# PROCEEDINGS OF THE 2016 AEHS FOUNDATION ANNUAL INTERNATIONAL CONFERENCES

## Volume 22

The 26th Annual International Conference on Soil, Water, Energy, and Air,
March 21 – 24, 2016
San Diego, CA

The 32nd Annual International Conference on Soils, Sediments, Water, and Energy,
October 17 – 20, 2016
Amherst, MA

AEHS Foundation

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# PROCEEDINGS OF THE 2016 AEHS FOUNDATION ANNUAL INTERNATIONAL CONFERENCES

## Volume 22

**Remedial Strategies**
**Fate and Transport**
**Site Characterization**
**Risk Assessment**

*Select manuscripts from*

*26th Annual International West Coast Conference on*
*Soil, Water, Energy, and Air*
*San Diego, California*
*March 21 – 24, 2016*

*32nd Annual International East Coast Conference on*
*Soils, Sediments, Water, and Energy*
*Amherst, Massachusetts*
*October 17 – 20, 2016*

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ISBN: 978-0-9888932-5-2
Volume 22 Proceedings of the 2016 AEHS Foundation Annual International Conferences

AEHS Foundation
150 Fearing Street
Amherst, MA 01002
www.AEHSFoundation.org

# Table of Contents

## REMEDIAL STRATEGIES

## FATE AND TRANSPORT

## SITE CHARACTERIZATION

## RISK ASSESSMENT

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# Foreword

In March and October of each year, two well-established and richly anticipated international symposia are held in San Diego, CA and Amherst, MA, respectively. San Diego in the spring and Amherst in the fall are excellent venues for the broad range of attending scientists and environmental practitioners, most of whom are very experienced.

Now that the West Coast Annual Conference is well into its third decade at age 26, and the East Coast Annual Conference is now a third of a century old, participants still attend, some on multiple occasions, to present, discuss, critique, and execute a wide variety of environmental investigations, approaches, and strategies that have been successful worldwide in one application or other. The Conferences exhibit a remarkable variety of scientific activities, represented in 2016 by a total of 400 platform and poster presentations, 20 participatory workshops on technically specialized areas, and featuring nearly 100 commercial exhibitors of practical and highly advanced environmental and analytical services or products. Many of the best meetings are the informal ones, not those from a podium, that take place over coffee in the hallway or at dinner. The technical sessions and discussions parse yet another year's efforts to assess and manage subtle and important environmental problems. It is a pleasure to participate in the daily discussions to see clearly why scientists, public organizations, governments, regulatory agencies, and commercial firms contribute their skills, time, funds, and life experiences to understanding and managing the fragile environmental systems we depend upon.

Many excellent papers are presented in this Proceedings compilation, including from the fields of Risk Assessment, Site Characterization, Remediation, Transport Modelling, and Water Supplies. It is a pleasure to present the collection to the reader, and we look forward to revisiting San Diego and Amherst in future years with other chemists, engineers, biologists, toxicologists, geologists, planners, regulatory agency personnel, other scientists, attorneys, and those in related fields who spend their time and skills describing, understanding, and improving our environment.

*Dr. Edward Calabrese*
*Dr. Paul Kostecki*
*Dr. Christopher Teaf*

Spring 2017

# 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 Soils, Sediments, Water & Energy 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: *Soil and Sediment Contamination* (1990); *Human and Ecological Risk Assessment* (1994); *International Journal of Phytoremediation* (1998); *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 (ISEF) 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 to 2011. He briefly left the University of Massachusetts Amherst to establish the online education program for Simmons College, Boston, Massachusetts (2011 to 2012). He is presently Professor Emeritus in the School of Public Health and Health Sciences, University of Massachusetts, Amherst, and President of the Association for Environmental Health and Sciences Foundation, Amherst, Massachusetts.

**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 commerce. Dr. Teaf is Director of the Florida State University Center for Biomedical & Toxicological Research and Director of Toxicology for Hazardous Substance & Waste Management Research.

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 site characterization and 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 35 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 for the state Petroleum Technical Advisory Committee. He served as Chair of the Toxic Substances Advisory Council for the Florida Department of Labor, as a member of the Peer Review Committee for the Florida DEP surface water criteria rule. 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 been Chair, then Treasurer, of the Dog Island Conservation District since 2004.

Dr. Teaf has served on editorial boards or as peer reviewer for many journals and is Co-Editor-in-Chief of the international journal *Soil and Sediment Contamination*. In addition to training, research and advisory services to many environmental agencies and private sector firms, he has provided toxicological support to the U.S. Attorney, Florida State Attorney, and Attorneys General of Florida, Oklahoma, and Washington. Chris has provided testimony in federal and state court, and administrative matters, on toxicology, health risk assessment, and environmental chemistry.

**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 the efficiency of the clinical trial, as well as the scientific foundations for risk assessment and environmental regulation for radiation and chemicals.

# COMPARISON OF PERMEABLE REACTIVE BARRIER MATRICES TO TREAT 1,2-DICHLOROPROPANE

*West Coast Conference, March 2016*

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## ABSTRACT

1,2-Dichloropropane (1,2-DCP) has been used in the past as a soil fumigant, chemical intermediate, an industrial solvent and in paint strippers, varnishes, and furniture finish removers. Due to its wide usage and environmental persistence it is present in groundwater at many sites. However, these treatments of 1,2-DCP have not been as well studied as the more common chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE).

A Permeable Reactive Barrier (PRB) is a passive treatment that relies on the natural flow of groundwater to bring the contaminants to the reactive media. The barrier serves as a reactive zone to intercept and treat contaminated groundwater. Physical, chemical, and/or biological processes can be used for the removal of contaminants within the reactive media of the PRB. Reactive media that are commonly used include Zero Valent Iron (ZVI), other iron media such as EHC®, organic media such as compost and emulsified vegetable oil (EVO), and granular activated carbon (GAC).

Groundwater at a train derailment site in Louisiana contains 1,2-DCP, which is migrating towards the property boundary and sensitive receptors. A PRB has been proposed to prevent off-site migration of the 1,2-DCP. A treatability study was performed to determine the most appropriate matrix for the PRB, the required hydraulic residence time (HRT), optimum dimensions of the PRB, and the estimated lifetime of the PRB. Several potential PRB matrices including ZVI, EHC®, compost, EVO and GAC were tested using different flow rates to produce different HRT using glass columns packed with the potential PRB matrices. The results of the study showed that several of the matrices would be effective for the treatment of the 1,2-DCP. A cost analysis was performed to select the optimal material.

The design, performance and results of the treatability study will be discussed.

**Keywords:** 1,2-dichloropropane, permeable reactive barrier, treatability study

## 1. INTRODUCTION

A permeable reactive barrier (PRB) has been proposed to treat 1,2-dichloropropane at a site in Louisiana. A treatability study was performed to determine the most appropriate matrix for the PRB and to determine the required hydraulic residence time (HRT), optimum dimensions of the PRB, and the estimated lifespan of the PRB.

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## 1.1 Permeable Reactive Barrier

A PRB is a passive treatment that relies on the natural flow of groundwater to bring the contaminants to the reactive media. It is a permanent structure, rarely relocated or modified. The barrier serves as a reactive zone to intercept and treat contaminated groundwater. Physical, chemical, and/or biological processes are the removal mechanisms for contaminants. When the contaminants make contact with the reactive media, chemical reactions take place to degrade or alter the contaminant allowing cleaner groundwater to pass through. When inorganic contaminants are in the presence of the reactive barrier, they can precipitate out of the soil and groundwater. This precipitation may cause the barrier material to become less reactive, reduce the hydraulic conductivity of the barrier, and result in breakthrough of the plume or overtopping of the barrier. Challenges facing PRB technology are the identification and evaluation of suitable media capable of providing a long-term treatment for organic and inorganic contaminants in groundwater. Adaptations in reactive media characteristics are continual. PRB media can consist of:

*Zero Valent Iron*

Iron can be used to treat chlorinated volatile organic compounds (CVOC) from soil and groundwater. Zero valent iron (ZVI) is the commonly used form of iron for the treatment of chlorinated organic compounds in soil and groundwater. ZVI dechlorinates organic compounds by creating extreme reducing conditions when the iron is oxidized to divalent iron ($Fe2^+$) and then trivalent iron ($Fe3^+$). Under these conditions, a proton can replace a chlorine atom on organic molecules. ZVI can also stimulate anaerobic biodegradation by creating an anaerobic environment and by serving as a proton donor for reductive dechlorination.

*Organic Media*

Organic media are substances such as wood chips, compost, humate, and soybean oil can be used to support the growth of bacteria that can degrade contaminants in soil and groundwater. For compounds that degrade under anaerobic conditions, such as trichloroethene (TCE), the addition of a carbon substrate to the subsurface will result in anaerobic conditions.

*EHC®*

EHC® is a controlled-release, integrated carbon and ZVI source that yields redox potential (Eh) in the -500 to -650 millivolts (mV) range. This Eh is lower than that achieved when using either organic materials (lactate, molasses, and sugars) or ZVI alone. EHC® dechlorinates organic compounds by an abiotic pathway similar to ZVI and also provides an additional carbon source for the stimulation of microbial degradation by reductive dechlorination. For an EHC® PRB, injection points would be used to inject a 40-percent slurry of EHC® in water. The final concentration of EHC® in the barrier would be about 3 percent

*Compost/Gypsum/Hematite*

Compost is a rich organic material that will create anaerobic conditions in the area where it is applied, as oxygen is used up by microorganisms feeding on the compost. Once anaerobic conditions are created, if sulfate is present, the environment is ideal for sulfate reducing bacteria (SRB). Gypsum is added as a source of sulfate to stimulate SRB activity. In the presence of $Fe3^+$, SRB activity causes the precipitation of iron sulfide (FeS). FeS chemically reduces chlorinated organic compounds in a manner similar to ZVI. Hematite is added to the barrier as a source of iron. This process is called biogeochemical reductive dechlorination (BiRD). For the PRB, a trench would be filled with a mixture containing 40 percent compost or other organic material, 3 percent gypsum, 3 percent hematite, 1 percent soil, and 53 percent sand.

*Granular Activated Carbon (GAC)*

GAC removes organic compounds from water since they are adsorbed onto the surface of the carbon particles and are held there. For a GAC PRB, a trench would be filled with a mixture containing 20 percent GAC and 80 percent sand.

# 2. MATERIAL AND METHODS

## 2.1 Objectives

The primary objectives of this laboratory study were to gather the data necessary to:

i) Assess the effectiveness of selected PRB active media for treatment of 1,2-dichloropropane in groundwater to below the target concentration of 9.4 milligrams per liter (mg/L). The target concentration was determined based on the project goals.
ii) Determine the most appropriate PRB medium for treatment of 1,2-dichloropropane in groundwater.
iii) Determine the optimum HRT for 1,2-dichloropropane treatment in each medium.
iv) Determine the optimum dimensions of the barrier wall.
v) Determine the estimated life of the PRB before replacement is needed for each medium.

## 2.2 Sample Acquisition

The treatability study was conducted using representative samples of groundwater collected from the Site. Thirty 1-gallon carboys of groundwater were collected. These samples were received at the GHD Services Inc. (GHD) Innovative Technology Group (ITG) laboratory in Niagara Falls, New York.

## 2.3 Task 1: Initial Characterization

Upon arrival at the laboratory, the samples were composited into one 30-gallon drum and analyzed for:

i) 1,2-dichloropropane
ii) pH
iii) Ammonia-Nitrogen
iv) Orthophosphate-phosphorus
v) Total Aerobic Microbial Population
vi) Total Anaerobic Microbial Population
vii) Total Metals

The analytical results provided a characterization of baseline conditions for the treatability study. The analysis was performed at the GHD laboratory. The results of the initial characterization are shown on Table 1.

## 2.4 Task 2: Column Tests

Six identical glass columns were packed as follows:

Column 1: 20 percent ZVI, 90 percent sand
Column 2: 2 percent EHC®, 98 percent sand
Column 3: 40 percent compost, 3 percent gypsum, 3 percent crushed hematite, 54 percent sand
Column 4: 100 percent sand with emulsified vegetable oil (EVO) and nutrients
Column 5: 20 percent GAC, 80 percent sand
Column 6: 100 percent sand (control)

The materials were measured on a weight-per-weight basis and thoroughly mixed manually to achieve good distribution of the medium throughout the sand. The mixtures were then poured into the glass columns. Groundwater from the drum was pumped into columns 2, 3, and 4 and allowed to stand in the columns to establish anaerobic conditions. Once anaerobic conditions had been established, additional groundwater was pumped into the bottom of each of the columns using a multi-channel pump. After the water had been flowing through the columns for about 4 pore volumes, a sample of the effluent water was collected from each column and analyzed for CVOC.

