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

**Volume 19**



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

**Volume 19**

**Remediation  
PCBs  
Risk Assessment  
Heavy Metals  
NAPL  
Soil and Sediments**

Selected manuscripts from the 29th Annual International Conference on  
Soils, Sediments, Water and Energy  
University of Massachusetts Amherst  
October 21 – 24, 2013

Edited by:  
Paul T. Kostecki  
Edward J. Calabrese  
David Ludwig  
Christopher M. Teaf

ISBN: 978-0-9888932-1-4

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Annual International Conference on Contaminated Soils, Sediments, Water, and Energy  
AEHS Foundation  
150 Fearing Street  
Amherst, MA 01002  
[www.AEHSFoundation.org](http://www.AEHSFoundation.org)

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## Contributing Authors

**Hashem Al-Mattarneh**, Engineering Department, Najran University, Najran, Saudi Arabia, 11001

**Abdullah Alwadie**, Engineering Department, Najran University, Najran, Saudi Arabia, 11001

**Daniel Boamah**, Geochemistry & Laboratories, Geological Survey Department, Accra, Ghana

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

**Jonathan Curran**, Antea Group, 500 Summit Lake Drive, Valhalla, New York, 10595

**Mohamad Dahim**, Engineering Department, Najran University, Najran, Saudi Arabia, 11001

**Michele M. Garber**, Hazardous Substance & Waste Management Research, Inc., 2976 Wellington Circle West, Tallahassee, Florida, 32309

**Gordon Hinshalwood**, Antea Group, 2 Bridgewater Road, Farmington, Connecticut, 06032

**Rabah Ismail**, Najran University, Engineering Department, Najran, Saudi Arabia, 11001

**Kingsley Kodom**, Department of Physics, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana

**Kennard F. Kosky**, Golder Associates, Inc., 6026 NW 1st Place, Gainesville, Florida, 32607

**Ahmad Malkawi**, Engineering Department, Najran University, Najran, Saudi Arabia, 11001

**Christopher Meyer**, Antea Group, 500 Summit Lake Drive, Valhalla, New York, 10595

**Joseph E. O'Connell**, Cardno ERI, 25371 Commercentre Drive, Suite 250, Lake Forest, California, 92630

**Mary O'Reilly**, SUNY School of Public Health, 7705 Farley Lane, Manlius, NY, 13104

**James D. Okun**, O'Reilly, Talbot & Okun Associates, Inc., 293 Bridge Street, Suite 500, Springfield, Massachusetts, 01103

**Kwasi Preko**, Department of Physics, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana

**Tarak Shrestha**, SUNY School of Public Health, 97 Lincoln Ave Fl-2, Albany, NY, 12206

**Włodzimierz A. Sokół**, Central Mining Institute, Plac Gwarkow 1, Katowice, Poland

**Nathan Stevens**, Gulf Oil Limited Partnership, 281 Eastern Avenue, Chelsea, Massachusetts, 01523

**Christopher M. Teaf**, Florida State University, Center for Biomedical and Toxicological Research, 2035 East Dirac Drive, Tallahassee, Florida, 32310

**Bruce J. Tuovila**, Hazardous Substance & Waste Management Research, Inc., 2976 Wellington Circle West, Tallahassee, Florida, 32309

**Gary M. Zwain**, Duplass, Zwain, Bourgeois, Pfister & Weinstock, 3838 N. Causeway Boulevard, Three Lakeway Center, Suite 2900, Metairie, Louisiana, 70002

## Foreword

Autumn in the Connecticut River valley around Amherst is a natural treasure. Led by sugar and Norway maples, the trees create a mosaic of colors that cannot be rivaled by artwork laid in the best glazed tiles. For a few weeks, the atmosphere itself reflects, refracts, magnifies, and propagates pigments spread on the landscape palette by the cyclical physiology of vegetation. The air is a hologram in red, orange, and yellow. At one level, a casual walk on a woodland path becomes a spiritual experience.

On another level, those stunning colors represent serious ecological processes at work. The plants are preparing to deal with the coming winter. Environmental realities demand hard work and complicated processes year after year. The bright colors are a lovely curtain, behind which the ecosystem machinery compels biology to meet the impending harsh geophysical challenges.

In similar fashion, scientists from many disciplines have convened each year in October at the Amherst Conference for nearly 30 years. That landscape has formed an annual backdrop for many important reports on environmental challenges and the tools we develop and invoke to meet those challenges. The Amherst Conference is a unique forum. A great diversity of environmental stewards attends, this year represented by nearly 200 platform and poster presentations, 10 highly focused preconference technical workshops, and approximately 50 exhibitors of applied environmental products and services. Each year, new environmental management tools or approaches are described, and their effectiveness is evaluated in the technical sessions, the poster presentations, and over coffee in the halls between meeting rooms. Emerging issues are identified and their impacts are quantified. Students, educators, regulators, land managers, scientists, and engineers have the opportunity to interact. Collectively, those meetings and discussions frame the state-of-the-art of another year's hard work on behalf of a sustainable biosphere. With the ecosystem on colorful display, the importance of our efforts is brought into sharp focus. If we want to understand

why we invest the time, money, and expertise that is behind each platform presentation and poster, we have only to step outside the building.

The best of the best from the 29<sup>th</sup> Annual International Conference on Soils, Sediments, Water and Energy are presented in this volume. We are proud to commend it to you. And we hope to see you in October 2014, when we will once again take a snapshot of the environment and discuss the tools that scientists, engineers, planners, regulatory personnel, attorneys and those in other related fields are applying to continue improvement of the environmental picture.

*Dave Ludwig*  
*Christopher Teaf*  
*Paul Kostecki*  
*Ed Calabrese*  
*Clifford Bruell*

## About the Editors

**Dr. Paul T. Kostecki's** professional career has focused on research, education and training in environmental contamination with an emphasis on human and ecological risk assessment and risk management of soils. His work includes soil ingestion estimates for children and adults; establishment of scientifically sound cleanup levels for soil; bioavailability of soil contaminants; fish as toxicological models for contamination assessment; and assessment and management of petroleum contaminated soils. Dr. Kostecki has developed and conducted over 55 conferences, workshops and courses both nationally and internationally, and has made presentations at over 100 national and international meetings. Since 1985, his conference at the University of Massachusetts Amherst on Contaminated Soils, Sediments and Water has attracted over 10,000 environmental professionals from over 50 countries. Dr. Kostecki has published over 100 articles and reports, co-edited/co-authored 35 Books and secured over \$15M in research support.

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

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

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

**Dr. Edward J. Calabrese** is a Professor of Toxicology at the University of Massachusetts, School of Public Health and Health Sciences, Amherst. Dr. Calabrese has researched extensively in the area of host factors affecting susceptibility to pollutants, and is the author of over 750 papers in scholarly journals, as well as more than 10 books, including Principles of Animal Extrapolation; Nutrition and Environmental Health, Vols. I and II; Ecogenetics; Multiple Chemical Interaction; Air Toxics and Risk Assessment; and Biological Effects of Low Level Exposures to Chemical and Radiation. Along with Mark Mattson (NIH) he is a co-editor of the recently published book entitled Hormesis: A Revolution in Biology, Toxicology and Medicine. He has been a member of the U.S. National Academy of Sciences and NATO Countries Safe Drinking Water committees, and on the Board of Scientific Counselors for the Agency for Toxic Substances and Disease Registry (ATSDR). Dr. Calabrese also serves as Chairman of the Biological Effects of Low Level Exposures (BELLE) and as Director of the Northeast Regional Environmental Public Health Center at the University of Massachusetts. Dr. Calabrese was awarded the 2009 Marie Curie Prize for his body of work on hormesis. He was the recipient of the International Society for Cell Communication and Signaling-Springer award for 2010. Dr. Calabrese received an honorary Doctor of Science from McMaster University, Hamilton, Ontario in 2013. Over the past 20 years Professor Calabrese has redirected his research to understanding the nature of the dose response in the low dose zone and underlying adaptive explanatory mechanisms. Of particular note is that this research has led to important discoveries which indicate that the most fundamental dose response in toxicology and pharmacology is the hormetic-biphasic dose response relationship. These observations are leading to a major transformation in improving drug discovery, development, and in the efficiency of the clinical trial, as well as the scientific foundations for risk assessment and environmental regulation for radiation and chemicals.

**Dr. David F. Ludwig** is a systems ecologist by training and a risk assessor by trade. He took an undergraduate Bachelor of Science degree from Rutgers University, a Master's in Marine Biology at the Virginia Institute of Marine Sciences, and a PhD in Systems Ecology at the University of Georgia Institute of Ecology. His career linked environmental consulting with university teaching. He worked in academia, the private sector, and for regulatory agencies, a breadth of background the gives him unique perspectives on environmental matters.

Dave's career spanned the globe. He worked in mainland Asia, Pacific Oceania, the Middle East, Europe, the Caribbean, and throughout North America. He is

broadly published in the technical literature, and co-author of books on urban ecology and the ecology and toxinology of true viper snakes. He provides weekly insights regarding environmental sustainability in a column published on the AEHS Foundation web site, titled “PeopleSystems and Sustainability: This Week in the Global Environment”.

**Dr. Christopher M. 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 Chair 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 as an expert in federal and state courts, as well as administrative proceedings, in a number of states regarding toxicology, health risk assessment, and environmental chemistry.



# DIELECTRIC MEASUREMENTS FOR CHARACTERIZING SANDY SOIL CONTAMINATED BY DIESEL

Hashem Al-Mattarneh<sup>§</sup>, Mohamad Dahim, Abdullah Alwadie, Ahmad Malkawi and Rabah Ismail

*Faculty of Engineering, Najran University, King Abdull Al-Aziz rood, Najran, Saudi Arabia, 11001*

## ABSTRACT

Soil contaminated by diesel isomers is associated with releases of petroleum products such as fuel-oil or gasoline, and human exposition to these compounds can have serious health consequences. Several geophysical methods have been developed which measure dielectric effects of contamination on physical properties of the soil. The potential of dielectric measuring techniques for soil characterization has not been fully explored. The objective of research reported here is to develop an empirical dielectric mixture model for soil hydrocarbon contamination applications. A parallel plate capacitor was developed for accurate measurement of soil dielectric properties. Twenty five samples were prepared with moisture content varied from 0% to 40% by weight. At each soil moisture content, 5 levels of diesel content were evaluated. The separate real and imaginary components of soil impedance measurements were investigated in the frequency range of 100 kHz to 1000 kHz. In saturated diesel contaminated soil and over a frequency range of 100 to 1000kHz, both dielectric constants and loss factors of soil samples decrease with increasing diesel content. This can be attributed to the decrease of conductivity of the soil when high conducting water is replaced by low conducting diesel. Unsaturated diesel contaminated soil exhibits different trends due to changes in conducting channels in the pore structures. Analyses indicate that the best extant model fit to experimental data is Silberstein (linear). All analytical models under-estimated the loss factor of contaminated soil. Since the power model is the most general, the best fit of the experimental measurement with the power function was obtained at  $\beta = 0.9$  for dielectric constant and 1.2 for loss factor. Based on these findings, a new dielectric model is proposed that considers the interactions between soil phases.

**Keywords:** petroleum, soil contamination, dielectric properties, mixture model

<sup>§</sup>Corresponding Author: Assoc. Prof. Dr. Hashem Al-Mattarneh, Head of Development and Quality Unit, Faculty of Engineering, Najran University, Najran, Saudi Arabia, 11001; +966-565212007; drhashem2010@yahoo.com

## **1. INTRODUCTION**

Determination of petroleum hydrocarbon contamination in soil using measurements of dielectric properties relies greatly on models relating the measured dielectric constant to the volume fractions of the pore fills and various soil phases including solids, water, air and contaminants. In recent years, numerous papers have appeared proposing models for the explanation and analysis of dielectric measurements on various types of soil that are based on physical principles. These models are based on various formulations of effective medium theories. The large number of available models suggests that theoretical problems in the understanding of dielectric phenomena remain.

Recently, research utilizing dielectric properties for the investigation of subsurface contamination has been reported (Kaya & Fang, 1997; Carrier & Soga, 1998; Darayan et al, 1998). However, the dielectric behavior of contaminated soil has not yet been fully established.

## **2. BASIC THEORY**

Materials which have the outermost electron shell of their atoms almost completely filled are called dielectric materials. Once the shells are completely filled, electrons are bound and it is relatively difficult to dislodge them. Dielectric materials have a few electrons available for conduction and are classified as insulators. These materials usually exhibit or can be made to exhibit a dipole structure, which is the separation of two point charges of equal magnitude and opposite sign by a small distance.

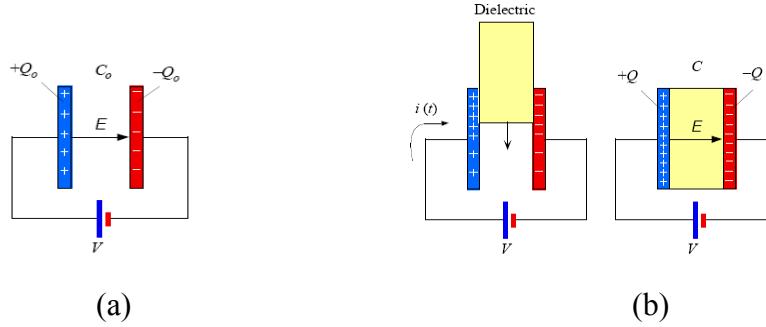
The ability of a dielectric material to store a charge can be explained using a parallel plate capacitor. When the space between the plates is a vacuum, the capacitance,  $C_0$ , which is the ratio of the charge on either plate to the potential difference between the plates, is directly proportional to the area of the plates,  $A$ , and inversely proportional to the distance between the plates,  $d$ . Therefore, the relationship can be given by:

$$C_0 = \epsilon_0 A / d \quad (1)$$

Where,  $\epsilon_0$  is the permittivity of a vacuum, and has a value of  $8.85 \times 10^{-12}$  F/m.

Figure 1a shows the charge between the plates when the space between them is a vacuum. When the space between the plates is filled with a dielectric material and an electric field applied, the dielectric material becomes polarized. While the interior of the dielectric material remains neutral, there is a concentration of

charges on the ends. This results in an increase in charges on the plates that is due to the polarization.



*Figure 1.* The charge between the plates when the space between (a) filled with vacuum (b) filled with the dielectric material.

Figure 1b shows the increased charge between the plates when the space between them is filled with the dielectric material. This increased capacitance is given by:

$$C = \epsilon_0 \epsilon_r A / d \quad (2)$$

From Equations 1 and 2, Dielectric constant of material is given by:

$$\epsilon_r = C / C_0 \quad (3)$$

Any dielectric material polarizes more than a vacuum. The permittivity of dielectric material  $\epsilon^*$  is greater than the permittivity of vacuum,  $\epsilon^* \epsilon_0$ . The permittivity of a material is usually expressed relative to that of a vacuum. The dielectric constant,  $\epsilon^* r$ , is a complex number where the real part represents the actual insulating behavior of the material and the imaginary part represents the lossy behavior of the material to an external electric field.

### 3. DIELECTRIC MIXTURE THEORY

A precise electromagnetic explanation for the structural complexity of natural materials is not possible with present knowledge. Two approaches are available for approximations, the analytical approach and the empirical approach.

Analytical mixing formulas idealize geometry and model the microstructure using simple forms, like spheres and ellipsoids. Dielectric mixing rules are algebraic formulas with which the effective permittivity of the mixture can be calculated as a function of the constituent permittivities, their fractional volume, and possibly other parameters characterizing the microstructure of the mixture (Sihvola, 2000).

The early history of dielectric mixing rules can be traced back to the mid-1800s. Famous names like Clausius, Mossotti, Maxwell, L.V. Lorenz, H.A. Lorentz, Rayleigh, and Garnett are affiliated with exposition of the dielectric properties of materials. During the last century, as experimental results on dielectric properties of materials began to accumulate, shape effects in the microstructure of the mixture on the theoretical models were given particular attention. Another direction of research was opened by the finding that different mixing rules predicted different results for the same mixture. This forced researchers to seek upper and lower bounds for the effective permittivity of a given mixture, and pioneering work by Hashin and Shtrikman (Hashin & Shtrikman, 1962) is the basic reference. For a review of developments throughout the century, see Landauer (Landauer, 1978) and Sihvola (Sihvola, 1999). The present-day research on mixing formulas focuses on mixtures of complex materials, for example bi-anisotropic and non-linear media.

### 3.1 Analytical Models

A special case of the family of mixing models (Equation 4) is the Lichtenecker's formula or mean geometrical model.

$$\ln \varepsilon_{soil} = \sum_{i=1}^n \phi_i \ln \varepsilon_i \quad (4)$$

A widely used class of mixing formulas is that of the power-law form

$$\varepsilon_{soil}^\beta = \sum_{i=1}^n \phi_i \varepsilon_i^\beta \quad (5)$$

Where a certain power of the bulk dielectric constant ( $\varepsilon_{soil}$ ) of the soil is averaged by volume weighting ( $\sum \phi_i = 1$ ) of the permittivity ( $\varepsilon_i$ ) of the soil components considered ( $n$ ). Most power law models take into account either three ( $n = 3$ : air, free water and solid particles) or four ( $n = 4$ : solid particles, air, free water and hydrocarbon) phases. The parameter in Equation (5), reflects the geometry of the media with respect to the applied electromagnetic field, with  $-1 < \alpha < +1$  (Roth et al, 1990; Roth et al, 1992).

Birchak formula, with  $\alpha = 0.5$  (Birchak et al, 1974) is given by Equation (6). This is also known as the “refractive index model” or (CRIM).

$$\sqrt{\varepsilon_{soil}} = \sum_{i=1}^n \phi_i \sqrt{\varepsilon_i} \quad (6)$$

Other mixing laws derivable from Equation (7) include the Looyenga formula (Looyenga, 1965) for which  $\beta = 1/3$ ,

$$\sqrt[3]{\varepsilon_{soil}} = \sum_{i=1}^n \phi_i \sqrt[3]{\varepsilon_i} \quad (7)$$

Other mixing laws derivable from Equation (8) include the linear law or Silberstein formula, which corresponds to  $\alpha = 1$ .

$$\varepsilon_{soil} = \sum_{i=1}^n \phi_i \varepsilon_i \quad (8)$$

The mixing rules that have been discussed so far are actually rather simple algebraic formulas that combine the component permittivity and some structural parameters of the mixture. A surprising range of real-life phenomena are predicted by these rules. The mixing process sometimes gives rise to qualitatively new effects such that the mixture displays properties that are absent in the component materials. These phenomena are especially prominent when materials are moist, in other words, when one of the components in the mixture is water. This is because of the strong dispersion in the permittivity of water on one hand, and the fact that water permittivity has very high values on the other.

### 3.2 Empirical Models

Empirical models are sometimes preferred by soil scientists because they are easy to use, accurate and can handle complex materials, such as soil, with no implicit assumptions (Topp et al, 1980; Wang & Schmugge, 1980; Tomer et al, 1999; Regalado et al, 2003). As possible disadvantages we may point to their limited predictive capability and that these may be only applicable to the specific data used to develop the model. Several empirical models were developed using statistical regressions to relate the soil properties of interest such as moisture content, porosity, hydrocarbon and salt content with soil dielectric properties. Several examples of these models are widely used in soil science applications. (Tomer et al, 1999) and (Regalado et al, 2003) proposed a logarithmic model for soil moisture content given in equation (9). The most widely used model for soil moisture content is proposed by (Topp et al, 1980) as shown in equation (10). Other model related dielectric of soil to soil porosity (Abidin, 2002) and specific gravity (Dobson et al, 1985). These models are given in equations (11) and (12) respectively.

$$M = a \ln \varepsilon_{soil} + b \quad (9)$$

$$M = -5.3 \times 10^{-2} + 2.92 \times 10^{-2} \varepsilon_{soil} - 5.5 \times 10^{-4} \varepsilon_{soil}^2 + 4.3 \times 10^{-6} \varepsilon_{soil}^3 \quad (10)$$

$$\phi = 0.0136 \varepsilon_{soil} + 0.02 \quad (11)$$

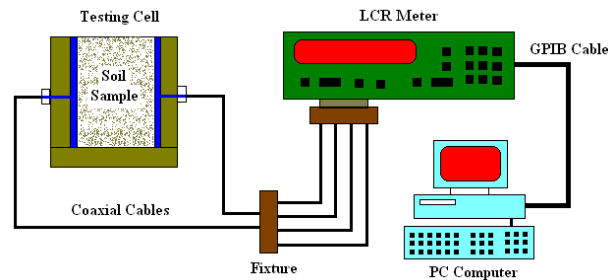
$$\varepsilon_s = (1.01 + 0.44 \rho_s)^2 - 0.062 \quad (12)$$

Demand for more reliable and practical dielectric models which can be used to predict various soil properties from the measured dielectric properties is ever increasing.

## 4. EXPERIMENTAL PROGRAM

### 4.1 Dielectric Measurement System

Figure 2 gives a schematic diagram of the dielectric measurement system used in this study. The system consists of a soil cell 80mm by 80 mm by 40 mm. Conductive metal plates were connected through coaxial cables to a fixture to connect the 2-port cell cables to the 4-port LCR-Meter. The LCR meter was used to excite the soil sample by AC signal and measured the impedance of the system. The LCR-Meter was connected via GPIB cable to a PC computer for data acquisition and measurement automation.



*Figure 2.* Schematic diagram of the dielectric measurement system.

### 4.2 Materials and Properties

Soil used for this study was white gray, quartz sand. Grain size distribution of the soil was determined by sieve analysis in accordance with ASTM Standard D 442. Results of this analysis are presented in Figure 3. The specific rules for classification are summarized and described in detail in ASTM D 2487. Based on the Unified Soil Classification System (USCS), the soil is classified as well-graded sand (SW).

### *Dielectric Measurements for Characterizing Sandy Soil*

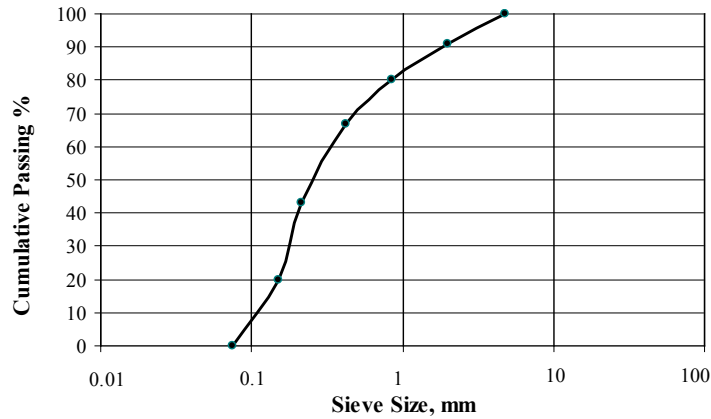


Figure 3. Grain size distribution of soil Material (Quartz sand).

The petroleum hydrocarbon used in this study was diesel supplied by ARAMCO. The density of the diesel was 0.865 g/m<sup>3</sup>. To provide diesel contamination levels of unsaturated soil for this study, 25 soil samples were prepared from dry sand. The weight of each sample was 500g. The sand samples were divided into 5 groups, each consisting of five samples. The first group was kept dry (moisture content 0%). Water was added to the other sets of sand samples, groups 2, 3, 4, and 5. The amount of water for sets 2, 3, 4, and 5 were 20g, 40g, 60g and 80g respectively to yield moisture contents of 4%, 8%, 12%, and 16% by weight of dry sand. The five samples in each set were contaminated by diesel amendments at 0%, 2%, 4%, 6% and 8% by weight of dry sand. The amounts of diesel were 0g, 10g, 20g, 30g and 40g. The soil samples were shaken for 15 min then kept for three hours in sealed plastic containers to avoid evaporation. The aim of this operation is to insure a uniform diesel and moisture distribution within the sample for consistent diesel and water adsorption by the soil grains. The soils were placed in 80×80 mm and 40 mm thick test cells. Three impedance measurements were obtained at each frequency and the average value was determined. The suite of diesel contaminated soil samples supports a 5 full factorial analysis as presented in Figure 4.

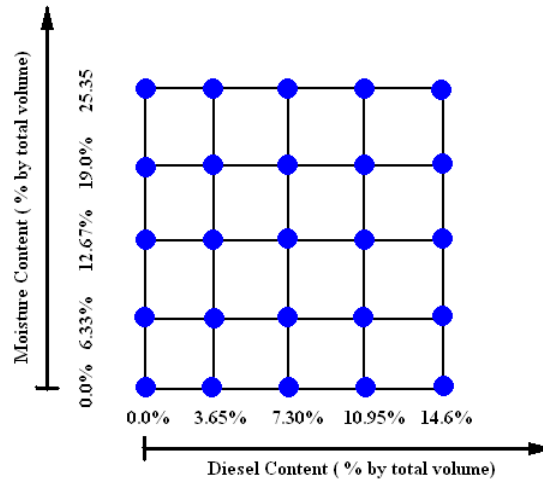


Figure 4. Combination of moisture and diesel content using 5-level 2-factorial design.

## 5. RESULTS AND DISCUSSION

### 5.1 Experimental Results

Variations of dielectric constant and loss factor of unsaturated contaminated soil with different diesel contents are shown in Figures 5 and 6. In general, the dielectric constant (real part of permittivity) increased with increasing diesel content while the loss factor (imaginary part of permittivity) showed three different trends similar to the trends observed for resistivity. The loss factor of unsaturated soil contaminated with diesel depends on the relative resistivity of water and hydrocarbons and the relative volume fraction of the three phases in the pore structure of the soil (water, diesel and air). To draw a clear picture about the effect of diesel content on the loss factor of unsaturated soil, unsaturated soils were categorized as low, medium and high moisture content.

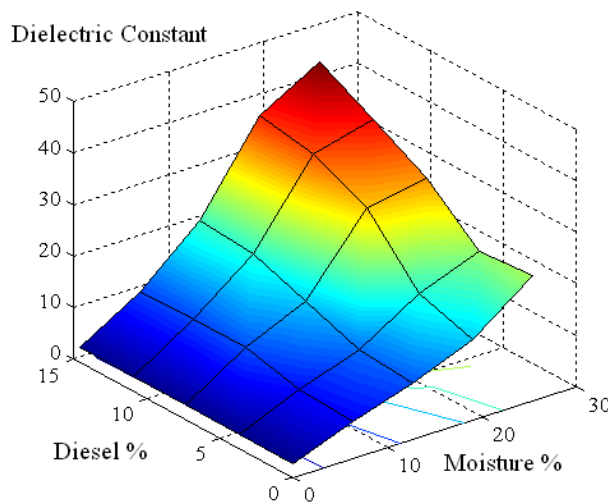
The loss factor of low moisture contaminated soil increased with increasing diesel content up to certain level, then the trend changed and decreases in the loss factor were recorded at high diesel content. The loss factor of medium moisture contaminated soils shows an increase with increasing diesel content. The resistance of high moisture contaminated soil increased with low diesel content, then decreased with further increases in diesel content. These results indicate that the electromagnetic properties of soil are dependent on the interaction of the various phases (water, diesel and air) in the voids of unsaturated soil. In addition, electromagnetic properties depend on the structure of conducting channels in the pore spaces of soil.



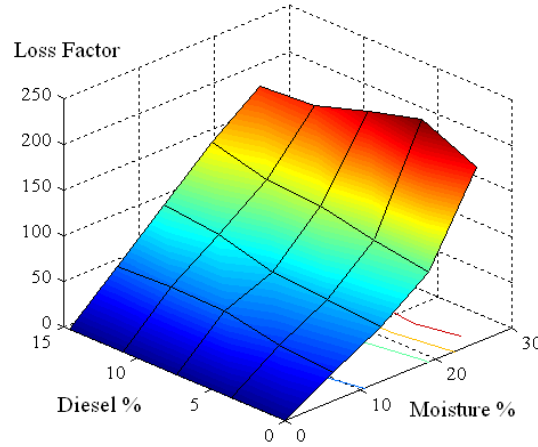
At low moisture content, unsaturated soil tends to form a few conducting channels through the pore structure, and other channels terminate in air voids. Adding diesel liquid to such soils fills some of the air voids, and some of the diesel displaces water and the displaced water forms additional conducting channels. Additional increases of diesel limit the space of air voids and interrupt existing conducting channels of the water phase, increasing overall resistivity of the soil column.

Adding diesel to unsaturated contaminated soils having medium moisture content helps to form more conducting channels by displacing water that then links otherwise unconnected channels in the pore structures. This phenomenon explains the continuous decrease of resistivity of soil with increasing diesel content as a result of increasing the overall conductivity of the soil column..

Unsaturated contaminated soils of high moisture content tend to have abundant conducting water channels and few air voids. Adding small amounts of diesel increases conducting channels by displacing water that then completes the few available non-conducting water channels. Increasing the diesel content further, cuts water conducting channels in the soil which increases resistivity, making the behavior similar to that in saturated soil.



*Figure 5.* Dielectric constant of contaminated soil at various levels of moisture and diesel.



*Figure 6.* Loss factors of contaminated soil at various levels of moisture and diesel.

## 5.2 Results of Analytical Models

To investigate the dielectric properties of hydrocarbon-contamination, soils were modeled using four phases (solid, water, diesel and air). The five models discussed in the previous sections can be written as:

$$\varepsilon_{Soil}^* = \phi_S \varepsilon_S^* + \phi_W \varepsilon_W^* + \phi_D \varepsilon_D^* + \phi_A \varepsilon_A^* \quad (13)$$

$$\sqrt{\varepsilon_{Soil}^*} = \phi_S \sqrt{\varepsilon_S^*} + \phi_W \sqrt{\varepsilon_W^*} + \phi_D \sqrt{\varepsilon_D^*} + \phi_A \sqrt{\varepsilon_A^*} \quad (14)$$

$$(\varepsilon_{Soil}^*)^{1/3} = \phi_S (\varepsilon_S^*)^{1/3} + \phi_W (\varepsilon_W^*)^{1/3} + \phi_D (\varepsilon_D^*)^{1/3} + \phi_A (\varepsilon_A^*)^{1/3} \quad (15)$$

$$\varepsilon_{Soil}^* = \phi_S \ln(\varepsilon_S^*) + \phi_W \ln(\varepsilon_W^*) + \phi_D \ln(\varepsilon_D^*) + \phi_A \ln(\varepsilon_A^*) \quad (16)$$

$$(\varepsilon_{Soil}^*)^\beta = \phi_S (\varepsilon_S^*)^\beta + \phi_W (\varepsilon_W^*)^\beta + \phi_D (\varepsilon_D^*)^\beta + \phi_A (\varepsilon_A^*)^\beta \quad (17)$$

The calculated dielectric constants and loss factors using the analytical models versus experimental values for soil contaminated with diesel are shown in Figures 7 and 8.

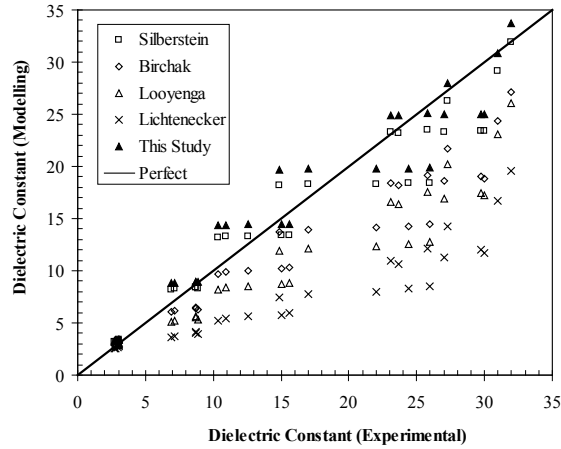


Figure 7. Various mixture models for dielectric constant of diesel contaminated sand with four phases.

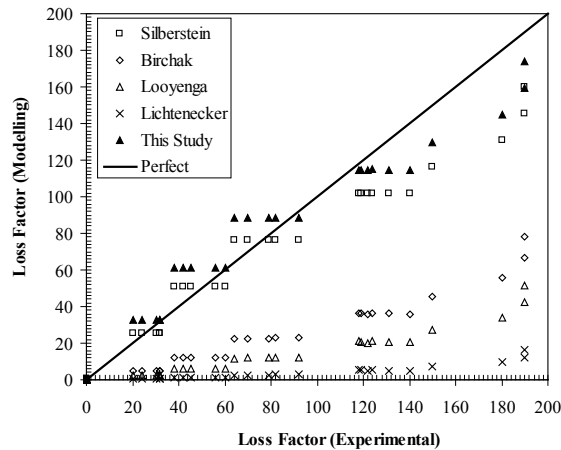


Figure 8. Various mixture models for loss factor of diesel contaminated sand with four phases.

## 6. CONCLUSION

Diesel has no substantive effect on the electromagnetic properties of dry soil, as expected given the nonconductive character of diesel. It is clear from the results of diesel contamination of saturated soils that both dielectric constant and loss factors are decreased with increasing diesel content. The dielectric constant shows a linear decrease with increasing diesel content while the loss factor shows a high rate of decrease with increasing diesel content. This can be attributed to the

decrease of conductivity of the soil when the high conducting water is replaced by low conducting diesel hydrocarbons.

Analytical models of dielectric properties of soil indicate that the best model fit to experimental data is Silberstein (linear). All analytical models under-estimate the loss factor of contaminated soil. Since the power model is the most general model, the best fit of experimental measurements to the power function were obtained at  $\beta = 0.9$  for dielectric constant and 1.2 for loss factor.

## **7. ACKNOWLEDGEMENTS**

This work was supported by grant “No. NU064/12 Petroleum Soil Contamination” from Deanship of Scientific Research, Najran University, Kingdom of Saudi Arabia. The authors would like to acknowledge staff members in the faculty of engineering for help and providing access to the testing facilities.

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# DIELECTRIC SPECTRA AND MODELING FOR DETERMINING SOIL MOISTURE CONTENT

Hashem Al-Mattarneh<sup>§</sup>, Abdullah Alwadie, Mohamad Dahim, Rabah Ismail and Ahmad Malkawi

*Faculty of Engineering, Najran University, King Abdull Al-Aziz rood, Najran, Saudi Arabia, 11001*

## ABSTRACT

Knowledge of soil moisture is necessary for agriculture, geology and civil engineering. Ground-based estimation of surface soil moisture over large areas is important for understanding hydrology, including climate and land surface modeling. The most accurate method of estimation is gravimetric sampling, but this is a time intensive procedure. A parallel plate capacitor was developed for accurate measurement of soil impedance at various moisture contents ranging from 0% to 40% by weight. The separate real and imaginary parts of soil dielectric were investigated in the frequency range of 100 kHz to 1000 kHz. Moist soils exhibit different complex dielectric spectra from dry soils. Increases of the imaginary part of the dielectric constant with volumetric water content can be explained by the increase of conduction loss caused by the increase of continuous current path in soil samples. In addition, both real and imaginary part of dielectric constant of soil sharply decrease with frequencies at higher volumetric water content. The result shows that decreases in dielectric constant with frequency depend on volumetric water content. The result of dielectric constant analytical models of dielectric properties of soil indicate that the best model fit to experimental data was Birchak for low moisture content while for high moisture content the best analytical model was Silberstein (linear). All analytical models under-estimate the loss factor of soil moisture. The power model is most generally applicable, and the best fits of experimental measurements were obtained with the power function.

**Keywords:** moisture, soil contamination, dielectric properties, mixture model

<sup>§</sup>Corresponding Author: Assoc. Prof. Dr. Hashem Al-Mattarneh, Head of Development and Quality Unit, Faculty of Engineering, Najran University, Najran, Saudi Arabia, 11001; +966-565212007; drhashem2010@yahoo.com

## 1. INTRODUCTION

Requirements for fast, reliable and automated spatially distributed soil water content monitoring are not fully satisfied by current commercially available technology measurements. Scientists and engineers are conducting research and building prototypes to develop new soil water sensors. Physical models are being revised to increase measurement selectivity, accuracy, ease of operation and availability, and to make them economically accessible for mass applications. Nondestructive and in situ measurements of soil water content are fundamental in agricultural applications including hydrology, precision watering and irrigation scheduling (Robinson et al. 2003; Walker et al. 2004 and Jones et al. 2005).

Dielectric soil moisture sensors determine soil moisture by measuring the dielectric constant, an electrical property that is highly dependent on moisture content. The dielectric constant ( $\epsilon'$ ) for dry soil is between 3 and 5; it is about 1 for air; and about 80 for water. Changes in moisture content cause a substantial change in the dielectric constant of soil. Soil moisture has two components, free and bound water, where bound water refers to the first few molecular water layers near solid surfaces that are rotationally hindered by surface forces (Bockris et al. 1966). The dielectric permittivity of bound water is typically in the range of 6–30 for the first and second molecular layers, respectively, and is temperature dependent (Bockris et al. 1966; Dobson et al. 1985; Jones & Or 2002; Or & Wraith 1999; Serbin 2001; Serbin & Or 2003, 2004).

Several models are available for relating measured bulk dielectric permittivity to water content, including the relationships of Topp et al. (1980) for mineral soils, and those of Schaap et al. (1997) and da Silva et al. (1998) for organic soils.

Topp et al. (1980) found that the real part of the dielectric constant ( $\epsilon_{soil}$ ) seems to be highly sensitive to volumetric water content, but only weakly sensitive to soil type and density. They used a wide range of soil samples to derive an empirical relationship between the apparent (measured) dielectric constant and volumetric water content:

$$M = -5.3 \times 10^{-2} + 2.92 \times 10^{-2} \epsilon_{soil} - 5.5 \times 10^{-4} \epsilon_{soil}^2 + 4.3 \times 10^{-6} \epsilon_{soil}^3 \quad (1)$$

## 2. DIELECTRIC THEORY

Materials which have the outermost electron shell of their atoms almost completely filled are called dielectric materials. Since the shells are completely filled, the electrons are bound and it is relatively difficult to dislodge them. Therefore dielectric materials have few electrons available for conduction and are

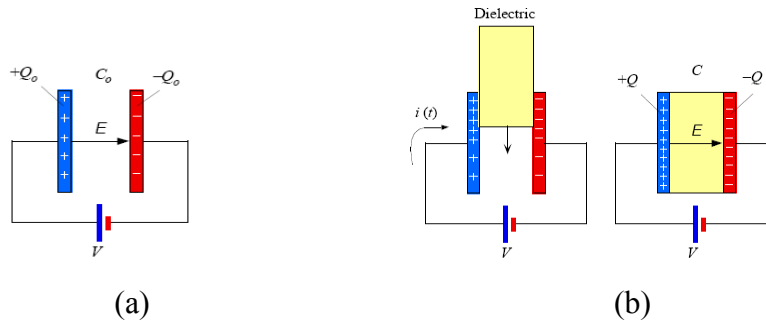
classified as insulators. These materials usually exhibit or can be made to exhibit a dipole structure, which is the separation of two point charges of equal magnitude and opposite sign by a small distance.

The ability of a dielectric material to store a charge can be explained using a parallel plate capacitor. When the space between the plates is a vacuum, the capacitance,  $C_o$ , which is the ratio of the charge on either plate to the potential difference between the plates, is directly proportional to the area of the plates,  $A$ , and inversely proportional to the distance between the plates,  $d$ . Therefore, the relationship can be given by:

$$C_o = \frac{\epsilon_o A}{d} \quad (2)$$

Where,  $\epsilon_o$  is the permittivity of vacuum, and has a value of  $8.85 \times 10^{-12}$  F/m.

Figure 1a shows the charge between the plates when the space between them is a vacuum. When the space between the plates is filled up with a dielectric material and an electric field applied, the dielectric material becomes polarized. While the interior of the dielectric material remains neutral, there is concentration of charges on the ends. This results in an increase in charges on the plates that is due to the polarization.



*Figure 1.* The charge between the plates when the space between (a) filled with vacuum (b) filled with the dielectric material.

Figure 1b shows the increased charge between the plates when the space between them is filled with the dielectric material. This increased capacitance is given by:

$$C = \frac{\epsilon_o \epsilon_r A}{d} \quad (3)$$

From Equations 2 and 3, Dielectric constant of material is given by:



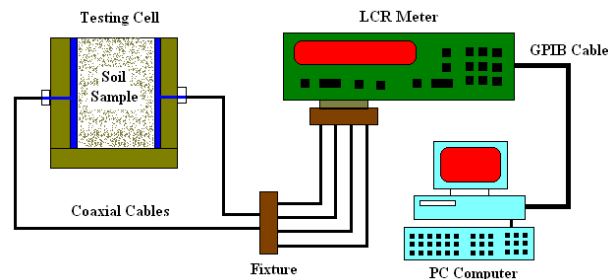
$$\epsilon_r = \frac{C}{C_o} \quad (4)$$

Any dielectric material can polarize more than a vacuum. Hence, the permittivity of the dielectric material  $\epsilon^*$  is greater than the permittivity of vacuum,  $\epsilon^*_o$ . The dielectric constant,  $\epsilon^*_r$ , is a complex number where the real part represents the actual insulating behavior of the material and the imaginary part represents the amount of electromagnetic energy loss by soil material as conducting current from an external electric field.

### 3. EXPERIMENTAL PROGRAM

#### 3.1 Dielectric Measurement System

Figure 2 gives a schematic diagram of the dielectric measurement system used in this study. The system consists of a soil cell 80 mm by 80 mm by 40 mm. The conductive metal plates are connected via coaxial cables to a fixture connecting the 2-port cell cables to the 4-port LCR-Meter. The LCR meter is used to excite the soil sample by AC signal and measure the impedance of the system. The LCR-Meter is connected via GPIB cable to a computer for data acquisition and automation of the measurements.



*Figure 2.* Schematic diagram of the dielectric measurement system.

#### 3.2 Materials and Properties

The soil used for this study is a white gray quartz sand. Grain size distribution was determined by sieve analysis in accordance with ASTM Standard D 442. The results of this analysis are presented in Figure 3. The specific rules for classification are summarized and described in detail in ASTM D 2487. Based on the Unified Soil Classification System (USCS), the soil is classified as well-graded sand (SW).

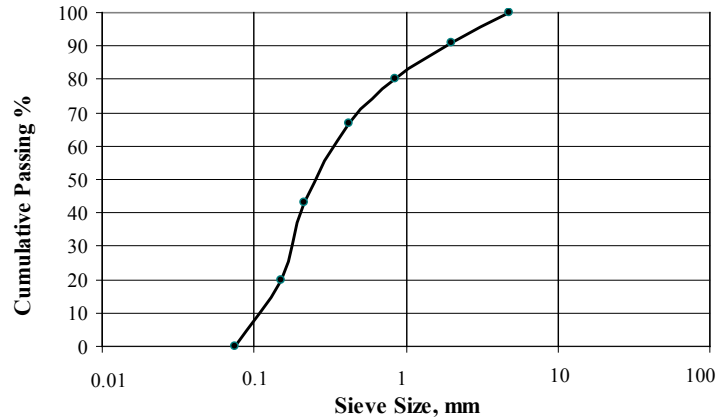


Figure 3. Grain size distribution of soil material (Quartz sand).

## 4. RESULTS AND DISCUSSION

### 4.1 Experimental Results

Dielectric properties (dielectric constant and loss factor) were deduced from the measured impedances of sandy soil using Equation 9. The relationship between dielectric properties and frequency of sand soil at various moisture contents is shown in Figure 4. To better visualize the relationship between dielectric properties of soil and soil moisture content, 28 samples were prepared with moisture content ranging between 0% by volume (dry sample) and 40% by volume (saturated sample). Relationship between the measured dielectric constant loss factors and frequency are shown in Figure 5.

Dielectric constant and loss factor of moist samples decrease with increasing frequency. The rate of decrease in the dielectric properties of sand is high at low frequency (less than 300 kHz). The rate slows and becomes almost constant at high frequency. Loss factor has a higher rate of change with frequency. This can be attributed to higher conductivity. Sand samples of high moisture content have a greater decrease of dielectric properties (specially the loss factor). This is due to the high conductance and low resistivity of water relative to solid particulates and air space voids.

