	5.76	406	4.42	146	
	10	7.32	5.75	418	3.92	146	
	15	7.35	5.75	438	3.32	143	
	20	7.40	5.79	447	3.02	136	
	25	7.30	5.81	445	3.02	131	10
1000 ml/min	0	7.15	5.91	445	3.27	107	
	5	7.33	5.83	432	3.50	117	
	10	7.38	5.82	429	3.71	121	
	15	7.40	5.82	432	3.63	123	10

Summary of Geochemical Parameters at Equilibrium per Purge Treatment and Statistical Differences

Purge Treatment (ml/min)	Temp	pH	COND	DO	redox	NTUs
50 (a)[1]	8.86	5.80	382	5.38	148	77
100	8.44	5.74	406	4.61	149	24
500	7.30	5.81	445	3.02	131	10
1000 (b)[2]	7.40	5.82	432	3.63	123	10
Standard Deviation	0.77	0.04	28.0	1.04	13.0	31.9
Mean	8.00	5.79	416	4.16	138	30.3
US EPA Equilibrium Criteria	+/- 3%	+/- 0.1	+/- 3%	+/- 0.3	+/- 10	+/- 10%

downgradient receptors, the disturbance and collection of soil-bound contaminants results in the recovery of unrepresentative groundwater samples.

Middle distillate petroleum hydrocarbons (diesel/fuel oil) have a greater affinity for soil as indicated by their higher partitioning coefficients and lower water solubility than lighter gasoline-related fractions (Gschwend and Wu, 1985, MassDEP, 2002 and 2004 Rev 1.1). The two data sets presented in Tables 1 and 3 demonstrate the additive effect of suspended solid-bound petroleum hydrocarbons on dissolved-phase concentrations particularly at purge rates above 100 ml/min. EPH concentrations were not detected above minimum laboratory reportable detection limits in samples that were field filtered. Critical to demonstrating this additive effect is the monitoring of turbidity levels in filtered samples, given the potential for filter breakthrough. Turbidity levels of 10-50 NTUs are not uncommon in field-filtered samples.

The MassDEP VPH/EPH Final Policy #WSC-02-411 (2002 and Revision 1.1 2004), recommends sample filtration at fuel oil impacted sites where suspended solid content can’t be reduced through low flow sample collection methods alone. Conversely, the data set presented in Table 2 demonstrates the limited effect suspended solids have on influencing mobile dissolved-phase gasoline hydrocarbon concentrations; the MassDEP VPH/EPH Policy does not recommend filtration for VPH-related compounds for this reason, and given the potential for volatilization during the filtration process.

4.2 Field Experiment

The absence of a correlation between VPH concentrations and turbidity in the field experiment, and the variable trends observed in VPH fraction concentrations in groundwater samples from the various purge treatments, imply the presence of sampling-induced factors other than suspended solids that can affect contaminant concentrations. The field experiment demonstrated the dissimilarity that can occur in the analytical as well as geochemical results as a consequence of inconsistent groundwater purge rates. Understanding the potential sources of sample variability is critical to the ability to differentiate real concentration trends from those occurring as artifacts of sample collection.

When groundwater is recovered from a monitoring well, the flow rate should be consistent among wells and between sampling events in order to justify an accurate comparison of analytical data collected spatially and temporally. Groundwater within a monitoring well can be viewed as having three source areas: (1) water within the well casing, (2) sand-pack pore water outside the well casing within the bore hole, and (3) formation pore water located outside the bore hole. In theory, if soil conditions permit and the well is constructed properly, a sufficient hydraulic connection is established between formation and well such that the three source areas are in equilibrium with each other. In practice, however, it is not uncommon for the three areas to be distinct due to heterogenic soils, inappropriate well construction and/or age. In this case, the concentration of dissolved phase components of a groundwater sample can vary substantially depending upon where the sample originated from.

Another source of sample uncertainty involves the recovery of mobile versus immobile groundwater. The more water soluble a particular analyte is, the more likely it is to be present in higher concentrations in groundwater that readily flows through the formation (i.e. mobile groundwater). Over time the contaminant concentrations will decrease as this groundwater effectively purges the source area. Conversely, groundwater occupying smaller soil pores retained through capillary forces is considered to be immobile under normal hydraulic gradients. Due to the static nature of this groundwater fraction and its close proximity to more hydrophobic contaminants that have a tendency to associate with soil surfaces due to lower water solubility levels, the concentrations of contaminants in immobile groundwater tend to be higher. During more aggressive well purging actions, the substantial but artificial hydraulic gradients produced are sufficient to overcome the capillary and hydrophobic forces resulting in the recovery of high contaminant concentrations present in immobile groundwater. The observations made during the field experiment are further discussed below as they relate to these sources of groundwater variability.