# 3. RESULTS

*Table 1.* Initial characterization of groundwater results

| **Parameter** | **Units** | **Groundwater** |
|---|---|---|
| 1,2-Dichloropropane | µg/L | 73,600 |
| pH | S.U. | 7.23 |
| Ammonia-Nitrogen | mg/L | ND (0.25) |
| Orthophosphate-phosphorus | mg/L | 0.681 |
| Total Aerobic Microbial Population | CFU/mL | 6.62E+03 |
| Total Anaerobic Microbial Population | CFU/mL | 3.66E+03 |
| Total Calcium | µg/L | 74,600 |
| Total Magnesium | µg/L | 99,200 |
| Total Sodium | µg/L | 397,000 |

### 3.1 Column 1 (ZVI Column)

Groundwater was initially pumped through this column at a flow rate of 1 milliliter per minute (mL/min) (HRT of 3 hours). Treatment of 6 percent of the 1,2-dichloropropane when compared to the sand column was observed. The flow was reduced to 0.1 mL/min (HRT of 30 hours) and no treatment of the 1,2-dichloropropane was observed. The column was repacked with a mixture containing 40 percent ZVI/60 percent sand and run at a flow rate of 0.1 mL/min. Treatment of 17 percent 1,2-dichloropropane when compared to the sand column was observed. Significant plugging of the column was noted. Pumping of the column continued to improve the conditioning of the column, but removal of the 1,2-dichloropropane did not increase and plugging continued to be observed. Therefore, the column was repacked a second time with 75 percent ZVI/25 percent sand and run at a flow rate of 0.1 mL/min. Treatment of 48 percent of the 1,2-dichloropropane when compared to the sand column was observed. This 48 percent reduction was not enough to bring the concentration of 1,2-dichloropropane to below the target of 9.4 mg/L. These data are shown in Table 2. Significant plugging was observed with this packing material. The plugging observed in the ZVI volume may have been caused by the precipitation of carbonate in the column matrix since the high calcium and magnesium concentrations in the groundwater suggest that the groundwater may have contained dissolved carbonates. Alternatively, the plugging may have been caused by precipitation of iron sulfide, which can be formed if significant levels of sulfate are present in the groundwater.

### 3.2 Column 2 (EHC® Column)

Groundwater was initially pumped through this column at a flow rate of 1 mL/min (HRT of 3 hours). Treatment of 3 percent 1,2-dichloropropane when compared to the sand column was observed. The flow was reduced to 0.1 mL/min (HRT of 30 hours) and no treatment of the 1,2-dichloropropane was observed. Conditioning of this column was continued since EHC® relies partially on a biological mechanism, and the microbial population can take time to develop and acclimate. However, although a further 12 pore volumes of groundwater were run through this column, only 9 percent treatment of the 1,2-dichloropropane was observed. The target concentration of 9.4 mg/L was not met with this column.

### 3.3 Column 3 (Biochemical Reduction Column)

Groundwater was initially pumped through this column at a flow rate of 1 mL/min (HRT of 3 hours). Treatment of 6 percent of 1,2-dichloropropane when compared to the sand column was observed. The flow was reduced to 0.1 mL/min (HRT of 30 hours) and no treatment of the 1,2-dichloropropane was observed. Conditioning of this column was continued since biochemical reduction relies partially on a biological mechanism, and the microbial population can take time to develop and acclimate. However, although a further 12 pore volumes of groundwater were run through this column, treatment of the 1,2-dichloropropane did not improve. The target concentration of 9.4 mg/L was not met with this column.

### 3.4 Column 4 (Anaerobic Biological Column)

Groundwater was initially pumped through this column at a flow rate of 1 mL/min (HRT of 3 hours). Treatment of 6 percent of 1,2-dichloropropane when compared to the same column was observed. The flow was reduced to 0.1 mL/min (HRT of 30 hours) and treatment of 24 percent of the 1,2-dichloropropane was observed. Conditioning of this column was continued since the microbial population can take time to develop and acclimate. After about 3 pore volumes passed through, treatment of 95 percent of the 1,2-dichloropropane was observed, bringing the 1,2-dichloropropane concentration to 2.3 mg/L, which is below the target concentration of 9.4 mg/L. After an additional 15 pore volumes passed through, treatment of greater than 99 percent of the 1,2-dichloropropane was observed, bringing the 1,2-dichloropropane concentration to 0.002 mg/L.

### 3.5 Column 5 (GAC Column)

At a flow rate of 1 mL/minute (HRT of 3 hours), all CVOC were treated to non-detect levels in the GAC column. The flow rate was increased to 20 mL/minute (HRT of 9 minutes), and the effluent concentrations of all the volatile organic compound (VOC) remained at non-detect levels. The flow rate was further increased to 40 mL/min, 50 mL/min, and 60 mL/min (HRT of 4.4 minutes, 3 minutes, and 2.5 minutes, respectively). Breakthrough of CVOC was observed at 60 mL/min showing 1 µg/L of 1,2-dichloropropane.

### 3.6 Column 6 (Control Column)

The control column showed consistent 1,2-dichloropropane results compared to the initial results at a flow rate of 1 mL/min. The results from the other samplings showed a slight decrease in the 1,2-dichloropropane concentration at a flow rate of 0.1 mL/min, but remained consistent throughout the remainder of the study.

## 4. DISCUSSION/CONCLUSION

The results of the treatability study showed that a PRB of a specific type would be effective in treating the groundwater to below the target concentration. A ZVI PRB containing 75 percent ZVI only treated up to 49 percent of the 1,2-dichloropropane, but did not treat the groundwater to below the target concentration of 9.4 mg/L. Significant plugging of the column was observed which suggested that a ZVI PRB would experience a reduction in permeability within a short time frame. The EHC® and biochemical reduction columns achieved some treatment of the 1,2-dichloropropane; however, due to the high influent concentrations, it is unlikely that these technologies would result in sufficient treatment of groundwater.

The results of the treatability study showed that an anaerobic biological PRB and a GAC PRB would be effective in treating the groundwater to below the target concentration. However, a GAC PRB would require trenching and replacement of the GAC every 5 years. A biological PRB would be applied by injecting EVO using injection wells. The EVO would likely need to be reinjected every 2 years. The use of a biological PRB would be more cost effective and would not generate a spent carbon waste stream, therefore, an anaerobic biological PRB is recommended. The addition of nutrients and a carbon source will produce conditions favorable for the anaerobic degradation of the 1,2-dichloropropane in the PRB. A dose of 0.05 pound (lb) of ammonium sulfate, 0.005 lb of sodium phosphate, 4.0 lb of EVO, and 0.1 lb of Accelerite (a B12 nutrient) would be required per cubic yard of PRB.

An HRT of 30 hours would be required for the anaerobic biological PRB to meet the target concentration of 9.4 mg/L. To achieve an HRT of 30 hours, a 0.3-foot thick PRB would be required if the groundwater flow rate is 100 feet/year. The cost of an anaerobic biological PRB would be approximately $15 per cubic yard of PRB.

# UTILIZATION OF COLUMN STUDIES FOR DESIGN OPTIMIZATION OF FIELD PILOT AND FULL SCALE DENITRIFYING PERMEABLE REACTIVE BARRIERS

*East Coast Conference, October 2016*

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## ABSTRACT

Column studies are underway using soil and ground water from a Falmouth, MA site contaminated with nitrate from septic systems. The columns were 46 inches long and 2 inches in diameter and were packed with 11 pounds of soil and had pore volumes of 592 mL. The column flow rates were about 1.2 feet/day. The tests are designed to evaluate the effectiveness of biological nitrate reduction using two loadings of Terra Systems, Inc. emulsified oil product, SRS in columns 1 and 2, and SRS-Z, a combination of SRS and zero-valent iron (ZVI) in column 3. The SRS-SD formulation with a small droplet (average 0.6 μm), a non-ionic surfactant package, with sodium lactate and inorganic nutrients, was used. The emulsion no longer appeared in the effluent after 1.3 to 2.4 pore volumes in columns 1 and 2. Complete removal of nitrate-nitrogen was observed shortly after column start-up and continued to be observed for all columns over 300 days from SRS injection, equivalent to 83 to 89 column pore volumes. Nitrate-nitrogen levels began to increase after 300 days. Sulfate was completely consumed until about 62 to 64 pore volumes. TOC levels in the effluent from the column reached as high as 3,900 mg/L as the emulsion was washed out of the columns for 3 pore volumes for columns 1 and 2 and about 11 pore volumes for column 3 with the SRS-Z. TOC levels had fallen to between 1.1 and 1.4 mg/L by day 340.

On Day 355, the columns were connected. A second application of a SRS product was applied to column 1. The SRS-NR formulation was designed to be retained on the soil and used an anionic surfactant package with a 5 μm average droplet size, but without the inorganic nutrients. The connected columns have been operated for another 139 days. Phosphate was added to the influent on Day 431. Complete denitrification has been observed. TOC levels only reached a maximum of 43 mg/L and the emulsion did not break through the 138 inches of combined columns. Ortho-phosphate as phosphorus was not detected in the effluent of the columns in the 63 days since it was added to the influent at an average concentration of 0.5 mg/L.

The column studies have shown that EVO can be effectively applied to stimulate naturally occurring denitrifying bacteria in Cape Cod soil, and groundwater and PRBs show promise for nitrate removal. Up to 2,244 mg of nitrate-nitrogen have been consumed by the additions of SRS. Data generated from the column study will aid in the design of the next proposed step, a field PRB demonstration on Cape Cod.

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**Keywords:** nitrate, permeable reactive barrier, column studies, septic tank pollution, emulsified vegetable oil

# 1. BACKGROUND

Nitrate contamination of surface waters can cause excess growth of algae which can create “dead zones”. To meet the estuary nitrate Total Maximum Daily Load (TMDL) on Cape Cod, MA sustainable technologies like permeable reactive barriers (PRBs) are being evaluated as non-traditional treatment alternatives (Cape Cod Commission, 2015).

Septic systems, lawn fertilizer, and road runoff on Cape Cod, MA have led to widespread nitrate contamination of the groundwater. Large dilute plumes of nitrate are moving into estuaries causing eutrophication. Concerns about water quality and a recent update of the Cape Cod Wastewater Management Plan developed under Section 208 of the Clean Water Act have prompted municipalities to look for ways to address the nitrate plumes (Cape Cod Commission, 2015). Potential management actions include new and updated wastewater treatment facilities along with innovative and sustainable green infrastructure approaches.

Permeable reactive barriers (PRB) are one potential solution. One PRB approach uses emulsified vegetable oil (EVO) to treat the nitrate. Microbes consume the nitrate under reducing conditions and generate nitrogen gas. EVO is widely used for chlorinated solvent treatment because it is relatively inexpensive, long-lasting, can be readily injected into wells or by direct push, and can be widely distributed in the subsurface. Concerns about the application of PRBs on Cape Cod from stakeholders include the expense for installation, longevity of the substrate, minimize intrusion, and that the substrate stays where it is emplaced and does not move into nearby water bodies.

# 2. INITIAL COLUMN STUDIES

Terra Systems is conducting column studies to evaluate PRB using emulsified vegetable oil (EVO) to treat the nitrate. Column studies using soil and ground water were conducted to evaluate the effectiveness of biological nitrate reduction using TSI’s emulsified vegetable oil products, SRS-SD®, and SRS-Z®, a combination of SRS and zero-valent iron (ZVI).

Twenty gallons of groundwater were collected from a well in a septic tank-impacted zone, MTER-3 which is screened from 4 above to 6 feet below sea level. Soil were collected using Geoprobe cores from 19 to 85 ft below ground surface (bgs).

Well MTER-3 is a water table well screened between -6 and 4 feet below mean sea level. The pH is mildly acidic (5.9 SU). Aerobic dissolved oxygen levels were seen with oxidizing redox potential. Nitrate-N was 0.63 mg/L, which is near background levels. Nitrite-N, ammonia, and total Kjeldahl nitrogen were not detected. There was little alkalinity, 9.5 mg/L. Chloride ranged from 13.3 mg/L and sulfate from 8.0 mg/L. Well MTER-3 had little dissolved iron (0.064 mg/L), dissolved manganese (0.24 mg/L), or boron (0.0085 mg/L). As expected, the dissolved organic carbon level in MTER-3 was low (1.2 mg/L). The soil contained 2,480 milligrams per kilogram (mg/kg) total iron, 29.5 mg/kg total manganese, and 15.7% moisture.

Three 46 in long, 2 in diameter clear PVC columns were prepared with the soil and groundwater collected from the Falmouth Site. Each column required about 5,200 grams (g) of soil. Assuming 25% porosity, the pore volume was estimated to be 592 mL for each column. The columns were prepared by installing a 0.95 cm plastic bushing to a small luer outlet onto both endcaps. The endcaps had a geotextile membrane layer at the bottom and were glued onto the columns. The soil was added to the column while maintaining the groundwater level (to prevent trapping air bubbles) and periodically tapped.

Nitrate-spiked groundwater was pumped up through the columns. The influent target for nitrate is 20 milligrams per liter (mg/L) $NO_3$-N or 89 mg/L nitrate; each liter (L) of influent groundwater received 121 milligrams (mg) of sodium nitrate. A flow rate of 1.2 ft/day or the equivalent of 187 milliliters per day (mL/day) or 0.13 mL/min gave a residence time in the columns of about 3.2 days. The groundwater was pumped into the bottom of the column using a peristaltic pump. Once the columns were filled with groundwater and pumped for two days, SRS-SD® diluted at a ratio of 1:10 with groundwater was added to the columns. The diluted SRS-SD® loadings were 308 mL (sufficient to fill the column to 53 cm and provide about 15.4 g carbon) for the first column and 616 mL (sufficient to fill the second column to 69 cm and provide about 30.8 g carbon, double the loading in the first column). The third column received 61 g of the SRS-SD® with 24.6 g of Ferox Flow ZVI (50 to 150 microns) and stabilizer (sufficient to fill the column to 69 cm and provide about 30.8 g carbon) and then was chased with 513 mL of groundwater. The flow to the columns was turned off for one to two days to allow the SRS-SD® to coat the soil and not advance further than the target distances up the columns. On Day 128, the groundwater was consumed and the influent was prepared with aerated tap water spiked with sodium nitrate and sodium sulfate. As the tap water was determined to have about 23 mg/L sulfate, on Day 234 the additions of sodium sulfate to the influent was discontinued.