*Dielectric Spectra and Modeling for Determining Soil Moisture Content*

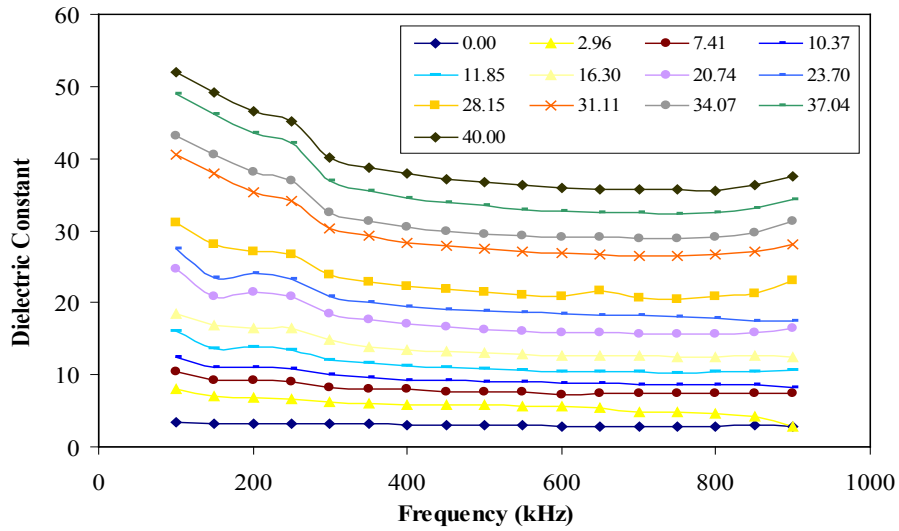


Figure 4. Relations between soil dielectric constant and frequency at different moisture content.

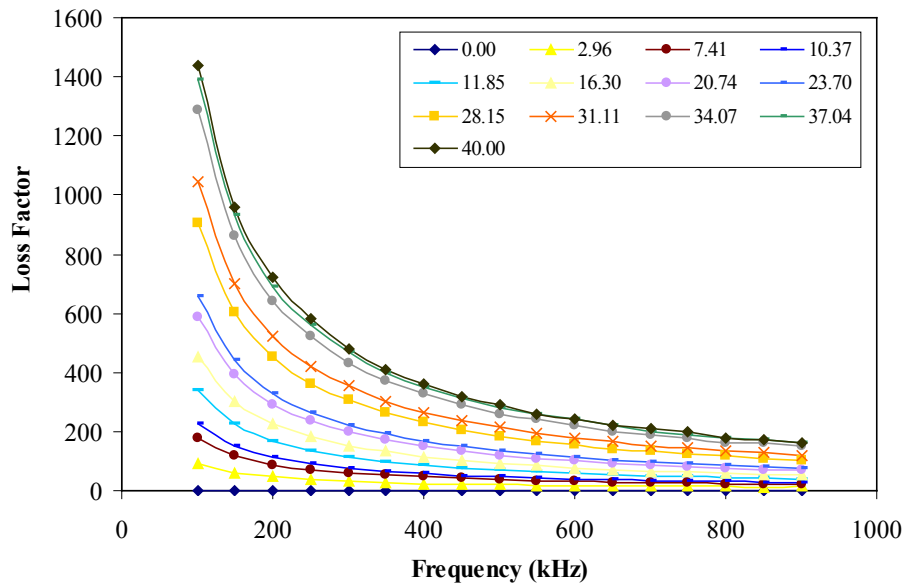


Figure 5. Relations between soil loss factor and frequency at different moisture contents.

Relationships between dielectric constant, loss factor and soil moisture content are shown in Figures 6 and 7 respectively. Both dielectric constant and loss factor increase with increasing moisture content. This result clearly shows that dielectric

properties can be used to determine the moisture content of soil. Since the dielectric constant of water is 80 and the loss factor ranges from 200 to about 600 while the dielectric constant of solid phase and air are 4.66 and 1 respectively, and their loss factors are 0.5 and 0, therefore, increasing the amount of water in soil sample will significantly increase its dielectric properties.

The real part of the dielectric constant of soil increases with its volumetric water content because the real part of the dielectric constant of water—80-- is larger than that of soil particulates or air. Increases of the imaginary part of the dielectric constant with volumetric water content can be explained by the increase of the conduction loss caused by the increase of continuous current path in a soil sample. In addition, both real and imaginary parts of the dielectric constant of soil sharply decrease with frequencies at higher volumetric water content. This result is in agreement with other research. The result shows that the decreases in dielectric constant with frequency depend on volumetric water content.

The real and imaginary part of soil dielectric constants had a tendency to decrease with frequency, a phenomenon known as dispersion, which is similar to the reported dielectric behaviors in the literature (Ju et al. 2003). When an external electric field is applied to a soil sample, water molecules (permanent electric dipole) in the soil sample realign in the direction of the electric field and cause the orientation polarization. The water molecules, which possess an electric dipole moment, tend to orient themselves in a strong electric field so that the positive poles face the negative electrode and the negative poles face the positive electrode. Also, the negative electron cloud around the oxygen nucleus is deformed or polarized in an electric field. Thus, an induced dipole is formed and adds its moment to that of the permanent dipole. But, as the frequency increases, the dielectric constant decreases because the polarized dipoles do not have enough time to realign and only a small number of water molecules can cause orientation polarization. If the frequency reaches a certain value and the period of electric field gets shorter than the smallest time that the dipoles can rearrange, the dielectric constant of soil is not affected by this polarization (Kaya & Fang 1997).

*Dielectric Spectra and Modeling for Determining Soil Moisture Content*

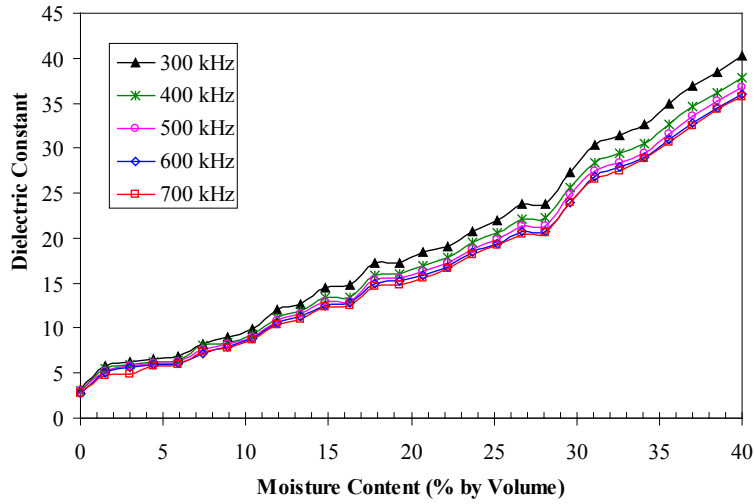


Figure 6. Relations Between Soil Dielectric Constant and Moisture Content at different frequency.

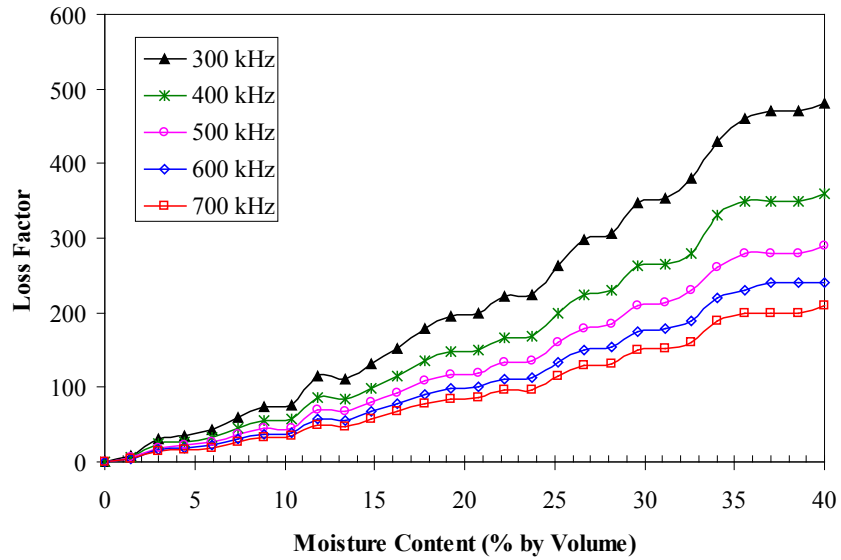


Figure 7. Relations between soil loss factor and moisture content at different frequency.

Dielectric properties of moist soil can be expressed by modeling the soil mixture as three phases (soil, air and water). The dielectric property of the soil mixture is a function of the dielectric properties of the soil phases and the volume fraction of each phase.

## 4.2 Dielectric Models

Analytical models developed for soil material were investigated. These models include Silberstein, Birchak, Looyenga and Lichtenecker. These models are used to determine the dielectric constant and loss factor of soil based on the volume fraction of the components of the soil material and the dielectric properties of each phase (component). The formulas of these models are given in Equations 5, 6, 7 and 8. As can be seen from these equations, the power model given in Equation 9 is the general formula of all these models.

Silberstein model

$$\epsilon_{Soil}^* = V_s \epsilon_{Solid}^* + V_w \epsilon_{Water}^* + V_A \epsilon_{Air}^* \quad (5)$$

Birchak model:

$$\sqrt{\epsilon_{Soil}^*} = V_s \sqrt{\epsilon_{Solid}^*} + V_w \sqrt{\epsilon_{Water}^*} + V_A \sqrt{\epsilon_{Air}^*} \quad (6)$$

Looyenga model:

$$(\epsilon_{Soil}^*)^{1/3} = V_s (\epsilon_{Solid}^*)^{1/3} + V_w (\epsilon_{Water}^*)^{1/3} + V_A (\epsilon_{Air}^*)^{1/3} \quad (7)$$

Lichtenecker model:

$$\epsilon_{Soil}^* = V_s \ln(\epsilon_{Solid}^*) + V_w \ln(\epsilon_{Water}^*) + V_A \ln(\epsilon_{Air}^*) \quad (8)$$

The general power model

$$(\epsilon_{Soil}^*)^\beta = V_s (\epsilon_{Solid}^*)^\beta + V_w (\epsilon_{Water}^*)^\beta + V_A (\epsilon_{Air}^*)^\beta \quad (9)$$

The result of the calculated dielectric constant and loss factor of clean soil at various moisture contents using these analytical models are presented and compared with the measured valued from this study (see Figure 8 and Figure 9). Analytical models of dielectric properties of soil indicate that the best model fit to the experimental data was Birchak for low moisture content and Silberstein (linear) for high moisture content. All analytical models under-estimated the loss factor of moist soil. Since the power model is the general model, the best fit of the experimental measurement with the power function were obtained at  $\beta = 0.9$  for dielectric constant and 1.2 for loss factor.

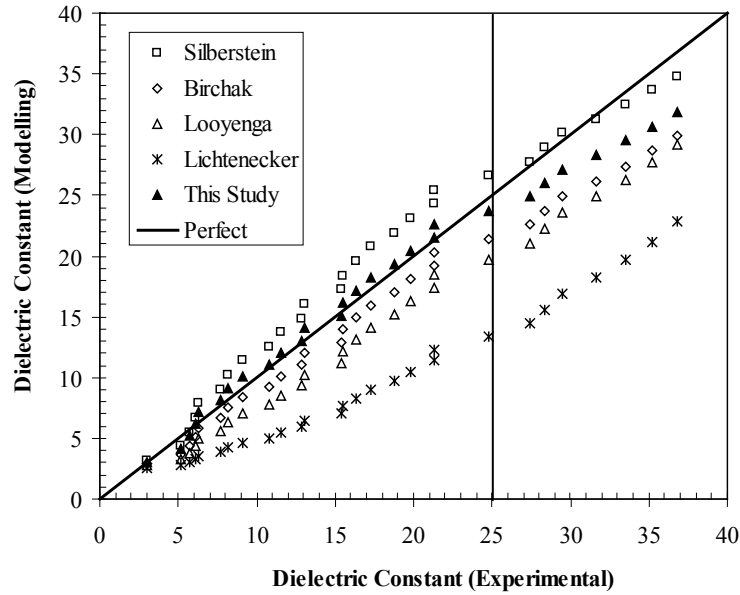


Figure 8. Various mixture models for dielectric constant of sand with three phases.

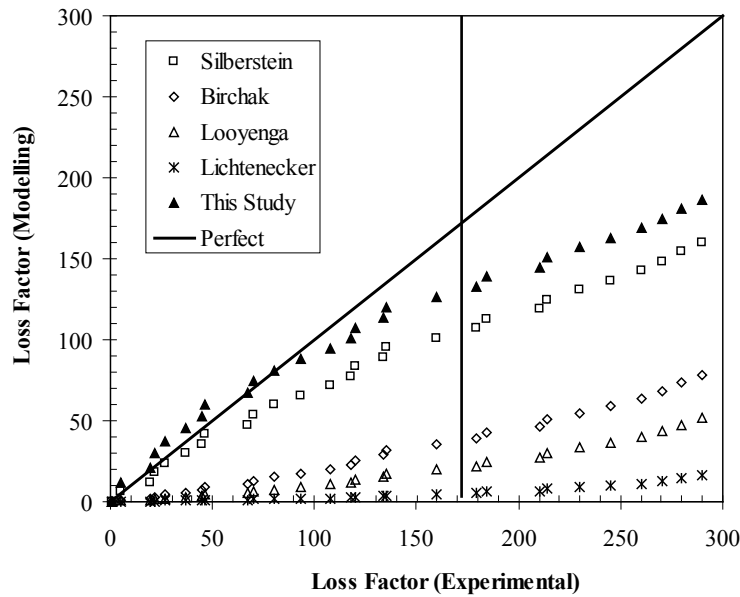


Figure 9. Various mixture models for loss factor of sand with three phases.

Several statistical models were investigated using multi-linear and multi-nonlinear regression analysis using MATLAB. A MATLAB program was prepared to develop the regression models and to evaluate these models. The formulas of the

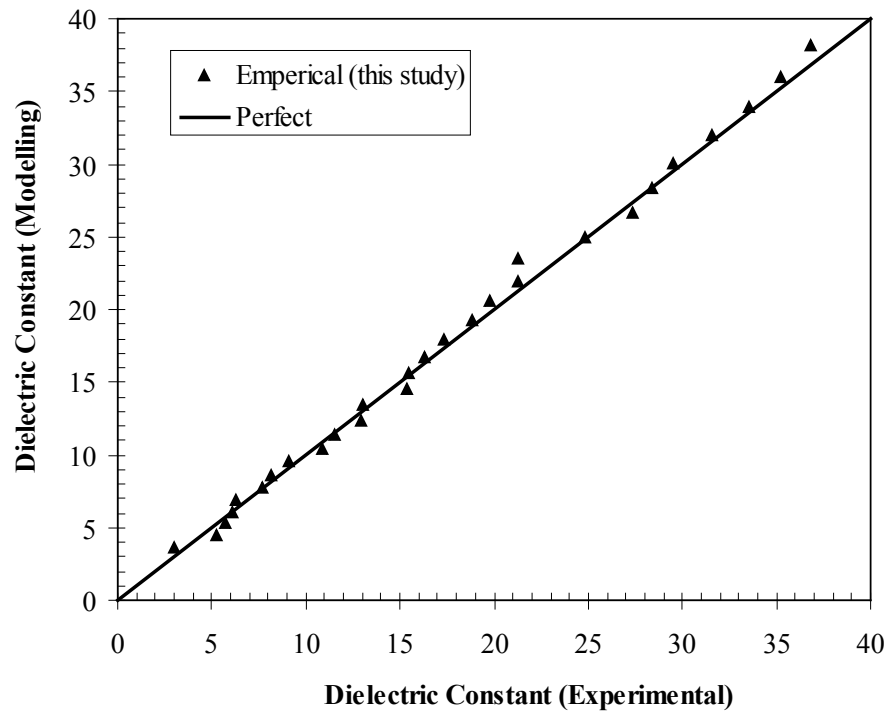
models are shown in Equations 10 and 11. Model coefficients and statistical analysis of the best model are shown in Tables 1. This model is similar to the model proposed by (Topp et al 1980). This model shows the highest correlation coefficient ( $R^2 = 0.996$ ) and lowest mean square error. In addition the residual value of this model was very small and lowest among several other models investigated. Figure 10 shows the quality fit of the proposed empirical model with the experimental results of moisture content.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_1^2 + \beta_3 X_1^3 \quad (10)$$

$$Y = 3.77 + 54.3X_1 - 6.4X_1^2 + 197X_1^3 \quad (11)$$

*Table 1.* Empirical models for dielectric constant of moist soil.

<b>Corr. Coef. (<math>R^2</math>)</b>	<b><math>R^2</math> (Adjusted)</b>	<b>(MSE)</b>	<b>F-Value</b>	<b>P (significance)</b>
99.6%	99.6%	8.200	146.081	0.000



*Figure 10.* Quality fit of the proposed empirical model with the experimental results of moisture content.



## **5. CONCLUSION**

The real part of dielectric constant of soil increases with volumetric water content. Increases of the imaginary part of the dielectric constant with volumetric water content can be explained by the increase of the conduction loss caused by the increase of continuous current path in soil sample. In addition, both real and imaginary parts of the dielectric constant of soil sharply decrease with frequencies at higher volumetric water content. This result is in agreement with other research.

The real and imaginary parts of soil dielectric constants have a tendency to decrease with frequency, which is again similar to reported dielectric behaviors in the literature. When an external electric field is applied to a soil sample, water molecules (permanent electric dipole) in the soil sample realign in the direction of electric field and cause the orientation polarization.

Several analytical mixture models and empirical data for dielectric properties of soil material were evaluated and developed. The following conclusions regarding dielectric mixture models can be made:

The best model fit to experimental data was Birchak for low moisture content and Silberstein (linear) for high moisture content. All analytical under-estimate the loss factor of moist soil. Since the power model is the general model, the best fit of the experimental measurement with the power function was obtained at  $\beta = 0.9$  for dielectric constant and 1.2 for loss factor.

Empirical dielectric models have the capability to estimate the dielectric properties of hydrocarbon-contaminated soil. Among several empirical models developed in this study, the interaction model shows the highest accuracy for determining the dielectric properties of moist soil.

## **6. ACKNOWLEDGEMENTS**

This work was supported by grant “No. NU502/13 Water Quality” from Deanship of Scientific Research, Najran University, Kingdom of Saudi Arabia. The authors would like to acknowledge the staff members in the faculty of engineering for help and providing access to the testing facilities.

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# PERFLUORINATED COMPOUNDS: POTENTIALLY APPLICABLE SOIL SCREENING LEVELS FOR THE CONTAMINANT DU JOUR

Christopher M. Teaf<sup>1</sup> and Douglas J. Covert<sup>2§</sup>

<sup>1</sup>Center for Biomedical & Toxicological Research, Florida State University, 2035 E. Dirac Dr., Tallahassee, FL, 32310; <sup>2</sup>Hazardous Substance & Waste Management Research, Inc., 2976 Wellington Circle West, Tallahassee, FL, 32309

## ABSTRACT

Over the past decade, manufacturer phaseouts, increased regulation, and improved water treatment practices have dramatically reduced reported human body burdens of perfluorinated compounds (PFCs) in the US. In particular, serum perfluorooctane sulfonic acid (PFOS) levels have seen a reduction of nearly 70% between the 1999-2000 and the 2009-2010 NHANES monitoring. Focused, state-specific monitoring programs at sites with perfluorinated compounds have seen even more impressive results. Regarding human health effects from reported blood levels of PFCs, the number of statements concluding no effects or insufficient information to suggest adverse effects far outweigh the sporadic, poorly supported reports of adverse health effects in humans. USEPA has provided provisional health advisories for drinking water exposure, and in 2009, Tier 3 toxicity guidance was proposed, including preliminary soil screening levels for residential exposure. Nonetheless, based on their ubiquitous detection in environmental media, animal tissues and human samples, PFCs are rapidly becoming the latest in the line of substances for which presence of detectable levels in the environment and/or bodily tissues is automatically assumed to indicate toxicological concern. We discuss reported soil levels from representative contamination sites and background locations, and also present the current state of the science on PFC toxicity, including evaluation of the USEPA provisional health advisories and toxicity values. Finally, we present potentially applicable risk-based concentrations for soil under commonly employed exposure scenarios.

**Keywords:** perfluorinated compounds, perfluorochemicals, PFCs, PFOS, PFOA, health risk, exposure, assessment, soil screening

<sup>§</sup>Corresponding Author: Douglas J. Covert, 2976 Wellington Circle West, Tallahassee, FL, USA, 32309; (850) 681-6894; dcovert@hswmr.com

## 1. INTRODUCTION

Perfluorinated compounds (PFCs; or perfluoroalkyls) are manmade, fully fluorinated compounds that are not found naturally in the environment. These compounds are used, or historically were used, in such products as fire fighting foams, non-stick coatings, stain blockers, and cleaning products. There are many PFCs, but the most industrially significant members of the PFCs, and thus the compounds with the most information toxicologically, are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). Since the early 2000s, PFC manufacturers have been working with EPA to phase out the use of several PFCs (ATSDR, 2009; U.S. EPA, 2012). 3M discontinued the production of PFOS and related chemicals in 2002, and, through the U.S. EPA PFOA Stewardship Program, DuPont and several other manufacturers committed to achieve by 2010 (and were largely successful; U.S. EPA, 2012), 95% reductions of plant emissions and product content of PFOA and PFOA precursors from 2000 baselines. Further Program goals are to achieve 100% reductions by the year 2015.

In 2003, the Environmental Working Group (EWG, 2003) stated that “As more studies pour in, PFCs seem destined to supplant DDT, PCBs, dioxin and other chemicals as the most notorious, global chemical contaminants ever produced.” Since a few years before that statement was made, and corresponding with manufacturer phaseouts, increased regulation, and improved water treatment practices, serum PFC levels in the U.S. population for PFOA and PFOS have decreased by 41% and 69%, respectively (CDC, 2009b; CDC, 2013; see *Table 1*, below). This is certainly a welcome trend, but continued close attention to the existence or extent of potential health and environmental impacts is warranted.

*Table 1.* From CDC, 2013. Geometric mean serum levels for U.S. population.

Survey years (NHANES data)	Serum PFOA (ug/L)	Serum PFOS (ug/L)	Sample Size
99-00	5.21	30.4	1,562
03-04	3.95	20.7	2,094
05-06	3.92	17.1	2,120
07-08	4.12	13.2	2,100
09-10	3.07	9.32	2,233

Because most human exposures are expected to occur via contaminated food and drinking water (ATSDR, 2009), the scientific literature predominantly addresses those routes of exposure. In this summary paper, we provide relevant environmental data and exposure recommendations for soil-borne PFCs, primarily PFOA and PFOS.

## **2. ENVIRONMENTAL SOIL LEVELS**

Although some information on soil concentrations of PFCs is available from at least one NPL site, the best long-term evaluation of PFCs in soil is from a study of agricultural land in Alabama on which biosolids containing PFCs from a wastewater treatment plant were applied for many years (Sepulvado et al., 2011).

Two long-term control plots, on which no biosolids were applied, were monitored during the Sepulvado study. Concentrations for all PFCs except PFOS were below 1 ug/kg. PFOS in soil on the two control plots was reported to be  $22 \pm 2$  ug/kg and  $96 \pm 4$  ug/kg. The study authors suspect that the results are skewed due to cross-contamination from nearby plots that received PFC-impacted biosolids (Sepulvado et al., 2011).

The plots on which PFC-impacted biosolids were applied reported PFC concentrations ranging from <10 ug/kg to 70 ug/kg for PFOA, and from 90 ug/kg to 225 ug/kg for PFOS (Sepulvado et al., 2011).

## **3. TOXICITY BRIEFS AND EXPOSURE GUIDELINES**

### **3.1 Perfluorooctanoic Acid**

Perfluorooctanoic acid (PFOA; perfluorooctanoate; C-8) is a fully substituted, long chain fluorinated compound that does not occur naturally in the environment. For many years, PFOA was used in the manufacture of fluoropolymer coatings for products requiring resistance to heat, oil, grease and water. Since 2002, most manufacturers have used a new process that does not utilize PFOA (CDC, 2009a; DuPont, 2011; 3M, 2012). Due in large part to its hydrophobic (water resistant) and oleophobic (oil resistant) properties, PFOA does not readily degrade on its own, and detectable environmental levels of PFOA are ubiquitous on a global scale. Human serum levels have decreased dramatically since the discontinuation of PFOA use in manufacturing processes (Calafat et al., 2007; Kato et al., 2011; CDC, 2013), principally due to decreased exposure and normal metabolic processes. Reported aqueous solubilities for PFOA in the range of 3,400 mg/L to 9,500 mg/L are questioned by some as being microdispersion of micelles, rather than true solubility (EFSA, 2008). This has may have notable implications in drinking water exposure studies.

Some animal studies with PFOA have reported significant developmental and other adverse effects at high exposure levels. Limited human health studies have demonstrated varying and mostly inconclusive correlations (ATSDR, 2009; U.S. EPA, 2005; CDC, 2009b). Toxicokinetic differences across species, genders and individuals in both animal and human studies appear to be substantive. . Additional studies are needed and are ongoing to better understand the broad presence of PFCs (including PFOA) in the environment (ATSDR, 2009; U.S. EPA, 2013).

Under conditions of sufficient exposure to PFOA, developmental, liver, and other adverse health effects have been reported in mice, rats and monkeys (HSDB, 2013; ATSDR, 2009; U.S. EPA, 2005; Lau et al., 2006; CDC, 2009a; CDC, 2009b).

The size and relative weight of the liver increased in male mice treated with PFOA in drinking water for 21 days. Dose-dependent hepatic damage also was observed at the higher doses. Similar results were not induced in kidneys of the test animals (Son et al., 2008).

In a 26-week oral dosing study with *Cynomolgus* monkeys, the lowest dose tested (3 mg/kg•day) resulted in a 36% increase in absolute liver weight, and dose-dependent increases were observed in all dosage groups (Butenhoff et al., 2002).

Lau et al. (2006) reported maternal and developmental toxicity of PFOA in a mouse study with doses of 1, 3, 5, 10, 20 and 40 mg/kg. Maternal enlarged livers were reported at all dosages, postnatal survival was compromised at the higher dosages (10 and 20 mg/kg; 40 mg/kg dosed animals were not in the postnatal survival test group), significant delays were reported in eye-openings at 5 mg/kg and higher, and male offspring (but not female) experienced accelerated sexual maturation (Lau et al., 2006).

PFOA has been reported to cause tumors of the liver, thyroid and mammary glands in high dose animal studies (ATSDR, 2009; OECD, 2002), but the applicability of these data for human risk assessment has not been demonstrated.

In 2005, the U.S. EPA Draft Risk Assessment of the Potential Human Health Effects Associated with Exposure to Perfluorooctanoic Acid and its Salts identified human Margins of Exposure (MOEs) for noncancer effects ranging from 398 to 78,546, suggesting limited risk potential under normal conditions. The MOEs were calculated as ratios between Lowest Observed Adverse Effect Levels (LOAELs) or No Observed Adverse Effect Levels (NOAELs) in animal studies involving non-human primates and rats, as compared with estimated exposure levels in humans. As MOE values increase, the concern for potential health effects decreases. Even the lowest reported 90th percentile MOE of 195 is well above the typical MOE threshold of concern of 100 (U.S. EPA, 2005). Thus, exposures typically were not judged to be toxicologically significant. Regarding potential carcinogenicity of PFOA, the EPA risk assessment concluded that... “PFOA may best be described as suggestive evidence of carcinogenicity, but not sufficient to assess human carcinogenic potential.”

In a 2006 study of 371 residents in an area known to have PFOA-impacted drinking water, either from the municipal water supply or private wells, no association was found between elevated serum PFOA levels and liver or renal function tests, cholesterol, thyroid-stimulating hormone, or with red cell indices, white cell, or platelet counts (Emmett et al., 2006). The study subjects were exposed for at least two years, drinking water from the municipal supply that had a reported mean PFOA level of 3.5 ug/L, and subject serum PFOA levels ranged from 181 to 571 ug/L.

A 2007 study of cord serum concentrations of PFOA and PFOS in relation to birth weights and sizes of newborns reported a limited statistical association between serum concentrations and reduced birthweight, ponderal index (a measure relating mass to height) and head circumference (Apelberg et al., 2007). The authors suggest "...cautious interpretation of this study until the findings can be replicated in other populations." No such replication has been reported.

A review panel established as a result of a lawsuit settlement involving releases of PFOA near a manufacturing plant in West Virginia has conducted multiple Probable Link evaluations for PFOA and adverse human health effects (C8 Science Panel, 2012a). As of October 2012, the science panel concluded that no probable link exists between PFOA exposure and birth defects, miscarriage or stillbirth, preterm births, low birthweight, Type II diabetes, metabolic syndrome, childhood obesity, childhood asthma, "other" autoimmune diseases, common infections, neurodevelopmental disorders in children, respiratory disease, stroke, hypertension, coronary artery disease, chronic kidney disease, liver disease, osteoarthritis, Parkinson's disease, thyroid cancer, melanoma, liver cancer, pancreatic cancer, prostate cancer, or breast cancer (C8 Science Panel, 2012a; 2012b). The panel has reported that a probable link exists between exposure to PFOA and pregnancy-induced hypertension, ulcerative colitis, thyroid disease, and diagnosed high cholesterol, as well as testicular cancer and kidney cancer, although a mechanism for the cancer occurrences has not been identified.

In 2012, the European Food Safety Authority (EFSA) affirmed their earlier conclusion that it was unlikely that adverse effects from exposure to PFOA were occurring in the general population, and they further concluded that dietary exposures to PFOA are highly unlikely to exceed health-based guidance values (EFSA, 2012).

In 2009, in response to reported concerns over low level PFC impacts in the environment and in human biomonitoring studies, the U.S. EPA Office of Water developed provisional health advisories (PHAs) for drinking water exposure to PFOA and PFOS (U.S. EPA, 2009a). The PFOA PHA was based on a subchronic developmental toxicity study in mice (Lau et al., 2006). Although not explicitly discussed in the Lau study, a 95% lower bound benchmark dose (BMDL10) of 0.46 mg/kg•day was calculated by the European Food Safety Authority (EFSA, 2008), based on raw data provided to them from the principal author of the Lau et al. (2006) study. The EFSA report identified a range of BMDL10 values from 0.3 to 0.7 mg/kg•day. As a midpoint in the range, the Office of Water selected the 0.46 mg/kg•day value for development of their PHA. Along with this BMDL10 value and assumptions of a 10 kg child drinking 1 liter/day of water, a relative source contribution of 20%, and various uncertainty factors totaling 2,430, the Office of Water calculated a 0.4 ug/L short-term PHA for PFOA (U.S. EPA, 2009a). Although based on a subchronic animal feeding study, and identified as a short-term health advisory calculated to protect the sensitive subpopulation of children, the Office of Water (U.S. EPA, 2009a) states that "The value should be protective of all population subgroups and lifestyles."

To evaluate exposures other than short-term drinking water scenarios, there was need of a toxicological guidance value (reference dose; RfD) for PFOA. Following the development of the PHA by the Office of Water, the U.S. EPA Office of Solid Waste and Emergency Response (OSWER) proposed a subchronic RfD using the same BMDL10 and Uncertainty Factors (UFs) that were used for the PHA. The UFs that were applied for the PHA, and for the RfD as well, included a factor of 30 for interspecies and intraspecies differences, as well as a factor of 81 to account for toxicokinetic differences in clearance rates between mice and humans (U.S. EPA, 2009b). Thus, the BMDL10 of 0.46 mg/kg•day divided by the total UF of 2,430 resulted in a proposed RfD of 2E-4 mg/kg•day (rounded to one significant digit from the calculated value of 1.89E-4 mg/kg•day, as typically is done in the U.S.).

In the interest of putting pervasive low level human serum concentrations of PFCs reported throughout Europe in perspective, the European Food Safety Authority (EFSA) had developed a Tolerable Daily Intake (TDI) for PFOA (EFSA, 2008). A TDI value is analogous to an RfD in that they both are defined as safe doses for lifetime exposure. For development of a TDI (or RfD) when sufficient human studies are not available, there is a requirement for animal studies that report dose-response data in the form of a benchmark dose or reasonably supported No Observed Adverse Effects Level (NOAEL). The lowest NOAEL identified by EFSA (2008) was 0.06 mg/kg•day from a subchronic rat study on liver effects. However, higher rat study NOAELs were identified from long-term studies, so the NOAEL approach was dismissed. Several mouse and rat studies reviewed by EFSA reported 95% lower confidence limit BMDs (BMDL10) ranging from 0.3 to 0.7 mg/kg•day. The authors conservatively selected the lowest dose of 0.3 mg/kg•day and applied an overall Uncertainty Factor (UF) of 200 to calculate a TDI for PFOA of 1.5E-3 mg/kg•day. The UF was composed of a factor of 100 for interspecies and intraspecies differences and a factor of 2 for differences in internal dose kinetics.

The RfD/TDI values derived by U.S. EPA (2009b; 2E-4 mg/kg•day) and EFSA (2008; 1.5E-3 mg/kg•day) differ by approximately an order of magnitude due primarily to different approaches in applying uncertainty factors. Both values are based on animal studies with similar critical effects, and both sets of uncertainty factors are fairly well-supported.

### **3.2 Perfluorooctane Sulfonic Acid**

Like PFOA, perfluorooctane sulfonic acid (PFOS; perfluorooctane sulfonate) is a fully substituted, long chain fluorinated compound that does not occur naturally in the environment. PFOS originally was the key ingredient used to manufacture 3M's Scotchgard® fabric and carpet protectant. In May 2000, 3M began a phase out of perfluorooctanoic acid (PFOA), PFOS and PFOS-related products, and in 2002 they had ceased producing any PFOS-containing products (3M, 2012). In 2002, EPA published two Significant New Use Rules under the Toxic Substances Control Act (TSCA) to limit any future manufacture or import of 88 perfluoroalkyl sulfonates, including PFOS (U.S. EPA, 2012).



Animal studies with PFOS have reported significant reproductive, developmental, liver and other adverse effects. Limited human health studies have demonstrated varying and mostly inconclusive correlations (Stein et al., 2009; ATSDR, 2009). Toxicokinetic differences across species, genders and individuals in both animal and human studies appear to be substantive. Additional studies are needed and are ongoing to better understand the broad presence of PFCs (including PFOS) in the environment (ATSDR, 2009; U.S. EPA, 2013).

Maternal and developmental toxicity was reported by Thibodeaux et al. (2003) in a rat and mouse study. Pregnant Sprague-Dawley rats were dosed daily by gavage with 1, 2, 3, 5 or 10 mg/kg and pregnant CD-1 mice were treated similarly with 1, 5, 10, 15 or 20 mg/kg PFOS. Maternal weight gains were reduced in both species in a dose-dependent manner, and maternal liver weights were notably increased in the mouse at the 10 mg/kg and higher dose levels. Fetuses in both species exhibited a series of birth defects including cleft palate, anasarca, ventricular septal defect, and enlargement of the right atrium (Thibodeaux et al., 2003).

Liver toxicity in rats was significantly associated with PFOS doses  $> 0.1$  mg/kg•day in a 2-year feeding study (Thomford, 2002). The 0.1 mg/kg•day level was identified as the LOAEL for the study, and the NOAEL was 0.03 mg/kg•day.

A 2009 study of self-reported pregnancy outcomes for women with elevated serum PFOS identified modest associations with preeclampsia and low birth weight (Stein et al., 2009). The authors correctly cautioned that the associations were small, limited in precision, and based only on self-reported outcomes.

A 2007 study of cord serum PFOA and PFOS levels related to birth weight and newborn size reported limited association between serum concentration and birthweight, ponderal index (measure relating mass to height) or head circumference (Apelberg et al., 2007). The authors said "...cautious interpretation of this study until the findings can be replicated in other populations."

A review panel established from lawsuit settlement proceeds involving releases of PFOA near a manufacturing plant in West Virginia conducted multiple Probable Link evaluations for PFOA and other perfluoroalkyl chemicals (including PFOS) and adverse human health effects (C8 Science Panel, 2012a). Although primarily reporting on PFOA, the panel reported that a probable link existed between exposure to PFOS and onset of puberty for male and female children (C8 Science Panel, 2012a).

In 2012, as with PFOA, the European Food Safety Authority (EFSA) affirmed an earlier conclusion that it was unlikely adverse effects from exposure to PFOS were occurring in the general population, further concluding that dietary exposure to PFOS are highly unlikely to exceed health-based guidelines (EFSA, 2012).

In 2009, in response to reported concerns over low level PFC impacts in the environment and in human biomonitoring studies, the U.S. EPA Office of Water developed provisional health advisories (PHAs) for drinking water exposure to PFOS and PFOA (U.S. EPA, 2009a). The PFOS PHA was based on a subchronic

toxicity study in *Cynomolgus* monkeys (Seacat et al., 2002). Groups of male and female monkeys were given oral doses of potassium PFOS at 0, 0.03, 0.15, or 0.75 mg/kg•day for 183 days. At the 0.15 mg/kg•day level, males exhibited increased estradiol-stimulating hormone, males and females exhibited reduced total triiodothyronine levels, and reduced levels of high-density lipoproteins were observed in females. A No Observed Adverse Effects Level (NOAEL) of 0.03 mg/kg•day was identified in the study (Seacat et al., 2002). Along with this NOAEL and assumptions of a 10 kg child drinking 1 liter/day of water, a relative source contribution of 20%, and various Uncertainty Factors totaling 390, the Office of Water calculated a 0.2 ug/L short-term PHA for PFOS (U.S. EPA, 2009a). Although based on a subchronic animal feeding study, and identified as a short-term health advisory calculated to protect the sensitive subpopulation of children, the Office of Water (U.S. EPA, 2009a) states that “The value should be protective of all population subgroups and lifestages.”

Following development of the PHA by the Office of Water, U.S. EPA Office of Solid Waste and Emergency Response (OSWER) proposed a subchronic RfD using the same NOAEL and Uncertainty Factors (UFs) as used for the PHA. The UFs that were applied for the PHA, and for the RfD as well, included a factor of 10 for interspecies and intraspecies differences, as well as a factor of 39 to account for toxicokinetic differences in clearance rates between monkeys and humans (U.S. EPA, 2009b). Thus, the NOAEL of 0.03 mg/kg•day divided by the total UF of 390 resulted in a proposed RfD of 8E-5 mg/kg•day (rounded to one significant digit from calculated value of 7.69E-5 mg/kg•day, as typically done).

Consistent with the development of a Tolerable Daily Intake (TDI) for PFOA in 2008 (EFSA, 2008), the European Food Safety Authority (EFSA) also proposed a TDI value for PFOS. For development of a TDI (or RfD) when sufficient human studies are not available, there is a need for animal studies that report dose-response data in the form of a benchmark dose or reasonably supported No Observed Adverse Effects Level (NOAEL). The lowest NOAEL identified by EFSA (2008) was the same 0.03 mg/kg•day level identified for development of the PHA from the Seacat et al. (2002) monkey study. The authors conservatively selected the lowest dose of 0.3 mg/kg•day and applied an overall Uncertainty Factor (UF) of 200 to calculate a TDI for PFOS of 1.5E-4 mg/kg•day. The UF was composed of a factor of 100 for interspecies + intraspecies differences and a factor of 2 for internal dose kinetics differences (EFSA, 2008).

The RfD/TDI values derived by U.S. EPA (2009b; 8E-05 mg/kg•day) and EFSA (2008; 1.5E-04 mg/kg•day) are based on the same critical effect in the same cited animal study, but differ by approximately fifty percent due primarily to different approaches in applying uncertainty factors. Each agency presents reasonable supporting data for their choice of uncertainty factors.

#### 4. POTENTIALLY APPLICABLE SOIL RBCs

In 2009, U.S. EPA Region 4 utilized the Tier 3 RfDs for PFOA and PFOS to calculate residential soil screening levels of 16 mg/kg (16,000 ug/kg) and 6 mg/kg (6,000 ug/kg), respectively. These values were developed using the U.S. EPA Superfund Program’s risk-based Regional Screening Level (RSL) calculator, assuming six years of childhood exposure to soil 350 days/year. For evaluation of potential noncarcinogenic effects from exposure to a nonvolatile organic substance (or essentially nonvolatile, as is the case with PFOA and PFOS), the equations and associated parameters embedded in the RSL calculator can be summarized as follows, with, for the purposes of this paper, “ARBC” (Alternative Risk-Based Concentration) replacing the U.S. EPA designation “RSL”:

$$ARBC = \frac{THQ \times BW \times AT}{EF \times ED \times [(1/RfD_o \times IR_o \times CF) + (1/RfD_d \times SA \times AF \times DA \times CF)]}$$

where,

THQ=Target Hazard Quotient	BW=Body Weight
AT=Averaging Time	EF=Exposure Frequency
ED=Exposure Duration	RfD=Reference Dose; oral, dermal
IR=Intake Rate; oral	CF=Conversion Factor for kg/mg
SA=Skin Surface Area	AF=Soil-to-skin Adherence Factor
DA=Dermal Absorption	

While the Region 4 residential screening levels are appropriate as conservative unrestricted-use values below which there should be no need for further evaluation, Table 2 presents potentially applicable ARBCs for common relevant exposure scenarios for application in specific investigations.

Table 2. Potentially applicable risk based concentrations for PFCs.

Scenario-/Chemical-Specific Values	Adult Worker	Construction Worker	Adolescent Trespasser
<b>PFOA ARBC (mg/kg)</b>	360	87	620
<b>PFOS ARBC (mg/kg)</b>	140	35	250
THQ	1	1	1
BW (kg)	70	70	45
AT (days)	9,125	91	3,650
EF (days/yr)	250	250	50
ED (years)	25	0.25 (3 months)	10
RfD oral (mg/kg•day)	2E-04 (PFOA) 8E-05 (PFOS)	2E-04 (PFOA) 8E-05 (PFOS)	2E-04 (PFOA) 8E-05 (PFOS)
RfD dermal (mg/kg•day)	2E-04 (PFOA) 8E-05 (PFOS)	2E-04 (PFOA) 8E-05 (PFOS)	2E-04 (PFOA) 8E-05 (PFOS)
IR (mg/day)	50	227 (480 for first	100

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		month, 100 for next two months)	
CF (kg/mg)	1E-06	1E-06	1E-06
SA (cm <sup>2</sup> )	3,300	3,500	3,300
AF (mg/cm <sup>2</sup> /day)	0.2	0.2	0.2
DA (dimensionless)	0.01	0.01	0.01

## **5. CONCLUSION**

With ongoing efforts to refine toxicological guidance for the most relevant PFCs, and with the lack of consensus on several basic questions (e.g., are they or are they not carcinogenic to humans), it seems prudent to forego development of formal soil screening levels at this time. The U.S. EPA residential/unrestricted use soil screening levels for PFOA and PFOS, based on the Tier 3 (i.e., non IRIS or PPRTV) toxicological guidance, represent reasonable, conservative values below which it is unlikely that soils will be of any concern. In the event that those levels are exceeded, we have provided in this paper a range of potentially applicable alternative risk based soil concentrations that may be considered for sites that are not subject to unrestricted use circumstances.

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# CHALLENGES RELATED TO 1,4-DIOXANE CHARACTERIZATION, EVALUATION AND TREATMENT: THREE CASE EXAMPLES

Christopher M. Teaf<sup>1</sup> and Michele M. Garber<sup>2§</sup>

<sup>1</sup>Center for Biomedical & Toxicological Research, Florida State University, 2035 E. Dirac Dr., Tallahassee, FL, 32310; <sup>2</sup>Hazardous Substance & Waste Management Research, Inc., 2976 Wellington Circle West, Tallahassee, FL, 32309

## ABSTRACT

As a result of improved analytical methods, 1,4-dioxane has emerged as a common chemical of interest at many state and federal remediation soil and groundwater sites. It is driving retrospective attention at sites where investigators are finding it necessary to modify study and remediation plans to account for 1,4-dioxane detections. Physical and chemical properties including low volatility, miscibility in water, extreme environmental mobility, and recalcitrance to degradation make 1,4-dioxane an unusual and cumbersome chemical to deal with in the laboratory and in the field. 1,4-dioxane was used as a solvent stabilizer in the historically common degreasing solvents 1,1,1-trichloroethane (1,1,1-TCA), and trichloroethene (TCE), among others. Other less common uses included leather surface treatments, adhesives, sealants and cements, and pharmaceutical applications. Recent changes have been made in the toxicity values and criteria assigned to 1,4-dioxane by U.S. EPA and other agencies. These changes generally have resulted in health-based target levels becoming more stringent. This paper addresses the evolving toxicological issues, along with various state recommended guidelines for 1,4-dioxane, and discusses significance of these parameters for potentially responsible parties (PRPs) who may be accountable for clean up at affected sites. Three case examples are presented.

**Keywords:** dioxane, health risk, exposure, assessment, remediation

§Corresponding Author: Michele Garber, 2976 Wellington Circle West, Tallahassee, FL, USA, 32309; (850) 681-6894; mgarber@hswmr.com

## **1. INTRODUCTION**

1,4 dioxane is the one that got away, or didn't. Does its presence truly increase risks at a site, or does it unnecessarily complicate the investigation and clean up process? 1,4-Dioxane has been in use for many decades, but its emergence as a contaminant of concern at an increasing number of sites has only recently occurred as a result of advances in analytical methods, along with increased awareness by regulators and decreases in regulatory limits.