4.3 Variations Attributed to Multiple Groundwater-Source Areas within a Monitoring Well

The effect groundwater purge rate has on contaminant concentrations can be demonstrated by comparing the volume of groundwater recovered to the volume available within the various source areas of a monitoring well. At lower purge volumes, which tend to be collected at lower flow rates (e.g. 10-50 ml/min) the potential exists for more of the recovered sample to contain groundwater that resided mainly within the well screen than that within the pore spaces of the well sand pack or formation. As recorded during the four low flow purge treatments, the time for geochemical parameter stabilization to occur was between 15-20 minutes for each treatment. Therefore, the volume of groundwater purged was directly related to purge rate.

The volume of groundwater within a typical two-inch diameter PVC monitoring well, constructed of 10-feet of well screen that provides approximately 5 feet of water column, is 0.75 gallons or 3,000 milliliters (ml), with 9 gallons (36,000 ml) available from the pore space of the sand pack.[2]

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[2] US EPA recommends the placement of a sand pack 3-5 inches beyond the well casing. Assuming a 3-inch sand pack distance surrounding a 2-inch diameter well screen, the groundwater storage capacity within a 5-foot tall sand pack in cubic feet is equal to:

(3.14 x bore radius^2 x length x 25% porosity for standard well grade sand) – (3.14 x well radius^2 x length)

(3.14 x 0.33^2 x 5 x 0.25)-(3.14 x 0.08^2 x 5) = 1.30 – 0.10 = 1.2 cubic feet x 7.5 gallons/cubic foot = 9 gallons

Under relatively permeable soil conditions, and groundwater drawdown of less than 0.3 foot, the groundwater removed from the well casing is replenished by sand-pack pore water, which in turn gets replenished by a virtually unlimited volume of formation pore water.

One of the founding principles of the US EPA low flow method is that groundwater recharge occurs more laterally than vertically such that the inlet of the sample tubing placed at a specified depth is recovering groundwater from a similar depth. For comparative purposes, an estimate of the vertical zone from which groundwater enters the sample tube inlet will not likely exceed one foot, unless aggressive purge treatments are applied, or under conditions of poor well recharge. In the latter case, the requirements for low flow sampling are voided and such conditions require a different approach to sample collection altogether.

Using the assumed vertical recovery zone estimate of one foot, the known monitoring well and sand-pack diameters, and soil porosity estimate, an approximation of the volume of groundwater available and/or likely recovered from a given source area can be obtained for each of the well purging/sampling treatments (see Table 6). Whether the sand pack pore space is replenished by groundwater from soil pores directly outside the well sand pack will be dependent upon the degree of mixing that occurs between sand pack and native formation pore water, which is directly related to the permeability of soil pores or grain size. For the purpose of this exercise, which also is consistent with the conditions present in the field experiment, the permeability of sand pack material and surrounding soils is considered sufficient to permit unrestricted well recharge.

The calculations presented in Table 6 imply that the 50 ml/min sample originated primarily from the well casing with potentially 12% occurring from the sand pack pore space, whereas the 100 ml/min sample was comprised mostly of groundwater originating from the sand pack (67%); formation pore water (groundwater originating from soil pores outside the well sand pack) was not considered to have contributed to either the 50 ml/min or 100 ml/min sample volumes. Formation groundwater accounted for approximately 85% of the groundwater sample volumes collected during the 500 ml/min and 1,000 ml/min purge treatments. Due to the substantial drawdown incurred during hand bailing (3.5 feet), the groundwater sample collected was considered to be comprised of approximately equal amounts of sand pack and formation water. Given that the drawdown exceeded one foot, the potential vertical recovery zone was over three times greater than the other treatments, such that the proportions of groundwater originating from the well casing and sand pack were greater than those from the formation water for the hand bailer samples compared to the other purge treatment samples.

Table 6. Summary of Groundwater Table Drawdown and Source Estimates for the Well Purging Treatments Applied During the Field Experiment

	Units	50 ml/min	100 ml/min	500 ml/min	1,000 ml/min	Hand Bailer
Total sampling time	minutes	15	20	25	15	NA
Total volume collected	milliliters	750	2,000	12,500	15,000	18,000[1]
Depth to groundwater at start of purging	feet	6.67	6.73	7.59	8.00	8.88
GW drawdown at end of purging	feet	0.02	0.05	0.63	0.88	3.54
Volume immediately purged within well [2]	milliliters	660	660	660	660	2,340[3]
Volume immediately purged outside of well	milliliters	90	1,340	11,840	14,340	15,660
Volume available in 1 foot of sand pack[4]	milliliters	2,000	2,000	2,000	2,000	7,000[5]
Volume of formation water purged or sampled	milliliters	0	0	9,840	12,340	8,000