Figure 1 shows the columns after 130 days. A black coloration is evident near the bottoms of the columns from sulfate and iron reduction leading to a ferrous sulfide precipitate.

The three columns have been run for a total of 500 days. Influent samples were collected periodically and analyzed for nitrate and sulfate by Lancaster Laboratories. Effluent samples from the columns were submitted to Lancaster Laboratories to be analyzed for nitrate, sulfate, and total organic carbon (TOC). The flow rate, dissolved oxygen, pH, redox potential, and nitrate by Hach concentrations were monitored one to three times weekly using laboratory meters and probes and Hach test kits.

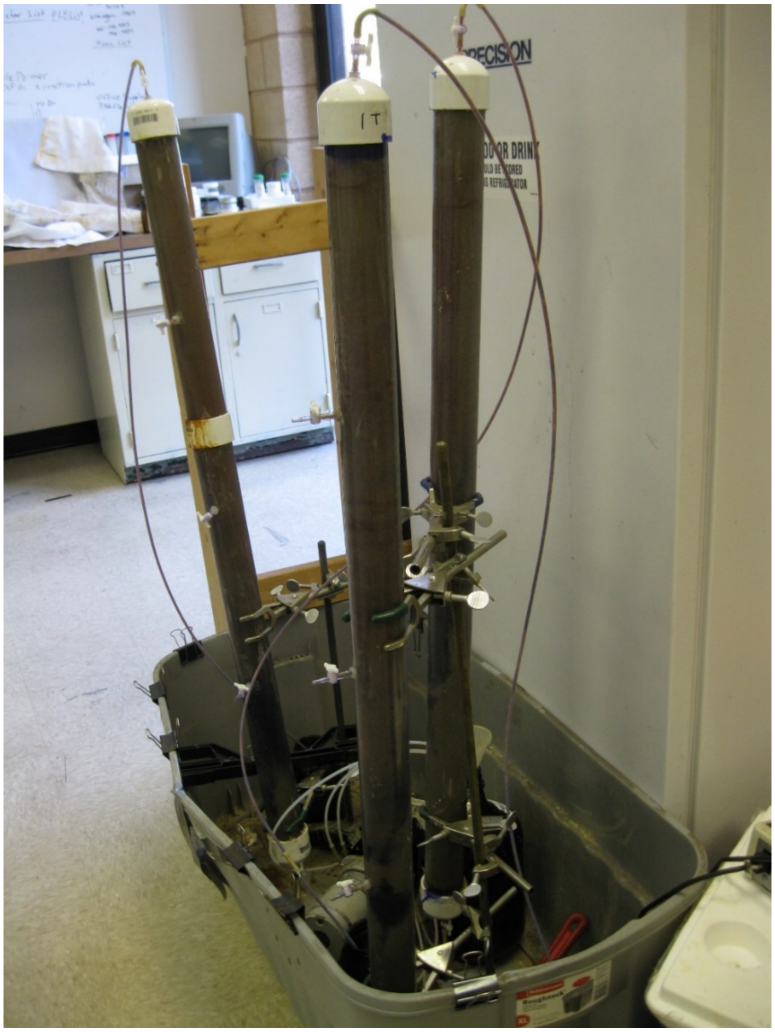

*Figure 1.* Columns after 130 days

The flow rates over the first 350 days have generally ranged from 0.09 to 0.19 mL/min with occasional dips due to clogged lines or leaks. The effluents are collected in open containers exposed to the atmosphere and the measured oxidation reduction potential (ORPs) are likely higher than the water existing within the columns. Dissolved oxygen measurements are also likely biased high due to the exposure to air. However, the dissolved oxygen levels in the influent are almost always higher than the column effluents suggesting that there is oxygen reduction within the column due to an oxygen demand from the substrate.

Over 350 days elapsed since the first SRS injection and as Figure 2 demonstrates, complete removal of the 19.5 to 26.9 mg/L of nitrate-nitrogen (measured by ion chromatography) in the influent was observed for all columns 317 days after the SRS injection or the equivalent of between 95 and 99 pore volumes. The nitrate-nitrogen level was low (0.68 mg/L) in the influent sample collected before the SRS-SD® was introduced and between 2.4 and 13.3 mg/L was found in the initial effluent samples from the columns. By day 25 (the first post-injection monitoring event by Lancaster Laboratories), all of the nitrate-nitrogen was consumed. Nitrite-N and ammonia were measured, but not detected. Consumption of an estimated 1,254 to 1,423 mg of nitrate-nitrogen have been consumed by the additions of 15,400 to 30,800 mg of SRS-SD in the first application to the columns. Sulfate was initially completely consumed (Figure 3). Sulfate levels began to increase after 210 days or 62 to 64 pore volumes and reached levels above the influent after 276 days (precipitated ferrous sulfide is likely being oxidized). TOC levels in the effluent from the column reached as high as 3,900 mg/L as the emulsion eluted out of the columns from approximately 0.5 to 2.4 pore volumes for columns 1 and 2 and for about 8.6 pore volumes for column 3 with the SRS-Z. The remaining EVO was attached to the soil. TOC levels fell to between 1.1 and 1.5 mg/L after 350 days (Figure 4). On a mass balance basis, between 6.0 and 48.3% of the initial TOC mass was collected in the effluents of the columns.

The following conclusions can be reached from the initial column studies:

- There was a complete and continuous removal of between 19.5 to 26.9 mg/L of nitrate-nitrogen in influent for over 317 days, equivalent of 83 to 89 column pore volumes, by the naturally occurring bacteria after the first application of SRS to the three separate columns.
- After the initial SRS-SD injection, TOC reached 626 to 3,900 mg/L in effluents. The emulsion no longer appeared in effluent after 1.3 to 2.4 pore volumes in columns 1 and 2. This demonstrates the limited potential for migration of EVO in the groundwater.
- Consumption of an estimated 1,254 to 1,398 mg of nitrate-N has been supported by the 15,400 to 30,800 mg of SRS initially applied to the columns.
- TOC concentrations in the effluent of the columns fell to between 1.1 and 1.5 mg/L. TOC levels above 2.3 mg/L supported complete denitrification.
- There was no obvious difference in the longevity with the increased loading of the SRS-SD or in combination with the ZVI.