1,4-Dioxane, a clear liquid with a faint pleasant odor, is a synthetic chemical used in a wide range of industrial applications as a solvent, stabilizing agent in chlorinated solvents (although this use has been discontinued; NHDES, 2011), and is a byproduct of polyester manufacturing. 1,4-Dioxane is found in many products including paint thinners, dyes, and waxes. Residues may be present in manufactured food additives, food packaging materials and on food crops treated with pesticides that contain 1,4-dioxane (USEPA, 2009b).

Commercial production of 1,4-dioxane was first reported in the U.S. in 1951, although semi-commercial quantities were available as early as 1929 (NTP, 2011). A patent application was filed for the use of 1,4-dioxane as a stabilizer in 1,1,1-trichloroethane (TCA) in 1954 (Doherty, 2000). The two remaining manufacturers of 1,4-dioxane in the U.S. are Dow Chemical Company (DOW) in Freeport, TX and Ferro Corporation in Baton Rouge, LA (ATSDR, 2012). In the mid-1960s, TCA replaced trichloroethylene (TCE) as a degreaser, with the production of TCA peaking in the mid-1980s. In 1995, the Montreal Protocols limited the use of TCA as a degreaser. Mohr et al. (2010) concluded that 1,4-dioxane was not used as a stabilizer in TCE due to smaller boiling point differences between 1,4-dioxane and TCE than between 1,4-dioxane and TCA; and because TCE is more stable than TCA, requiring smaller quantities of stabilizer. Mohr et al. (2010) also reported that based on chemical market reports, ~90% of all 1,4-dioxane produced in the U.S. was used as a stabilizer for TCA. TCA and TCE were used in similar manufacturing situations at various times in history and both TCE and TCA, as well as several TCE degradation products, such as cis-1,2-dichloroethylene (cis-1,2-DCE), are often found together at clean-up sites.

1,4-Dioxane has been identified at 31 of 1689 hazardous waste sites in the U.S. (ATSDR, 2012). For reasons discussed in this paper it is likely to be present at others, yet not analyzed for or not reported due to high analytical detection limits. Its relatively high boiling point (101.1°C) can cause the concentration of 1,4-dioxane to increase in solvents during the solvent vapor degreasing process, leading to possibly higher than anticipated concentrations in groundwater (USEPA, 2006b). In October 2009, 1,4-dioxane was added to the final third



Contaminant Candidate List (CCL) as one of 104 chemicals or chemical groups believed to have the potential to present health risks through drinking water exposure (USEPA, 2009a).

1,4-Dioxane is seldom found in the environment apart from chlorinated solvent contamination situations, and it has been known to precede the TCA plume at some waste sites due to its miscibility in water (Anderson et al., 2012; Zenker et al., 2003). Because 1,4-dioxane plumes have been measured at twice the length of the associated chlorinated solvent plume, with an area up to six times greater, defining, capturing, and remediating a 1,4-dioxane plume can be challenging. 1,4-Dioxane has gained widespread attention from regulators due to its physical and chemical properties, including low volatility, miscibility in water, extreme environmental mobility, and resistance to degradation. As a result of its structure, 1,4-dioxane is highly stable and relatively immune to reactions with acids, oxides, and oxidizing agents. Concentrated acids and strong oxidizers are required to break the ring structure under high temperature and pressure (Mohr et al., 2010). 1,4-Dioxane has a low potential for bioaccumulation and does not bind strongly to organic matter, resulting in a high potential to leach to groundwater from soils. Thus, groundwater typically is the primary medium of concern (Stickney et al., 2003; USEPA, 2006b; NTP, 2011). Many Potentially Responsible Parties (PRPs) are being required to modify existing remediation and/or monitoring plans to account for newly discovered, often very low quantities, of 1,4-dioxane in groundwater. The calculated health risks at a particular site are specific and unique to that site and the discovery of 1,4-dioxane may or may not affect the overall aggregate risk posed by contaminants. However, the highly restrictive U.S. Environmental Protection Agency (USEPA) Regional Screening Level (RSL) of 0.67 µg/L often dictates specific attention.

## **2. TOXICITY SUMMARY AND HEALTH GUIDELINES**

The primary routes of exposure from environmental or occupational sources include inhalation and ingestion. 1,4-dioxane is well absorbed via these exposure routes, while dermal exposure results in much less absorption (USEPA, 2010). 1,4-Dioxane does not accumulate in the body and is not highly toxic to aquatic organisms (WHO, 2005). Irritation of the eyes, nose, throat, and lungs may follow airborne exposure, while drowsiness, vertigo, headache, and anorexia may accompany all routes of exposure (USEPA, 2009b). Genotoxicity data for 1,4-dioxane are generally negative or show it to be weakly genotoxic. Reproductive effects are undescribed to date (ATSDR, 2012). Most available toxicity information is from laboratory animal studies. There are limited data from human exposures. There are no human studies regarding reproductive or developmental

effects, and the animal studies show some reduced body weights and minor bone malformations following administration of large amounts of 1,4-dioxane to pregnant females (NHDES, 2011). No data were found regarding the health effects of human exposure via the oral route (OEHHA, 1998).

Primary noncancer effects in humans and animals affect the liver and the kidney (DeRosa et al., 1996; USEPA, 2010) at exposure to very high concentrations. 1,4-Dioxane is largely metabolized to  $\beta$ -hydroxyethoxy acetic acid (HEAA), which is excreted in urine (USEPA, 2010). High-level exposure to several species in two year drinking water bioassays caused increased liver tumors. In other rat studies, nasal turbinate tumors were observed (ATSDR, 2007).

1,4-Dioxane was first listed in the 2nd Annual Report on Carcinogens by the Department of Health and Human Services in 1981 as “reasonably anticipated to be a human carcinogen” and continues to be listed as such (NTP, 2011). In 1988, USEPA classified 1,4-dioxane as a B2 “probable carcinogen” with a cancer slope factor (CSF) of  $0.011 \text{ (mg/kg}\cdot\text{day)}^{-1}$  derived from tumor incidence data for nasal squamous cell carcinoma in male rats exposed for 2 years in drinking water (USEPA, 2010). Under the current Guidelines for Carcinogen Risk Assessment (USEPA, 2005), 1,4-dioxane is classified as “likely to be carcinogenic to humans” based on liver carcinogenicity in several animal species. A revised CSF of  $0.1 \text{ (mg/kg}\cdot\text{day)}^{-1}$  was derived based on the incidence of hepatocellular adenomas and carcinomas in female mice exposed for 2 years to 1,4-dioxane in drinking water (USEPA, 2010). An inhalation unit risk (IUR) and reference dose (RfD), as listed in Table 1, also have been derived (Kano et al., 2009; USEPA, 2013b). Two small cohort studies in humans in the 1970s found no conclusive evidence for a causal link between exposure to 1,4-dioxane and cancer (USEPA, 2010). IARC (1999) classified 1,4-dioxane as a possible carcinogen to humans, Group 2B, based on inadequate evidence in humans and sufficient evidence in experimental animals.

Table 1. Risk Values for 1,4-Dioxane.

	CSF $(\text{mg/kg}\cdot\text{day})^{-1}$	IUR $(\mu\text{g}/\text{m}^3)^{-1}$	RfD $(\text{mg/kg}\cdot\text{day})$	RfC $(\text{mg}/\text{m}^3)$
1988	0.011	ND	ND	ND
2010	0.1	ND	0.03	ND
2013	0.1	$5 \times 10^{-6}$	0.03	0.03

ND-Not determined

USEPA has not established an enforceable Maximum Contaminant Level (MCL) for 1,4-dioxane in drinking water. That agency determined exposure to 1,4-dioxane in drinking water at 4 mg/L for one day or 0.4 mg/L for 10 days is not expected to cause adverse effects in a child (ATSDR, 2012). Although a legally enforceable level is absent in all states except for Colorado, 1,4-dioxane can be subject to regulation through clean up requirements (USEPA, 2006b). In 1998, the California Department of Public Health (CDPH) published an initial “notification level” of 3 µg/L based on the 1988 USEPA Integrated Risk Information System (IRIS) evaluation, but subsequently revised its notification level to 1 µg/L in November 2010 following USEPA’s revised number (CDPH, 2011). Colorado has the only legally binding MCL for groundwater, which started out in 2005 at 6.1 µg/L, followed by a decrease to 3.2 µg/L, with a further downward revision to 0.35 µg/L, the current value listed in regulation No. 41 (USEPA, 2011; CDPHE, 2013). Table 2 shows the variety of regulatory numbers across the states for 1,4-dioxane in drinking water as well as other important applicable federal guidance values.

The current USEPA RSL of 0.67 µg/L was derived using an age-adjusted drinking water ingestion rate of 1.086 L instead of the standard 2 L per day value that was used to obtain the health advisory value of 0.35 µg/L. USEPA released the final Toxicological Review for 1,4-dioxane in September 2013, which includes an inhalation exposure update. ATSDR released a Toxicological Profile for 1,4-dioxane in April 2012 to update the older 2007 version.

*Challenges Related to 1,4-Dioxane Characterization, Evaluation and Treatment*

*Table 2. Drinking Water Regulations & Guidelines for 1,4-Dioxane.*

<i>Agency</i>	<i>Regulatory Number</i>	<i>Value</i>	<i>Units</i>
Colorado Department of Public Health and Environment (CDPHE)	Maximum Contaminant Level (MCL)	0.35	µg/L
Maine Center for Disease Control and Prevention (Maine CDC)	Maximum Exposure Guidelines (MEG)	4	ppb
Massachusetts Department of Environmental Protection (Mass DEP)	Drinking Water Guidelines (ORSG)	0.3	µg/L
Michigan Department of Environmental Quality (Michigan DEQ)	Risk-based Screening Level (RBSL)	85	ppb
Florida Department of Environmental Protection (FDEP)	Groundwater Cleanup Target Level (GCTL)	3.2	µg/L
California Department of Public Health (CDPH)	Notification Level	1	µg/L
United States Environmental Protection Agency (USEPA)	Health Advisory Level (HAL)	0.35	µg/L

*Sources: Maine CDC 2012. Mass DEP 2012. Michigan DEQ 2012. CDPHE 2013. FDEP 2005. CDPH 2011. USEPA 2011.*

### **3. ANALYTICAL METHODS FOR DETECTION**

The first sensitive and reliable analytical method for 1,4-dioxane became available in 1997 when the California Department of Health Services developed a method for “low detection” (Draper et al., 2000). One of the challenges associated with detecting 1,4-dioxane is that the method has to be capable of extracting low levels of this very hydrophilic contaminant from water samples (Mohr et al., 2010). The high water solubility and poor purging efficiency of 1,4-dioxane requires modifications to existing methods to achieve the sensitivity necessary for low detection limits. Some modifications that can be made to USEPA Method 8260 include a moisture control module, addition of sodium sulfate to increase purge efficiency and heated sparging (Mohr et al., 2010). Purging at elevated temperatures allows more 1,4-dioxane to be removed from the water (USEPA, 2006b), and selected ion monitoring (SIM) can improve the sensitivity of the mass spectrometer (MS). Sample preparation techniques listed as appropriate for USEPA Method 8260 include azeotropic distillation (5031), closed system vacuum distillation (5032) and direct injection (USEPA, 1996; USEPA, 2006b) but the detection limits for these methods are around 12 µg/L (USEPA, 1996) which is still not low enough to meet the challenges of sub ppb (parts per billion; µg/L) guidance values and standards.

Another challenge to analyzing water samples for 1,4-dioxane is the issue of “dirty” samples. Some samples may be submitted that have much higher concentrations of other volatile organic compounds (VOCs), such as TCA, and require dilution which elevates the reporting limit of 1,4-dioxane in that particular sample (Mohr et al., 2010). If the “dirty” samples are not diluted and are analyzed on sensitive instrumentation, increased maintenance and replacement of equipment parts may be necessitated, which can increase time and costs. 1,4-Dioxane samples analyzed alone yield optimum results.

In the past, USEPA methods such as 8260B, 8270D, 1624, and 524.2 have been used for detecting 1,4-dioxane in water samples. In 2008, USEPA developed Method 522, which is specific for low detection limit analysis for 1,4-dioxane (USEPA, 2008). In 2010, the Florida Department of Environmental Protection (FDEP) evaluated the advantages and disadvantages of a group of analytical methods for 1,4-dioxane including USEPA Methods 8260C, 8261, 8270D, and 522 (FDEP, 2010). FDEP does not recommend 8270D because of 1,4-dioxane’s high water solubility and potential loss during the concentration step in sample preparation. USEPA’s drinking water Method 522 for analysis of groundwater and surface water proved robust and provides detection limits far superior to the other analytical methods evaluated, though the main limitation of Method 522 is its narrow application to only one chemical (FDEP, 2010). Although some

laboratories may be able to make modifications to older methods in order to achieve sub ppb detection limits, such as isotope dilution and large injection volume, the FDEP results suggest that USEPA Method 522 is a better choice for detecting sub ppb levels of 1,4-dioxane in water samples.

#### **4. TREATMENT TECHNOLOGIES INVESTIGATED**

The same properties that make 1,4-dioxane difficult to detect in water samples also make it difficult to treat in groundwater. 1,4-Dioxane is not efficiently removed by air stripping, coagulation, or oxidation by chlorine or potassium permanganate, while granular activated carbon can achieve about 50% removal (Zenker et al., 2003). Technologies that are used for chlorinated solvents often are not effective for treating 1,4-dioxane because of differences in physical properties. Due to its high solubility and low tendency to adsorb to soils, 1,4-dioxane is not well-suited for groundwater extraction and treatment (Moyer, 2008). Volatilization and sorption are not significant attenuation processes because of the low Henry's law constant, low octanol-water partition coefficient, and infinite water solubility (Zenker et al., 2003). Pump and treat remediation using *ex situ* treatment technologies tailored for 1,4-dioxane's unique physical and chemical properties have been applied successfully in some instances (USEPA, 2006b).

Due to its heterocyclic nature and two ether linkages, 1,4-dioxane is resistant to abiotic and biologically mediated degradation, although some laboratory results have shown that biodegradation may be possible under specified conditions (Zenker et al., 2003). Chiang et al. (2008) showed decreasing concentrations of 1,4-dioxane in groundwater during Monitored Natural Attenuation (MNA) at a site where the source of contamination had been removed.

##### **4.1 *Ex Situ* Pump-and-Treat Technologies**

Advanced oxidation processes (AOPs) appear to be most commonly used for full scale *ex situ* 1,4-dioxane treatment (Mohr et al., 2010). AOPs are available for above ground treatment of 1,4-dioxane in groundwater and can be used alone or in combination with other remediation processes (USEPA, 2006b). Two common AOPs used for 1,4-dioxane treatment are hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) with ultraviolet (UV) light, and H<sub>2</sub>O<sub>2</sub> with ozone. UV light and ozone combined with hydrogen peroxide cause hydroxyl radicals to be released, with an oxidation potential of 2.7 electron volts (eV), yielding one of the strongest oxidizers available (DiGuseppi and Whitesides, 2007). Coleman et al. (2007) demonstrated good results with several photolysis systems in addition to the

H<sub>2</sub>O<sub>2</sub>/UV process. There are some limitations to using AOPs, including the formation of bromate if the contaminated water contains bromide, as well as other decomposition products, and the limited ability to handle concentrations of 1,4-dioxane above 1 milligram per liter (mg/L) unless multiple units in a series are utilized (USEPA, 2006b).

Based on the properties of 1,4-dioxane, one would not expect adsorption to work; however, granular activated carbon (GAC) as a sorbent has been found to remove at least some 1,4-dioxane from groundwater based on analytic results of influent and effluent water samples (USEPA, 2006b). This may have been due to low influent concentrations, very low flow rates (0.5 gallons per minute [gpm]), or possible biodegradation of 1,4-dioxane on carbon surfaces in the presence of tetrahydrofuran (THF; USEPA, 2006b). In most cases, its low tendency to adsorb 1,4-dioxane makes GAC an inappropriate treatment technology (Mohr et al., 2010).

Microcosm studies show that aerobic co-metabolic bioremediation is promising but that anaerobic bioremediation is not effective (Mohr et al., 2010). Steffan (2007) tested bioremediation and found that several organisms were able to degrade 1,4-dioxane via cometabolism during growth on propane or THF, but 1,4-dioxane was not consistently degraded in microcosms with samples from different 1,4-dioxane contaminated aquifers. Biological treatment and MNA are unlikely to successfully remediate 1,4-dioxane in groundwater (Steffan, 2007).

Because 1,4-dioxane was used as a solvent stabilizer in TCA and other chlorinated solvents, some solvent breakdown products, including 1,1-dichloroethylene (1,1-DCE), are commonly found in association with 1,4-dioxane in groundwater. Mahendra et al. (2012) evaluated the effects of TCA and 1,1-DCE on 1,4-dioxane degradation by *Pseudonocardia dioxanivorans* CB1190, *Pseudomonas medocina* KRI, and *Escherichia coli* and found that the presence of these chlorinated chemicals inhibited degradation of 1,4-dioxane in all strains of bacteria tested (Mahendra et al., 2012).

## 4.2 In-Situ Technologies

Treatment technologies are available which incorporate soil vapor extraction, air sparging, air stripping, flushing, and enhanced bioremediation/oxidation in a single groundwater well with a minimum diameter of 4 inches (Accelerated Remediation Technologies, Inc. (ART), no date). Odah et al. (2005) showed a 70% reduction of 1,4-dioxane at a 10 foot distance from an ART treatment well and 91% reduction at a 20 foot distance from the treatment well within 3 months.

Phytoremediation technologies, which use vegetation as an uptake vehicle, are being explored. However, it is unclear if plants are able to take up 1,4-dioxane in

appreciable amounts (USEPA 1999; USEPA, 2013a). Aitchison et al. (2000) found that hybrid poplar trees, which were chosen because they are easily propagated, develop deep root systems, exhibit high water uptake rates, and are tolerant to high levels of organics, were effective at removing 1,4-dioxane from water samples and soil samples in the laboratory. Most of the 1,4-dioxane taken up by the roots was volatilized by transpiration from leaf surfaces (Aitchison et al., 2000).

## 5. CASE STUDIES

Case studies from Colorado, Arizona and South Carolina (Table 3) are described as examples where the identification of 1,4-dioxane in groundwater samples resulted in changes to remediation plans and/or monitoring of the sites and surrounding off-site properties. A common theme is that successful conventional VOC cleanup resulted in anticipated remediated water being released while it may in fact still have contained detectable levels of 1,4-dioxane. Had the engineers and scientists been aware of this contaminant prior to the first round of remediation they could have tailored their techniques accordingly, which would have prevented the need to revisit the remediation. The case studies that follow include background information on the site, examples of some quantities of 1,4-dioxane detected on or near the site, treatment technologies used at the site, and the current status.

Table 3. Three Case Studies.

Site Name	Location	Size of Site	Date of 1,4-Dioxane Discovery	Treatment Technology
Case 1	Colorado	507 Acres	2003	Groundwater extraction and treatment
Case 2	Arizona	6400 Acres	2002	Advanced Oxidation Process
Case 3	South Carolina	670 Acres	1992	Perimeter extraction System and UV peroxide treatment

### 5.1 Site 1

Site 1 is located on approximately 507 acres in Arapahoe County, Colorado. The City and County of Denver operated an industrial waste and municipal solid waste



landfill from the mid-1960s until 1980 at the Site and currently own it. In 1980, co-disposal of municipal and industrial waste stopped, while landfilling of municipal solid waste continued until 1990 when all landfilling operations ceased. USEPA estimated that approximately 138 million gallons of industrial wastes were disposed at the Site during this time (USEPA, 2012c). Waste, including sewage sludge, paints, pesticides, and industrial solvents, were dumped into about 78 unlined pits spanning over 200 acres, which was common practice at the time, and later covered with trash/debris, tires, and soil to absorb the liquids. Some liquids were sprayed onto the soil in large “leachate spraying” areas located in the northern part of the site. Over time, some of the contaminated liquids seeped out of the pits and contaminated surrounding soils, surface water, and groundwater (USEPA, 2000; USEPA, 2012c).

The Site was added to the National Priorities List (NPL) in 1984 and investigations have been ongoing since then by USEPA, and others, to determine the nature of the contamination and determine possible risks and remediation options (USEPA, 2006a). A Record of Decision (ROD) was signed in March 1994 by USEPA and the state agency which set out a comprehensive plan for the Site to protect human health and the environment by addressing groundwater, surface water, landfill gas, landfill solids, soils and sediment issues (USEPA, 2001). At the time of the ROD, USEPA identified approximately 50 chemicals of concern at the Site, which did not include 1,4-dioxane, since it was not a known contaminant and laboratories were not routinely testing for it. The site-wide remedy is based on “containment”, which means that hazardous substances, pollutants, or contaminants will remain on-site while protective measures are put in place to prevent off-site movement. This containment strategy avoids public health and environmental risks associated with removing large amounts of contaminated materials, accepts the relatively low long-term threat posed by leaving hazardous materials in place, and acknowledges that treatment is impractical because of the size and diversity of landfill contaminants.

1,4-Dioxane contamination was detected in 2003 during routine monitoring of the compliance wells, and investigations continued through 2007 to characterize the plume (USEPA, 2008). In 2005, the Colorado Water Quality Control Commission established a groundwater standard of 6.1 µg/L, which was considerably less than the 200 µg/L that USEPA was requiring the landfill to meet for cleanup (USEPA, 2006a). As a result, newly developed laboratory methods were selected that were capable of detecting 1,4-dioxane at or below this new standard, which subsequently was decreased to 0.35 µg/L, as mentioned in section 2 above. Detections in shallow groundwater and surface water approximately 1 mile (1.6 kilometer) north of the Site initiated a larger study to characterize the extent of the off-site contamination (USEPA, 2006a). Most residents in the area

of the Site drink water provided by the City. However, a few wells used for drinking water were tested, and these wells did not contain detectable levels of 1,4-dioxane.

It is believed that the 1,4-dioxane was present in the groundwater prior to installation of the North Boundary Barrier Wall (NBBW) and before the standard changed from the earlier practice of re-injecting water contaminated with 1,4-dioxane north of the NBBW and thus, is not believed to be a current source of 1,4-dioxane in groundwater (USEPA, 2008). Further improvements in 2007 included the installation of additional wells to capture and remove the 1,4-dioxane from the groundwater north of the boundary.

Health risks at the Site are limited because access to the site is restricted and off-site groundwater used as drinking water is not contaminated. USEPA evaluated health risks associated with public exposure to 1,4-dioxane north of the site and found no significant health risks associated with surface water or groundwater (USEPA, 2008). USEPA considered the possibility of occasional contact with contaminated groundwater entering a nearby creek and evaluated scenarios where children may play in the creek and golfers may possibly be exposed and found no significant health risks (USEPA, 2008). Concentrations of 1,4-dioxane measured in the nearby creek ranged from non-detect up to 79 µg/L north of the landfill (USEPA, 2008) and in other areas of the Site concentrations of 1,4-dioxane in groundwater ranged from non-detect to 230 µg/L. However, in nearby neighborhoods, values were much lower, ranging from non-detect to 42 µg/L and affected groundwater is not located under any existing residences.

The North Toe Extraction System (NTES) was constructed in 1998 but did not go into full effect until approximately 6 years later following completion of studies on how to treat this contaminated water. Water from the NTES is mixed with water from the main WTP and then biologically treated. The effluent is returned to the WTP for additional blending, treatment and discharge to the Publicly Owned Treatment Works (POTW; USEPA, 2007). In addition, there are early warning monitoring wells that are tested twice a year to determine if modifications to the treatment plant are needed. Land use controls, such as fences and warning signs, are in place to protect people from exposure to site contaminants (USEPA, 2001). Deed and development restrictions also are in place to limit future use of the property in the vicinity of the Site (USEPA, 2001). Remedies conducted at the Site include landfill cover, a slurry wall, NTES, NBBW, surface water remediation, landfill gas extraction, remediation of the former tire pit area, and long-term monitoring for all media to evaluate effectiveness and overall protectiveness of the cleanup actions taken (USEPA, 2012c). A 200-acre soil layer now covers the main landfill and an 8,800-foot long

underground groundwater barrier wall of soil and clay encloses the west, east, and south sides of the main landfill.

Following years of efforts at the Site, the second five-year review report released in February 2007 found that the remedy for all six operable units was protective of human health and the environment (USEPA, 2007) and this was the case again for the third five-year review (USEPA, 2012b).

## **5.2 Site 2**

Site 2 is an example of a superfund site that is currently spending millions of dollars to construct a treatment facility that would be able to treat contaminated water for 1,4-dioxane at levels that are below the previous USEPA Health Advisory level of 3 µg/L. Site 2 has been divided into 7 project areas on approximately a 10 square mile area (6400 acres, 2590 hectares) in Pima County, Arizona where more than 20 separate facilities have operated since 1942.

Initial contamination was discovered in the early 1950s, improper waste disposal at the Site stopped by the early 1970s, and in 1981 USEPA and the City conducted groundwater sampling and analysis from city municipal water wells. Unsafe levels of TCE were discovered in several south-side City water wells and the Site was officially listed as an NPL site in September 1983. Subsequent sampling identified the primary plume of groundwater contamination approximately ½ mile wide and 5 miles in length resulting in the shut down of 11 city drinking water wells and several more private wells.

In 1987, a pump and treat facility in one area began removing chlorinated solvents from groundwater and reinjecting most of the treated water back into the regional aquifer at the site (Tillman, 2009). In 1994, an additional water treatment facility was completed in the north portion of the Site, and extraction of groundwater from the northern portion of the plume began in order to manage a 4-mile (6.4 kilometer) long, 1-mile (1.6 kilometer) wide plume of groundwater contamination (USEPA, 2012a). In 1997, the treatment system in the south area of the Site was upgraded to a dual phase extraction system, the holding ponds were closed and it became a nondischarging plant that recycles 97% of its water.

In 2002, the City began analyzing samples at the northern treatment facility for 1,4-dioxane and discovered a plume extending for more than 5 miles (8 kilometers) throughout this area. USEPA issued an Administration Order in July 2007 requiring installation of an advanced oxidation process (AOP) treatment system at this location to remove 1,4-dioxane from water being recharged to the aquifer (Tillman, 2009). The AOP began operations at the southern facility fulltime in September 2009, which replaced the existing dual phase extraction system coupled with air stripping towers that, after nearly 10 years of operation,

was not meeting the clean up goals at the site (USEPA, 2012a). The U.S. Geological Survey (USGS) results indicated that 30% of the sample concentrations were less than reportable limits, while 46% of the samples collected had concentrations of 1,4-dioxane greater than the USEPA health advisory level of 3 µg/L which was in place at that time (Tillman, 2009). The highest concentration detected from any of these samples was 16 µg/L found at one well on two occasions, while most other sample results were in the single digit ug/L range (Tillman, 2009). The most recent sampling event in July 2013 showed non-detects in 9 of 11 sample well locations, with the other two at 0.2 µg/L, which is the minimum reporting limit and is below the health advisory level of 0.35 µg/L (Tucson, 2013).

When USEPA issued a health advisory of 0.35 µg/L for 1,4-dioxane in 2011 planning and designing began for a new facility to treat the northern portion of the Site with state of the art technology to remove 1,4-dioxane from the water to these low levels. Construction of the AOP facility, utilizing H<sub>2</sub>O<sub>2</sub> and UV light, started in July 2012 and is expected to be finished in early 2014 with a budget of approximately 18 million dollars. Use of this new AOP facility along with the existing groundwater treatment plant is expected to treat 8 million gallons (30 million liters) of water daily (USEPA, 2012a). In August 2012, private well monitoring indicated no significant adverse changes and in some cases the contaminant levels were less than the previous year. 1,4-Dioxane was detected in two of the four wells at a maximum concentration of 1.7 µg/L (PCDEQ, 2012).

All public health assessments have determined that there are no immediate threats to human health or the environment. Groundwater clean up actions and quarterly monitoring are currently ongoing at the Site.

### **5.3 Site 3**

Site 3 differs from the other two sites in that 1,4-dioxane concentrations were higher in the historical data on-site than the older detection limits (i.e., 50 µg/L). The Site is located on about 670 acres (271 hectares) in rural South Carolina. The Site has been used for several industrial operations by numerous owners since 1966 and is not a listed USEPA NPL site. The primary issues at the site involve 1,4-dioxane, DowTherm A (1,1 biphenyl + biphenyl ether), and chlorinated solvents, including chloroform. The state environmental agency has been overseeing assessment and cleanup since the late 1980s. Groundwater contamination was discovered in 1988 and remediation began about 1992 with the installation of a distillation column to recover 1,4-dioxane from plant effluent prior to discharge to the wastewater treatment plant, and the installation of extraction wells. There were no contaminants of potential concern (COPCs)

identified in nearby surface water bodies in the early-1990s. 1,4-Dioxane was found in several parts of the site with inconsistent detections suggesting the absence of a single coherent plume. Remediation at the site for 1,4-dioxane has included the use of a perimeter extraction system and a UV/H<sub>2</sub>O<sub>2</sub> treatment system. Several areas have achieved success at site boundaries. Other clean up activities at the site have included removal of soil and sludge from wastewater treatment plant impoundments and basins, upgrades to the wastewater treatment plant and removal of liquid DowTherm A from the groundwater. 1,4-Dioxane has been detected sporadically in surface water samples at a detection limit of 10 µg/L (ppb). There is currently an off-site investigation underway to assess site-related impacts off-site. Levels off-site are unlikely to represent a human health risk.

Future actions at the site include defining the extent of offsite detections, evaluating data trends, continued monitoring, evaluating sediment issues, and continuing to evaluate cleanup efforts. The state agency continues to monitor off-site drinking water wells for contamination. Levels of 1,4-dioxane continue to be detected in wells on-site but there has been no consistent evidence, based on the detection limits used, of 1,4-dioxane being detected in surface water samples or at off-site groundwater sample locations at levels of significance.

## **6. CONCLUSION**

1,4-Dioxane has emerged as a contaminant of interest at many waste sites around the country and, while its presence may or may not translate to a substantive human health risk, its occurrence is receiving regulatory attention. Laboratories now can detect 1,4-dioxane concentrations in the sub ppb range. As seen from the three examples, discovery of 1,4-dioxane at existing sites, or where cleanup is being performed for other chemicals of interest, can complicate remedial activities. These may include increased monitoring, and costs associated with more sensitive analytical techniques required to detect 1,4-dioxane at sub ppb. This can be a significant consideration when these levels may not factor into the calculation of human health risk at a site. It is important for responsible parties to be aware that if VOCs, especially TCE or TCA, are found at a site they may consider analysis of samples for 1,4-dioxane to ensure that the chosen treatment strategy will effectively remove contaminants of interest from the site.

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# **ANAEROBIC BIOSTIMULATION AS A SECONDARY TREATMENT OPTION FOR THE REMEDIATION OF PETROLEUM HYDROCARBON IMPACTS AT TWO GASOLINE SERVICE STATIONS ON LONG ISLAND, NY**

Gordon Hinshalwood,<sup>§1</sup> Jonathan Curran<sup>2</sup> and Christopher Meyer<sup>2</sup>

*Antea Group,<sup>1</sup> 2 Bridgewater Road., Farmington, CT 06032; <sup>2</sup> 500 Summit Lake Drive, Valhalla, NY 10595*

## **ABSTRACT**

Treatment of contaminated soil and ground water through the addition of oxygen to an aquifer to stimulate aerobic remediation is a common cleanup method. Anaerobic biostimulation through the application of alternate electron acceptors, though not as common, can also be effective in treating impacted media. Two case studies are presented, both involving gasoline service stations on Long Island, NY. Both sites were initially treated using other methods (air sparge/soil vapor extraction and ground water pump-and-treat) to address the impacted source materials, but acceptable end point concentrations with respect to ground water quality were not met in either case. Secondary treatment via the injection of alternative electron acceptors (sulfate and sulfate/nitrate mix) to stimulate indigenous anaerobic microbiological activity successfully brought ground water quality to acceptable end points at both sites.

**Keywords:** site remediation, sulfate-reducing, anaerobic biostimulation, petroleum hydrocarbons

<sup>§</sup>Corresponding Author: Gordon Hinshalwood, 2 Bridgewater Road, Farmington, CT 06032; (860) 371-1220; Gordon.hinshalwood@anteagroup.com

## 1. INTRODUCTION

Site remediation of soil and ground water contaminated with petroleum hydrocarbons has traditionally been completed through a combination of excavation/disposal of impacted soils followed by the application of some *in situ* extraction technology such as pump-and-treat (ground water), soil vapor extraction (soil only), or multi-phase extraction (soil and ground water) (ITRC, 2004). Although generally effective at reducing the total contaminant mass present, these technologies do not always achieve their desired goal (typically the reduction of contaminant soil and/or ground water concentrations to a predetermined regulatory standard or an acceptable risk level) (Khan et al, 2004). Soil excavation, while highly effective for removing a contaminant source, frequently cannot be fully completed due to practical limitations or site constraints. Furthermore, significant dissolved-phase contaminant mass may remain in site ground water after impacted soils are removed. Extraction technologies can effectively remove additional contaminant mass post excavation, but are often limited by such factors as site hydrogeological features and contaminant mass distribution in the subsurface.

One possible “secondary” treatment option to address lingering post-excavation/extraction concentrations both in the dissolved-phase and sorbed to soils in and below the capillary zone is the injection of oxygen or an alternative electron acceptor to stimulate microbiological activity. Two case studies are presented here, both involving gasoline service stations on Long Island, NY. Both sites were initially treated using other methods (air sparge/soil vapor extraction and ground water pump-and-treat) to address the impacted source materials, but acceptable end point concentrations with respect to ground water quality were not met in either case. Secondary treatment through the injection of alternative electron acceptors (sulfate and sulfate/nitrate mix, respectively) to stimulate indigenous anaerobic microbiological activity subsequently brought ground water concentrations to acceptable end points at both sites.

The sites are located in similar hydrogeological settings, underlain by Pleistocene-age glacial outwash consisting of fine to coarse grained gravel and sand remnants of post-glacial fluvial deposition (Cadwell, 1989). The deposits consist primarily of well-sorted, highly permeable sediments deposited as deltas, fans and flood plains. Site 1 is covered with extensive fill material to a depth of approximately 13 feet (4 meters) below ground surface (bgs), which is underlain by coarse-grained sand and gravel. Depth to ground water averages 21 feet (6.4 meters) bgs and, based on slug testing performed on several site ground water monitoring

wells, hydraulic conductivity is estimated to range from 175 – 200 feet per day (ft/day). Site 2 exhibits an average depth to ground water of 26 feet (8 meters) bgs, with an estimated hydraulic conductivity of 275 ft/day.

Hydrocarbon impacts were originally identified at Site 1 when the underground storage tank (UST) system failed a routine pressure tightness test, which was traced back to a leaking elbow in one of the dispenser lines (Figure 1). The leaking component was repaired, but the amount of impacted soil excavated was minimal (less than 10 cubic yards, 7.6 cubic meters) due to site constraints. Investigations were subsequently conducted over several years using a combination of soil gas survey, electrical resistivity, direct-push drilling, and conventional drilling techniques to define the extent of subsurface impact. Figure 1 summarizes the results of these delineation efforts, which collectively defined two areas of soil impact adjacent to the canopy on its eastern and western sides, as well as measureable non aqueous phase liquid (NAPL) in five of the on-site ground water monitoring wells.

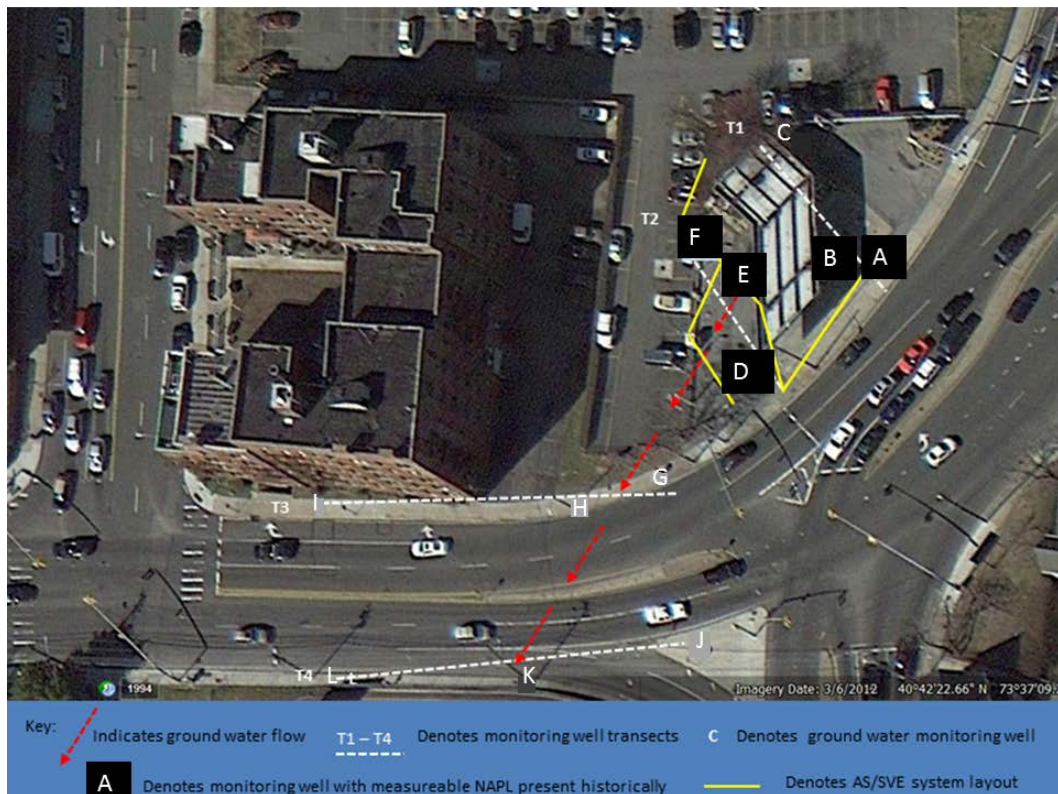


Figure 1. Aerial view of Site 1 depicting identified source area (boxes A through F), ground water monitoring wells used to form “transects” for contaminant mass flux calculations, and ground water flow direction.

Given the extent and depth (greater than 20 feet, 6 meters,bgs) of the impacts identified, additional excavation was not considered practical. A combination of air sparging and soil vapor extraction (AS/SVE) was implemented instead to treat all impacted media (Figure 1). The AS/SVE system operated for a 37 month period, during which total hydrocarbon recovery was estimated to be 421 pounds (191 kilograms) of total BTEX (benzene, toluene, ethylbenzene and xylene isomers), 432 pounds (196 kilograms) of methyl tert-butyl ether (MTBE), and 5,355 pounds (2429 kilograms) of total petroleum hydrocarbons (TPH).

During the lateral stages of operation, the AS/SVE system exhibited lower recovery rates (Figure 2) as hydrocarbon mass in and around the source area was significantly reduced, and source zone soil sampling confirmed that concentrations had been reduced to acceptable levels. However, ground water hydrocarbon concentrations in source area monitoring wells, although significantly reduced following AS/SVE treatment (Figure 2), remained above regulatory limits, and concentration increases indicative of “bounce back” were observed throughout the source area monitoring wells within a year of system shut down (Figure 2).

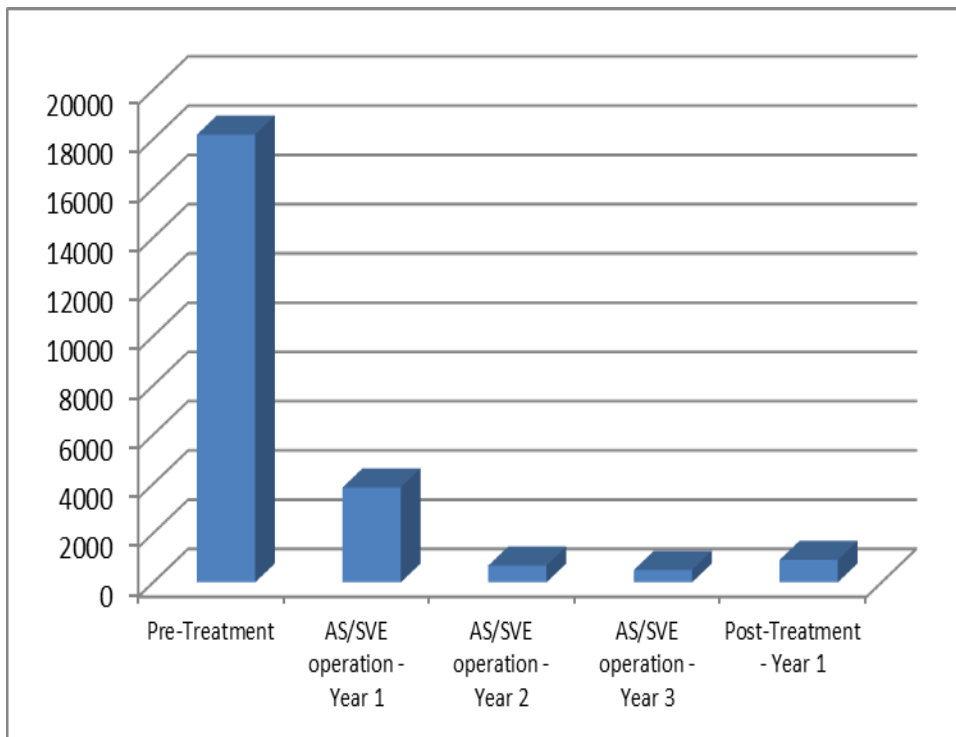


Figure 2. Source area average annual total BTEX concentrations at Site 1, in ug/L. Annual average concentrations were first calculated at each source area monitoring well with concentrations initially exceeding 100 ug/L total BTEX. These values were then averaged in turn to represent annual average source area concentration as a single value (ug/L).

Site 2 has a somewhat more complicated history, with multiple remedial strategies implemented prior to anaerobic biostimulation. Hydrocarbon impacts were initially identified when a product line was ruptured during subsurface construction activities. Repairs were rendered, and the extent of impacted soil excavation/removal was again limited to a minimal effort by site constraints (5 cubic yards, 3.8 cubic meters). Following an initial soil and ground water investigation, pump-and-treat (P & T) was selected as the remedy to address dissolved-phase impacts, and a treatment system consisting of a single extraction well, a shallow-tray air stripper unit with carbon filtration, and a re-infiltration gallery to discharge treated water was installed (Figure 3).

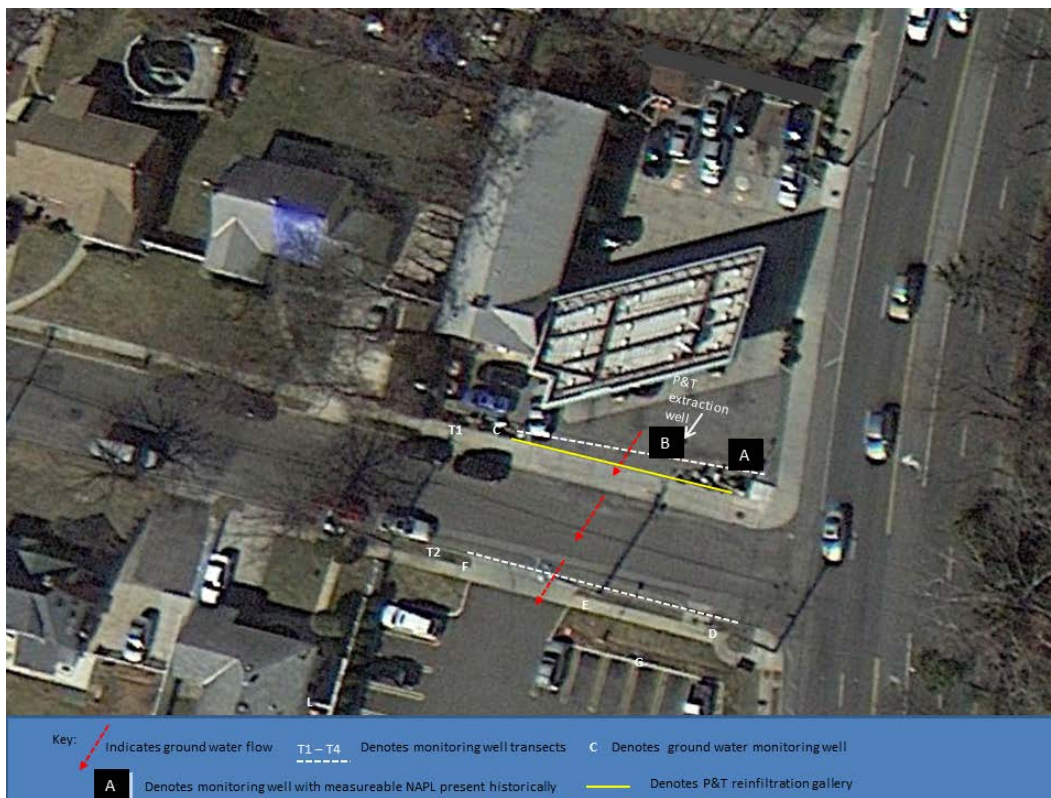


Figure 3. Aerial view of Site 2 depicting identified source area (transect T1), ground water monitoring wells used to form “transects” for contaminant mass flux calculations, ground water flow direction, and pump-and-treat system features.