NA = not applicable GW = groundwater

[1] 18 bailers (1 liter capacity) were used to purge well prior to sample collection

[2] drawdown in ft x 0.022 sf [surface area of 2 in. well] = cf x 7.5 gall./cf x 4 qrts/gall x 1000 = milliliters in well

[3] Volume based on 3.54 foot drawdown of groundwater vs 1-foot estimate

[4] 1 ft sand pack length x 0.33 ft bore hole radius^2 x 3.14 x 0.25 porosity)-(3.14 x 0.08^2 well radius x 1 ft)
0.085-0.020 = 0.065 cubic foot x 7.5 gallons/cf = 0.5 gallons = 2 liters = 2,000 ml

[5] 3.54 ft sand pack length x 0.33 ft bore hole radius^2 x 3.14 x 0.25 porosity)-(3.14 x 0.082 well radius x 1 ft)
0.255-0.020 = 0.235 cf x 7.5 gall/cf = 1.76 gall = 7 liters = 7,000 ml = volume in sand pack based on 3.54 ft
of drawdown after hand bailing three well volumes

The above exercise demonstrates the potential for variability of contaminant concentrations and may explain the lower total VPH concentrations detected and the poorest precision observed in the 50 ml/min purge treatment triplicate samples compared to the other sample sets. The differences observed in the geochemical parameter levels detected may also be explained by variation in potential well source areas. Under non-sampling conditions, groundwater within a properly functioning well should be in equilibrium with the surrounding aquifer provided the hydraulic connection between well and formation is sufficient to sustain the natural flow of groundwater across the well screen. Given the low volumes of groundwater purged during the 50 ml/min treatment (750 ml), the potential exists for groundwater within the well screen to have not been adequately purged (accounting for the majority of the sample collected), which is not considered to be representative of site groundwater conditions.

4.4 Variations Attributed to the Recovery of Mobile versus Immobile Groundwater

The VPH fraction concentrations detected in samples collected at the 50 ml/min, 100 ml/min, and 500 ml/min purge treatments exhibited increasing trends for all three fractions, as depicted in Figure 1. The concentrations of the C9-12 VPH and C9-10 VPH fractions, however, tailed off in the 1,000 ml/min and hand bailed samples, whereas the C5-8 VPH fraction concentrations did not exhibit this break in concentration. The 100 ml/min purge treatment yielded the sample replicate concentrations with the greatest precision; the C9-10 VPH fraction exhibited the greatest precision among all three fractions and for all purge treatments.

The C9-12 and C5-8 aliphatic VPH fractions have the lowest water solubility (0.07 mg/l and 11 mg/l) and greatest soil partitioning coefficients (150,000 Foc and 2,265 Foc) compared to the C9-10 aromatic VPH fraction, which has the highest water solubility (51 mg/l) and lowest soil partitioning coefficient (1,778 Foc). It may be possible that the C9-10 VPH fraction was least affected by purge rate since it was most likely present in the dissolved phase of the mobile groundwater, whereas the other VPH fractions have a greater potential of being associated with immobile groundwater resulting in greater variability in concentrations as the contaminants present at higher concentrations in the immobile groundwater mixed with the contaminants present at lower concentrations in the mobile groundwater.

Combining the two potential sources of groundwater variability, samples collected at sufficient flow rates to permit the recovery of groundwater mainly from the sand-pack should be more representative of mobile groundwater than samples collected at lower or higher purge rate extremes, and have the least variability in contaminant concentration. Groundwater localized in sand pack pores are also protected from adverse conditions within the well screen (i.e. volatilization, aerobic degradation as a result of elevated dissolved oxygen concentrations from the atmosphere) and less likely to be influenced by the recovery of immobile groundwater from formation pore water outside the bore hole.

The groundwater replicates collected during the 100 ml/min purge treatment likely originated mainly from sand pack pore water and had the greatest precision among all replicate samples. Samples from the 500 ml/min and 1,000 ml/min treatments likely originated mainly from formation pore water given the large volumes purged. The 500 ml/min treatment samples contained the highest total VPH fraction concentrations and poorest precision among all treatment samples, along with the 50 ml/min treatment samples. The 1,000 ml/min and hand bail treatment samples exhibited lower VPH fraction concentrations than the 500 ml/min treatment samples and exhibited similarly poorer sample precision.