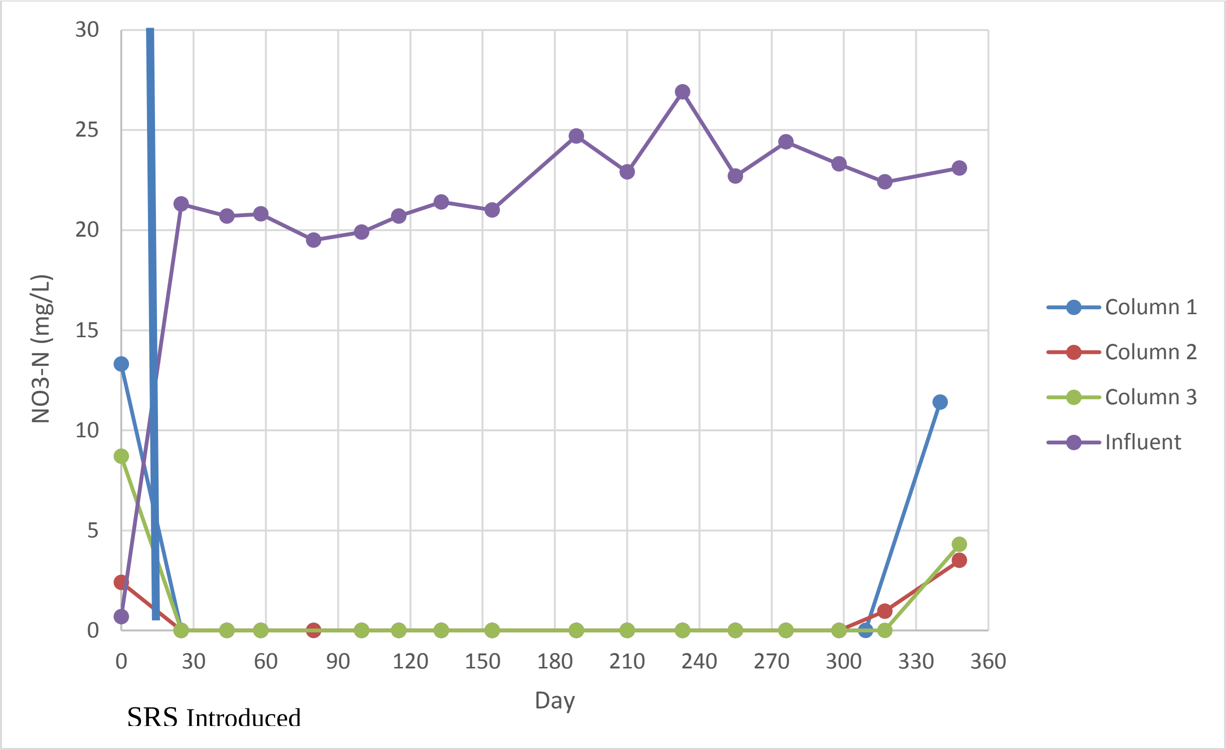

*Figure 2.* Nitrate-N concentrations by ion chromatography, days 0 to 355

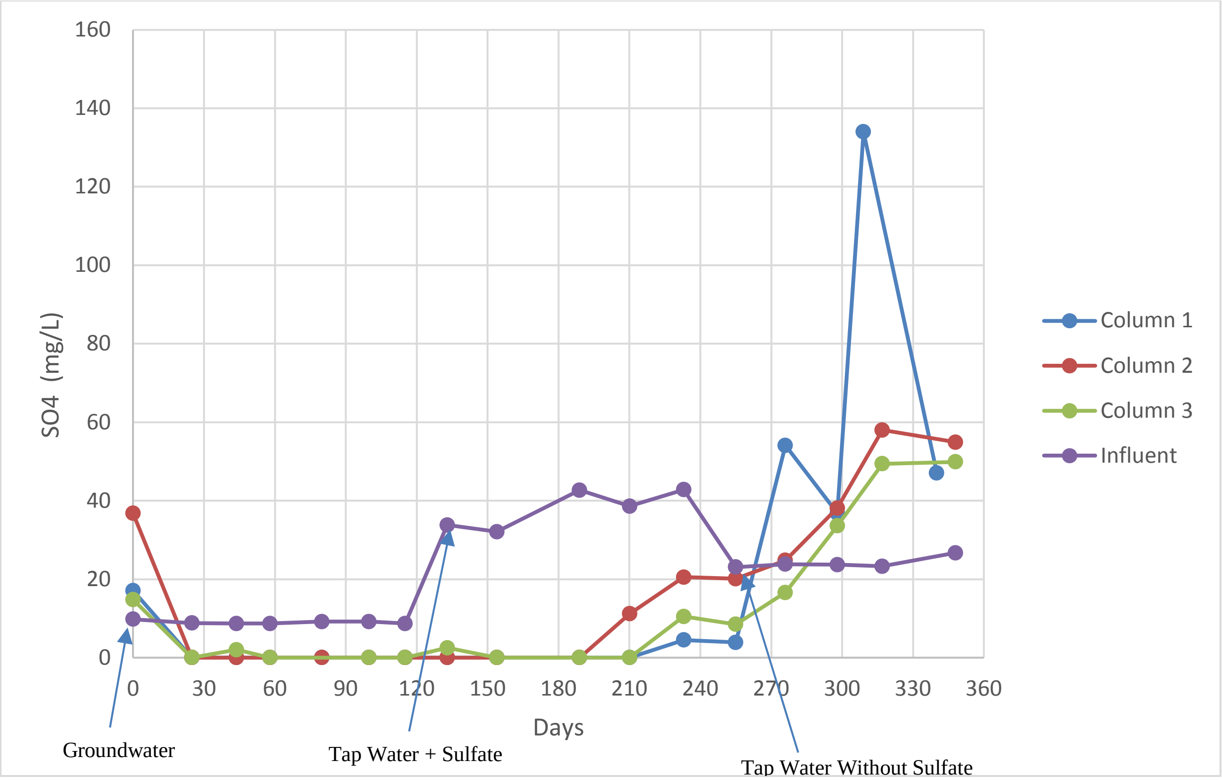

*Figure 3.* Sulfate concentrations by ion chromatography, days 0 to 355

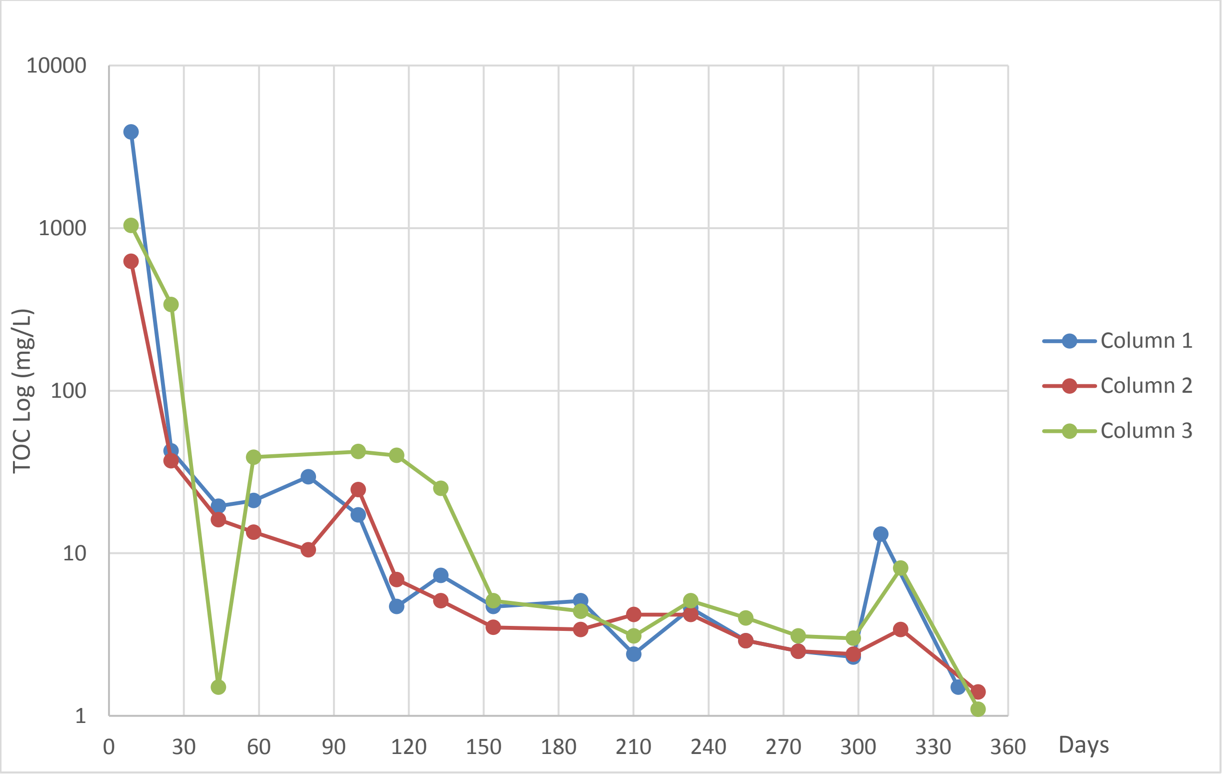

*Figure 4.* Log TOC concentrations, days 0 to 355

# 3. COMBINED COLUMNS

On Day 355, the three columns were connected with flow from Column 1 to Column 2 to Column 3. A second application of 30.8 g of the SRS-NR product diluted 1:10 was applied to column 1 (the TOC of the solution was 12,600 mg/L). The SRS-NR formulation was designed to be retained on the soil and used an anionic surfactant package with a 5 μm average droplet size, but without the inorganic nutrients. The connected columns were operated for another 139 days. Phosphate was added to the influent on Day 431. Ortho-phosphate as P analyses were conducted by Lancaster Laboratories.

As seen in Figure 5, the 21.2 to 24.2 mg/L of nitrate-N in the influent was completely denitrified (except for one time point at Day 440) for over 139 days and 70 pore volumes since the second SRS-NR application. Most of the 25 to 32 mg/L of sulfate in the influent has been consumed (Figure 6) except at Day 440 where there was a flow interruption. The flow rate ranged from 63 to 567 mL/day or an average of 1.9 ft/day. As seen in Figure 7, the maximum TOC in column 3 effluent was 43.2 mg/L with no evidence for the movement of the emulsion through the combined columns. TOC levels have fallen as low as 2.9 mg/L while still supporting complete denitrification. On day 410, the effluent from column 3 was collected in a Tedlar bag (to prevent exposure to oxygen) and dissolved iron and manganese and methane were measured. The dissolved iron was 3.3 mg/L, dissolved manganese was 0.51 mg/L, and methane was 0.33 mg/L. Figure 8 shows that ortho-phosphate as P was reduced from 0.44 to 0.56 mg/L in the influent over the 63-day monitoring period to below the detection limits of 0.03 to 0.06 mg/L in the effluent of Column 3 by biological uptake or adsorption onto the soil.