The system was operated for a 78 month period, beginning 3 years after the initial spill discovery. During the first 22 months of operation, NAPL was intermittently found in both the extraction well and a neighboring monitoring well in the treatment zone. A combination of hand bailing and skimming was initiated to

remove measureable NAPL from these wells concurrent with P&T system operation, yielding approximately 35 gallons (133 liters) of recovered NAPL. After 22 months of operation, the system was enhanced with soil vapor extraction at the extraction well to address both soil impacts and the ongoing NAPL accumulation. During this period, the ongoing remediation efforts were supplemented with two multiphase (vapor and liquid removal) vacuum extraction events and five limited chemical oxidation events using hydrogen peroxide as the oxidant (55 gallons, 208 liters) of 35% peroxide solution at each event). These events were all performed within and immediately downgradient of the source area between 12 and 36 months after the P&T system startup.

The SVE enhancement operated for a total of 21 months, and was then shut down when influent vapor recovery levels dropped below detectable concentrations. The P&T system was subsequently shut down after 78 months due to operational and iron fouling issues. Total hydrocarbon recovery over the P&T system lifecycle was estimated at 840 pounds (381 kilograms) of total BTEX, with about 16.6 million gallons (63 million liters) of water treated. SVE operation increased the contaminant mass removal with an additional estimated 339 pounds (154 kilograms) of total BTEX and 3,880 pounds (1760 kilograms) of MTBE. The multiphase vacuum extraction events added an estimated 17 pounds (7.7 kilograms) of hydrocarbon vapor recovery along with an estimated 1,180 gallons (4467 liters) of liquid recovery.

Similar to Site 1, Site 2 exhibited dramatic reductions of contaminant mass in the source area following the various remedial actions taken, but ground water concentrations remained above target levels post-remediation and concentration bounce back was also observed within a year following P&T system shutdown (Figure 4).

At both sites, continued delineation efforts had identified off-site ground water impacts while source area treatments were ongoing. When the systems showed reduced performance and were shut down, in both cases the sites were left with significantly reduced source area hydrocarbon mass, but ground water concentrations above acceptable limits in and downgradient of the treatment zones. Additional remedial actions post-treatment were therefore needed at both sites to reach acceptable ground water concentrations.



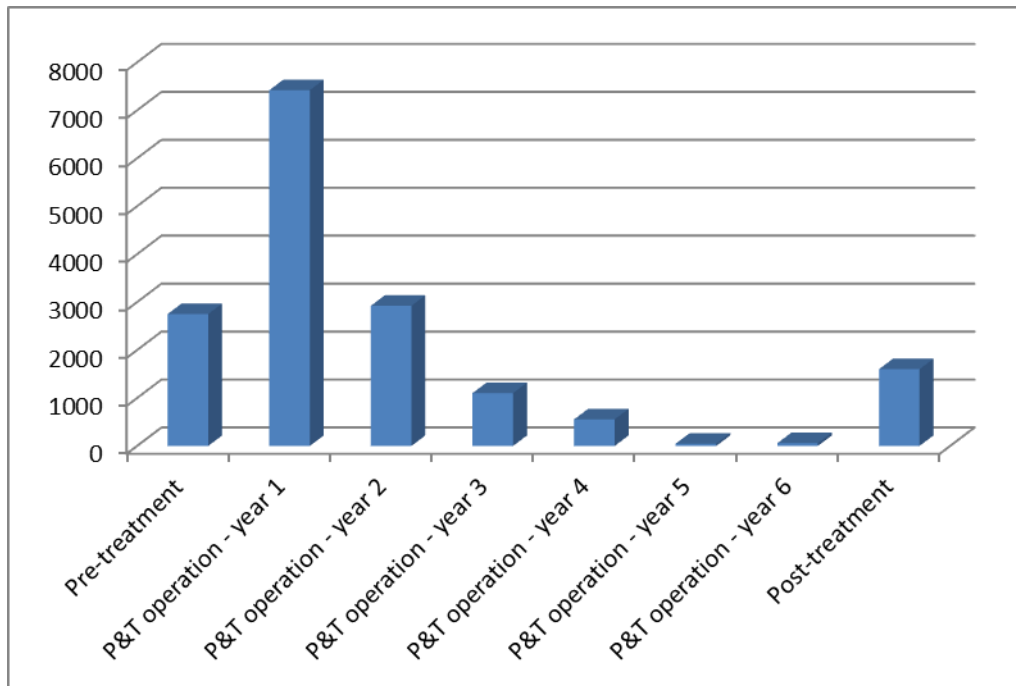


Figure 4. Source area average annual total BTEX concentrations at Site 2 in ug/L. Of note, a surficial gasoline spill was washed into an on-site drywell during the final year of P&T system operation, contributing to the magnitude of post-treatment concentrations in the source area.

## 2. EXPERIMENTAL MATERIALS AND APPROACH

Intrinsic biodegradation of petroleum hydrocarbons under a variety of aquifer redox conditions has been well established in the literature (Lovely, 1997). Ground water geochemical data were therefore initially collected at both sites to evaluate the potential for anaerobic biostimulation as a treatment method to bring dissolved-phase hydrocarbon concentrations within acceptable limits. Both aquifers exhibited indicators of reducing conditions, with lower oxygen content evident within the plume footprints (Table 1). These data are indicative of increased microbiological activity within the plume footprint, as would be anticipated in a substrate-rich, microbiologically active zone. Site 1 showed depleted nitrate and sulfate concentrations within the plume, while Site 2 was mixed; clearly reduced with respect to nitrate, but not sulfate. Anaerobic biostimulation was therefore piloted using sulfate alone as an electron acceptor at Site 1, and a nitrate/sulfate mix as electron acceptors at Site 2.

Table 1. Average concentrations of select ground water geochemical parameters at Sites 1 and 2 prior to biostimulation. Concentrations of all wells sampled within the hydrocarbon plume footprint were averaged to represent plume conditions as were all wells sampled outside the plume footprint, representing background aquifer conditions.

Analytical Parameter	Site 1		Site 2	
	Within Ground Water Plume	Beyond Ground Water Plume	Within Ground Water Plume	Beyond Ground Water Plume
Dissolved Oxygen (mg/L)	0.3	1.5	1.0	3.9
ORP (mV)	-90.3	48.5	-32.0	47.5
Alkalinity, Total as CaCO <sub>3</sub> (mg/L)	105.9	82.4	131.0	28.0
Total Iron (mg/L)	21.1	4.0	42.1	3.6
Nitrate, as Nitrogen (mg/L)	0.6	4.1	0.0	1.8
Sulfate (mg/L)	9.0	29.4	13.0	12.7
Methane (mg/L)	101.9	19.5		

Pilot tests involving biostimulant injection into a single on-site monitoring well followed by observation in downgradient monitoring wells were initially conducted at both sites to help define reagent concentrations and injection volumes. Based on these results, 2,000 gallons (7,580 liters) of 25,000 mg/L sulfate solution was selected as the injection volume and concentration at Site 1. Two injection wells located upgradient of and within the source area were selected: one upgradient of the contaminant source area to address residual source area impacts post AS/SVE treatment, the other near the downgradient source area limit to address the off-site contaminant plume (Figure 1). Both wells featured 10-foot (3.3 meter) screen intervals constructed of 2-inch (5.1 centimeter) diameter, Schedule 40 slotted PVC screens with Morie #2 well sand packs and bentonite seals above the filter packs.

Due to site constraints, the sulfate solution was mixed off-site and transported to the property in 55-gallon (208 liter) drums. Once on-site, the solution was applied using a diaphragm pump at ground surface, which was connected to both the reagent drums and the wellhead with 1-inch (2.54 centimeter) reinforced PVC tubing secured with camlock fittings at all end points. The solution was gravity-fed into the aquifer without any pressure assistance. Using this protocol,



approximately 2,130 kg (4,686 pounds) of sulfate was injected over 11 events during a 28-month period beginning 36 months after the system was shut down. Aquifer sulfate concentrations were monitored frequently (weekly or biweekly) during periods following an event, and quarterly otherwise. Benzene, toluene, ethylbenzene, xylene isomer (BTEX) and MTBE ground water concentration data were collected quarterly throughout the treatment period.

Site 2 was equipped with an infiltration gallery on-site originally constructed for the pump-and-treat system, which was used to inject the biostimulant solution into the aquifer (Figure 3). This location served as the application point for treatment of both on-site and off-site dissolved-phase impacts.

The solution administered contained 725 mg/L nitrate and 4,000 mg/L sulfate: 1,000 gallons (3,790 liters) each for 2,000 gallons (7,580 liters) total volume at each application. Approximately 80 kg (176 pounds) of nitrate and 1,500 kg (3,300 pounds) of sulfate were injected over a 35 month period beginning 12 months following the P & T system shutdown.

### **3. RESULTS AND DISCUSSION**

With the contaminant extraction systems initially used at the subject sites, progress was measured directly by the amount of contaminant mass removed over time. Evaluating progress with *in situ* remediation technologies is more challenging since the degradation reactions cannot be observed directly and reaction products are not extracted. Although a variety of molecular and isotopic tools useful for identifying contaminant biodegradation *in situ* have become widely available in recent years (USEPA, 2008), these tools generally do not quantify the contaminant mass degraded, which is more commonly estimated through spatial and temporal analyses of ground water data.

At both sites, contaminant concentration data (total BTEX) were collected quarterly throughout the sites' histories, and electron acceptor ground water concentration data (sulfate and sulfate/nitrate) were collected throughout the biostimulation treatment periods. To analyze the data, monitoring well locations were aligned into linear transects orthogonal to the direction of ground water flow (Figures 1 and 3). Interpolating the contaminant or electron acceptor mass in between transect wells yielded an estimate of mass "fluxing" through each transect at a given point in time. Completing this analysis using data from multiple time periods provided annual mass flux estimates for the time periods for

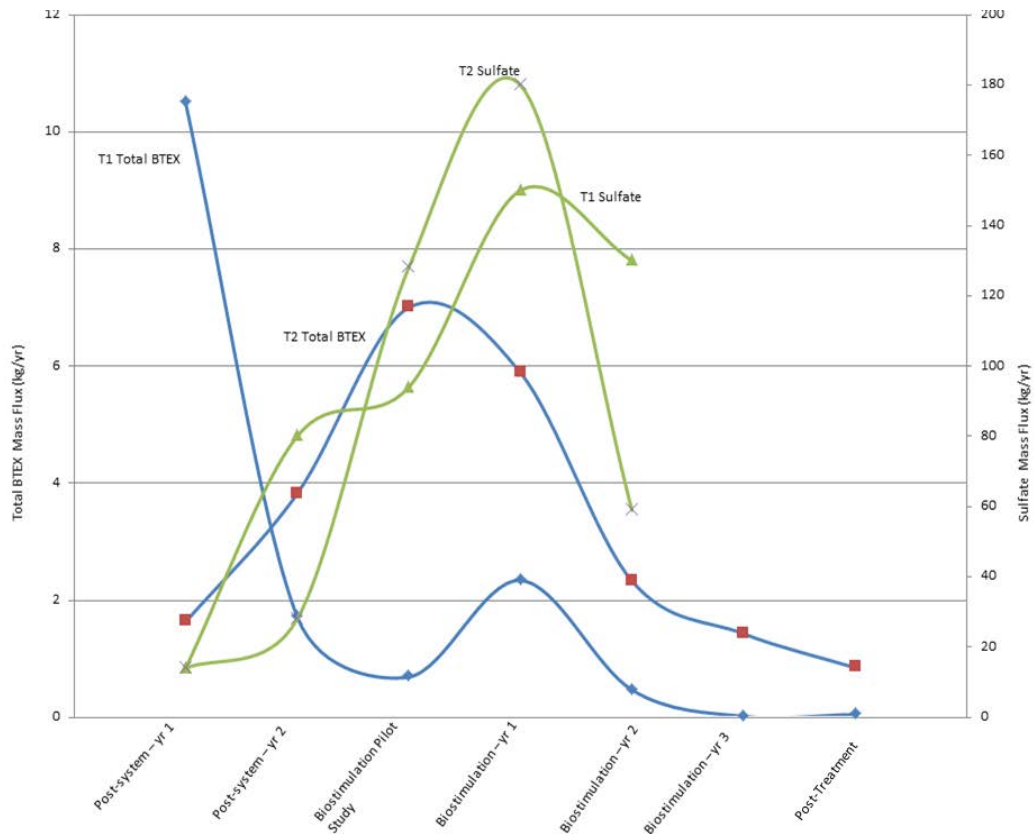
which data were available. These mass flux estimates were completed in accordance with Interstate Technology and Regulatory Council guidance (ITRC, 2010) using the Mass Flux Toolkit software developed by GSI for the Department of Defense (Farhat et al, 2006). Time-weighted annual averages of contaminant and electron acceptor concentration data were calculated for each transect well, then input into the model along with estimated hydrological parameters for each site (hydraulic conductivity, porosity, hydraulic gradient, and cross-sectional area estimates). Annual mass fluxes were then calculated through simple linear interpolation of the averaged well data at each transect.

Of the two study sites, Site 1 had a more extensive monitoring well network, allowing the selection of two well transects in the source zone (T1 and T2 on Figure 1) and two more downgradient of the source zone extending into the off-site contaminant plume (T3 and T4 on Figure 1). At Site 2, a single transect was formed in the source zone (T1, Figure 3), with a second transect formed within the downgradient contaminant plume (T2, Figure 3).

Figure 5 shows the annual average contaminant mass flux trends in the Site 1 source zone following the AS/SVE system shutdown, from the commencement of biostimulation treatments through treatment completion. Also shown are sulfate mass flux trends in the source area during biostimulation treatments.

In the period following AS/SVE system shutdown, contaminant concentration “bounce back” was apparent within the source area, as evidenced in T2 mass flux trends initially and T1 trends laterally. Prior to the biostimulation pilot study, contaminant mass flux in both transects was increasing. As sulfate mass flux rose above 130 kg/yr (286 pounds per year) and continued climbing in T2, the contaminant mass flux trend reversed, then continued to decline. Transect 2 followed a similar pattern as sulfate mass flux rose above 130 – 140 kg/yr (286 - 308 pounds per year).

*Anaerobic Biostimulation as a Secondary Treatment Option for Remediation*



*Figure 5.* Contaminant and electron acceptor mass flux through the Site 1 source zone. Contaminant mass flux is shown in blue (T1 and T2), while sulfate mass flux is shown in green (also T1 and T2). Left-side Y axis is scaled for total BTEX mass flux values, right-side Y axis is scaled for sulfate mass flux. All values are expressed in kg/yr, and were calculated through a two step process: time-weighted average annual concentrations were first calculated for each transect well, then mass flux was calculated for each transect through linear interpolation of the concentrations calculated in the first step.

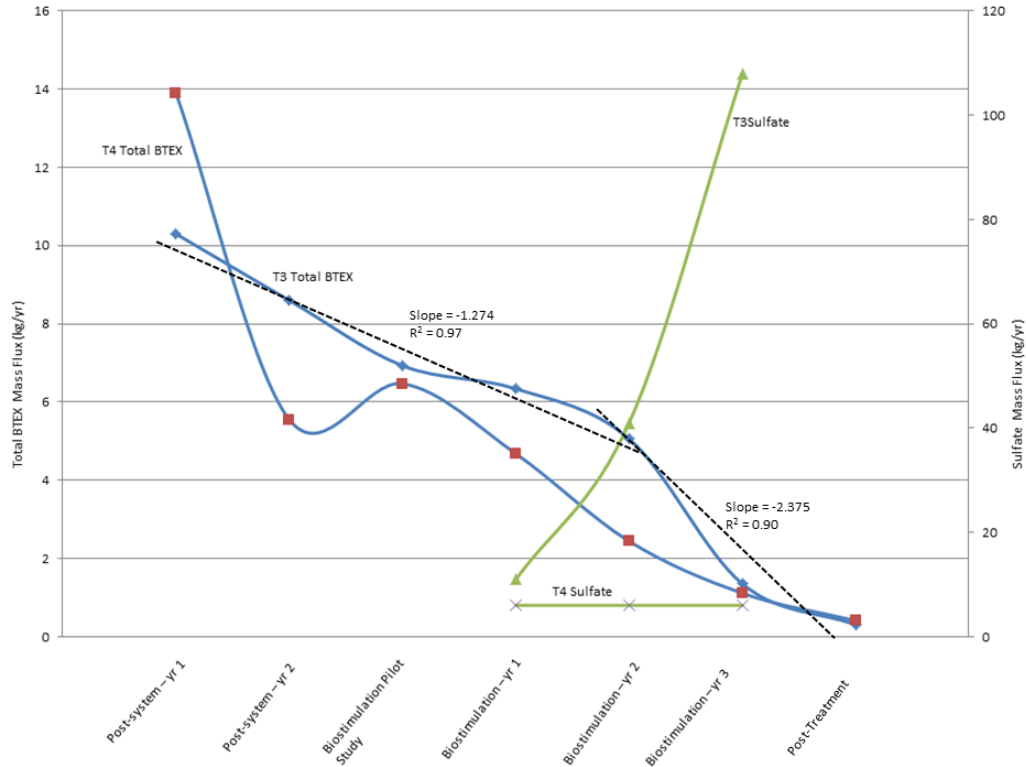


Figure 6. Contaminant and electron acceptor mass flux through the downgradient transects at Site 1. Contaminant mass flux is shown in blue (T3 and T4), while sulfate mass flux is shown in green (also T3 and T4). Left-side Y axis is scaled for total BTEX mass flux values, right-site Y axis is scaled for sulfate mass flux (kg/yr). Best-fit regression slopes are shown for T3 pre-biostimulation through treatment year 2, and treatment year 2 to post-treatment.

Results downgradient of the source zone at Site 1 were mixed: at T3 (located approximately 75 ft (24.6 meters) downgradient of the lower injection point) contaminant mass attenuated at a steady rate (-1.27 kg/yr, -2.8 pounds per year) throughout the post AS/SVE system period and during the first two years of biostimulation (Figure 6). Throughout this period, sulfate mass flux never reached 50 kg/yr (110 pounds per year). When T3 sulfate mass flux rose above 100 kg/yr (220 pounds per year) (biostimulation year 3 on Figure 6) the contaminant attenuation rate increased to -2.38 kg/yr (5.2 pounds per year). This

rate increase resulted in the achievement of reduced contaminant concentrations in the T3 area about 3 years earlier than anticipated based on the pre-treatment regression slope.

At transect T4, however, contaminant mass flux declined at a steady rate (-1.57 kg/yr, 3.5 pounds) throughout the biostimulation treatment period, while sulfate mass flux never changed (Figure 6). Sulfate added to the aquifer therefore never reached T4, and contaminant attenuation proceeded unaffected by the biostimulation efforts in this part of the contaminant plume.

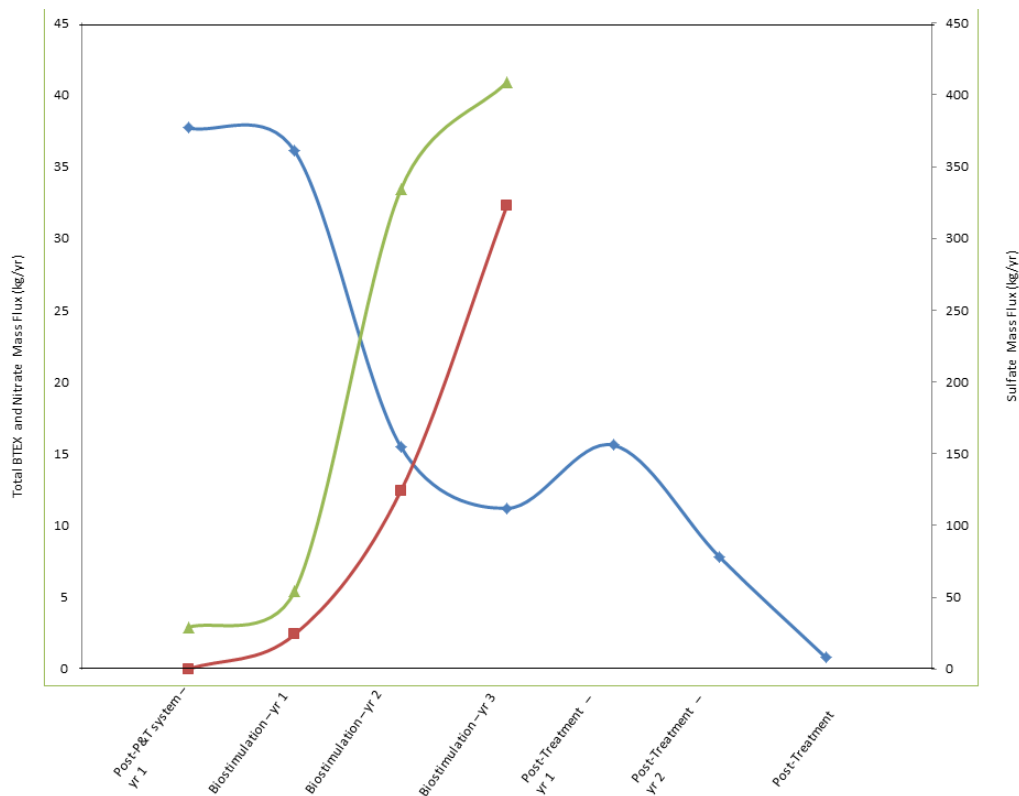


Figure 7. Contaminant and electron acceptor mass flux through the downgradient transect T2 at Site 2. Contaminant mass flux is shown in blue, nitrate mass flux in red, and sulfate mass flux in green. Left-side Y axis is scaled for total BTEX and nitrate mass flux values, right-side Y axis is scaled for sulfate mass flux.

At Site 2, source zone contaminant concentrations were low following the P&T system shut down, but off-site delineation had shown that elevated concentrations persisted downgradient of the source zone, beyond the P&T system radius of influence. Biostimulation treatment was therefore designed primarily to address

the off-site contaminant plume. This was accomplished by injecting biostimulants through the existing infiltration gallery (Figure 3).

During the biostimulation treatment period, contaminant mass flux in the source zone (transect T1, Figure 3) increased (0.1 kg/yr (0.2 pounds) to more than 3 kg/yr (6.6 pounds), data not shown), before steadily attenuating until transect wells reached acceptable concentrations. This was more likely related to “bounce back” from sorbed, untreated contaminant mass in the source zone than from the introduction of electron acceptors into the aquifer, since the biostimulants were introduced downgradient of the source area center of mass (Figure 3). Electron acceptor data was not collected in the T1 well transect during the biostimulation treatment period, but it is evident from contaminant mass flux during this period that biostimulation did not reduce source area mass.

The downgradient well transect at Site 2 (T2, Figure 3) was not installed prior to P&T system shut down, so data in this zone from the system treatment period does not exist. After the transect wells were installed, they exhibited a steady mass flux in excess of 35 kg/yr (77 pounds) during the post-P&T treatment period and the first year of biostimulation (Figure 7 above). During this period, sulfate and nitrate mass flux did not increase appreciably, remaining at or below 50 and 5 kg/yr (11 – 110 pounds/yr), respectively. During the second year of biostimulation, sulfate mass flux increased significantly, exceeding 300 kg/yr (660 pounds), as contaminant mass flux correspondingly decreased by approximately 50% (Figure 7). Nitrate mass flux also increased, but not as much (15 kg/yr, 33 pounds). Sulfate mass flux continued to increase for the remainder of the biostimulation treatment period, as contaminant mass flux decreased both during and post biostimulation treatment. Nitrate mass flux also continued to increase during the treatment period, but never exceeded 50 kg/yr (110 pounds).

## **5. CONCLUSIONS**

This study examined the efficacy of applying anaerobic biostimulation as a secondary treatment option following mass extraction from contaminant source areas at two sites impacted with gasoline-range hydrocarbons. At Site 1, the addition of sulfate as a terminal electron acceptor to stimulate microbiological activity under sulfate-reducing conditions was effective in reducing contaminant mass flux where sulfate mass fluxes of 130 – 140 kg/yr (286 – 308 pounds) or greater were sustained. Where sulfate mass flux did not exceed 50 kg/yr (110

pounds), contaminant biodegradation was not enhanced by the added sulfate, and contaminant mass attenuation rates didn't change.

Site 2 showed a similar pattern of contaminant mass flux reduction downgradient of the source area when sulfate mass flux exceeded 100 kg/yr (220 pounds). Nitrate was also added as an electron acceptor, but its mass flux, although increasing throughout the treatment period, never exceeded 15 kg/yr (33 pounds), which may not have been sufficient to significantly stimulate nitrate reducing microbiological activity. The source area of Site 2 remained unaffected by the biostimulation treatments; however, downgradient dissolved-phase concentrations were reduced to acceptable levels.

Overall, these results indicate that anaerobic biostimulation through the addition of sulfate as a terminal electron acceptor under sulfate-reducing conditions can be an effective method of reducing dissolved-phase petroleum hydrocarbon contaminant mass following more conventional source zone treatments, provided a critical sulfate mass flux is sustained in the treatment zone. Sulfate mass fluxes in excess of 100 kg/yr (220 pounds) were observed in the effective treatment areas of both sites, but it is not clear from these data that this mass flux represents a universal critical threshold; such a threshold is more likely site-specific and based on total contaminant mass and characterization.

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# GEOSTATISTICAL ANALYSIS OF HEAVY METAL POLLUTION IN SOILS FROM AN INDUSTRIAL COMPLEX IN KUMASI, GHANA

Kingsley Kodom<sup>§1</sup>, Kwasi Preko<sup>1</sup>, Daniel Boamah<sup>2</sup>

<sup>1</sup>*Department of Physics, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana;*

<sup>2</sup>*Geochemistry & Laboratories, Geological Survey Department, Accra, Ghana*

## ABSTRACT

This paper documents the extent of trace metal pollution in surface soils at the “Suame-Magazine” industrial area of Kumasi, and evaluates potential for associated industrial impacts. Concentrations of *Pb*, *Cu*, *Ni*, *Hg*, and *As* were estimated by ED-X-ray Fluorescence (XRF) analysis. Sampling sites were selected from areas reflecting a gradient of industrial activity. Surface soils (0-15cm) were collected and analysed. Mean concentration values of *Pb*, *Cu*, *Ni*, *Hg*, and *As* respectively ranged from, 133.7- 571.3 mgkg<sup>-1</sup>, 62.9 - 334.6 mgkg<sup>-1</sup>, 12.4 - 30.9 mgkg<sup>-1</sup>, 5.5 - 10.4 mgkg<sup>-1</sup> and 2.3 - 18.6 mgkg<sup>-1</sup>. Apart from *Ni* and *As*, all the trace metals exceeded respective threshold limit values (TLVs). Spatially, the distribution of metals demonstrates significant correlations along a gradient of industrial activity. Findings are of sufficient concern to warrant additional investigation and risk assessment.

**Keywords:** heavy metals, x-ray fluorescence (xrf), soil pollution, threshold limit values (tlvs), geostatistical analysis

<sup>§</sup>Corresponding author: Kingsley Kodom, Department of Physics, Kwame Nkrumah University of Science & Technology, Kumasi, Ghana; +233 24 4868221; kwakingko@yahoo.co.uk

## **1. INTRODUCTION**

### **1.1 Geostatistical Analysis**

Geostatistical techniques deal with the characterization of spatial attributes, employing primarily random models in a manner analogous to time series analysis of temporal data (Olea, 1999). It is therefore considered by Deutsch, 2002 as a study of phenomena that vary in space and/or time. Geostatistics (Korre *et al.*, 2002; Fierreira da Silva *et al.*, 2004; Hooker and Nathanail, 2006; Kumi-Boateng, 2007) have been used to investigate and map soil pollution by heavy metals. Geostatistical methods facilitate quantification of spatial features and enable spatial interpolation (Liu *et al.*, 2004; McGrath *et al.*, 2004). According to Goovaerts (2008), effective analysis of cause-effect relationships involving point source pollution and health outcomes requires measurements and/or models of chemical exposure at spatial and temporal scales coincident with health data. Geostatistical tools allow analysis at various spatial scales, and can incorporate field data and model output for evaluating cause and effect relationships.

### **1.2 Autocorrelation analysis**

Geostatistical analysis deals with spatially correlated data. Observations that are temporally or spatially independent can be evaluated by various parametric and nonparametric statistical methods. Data that manifest temporal or spatial dependence can be addressed by methods derived from regionalized variable analysis and applied time series techniques. The three major functions used in Geostatistics for describing spatial correlation of observations are the correlogram, the covariance, and the semivariogram (or Variogram). Autocorrelation analysis is normally employed to determine relationships between variables observed at different locations. The degree of linear association between pairs of values separated by a given distance is reflected in the autocorrelation coefficient (Nielsen and Ole Wendroth, 2003).

## **2. MATERIALS AND PROCEDURE**

### **2.1 Sampling and analyses**

The study area is “Suame Magazine” which is a cluster of metal work industries in Suame, a northern suburb of Kumasi in the Ashanti Region of Ghana. A total of 100 soil samples were collected from six sampling locations in the year 2009. Four of the areas are subject to high levels of industrial impact, the remaining two areas are residential communities. Forty (40) of the soil samples were selected for

spatial autocorrelation analyses. Kodom, 2011 and Kodom *et al.*, 2012 provide descriptive details of the study area, methods for soil sample collection, processing, characterization and analysis, and documents the distribution of soil samples. Sample preparation and elemental analysis methods are presented in, Buhrke *et al.*, 1998; Brouwer, 2006; Guthrie, 2007; Kodom *et al.*, 2010 and Kodom *et al.*, 2012.

## **2.2 Autocorrelation model**

An illustrative plot of autocorrelation coefficients (correlogram) versus separation distance (lag) between pairs of measurements is shown in Figure 1. In general, if points are not correlated, correlation coefficient values fall on the line parallel to the lag or separation distance axis. If however, the autocorrelogram is such that at separation distance of zero one obtains a value which decreases exponentially as the separation distance increases, then the physical values at the various points are correlated. The distance (correlation length)  $\lambda$ , beyond which the values obtained are random and without mutual correlation can be determined. For example if  $\lambda = 2.2$  m as shown in figure 1, then any separation distance from any particular chosen point greater than 2.2 m will give uncorrelated points.

Since the autocorrelation function (the correlogram) gives a primary diagnostic measure that indicates whether or not a spatial or temporal interpretation of on-site sampled data will effectively be achieved, if a correlation length can be

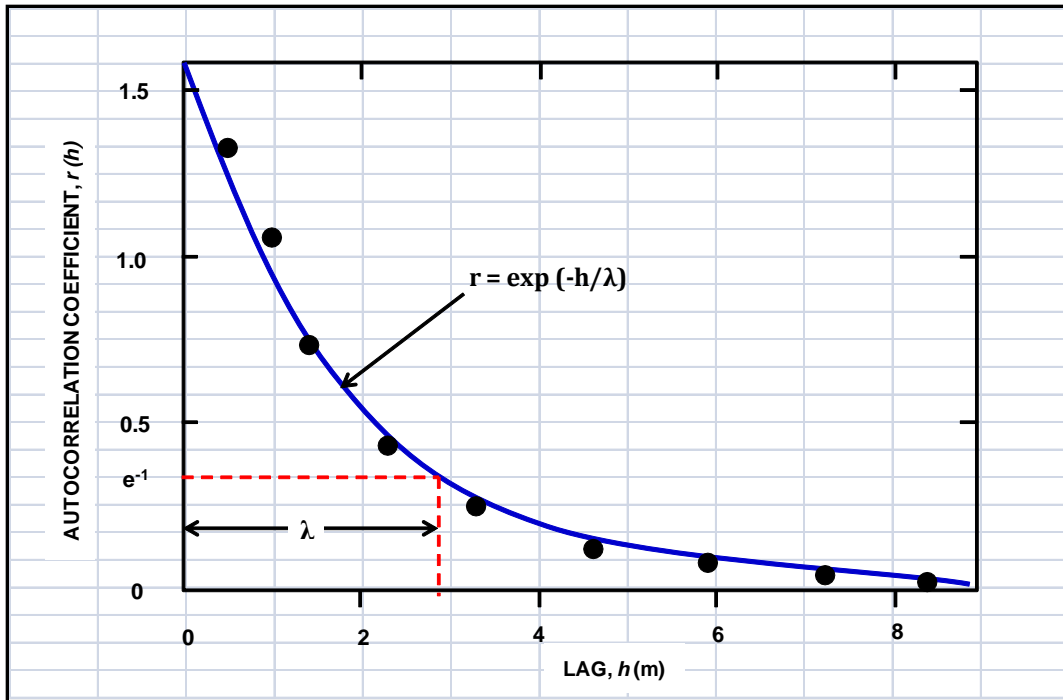


Figure 1. Autocorrelogram showing parameters that characterizes autocorrelation analysis.

determined, one is not limited to comparisons between treatment means. But also, according to Nielsen and Ole Wendroth, 2003, if data reflect sampling other underlying and spatially or temporally correlated properties, techniques such as cross correlation, semivariogram (or Variogram) analysis, and Kriging may be applied. Considering a set of number of measurements,  $n$  of a soil property,  $A_i$  taken at specific intervals along a transect at locations,  $x_i$ , the autocorrelation coefficients for pairs separated by a specified distance,  $h$  can be computed using the relation;

$$r(h) = \frac{cov[A_i(x), A_i(x + h)]}{\sqrt{var[A_i(x)]}\sqrt{var[A_i(x + h)]}} \quad [1]$$

Where  $A_1(x_1)$  and  $A_2(x_2)$  are the pair values of  $A$  at respective locations of  $x_1$  and  $x_2$ . Covariance and variance are designated by  $cov$  and  $var$  respectively. The covariance, according classical statistics, is the variance between two different kinds of observations which describes their joint variations about their respective means (Nielsen and Ole Wendroth, 2003). The variance is expressed as the square of the standard deviation. The distance between neighbours (pair values) is called

the lag  $h$ , while the distance over which a significant correlation exists is referred to as the autocorrelation length,  $\lambda$  (or autocorrelation range). For a particular transect, the autocorrelation length,  $\lambda$  is deduced from the relation;

$$r(h) = r_o \exp\left(-h/\lambda\right) \quad (2)$$

when  $r_o = 1$  at a lag distance of  $h = \lambda$  then,  $r(h)$  is reduced to  $e^{-1}$ . Therefore, the magnitude of  $\lambda$  is clearly defined in an autocorrelogram when  $r_o = 1$ . Consequently, the magnitude of the autocorrelation length,  $\lambda$  is expressed from the general relation;

$$\sum_{i=1}^{n-1} \left[ r_i(h) - \exp\left(h/\lambda\right) \right] = 0 \quad (3)$$

where  $n$  is the number of observations along a specified transect, with  $h$  and  $\lambda$  being the lag- distance and autocorrelation length respectively.

### **3. DATA AND ANALYSIS**

#### **3.1 Heavy Metal Concentration and Distribution**

Results obtained from the elemental analysis for the forty (40) soil samples collected from the six (6) different locations at the study area are shown in Table 1. From this elemental analysis, concentrations of Arsenic (As), Lead (Pb), Mercury (Hg), Nickel (Ni), Copper (Cu) were identified and quantified using XRF spectrometry. Each of these heavy metals was analyzed using descriptive statistical analysis, with the mean measured values compared with their respective threshold limit values, TLVs (as shown in Tables 2 & 3). Zone 4 results were used for the geostatistical analysis for spatial distribution along a specified 38m transect. Table 4 shows the computed autocorrelation coefficients obtained from the measured concentrations for Zone 4, which is the sample location with the highest number of samples.

*Geostatistical Analysis of Heavy Metal Pollution in Soils*

*Table 1. Mean Heavy Metal concentration values for all sampled locations.*

<b>Zone (Community)</b>	<b>No. of samples</b>	<b>As</b>	<b>Pb</b>	<b>Hg</b>	<b>Cu</b>	<b>Ni</b>
		<b>mgkg<sup>-1</sup></b>				
<b>Zone 4</b>	20	18.6	481.0	8.4	334.6	30.9
<b>Zone 7</b>	4	2.3	133.7	9.8	62.9	20.6
<b>Zone 12</b>	4	7.7	571.3	5.5	254.2	29.4
<b>Anomanye Junc. (Kwantwima)</b>	4	5.3	380.5	10.4	75.5	12.4
<b>(Abusuakrowa)</b>	4	1.4	43.7	3.3	19.9	9.7
<b>(Abusuakrowa)</b>	4	1.9	23.3	3.5	19.0	10.0

*Table 2. Zone 4 summary results of descriptive statistical analysis of selected heavy metal concentrations with TLVs.*

<b>Heavy metal</b>	<b>Min</b>	<b>Max</b>	<b>SD (<math>\sigma</math>)</b>	<b><math>\lambda</math></b>	<b>Mean Value</b>	<b>TLV</b>
		<b>(mgkg<sup>-1</sup>)</b>	<b>(mgkg<sup>-1</sup>)</b>	<b>(m)</b>	<b>(mgkg<sup>-1</sup>)</b>	<b>(mgkg<sup>-1</sup>)</b>
As	1.5	33.6	8.16	1.22	18.6	20
Pb	126.9	760.8	154.35	1.04	481.0	100
Hg	4.3	15.4	2.89	0.90	8.4	1
Ni	18.8	43.3	6.60	1.08	30.9	50
Cu	66.5	589.8	145.30	1.52	334.6	100

TLV = Threshold Limit Value. SD ( $\sigma$ ) = standard deviation.  $\lambda$  = Autocorrelation length.  
Min. = Minimum concentration value. Max. = maximum concentration value.

### **3.2 The Spatial Distribution**

The autocorrelogram, the plot of autocorrelation coefficient against lag (the distance between pairs of measurement), is shown in Figure 2 through figure 6 for each of the heavy metals (Pb, Cu, Ni, Hg, and As).

*Geostatistical Analysis of Heavy Metal Pollution in Soils*

*Table 3.* Autocorrelation coefficients calculated from the concentration values of Zone 4. (n=20)

<b>Lag</b>	<b>Pb</b>	<b>Cu</b>	<b>Ni</b>	<b>Hg</b>	<b>As</b>
2	-0.0077	0.04451	0.0022	-0.0394	0.06865
4	-0.0262	0.08917	0.03684	-0.2858	0.045
6	-0.1308	0.01554	-0.0967	0.52848	-0.2131
8	-0.2204	-0.4285	-0.1771	-0.1051	-0.418
10	0.27593	0.07716	-0.0895	-0.4738	0.06742
12	-0.2475	-0.1988	-0.117	0.03706	0.09722
14	-0.6169	-0.3581	-0.0423	-0.0242	0.46779
16	-0.3516	-0.1717	-0.2595	-0.265	-0.4117
18	-0.2513	-0.29	-0.1883	-0.1896	-0.1861
20	0.33561	-0.2519	-0.0578	0.29661	-0.6888
22	0.48894	0.12215	0.31387	0.436	-0.3674
24	0.23079	0.08034	-0.4459	-0.0941	0.3406
26	0.15727	0.34301	0.57776	0.33681	-0.0088
28	-0.4445	-0.8748	0.42881	0.60082	0.48264
30	0.45157	0.80426	-0.8116	-0.7429	-0.1987
32	0.35189	-0.5997	-0.2978	0.41242	-0.5501

*Table 4.* Summary results of descriptive statistical analysis of selected measured heavy metal Concentrations for Zone 4.

<b>Element</b>	<b><math>\sigma</math></b>	<b>Variance</b>	<b>CV</b>	<b>95 %</b>	<b><math>\lambda</math></b>	<b>Mean</b>	<b>TLV</b>	<b>Extent of</b>
			<b>%</b>	<b>CI</b>	<b>m</b>	<b>mgkg<sup>-1</sup></b>		<b>pollution</b>
								<b>%</b>
As <sup>(1)</sup>	8.16	66.64	44.01	0.171	1.22	19	20	5 <sup>b</sup>
Pb <sup>(2)</sup>	154.35	23822.95	32.09	0.166	1.04	481	100	79.2
Hg <sup>(3)</sup>	2.89	8.34	34.52	0.187	0.90	8	1	87.9
Ni <sup>(53)</sup>	6.60	43.59	21.38	0.162	1.08	31	50	61.3 <sup>b</sup>
Cu <sup>(128)</sup>	145.30	21112.56	43.43	0.192	1.52	335	100	70.1

Elements are arranged according to ATSDR order of toxicity (superscript indicates order)

\*For hexavalent chromium Cr <sup>6+</sup> CV = Coefficients of variation. CI = confidence interval

<sup>b</sup>against value means, the mean concentration value is below the TLV

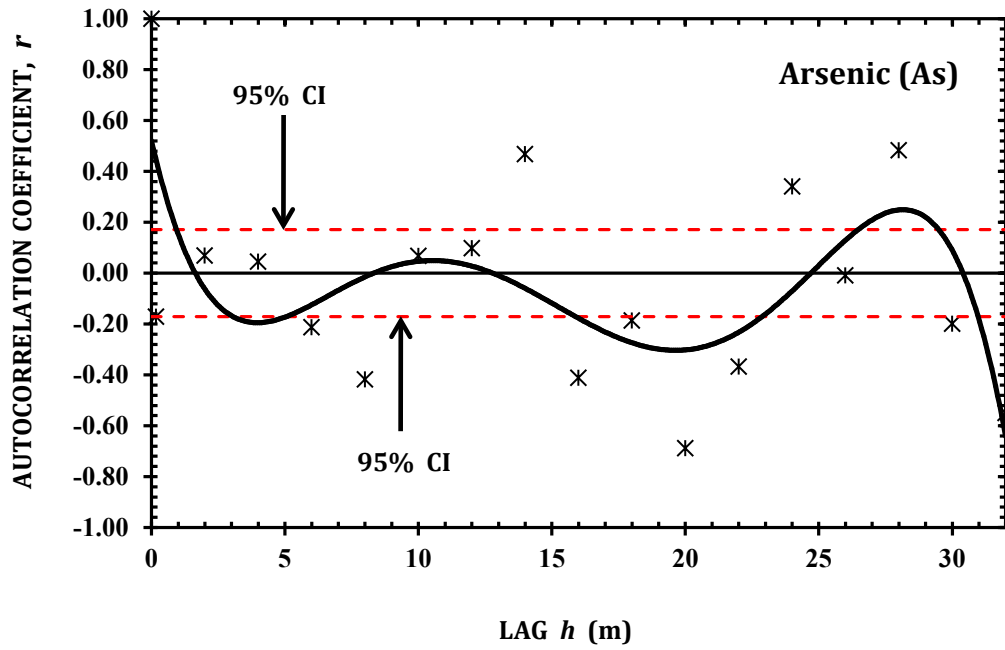


Figure 2. Autocorrelogram for the soil heavy metal concentration of Arsenic.

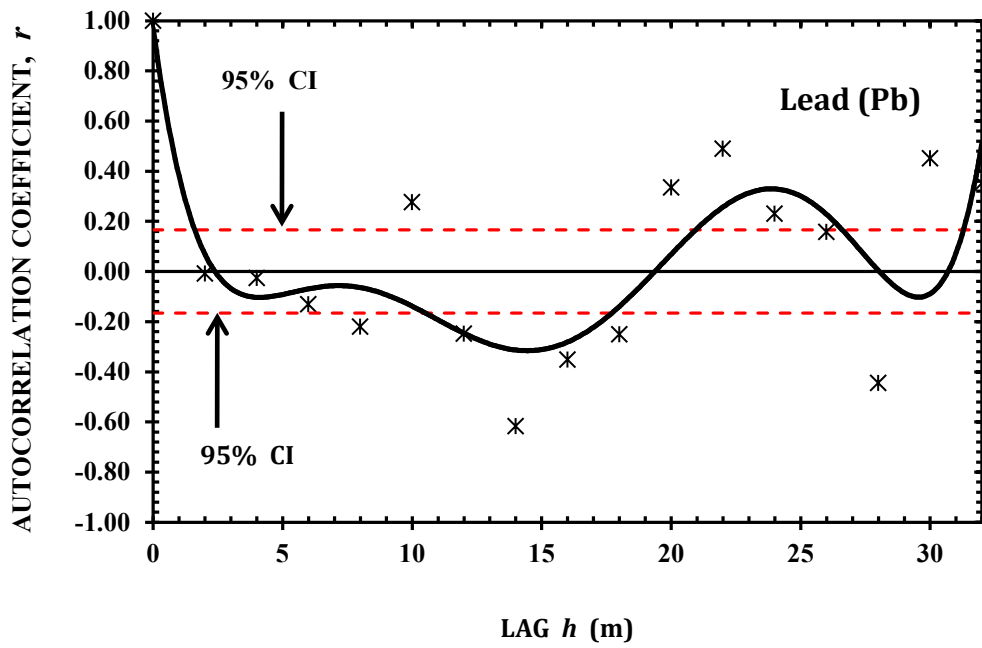


Figure 3. Autocorrelogram for the soil heavy metal concentration of Lead.