The need for precision (i.e. reproducibility of a result) and accuracy (i.e. how close a result comes to the true value) in the collection and analysis of samples is critical to trend analysis, as it is this information that is used to develop and/or support professional opinions concerning risk to sensitive receptors. The emphasis placed on analytical results is magnified at sites that pose a greater risk as indicative of more stringent standards. Conversely, precision and accuracy become lesser commodities when exposure potential is minimized and regulatory standards are less rigorous. For example, the C9-10 VPH fraction concentrations detected in the replicate samples A, B and C for the 500 ml/min purge treatment were 185 ug/l, 179 ug/l, and 210 ug/l, respectively. Given that the applicable GW-1 Method 1 Risk Characterization Standard at this site for this VPH fraction is 200 ug/l, accuracy and precision play a more important role. Conversely, if the level of risk for this fraction is reduced, as is the case at sites where the less stringent Method 1 Risk Characterization Standards GW-2 (7,000 ug/l) or GW-3 (50,000 ug/l) apply, the variation in this data set is irrelevant.

In situations where risk is low, or concentrations are so high that precision and accuracy play a secondary role to general characterization, and likely site closure is far in the future, groundwater sampling at higher flow rates and/or following hand bailer methods may be acceptable. Under certain conditions, the recovery of immobile groundwater may be the desired outcome, as is the case when calculating the total mass of contaminant and remedial additive. Analysis of mobile groundwater conditions alone may underestimate the amount of chemical oxidant or reducing agent.

5. CONCLUSIONS

The concentration of geochemical parameters and petroleum hydrocarbons was shown to be affected by the rate at which groundwater is recovered from monitoring wells. Inconsistency in groundwater purge rate among site specific monitoring wells and between sampling events can complicate the assessment of analytical results by inducing uncertainty in data precision and accuracy.

In addition to the disturbance and collection of suspended solids that results in the contribution of solid bound contaminants to dissolved phase concentrations, aggressive groundwater purge treatments have the potential of extracting what is typically immobile groundwater, overcoming the hydrophobic and capillary forces that contribute to the retention of groundwater located in tight soil-pore spaces. The US EPA low flow method is intended to minimize the introduction of suspended solids by minimizing groundwater table drawdown and thus maintaining shallow hydraulic gradients during well purging, and thus allowing the recovery of mainly mobile groundwater.

In addition to validating the additive effects that suspended solid-bound contaminants have on dissolved phase concentrations of middle distillate petroleum hydrocarbons, common to fuel oil, the effect of varying purge rates on the source area from which groundwater is recovered was demonstrated during the field experiment. Despite achieving stabilization, the geochemical parameters differed quantitatively among the various purge treatments suggesting the recovery of groundwater from different source areas within the test well. Utilizing the purge volumes collected for each treatment, the well screen, well sand pack pore space, and formation pore space, were considered to represent three separate and distinct sample source areas.

The sample set collected during the 100 ml/min purge rate, which exhibited the greatest precision in analytical results, was considered to have originated from the sand pack pore water and be most representative of mobile groundwater. The C9-10 VPH fraction concentrations exhibited the greatest precision of all fractions regardless of purge treatment. This may be explained at least in part by this fraction being predominant in mobile groundwater due to having the highest water solubility and lowest affinity for soil partitioning of the three fractions. The higher VPH fraction concentrations detected in samples collected during the 500 ml/min purge treatment are considered to be attributed to the recovery of immobile groundwater from primarily formation pore water. The recovery of higher contaminant concentrations associated with immobile groundwater is not representative of mobile groundwater and contributes to the diminished precision and accuracy noted in analytical results obtained.

The need for precision and accuracy in the collection and analysis of groundwater samples is critical to trend analysis, as this information is used to develop and/or support professional opinions concerning risk to sensitive receptors. The emphasis placed on analytical results is magnified at sites that pose a greater risk and, therefore, are regulated by more stringent standards. Conversely, sites where exposure risks are reduced and less restrictive standards exist may not warrant the same demand for analytical precision and accuracy. While hand bailing methods would not be suitable for fuel oil impacted groundwater or at sites where the degree of risk is high (i.e. low standards), the use of hand bailing at gasoline impacted sites where risk is low and standards are high may be a better use of limited resources than the more costly low flow sampling method.

Trend analysis involves more than the plotting of data over time. Knowledge of the soil conditions associated with a given monitoring well, the presence of contaminant smear zones or preferential migration pathways, decisions behind the selection of groundwater purge rates, the positioning of low flow sample tubing or the selection of hand bailing methods must also be considered before conclusions are drawn from the analytical results. Failure to address these variables can lead to prolonged site closure and unnecessary assessment and/or remedial actions.

6. REFERENCES

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