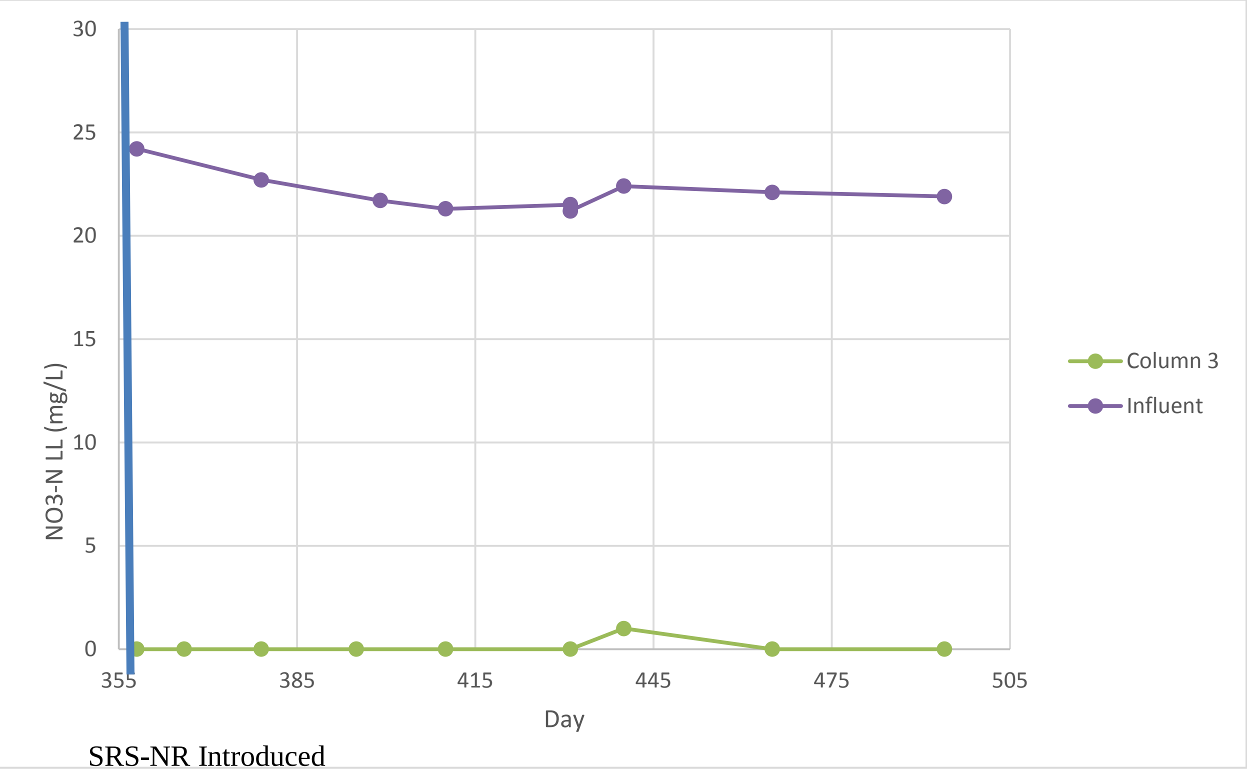

*Figure 5.* Nitrate-N in combined columns

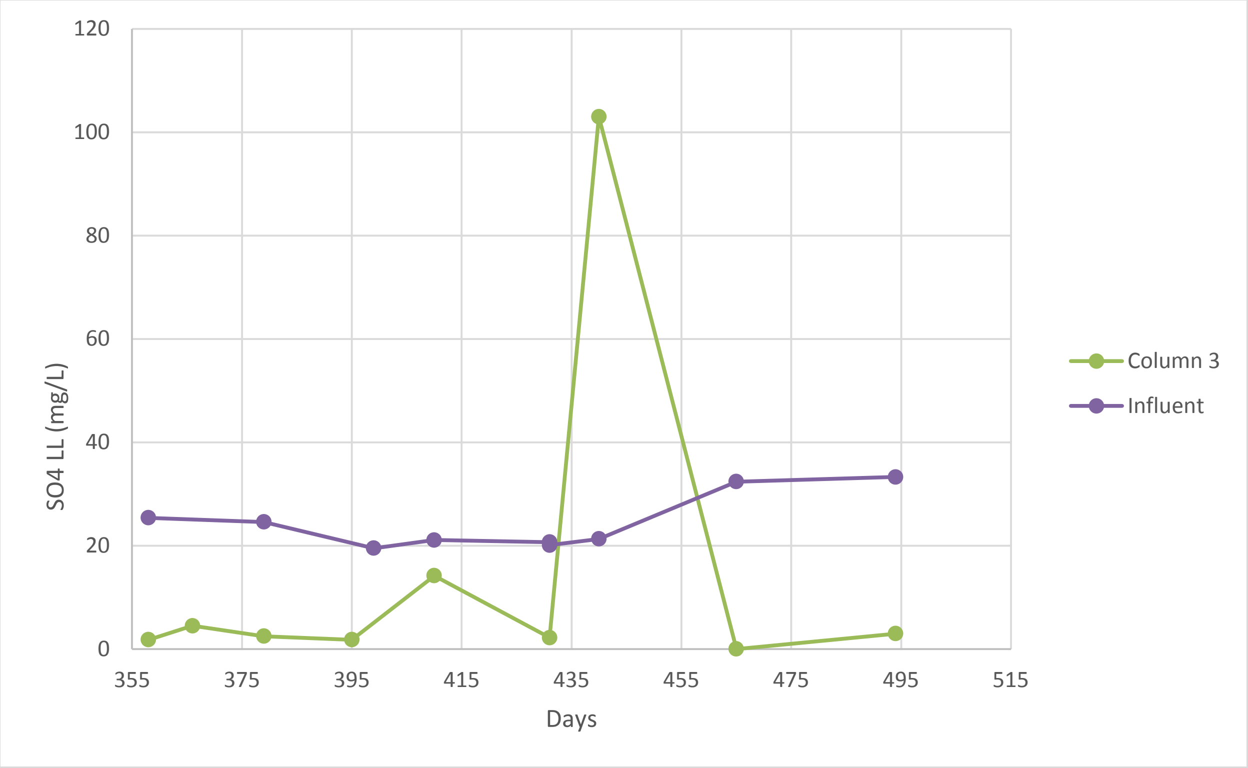

*Figure 6.* Sulfate concentrations in combined columns

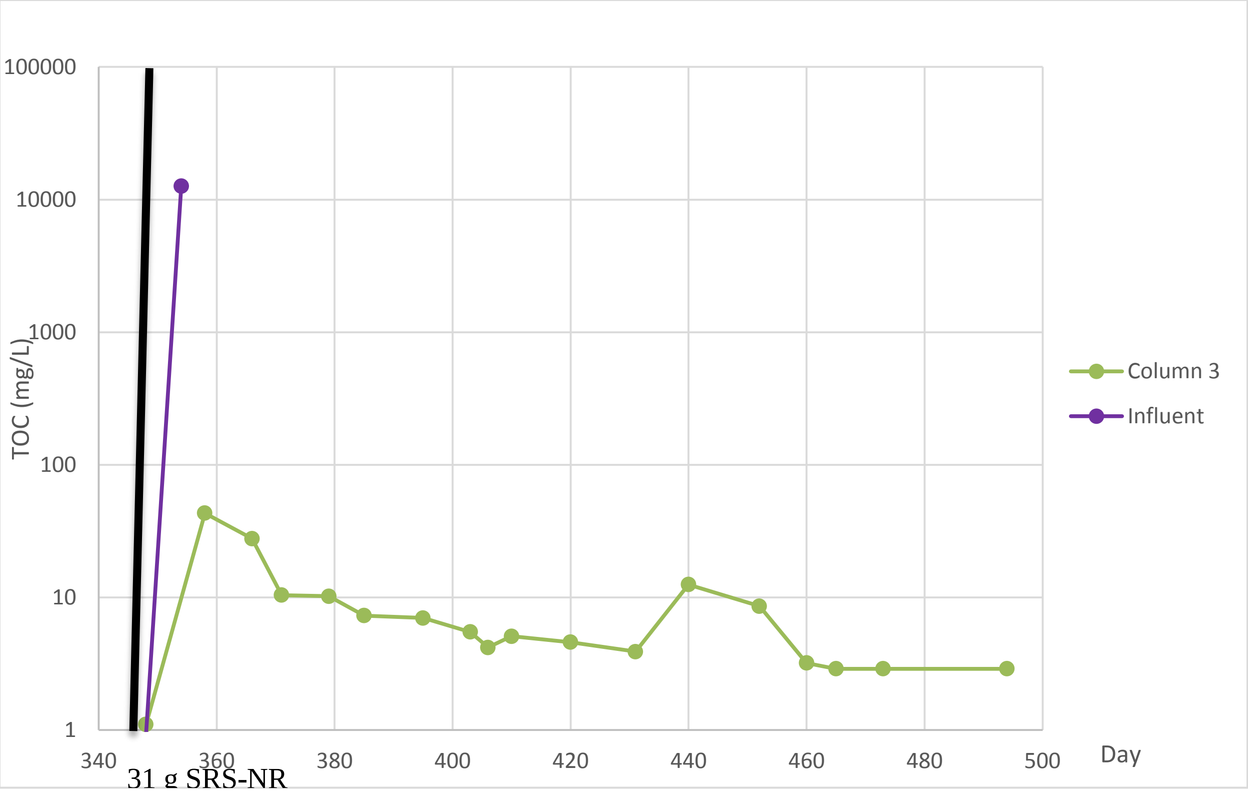

*Figure 7*. TOC concentrations in combined columns

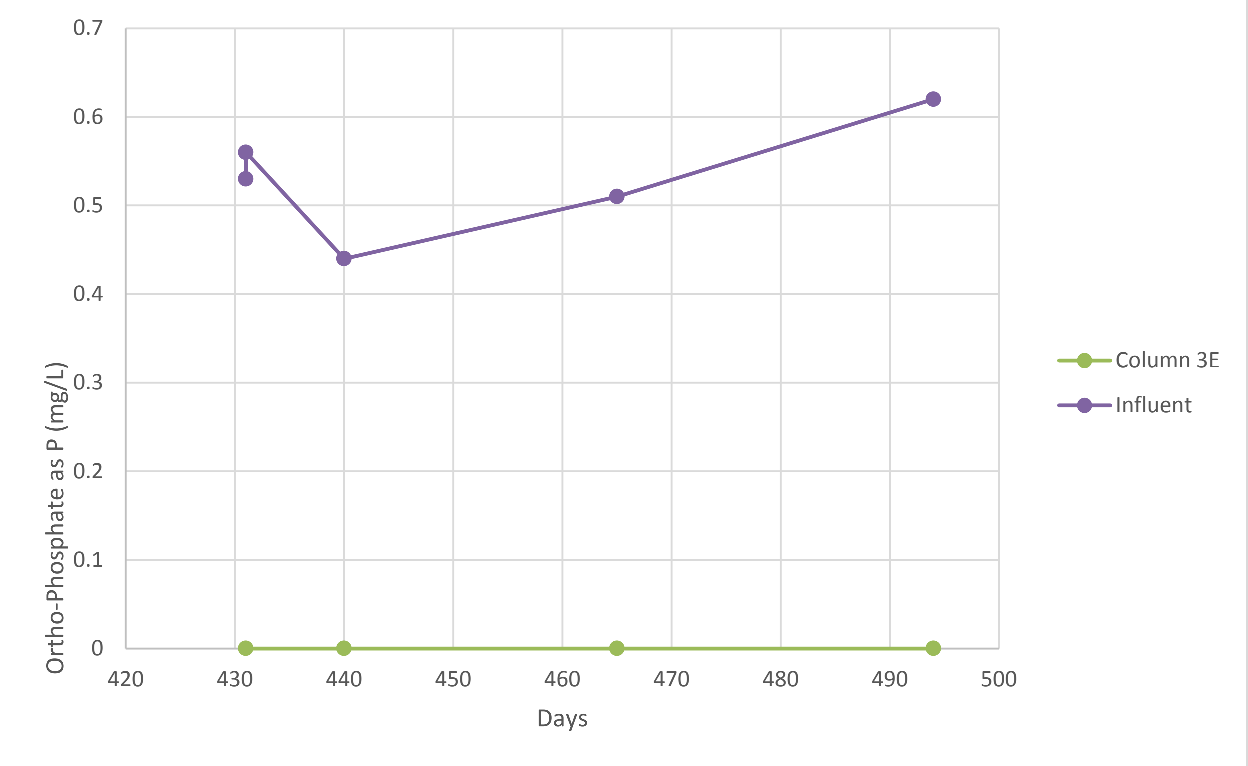

*Figure 8.* Ortho-phosphate as P concentrations in combined columns

## 4. CONCLUSIONS

- The continued effectiveness of an EVO barrier to completely remove nitrate even at low residual EVO concentrations demonstrated the longevity an EVO barrier will have in mitigating nitrate in groundwater and eliminate its impact to surface waters, even in Cape Cod soils with high groundwater flowrates.
- After injection, TOC reached 43 mg/L in column 3 effluent from the combined columns. Emulsion did not appear in effluent based upon low turbidity. TOC in effluent as low as 2.9 mg/L sustained complete nitrate removal.
- Phosphate removal was due to adsorption onto soil or biological uptake.
- SRS-NR formulation with anionic surfactant retained on soil matrix was better than SRS-SD formulation.

## 5. RECOMMENDATIONS

A field scale permeable reactive barrier pilot will be conducted to evaluate SRS transport and denitrification. We recommend the SRS-NR formulation with a larger droplet size and stickier, anionic surfactant mixture for maximum retention and longevity.

# 6. REFERENCES

Cape Cod Commission. 2015. Cape Cod Area Wide Water Quality Management Plan Update. Barnstable, MA.

# WATER SUPPLY TO URBAN POOR COMMUNITIES - THE COST AND TECHNIQUES INVOLVED: CASE STUDY IN THE ASHANTI REGION, GHANA

*West Coast Conference, March 2016*

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## ABSTRACT

The urban slums and low-income communities of urban areas in developing countries have inadequate access to water supply and sanitation. The aim of the study is to identify technical options, the cost of water price and how poor urban inhabitants can be provided with water at affordable prices. The daily consumption of households with the corresponding household size and households' choice of domestic water sources was studied. The study also assessed the relationship between water distance, consumption and cost. The analysis was built on primary data collected from 135 households from three communities. Both qualitative and quantitative form of interview was implemented during the survey. The major statistical tools used to analyze the collected data were SPSS and ANOVA software. Results showed that the main sources of water include Ghana Water Company Limited (GWCL) household connection, borehole, Water Health Ghana (standpipe), GWCL community standpipe, hand dug wells and vendors (tank service). The use of water is restricted by the cost and time needed to access a particular source of water. The cost of using water purchased from mobile tankers and GWCL community standpipes was higher than that of a household connection. About 85% of the respondents preferred borehole water and household connection to public standpipes and water bought from the mobile tankers due to the long distance covered to access the water and the high cost of water from water vendors respectively. Most of the inhabitants were aware of each individual's right to basic clean and potable water, the inhabitants also raised concerns about the governments' negligence on responsibilities concerning water supply.

**Keywords:** water, water supply, urban poor, water quality, hygiene

## 1. INTRODUCTION

In recent decades, one of the greatest challenges of sustainable development of quickly developing urban regions in developing countries is providing safe and affordable drinking water to the residents (UN, 2007). Delivery of clean water service transforms lives, combats poor health and brings sustainable economic benefits (WaterAid, 2012). The ambition of all developing countries is to make water sustainable for all. Sustainable access to drinking water implies that the source is under 1 kilometer far from places of utilization and that it is

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conceivable to dependably get no less than 20 liters for each individual of a family unit for every day. Also, the water must be safe for drinking, thus, the chemical and physical characteristics of the water should meet World Health Organization (WHO) guidelines or national standards (UN, 2015). According to WHO, 1.1 billion individuals around the globe needed access to “improved water supply” in 2000. In response, WHO and United Nations International Children's Emergency Fund (UNICEF) set up a Joint Monitoring Program (JMP) to screen the status for water supply all inclusive. According to the 2015 millennium development goals, 91% worldwide populace is utilizing an improved drinking water source, contrasted with 76% in 1990. Although the figures seem positive, poor urban communities in developing countries still face challenges in water accessibility according to the 2015 JMP report (JMP, 2015). Some the reasons why developing countries still face challenges is due to poor governance, lack of political will, financing, cost recovery and choice of technical options, insufficient continued investment, inefficient systems and lack of training, and spares to maintain systems in working order (Abdul-Nashiru, 2006). In addition, the low level of creativity and innovativeness of service providers, no pro-poor regulation by the government, and no separation between regulator and operator are some of the other factors affecting the water supply to poor communities. The poor are also not served because of the high connection cost required to be paid by the poor households. (Mcintosh, 2003; McGranahan and Owen, 2006; Van Rooijen, 2011; Bardhan, 2013).The poor economic conditions in Ghana coupled with low annual income by household heads has made water accessibility difficult. Research shows that funds obtained by developing countries through loans and grants with the aim of improving water supply in urban areas are mostly channeled into pipe borne water supply expansions, which are mostly benefited by high-income earners. In effect, the rich turn to benefit more from subsidies than the poor, thus the poor consume less water and pay more water than the rich (Blokland et al., 1999; Baker and Trémolet, 2000). Research also shows that households receiving intermittent water supply were willing to pay more in order to receive a continuous water supply (Lovei and Whittington, 1993). Water produced for supply does not meet the required demand due to urbanization. In addition, the amount of pollution is increased tremendously in urban towns due to overcrowding. This results in an increase in the cost of production at water pumping stations, which ultimately affects the amount of water produced for the urban areas (Zhu Zhongie, 2003). Cost-recovery and subsidies are key components in ensuring efficient water supply to people residing in the poor urban communities. Cost-recovery is most likely to be achievable where the quality and quantity of service is sufficient to encourage payment for services (Hukka and Katko, 2003). Studies also show that unaccounted-for- water exceeds accounted-for-water in urban piped water supplies in developing countries. Recovering this lost water would provide more water to extend services into new areas. Reducing leakage has additional benefits for reducing the likelihood of ingress of contaminated water into the supply, which may lead to disease outbreaks (WasteCare Limited, 2005). Delivery of utility services (water and sanitation) should be purely exclusive and expert-driven rather than inclusive and communicative (Blokland et al., 1999). Poor urban people suffer the most because they tend to be excluded and do not understand or influence utility procedures (Thackray, 1992).

This report tends to compare the various techniques by which sustainable water is delivered to poor urban communities. The techniques used to deliver water to the poor communities include; Water Health Ghana (WHG) standpipe, boreholes, hand dug wells, GWCL standpipe, vendors/ water tankers and GWCL house connection. The various techniques are compared based on the people's perception, cost and water consumption rate. The study also assesses the relationship between water distance, consumption and cost.

## 2. MATERIALS AND METHODS

The study area was the Ashanti Region of Ghana. The three poor urban communities were Mampong, Nsuta and Abenkro as shown in Figure 1.

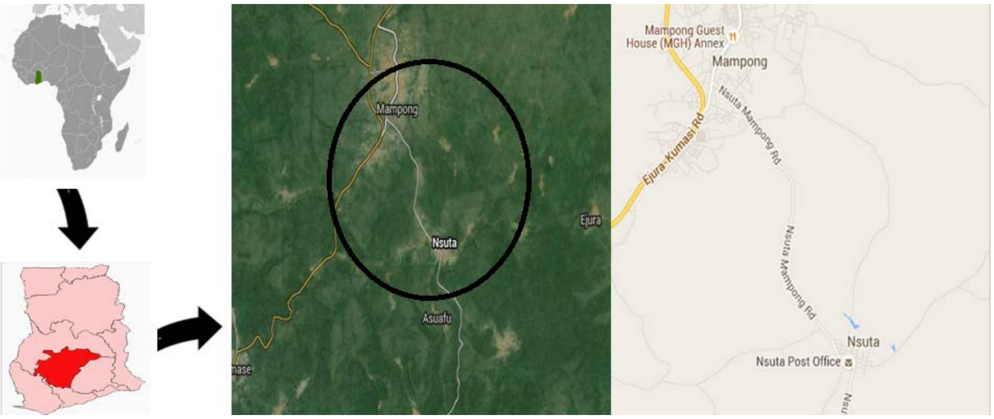

*Figure 1.* Study area (Source: Google Map)

Random sampling method was used in order to get information across the communities. The households were selected at random in the administration of a questionnaire to community members. A representative of each household, irrespective of gender, was interviewed. However, only 18 years and above were considered. Both the qualitative and quantitative form of an interview was conducted during household surveys. The quantitative method involved the use of semi-structural questionnaires while the qualitative method was done through focus group discussion. Statistical analysis was performed using SPSS, Microsoft Excel and one-way ANOVA (Analysis of Variance). A confidence level of 95% was used during the descriptive statistics analysis while an alpha value of 0.05 was used in the one-way ANOVA. During the survey, the people's perception about the existing water facilities (i.e. quality, reliability, accessibility) was also analyzed. Household expenditures were used to estimate household income because of the difficulty in estimating the total income of the households, especially those households involved in occupations that yield irregular incomes. In all, 135 households within 3 communities were selected for an interview. The entire three communities considered in this study were divided into zones as per the number of interviewers, and then a random selection of houses was performed in the ratio of nearly 1 in 5. The questionnaire was organized so as to get information on four broad perspectives: socioeconomic, infrastructure, environmental health, and behavior and environmental awareness. However, this research will be mainly focused on linking the cost of water supply and the various technical options that can be adapted to ensure the poor urban community is served. Comparative analysis was made between the services offered by the sources of water based on reliability, adequacy and suitability and establish factors which explain the differences in cost of each source. One way ANOVA was used for data analysis. The F-statistics was lower than the F critical. The variance is the same, thus the null hypothesis is not rejected. The alpha value was greater than 0.05, thus we can confidently say that the data was equal at the alpha level 0.05.

*Table 1.* Source: Statistical Service Ghana 2010 population (PHC 2012)

| Name of community (district) | No. of households interviewed | Municipal/ District Population |
|---|---|---|
| Nsuta (Sekyere Central District) | 45 | 71,232 |
| Abenkro (Ejisu Juaben Municipal) | 45 | 143,762 |
| Mampong ( Mampong Municipal) | 45 | 88,051 |

# 3. RESULTS

## 3.1 Technical Options for Water Supply to Urban Poor

The majority (41%) of the 100 respondent interviewed were 45 years and above. 33% were in the age group of 30 – 44 years, which constituted the second majority, while 26% were in the age group 18 – 29 years, constituting the minority. 60% of the respondents were females whilst 40% were males. 60% were self-employed, 5% are government employed and 10% are privately employed. 15% are students and 10% are unemployed. Most of the self-employed were petty traders and farmers. 19% did not have any formal education. However, the majority (56%) however had education up to the basic level, 10% to secondary level, and 10% had education up to the tertiary level. The pattern of answers to the above question presupposes the economic status of the individual respondents. Table 2 shows the various water techniques available in the three communities.