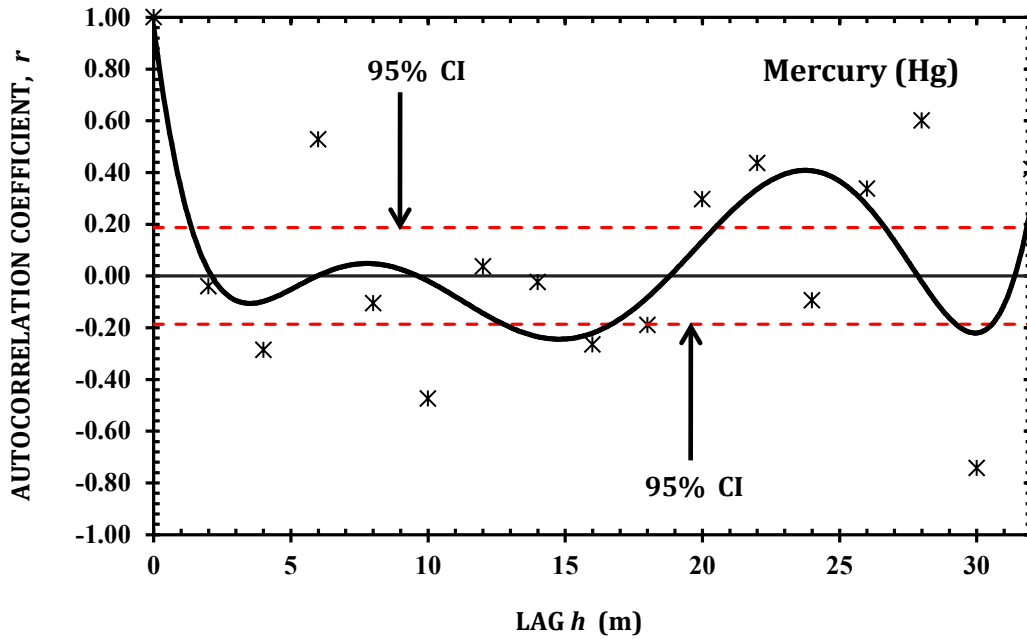


Figure 4. Autocorrelogram for the soil heavy metal concentration of Mercury.

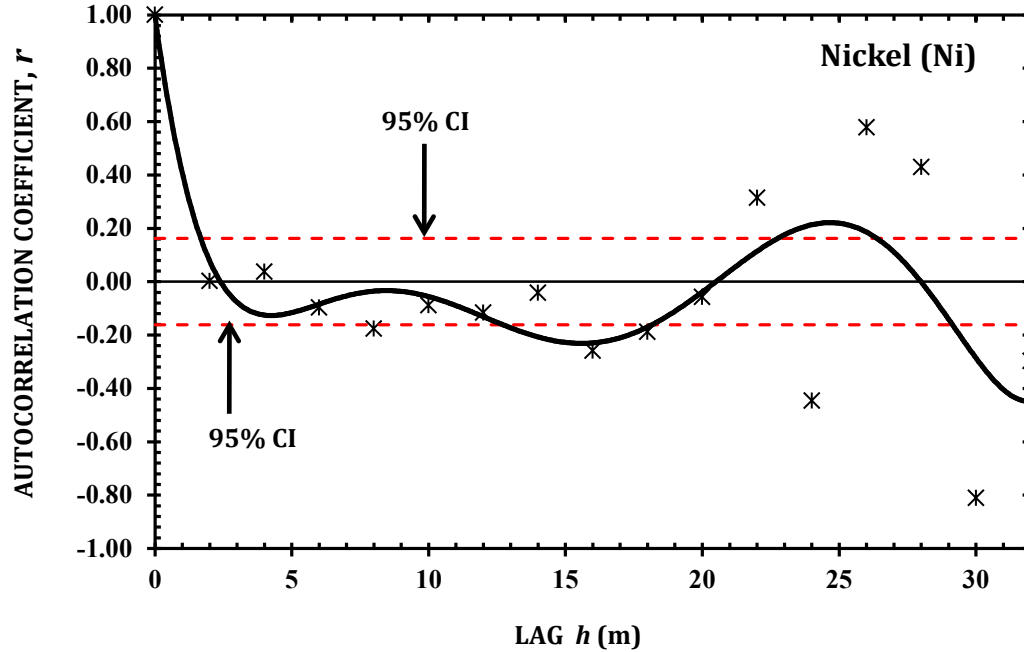


Figure 5. Autocorrelogram for the soil heavy metal concentration of Nickel.

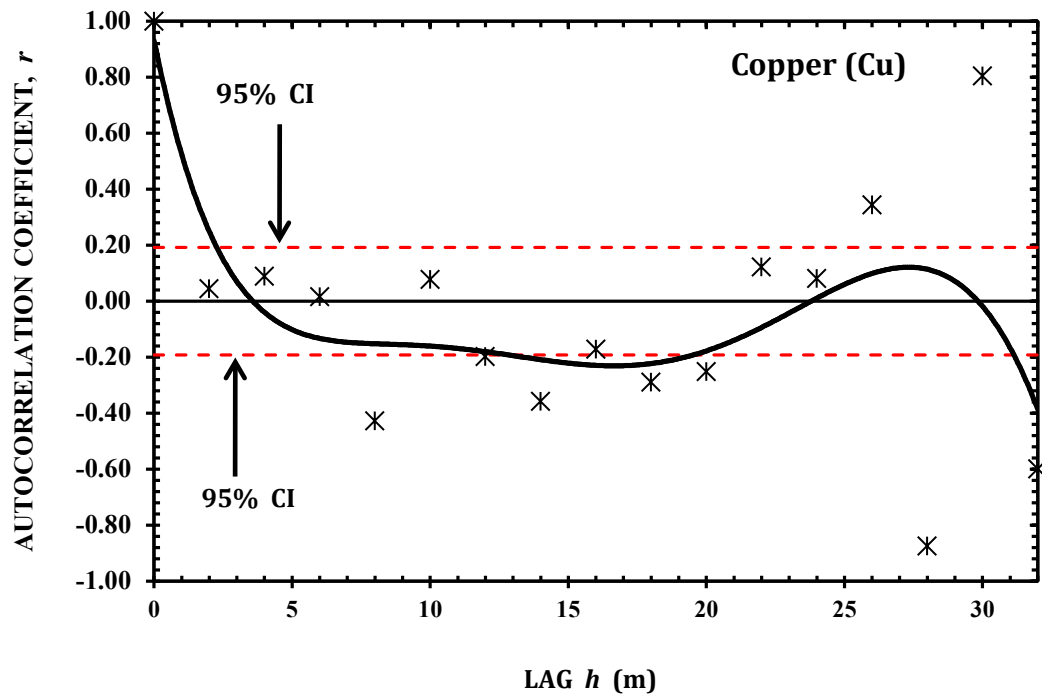


Figure 6. Autocorrelogram for the soil heavy metal concentration of Copper.

### 3.2.1 Arsenic (As)

Spatially, the autocorrelogram in Figure 2 for arsenic has few values of autocorrelation coefficients  $r$  scattered about the horizontal axis and as described by equation 2, the value of  $\lambda$  was calculated to be 1.22 m which is greater than one lag. For any separation greater than 1.22 m with respect to any particular point as a reference, the data will be found to be random and there is no correlation between them. Data points within the 95% confidence interval are insignificant since data points are randomly distributed within and outside the 95% CI, with the majority found outside the confidence interval. The autocorrelation coefficient has an initial value of approximately 0.5 and it decreases gradually to cut the lag axis. It shows that indeed, there is correlation between the data points. Zone 4 recorded the highest mean arsenic concentration value of  $18.6 \text{ mgkg}^{-1}$ . Even though the mean concentration value for arsenic does not exceed the threshold limit value (TLV), most data points are above the TLV as shown in the plots of concentration against separation distance according to Kodom *et al.*, 2012.

Arsenic is a common cause of acute heavy metal poisoning (Lenntech, 2008), making it a potential threat to human health, animals, plants, and aquatic life.

### **3.2.2 Lead (Pb)**

Figure 3 shows that there is correlation between data points with a correlation length of 1.04 m. This means that beyond 1.04 m the data points are random and become uncorrelated. Like arsenic, most of the data points are outside the 95% CI. This shows a high level of significant correlation between the data points. As expected, the autocorrelation coefficient is initially a large value, and this decreases steadily to cut the lag axis. This confirms the existence of correlation between Pb data points. Considering the entire study area, Zone 4 recorded the second highest Pb concentration value of  $481.0 \text{ mgkg}^{-1}$  (Table 1), which is attributed to industrial activities and improper waste disposal from smelting plants and car batteries. The mean concentration value of Pb at this Zone exceeds the TLV (Table 2).

According to ATSDR 2007, Pb is an important toxic heavy metal (see table 4). Globally, Pb pollution accounts for many cases of paediatric heavy metal poisoning.

### **3.2.3 Mercury (Hg)**

From the autocorrelogram of Hg (Figure 4), most of the data points are outside the 95% CI. The autocorrelation length,  $\lambda$  was determined to be 0.90 m which is less than one lag. This suggests that, with respect to any particular point as a reference, for any separation greater than 0.9 m, the data points will be found to be uncorrelated.

Considering a TLV of  $1 \text{ mgkg}^{-1}$  for Hg, concentration values obtained from all locations exceed, with Zone 4 recording a value of  $8.4 \text{ mgkg}^{-1}$  (see Table 1). These recorded values constitute a high level of pollution associated with industrial activity, and exceed natural background levels.

### **3.2.4 Nickel (Ni)**

The autocorrelogram of Ni (Figure 5) indicates that, after the high initial autocorrelation coefficient value of one (1), almost all the data points are within the 95% CI. Data points within the 95% CI are significant and considered to be zero, outliers indicate some level of correlation. The autocorrelation length,  $\lambda$  was determined to be 1.08 m and beyond this length ( $\lambda$ ), no significant correlation exists.

All the observations in Zone 4 registered concentration values below the TLV (see Tables 1 & 2). However, all the values are above the “normal” level of 2-5 mg kg<sup>-1</sup> proposed by Kloke, 1980.

### **3.2.5 Copper (Cu)**

From Figure 6, most data points are found within the 95% CI, and a minority are outliers. The autocorrelation coefficient has an initial expected value of one (1) and this gradually decreases to cut the lag axis with increase in lag. The autocorrelation length  $\lambda$  was calculated to be 1.04 m. This means that beyond a distance of 1.04 m, the data points are random and are not correlated. Since few of the data points are outside the 95% CI, the correlation between the data points, is comparatively weak.

Most locations recorded concentration values below the TLV, although zones 4 and 12 (see Tables 1, 2 & 4) registered high concentration values. These high values are due to smelting operations and poor management of metallurgical wastes.

## **4. CONCLUSION**

High concentration levels of *Pb*, *Cu*, and *Hg* are a result of heavy metallurgical and industrial activities in the study area. *As* and *Ni* concentrations were generally below threshold limits. Samples from the residential communities showed similar patterns of metal distribution according to Kodom *et al.*, 2012.

Spatially, the distributions of the various metals indicate a concentration gradient reflecting site-specific intensity of industrial activity. Since areas of high industrial activities recorded high concentration values, it is recommended that research should be extended to cover the entire industrial complex to further monitor and delineate other pollution sources. In addition, sampling should be conducted at depth within the soil column to test for potential deep soil and/or ground water contamination. Such a sampling program should be followed by risk assessments to estimate potential threats to human health and ecosystem quality.

## **5. ACKNOWLEDGEMENT**

This study was partly supported by Geochemistry and Laboratories at Geological Survey Department, Accra, Ghana. The authors wish to acknowledge the technical assistance with sampling and analysis of Mr. Emmanuel Effum and Mr. Edwin Bawa. The first author further expresses in gratitude to his lovely uncle,

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Mr. Kwasi Boahen, for his invaluable financial and moral support during the preparation of this paper.

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# REMEDICATION OF MTBE & TBA IN GROUNDWATER USING A FLUIDIZED BED BIOREACTOR

Joseph E. O'Connell<sup>§</sup>

25371 Commercentre Drive, Suite 250, Lake Forest, CA 92630

## ABSTRACT

Biological fluidized bed reactors are being used at more than 30 sites around the country to remove the fuel oxygenates tertiary-butyl alcohol (TBA) and methyl tertiary-butyl ether (MTBE) from groundwater and convert them to carbon dioxide and water. Although most of the systems operate in California, where rainfall is scant and groundwater is at a premium, the bioreactors have been adapted for use in a variety of conditions around the country. In New Hampshire accommodation was made for freeze protection and for iron and manganese found in the incoming water. Near the end of the project treated water was re-injected up-gradient of the plume, greatly speeding up the remediation process. A bioreactor operated at a service station site in South Florida for about one and a half years until the site was cleaned up. Treated water was also re-injected at the Florida site up-gradient of the source. At a site in the Los Angeles basin, two bioreactors were required to accommodate the high volume of water needing to be processed. Here pH adjustment was required when exposure to air elevated the pH. A new site in Auburn New Hampshire is being set up to re-inject treated water from the outset, thus promoting an *in-situ/ex-situ* operation and speeding up the final clean-up. The bioreactor being used here is portable and can be trailered from site to site. In many cases, bioreactors have been picked up and moved to another site when remediation was complete. This paper describes the bioreactor operating principles, process, equipment, and field experiences. Analytical data for the water being treated at the various sites are presented and capital and operating costs are reviewed.

**Keywords:** Bioremediation, TBA, MTBE, groundwater, fuel oxygenates

<sup>§</sup>Corresponding Author: Joseph O'Connell, Sc.D., P.E., Cardno ERI, 25371 Commercentre Drive, Suite 250, Lake Forest, CA 92630; (949) 457-8950; joe.oconnell@cardno.com



## **1. INTRODUCTION**

Cardno ERI (formerly Environmental Resolutions, Inc.), in conjunction with Drs. Kate Scow, Edward Schroeder, and Daniel Chang at the University of California at Davis (UC Davis), has developed a biological treatment process for removing fuel oxygenates, such as methyl tertiary butyl ether (MTBE) and tertiary butyl alcohol (TBA), from water. The original source of the biomass was a vapor-phase biofilter located at the Joint Water Pollution Control Plant in Carson, California, used in 1997 to remove volatile organic compounds (VOCs) and odors in the off-gas from a sewage treatment plant. After about 370 days, the biomass adapted to consume MTBE. The culture was harvested in 1998 and further developed by UC Davis, who isolated the active microbes and named them *Methylobium petroleophilum*, or PM-1.

UC Davis and Cardno ERI each set up trickling bed filters, all of which developed a problem with solids build up. Cardno ERI then began the development of a high surface area fluidized bed bioreactor in Orange County, California. Since the first prototype began operating in 2000 at a site in Palo Alto, California, Cardno ERI's fluidized bed bioreactors have been put into operation at more than 30 other sites in California, New Hampshire, Maryland, and Florida.

Although MTBE is no longer used in gasoline, past fuel releases have introduced enough MTBE and TBA into the subsurface to affect groundwater quality for years to come. Bioreactors offer a green solution that permanently destroys these compounds, converting them to carbon dioxide and water, rather than merely transferring them to another medium, such as air or granular activated carbon (GAC).

## **2. MATERIAL AND METHODS**

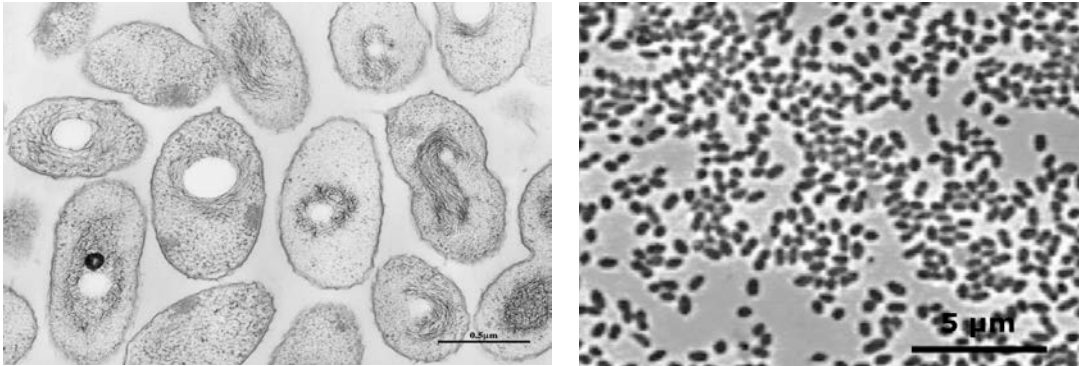
### **2.1 Fluidized Bed Bioreactor Principles**

This bioreactor is a two-phase system (solid sand and liquid water, no gas) with a recirculating water stream. The biomass is confined to the reaction vessel by its adherence to fine sand. The biomass is distributed within the bioreactor by fluidization with an upward flow of recirculating water. The water passes upward through the sand where the biomass removes VOCs as the water passes by. The reaction is rapid and thorough. During the 15 minutes the solution resides in the reactor the MTBE and TBA are reacted to yield exit concentrations of ND<5 micro grams per liter ( $\mu\text{g/L}$ ).

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Experience to date indicates that the bioreactor operates best between 10°C and 35°C (50°F and 95°F) at a partial pressure of oxygen above 0.21 atmospheres. The bioreactor is capable of complete reaction in one pass through the fluidized bed as long as the dissolved oxygen (DO) is not consumed completely and sufficient nutrients, such as nitrogen, phosphorus, and potassium (N, P, and K) are available. In addition, pH needs to be in the range of 6.5 to 8.5 standard units.

PM-1 is a naturally occurring bacterium, or consortium of bacteria, that has been identified at locations in California, New York, and Europe. It has been found at both contaminated and uncontaminated sites. PM-1 is characterized by a very slow growth rate. Its doubling time is on the order of weeks rather than on the order of hours, as is typical for many other common aerobic bacteria. The slow growth results in a low yield, meaning very little biomass is produced per pound of organic material consumed. This is advantageous in that excess biomass (sludge) requiring removal from the system is rarely generated. On the other hand, it means that a bioreactor should be started up with a large amount of biomass to avoid delays while waiting for the population to grow. Generally, a bioreactor is started up with half the biomass that will ultimately be needed so that within several weeks the population will be sufficiently large. PM-1 consumes TBA, ethers, and petroleum hydrocarbons as food, breathing oxygen in the process. Photomicrographs of PM-1 are included in Figure 1.



*Figure 1.* Photomicrographs of PM-1.

The bacterial consortium, while capable of consuming fuel oxygenates, actually prefers to dine on BTEX and other petroleum hydrocarbons. If high concentrations of petroleum hydrocarbons are present in the water being treated, petroleum hydrocarbon degraders that may be present will tend to out-compete

the fuel oxygenate degraders, and the bioreactor may lose the ability to degrade MTBE and TBA. If the total concentration of BTEX and other petroleum hydrocarbons exceeds half the total fuel oxygenates concentration, pretreatment using GAC or air stripping is generally recommended ahead of the bioreactor for removal of these more easily metabolized compounds. The fuel oxygenates will break through the GAC or air stripping unit and enter the bioreactor for treatment. This strategy keeps the bacteria focused on consuming the fuel oxygenates.

## 2.2 Bioreactor Operation

The key to bioreactor sizing and operation is contaminant mass loading, which is the product of the flow rate of groundwater from the site recovery wells times the average total VOC concentration in the groundwater from the site recovery wells. As an example, bioreactor operation for a system to process 10 gallons per minute (gpm) containing 5,000 parts per billion (ppb) or micrograms per liter ( $\mu\text{g/L}$ ) of MTBE and 5,000  $\mu\text{g/L}$  of TBA (10,000  $\mu\text{g/L}$  total) is shown schematically in Figure 2. The mass loading in this example is 10 gpm times 10,000  $\mu\text{g/L}$ , or 100,000 gpm- $\mu\text{g/L}$  (this is the equivalent to 1.3 pounds/day). Alternatively, the reactor could be fed 1 gpm at a concentration of 100,000  $\mu\text{g/L}$ .

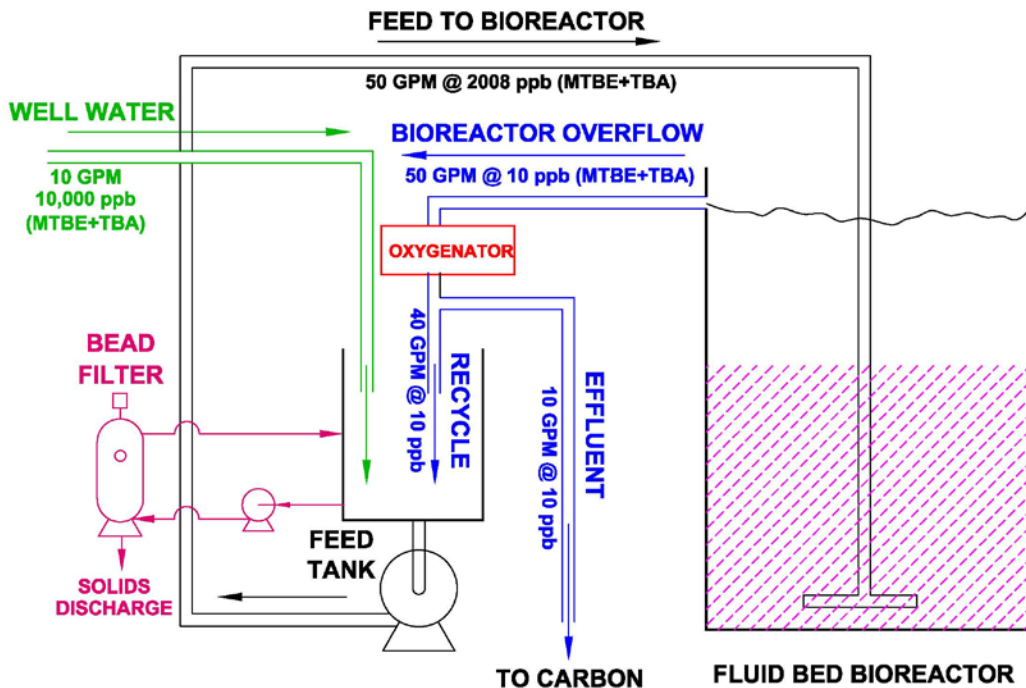


Figure 2. Schematic Flow Diagram.

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The constant recirculation rate for this bioreactor to keep the sand medium fluidized is 50 gpm. Well water enters the feed tank where it is diluted with 40 gpm of clean treated water to achieve a diluted MTBE/TBA concentration of 2,008 µg/L and a DO of about eight mg/L. Fifty gpm of the mixture of influent and treated water are pumped into the bottom of the fluidized bed. After spending 15 minutes in the bioreactor, water exiting the top of the bioreactor has low DO and non-detectable MTBE/TBA (<10 µg/L). The treated water passes through an oxygenator where it is replenished with DO. An exit flow of 10 gpm leaves 40 gpm to dilute the incoming 10 gpm stream and cycle through the fluidized bed.

Higher concentrations of MTBE/TBA can be handled by reducing the influent flow rate from the recovery wells so the mass loading on the system is maintained at 100,000 gpm-µg/L. Another alternative would be to add an oxygen booster. With increased oxygenation from an oxygen booster, the mass loading can be raised to 240,000 gpm-µg/L (three pounds per day).

Treated effluent can be discharged back to groundwater, surface water, or a publicly owned treatment works (POTW). The concentrations of MTBE and TBA exiting the fluidized bed are typically below the detection limit of the laboratory method being used. For most Regional Water Quality Control Boards in California, a detection of 10 µg/L is satisfactory. However, some require a limit of less than 5 µg/L.

### **2.3 Solids Removal**

When water is oxygenated, sticky solids can form from the interaction of the biomass with precipitates formed from dissolved iron, manganese, and/or hardness. A filter containing spherical polyethylene beads is used to remove solids from the system (see Schematic Flow Diagram - Figure 2). A separate recycle loop is passed through the filter in up-flow mode until enough solids accumulate on the filter beads to require a backwash. The filter is then isolated with a three-way valve and a motorized agitator is activated to knock the accumulated material off of the beads. When the agitation stops, the beads rise and the solids settle to the bottom of the filter chamber where they are drawn off as a slurry. About five to seven gallons of slurry are accumulated for each backwash. Backwashing frequency varies with the solids loading, but most systems require backwashing less than once per week.

## **2.4 Bioreactor Size and Application**

Either of two off-the-shelf Cardno ERI bioreactors (a five-foot diameter unit or a two-foot diameter unit) can accommodate a wide range of mass loadings. For a custom design, the sizing is changed by altering the footprint of the bioreactor vessel, leaving the height relatively constant. The recirculation flow rate is then adjusted to maintain bed fluidization and a hydraulic residence time of approximately 15 minutes.

The five-foot diameter bioreactor fits on a 10-foot by six-foot skid and stands about 11.5 feet tall. The empty weight is about 3,800 pounds and, when loaded with sand and water, the total weight is about 18,000 pounds. This bioreactor is designed to metabolize about 1.3 pounds of VOCs per day (or 100,000 gpm- $\mu$ g/L). The mass loading can be increased to three pounds per day with an oxygen booster.

The two-foot diameter bioreactor fits on a four-foot by four-foot skid and stands about 10.5 feet tall. The empty weight is about 400 pounds. Sand and water bring the total weight to about 3,000 pounds. This bioreactor is designed to metabolize 0.2 pounds of VOCs per day (or 20,000 gpm- $\mu$ g/L). The mass loading can be increased to 0.4 pounds per day with an oxygen booster.

Both of these bioreactors are commercially available and can be delivered and set up virtually anywhere. Clearly some precautions must be taken when the unit is to be operated in extremely cold or hot climates to keep the biomass in the optimal temperature range of 50 to 95°F (10 to 35°C). Once the biomass is established, it generally self regulates the pH at 7.5 + 0.5 by generating carbon dioxide, which produces a bicarbonate buffer. At several sites, this was not the case and the pH fell below 6.5 or rose above 8.5. An inexpensive automatic pH adjustment system was added to regulate the pH by adding either acid or base as needed. Based on performance of the bioreactor in New Hampshire, iron and manganese do not appear to have any deleterious effect on the performance of the biomass; however, these metals exert an oxygen demand. Copper is a known biocide and should generally be avoided.

## **3. RESULTS**

### **3.1 Bioreactor Performance in the Field**

Cardno ERI fluidized bed bioreactors have operated at fuel spill sites in California, New Hampshire, Maryland, and Florida. Some of these bioreactors are discussed below.

### **3.1.1 Palo Alto, California**

At this site, MTBE in groundwater was originally being treated with GAC and was then discharged to a POTW via a sanitary sewer. Initially, there was no TBA restriction on the discharge, so TBA values were not measured at the outset. The bioreactor was started up in early August 2000 as a side stream treating a portion of the 20 gpm being processed by the GAC system. The first effluent sample, collected on August 9<sup>th</sup>, indicated complete reaction. The incomplete reaction of August 29<sup>th</sup> was due to a depletion of essential nutrients, which was corrected by supplementing with N, P, and K on a regular basis. The incomplete reaction of September 22<sup>nd</sup> was due to overfeeding (164,000 gpm- $\mu$ g/L, well above the 100,000 gpm- $\mu$ g/L design mass loading). This was cured by adding an oxygen booster.

On November 9<sup>th</sup>, with the oxygen booster in operation, the loading was 204,000 gpm- $\mu$ g/L and reaction was complete for both MTBE and TBA. The oxygen booster was turned off in February 2001 as concentrations appeared to be dropping, and then on February 14<sup>th</sup>, a surge in concentration required the booster to be turned back on. The booster was restarted in mid-February and ran until it was turned off in September 2001. With the exception of May 8, 2002, TBA was not detected. Over 26 million gallons of water were treated by this bioreactor in the three years it was used. Carbon was not changed out in the last 1.5 years of operation.

The concentrations of oxygenates in site groundwater seemed to rise and fall until the tank tops and dispenser piping were exposed and repaired in January 2003. Vapor leaks were found and corrected. After those repairs, the concentrations of oxygenates dropped steadily until they reached target levels agreed to by the regulating authorities. The bioreactor was moved to another site in September of 2003. Bioreactor treatment was followed by a period of pump and treat with GAC only, and then a period of monitored natural attenuation (MNA), which is on-going.

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Data from the operation at Palo Alto, Cardno ERI's first full-scale fluidized bed bioreactor, are shown in Table 1.

*Table 1. Performance Data for Five-Foot Fluidized Bed Bioreactor – Palo Alto, California. Demonstration of Basic Bioreactor Principles.*

Date	Flow Rate (gpm)	MTBE Influent (µg/L)	MTBE Effluent (µg/L)	TBA Influent (µg/L)	TBA Effluent (µg/L)	
9-Aug-00	10	6,200	ND<2.5	NA	NA	
29-Aug-00	10	8,000	2,330			N, P, & K needed
19-Sep-00	10	7,600	ND<2.5			
22-Sep-00	12	13,700	30.6			Loading above 100,000 gpm-ppm
26-Oct-00	17	9,670	6.1	980	ND<4	
9-Nov-00	17	12,000	ND<0.5	300	ND<5	
21-Nov-00	17	5,300	1.2	120	ND<5	
20-Dec-00	19	3,600	0.7	260	ND<5	
8-Feb-01	19	4,300	ND<2			Removed O <sub>2</sub> booster
14-Feb-01	19	7,600	300			Restarted booster
22-Feb-01	19	4,700	ND<2			
7-Sep-01	16	2,300	ND<2	1,000	ND<5	
4-Oct-01	15	1,300	ND<2	740	ND<5	
6-Nov-01	14	1,300	ND<2	530	ND<5	
6-Dec-01	17	1,100	ND<2	1,100	ND<5	
8-May-02	15	710	6	2,100	15	
7-Aug-02	15	670	3.6	1,100	ND<20	
4-Sep-02	15	3,600	1.1	1,500	ND<20	Suspicious rise in concentration
2-Oct-02	15	4,200	0.8	1,100	ND<5	
6-Nov-02	15	900	1	2,000	ND<5	
4-Mar-03	12	120	ND<0.5	1100	ND<5	
8-May-03	10	49	ND<0.5	570	ND<5	
6-Aug-03	11	23	ND<0.5	150	ND<5	

NA=not analyzed

### 3.1.2 Milpitas, California

The initial design called for a system to treat 10 gpm with a concentration (MTBE+TBA) of 10,000 µg/L – (100,000 gpm-ppb). In this case, the bioreactor turned out to be considerably oversized for the loading actually produced from the recovery wells. The highest loading occurred on February 22, 2002 and was two gpm with 787 µg/L MTBE plus 194 µg/L TBA, which is just under 2,000 gpm-ppb. The bioreactor had difficulty sustaining a biomass at 2% of design loading and a supplemental feed was required. A small amount of MTBE was added to the nutrient feed drum to maintain a concentration in the bioreactor of 100 µg/L.

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The bioreactor was employed to meet the five µg/L limit for discharge of TBA to the storm water system in Milpitas. The data shows that these limits were met in the effluent from the bioreactor in each case. This case points out the importance of carrying out a sufficiently long pumping test (e.g., at least 24 hours long in a sandy environment, and longer in a less permeable setting) to properly estimate the mass loading from the site based on approximate steady-state flow rate contaminant concentrations determined after a number of hours of pumping. The data also demonstrate that, by adding supplemental feed, the bioreactor can reliably produce a very low effluent concentration even if the influent concentrations fall below that required to sustain a viable bioreaction. The large bioreactor has been moved to another location, and this site has been closed, but a smaller bioreactor could have done the job for lower cost. Data for the bioreactor operating in Milpitas are summarized in Table 2.

*Table 2.* Performance Data for Five-Foot Fluidized Bed Bioreactor – Milpitas, California. Demonstration of the Need for Adequate Pretesting (flow-concentration).

<b>Date</b>	<b>Flow Rate (gpm)</b>	<b>MTBE Influent (µg/L)</b>	<b>MTBE Effluent (µg/L)</b>	<b>TBA Influent (µg/L)</b>	<b>TBA Effluent (µg/L)</b>
19-Dec-01	2	420	300	NA	NA
18-Jan-02	2	530	27	NA	NA
15-Feb-02	2	797	0.8	65	ND<5
22-Feb-02	2	787	ND<0.5	194	ND<5
01-Mar-02	2	513	0.6	105	ND<5
08-Mar-02	2	613	0.7	11	ND<5
15-Mar-02	2	737	ND<0.5	24	ND<5
09-Sep-02	2	120	ND<0.5	6	ND<5
22-Oct-02	2	61	ND<0.5	6	ND<5
19-Nov-02	2	73	ND<0.5	16	ND<5
12-Dec-02	2	69	ND<0.5	ND<5	ND<5
16-Dec-02	2	73	ND<0.5	ND<5	ND<5

### **3.1.3 Bedford, New Hampshire**

At the Bedford site, the small Bio-500 bioreactor (Figure 3) was introduced to freezing temperatures, high iron (30 mg/L as Fe), and high manganese (10 mg/L as Mn), in addition to the usual TBA, MTBE, and BTEX. The treatment train consisted of an air stripper to remove BTEX and iron (not shown), a bioreactor to remove MTBE and TBA (green), and activated carbon (gray) for a final polish. The bioreactor was enclosed in a heated building, the iron was removed in the stripper, and the manganese precipitated out in a separate layer in the bioreactor. The biomass adapted to perform well at groundwater temperatures as low as 49°F, the lowest groundwater temperature measured at the site. The increased solubility



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of oxygen in cold water is believed to partially offset the slowdown in metabolism expected with cooler temperatures.

When BTEX concentrations in the incoming groundwater decreased to less than those of MTBE and TBA, the stripper was replaced with an ion exchange unit to control the iron and manganese. Eventually the iron and manganese concentrations decreased to 10 mg/L iron and five mg/L manganese and the ion exchange system was removed. Finally, the carbon polishing unit was taken out of service. The system was then operated as an in-situ/ex-situ bioremediation treatment unit. Water pumped from the wells down gradient of the source area was treated in the bioreactor to produce water meeting the discharge requirements for the State of New Hampshire. A portion of that water was infiltrated upgradient from the source and the rest was discharged to surface waters. Remediation at the site is nearly complete. Water discharged from the bioreactor has consistently been reduced from 7,000 µg/L to less than 20 µg/L of TBA, the discharge limit for this site.



*Figure 3. Small Bio-500 Located in New Hampshire.*

### **3.1.4 Hollywood, Florida**

A five-foot diameter bioreactor was set up in Hollywood, Florida to treat a groundwater stream containing TBA at an initial concentration of 100,000 µg/L, with trace amounts of BTEX (<500 µg/L) and some MTBE. The system was set up to re-inject treated water downgradient of the impacted zone. An attempt was

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made to start the system in August, but the hot weather proved problematic. In addition, regulatory requirements mandated batch analysis prior to discharge. Long laboratory turnaround times would have resulted in a high volume of effluent generated before the receipt of laboratory results. Therefore, the bioreactor was placed in recycle mode during samplings. The weather was so hot that the biomass consistently overheated during periods of recirculation.

During one of the recirculation periods, the temperature of the fluidized bed reached 103°F and the biomass lost much of its activity, requiring partial replacement. To overcome the overheating problem, special provisions were made with the agency to allow re-injection of partially treated groundwater into the source area. This continuous flow of groundwater through the bioreactor kept the internal bioreactor temperature down and allowed the biomass to develop in a few weeks.

Re-injection of treated groundwater into the source area also introduced oxygenated water, with a DO of approximately seven mg/l, promoting in-situ bioreaction in the subsurface and reducing the lifecycle of the system. The bioreactor operation combined with the re-injection reduced TBA concentrations in groundwater to monitoring levels only (concentrations decreased by 99.6%) within one year of system activation.

#### **3.1.5 Norwalk California**

Two five-foot diameter bioreactors were set up in Norwalk, California to treat up to 25 gpm each (for a total of 50 gpm) of water containing 1,200 µg/L of TBA and 400 µg/L MTBE, as well as containing 2,500 µg/L of BTEX. Sacrificial carbon was used ahead of the bioreactors to remove most of the BTEX allowing the bioreactor system to focus on metabolism of the TBA and MTBE.

The groundwater is unusually hard at this site (hardness of 800 to 1200 ppm as CaCO<sub>3</sub>). When groundwater contacted air in the bioreactor, the pH rose and solids precipitated, clogging the injectors, the circulating piping, and the final polishing carbons. A pH control system was installed to keep the pH below 7.2, which largely eliminated the solids problem. A picture of the site is shown in Figure 4.

During the last year and a half, over 12 million gallons of water were processed, achieving discharge concentrations of <5 µg/L TBA and <5 µg/L MTBE. At present the groundwater through-put is limited by the filtration rate on the incoming stream. The solids to be removed are gummy in nature and appear to be biological. Current efforts are being directed at finding a system to control or

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reduce the bio solids (perhaps with a biocide), while protecting the biomass that is needed to metabolize the TBA and MTBE.



Figure 4. Bioreactor System in Norwalk, California showing an incoming process water surge tank (dark green), bioreactors (light green), HCl storage tank (white), and Nutrient and MTBE feed drums (blue).

### 3.1.6 Auburn, New Hampshire

A mobile bioreactor was built and placed on a fuel spill site in Auburn, New Hampshire. The system was designed to re-inject treated water upgradient of the source area to promote *in-situ/ex-situ* reaction. The biomass was grown and replenished in the aboveground reactor. Treated water containing some biomass and oxygenated water infiltrated into the subsurface through two perforated horizontal pipes upgradient of the source of the plume. The bioreactor was contained in an enclosed, insulated trailer as shown in Figure 5, to protect it from freezing weather. A layout of the system is shown in Figure 6. The injected water formed a 1-2 foot mound as measured in MW-102 adjacent to the horizontal infiltration gallery. Water was extracted from EW-1, EW-2, and MW-BR. As of publication, the system has been running for only a few weeks. Concentrations in EW-1 and EW-2 have dropped in half and MW-BR has just been put on line.

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Figure 5. Transportable bioreactor in Auburn. Insulated to protect the biomass from New Hampshire winters.

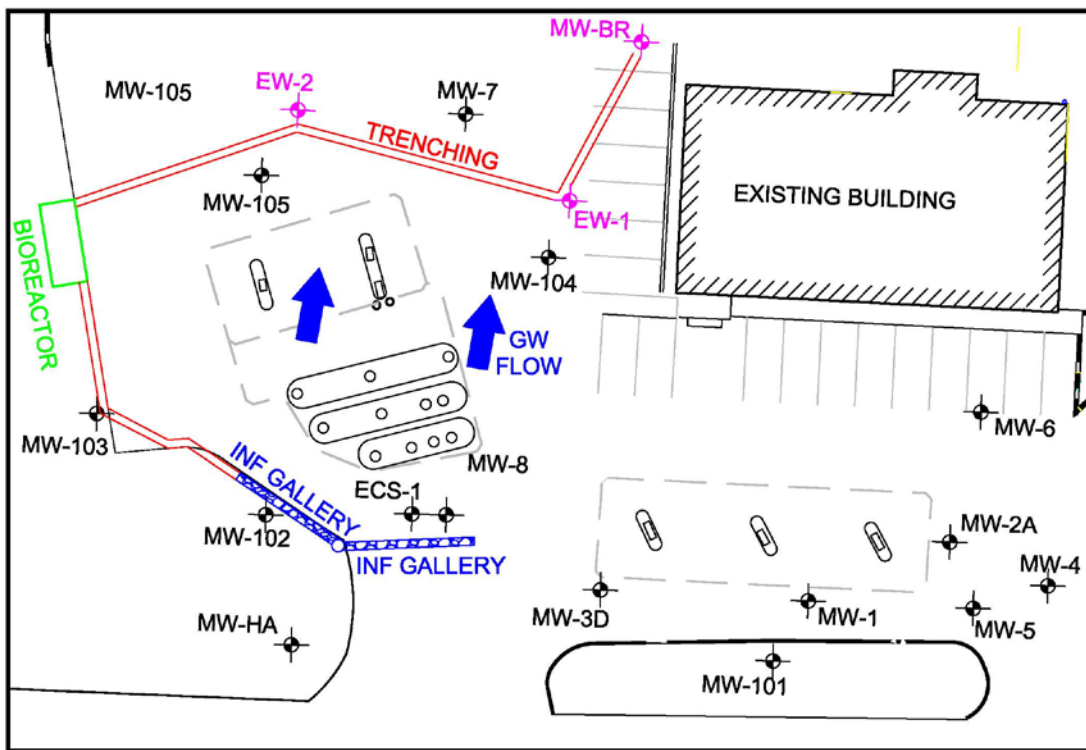


Figure 6. Flow through bioreactor system generating biomass aboveground and extending the reaction underground via infiltration.

## **4. DISCUSSION**

### **4.1 Bioreaction in the Presence of Surfactants**

Pilot studies have confirmed that these bioreactors are able to metabolize hydrocarbons and oxygenates in the presence of surface active materials like detergents.

#### **4.1.1 Deliberate Addition of Biodegradable Surfactant**

A current bioreactor user wanted to inject a citrus based biodegradable surfactant to enhance the recovery of non-polar hydrocarbons (BTEX) from the subsurface. A pilot study was run on a two-foot diameter bioreactor in Cardno ERI's laboratory to determine the effect of added surfactant. The results showed no foaming in the bioreactor and after a short period of acclimation, the BTEX and oxygenates were consumed at previous rates obtained before surfactants were added.

#### **4.1.2 Reaction of BTEX in Presence of Alkyl Benzene Sulfonates**

Surfactants (suspected to be alkyl benzene sulfonates) were present from previous land use with groundwater containing high concentrations of benzene (>30,000 ppb). Air sparging at the site produced foam in the groundwater wells. Groundwater extraction for treatment with carbon was ineffective because the surfactants solubilized the benzene and it went right through the carbon. As an alternative, a three-week pilot study in a two-foot diameter bioreactor using groundwater from the site confirmed that the benzene could be metabolized in the presence of the surfactants to yield an exit concentration of less than one ppb.

### **4.2 Bioreactor Costs**

Current cost information for the two off-the-shelf Cardno ERI bioreactors is summarized below in Table 3. Incremental operation and maintenance (O&M) costs are estimated on the assumption that O&M is already required at the site for other purposes. Some costs not included in the table tend to be site-specific and will vary. Not included below are site-specific costs for transportation, installation, system enclosure, groundwater extraction, GAC and other filters, underground piping, effluent discharge, sampling and analysis, or project management.

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Table 3. Bioreactor Cost Information.

Cost Item	Two-Foot Bioreactor	Five-Foot Bioreactor
Bioreactor, sand, and biomass	\$40,000	\$70,000
Oxygen booster (optional)	\$3,500	\$3,500
On-site O&M labor (hours/week)	1.5-2.5	4-5
Power for bioreactor (kilowatts)	0.9	1.5
Materials, chemicals, parts, solids disposal	\$100/month	\$200/month

## 5. CONCLUSIONS

The use of fluidized bed reactors to treat fuel oxygenates and petroleum hydrocarbons offers the following features and benefits:

- The process actually destroys fuel oxygenates and petroleum hydrocarbons, mineralizing them to carbon dioxide and water, rather than merely transferring them to another medium.
- The partial recycle loop in the bioreactor provides operational flexibility allowing the bioreactor to treat highly contaminated groundwater.
- The technology has been proven in full-scale operation at over 30 sites.
- The process uses naturally occurring microorganisms.
- The biomass is extremely resilient, adapting well to gradual changes in contaminant concentrations, temperature, and other conditions.
- Because of its slow growth rate, excess biomass is rarely generated.
- The biomass performs well at temperatures ranging from 50°F to 90°F.
- The process provides one of the very few treatment options for TBA.
- Groundwater extraction and treatment can provide hydraulic control at the site and is often a good strategy for dealing with soluble non-adsorptive contaminants, such as MTBE and TBA.
- The cleaned, aerated, and bacterially seeded effluent can be re-injected to flush the smear zone and promote *in-situ* bioremediation.
- The bioreactors can be scaled to any mass loading.
- Two off-the-shelf sizes are available and larger sizes can be custom manufactured.

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- The bioreactors are minimally impacted by clogging and precipitates compared to other technologies. In particular, high manganese concentrations are well tolerated.
- The bioreactors are compact, quiet, and odor-free.
- When remediation is complete, the bioreactor may be reused at the next site.

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# PCBS, YUSHO DISEASE AND TSCA: A CASE STUDY OF THE INTERPLAY BETWEEN RISK PERCEPTION AND RISK ASSESSMENT

James D. Okun<sup>§</sup>

*O'Reilly, Talbot & Okun Associates, Inc., 293 Bridge Street, Suite 500, Springfield, Massachusetts, 01103*

## ABSTRACT

Prior to the 1968 Yusho rice oil poisoning incident in Kyushu Japan, polychlorinated biphenyls (PCBs) were considered a benign and useful class of organic chemicals. Prized for chemical stability, inflammability and low toxicity, they were used in liquid products (e.g. dielectric fluids and lubricants) and solid products (e.g. carbon paper, building caulk and surface finishes). The perception of PCBs changed dramatically for the worse following Yusho. The Toxic Substances Control Act (TSCA) and resulting regulations banned the manufacture of PCBs and established strict management and disposal requirements for the existing stock. The regulations did contain a provision allowing PCBs already in-service to remain in-service until the end of their useful life (the “in-service rule”). In the mid-1980s researchers discovered that PCBs had not been the causative agent for Yusho disease, but this finding had little if any effect on the strict regulatory regime. In 1998 the PCB regulations were substantially rewritten and the in-service rule was eliminated. This meant that only those PCB uses specifically authorized in the regulations were permitted to continue, all other uses were illegal. None of the uses of PCBs in building materials were authorized. While not initially understood, this regulation change set the stage for PCBs to become a problem in schools. In the late 1990s, researchers began using more powerful tools to measure trace contaminants in indoor air including PCBs. PCBs in air were often correlated with the presence of PCBs in building materials. Although measured air concentrations were low and no adverse health effects were noted, USEPA risk assessment models suggested possible health risks. Schools became “lightning rods” for toxic exposure concerns despite no evidence of harm. Costs to remove PCBs from buildings proved difficult to estimate and surprisingly high. Nationally, the cost to remove PCBs from K-12 schools may approach or exceed \$100 Billion.

**Key Words:** PCBs, Yusho Disease, PCDFs, PCBs in Schools

<sup>§</sup> Corresponding Author: James D. Okun; O'Reilly, Talbot & Okun, Associates, Inc.; 293 Bridge Street, Suite 500, Springfield, MA 01103; (413) 788-6222; okun@oto.env.com

## **1. INTRODUCTION**

A considerable body of research has been published regarding differences between risk assessment and risk perception (Ropeik, 2010). This paper describes the discrepancy between perceived risk and actual documented human health effects for polychlorinated biphenyls (PCBs). In the US, PCBs are among the most regulated chemical products ever produced; in news stories they are often described as dangerous carcinogens (The Wave, 2011; Navarro, 2011). Yet long-term epidemiological studies have consistently failed to find a reproducible cause and effect relationship between PCB exposure and human cancer or other chronic disease (Golden, 2004, 2009; Sheilds, 2006).

This is a subject of more than academic interest. While most of the PCB regulatory burden has fallen on industry, there are increasing reports of PCBs in schools that have alarmed parents and school staff (Lefkowitz, 2013). While there is often a fast decision by school administrators to remove PCBs from the school, implementing that decision has generally proven more difficult and expensive than anticipated. Few school system budgets can be stretched to undertake unplanned multi-million dollar PCB removal projects. As discussed in Section 5.4, on a national basis the cost of PCB removal from schools could approach or even exceed \$100 billion.

PCB removal projects are not motivated solely by stakeholder concerns; federal PCB regulations ban the use of PCBs in building materials even when that use began while still legal. Uses of PCBs that are not specifically authorized under the regulations are prohibited. This means that when a building owner becomes aware of PCBs in building materials there is an affirmative obligation to eliminate or at least actively manage those PCBs in a manner to prevent exposures.

The negative perception of PCBs and federal PCB laws are both at least partially attributable to the 1968 Yusho rice oil poisoning incident in Kyushu, Japan (Kuratsune et al., 2007). Prior to the Yusho event, PCBs were considered benign, useful chemicals. That perception changed as news of the poisoning spread. While initial reports attributed poisoning to PCB contamination of the edible oil, subsequent research demonstrated that PCBs played little if any role in the toxic effects (Kashimoto et al., 1985). However, by the time these findings were published, negative public opinion and prohibitive regulatory programs had been firmly established.

In the US, schools are among our most important public and private institutions. Threats to schools elicit a strong protective response; the discovery of PCBs in schools being no exception. Considered holistically, PCBs pose two threats to schools: possible health effects, although harm to health has yet to be demonstrated (Okun, 2011), and economic burdens accruing from the substantive costs of eliminating PCBs from buildings. Considering the magnitude of the problem, an explicit national discussion of risks, costs, and benefits of PCB management in schools would be useful. This paper is intended to contribute to such an inquiry.

## **2. PERCEPTION OF PCB HEALTH RISK PRIOR TO THE YUSHO INCIDENT**

The following quotes from a 1960 Monsanto sales brochure capture the perception of PCBs (sold under the trade name “Aroclors”) prior to the 1968 Yusho poisoning. These quotes are verbatim, we have not attempted to correct grammar and usage.

“The Aroclor<sup>®</sup> compounds are among the most unique, most versatile chemically-made materials in industry. Aroclors are so useful in so many ways in so many applications, primarily because of one outstanding characteristic: inertness.

“The Aroclors do not burn . . . and they impart fire-retardance to compositions in which they are mixed. The Aroclors do not “break down” under mechanical stress; therefore, they make good lubricants, sealants, and expansion media. The Aroclors are not decomposed by, nor do they conduct even tiny amounts of, electricity; therefore they are outstanding dielectrics. Heat has little effect on the compounds, hence the Aroclors are excellent heat transfer fluids. Since they are compatible with a wide range of synthetic resins, Aroclors make excellent plasticizers. Because Aroclor formulations “trap” and hold more volatile ingredients, they make volatile insecticides and repellents “last longer” in residual activity”.

First produced in the 1880s as a chemical novelty, PCBs were used commercially in a wide range of applications by the 1930s (Fiedler, 2002). Non-flammability, low volatility, and chemical stability made PCBs useful in the formulation of many products. PCBs were generally believed to have relatively low toxicity. For more than 40 years the variety of PCB applications increased. Over that period, potential health risks were considered and the perception was that PCBs were generally benign (Monsanto, 1962).

The few symptoms attributed to PCB exposure generally disappeared when exposure ended (Hara, 1985). Pre-Yusho occupational exposures to PCBs were large relative to present industrial exposure standards. There was considerable experience with occupational PCB exposures during the manufacture of capacitors and transformers. The typical indication of over-exposure was the appearance of skin lesions known as chloracne. Long-term health effects were rare, but not unknown. End users of PCB containing products (including building materials) were generally not known to experience health effects. That was representative of the PCB toxicity experience for the 40 years prior to Yusho.

While the concepts of human health and environmental risk were analyzed less rigorously in the pre-Yusho period, based on the available documentation from that period it is reasonable to conclude that PCBs were not considered particularly risky. There were some researchers who did express concerns about PCBs before Yusho, but they were in the minority were generally not persuasive.

### **3. THE YUSHO POISONING**

The 1968 Yusho mass poisoning in Kyushu, Japan brought world-wide attention to PCBs and their toxicity (Pfafflin and Ziegler, 2006). This tragic incident occurred when rice bran oil became contaminated with PCB containing heat exchange fluid. While little known in the US, rice bran oil is popular in Asia and valued for its health benefits. The toxic Yusho oil was prepared by a process that included the use of an industrial heat exchanger containing PCB heat transfer fluid. The heat exchanger leaked and the PCB heat transfer fluid contaminated the rice bran oil. The contaminated oil was sold and consumed. The victims of the poisoning experienced health symptoms that began as skin lesions and spread across physiological systems resulting in pronounced and horrific toxicity. The effects were long-lasting and, in some cases, irreversible.

Ten years after the Yusho incident, in 1978, there was a similar poisoning, also with rice bran oil, in Taiwan (the “Yu Cheng” incident). The circumstances and particulars of the two poisonings were quite similar, although subsequent studies suggested the Taiwanese poisoning was somewhat less severe.

The initial Yusho poisoning assessment concluded that the PCBs from the heat exchange fluid caused the toxic effects. However, as more sensitive analytical chemistry methods were developed, chemists retesting the fluid discovered the cause was more complex (Kuratsune et al., 2007). The Yusho oil contained a range of chlorinated organic chemicals, most notably polychlorinated dibenzofurans (PCDFs) and polychlorinated quaterphenyls (PCQs). PCDFs are chemically similar to PCBs, but contain a single oxygen atom bridge between the 2 and 2' carbon atoms thereby forming a furan. PCQs are dimers of PCBs. Testing showed that neither PCDFs nor PCQs would have been present in significant concentrations in the original PCB heat transfer fluid.

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

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

To aid in evaluating the relative toxic potency of chemical mixtures containing PCDDs, PCDFs and/or PCBs, toxicity equivalence factors (TEF) have been developed for each of the individual congeners. The relative toxicity of a mixture may be estimated by multiplying the concentration of each congener times its TEF and then summing these products. When the TEF calculation was made for the Yusho rice oil, it was demonstrated that the vast majority of the oil's toxicity can be explained by the presence

of just two chemicals in the oil: 2, 3, 7, 8-tetrachlorodibenzofuran and 2, 3, 4, 7, 8-pentachlorodibenzofuran. While present at much higher concentrations, it was concluded that the PCB congeners played no or almost no role in causing the poisonings (Dyke and Stratford, 2002).

Another observation from the Yusho and Yu-Cheng incidences that was inconsistent with known cases of occupational PCB poisoning was the severity and persistence of the symptoms. The symptoms of occupationally-induced PCB toxicity were generally reversed once the continuing exposure was curtailed. However, the victims of the Yusho and Yu-Cheng poisonings did not experience relief until very long after the exposure was stopped. The symptoms of Yusho/Yu-Cheng poisoning were significantly more extensive, severe and persistent than had previously been seen with human PCB toxicity.

### **3.1 Could a Yusho-type Poisoning Occur due to Exposure to PCB Building Materials?**

The Yusho and Yu-Cheng poisonings were caused by the consumption of rice bran oil containing toxicologically significant concentrations of PCDFs. While the oil also contained PCBs, we now know they were not the cause of Yusho symptoms. The commercial mixtures of PCBs manufactured in the US have been tested and found not to contain toxicologically significant concentrations of PCDFs. The conditions required to convert PCBs to PCDFs do not occur in a building under normal operating conditions, even when materials are exposed to direct sunlight in a tropical setting. Therefore, under normal building conditions, there is no realistic possibility of building occupants being exposed to PCDFs from building materials. Without PCDF exposure, a Yusho-type poisoning has not been observed. No evidence of toxicologically significant PCB exposures have been observed from occupying buildings containing PCBs (Herrick et al., 2004)

### **3.2 The Post-Yusho Perception of PCB Risk**

Following the Yusho incident the public perception of risks from PCBs changed quickly. No longer seen as a benign chemical mixture, PCBs came to symbolize an entire chemical industry that seemed insensitive to the underlying societal costs of their products. A pronounced public sentiment against chemicals in general and PCBs in particular had developed; not surprisingly, government policy makers took note of this attitude shift and responded. It was this post-Yusho focus on environmental policy that gave form to the key federal and state environmental laws of the 1970s and 1980s.

## **4. TSCA AND THE US PCB REGULATIONS**

The Toxic Substances Control Act (TSCA, 1976) was initially developed in President Richard Nixon's Council on Environmental Quality (CEQ) in 1969, but it was not passed into law until December, 1976 (CEQ, 1971). The version of TSCA produced by CEQ

and that was first presented to Congress in 1970 made no mention of PCBs (Blodgett, 1976). It was not until 1976, just prior to its final passage, that the law was amended to contain Section 6(e) that specifically directed the EPA Administrator to regulate PCBs. The PCB regulations called for in the statute were issued 1978 and 1979; ten full years after the Yusho incident that triggered their promulgation. While the early regulations received minor revisions from time to time, it would be 20 years before they were substantially redrafted.

#### **4.1 The “1998 PCB Mega-Rule”**

EPA began work on major revisions to the PCB regulations in the early 1990s. When they were finally issued, the new regulations were referred to as the “1998 PCB Mega Rule” because of the large number of revisions that were included. Among other changes, the Mega Rule introduced a more sophisticated approach to the management of PCB-contaminated remediation waste.

#### **4.2 Elimination of the “PCB In-Service-Rule”**

One of the other Mega Rule changes was the elimination of the PCB “in-service rule”. The in-service rule was included in the 1978 regulations as a regulatory mechanism to permit the continued use of PCBs that were already in-service in applications that were not totally-enclosed. The in-service rule was intended to prevent the abrupt discontinuation of PCB use in situations where PCBs had been incorporated into a variety of products before the effective date of the regulations. The in-service rule (*Introduction to Subpart D, Pre-1998 PCB Regulations*) reads as follows:

*“Note: This subpart does not require removal of PCBs and PCB Items from service and disposal earlier than would normally be the case. However, when PCBs and PCB Items are removed from service and disposed of, disposal must be undertaken in accordance with these regulations. PCBs (including soil and debris) and PCB Items which have been placed in a disposal site are considered to be “in-service” for purposes of the applicability of this subpart”.*

It is now apparent that in eliminating the in-service rule EPA changed the status of existing PCBs in building materials from that of being permitted to that of being illegal. However, in 1998 this particular consequence was apparently not fully understood, as there is no discussion of the change in either the preamble or in the regulations themselves. Without the in-service rule, anytime that PCB-containing building material is identified it constitutes an illegal use of PCBs.

## **5. PCBs IN SCHOOLS AND OTHER BUILDINGS**

In the late 1990s, two events set the stage for the PCBs in schools problem. The first was the 1998 PCB regulation changes, particularly the elimination of the in-service rule, as

discussed in the previous section. The second was the advances in analytical chemistry that permitted the routine measurement of PCBs in air at very low concentrations.

## **5.1 Measuring PCBs in Air**

Until the 1990s, PCBs had not been considered significant air contaminants. Generally, air contaminants include substances that are either gasses (meaning they can exist in the vapor phase at ambient temperatures) or they are particulates (meaning they exist as or on particles small enough to remain suspended in air for some period of time). Contaminants that exist as vapors at ambient temperature are described as being volatile; in practice this means those with vapor pressures  $> 0.1$  millimeters of mercury (mm Hg) are considered volatile; those with vapor pressures  $< 0.1$  mm Hg are considered nonvolatile or semi-volatile (USEPA, 2011).

PCBs are generally considered to be nonvolatile organic chemicals (Foreman and Bidleman, 1985). The vapor pressure of Aroclor 1221, the most volatile of the PCB Aroclor mixtures, is estimated to be  $6.7 \times 10^{-3}$  mm Hg; the vapor pressure of Aroclor 1260, one of the least volatile Aroclors has been measured at  $4.05 \times 10^{-5}$  mm Hg (USEPA, 1983; Foreman and Bidleman, 1985). Due to their low vapor pressures, it was sometime before the inhalation of PCBs was considered a significant potential route of exposure for people.

By the early-1990s, environmental scientists were publishing accounts of PCBs being detected in indoor air, with much of this early work taking place in Germany (Benthe et al., 1992; Balfanz et al., 1993). Although their vapor pressure is quite low, it was shown that low concentrations of PCBs could volatilize out of building materials and into indoor air. A survey article on the state of PCB testing in indoor air appears in Spengler et al.'s 2000 Indoor Air Quality Handbook (Spengler et al., 2000).

Since 2000, there have been increasing reports of PCBs in building materials and indoor air, particularly in schools (Daley, 2009; Egbert, 2008). There is a widely held assumption that PCBs in building air is correlated with their use in specific building materials like paint, adhesives or caulk. While this assumption seems reasonable, the comparison of test results before and after the removal of PCB containing building materials often shows little change. The reasons for this are not yet understood.

## **5.2 PCBs in Schools: A Two Sided Problem**

From the perspective of a school administrator, PCBs pose at least two problems: 1) the perception that their presence in the building poses a health risk to students and staff; and 2) compliance with the rigorous regulatory requirements.

### **5.2.1 Perceived Health Risk**

PCBs are known to be present in many buildings constructed between 1950 and 1978 (USEPA, 2012). Studies to assess possible adverse health effects to students and staff

that have spent time in these buildings have not found such effects. These results are consistent with those observed for PCB workers where exposures were often 1,000 times greater than those that occur in school buildings (Wolff, 1985). Further, PCB exposures from buildings are generally a small fraction of the PCB dose the average person receives in their diet. Despite available data, the perception of health risk from PCBs in schools is still able to elicit a powerful fear reaction among some parents and educators.

Managing the school system's response to a PCB problem typically falls to the school and municipal administrations. This is a task in which few have received direct training. Managing the actual presence of PCBs often becomes confused with the parallel burden of managing the perceived risk of PCBs.

Responsible administrators must often rely on outside experts for guidance. These experts sometimes lack complete information or may have interests that conflict with those of the school system.

### **5.2.2 Meeting Regulatory Requirements**

The regulatory process for the management of PCBs in building materials is fairly clear; once discovered, the presence of these materials becomes a violation of the federal PCB regulations. The next step is to develop a plan to address and remove the materials. This is often done in consultation with USEPA representatives. This means that testing of building materials for PCBs should be undertaken with the understanding that beginning this process may inevitably lead to the removal and disposal of those materials. In addition, when the results of a limited testing program become available, the scope of the testing may expand in a way not anticipated or controlled by those who set the testing in motion.

### **5.3 Linking Regulatory Compliance to Indoor Air Concentrations**

When the presence of PCBs is documented in building materials and the USEPA is overseeing the PCB removal, the agency may require that indoor air testing be conducted to demonstrate the effectiveness of the PCB removal process. In these situations the PCB removal process may not be considered complete until air concentrations drop below a predetermined level.

When cleanup effectiveness is determined based on indoor air test results, an iterative search and removal process begins that may have unanticipated and very costly results.

### **5.4 PCB Removal Costs**

The cost of removing PCB containing materials from buildings often exceeds estimated budgets. This happens because, once in place, PCBs have a tendency to migrate into surrounding materials. The extent of this migration is small, but still sufficient to make these abutting materials subject to regulation and removal. In practice this means that if a PCB-containing window is removed it may also be necessary to remove the surrounding



brick, concrete or wood the window was set into. Or in the case of floor tile or carpeting held down with a PCB-containing adhesive, the cost of replacing the floor and a portion of the underlying concrete slab may also be a factor. This additional work can significantly increase removal project cost.

National studies to examine the costs of PCB removals in schools have not been conducted yet. However, two school PCB removal projects where a significant amount of public information is available are the Estabrook School in Lexington, Massachusetts and the Middle School in Westport, Massachusetts. In the case of the Estabrook School, after expenses in excess of \$1 million the administration determined it would be less costly to demolish and dispose of the existing school and build a new one than to remove all of the PCBs. At the Middle School in Westport initial projected costs of \$300,000 quickly escalated. To date over \$3 million has been spent and the project is not yet completed. These are not unusual cases where PCBs have been found in schools.

No published estimates are available for the national costs of removing PCBs from schools. There are approximately 132,000 public and private schools in the US (US Dept. of Education, 2013). If one third of these schools contain PCBs, and the average cost of removing the PCBs were \$2 million per school, then the national school PCB removal cost would be \$88 billion. By way of comparison the national cost of the federal Superfund cleanup program is estimated by the USEPA to be \$250 billion through to the year 2075. This includes public and private spending.

## **6. CONCLUSIONS**

It was 45 years ago that PCBs were cast into the international spotlight as the result of the Yusho poisoning incident. PCBs came to symbolize all that had gone wrong with toxic chemicals in the environment. Over the following years strict regulatory regimes were implemented to ban further manufacture and rigorously manage the remaining stock of PCBs. Then, 28 years ago, scientists reported that PCBs were in fact not the causative agent in the Yusho poisonings, but there has never been a corresponding change in the regulatory regime or in public perceptions to reflect the knowledge that PCBs were much less toxic to than scientists had previously thought. The public continued to perceive the health risk from PCBs as being very serious.

Researchers began reporting on the presence of PCBs in building air 20 years ago., That, combined with the discovery of PCBs in building materials, began the problem of known as PCBs in schools. Schools have become a flash point in the conflict between risk perception and risk assessment for PCBs.

School systems faced with the prospect of managing PCB assessment and removal projects are in very challenging circumstances. They often confront a portion of their parents in educators who are in genuine fear that their health (or the health of their children) is at risk. In many cases, this fear can become the primary driver of school system decision making. System administrators are also faced with a complex and

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demanding set of federal regulations that require experts to decipher. These very experts that school systems rely on may have divided interests that are not always be aligned with those of the school system itself. Finally, system administrators hear conflicting evidence from government (MADPH, 2009) and independent professionals to the effect that there is no good evidence that PCBs in buildings are actually causing any harm.

It is the author's conclusion that the current response to PCBs in schools has not been adequately considered from the national perspective. As a result, inconsistent policies and project implementation have led to a potential for the mismanagement of scarce school system resources. The author recommends that the EPA forestall further requirements for school PCB remediation projects until panels of scientific and engineering experts can be convened to evaluate the health and remediation issues involved and develop a uniform national policy towards PCBs in schools.

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# **HIGHWAY RIGHT OF WAY MAINTENANCE: ENERGY USE PER ACRE IN MOWING COMPARED TO HERBICIDE APPLICATION**

Mary O'Reilly<sup>§1</sup>, Tarak Shrestha<sup>2</sup>

<sup>1</sup>*SUNY School of Public Health 7705 Farley Lane Manlius, NY 13104;* <sup>2</sup>*SUNY School of Public Health 97  
Lincoln Ave FI-2 Albany, NY 12206*

## **ABSTRACT**

Vegetation control along highway rights-of-way (ROWs) is important to promote proper drainage, to provide adequate sight distances to motorists, to maintain sign visibility and to protect highway maintenance workers. Although new methods are being sought and developed to control ROW vegetation, the two main methods currently in use are mowing and herbicide application. Extensive data exists on energy use in both on-road and off-road vehicles, but very little data is available on energy consumed by either ROW mowing or herbicide application.

This study uses data from actual highway maintenance practice supplemented with reference data from the U.S. Environmental Protection Agency (U.S. EPA), the U.S. Department of Energy (U.S. DOE) and the open literature to calculate energy use per acre of highway ROW. For mowing operations the fuel energy in BTUs and the legacy energy of the equipment itself also in BTUs were added to calculate the final energy cost per acre in BTUs. For herbicide application the energy in BTUs to manufacture the herbicide, the fuel used and the legacy energy of the equipment itself were added to calculate the final energy cost per acre in BTUs.

Using data obtained from the open literature (Pimentel, 1980; Clemens et al, 1995) the energy cost to manufacture one of the herbicides used along the ROW is about 108,000 Kcal/kg, which is about 428,000 BTUs/kg. The energy used in herbicide manufacture drives the energy use of herbicide application per acre to about four times the energy used per acre by mowing.

Several studies report that monetary costs are lower for herbicide application compared with mowing (Environment and Energy Bulletin, 2009). Conventional wisdom suggests that monetary cost should parallel energy cost. The transparency of life cycle analysis facilitates productive discussion of this discrepancy as well as other environmental health considerations.

<sup>§</sup>Corresponding Author: Mary O'Reilly SUNY School of Public Health, 7705 Farley Lane, Manlius, NY 13104; (315) 682-3064; moreilly@albany.edu

**Keywords:** highway ROW, vegetation control, mowing, herbicide application, energy use

## **1. INTRODUCTION**

Highways have evolved since the early-1900s. Pre-World War II parkways, primarily in urban areas, were curvy roads with limited access built for leisurely travel. They often used vegetation, such as shrubs and flowering trees, to separate the traffic from the populated areas where they were located. The highway interstate system that we have today was built after World War II for high-speed, long-distance travel. Large tracts of land were cleared and fenced as ROWs surrounding the new interstate highway system. Beautification of the highway system, which often included mowing from fence line to fence line, was championed by Ladybird Johnson in the 1960s when fuel was abundant and cheap. With the advent of dwindling supplies of and increasing cost for fuel, highway ROW vegetation control needed cost effective ways to promote proper drainage, to provide adequate sight distances to motorists, to maintain sign visibility and to protect highway maintenance workers.

Since World War II, herbicides have been a part of highway vegetation control. Zukel and Eddy (1958) report that in the 1950s highway ROW was maintained for 10 feet out from the edge of shoulder on both sides of a two lane road, for a total of 2.5 acres per linear mile. New York had 12,964 miles of highway in 1955 and spent \$5,000 to \$7000 on herbicides, primarily 2,4-D, 2,4,5-D, dalapon and monuron. Ohio reported that it cost \$126.62/mile/season for mowing but \$108.17/mile/season when both mowing and herbicide application were used. Zukel and Eddy (1958) reported very few details. The interstate system was under construction at the time of their publication.

Departments of Transportation often calculate the value of assets using linear measurements. This approach works quite well for linear assets such as guide rail, paint striping, culverts and ditches. The system of linear reference markers along highways fosters their use to measure work done between them. Herbicide applicators keep track of their work by noting reference markers in their daily logs, even though they calibrate their spray equipment each morning by measuring the two dimensional pattern it makes on the pavement before the

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herbicide is added to the spray tank. In most cases linear measurement works well. To compare mowing operations with herbicide application, however, a better unit of measurement is to use two dimensions, such as square feet or acres.

The current study relies on data generated by others for several parameters including the energy to make tractors and trucks, the energy contained in fuel and the energy requirements to manufacture pesticides. Although no direct measurements of energy input to manufacture agricultural equipment are available, parallels between tractor and automobile manufacture support using information from the auto industry to approximate energy inputs to manufacture tractors, summarized in Table 1 (Mikkola and Ahokas, 2010). Mikkola and Ahokas (2010) make the argument that proportionately similar amounts of steel have been replaced in both automobiles and farm equipment and that, because it takes more energy to manufacture synthetic materials, the total energy has not decreased as much as would be expected from calculating the decreased percentage of steel in both type of vehicles

Table 1. Reported energy required to manufacture automobiles (Mikkola and Ahokas, 2010).

Energy input MJ/kg	Reference
81.2	Berry and Fulton Fels, 1972 “average car”
86.6	MacLean and Lave, 1998 Ford Taurus
74.9	Schweimer and Levin, 2002 VW diesel

There are a variety of values reported for the energy in BTUs (British Thermal Units) contained in a gallon of diesel, number 2 fuel (Table 2). Similarly there is a range of BTUs contained in a gallon of gasoline from 116,090 to 124,340 BTUs ([http://www.afdc.energy.gov/fuels/fuel\\_comparison\\_chart.pdf](http://www.afdc.energy.gov/fuels/fuel_comparison_chart.pdf)).

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Table 2. Energy values reported for a gallon of diesel, number 2 fuel.

Energy BTUs/gallon	Reference
128,450	U.S. Department of Energy, 2013. <a href="http://www.afdc.energy.gov/fuels/fuel_comparison_chart.pdf">www.afdc.energy.gov/fuels/fuel_comparison_chart.pdf</a>
137,380	U.S. Department of Energy, 2013. <a href="http://www.afdc.energy.gov/fuels/fuel_comparison_chart.pdf">www.afdc.energy.gov/fuels/fuel_comparison_chart.pdf</a>
139,000	U.S. Department of Energy, 2014 ( <a href="http://www.netl/doi.gov/research/coal/crosscutting/energy-calculator">http://www.netl/doi.gov/research/coal/crosscutting/energy-calculator</a> )

The CRC Handbook of Energy Utilization in Agriculture reports on several herbicides with Dinoseb requiring 19,000 kcal/kg and glyphosate requiring 108,100 kcal/kg. Energy requirements to manufacture glyphosate, as reported by several sources, are in good agreement and summarized in Table 3.

Table 3. Energy required to manufacture glyphosate.

Energy required	Reference
454 MJ/kg <sup>1</sup>	Green (1987)
195,313 BTU/lb <sup>2</sup>	Fluck (1992)
108,100 kcal/kg	Pimental (1980)

<sup>1</sup> 1 MJ = 239 kcal. 454 MJ = 108,506 kcal

<sup>2</sup> 1 BTU = 0.252 kcal; 1 lb = 0.454 kg. 195,313 BTU/lb = 108,412 kcal/kg



## **2. MATERIALS AND PROCEDURE**

As part of a larger study (Gao et al, 2010) conducted by Cornell University for New York State Department of Transportation, a modified life cycle assessment comparing energy use between mowing and herbicide application was done. To compare both operations by the same unit of measure, the energy consumed per unit area (acre) is used. Total energy consumption requires calculation of the energy used to make the equipment used in both operations plus the energy consumed during the operation. For mowing, the energy costs include the energy to manufacture the tractor and the cutting apparatus, plus the fuel consumed during the mowing operation. For herbicide application the energy costs include the energy to manufacture the herbicide truck, the fuel consumed during the herbicide operation, plus the energy used to manufacture the herbicide.

### **2.1. Mowing**

Energy use during mowing was calculated by dividing the fuel used by the area mowed in a day. Fuel use during mowing was measured in gallons of diesel consumed as observed in the field. The reference marker from the beginning of the work to the end of the work was used to calculate linear feet mowed. Only 75% of the linear distance derived from the reference markers was used in this calculation to account for interrupted mowing due to guide rail, intersections (on state roads), bridges and other impediments to mowing. The linear distance was then multiplied by the width of the mowing equipment to calculate the area mowed. The area was converted to acres. The energy contained in a gallon of diesel consumed was converted to BTUs.

### **2.2. Herbicide application**

Energy use during herbicide application was calculated by dividing the fuel used during application plus the energy consumed in the manufacture of the herbicide by the area to which the herbicide was applied. The product used in this study was RazorPro manufactured by Nufarm. The Material Safety Data Sheet (March 27, 2007) indicates that the density of the product is 9.67 pounds/gallon and that the active ingredient, glyphosate (N-(phosphonomethyl) glycine, in the form of its isopropylamine salt), is 41% by weight. If the active ingredient (AI) is 41% of

the product then there are 3.96 pounds of glyphosate per gallon of product. The product was diluted to a 5% solution before application reducing the concentration of AI to 0.198 pounds (90 grams) per gallon. The herbicide solution was applied at the specified rate of 25 gallons per acre.

### **3. DATA AND ANALYSIS**

Mowing operations are quite variable due to differences in slopes, vegetation height and type as well as cutting equipment and tractor type. The main types of cutting equipment evaluated were sickle bar, flail attachments, batwings and over-the-rail mowers. Tractor models also varied from older tractors from the eighties to newer turbo-charged ones manufactured within the last 10 years. The tractors and cutting equipment were used in a variety of combinations that does not remain constant from one year to the next.

The six tractors and their associated mowing equipment in this study are listed in Table 4. Each of the different types of mowing equipment has a different width, so just recording linear travel can be misleading. In addition, some of the travel distance logged by mowing tractors is driving to and from the mowing location as well as driving over bridges. The gallons of fuel per acre is fairly consistent at just under a half a gallon per acre except for the 1984 Ford tractor pulling the sickle bar mower. This tractor also has a significantly higher energy use per acre than the others. This difference is primarily due to the smaller width of the sickle bar mower attachment.

Table 4 underscores the difficulty of using a single number for energy use per acre during mowing due to the large number of variables that go into calculating that number. Nevertheless, the mean and standard deviation for gallons per acre using all six tractors is  $0.48 + 0.21$ , and the BTUs per acre are  $65,878 + 29$ .

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Table 4. Fuel usage per acre for mowing tractor.

ID number	Make	Mower type	Width of mower (feet) <sup>3</sup>	Distance mowed (miles) <sup>1</sup>	Diesel used (gallons) <sup>1</sup>	Area mowed (acres) <sup>4</sup>	Fuel use/acre (gallons/acre) <sup>5</sup>	Energy use/acre (BTUs/acre) <sup>6</sup>
84 7107	Ford	Sickle bar	7.5	2.9	1.70	1.98	0.86	119,273
84 7153	John Deere	Flail	13	4.0	2.14	4.73	0.45	62,411
89 7074	Ford	Flail	13	5.6	2.79	6.62	0.42	58,250
90 7160	MF	Flail	13	5.0	1.30	5.91	0.22	30,512
94 7030	Case IH	Flail	13	6	3.40	7.10	0.48	66,571
83 7091	Ford	Batwing	15	3.5	2.00	4.77	0.42	58,250

<sup>3</sup> Measured in the field

<sup>4</sup> Calculated by multiplying the number of miles by 5280 feet and the width of the mower in feet. That sum is divided by 43,560 square feet to obtain the number of acres mowed. The total number of acres mowed is multiplied by .75 to account for non-mowing travel time.

<sup>5</sup> Calculated by dividing the number of gallons of diesel used by the number of acres mowed.

<sup>6</sup> Obtained by using the online DOE calculator to convert gallons of diesel to BTUs. 1 gallon #2 diesel = 138,690 BTUs.

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In addition to the fuel used during mowing, the energy used to manufacture the tractor and mower should be evaluated. The weight of each tractor is known (Table 5). The default value of 75 MJ/kg (Mikkola and Ahokas, 2010) can be used to calculate the manufacturing energy. The total manufacturing energy can be prorated to a per acre amount based on either total time divided by total expected time for the life of the tractor or total miles divided by the total miles expected for the lifetime of the tractor. The sickle bar, flail and batwing mowers have masses of approximately 182 kg, 591 kg and 1591 kg, respectively.

From these considerations it is clear that there is a range of energy costs to perform mowing. The largest single driver of the mowing energy consumption at this point in time, however, is the diesel fuel to power the tractor and mower.

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Table 5. Manufacturing energy for tractors pro-rated for specific mowing event.

Tractor	Weight (kg)	Mfg energy (MJ) <sup>1</sup>	Task time (hours)	Task energy (MJ) <sup>2</sup>	Area mowed (acres)	Legacy energy (BTUs/acre) <sup>3</sup>
84 7107 Ford 2910 (sickle bar)	2109	158,175	2	31.6	2.0	14,976
84 7153 JD 401B (flail)	2019	151,425	1.1	16.7	4.7	3368
89 7074 Ford 5610 (flail)	2627	197,025	1.7	33.5	6.6	4811
90 7160 MF 383 (flail)	2903	217,725	2.5	54.4	5.9	8739
94 7030 Case IH 695 (flail)	2567	192,525	2.2	42.4	7.1	5660
83 7091 Ford 5610 (batwing)	2627	197,025	1.6	31.5	4.7	6352

<sup>1</sup> The manufacturing energy is calculated by multiplying the mass of the tractor by the energy per kg of output for manufacturing (75 MJ/kg)

<sup>2</sup> The operation energy is calculated by multiplying the total manufacturing energy by the hours required for the task divided by the total expected hours that the tractor will operate (10,000 hours).

<sup>3</sup> The legacy energy (the proportion of the total manufacturing energy used during specific tasks) was calculated by converting MJ to BTUs and dividing by the number of acres mowed in the task. 1MJ = 947.82 BTUs.

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A very different set of variables needs to be evaluated to determine energy costs of herbicide application along the highway ROW. The application rate is specified in standard operating procedures which, in turn, must be in compliance with state and federal regulations governing herbicides. Different herbicides have different specified application rates. The application rate for glyphosate-containing herbicides along highway ROWs in New York State at the time of this study was 25 gallons of a 5% solution of product per acre. Given the application rate of 25 gallons per acre, 2.25 kg of glyphosate is applied to each acre of ROW. From the literature the energy required to manufacture 1 kg of glyphosate is 108,100 kcal, equivalent to 243,225 kcal/acre or 964,549 BTUs/acre.

The energy used to manufacture the herbicide truck and the gasoline used to drive the truck also needs to be evaluated. Although a variety of trucks is used in herbicide application, one of the truck types commonly used is the Ford F250 which weighs between 5,500 and 6,000 pounds, or between 2,500 and 2,700 kg. Using the default value of 75 MJ/kg (Mikkola and Ahokas, 2010) the manufacturing energy for the herbicide truck is between 187,500 and 202,500 MJ.

It is difficult to estimate fuel usage during herbicide application because when herbicide is actively being applied a speed of about 10 miles per hour is maintained. When herbicide is not being actively applied, for example when close to stream and wetlands or when returning at the end of the day, speeds are much higher. Herbicide trucks typically use gasoline.

The fuel use for herbicide application was estimated by using 4 hours of actual travel and application time at 10 mph and an additional two hours for travel time from and to the home facility at 45 mph. Using the default values of 0.114 gallons per mile for a medium sized truck from the EPA MOVES model, 12.5 gallons of gasoline would be used to apply glyphosate to 20 acres (US EPA, 2009). Using an energy content of gasoline of 120,000 BTUs per gallon the total energy consumed in the fuel is 1,500,000 BTUs per day and, assuming herbicide is applied to 20 acres per day, the energy cost for fuel would be 75,000 BTUs/acre. This is close to the BTUs used per acre for tractor operation.

The results from the analysis of mowing and herbicide application are summarized in Table 6.

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Table 6. Summary of Results.

Table 6a. Energy Requirements for Equipment.

<b>Activity</b>	<b>Equipment</b>	<b>Weight (kg)</b>	<b>Energy (MJ)</b>	<b>Energy Totals (MJ)</b>
Mowing	tractor	2019 – 2903	151 – 218 x 10 <sup>3</sup> MJ	164.7 – 337 x 10 <sup>3</sup> MJ
	mower	182 – 1591	13.7 – 119 x 10 <sup>3</sup> MJ	
Herbicide Application	Truck Ford F250	2500 – 2700	188- 203 x 10 <sup>3</sup> MJ	188- 203 x 10 <sup>3</sup> MJ

Table 6b. Energy Requirements for Consumables per acre.

<b>Activity</b>	<b>Consumable</b>	<b>Calculation</b>	<b>Energy used (BTUs/acre)</b>	<b>Totals (BTUs/acre)</b>
Mowing	Diesel fuel	0.22 – 0.86 gallons/acre (from Table 5)	65878 ± 29088	65878 ± 29088
Herbicide Application	Gasoline	70 miles @0.114 gal/mile for total of 12.5 miles	75,000	1,040,600
	glyphosate	2.25 kg/acre x 108100 kcal/kg	965,600	

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The case can be made that the energy for manufacturing the mowing equipment and the herbicide application equipment is similar. Interestingly, the fuel energy consumed during both operations is quite similar even though different fuels are used. The energy cost of manufacturing glyphosate remains the dominant component of the increased energy use per acre observed during herbicide application.

From this work, it is clear that evaluation of energy consumption during specific operations is not a precise science. There are many branch points in the evaluation, and assumptions and default values are used in order to be able to perform the evaluation at all. The value of doing this type of exercise is that it requires the evaluator to identify energy use and assign a semi-quantitative value to the amount of energy being used. For comparisons to be made it is necessary to identify a common metric that can be used as the quantifier in each operation. The methodology to calculate that metric, as long as it is transparent and accurate, does not have to be identical, as evidenced in this study.

The Cornell study (Gao et al, 2010) used a portable 5-emission measurement system manufactured by Clean Air Technologies. The Axion, an updated version of the Montana System, measures fuel rate, engine speed, intake air temperature and boost pressure (for turbo-charged engines), as well as providing emission rates for hydrocarbons, carbon monoxide, carbon dioxide and particulate matter (Clean Air Technologies International Inc., 2008). The Cornell study evaluated ten tractors with mowers with the Axion during 10 minute mowing trials along the ROW. Six of the tractors with mowers were evaluated in our study under field conditions. The average fuel rate of  $0.48 \pm 0.21$  gallons/acre determined by field measurements in the current study (Table 4) compares well with the average fuel rate of  $0.55 \pm 0.14$  reported by Gao et al (2010).

In addition, the Cornell study (Gao et al, 2010) performed four 10 minute trials on over-the-rail (OTR) mowers with the Axion (Clean Air Technologies International Inc., Axion System, 2008). The OTR mower is attached to a tractor through a hydraulic arm that allows the 4 foot wide mowing head to be positioned just on the other side of guide rail. A guide rail is used to keep errant vehicles on the highway and is typically placed along roadside with steep slopes where regular tractors pulling mowers would not be able to work. Gao et al (2010) report that the OTR mowing operation consumes an average of 5.3 gallons of



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diesel per acre. This is equivalent to 743,000 BTUs/ acre. Our study did not include a field evaluation of the OTR mowing operation. The data from Gao et al (2010), however, indicate that although significantly more fuel is used in the OTR operation than in flatter, easier-to-mow ROWs, it is still less than the 1 million BTUs/acre reported for glyphosate application.

Although herbicide application consumes more energy per unit area than mowing does, there is widespread perception that it is less expensive along highway ROWs. The Environment and Energy Bulletin, published by the Business Council of British Columbia (Environment and Energy Bulletin, 2009), reports that integrated vegetation management (IVM), using both chemical and mechanical control of vegetation, is more cost effective than just using mechanical control. They base their conclusion on a survey by CN Utility Consulting (CNUC, 2009) which reports “that mowing transmission line corridors costs an average of \$400 (US) per acre, while herbicide application costs an average of \$224.” They go on to say that the cost can be further reduced to \$100 – \$150 per acre with a well-developed IVM system. They do not explain the derivation of their numbers. In addition, most of the discussion in the Business Council of British Columbia’s article is based on railroads and various utility ROWs. Although similar, utility ROWs and highway ROWs are very different in some important aspects. Utility ROWs are often located away from human populations whereas highways may be located in densely populated areas. Herbicide application can be done aurally along many utility ROWs, but not along highway ROWs. The public typically does not complain about the aesthetic appearance of utility ROWs but can be quite vocal about highway ROWs. The cost saving reported by the Business Council of British Columbia cannot be unilaterally applied to highway ROWs.

Our study did not evaluate the costs of herbicide application or mowing so we cannot directly address cost. Typically increased energy use results in increased cost. There are several aspects of the relationship between energy use and cost, however, that might help to explain a discrepancy, if one exists, including corporate pricing, hidden energy costs, the methods of calculating both cost and energy use, and timeframe in which the calculations were done.

Pimentel (1980) lists the energy inputs for several herbicides. Paraquat is the most energy-intensive at 109,520 kcal/kg, followed by glyphosate at 108,100 kcal/gk. The least energy intensive herbicide on the list is Dinoseb at 19,080

kcal/kg, followed by 2,4-D at 24,200 kcal/kg. The company could choose to lose some money on energy costs to manufacture some herbicides if it were able to recover those losses on the energy costs of other herbicides.

When a product is made in one country and used in another there often exist hidden energy costs, sometimes called “embodied” or “virtual energy” costs (Graedel and Allenby, 2010). With globalization and the spread of multinational corporations it is not always clear where the product has actually been manufactured. Because fuel costs in different countries vary widely, the kcal/kg of manufactured product may not reflect the same cost that would be incurred in the US. In addition, the analysis performed in this study did not take into account energy costs for transportation of products used. Although data to do this analysis may exist, it would be expensive both in time and money.

Another type of data that is difficult to obtain is cost per unit on materials used in large organizations with central purchasing typically far removed from where the product is used. Cost of materials often changes from year to year, and even within a shorter timeframe. Herbicides, if stored properly, can be used several years after they were purchased.

Finally, the time period in which the energy analysis was done greatly influences the cost estimate. Although energy used per gallon of fuel today is similar to what it was in the 1950s, the analysis reported by Zukel and Eddy (1958) was based on cost and not fuel use. Without considerably more data, the cost reported in their brief article cannot be translated into current dollars or energy use. Even though mowing and herbicide application are influenced by the same increases in the cost of energy and the increase should affect both operations proportionately the same, the information they present cannot be used as a yardstick against which to measure current usage without doing extensive research to determine how they derived the numbers they use.

#### **4. CONCLUSIONS**

1. Life cycle analysis is not a precise tool, but it is very useful to help identify energy use in areas that are not readily apparent by systematically analyzing energy inputs into a product and operation. These calculations must be transparent because there are many branch points that can use different default

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and/or calculated values. Furthermore, although the final number must be accurate, the accuracy required is in the range of orders of magnitude rather than significant decimal places. Life cycle analysis needs to be done carefully but it is most useful as a big picture tool.

2. Common wisdom supposes that financial costs reflect energy costs, but there are many reasons why that may not be the case. Because of the myriad ways to calculate both financial and energy costs, it is essential that conversions to a common unit of cost be done. In addition, there are often hidden costs, such as embodied energy and transferred and/or distributed financial costs.

3. Financial and energy costs will never exclusively determine ROW vegetation management policy, but energy and financial cost should be a part of the decision process. Without a detailed analysis their inclusion in policy decisions is based on perception, which can be misleading without factual basis and support.