*Table 2.* Household drinking water sources (technical options) in the poor urban communities

| Water Technique | Nsuta | Abenkro | Mampong |
|---|---|---|---|
| Borehole |  | ✓ | ✓ |
| WHG standpipe | ✓ |  | ✓ |
| Hand dug well | ✓ |  |  |
| GWCL standpipe | ✓ |  | ✓ |
| GWCL house connection |  |  | ✓ |
| Water tanker | ✓ | ✓ | ✓ |
| House connection |  | ✓ |  |
| Community managed system (standpipe) |  | ✓ | ✓ |

Figure 2 shows the inhabitants usage of water source (technical option). This usage was based on water quality, neatness, cost, adequacy and conveniences. Figure 3 shows the status of the various water technologies in the communities.

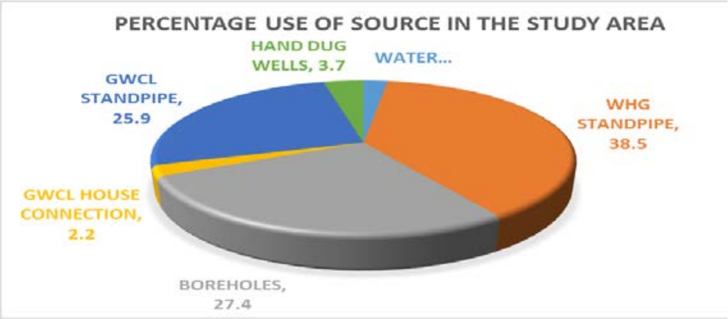

*Figure 2.* The number of respondents and the corresponding source of water used (Statistical analysis: n = 6; F = 1.31; $F_{crit}$= 3.1; P =0.3230; Confidence level = 95%, Descriptive statistics; α = 0.05, one-way ANOVA.)

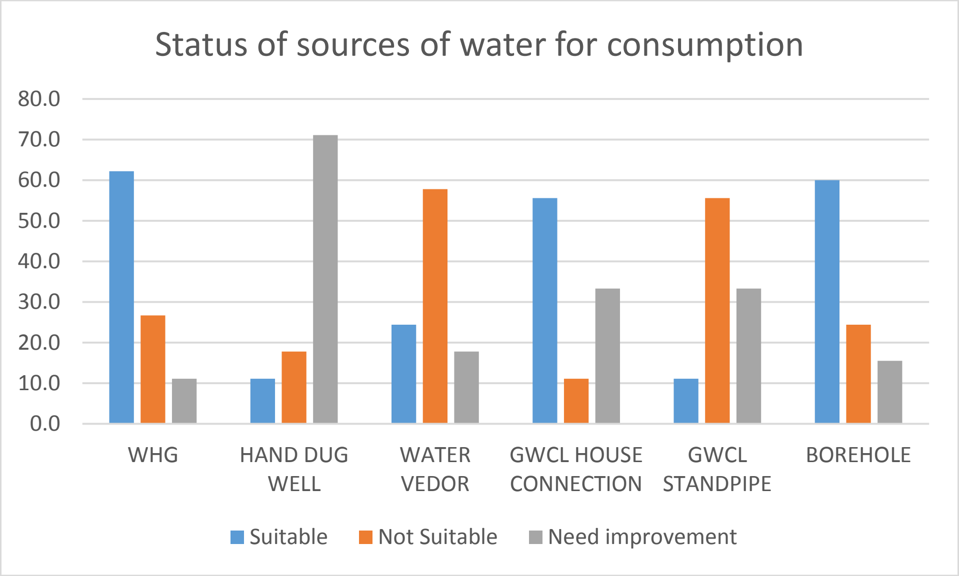

*Figure 3. S*tatus of source of water for consumption

## 3.2 Household Income, Cost and Quantity of Water Consumption

Household expenditures were used to estimate household income because of the difficulty in estimating the total income of the households, especially those households involved in occupations that yield irregular incomes. Table 3 shows the monthly income by the household heads (father) only.

*Table 3.* Average monthly income by household heads only

| Name of community | Average income* | Average household size |
|---|---|---|
| Nsuta | 322 | 8 |
| Abenkro | 314 | 9 |
| Mampong | 300 | 7 |

*235 Ghana pesewas (2.35 Cedis) is equivalent to 1 dollar (2013) (Source: FX Exchange rate)

The unit costs for each category of water supply as shown in Table 4 in the study area are used to estimate the cost of consumption per person per day, month and year for each household in the study area as seen in figures 4, 5, 6, 7 and 8.

*Table 4.* Unit costs (1000 liters) for each category of water supply

| Category of service Monthly Consumption (1000 Liters) | Approved Rates in GH pesewas*/1000 Liters |
|---|---|
| Metered Domestic 0-20m$^3$ | 80 |
| 20 m$^3$ and more | 120 |
| Unmetered Premises- Flat rate per house per month | 520 |
| (PURC Publication of Electricity &Water Tariffs, 26th May, 2010) | |
| GWCL standpipes | 434 |
| Water vendors (tank service) | 1300 |
| WHG Standpipe | 650 |
| Hand dug well | 860 |
| Borehole | 217 |

*235 Ghana pesewas (2.35 Cedis) is equivalent to 1 dollar (2013) (Source: FX Exchange rate)

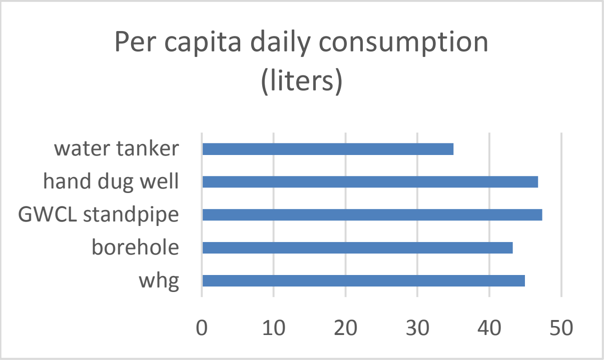

*Figure 4.* Per capita daily consumption in liters

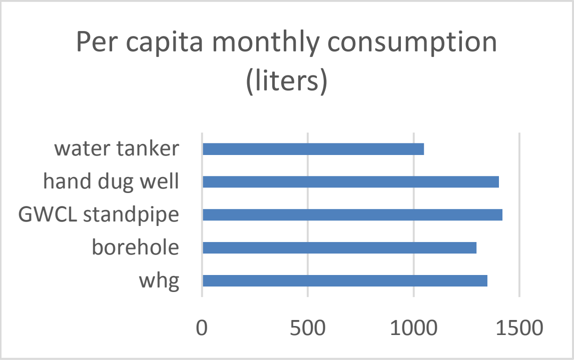

*Figure 5.* Per capita monthly consumption in liters

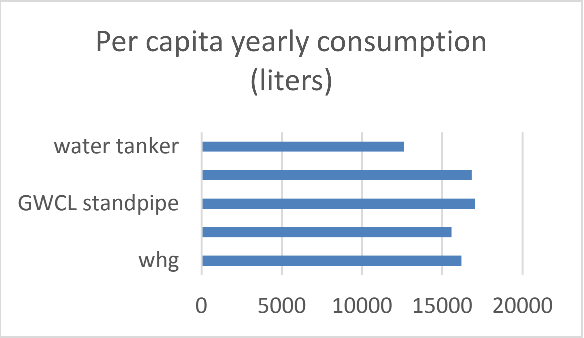

*Figure 6.* Per capita yearly consumption in liters

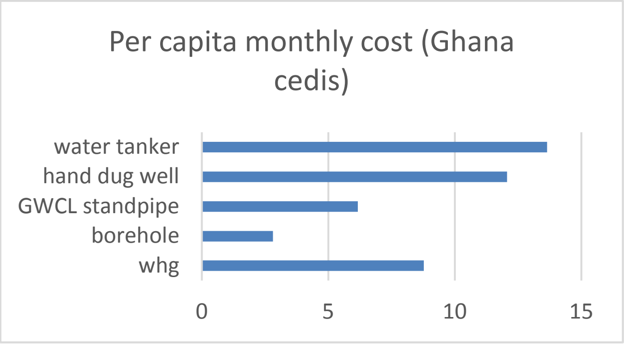

*Figure 7.* Per capita monthly cost in cedis

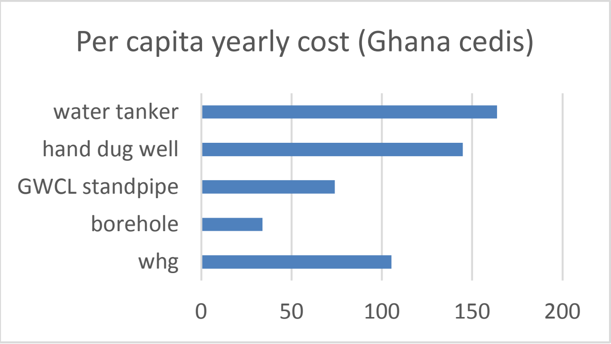

*Figure 8.* Per capita yearly cost in cedis

## 3.3 Community Participation in Water Supply

Figures 9 and 10 show the inhabitants' level of knowledge of an individual's basic right to potable water and the respondents' preferred source of water, respectively. The respondents' preference is based on water quality, serviceability, reliability, and accessibility.