4. Herbicide application, depending on a variety of factors including the herbicide used and inputs considered, is at least as energy intensive as mowing and, in most cases, more energy intensive than mowing. This information should be included in both the conceptual design and planning for maintenance operations of highways.

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# A METHODOLOGY FOR PRE-EVALUATION OF ECOEFFICIENCY OF ENVIRONMENTAL TECHNOLOGIES FOR SUSTAINABLE REVITALIZATION OF POST-INDUSTRIAL SITES

Włodzimierz A. Sokół<sup>§</sup>

*Central Mining Institute, Plac Gwarkow 1, Katowice, Poland, 40-166*

## ABSTRACT

Revitalization of post-industrial sites is a challenge. Holistic approaches based on integrated regional environmental management are necessary to prevent sites from becoming restricted-use liabilities in the developed landscape. Maintaining site attractiveness and preventing ongoing environmental degradation are important aspects of sustainability in urban areas. This paper describes methods for and examples of integrated regional environmental management systems. The incorporation of information on risk drivers, spatial and temporal components of exposure to various risks, and establishment of remediation and restoration priorities, allows such integrated regional management systems to provide best practices for decision making in the context of multiple risk influences and a range of site end-uses. Methods allowing preevaluation of responses intended to correct site degradation and maximize the range of possible end uses are valuable tools for sustainable development. Evaluation of potential impacts, costs, and benefits of responses and end-use alternatives is important for achieving sustainable environmental, economic, social, and land-use objectives during the planning process. Criteria for preevaluation of energy commitment, material requirements, and emissions to soil, water and air are presented and considered for method development. Example technologies were selected from databases of technologies and tools, and were evaluated in a framework of the international project called EFFECT.

**Keywords:** regional environmental management, risk management, post industrial sites, eco-efficiency

<sup>§</sup>Corresponding Author: Włodzimierz A. Sokół (D.Sc.Eng.), Central Mining Institute, Plac Gwarkow 1, Katowice, Poland, 40-166; +48 32 259 22 11; w.sokol@gig.eu

## 1. INTRODUCTION

Revitalization of post-industrial sites is recognized as an unsolved historical problem in the European Union and in Poland. Many sites here and elsewhere in the world need constructive development to achieve useful functions, and to protect against further site degradation. A difference between the sites currently used (Fig. 1, Site A) and degraded industrial areas called “Brownfields” (Fig. 1, Site B), lies in the fact that for the latter there is the need to reduce existing physical and/or chemical degradation to the level that allows implementation of new site use, and to carry out site development (i.e. achieve revitalization).

Variability in the use of sites is inevitable (Fig. 1 - Site State), but site degradation should be prevented or corrected. This means that we have to look at the degraded sites not solely as a relict of the past, but rather as a challenge for the present day.

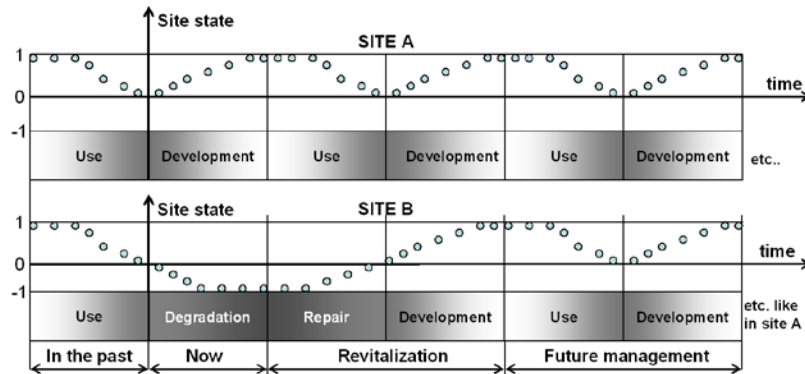


Figure 1. Dealing with two sites: Site A – free of degradation, Site B – degraded.

This is shown by the results of work carried out with the participation of the author, for sustainable development in business districts of major cities of the world (ISO IWA 9, 2011). The sites currently used, now or in a few years, will require changes or improvements (Fig. 1 - Development) to avoid loss of their attractiveness and gradual degradation again.

One way to solve problems of the past and protect against land degradation in the future, and to ensure sustainable development, is to apply approaches defined in the European Union "Action Plan for Environmental Technologies" (COM, 2004), which refers to the United Nations Agenda 21 (UN AGENDA 21, 1992). “Environmental technologies” are those technologies that are less harmful to the environment than their alternatives. This definition for anthropogenically transformed areas is beneficial because it allows application of an integrated methodology for ensuring identification, evaluation and selection of innovative technologies for repair of degraded areas and their development, with an appropriate set of tools, including management tools. Achieving this goal, especially in areas of anthropogenically transformed lands, requires a coherent management system, incorporating different

elements as shown on Figure 2, thus optimizing the likelihood of success. Considering the site life cycle is necessary, taking into account the relationship with surrounding areas, embracing all phases of the revitalization process, and managing environmental aspects, as well as local, regional and state economic and social elements.

Achieving a goal of adapting a site to its new use is an integrated environmental management process, typically organized at a regional level, using risk management approaches as a core tool for identification of significant environmental aspects, strategic/operational objectives, and implementation of investment projects as environmental tasks. Other core tools include environmental, economic and social performance evaluation. This business approach to risk management is essential to successful remediation and redevelopment of degraded sites.

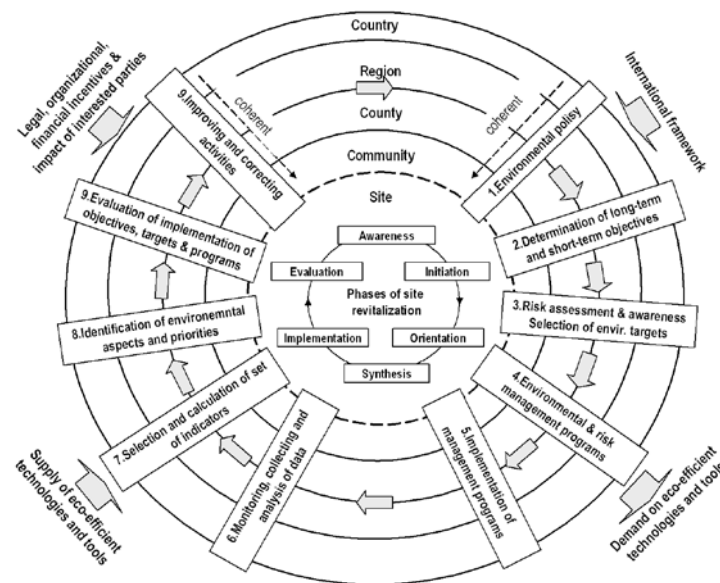


Figure 2. Aspects of site development and how they interact.

This paper is based on a methodology of integrated regional environmental management as presented at the 20<sup>th</sup> AHSC International Conference (Sokol, 2010) where the approach was defined, risk areas, risk factors and priorities were described for evaluation of environmental technologies, and projects were selected to represent Best Practices for proposed risk criteria.

This methodology was developed to allow precategorization of technology options and preevaluation of ecoefficiency for site remediation, as well as development of new uses of sites according to sustainable development principles. Preevaluation of ecoefficiency of environmental technologies is based on data and information submitted by the technology suppliers. The process considers impact of technologies for reduction of site contamination, development of new site uses, and probability that environmental, economic,

social and space-planning benefits will be achieved. Technology examples were identified from the ACT CLEAN, SPIN via ([www.actclean.gig.eu](http://www.actclean.gig.eu)) databases, and they were evaluated within the framework of an international project known as EFFECT (EFFECT, 2012).

## **2. ASSUMPTIONS OF THE INTEGRATED METHODOLOGY**

The essence of the methodology is shown in Figure 3. If we assume that the keys to the door to sustainable development of an affected site are environmental technologies, then finding the right combination of keys is likely to lead to success. The integrating element of the proposed methodology (Key 1 on Figure 3) is a model of the Regional Environmental Management System (REMAS; Sokol, 2011) shown in Figure 4, with its own uniform environmental procedures and software (e-REMAS), and access to external tools such as:

- Business risk management tools, adopting AIRMIC (2002; ISO 31000:2009), are applied to decisions at appropriate stages (Figure 3, Key 2);
- Review of specific revitalization procedures (Figure 5; Sokol, 2010), to manage the process of Brownfield revitalization and identification of environmental technologies, as well as potential obstructions in the process (Figure 3, Key 3);
- Preevaluation of environmental technologies and eco-efficiency (Figure 3, Key 4);
- External databases of environmental technologies and tools available (e.g., ACT CLEAN, SPIN, LONGLIFE) through the National Contact Point for Eco-efficient Technologies and Management Systems ([www.actcclean.gig.eu](http://www.actcclean.gig.eu)) (Figure 3, Key 5);
- External database of areas that require revitalisation, and data on pollutants and their sources (Reviewing Sheet) of REMAS (Figure 3, Key 5);and,
- Tools to provide participation of stakeholders in evaluation of projects, programs and decisionmaking at different stages of the site development process (Figure 3, Key 5).



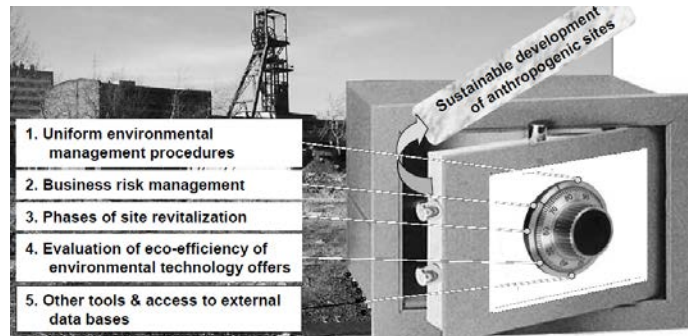


Figure 3. Basic keys to the doors of sustainable development at post-industrial sites.

In the environmental management process, business risks often are associated with achievement of regional strategic and operational objectives level, and in relation to specific sites ("Establishing objectives and risk assessment", Figure 4). If the land is contaminated, then it must be cleaned up (see Figure 1), reducing chemical and/or physical degradation to a level that allows implementation of new site functions. Other steps are the same as for redevelopment in degradation-free areas. The key to the environmental management system (Figure 4) is "Evaluation of projects, technologies and risk", which must interact with relevant phases of the revitalization process (Figure 5). In this step, potential technologies and availability are preevaluated based on supplier data and information.

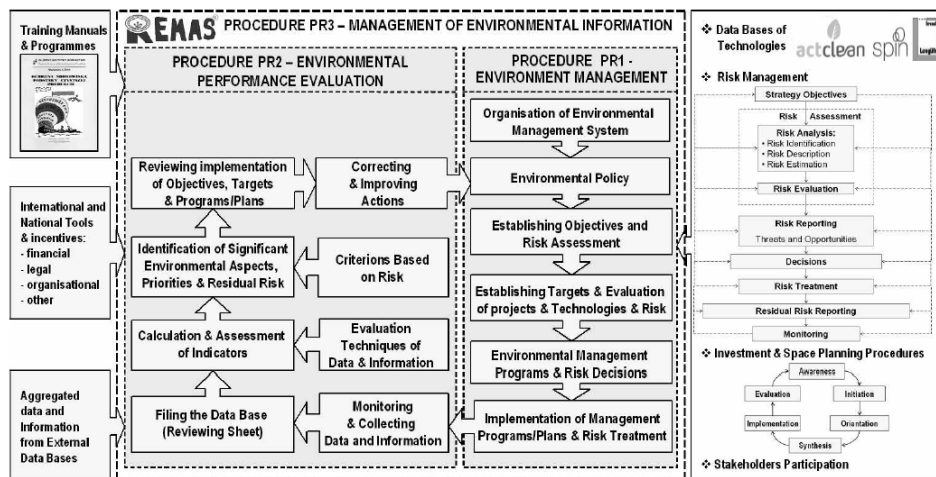


Figure 4. Regional Environmental Management System (e-REMAS tool).

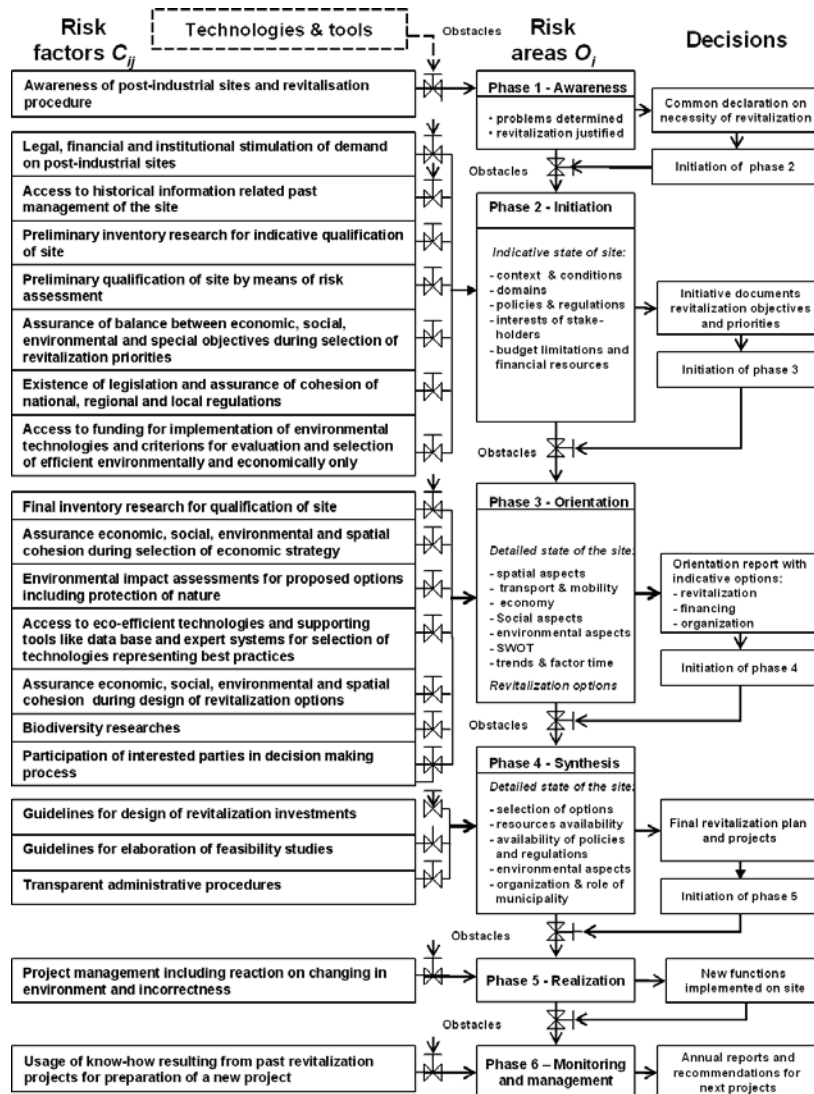


Figure 5. Revitalization procedure with obstacles during implementation (Sokol, 2010).

### 3. EVALUATION OF PROJECTS AND TECHNOLOGIES

#### 3.1 Evaluation of Revitalization Projects

In the site development process (Figure 4; Figure 5), use of ecoefficient technologies is indispensable, and a risk management approach leads to selection of the best projects. Implementation of each project involves risk, which can be characterized by:

- Risk areas ( $O_i$ ,  $i = 1 \div n$ ) that reflect sustainability areas in environmental management system or the specific phases of revitalization procedure (Table 1; Figure 5),
- Risk factors within the risk areas ( $C_{ij}$ ,  $i = 1 \div n, j = 1 \div m_i$ ) that reflect sustainability objectives in the framework of the sustainability areas or the specific technologies in the revitalization procedure,

Each risk factor  $C_{ij}$  for specific projects (Table 1, Figure 5) is described by:

- $I_{ij}$  – impact (significance of the factor),
- $P_{ij}$  – probability (the belief that the factor will really occur),
- $R_{ij}$  - risk (risk of defeat or a chance of success):

$$R_{ij} = I_{ij} \cdot P_{ij}, i=1 \div n, j=1 \div m_i \quad (1)$$

Impact  $I_{ij}$  and probability  $P_{ij}$  are evaluated by using a range of possible values 1 to 5 for each variable as shown on Figure 6 (1 = negligible, 2 = small, 3 = medium, 4 = big, 5 = very big).

After the evaluation of risk factors, including assessment of the proposed technology, the assessment of specific risk areas is performed, followed by evaluation of the entire project:

for the risk areas: 
$$R_i = \sqrt{\frac{1}{m_i} \sum_{j=1}^{m_i} R_{ij}^2}, i=1 \div n, j=1 \div m_i \quad (2)$$

for the whole project: 
$$R = \sqrt{\frac{1}{n} \sum_{i=1}^n R_i^2}, i=1 \div n \quad (3)$$

Risk lies in the range [0, 25], or [0, 100] if multiplied by 4 to get comparability of results with results from other methods (RESCUE, 2004). Proposed criteria are shown in Figure 6 (Sokol 2010). Depending on formulation of the problem, findings may indicate a threat of defeat (pessimistic) or chance of success (optimistic) associated with use of selected technologies.

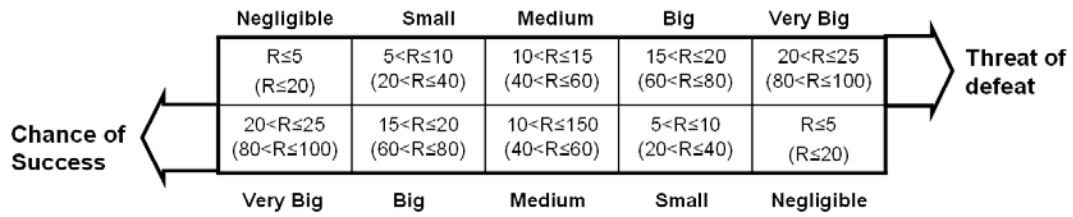


Figure 6. Criteria for evaluation of risk.

Assigning scores for  $I_{ij}$  and  $P_{ij}$  is supported by checklists using quantitative evaluation, qualitative evaluation, or a combination of the two, for example:

- assessment by individual experts, self-assessment by authors of a project, or group assessment during the workshop, using evaluator knowledge and experience;
- use of auxiliary tools such as: tests and measures, computer simulation, ecotechnology effectiveness evaluation (e.g., by life-cycle analysis; Guinee, 2002; ISO 14044:2006), ecoefficiency of the technology (ISO/CD 14045, 2010; Michelsen et al., 2006) etc., and software like Ecoindicator 99 (Goedkoop and, Effting and Collignon 2002) or other tools such as health risk assessment; and,
- combination of both assessment forms.

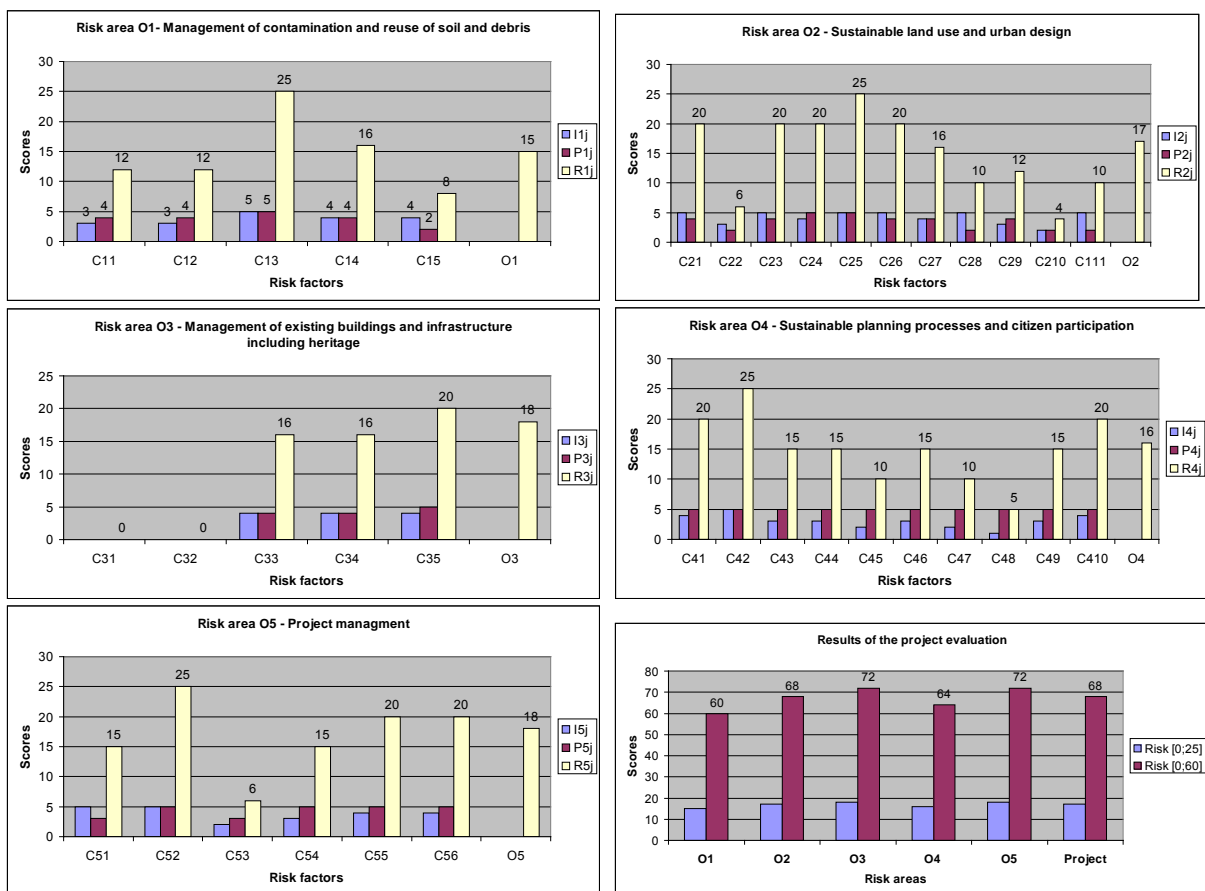
As an example, consider evaluation of a project known as "Dolomite Valley" in Bytom, Poland (Sokol, 2004, 2010) completed under a framework of Phase 5 of the revitalization procedure (Figure 5). It is a 38 ha area on the site of a former dolomite opencast mine, often termed a "stripmine". As a result of the revitalization process, this site now has an artificial ski slope, a restaurant, hotel, bike trails and other attractions. The revitalization project defined 5 risk areas ( $O_i$ ) and 37 risk factors ( $C_{ij}$ ) as presented in Table 1. The risk factors reflect sustainable development objectives identified as significant environmental aspects. Project results are presented in Figure 9.



Figure 7. Degraded site after closing the dolomite opencast -photo from 1997.



*Figure 8. Dolomite valley today after revitalization.*



*Figure 9. Results of the project evaluation.*

*Table 1.* Description of the project risk areas and risk factors.

<b>Risk areas</b>	<b>Risk factors (sustainability objectives)</b>	
<b>Risk area O1</b> – Management of contamination and reuse of soil and debris	C <sub>11</sub>	To reduce negative environmental impacts on the site and on the neighbourhood including human health risks
	C <sub>12</sub>	To minimise waste and maximise recycling/reuse of soil, debris
	C <sub>13</sub>	To ensure cost effectiveness and technical feasibility
	C <sub>14</sub>	To improve social acceptance through identification of all stakeholders and risk communication
	C <sub>15</sub>	To provide decision support tools for risk based land management
<b>Risk area O2</b> – Sustainable land use and urban design	C <sub>21</sub>	To promote land use functions that match regional socio-economic demands and needs
	C <sub>22</sub>	To integrate reuse of brownfield sites into regional land management
	C <sub>23</sub>	To integrate the reuse of brownfield sites into urban development
	C <sub>24</sub>	To achieve benefits for and prevent adverse impacts on the local neighbourhood
	C <sub>25</sub>	To generate and safeguard employment and economic development
	C <sub>26</sub>	To promote land use functions that suit the natural and man-made environment of the site and its neighbourhood
	C <sub>27</sub>	To save resources
	C <sub>28</sub>	To connect different city districts
	C <sub>29</sub>	To provide access for all means of transport
	C <sub>210</sub>	To achieve high urban design quality
<b>Risk area O3</b> – Management of existing buildings and infrastructure including heritage	C <sub>111</sub>	To create and maintain flexibility and flexible urban design
	C <sub>31</sub>	To protect heritage buildings
	C <sub>32</sub>	To minimise costs of protection of heritage buildings
	C <sub>33</sub>	To assure conservation of energy
	C <sub>34</sub>	To reduce consumption of resources
<b>Risk area O4</b> – Sustainable planning processes and citizen participation	C <sub>35</sub>	To reduce impact on environment and health
	C <sub>41</sub>	To integration of stakeholders into all steps of the process
	C <sub>42</sub>	To assure equal access to (critical) information
	C <sub>43</sub>	To assure information management
	C <sub>44</sub>	To assure two-way information flow
	C <sub>45</sub>	To publicize and document process and intermediate results
C <sub>46</sub>	To assure influence on decisions, procedures and process evolution	

	C <sub>47</sub>	To assure budget allocated for participation
	C <sub>48</sub>	To assure emergence of structures and institutional learning
	C <sub>49</sub>	To assure quality of process management
	C <sub>410</sub>	To assure satisfaction / contestation of results
<b>Risk area O5 – Project management</b>	C <sub>51</sub>	To adopt an interdisciplinary project team approach
	C <sub>52</sub>	To facilitate efficient project delivery
	C <sub>53</sub>	To promote and manage stakeholders participation
	C <sub>54</sub>	To provide a framework for transparency in decisions, flow of information and improved communication structures
	C <sub>55</sub>	To protect human health and safety during field work
	C <sub>56</sub>	To adopt an approach that integrates social, economical and environmental aspects

Comparison of the results of this project with the criteria shown in Figure 6 confirms that the project is likely to be successfully implemented, as illustrated in Figure 8.

### **3.2 Prevaluation of Probability That Technology Offers Are Relevant for the Project**

Preevaluation of probability that the technology offers are relevant is a part of the project evaluation. Depending on the importance of technology  $I_{ij}$  for the project, coupled with product knowledge which is provided with the technology offer, the technologies are categorized into different "baskets" because of probability  $P_{ij}$  of achieving a supplier-declared efficiency (defined in following bullets). Probability  $P_{ij}$ , that the project is able to achieve expected objectives after implementation of the selected technology in the framework of a given investment project, influences allocation of a technology to a specific basket.

- **Certified technology** – score of 5– technology parameters are certificated by an independent body (e.g., Environmental Technology Verification (ETV)),
- **Patented (innovative) technology** - score of 4 – technology is patented or subject to a process of property protection, <3 years on the market, <15% of the market sector,
- **Cleaner Production technology** – score of 3 – technology with confirmed pollution prevention efficiency in comparison to situation before technology implementation,
- **End of Pipe technology** - score of 2 – technology with confirmed pollution treatment efficiency in comparison to situation before technology implementation,

- **Ordinary technology** – score of 1 – ordinary solution available at market or lack of numerical data/indicators which prove novelty technology,
- **Unacceptable technology** - 0 score – obsolete or inappropriate technology.

The idea of preevaluation of probability that the technology offers are relevant for the project is presented on Figure 10. Putting a technology offer in a selected “basket” is valid assuming a supplier describes the technology in sufficient detail. If a supplier submits more reliable data and increases the user’s certainty, then the offer can be moved into the higher basket. For example, if the technology offer is in the basket 1 because there is a verbal description only, but the supplier subsequently submits results of measurements for this technology with comparison to an older one or provides comparison with a reference technology, then the technology offer can move from basket 1 to basket 2 or 3 depending on whether it relates to Cleaner Production or an End-of-pipe solution. If a supplier submits results of technology verification by an independent body (Lonsdale 2011; EPA ETV 2006), the technology may move from basket 1 to a higher basket.

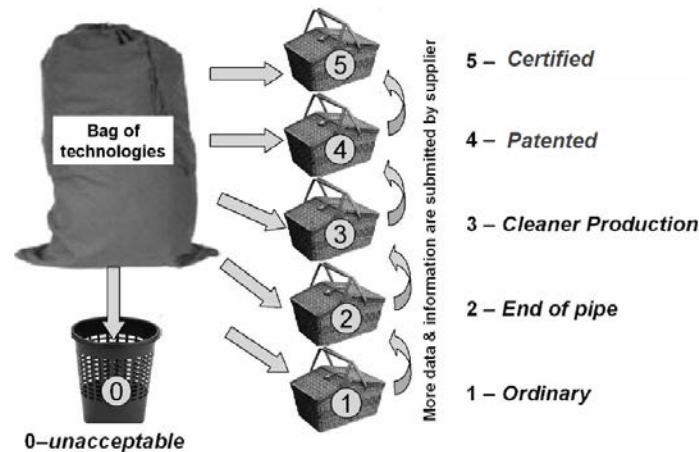


Figure 10. The idea of “Basket” approach.

### 3.3 Preevaluation of Ecoefficiency of Environmental Technologies

Potential buyers often seek innovative technologies and will expect recommendations relating to ecoefficiency. That’s why as a part of the project evaluation process, a simplified preevaluation approach was developed for assessment of a technology’s ecoefficiency, often based on limited numerical data. Inspired by JEMAI (2004), a simple approach to the enhancement of ecoefficiency of an improved technology developed is illustrated as follows:



$$\Delta E[\%] = 100 \cdot (E_{new} / E_{old} - 1) = 100 \left\{ \sqrt{3} / \sqrt{\sum_{i=1}^3 I_i^2} - 1 \right\} \quad (4)$$

where:

$$I_i = \sqrt{\frac{1}{n_i} \sum_{j=1}^{n_i} I_{ij}^2}, \quad i = 1 \div 3, j = 1 \div n_i \quad (5)$$

$$E_{new} = \frac{V_{new}}{I_{new}} = \frac{1}{(I_{new} / V_{new})} = 1 / \sqrt{\sum_{i=1}^3 I_i^2} \quad \text{and} \quad E_{old} = \frac{1}{\sqrt{3}} \quad (6)$$

In the equations,  $I_{ij}$  and  $I_i$  are relative environmental impact of a new technology (improved):

$$I_{ij} = \left( \frac{I_{ij,new}}{V_{new}} \right) / \left( \frac{I_{ij,old}}{V_{old}} \right) \quad (7)$$

and:

- $I_1$  – Efficiency of resources (degree of reduction in raw material consumption, e.g., water, natural fuels etc.),
- $I_2$  – Efficient use of energy (degree of reduction in consumption of energy),
- $I_3$  – Emissions released (degree of emission reduction to air, water and soil and content of environmentally harmful substances),
- $n_i$  – quantity of the parameters  $I_{ij}$  in framework of the environmental impacts  $I_i$ ,
- $E_{new}, E_{old}$  – the ecoefficiency of new and old technology respectively.
- $V_{new}, V_{old}$  – technology value of new and old solution,
- $I_{ij,new}, I_{ij,old}$  – environmental impact of new and old solution.

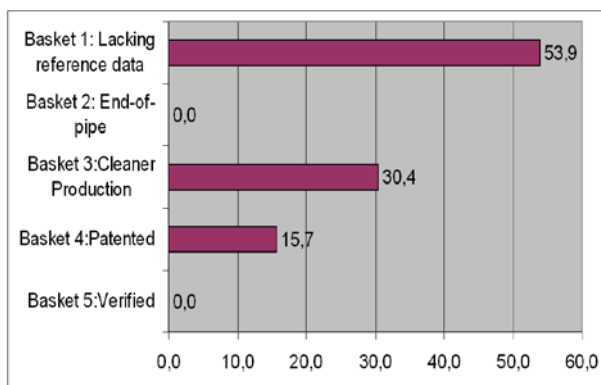
In equation (4), it is assumed that for an old technology (before implementation of improvements), each component of the environmental impact is represented by  $I_i = 1$ . If the new technology does not show improvement in a component, the value remains equal to 1. Equation (5) i.e. average sum of squares is used when a few improvements  $I_{ij}$  were implemented relating to one environmental impact  $I_i$ . If for example  $I_3$  reflects emission to air that consists of  $n_3=4$  emissions of CO<sub>2</sub> ( $I_{31}$ ), NO<sub>2</sub> ( $I_{32}$ ), SO<sub>2</sub> ( $I_{33}$ ) dust ( $I_{34}$ ), then we apply equation (5) for evaluation of  $I_3$ .

Preassessment of ecoefficiency enhancement ( $\Delta E$ ) assumes that the system boundaries apply to the technology only and that external changes are negligible. The accuracy of this evaluation depends on the numerical data submitted by the technology supplier. This approach can motivate a potential buyer to ask for more detailed data to allow assessment of ecoefficiency.

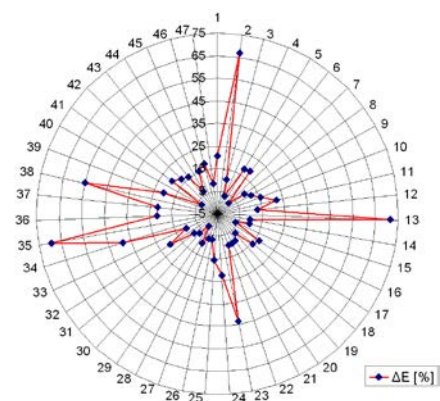
The methodology was tested against 102 selected offers of energy efficient technologies submitted by suppliers from the Baltic Sea Region countries (BSR), being considered for the SPIN and ACT CLEAN databases. It must be emphasized that the databases included labels of each technology only and not full descriptions. Results of preevaluation of the 102 offered technologies are presented on the Figure 11. Only 46% of the offered technologies were patented or under a similar legal protection process. It is positive that a significant percentage of the offered technologies from baskets 3 and 4 implemented Cleaner Production solutions and none from the basket 2 represented end-of pipe approaches. Almost 54% of offered technologies had only descriptive information on performance. None of the technologies included information on full life-cycle or that ecoefficiency evaluation was performed. Only 47 offers included numerical data, and in those cases it was limited.

Historically, this kind of evaluation is available for a limited number of products (Saling et al., 2002; Guinee, 2002; Michelsen et al., 2006; JEMAI, 2004; and ISO 14045, 2012). For the technology assessment, relevant methodologies are still being sought. Many evaluation efforts have failed because they lacked important data relating to the life cycle assessment (LCA) of the technology and relied upon simplified assumptions to overcome a lack of sufficient data for an ecoefficiency analysis. Moreover, the LCA depends on assumed system boundaries and on applied tools, such as ecoindicator 99 (Goedkoop, Effting and Collignon, 2002) and others.

The results of this preevaluation are presented on Figure 12. That simplified evaluation allows assessment of ways that a new or modified technology is more ecoefficient as compared with an old or standard/reference technology, given poor numerical data on performance.

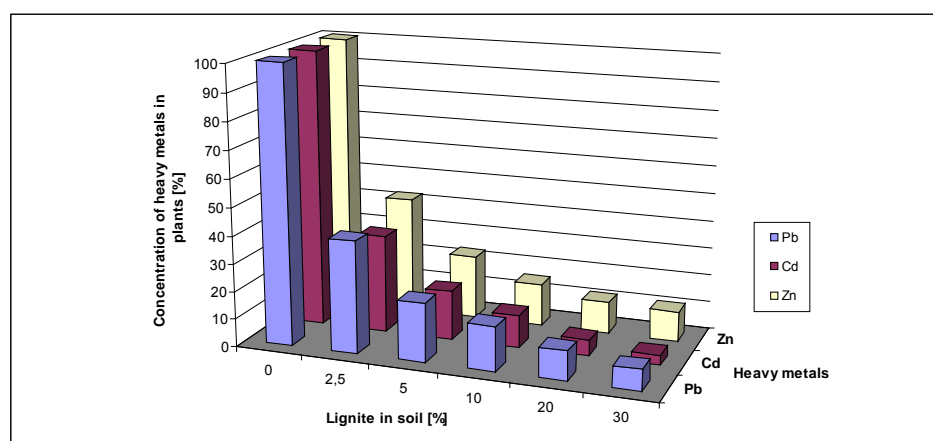


*Figure 11.* Allocation of selected technology offers from BSR into the baskets in (%).



*Figure 12.* Results of pre-evaluation of ecoefficiency  $\Delta E$  [%] of selected energy-efficient technology offers from BSR.

The scope of this paper makes limits a detailed discussion on the evaluated technologies, data on technology performance being analysed, and presentation of the full range of technologies selected within the framework of the e-REMAS tool. That is why only one example of preevaluation of technology ecoefficiency is presented for the case of chemophytostabilization of heavy metal-contaminated soil by means of lignite. Soil contamination by heavy metals is observed in sites related to mining industry, ironworks, waste treatment plants and others. Special attention should be paid to the sites where a soil contamination occurs in the vicinity of closed industry plants and currently operating facilities. An example is that of the Dolomite Valley (Figure 7). At such sites, high metal concentrations and bioavailability, coupled with poor vegetation, may create risks of heavy metal effects on the food chain. While that threat was not observed, different technologies were reviewed to be ready to manage this kind of contamination. Among the remediation methods, chemophytostabilization was considered for treatment of soil where the risk of heavy metals exists. Chemical amendments and selection of selected plants decrease metals bioavailability, and create good and dense plant cover. Plant cover diminishes soil erosion and incursion of heavy metals into the soil profile. Technology review that considers lignite for chemophytostabilization of metals in soil is a good example for preevaluation of technology ecoefficiency. Krzyzak (2010) considered different options to decrease metal bioavailability for cadmium, lead and zinc by various treatments of lignite to the soil, based on metal concentration in plants (*Festuca arundiancea* cv. Montserrat). Initial concentration of heavy metals in soil was as follows: lead – 470 mg/kg , cadmium – 850 mg/kg, zinc – 6,500 mg/kg. On Figure13, the option without addition of lignite (0% lignite ) is the reference option with concentration of heavy metals (100%). Dosing of soil with lignite at 2.5%, 5%, 10%, 20% and 30% results in a concentration decrease due to reduced bioavailability.



*Figure 13.* Reduction of heavy metal bioavailability by lignite soil dosing.

Reduction or increase of specific environmental impacts (e.g., use of resources,  $I_1$  = lignite; consumption of energy  $I_2$ ; and average concentration of heavy metals in plants,  $I_3$ ) is presented in Figure 14, along with preevaluation of ecoefficiency enhancement ( $\Delta E$ ). For evaluation of average concentration of heavy metals in plants, equation (5) was applied. All impacts  $I_i$  and ecoefficiency enhancement  $\Delta E$  are expressed in Figure 14 in %. The best technology option is the soil dosage of lignite (L on Figure 12) at 10%. It reduces the concentration of heavy metals in plants ( $I_3 = 14\%$ ) and increase ecoefficiency ( $\Delta E = 16\%$  increase) despite an increase in resources consumption by 10% ( $I_1 = 110\%$ ). Increases in lignite to L = 20% or L = 30% decrease the concentration of heavy metals in plants slightly ( $I_3 = 10\%$  and 8%, respectively) but technology ecoefficiency enhancement decreases ( $\Delta E = 11\%$  and 5%, respectively) due to increased consumption of resources (lignite) to 120% and 130%. Energy consumption wasn't presented in (Krzyzak 2010), that is why it was assumed as and unchanged value for  $I_3 = 100\%$ .

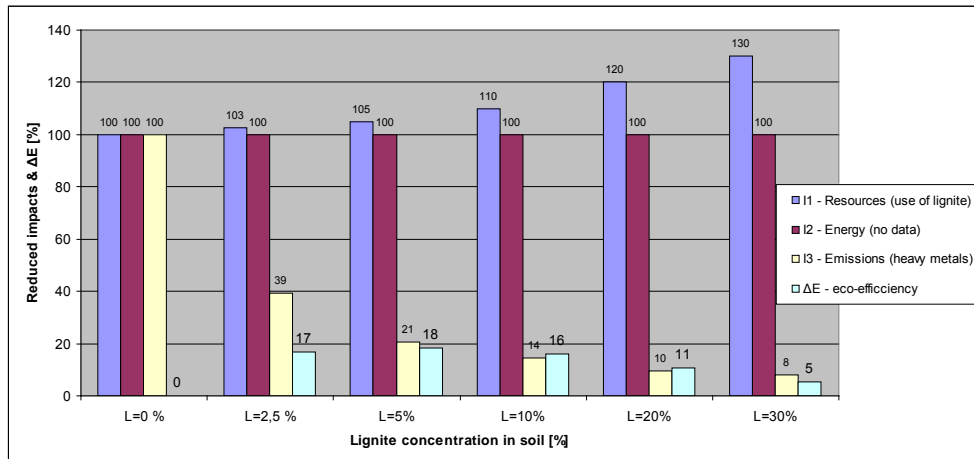


Figure 14. Ecoefficiency enhancement of chemophytostabilization technology options.

#### 4. THE POSSIBILITY OF USING THE METHODOLOGY FOR PROTECTION AGAINST DEGRADATION OF URBAN AREAS

In many places in Europe and around the world there is a need to change current land uses, and to significantly expand functions for existing site uses. The methodology presented herein was developed as well to allow precategorization of technology options and preevaluation of ecoefficiency for site development and degradation prevention. Around 40% of the energy consumption in the European Union is due to existing buildings. That is why development of the methodology is carried out, inter alia, for the construction sector. Currently the methodology is being tested during the development process at the campus of the Klaipeda University in Lithuania for evaluation

of energy efficiency and reduction of CO<sub>2</sub> emissions in a pilot low energy dormitory building (LONGLIFE-INVEST, 2012).

A chance for wider application of the proposed methodology beyond Poland is an initiative of the International Committee of the ISO International Workshop Agreement on Sustainable business districts (ISO IWA) in 24 major metropolitan areas across the world. Model REMAS was used for development of a general management system for the business districts.

A survey conducted by the French Institute (IAU; Romera and Mohamed, 2010), shown in Figure 15, concluded that among the 12 metropolitan areas surveyed, 10 business districts are located in city centers, and the development is carried out in a systematic manner. In many cases, there is a need to change the existing function of buildings including buildings with historical value. Planning by the cities regarding where the business districts are developed is dependent on a number of considerations, including:

- energy consumption reduction, diversification of energy sources, and production of energy within business areas with innovative technology (passive or low energy buildings) - 8 business districts,
- water consumption reduction and water recycling, including rainwater - 7 districts,
- reduction of waste production, materials recycling of materials/waste in or near district - 9 districts.



Figure 15. Business district being involved into ISO IWA - source (Romera and Mohamed, 2010).

#### **4. CONCLUSIONS**

1. Variability in site use is inevitable, but site degradation should be prevented. Sites currently used, or those in future years, will require changes or improvements to avoid losing attractiveness and becoming gradually degraded.
2. To solve past problems and protect against future land degradation in a sustainable way, it is worthwhile to initiate a voluntary regional environmental management system integrating management procedures with supporting tools like revitalization procedures, access to databases of ecoefficient technologies, and risk management approaches to assure achievement of strategic and operational objectives of the site and region. The REMAS model and its innovative tool e-REMAS suit this purpose.
4. Technology needs should be identified and evaluated within relevant procedures of regional environmental management systems. In selecting technology innovations it is necessary to preevaluate their ecoefficiency and efficiency of implementation projects. Results will lead to selection of the best solutions with high probability that technologies offered by the supplier will allow achievement of stated objectives.
5. Results of international projects for planning and implementation of sustainable development of degraded sites should be used. Useful technology highlights, tools and best practices have been identified, verified and implemented, as referred in this paper.

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# OBSERVED FIELD SCALE FIRST ORDER ATTENUATION RATES OF BTEX

Nathan Stevens<sup>§</sup>

*Gulf Oil Limited Partnership, 281 Eastern Avenue, Chelsea, MA 01523*

## ABSTRACT

Due to the widespread use of laboratory analyses of benzene, toluene, ethylbenzene, and xylenes to evaluate potential human health and environmental risks posed by releases of petroleum to the environment, an abundance of data regarding the concentration of these compounds in soil and groundwater at regulated sites is available. Characterization of the attenuation of these compounds is an important part of developing site closure strategies, forecasting fate and transport, and estimating the risk posed to area receptors. Evaluation of BTEX concentrations and first-order attenuation at more than 20 petroleum release sites located in the eastern US (over 1,400 samples) was recently performed. We present data on the apparent field scale attenuation rates of benzene, toluene, ethylbenzene, and total xylenes under varying release conditions. The size and geographic spread of the primary data set makes our findings potential applicable to a large number of petroleum release sites.

**Keywords:** first-order rates, natural attenuation, BTEX

<sup>§</sup>Corresponding Author: Nathan Stevens, Gulf Oil Limited Partnership, 281 Eastern Avenue, Chelsea, MA 01523; (617) 884-5980; [nstevens@gulfoil.com](mailto:nstevens@gulfoil.com)

## **1. INTRODUCTION**

According to the United States Environmental Protection Agency, as of September 2013, there is a backlog of 80,693 leaking underground storage tank (UST) sites to be evaluated and potentially remediated (*US EPA, 2013*). Residual petroleum hydrocarbon impacts to groundwater at a large number of these sites will be addressed, partially or entirely, through monitored natural attenuation (MNA). The decision process of many potentially responsible parties (PRPs) includes explicit evaluation of the relative and absolute risks posed by such sites, net present value of various remedial strategies, real estate and revenue concerns, and risk tolerance. MNA is frequently found to be a viable solution for risk management of impacted properties, especially following active source removal actions at sites which pose relatively low risk.

In evaluating the feasibility and appropriateness of MNA as a remedial action, temporal considerations are of great importance. The question of “How long will this take?” is paramount to regulators, PRPs, property owners, and the communities in which these sites are located. Fully and accurately addressing this simple question can require extensive evaluation of the stability of the impacted groundwater plume, the mass of contaminants in the subsurface, an understanding of the hydrodynamic regime of the impacted groundwater, land use considerations, and the rates of chemical reactions affecting the contaminants (*National Research Council, 2000*).

A basic evaluation component of the timing of MNA strategies is to determine the rate at which contaminant concentrations in the groundwater are changing. Such rates may be determined for both the downgradient distance to which concentrations of constituents of concern (COCs) will travel with the groundwater, and for the changes in concentration at a point such as a monitoring well over time. We recently evaluated the first order attenuation rates for benzene, toluene, ethylbenzene, and total xylenes in groundwater at 58 monitoring wells at 24 sites throughout the northeastern United States, using the methodology of *Newell et al.*[citation needs a date.] Attenuation rates were determined on a per-event basis, and compared over the monitoring periods, up to approximately 19 years. A brief discussion regarding possible applicability of this method for estimating long-term impacts is also presented.

## **2. METHODS**

All 24 sites studied are located in the northeastern United States, from Pennsylvania through New Hampshire. Each location is or was previously a retail gasoline station and convenience store, dispensing petroleum products from multiple USTs. Out of an available study group of some 300 locations, sites were selected based on several factors meant to maximize the comparability of the data.

1. Certainty of potential release dates.
2. Absence of additional apparent releases during the evaluated period.
3. Completion of basic source removal such as removal of leaking tanks and visibly impacted soil at or above the water table.
4. Monitoring periods prior to application of other active remediation techniques such as groundwater extraction and treatment, in-situ chemical treatments, air sparging, or soil venting.
5. Availability of groundwater sample analyses of benzene, toluene, ethylbenzene, and total xylenes with detected concentrations of all compounds.

Groundwater sample analyses had been conducted by a few widespread techniques, based on industry standards and regulatory requirements. No effort was made to independently evaluate the accuracy or quality of the data, other than that each sample result had been included in a final lab report from a third party lab, and subsequently submitted to the applicable regulatory agency. The primary analytical methods included US EPA 8021 (gas chromatography and photoionization detector [GC/PID]), US EPA 8260 (GC and mass spectrometer [GC/MS]), and Massachusetts Volatile Petroleum Hydrocarbon analysis (VPH, GC/PID with a flame-ionization detector connected in series). Determination of the first-order point attenuation rate was performed using the industry-standard method from ASTM (1998) as described in Newell et al. (2002).

Microsoft Excel 2007 was used for data analyses. Each well was evaluated separately. The COC concentrations as determined by laboratory analysis ( $[X]$ ) were log-transformed via the natural log ( $\ln$ ) of the concentration and plotted against time. Time ( $t$ ) in all cases was normalized by subtracting the original release date (in some cases the date of the first sample) from the sample date. Excel's LINEST function was used to calculate the slope of a best-fit line through the  $\ln[X]$  data against  $t$ . This slope is taken as the point attenuation ( $k_p$ ) rate and has units of per time. For each well, the  $k_p$  was determined for each COC from the first sampling event at  $t_0$  until the  $i^{th}$  sample.

Table 1 presents an example data set from this study. For each COC, at each sampling event the attenuation rate was calculated from the date of release to the

*Observed Field Scale First Order Attenuation Rates of BTEX*

sampling date. For example, the fifth sample, highlighted in the table, was collected August 5, 2005. Calculation of the first-order point attenuation rate  $k_p$  for benzene is therefore:

$$k_p = \frac{\ln(B_0) - \ln(B_4)}{t}$$
$$k_p = \frac{\ln(1840) - \ln(887)}{1.56 \text{ yrs}}$$
$$k_p = 0.47 \text{ yr}^{-1}$$

Where  $B_0$  is the initial measured benzene concentration,  $B_4$  is the fourth sample benzene concentration, and  $t$  is the time elapsed between the two. The same procedure was utilized for each COC for each sampling event, for each site. Correlations between each COC and total BTEX were evaluated using Excel's CORREL function:

$$\text{Correl}(X, Y) = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}}$$

Where  $x$  and  $y$  are values and means of each COC data set.

The entire  $k_p$  data set was then evaluated for changes in average  $k_p$  for each COC over time. To facilitate this, the data were stratified to produce samples representing results soon (up to 0.99 years) following the petroleum releases, two divisions of mid-term monitoring (1-4.9 years and 4.0-9.9 years), and longer-term (greater than 10.0 years) monitoring. For each temporal group, the average  $k_p$  was calculated for each COC and for Total BTEX.

Table 1. Example data set from this study. B is benzene, T toluene, E ethylbenzene, and X total xylenes. LN is natural logarithm. Kp is point attenuation rate. NA not applicable.

WELL ID	Sampling Date	Years	B (ug/L)	T	E	X	BTEX	LN B	LN T	LN E	LN X	LN BTEX	KpB (per year)	KpT	KpE	KpX	KpBTEX
MW-3	01/13/04	-	1840	4,710	3,680	19,100	29330	7.52	8.46	8.21	9.86	10.29	NA	NA	NA	NA	NA
MW-3	11/18/04	0.85	1210	1,350	2,030	8,450	13040	7.10	7.21	7.62	9.04	9.48	(0.49)	(1.47)	(0.70)	(0.96)	(0.96)
MW-3	02/04/05	1.06	462	821	1,210	5,620	8113	6.14	6.71	7.10	8.63	9.00	(1.30)	(1.64)	(1.05)	(1.15)	(1.21)
MW-3	05/05/05	1.31	550	626	1,340	5,570	8086	6.31	6.44	7.20	8.63	9.00	(0.92)	(1.54)	(0.77)	(0.94)	(0.98)
MW-3	08/05/05	1.56	887	1,350	2,050	8,090	12377	6.79	7.21	7.63	9.00	9.42	(0.47)	(0.80)	(0.37)	(0.55)	(0.55)
MW-3	11/04/05	1.81	628	727	1,710	6,600	9665	6.44	6.59	7.44	8.79	9.18	(0.59)	(1.03)	(0.42)	(0.59)	(0.61)
MW-3	02/07/06	2.07	1200	1,800	2,900	12,200	18100	7.09	7.50	7.97	9.41	9.80	(0.21)	(0.46)	(0.12)	(0.22)	(0.23)
MW-3	02/07/06	2.07	1100	2,000	2,500	10,800	16400	7.00	7.60	7.82	9.29	9.71	(0.25)	(0.41)	(0.19)	(0.28)	(0.28)
MW-3	05/08/06	2.32	981	1,170	1,910	8,640	12701	6.89	7.06	7.55	9.06	9.45	(0.27)	(0.60)	(0.28)	(0.34)	(0.36)
MW-3	08/14/06	2.58	841	560	1,490	5,830	8721	6.73	6.33	7.31	8.67	9.07	(0.30)	(0.82)	(0.35)	(0.46)	(0.47)
MW-3	11/13/06	2.83	934	766	2,090	8,490	12280	6.84	6.64	7.64	9.05	9.42	(0.24)	(0.64)	(0.20)	(0.29)	(0.31)
MW-3	11/13/06	2.83	846	675	1,760	5,550	8831	6.74	6.51	7.47	8.62	9.09	(0.27)	(0.69)	(0.26)	(0.44)	(0.42)
MW-3	03/21/07	3.18	967	1,280	2,400	9,610	14257	6.87	7.15	7.78	9.17	9.57	(0.20)	(0.41)	(0.13)	(0.22)	(0.23)
MW-3	03/21/07	3.18	971	1,260	2,350	9,380	13961	6.88	7.14	7.76	9.15	9.54	(0.20)	(0.41)	(0.14)	(0.22)	(0.23)
MW-3	05/24/07	3.36	629	567	1,620	6,420	9236	6.44	6.34	7.39	8.77	9.13	(0.32)	(0.63)	(0.24)	(0.32)	(0.34)
MW-3	08/16/07	3.59	695	576	1,680	6,710	9661	6.54	6.36	7.43	8.81	9.18	(0.27)	(0.59)	(0.22)	(0.29)	(0.31)
MW-3	08/16/07	3.59	686	561	1,630	6,600	9477	6.53	6.33	7.40	8.79	9.16	(0.27)	(0.59)	(0.23)	(0.30)	(0.31)

### 3. RESULTS

A total of 5,665 samples with measures of concentrations of benzene, toluene, ethylbenzene, and total xylenes were evaluated. Total BTEX concentrations were calculated for each sample. These represented analytical results from groundwater samples collected from 58 monitoring wells at 24 impacted sites over periods ranging up to 19.2 years. As shown on Table 2, maximum detected groundwater concentrations ranged up to hundreds of thousands micrograms per liter (ug/L) for toluene and total xylenes, and tens of thousands of ug/L of benzene and toluene. Minimum detected values approached the laboratory reporting limits. Samples which contained one or more non-detect values were eliminated.

Table 2. Basic statistics of 5,665 data points consisting of groundwater analytical data collected. All values are micrograms per liter (ug/L).

	Benzene	Toluene	Ethylbenzene	Total Xylenes	Total BTEX
Maximum	24000	320000	42000	248440	396300
Minimum	0.44	0.26	0.92	1.10	3.26
Mean	1192.21	5989.64	1559.20	7366.82	16107.87
Median	410	561	964	3660	6835
Standard Deviation	1940.90	17552.35	2620.15	14721.21	30571.18

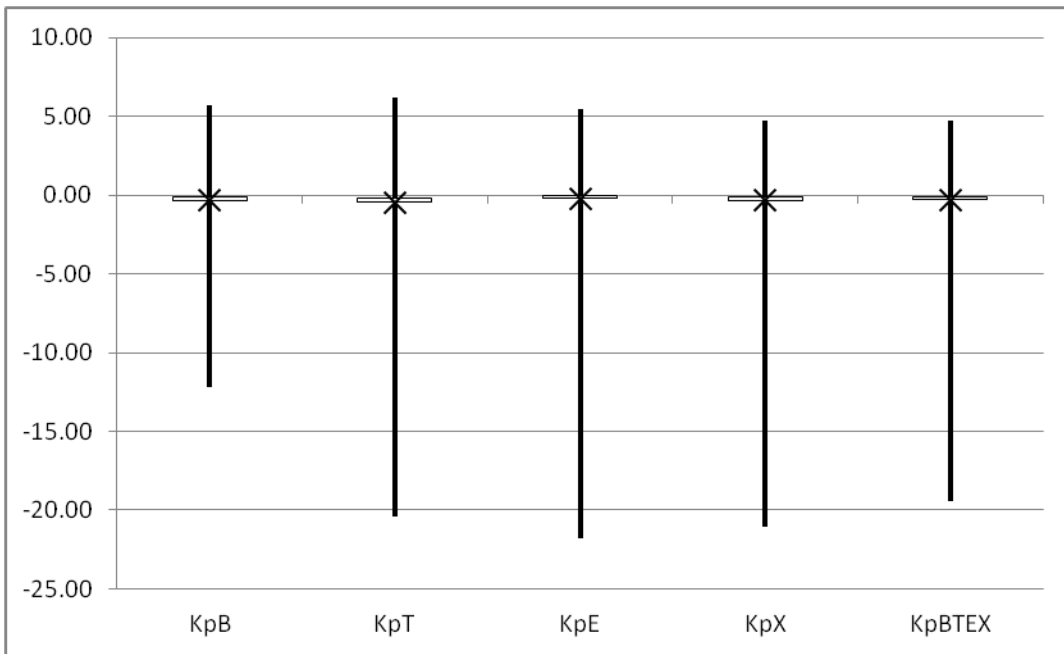
As shown on Table 3 correlations between detected COC ranged from 0.305 (benzene and ethylbenzene) to 0.836 (ethylbenzene and xylenes). Toluene exhibited the greatest correlation with Total BTEX concentration (0.864).

Table 3. Correlations of COC concentrations, as determined using Excel's CORREL function.

	Benzene	Toluene	Ethylbenzene	Xylenes	Total BTEX
Benzene	1.000				
Toluene	0.393	1.000			
Ethylbenzene	0.305	0.608	1.000		
Xylenes	0.365	0.441	0.836	1.000	
TOTAL BTEX	0.491	0.864	0.857	0.830	1.000

*Observed Field Scale First Order Attenuation Rates of BTEX*

As shown on Figure 1,  $k_p$  values varied over a wide absolute range, from a maximum  $6.18 \text{ yr}^{-1}$  rate calculated for toluene (indicating increasing concentrations, probably due to seasonal variability) to a minimum of  $-21.78 \text{ yr}^{-1}$  for ethylbenzene. Such an attenuation rate would indicate a half-life for ethylbenzene of approximately 12 days. 25<sup>th</sup> and 75<sup>th</sup> percentiles (Q1 and Q3, respectively)  $k_p$  were less variable, and were consistently negative (indicating attenuation). Table 4 summarizes the basic statistics of the calculated  $k_p$  rates for this study.



*Figure 1.* Box and Whisker diagram of  $K_p$  rates (per year) for benzene, toluene, ethylbenzene, total xylenes, and Total BTEX.

*Table 4.* Summary of point attenuation ( $K_p$ ) statistics for this study. Q1 and Q3 indicate 25% and 75% percentile, respectively.

	$k_pB \text{ (yr}^{-1}\text{)}$	$k_pT \text{ (yr}^{-1}\text{)}$	$k_pE \text{ (yr}^{-1}\text{)}$	$k_pX \text{ (yr}^{-1}\text{)}$	$k_pBTEX \text{ (yr}^{-1}\text{)}$
Median	-0.33	-0.44	-0.24	-0.33	-0.31
Q1	-0.75	-1.03	-0.61	-0.73	-0.68
Maximum (increasing concentrations)	5.69	6.18	5.42	4.76	4.75
Minimum (greatest attenuation rates)	-12.18	-20.37	-21.78	-21.05	-19.39

*Observed Field Scale First Order Attenuation Rates of BTEX*

Q3	-0.13	-0.22	-0.05	-0.09	-0.13
Standard Deviation	1.13	1.39	1.28	1.39	1.22
Median Half-life (yrs)	2.12	1.56	2.93	2.11	2.26

In general, correlations between attenuation rates were greater than those between absolute concentrations of COCs.

Table 5 summarizes correlations between the  $k_p$  values calculated in this study. Between individual COCs, the  $k_p$  of ethylbenzene and total xylenes was highest, as was the case with absolute concentrations. Total xylenes  $k_p$  also had the highest calculated correlation with  $k_p$  for Total BTEX.

*Table 5. Correlations of  $k_p$  rates for individuals COCs and Total BTEX.*

	$k_pB$	$k_pT$	$k_pE$	$k_pX$	$k_pBTEX$
$k_pB$	1.000				
$k_pT$	0.707	1.000			
$k_pE$	0.612	0.787	1.000		
$k_pX$	0.522	0.763	0.871	1.000	
$k_pBTEX$	0.681	0.891	0.910	0.933	1.000

Sufficient temporal data were available to attempt an evaluation of the change in first-order  $k_p$  over time. In general, the average attenuation rate decreased (i.e. less attenuation was occurring) with increased time from the release. As shown on Table 6, the first-order rate of attenuation falls with time for all individual COCs and Total BTEX. From one year to 10 years following a release, the average  $k_p$  decreases approximately 90% (i.e., the COCs are degrading at 10% the original rate a decade after the release).



*Observed Field Scale First Order Attenuation Rates of BTEX*

Table 6. Comparison of point attenuation rates for times since release of less than 1 year, 1 to 5 years, 5 to 10 years, and greater than 10 years.  $K_p$  in units of per year.

	n =	70	500	428	77
Years since release		0-0.9	1.0-4.9	5.0-9.9	10.0+
AVERAGE	$k_p$ B	-1.79	-0.59	-0.35	-0.21
	$k_p$ T	-2.62	-0.93	-0.44	-0.24
	$k_p$ E	-1.68	-0.61	-0.25	-0.10
	$k_p$ X	-1.61	-0.76	-0.32	-0.15
	$k_p$ BTEX	-1.80	-0.67	-0.31	-0.15

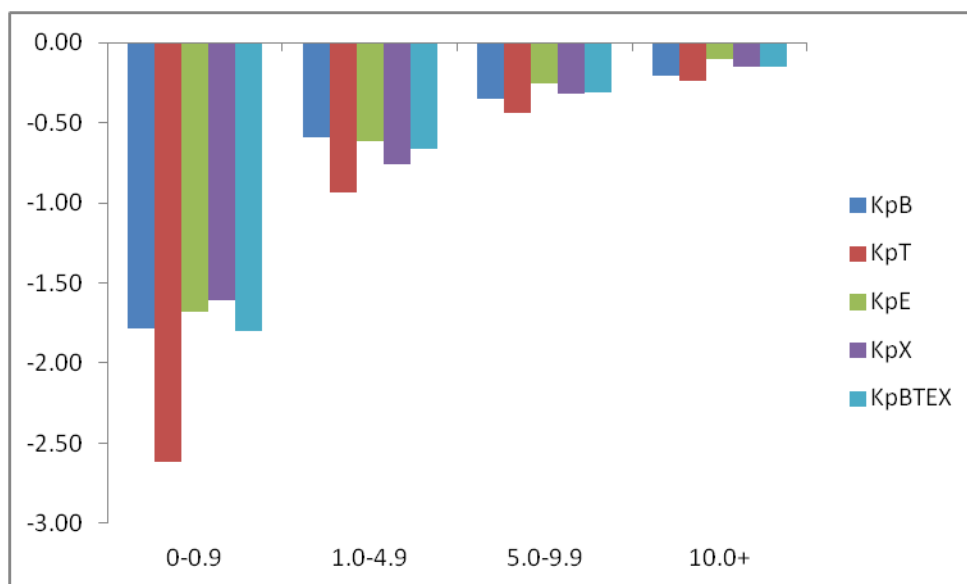


Figure 2. Comparison in average  $k_p$  rates (per year) for individual COCs and Total BTEX over time. Data provided in Table 6.

#### 4. DISCUSSION

As shown on Table 7, the observed  $k_p$  in this study agree broadly with those published by others. Median half-lives were approximately 2 years for individual COCs.

*Observed Field Scale First Order Attenuation Rates of BTEX*

Table 7. Comparison of previously published  $k_p$  and half-lives with this study.

Study	Compound	Average $k_p$ (yr <sup>-1</sup> )	Average half-life ( $t_{1/2}$ ) years
Reid & Reisinger (1999)	Benzene	0.46	1.5
Peargin (2002)	Benzene	0.14	5
Newell (2002)	Benzene	0.33 (mean)	2.1
Bruce <i>et al.</i> (2010)	Benzene	0.073-0.877	9.5-0.79
Bruce <i>et al.</i> (2010)	Toluene	0.110-1.31	6.3-0.53
Bruce <i>et al.</i> (2010)	Ethylbenzene	0.037-0.657	18.7-1.05
Bruce <i>et al.</i> (2010)	Xylenes	0.073-0.840	9.49-0.825
Stevens (2013)	Benzene	0.33	2.1
Stevens (2013)	Toluene	0.44	1.6
Stevens (2013)	Ethylbenzene	0.24	2.9
Stevens (2013)	Xylenes	0.33	2.1
Stevens (2013)	Total BTEX	0.31	2.2

A common practice in the consulting and remediation industry is to attempt to estimate the time a given plume of contaminated groundwater will take to achieve regulatory standards under monitored natural attenuation. Commonly, such estimates are made following the initial investigation of the nature and extent of impacted media, and again following a comprehensive assessment of the full horizontal and vertical extent of contamination. In each case, financial guarantees, bonds, escrow funds, or other monetary reserves may be committed to fund a long-term monitoring effort.

Clearly, evaluation of attenuation rates using straight-line fits to normal concentration data produces erroneous results, although this method is still occasionally seen in consulting reports. Logarithmically transformed data in many situations provides a population more amenable to linear models, which are relatively simple to apply and therefore cost-effective. The user should be cautioned (*National Research Council* (2000), *Wiedemeir et al.* (1999), and *Newell et al* (2002)) that while such models provide acceptable results in terms of goodness-of-fit or other correlative measures, the calculated rates will vary with time. The linear model is truly a description of the data already collected, and a potentially poor indicator of longer term (10+ year) attenuation rates.

In this study,  $k_p$  was found to decrease approximately 90% from the one-year to the ten-year monitoring periods. Such reductions in attenuation rates modeled as log-linear at early times will result in erroneously optimistic estimates of remediation times under monitored natural attenuation scenarios.

#### **4. CONCLUSION**

The application of  $k_p$  can be a useful tool with which to estimate the attenuation rate of COCs at a monitoring point over relatively short time frames. In this capacity it may support conclusions regarding the time line necessary for monitored natural attenuation to achieve clean-up goals. It is recommended that attenuation rate estimates be periodically updated over the course of the monitoring program, as this could signal potential changes in the geochemical regime which may affect the efficiency of natural attenuation.

$K_p$ , while based on a log-linear fit, is not constant. Over the course of nearly two decades of groundwater monitoring at multiple sites, it has been found to generally decrease with time, leading to cleanup times considerably longer than originally estimated in many cases.

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# EVALUATION OF REPORTED HEALTH EFFECTS ASSOCIATED WITH HYDROCHLORIC ACID RELEASE IN A RESIDENTIAL SETTING

Christopher M. Teaf<sup>1§</sup>, Bruce J. Tuovila<sup>2</sup>, Kennard F. Kosky<sup>3</sup>, Gary M. Zwain<sup>4</sup>

<sup>1</sup>Center for Biomedical & Toxicological Research, Florida State University, 2035 E. Dirac Dr., Tallahassee, FL, 32310; <sup>2</sup>Hazardous Substance & Waste Management Research, Inc., 2976 Wellington Circle West, Tallahassee, FL, 32309; <sup>3</sup>Golder Associates, Inc., 6026 NW 1<sup>st</sup> Place, Gainesville, FL, 32607; <sup>4</sup>Duplass, Zwain, Bourgeois, Pfister & Weinstock, 3838 N. Causeway Blvd., Three Lakeway Ctr., Suite 2900, Metairie, LA, 70002

## ABSTRACT

Following the accidental release of an estimated 470 gallons of hydrochloric acid (HCl) and subsequent volatilization of some of this material into the air, residents of a neighborhood adjacent to the release area complained of a variety of health effects from what they believed was exposure to the airborne HCl vapor. As part of legal action taken on behalf of some local residents, plaintiffs in the lawsuit filled out a questionnaire which provided detailed information regarding their recollections of physical location at the time of the spill and a listing of health effects which they believed were the result of their exposure. Based on the information contained in these questionnaires, together with air modeling of potential plume movement and dispersion, a statistical comparison was developed of the proportion of health effects reported by residents inside the modeled plume areas with those outside those areas. The frequency and distribution of reported health complaints were analyzed in a variety of ways. The analysis concluded that, despite a wide variety of health effects reported, these data do not support a conclusion that adverse health effects were caused by or associated with reported potential exposure to hydrochloric acid among residents in the vicinity of the release. This assessment underscores the importance of establishing concordance between toxicological properties of a substance, potential exposure characteristics, and reported health complaints.

**Keywords:** Hydrochloric acid, HCl, human health, exposure, air, residential

<sup>§</sup>Corresponding Author: Christopher M. Teaf, Center for Biomedical & Toxicological Research, Florida State University, 2035 E. Dirac Dr., Tallahassee, FL, 32310, 850-681-6894, cteaf@fsu.edu

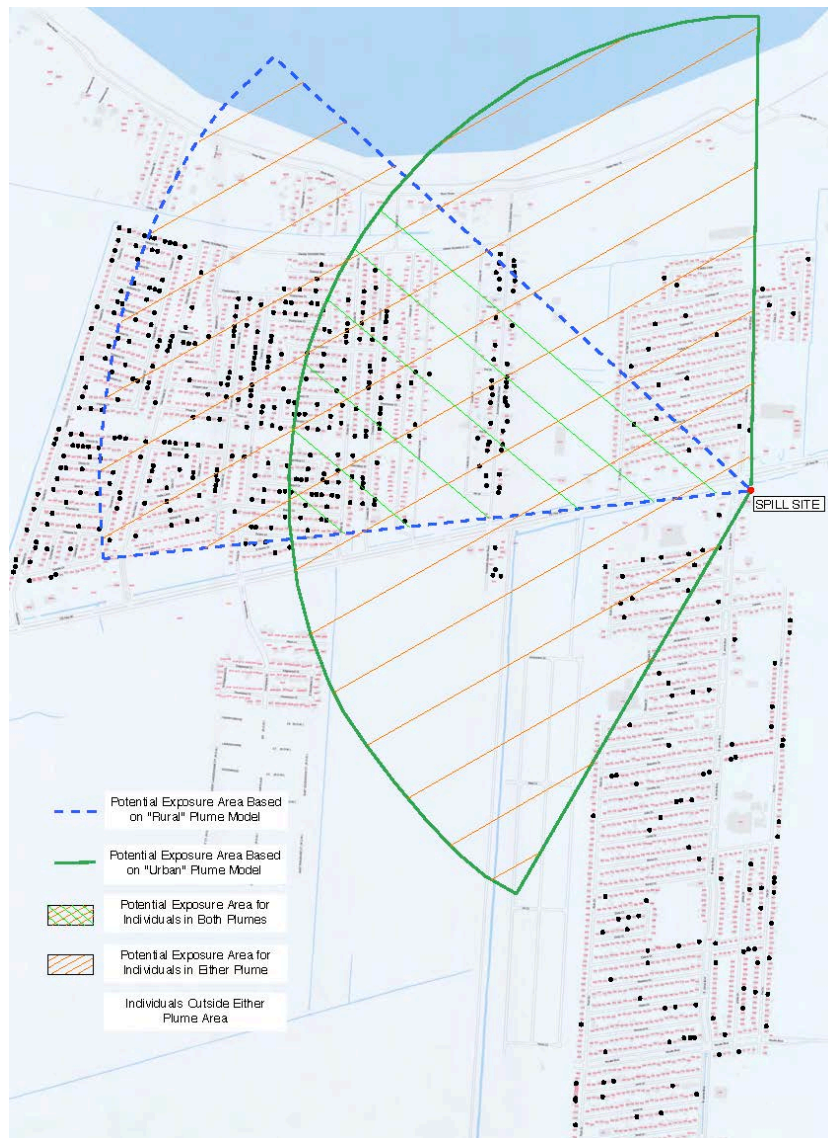
## **1. INTRODUCTION**

Hydrochloric acid (HCl) is one of the most widely used industrial chemicals, with a production volume of approximately 8 to 10 billion pounds (3.6 to 4.5 billion kilograms) in the U.S. for the 2000 to 2012 timeframe (HSDB, 2008; U.S. Census Bureau, 2012). It is likely that if HCl presented a significant and prevalent cause of adverse health effects at low air concentrations (e.g., low single digit parts per million, ppm) it would have been well-documented in the scientific and toxicological literature. Such is not the case. Individuals who encounter low levels of HCl in air may perceive an identifiable odor at levels of 1 ppm or less. However, this is well below the level that may cause serious injury (U.S. EPA, 1976; ACGIH, 2003; ATSDR, 2011). HCl can act as a sensory irritant at sufficient concentrations, but exerts its effects only at the site of contact (U.S. EPA, 1996; ACGIH, 2003). While HCl exposure may, in some cases, result in variable irritation of mucous membranes and skin, the respiratory tract is the critical target tissue at high concentrations (U.S. EPA, 1996). Occupational studies conducted by the National Institute for Occupational Safety and Health (NIOSH), and other authors, have reported HCl levels in workspace air at low concentrations (e.g., in the range of 0.5 to 5 ppm), and did not report that adverse health effects or health hazards were associated with HCl exposure at these concentrations (ACGIH, 2003; NIOSH, 1981; Bond et al., 1991; Kauppinen and Niemela, 1985; Williamson and Kavanagh, 1987).

In the early morning of April 5, 2001, a storage tank valve leak at a small oil extraction field in proximity to residences in the town of Avondale, Louisiana resulted in the release of an estimated 470 gallons of 31.4% HCl onto the ground, which consisted of sand, limestone/shell fragments, and native soil. Between about 3 AM and 5 AM, a vapor cloud was observed in the vicinity of the release. The hygroscopic nature of HCl (CalOEHHA, 1999) and local reported meteorological conditions suggest that this cloud consisted of a mixture of HCl and condensed water vapor. Measurements collected by emergency responders to the incident reported a maximum HCl air concentration of 2 parts per million (ppm). Although emergency personnel who were within this cloud did not report experiencing any symptoms, employees of several businesses in the vicinity of the vapor plume were ordered to shelter in place and roadblocks were established to prevent driving in the area until the cloud dissipated at approximately 5 AM.

Following the incident, litigation was initiated on behalf of some residents of Avondale based on concerns regarding personal injury and economic damages. Plaintiffs alleged that the reported effects were the result of exposure to HCl vapor released from the spill site, which was then transported to the residential neighborhood by the prevailing wind. In support of the allegation of HCl vapor

transport into the residential neighborhood, an air modeling expert for plaintiffs in the lawsuit developed two air dispersion models based on various modeling parameters. These modeled areas of putative exposure were designated the "Urban" plume model and the "Rural" plume model, as shown on Figure 1, and



*Figure 1.* Location of "rural" and "urban" modeled exposure plume areas in Avondale.

were intended to predict maximum concentrations of HCl in air within the zones described. An air modeling expert for Defendants developed an independent model which encompassed a significantly smaller area of potential exposure for

the plaintiffs. The results of that model indicated that very few of the plaintiffs would have been present in areas where there was a potential for exposure to HCl at concentrations that would be of health significance. For the evaluation described herein, the plaintiffs' modeled plume areas were chosen to test the extent to which that model reflected distinct differences in reported plaintiff health symptoms as related to projected exposure by the plaintiff transport model.

Approximately 5 years following the incident, in mid-2006, about 1,600 plaintiffs filled out questionnaire forms in which they provided variably detailed information including residence address on the date of the spill, specific time or range of times during which they believed that they were exposed to HCl from the spill, their activities and physical location at the time of the spill, health effects they experienced, and any preexisting health conditions. In some instances, the forms included information regarding health effects reportedly experienced by other individuals, typically a minor child or someone not capable of filling out their own questionnaire.

## **2. METHODS**

To evaluate the extent to which health effects from exposure to HCl from the 2001 spill may have occurred, a detailed comparison was conducted between reported health effects and location in the several hours believed to be associated with the presence of the airborne HCl. The operational hypothesis was that those plaintiffs who were located inside one or the other of the modeled plume areas should have reported a greater incidence of health effects, especially those effects most closely associated with exposure to HCl, than plaintiffs who were located outside these plume areas in the relevant time period. Absent that demonstration, it is not reasonable or scientifically plausible to conclude that reported health effects were the result of exposure to HCl from the spill.

According to the plaintiffs' modeling expert, the period during which the HCl plume existed was between approximately 3:00 AM and no later than 5:00 AM on April 5, 2001. plaintiffs who reported that they resided at an address inside either of the plume model areas, or who reported that they were driving inside either of these plumes, or who lived outside Avondale but reported that they were staying at a residence inside either plume during this time period were assumed for the purposes of this evaluation to have had potential exposure to HCl. Plaintiffs whose reported location information that placed them along the border of, but nominally outside, either plume model area also were considered to have been inside the plume, as a conservative measure.



In their questionnaires, plaintiffs reported health concerns using a wide variety of terms (e.g., "blurred eyes", "burning eyes", "itchy eyes", "dry eyes", "eye redness" to describe eye irritation). Terms that were related to a specific health concern (i.e., cough, eye irritation, nausea, etc.) were grouped into the 26 health effect categories presented in Table 1.

*Table 1.* Categories of physical symptoms reported by plaintiffs.

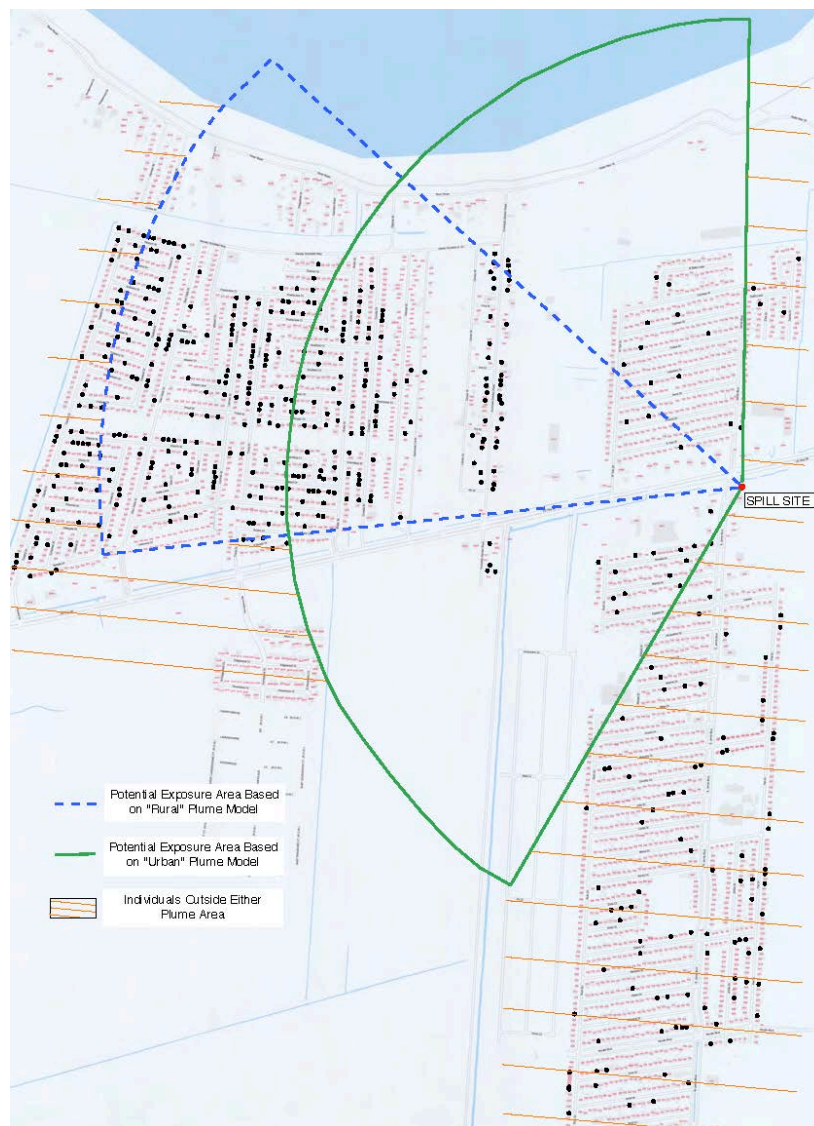
Physical Symptom Category
Aches/pains/chills/fever
Allergy symptoms
Anxiety
Asthma
Blood pressure problems
Breathing difficulty/SOB
Burning throat
Chest pain/congestion
Cough
Diabetes
Diarrhea
Dizzy/lightheaded
Ear irritation
Eye irritation
Fatigue/weakness/sleepiness
Headache
Heart problems
Mouth irritation
Nausea
Sinus/Nasal/Nose
Skin irritation
Sleep problems
Stomach/Abdominal pain
Unusual tastes
Vomiting
Miscellaneous

Five of these health effect categories (i.e., burning throat, cough, eye irritation, sinus/nasal problems, skin irritation) which have been reported in the scientific literature to be associated with exposure to HCl (U.S. EPA, 1976; ATSDR, 2002; U.S. EPA, 2007; NRC, 1987; ATSDR, 2011) were evaluated.

To determine the extent, if any, to which reported plaintiff health effects may have been related to potential exposure to HCl from the spill, plaintiffs were assigned to exposure scenarios based on the two plaintiff plume models. Based on these criteria, eight potential exposure scenarios were developed:

- plaintiffs located inside the "Rural" plume
- plaintiffs located outside the "Rural" plume
- plaintiffs located inside the "Urban" plume
- plaintiffs located outside the "Urban" plume
- plaintiffs located inside overlap of both plumes
- plaintiffs located outside overlap of both plumes
- plaintiffs located inside either of the plumes
- plaintiffs located outside both plumes

While analyses were conducted for all individual comparisons, for the purposes of this analysis only those scenarios most favorable to the plaintiffs are presented as an example. These include the difference in the proportion of reported health effects for plaintiffs inside the overlap of both of the modeled plume areas (cross hatched area, Figure 1) compared to those outside of the entire area encompassed by both plumes (hatched area, Figure 2), and the proportion of plaintiffs reporting health effects inside either of the modeled plume areas (single hatched area, Figure 1) compared to those outside of the entire area encompassed by both modeled plume areas (hatched area, Figure 2).



*Figure 2.* Location of individuals outside either modeled exposure plume area.

### **3. RESULTS**

The number of plaintiffs who reported health effects and the corresponding percentage of reported health effects in each symptom category are presented in Table 2 and Table 3. As shown in Table 3, the differences between the percentage of plaintiffs inside of the modeled plume areas who reported a health effect compared to those outside of these areas were relatively small. To determine which, if any, of the observed differences were statistically significant,

a statistical evaluation of the data was performed based on a two sample Z-test of proportions as described by the U.S. Environmental Protection Agency and other statistical literature (U.S. EPA, 2006; Sheskin, 2004; Zou et al., 2003).

*Table 2.* Number of plaintiffs in each exposure category.

Symptom Category	Inside Plume Overlap	Outside Both Plumes	Inside Either Plume	Outside Both Plumes
Burning throat	132	151	283	151
Cough	116	89	270	89
Eye irritation	318	281	773	281
Sinus/Nasal/Nose	152	126	352	126
Skin irritation	28	30	66	30
Total plaintiffs	459	434	1135	434

*Table 3.* Percentage of plaintiffs in each exposure category.

Symptom Category	Inside Plume Overlap	Outside Both Plumes	Inside Either Plume	Outside Both Plumes
Burning throat	28.76%	34.79%	24.93%	34.79%
Cough	25.27%	20.51%	23.79%	20.51%
Eye irritation	69.28%	64.75%	68.11%	64.75%
Sinus/Nasal/Nose	33.12%	29.03%	31.01%	29.03%
Skin irritation	6.10%	6.91%	5.81%	6.91%

Results of the Z-test are presented in Table 4. Although a greater proportion of plaintiffs inside of the modeled plume areas reported experiencing cough, eye irritation, and sinus or nasal irritation, none of these differences were statistically significant. The incidence of burning throat, however, was reported by a statistically significantly greater proportion of plaintiffs who were located outside both of the modeled plume areas. There was very little difference in the reported incidence of skin irritation between those inside and outside of the modeled plume areas. For the remaining 21 symptom categories presented in Table 1, only the proportions of reported allergy symptoms, asthma, and breathing difficulty/SOB were significantly different between those inside and outside of the modeled plume areas (data not shown). In each case for these symptom categories, the reported incidences were higher for those outside the modeled plume areas. Similar results were obtained from the statistical comparison of symptoms reported by plaintiffs inside and outside of either the "rural" or "urban" modeled plume areas when evaluated separately (data not shown). For the "rural" modeled

plume area, again, the incidence of burning throat and breathing difficulty/SOB was significantly greater for those outside the plume area. For the "urban" modeled plume area, the incidence of cough was significantly greater for those inside that plume area. This is the only instance in which a reported symptom was significantly greater for plaintiffs inside a modeled plume area compared to those outside that area. It is significant that even plaintiffs in the extreme instance, where exposure to HCl potentially could have occurred because they were located in the area encompassed by both of the plume models (cross hatched area, Figure 1), were no more likely to report a health effect compared to those who could not have received any exposure based upon the model projections (i.e., were never reported to be inside either exposure area; hatched area, Figure 2). In fact, statistically significant exposure for burning throat, a hallmark of significant HCl exposure, was reported more frequently by plaintiffs located outside of the modeled plume areas.

Table 4. Results of two sample Z-test of statistical significance between plaintiff exposure scenarios. Z value statistically significant at 95% confidence if  $Z > 1.96$  or  $Z < -1.96$ . A negative Z value indicates a greater proportion of plaintiffs outside the plume reporting the indicated health effect.

Symptom Category	Inside Plume Overlap v. Outside Both Plumes		Inside Either Plume v. Outside Both Plumes	
	Z Value	Difference Significant?	Z Value	Difference Significant?
Burning throat	-2.01	Yes	-3.91	Yes
Cough	1.69	No	1.38	No
Eye irritation	1.44	No	1.27	No
Sinus/Nasal/Nose	1.33	No	0.76	No
Skin irritation	-0.51	No	-0.81	No

In addition to the general lack of statistical significance of reported symptoms between plaintiffs inside vs. outside of the plaintiff modeled plume areas, the distribution of reported symptoms for Avondale residents is also of interest. From a toxicological perspective, it would be expected that a greater number of plaintiffs reporting health effects would be located closest to the release site and that the number of plaintiffs would decrease with greater distance from the release site. However, that is not the case, based on the location of residences where plaintiffs reported health effects within each of the modeled plume areas, as shown on Figure 1. Figure 1 shows that the number of plaintiff residences is lower for areas of the Avondale neighborhood closest to the area of the spill. That is not a pattern that would be consistent with an actual exposure-related event.

#### **4. DISCUSSION**

Although exposure to hydrochloric acid has been reported to be associated with a variety of health effects in humans, primarily respiratory and ocular, whether these effects can be attributed to HCl exposure inside a defined area, such as the modeled plume areas in this case, depends on the relative magnitude of reported health effects between individuals located inside that area compared to those outside. In the case presented here, it is apparent that the reported incidence of adverse health effects from alleged exposure to hydrochloric acid inside the modeled plume areas is not significantly different from the incidence reported by individuals outside of those areas.

A number of health-based guidance values for HCl in air are used for the purpose of providing protective exposure levels for employees in working circumstances. While occupational threshold values are not directly applicable to chemical releases which potentially may affect the general public, they provide evidence from health agencies regarding levels of HCl in air that are considered to be safe for humans for short-term or lengthier periods. The Occupational Safety and Health Administration (OSHA) and NIOSH both have established an occupational “Ceiling” value (not to be exceeded during a working day) for HCl of 5 ppm, and the American Conference of Governmental Industrial Hygienists (ACGIH) has designated a ceiling for HCl of 2 ppm, considered a safe level at which irritation should not occur, incorporating an adequate margin of safety (ACGIH, 2011a; ACGIH, 2011b). No measured air values for this incident exceeded 2 ppm at any location.

For the purpose of providing safe exposure levels for the general public in the event of a chemical release, the American Industrial Hygiene Association (AIHA) has developed Emergency Response Planning Guidelines (ERPGs) for HCl, which are defined as applicable and protective for nearly all individuals. At 3 ppm (the ERPG-1) for up to an hour exposure, the only expected effect from HCl would be objectionable odor or transient irritation, and even at 20 ppm (the ERPG-2) no serious or irreversible health effects would be expected to occur (AIHA, 2005; AIHA, 2011).

Controlled laboratory studies in mild asthmatics exposed to HCl do not support the conclusion that low concentrations of HCl in air cause or exacerbate serious adverse respiratory effects in typical circumstances (Stevens et al., 1992; Fine et al., 1987). In the Stevens et al. (1992) study of mild asthmatics, subjects were exposed to either filtered air alone, or to filtered air containing 0.8 ppm or 1.8 ppm HCl, with some individual air concentrations during the test exceeding 2.0

ppm. Experimental sessions included resting and exercise. The authors found no adverse respiratory effects resulting from inhalation of either HCl concentrations (maximum 1.8 ppm), based on baseline and postexposure pulmonary function tests.

## **5. CONCLUSIONS**

Alleged plaintiff injuries in this case involved people who reportedly resided in or were present in the vicinity of the site of the HCl release and for whom it is suggested that health has been affected by the release. Remarkably, for the one reported symptom that reached statistical significance (i.e., burning throat), reports of that symptom were higher for those individuals outside the modeled plume areas than for those inside.

The incidence of reported health effects for plaintiffs inside the modeled plume areas compared with those outside is not consistent with a conclusion that those health effects resulted from exposure to hydrochloric acid vapor released during the subject spill.

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