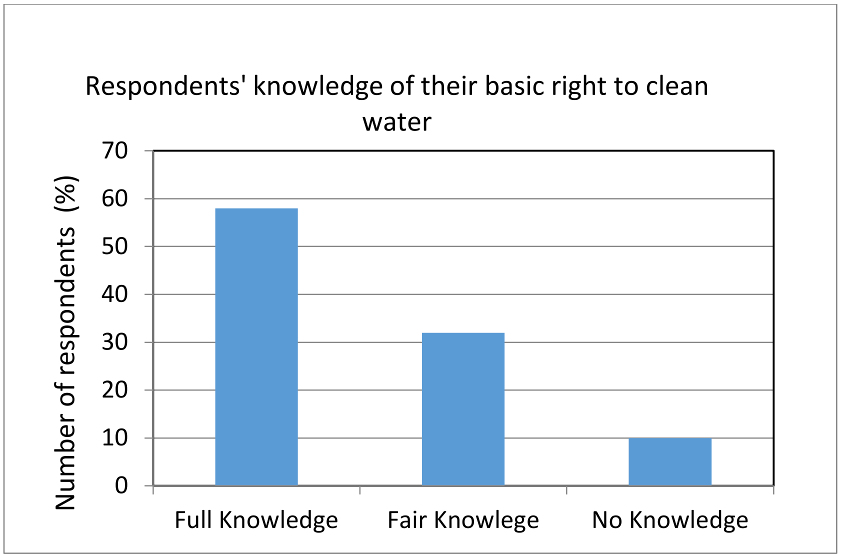

*Figure 9.* Respondents' knowledge of an individual's basic right to clean water

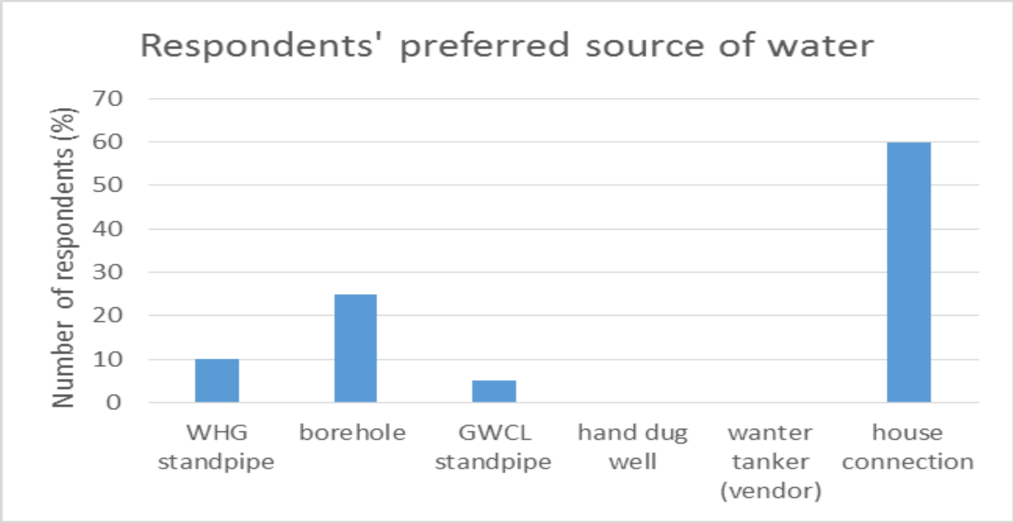

*Figure 10*. Respondents' preferred source of water

# 4. DISCUSSION/CONCLUSION

Most people preferred having the direct household connection of water for convenience, but due to the high cost of installation, the inhabitants resorted to other sources. The inhabitants turn to a water vendor as the last option due to the high cost compared to the other water sources. The benefits enjoyed by households who have access to improved water services include: savings on expenses from buying water from alternative providers, more time saved, improved health and sound mind for the household members (UN, 2007). The average time taken by the respondents to journey from homes to fetch water from GWCL standpipes and boreholes was between 10-20 minutes. This was, however, different when the flow of water ceased at certain periods during the day due to long queues which developed at the standpipes when the flow resumed. Some of the respondents indicated that it can take close to an hour to get a gallon of water when water becomes scarce. Figure 3 shows the observation and comments of each household on the various techniques used to supply water. The available technical options in the study were compared on the basis of affordability, suitability and reliability. The water consumption rate per head as shown in Figures 4, 5 and 6 indicates that water from the hand-dug well was consumed the most, followed by GWCL standpipe, WHG standpipe, boreholes and water vendors. Although a hand dug well was not suitable for inhabitants (Figure 3), the inhabitants consumed hand dug well water the most due to the short distance covered (i.e, convenience) to obtain water for use. The cost involved in using the various water technologies is shown in Figures 7 and 8. From Figures 4, 5, and 6 and Table 3, the cost of using water vendors (tank service) as a source of water was far more expensive than the other available sources. This is an indication that the poor urban community spends more money on less water than the rich since the rich conveniently use house owned connections as a source of water. The variations in the daily, monthly and yearly volume of water used as well the cost involved further proves that pipe borne water (e.g., own connection) is cost effective. The WHG standpipes and boreholes are more reliable than GWCL standpipes and water vendors (e.g., tank service) due to constant flow. The poor households in the study area decide, on a daily basis, which sources to use depending on the availability of time and money. The unit cost of water is a major constraint, and this affects the type of water source accessed daily. The income levels of the respondents support the fact that the poor urban community rarely has large enough sums of money in order to get connected to the GWCL network or construct mechanized boreholes, and as such consider the daily purchase of water from public standpipes, water vendors (e.g., tank service) and other sources as adequate. The trend of answers given shows that the major barrier to accessing utility-piped water is the cost of connection (e.g., fees and material). Moreover, beyond the cost of connection, the paperwork involved is cumbersome and intimidating. The bills issued every month from utilities are not suitable for the poor urban community because of lack of steady incomes. During the focus group discussion, inhabitants who owned WC (flush toilets), showers and other water consuming devices in homes consumed more water thus increasing water cost. The distance between the households and source of water was another determining factor that influenced the water consumption. Those who covered a short distance in order to get water consumed more water, thus paying more for water. Furthermore, dwelling type, house size, and the number of members in the household also contribute significantly to the amount of water used. Socioeconomic factors (i.e., education level, household income) also influenced the water consumption rate. The study showed that changes in season also affected water consumption rate and cost. During the dry season, households patronize water more from the technical sources than in the wet season. During the wet season, rainwater serves as a water supplement when harvested. The average distances covered by inhabitants to fetch water is acceptable. The inhabitants also consume more than 20 liters of water per day per head meeting the UN requirements on sustainable access to water. Household connection is convenient and the unit cost of 1000 liters is the cheapest followed by the borehole, GWCL standpipes, WHG standpipe, hand dug wells and water vendors (e.g., tank service). The research showed that the unit price (1000 liters) of water was too much from the poor person’s point of view due to the irregular source of income of the poor. 90% of the respondents had knowledge of an individual’s right to clean and potable water as shown in figure 9. The respondents express concerns as to why the poor urban areas lack reliable water supply systems. The provision of clean drinking water is critical to economic growth and is integral to human development, including education, gender equality and health. The government and stakeholders involved must implement policies to favor the poor urban communities in order to make clean water sources reliable, affordable and accessible to all.

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# PHYSICOCHEMICAL TREATMENT OF CYANOBACTERIA BY HYDRODYNAMIC CAVITATION

*West Coast Conference, March 2016*

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## ABSTRACT

Harmful algal blooms (HABs) continue to be a serious issue facing the maintenance of healthy waterways as they can rapidly degrade water quality. In this study we evaluated the effect of hydrodynamic cavitation and the removal of cyanobacteria and its associated toxins from water under various cavitation fields. It was hypothesized that the mechanism of hydrodynamic cavitation alone would structurally damage the membranes of the cyanobacteria while radicals generated from the cavitation process oxidize toxins released from the disrupted cell membranes. Three 400 gallon tanks with cyanobacteria were subjected to various cavitation intensities generated by circulating the tank water at through hoses with different nozzle configurations. Parameter measurements included pH, dissolved oxygen (DO), cell biomass, chlorophyll α, and turbidity. Following 40 minute treatments, the trends observed in algal biomass suggest that 2 of the 3 treatments were effective in reducing algal biomass that sustained for 168 hours. The least effective treatment reduced algal cell biomass immediately following treatment, but regenerated quickly after 48 hrs. Current findings from this study suggest that the process of cavitation may have promising application with further investigation.

**Keywords**: cyanobacteria, hydrodynamic cavitation, harmful algal blooms, microcystin

## 1. INTRODUCTION

To date, it is difficult to find a low-cost method to remove cyanobacteria as both chemical and physical methods of treatment have been explored. Chemical treatment methods that can control cyanobacterial growth have been found to affect the natural ecological processes of the environment, while physical methods often induces secondary pollution through the release of microcystins from disrupted algal cells (Wu et al., 2012). Due to the difficulty of removing microcystins from water bodies, the treatment of HABs in contaminated waters is a great challenge. In addition to algal removal, it is also necessary to treat the toxins generated by the algae. Disruption of the algae cells increases the release of toxins. The most current treatment technologies include the use of radical materials such as ozone ($O_3$) and hydrogen peroxide ($H_2O_2$) to effectively decrease microcystin concentrations in aquatic environments (Barrington et al., 2013). However, there are concerns that strong oxidants like $O_3$ and $H_2O_2$ may adversely impact other organisms (Fan et al., 2013). To overcome the obstacle of employing harmful oxidants, other less powerful oxygen radicals generated by cavitation will be investigated in this study. In previous work, superoxide anions ($O_2^-$) have been demonstrated to degrade

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microcystins (Mezyk et al., 2013), while potentially causing less harm to other organisms. In the present, oxygen radicals will be generated without the use of a specialized, commercial reactor. The objectives of this work are to evaluate the combined effect of hydrodynamic cavitation and advanced oxidation to 1) remove cyanobacteria and its associated toxins from water under various cavitation fields, and 2) determine the oxygen species generated from each cavitation field intensity.

## 2. MATERIALS AND METHODS

Four 400 gallon tanks were used to grow large cyanobacteria cultures. One tank was designated as the stock, and the remaining 3 tanks were for testing. The three experimental tanks were plumbed together to utilize one water pump to maintain pressure consistencies. The water circulation pump was 1/3 horse power (hp) with an output pressure of 25.6 psi. Six-foot hoses were connected to the pumps, in which 3 specialized nozzles were attached. Each nozzle consisted of different molding configurations to generate varying cavitation fields during treatment. Nozzles were identified as Treatment Nozzles #1, 2, and 3.

Cyanobacteria contaminated water samples collected from a lake affected by HABs were cultured for testing in the present study. A 5 gallon water sample collected from the contaminated lake was completed to a volume of 250 gallons in a 400 gallon stock culture tank. The bacteria were supplied with 50 doses of Shultz Plant Food Plus. After culturing the stock algae for 14 days, 5 gallons of the cultured cyanobacteria was used to culture each of the 3 treatment tanks. The total volume of each treatment tank was 250 gallons. Sample treatments began after 14 days of culturing. Before treatment, 500 ml samples were collected from each tank. Each tank was treated for 40 minutes. At 5, 10, 20, and 40 minutes, 500 ml samples were collected at 15 inches from the treatment impact area. Thereafter, samples were taken at 48, 96, and 162 hours. Measured parameters included pH, dissolved oxygen (DO), turbidity, biomass, and chlorophyll α. Samples collected for microcystin concentrations are currently stored at 4°C for future analysis.

## 3. RESULTS AND DISCUSSION

Following cavitation treatments, algal biomasses were moderately reduced in Treatment #1, but greatly reduced in Treatments #2 and 3 up to 96 hours. While this trend is encouraging, the rapid regeneration rate of the cyanobacteria observed at 168 hours in Treatments #2 and 3 is a highly unfavorable outcome. The algal biomass concentration increased by an average of 58% above the initial biomass concentrations. These data imply that the greater water pressures (observed in treatments 2 and 3) are effective for only up to 96 hours after treatment, while the treatment with the least pressure yielded only subtle changes in algal biomass. Seemingly, Treatment #1 impeded rapid proliferation of the algae rather than reducing algal biomasses. Turbidity measurements are shown in Figure 1.

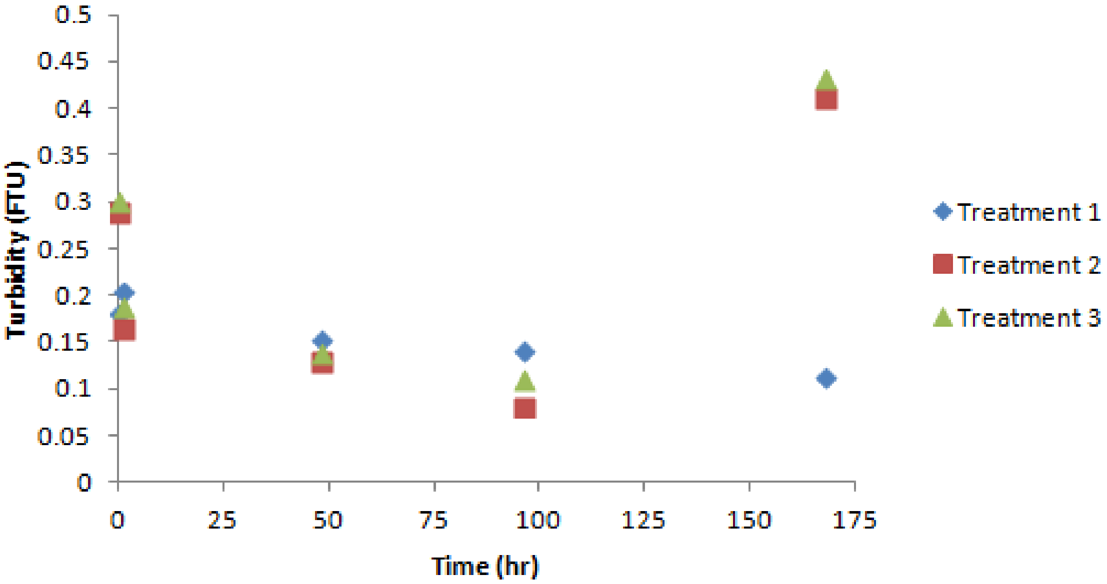

*Figure 1*. Turbidity measurements of samples collected after cavitation treatment over 168 hours

Comparing the results from the aforementioned treatments, an important factor to consider is that Treatment #1 comprised the lowest initial biomass concentration (despite the equal volumes of stock algae added to each tanks during cultivation). Considering this, additional cavitation treatments will be conducted with very low algal biomasses with sampling intervals exceeding 168 hrs.

In subsequent cavitation tests, treatment strategies were modified to be employed as a preventive means rather than treatment. Very low concentrations of cyanobacteria were treated before the algae reached its bloom stage. Results from this test follow the same trend as our previous submerged water tests for each treatment. Results from the previous test showed that Treatment #1 was not as effective in treating cyanobacteria as it was in hindering its growth, while Treatments #2 and 3 demonstrated a comparatively greater reduction in algal biomass immediately following treatment, and a significant increase after 96 hrs. No measurable indication (turbidity, chlorophyll, or particulate biomass) of cyanobacteria was detected in Treatment tank #1 until day 16 when chlorophyll α concentrations reached 0.9 mg/L (Figures 2 and 3).

In the Control and Treatment Tanks #2 and 3, cyanobacteria growth was observed 7 days after treatment (sample collection day 9) when chlorophyll α concentrations reached 3.1, 2.5 and 2.4 mg/L, respectively.

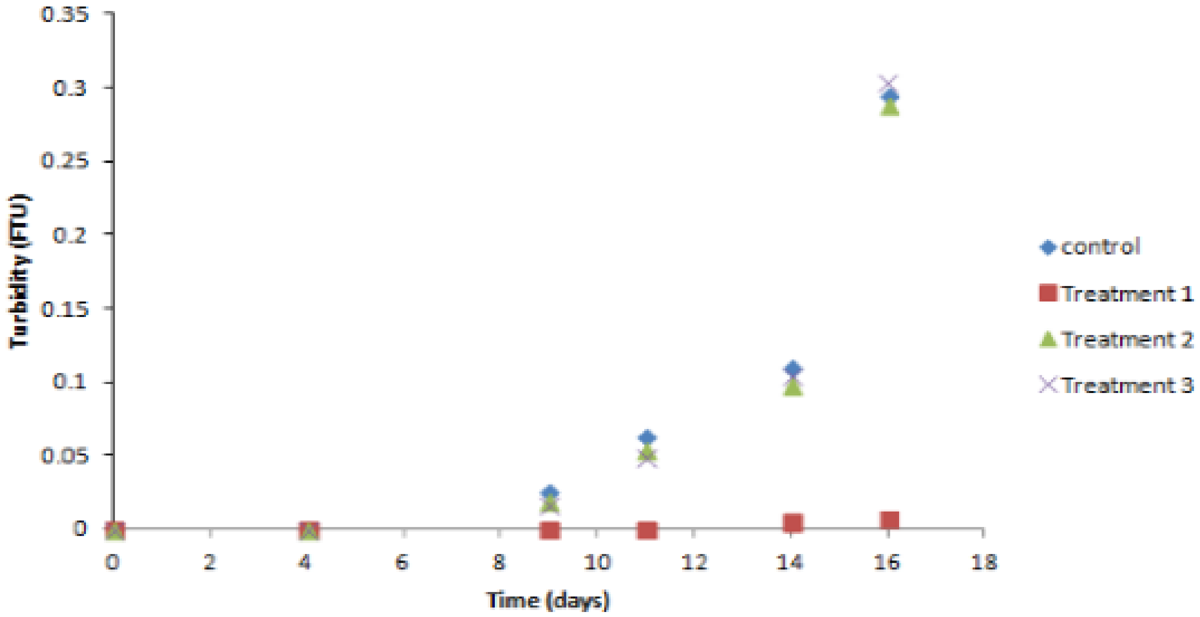

*Figure 2*. Turbidity measurements of samples collected after cavitation treatment of low concentration cyanobacteria culture over 16 days

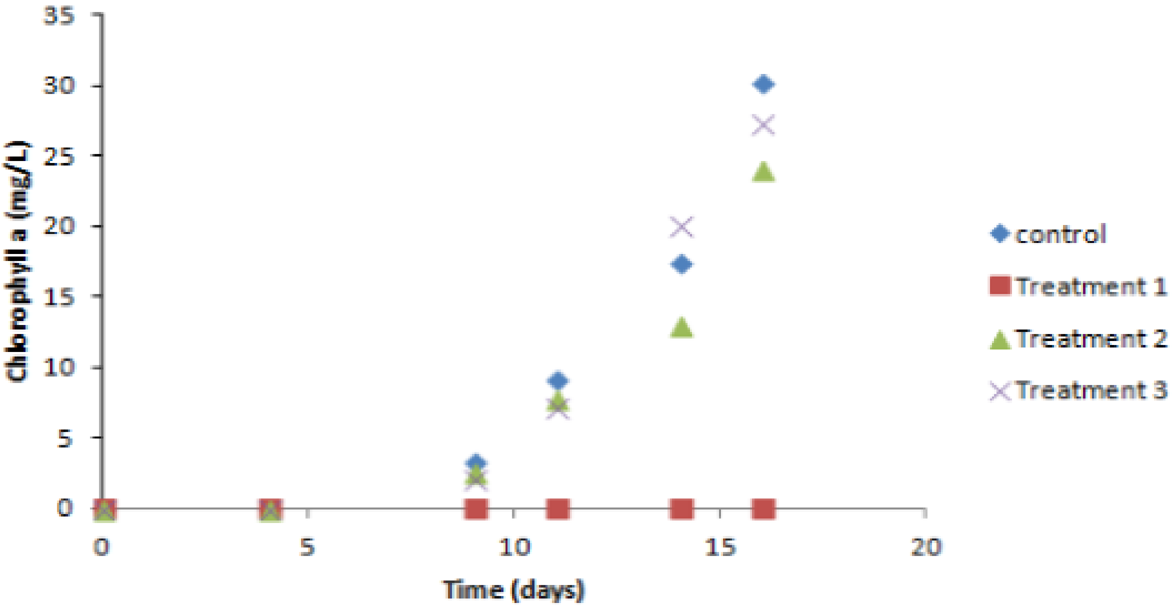

*Figure 3*. Chlorophyll a measurements of samples collected after cavitation treatment of low concentration cyanobacteria culture over 16 days

# 4. CONCLUSION

Considering that the nozzle configuration of Treatment #1 generates the least amount of pressure relative the nozzle configurations of Treatments #2 and 3, it is implied that greater water pressures in cavitation can promote algal growth over time, despite its ability to physically destroy the cyanobacteria during treatment. Taking into account the similar trends observed in the submerged water tests, future work will investigate 1) the frequency of low pressure treatments required to prevent algal growth from reaching measurable detection, and 2) the dual treatment of cyanobacteria using the higher pressure treatments (nozzle configurations #2 and 3) followed by a low pressure treatment (nozzle configuration #1) to prevent algal growth.

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# QUIETING THE IMPACT OF TRANSPORTATION WITH SOUND ACOUSTICAL PLANNING

*East Coast Conference, October 2016*

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## ABSTRACT

Hearing is one of the five basic sensory perceptions that we as human beings use to explore, understand and enjoy the world around us. As such, planning and designing for proper acoustics deserves at least 20% of our attention and resources to ensure a quality life. Transportation systems (highways, airports, railroads, transit systems), and associated construction projects, are the largest producer of environmental noise affecting our lives. Fortunately, several Federal and State agencies have established guidelines for how to measure, predict, evaluate and control these types of ubiquitous noise sources.

This paper will summarize the current state-of-the-industry with respect to transportation noise regulations and mitigation controls. Basic acoustical concepts will be defined; the technical approaches used to assess and identify noise impacts will be explained; and noteworthy examples of Federal, State and local noise policies will be provided. Lastly, examples of noise control mitigation options will be provided for each mode of transportation noise.

**Keywords:** noise, acoustics, measurements, modeling, criteria, mitigation, control

## 1. BASIC ACOUSTICS FUNDAMENTALS

Sound is what we hear when our ears are exposed to small pressure fluctuations in the air. Noise is generally defined as unwanted sound. It is measured in terms of sound pressure level, and is usually expressed in logarithmic decibels (dB) with respect to a reference level of $20x10^{-6}$ Pascals. In general, human sound perception is such that a change in sound level of 1 dB is just barely noticeable, a change of 3 dB is clearly noticeable, a change of 6 dB is obvious, and a change of 10 dB is perceived as a doubling or halving in sound level.

Humans are capable of hearing sound levels over the audible frequency range of 20 Hz to 20,000 Hz. However, humans are not equally sensitive to all frequencies, so noise measurements are weighted more heavily for frequencies to which humans are sensitive in a process called "A-weighting", with sound level decibels being abbreviated as "dBA". The A-weighted sound level is widely accepted by acousticians as a proper unit for describing environmental noise.

Typical A-weighted sound levels are show in Figure 1. The following noise descriptors are used for noise measurements, computations, and assessment of noise impacts from transportation projects as described below:

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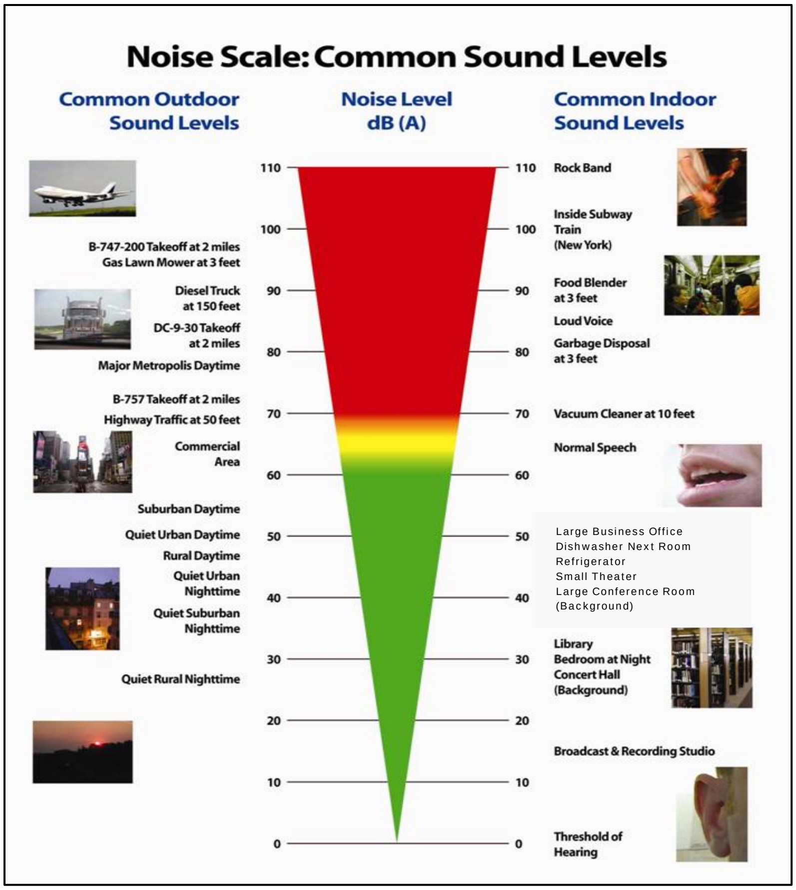


*Figure 1.* A-weighted decibel levels

**Lmax -** The maximum sound level (Lmax) during a single noise event. For example, as a vehicle approaches, passes by, and then recedes into the distance, the A-weighted sound level rises, reaches a maximum (Lmax), and then fades into the background noise.

**SEL -** The sound exposure level (SEL) describes a receptor's cumulative noise exposure from a single event, with the results normalized in time to a period of 1 second for relative comparison. Louder events have greater SELs then do quieter ones, and events that last longer in time have greater SELs than do shorter ones. The SEL it is not a sound level that humans would hear per se; rather, it is used to characterize noise sources in prediction models.

**Leq -** The equivalent sound level, Leq, is the cumulative energy-averaged sound level at a receptor during a defined period of time. It accounts for the moment to moment fluctuations due to all sound sources during that time period combined. The peak- or loudest-hour Leq(h) of the day is typically used for transportation noise analyses.

**Ldn -** The day-night sound level (Ldn or DNL) is an Leq over a 24-hour period with a 10 decibel penalty added to nighttime sound levels between 10 PM and 7 AM. The Ldn accounts for the greater sensitivity and lower background sound levels during nighttime hours, so it is used for transportation noise analyses at locations with nighttime use, such as residences, hospitals and hotels.

**Ln% -** The sound level percentile (Ln%) is a statistical measure of fluctuating sound levels exceeding a given level over a period of time. For example, the L10 sound level represents the sound level exceeded 10% of the time, and is often used to define intrusive sound levels.

Conversely, the L90 sound level would be the sound level exceeded 90% of the time, which is often used to define steady background sound levels.

## 2. FEDERAL NOISE GUIDELINES

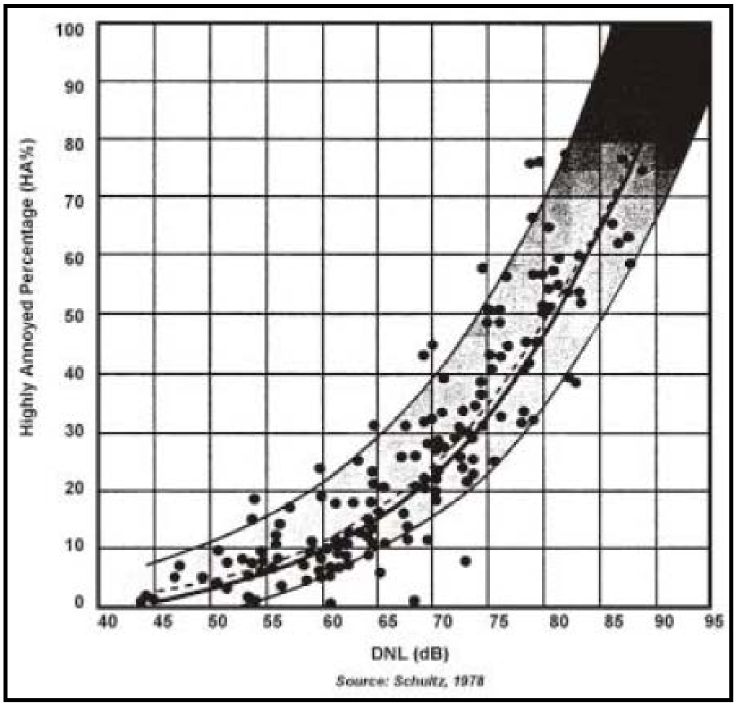
America made its decision in the 1950s that we were going to be a mobile society based primarily on the automobile. The Federal Aid Highway Act, signed by President Eisenhower in 1956, created the Federal Highway Administration (FHWA) and the first 41,000 miles of the Interstate highways. Its goals were two fold; to link all the contiguous states to promote free commerce and travel, but also to provide a network of roadways for national defense purposes if needed. For example, one mile out of every five along an Interstate highway had to be constructed in a straight line so that a heavy bomber could land on it in an emergency.

This is not to say that America did not vastly expand its heavy and light rail systems and airports as well. Those modes of transportation also expanded greatly due primarily to meet the growing commercial demands to move ever-more products and goods. In 1966, the US Department of Transportation (USDOT) was created which eventually would include the Federal Highway Administration (FHWA) to oversee Interstate highways; the Federal Railroad Administration (FRA) and the Federal Transit Administration (FTA) to oversee heavy and light railways, respectively; and the Federal Aviation Administration (FAA) to manage the growth and safety of the country's civilian airports.

But with all of these modes of transportation came an unwanted byproduct – noise. Noise regulations at the time mainly focused on hearing conservation, not community comfort. Early complaints were often met with the response, "Sorry, it's the price of freedom." However, is became anecdotally clear that high levels of community noise exposure were directly associated with depressed socio-economic areas, lower learning abilities in grade schools, and general social unrest and crime. There are also individual health concerns associated with long-term exposure to elevated noise levels such as hypertension, ischemic heart disease, annoyance, and sleep disturbance.

Then in 1970, the National Environmental Policy Act (NEPA) was signed into law by President Nixon, soon followed by the Noise Control Act of 1972 which created the US Environmental Protection Agency (USEPA). But it was not until 1978 when a seminal EPA community noise study was performed by Theodore Schultz that the adverse effects of community noise exposure were first quantified. The EPA report (USEPA, 1974), known as the "Levels Document", prescribed noise emission standards, identified major sources of noise, and determined appropriate noise levels that would not infringe on public health and welfare.

The results, known as the Schultz curve (Figure 2), established an empirical relationship between elevated community noise exposure and people's reaction to it. The percentage of people likely to be highly annoyed (HA%) was a predictable function of the Day-Night Sound Level (Ldn or DNL). The Ldn is a 24-hour acoustic-energy-averaged sound metric expressed in A-weighted decibels in which a 10 decibel penalty is added to the hours from 10 PM to 7 AM to account for people's greater sensitivity to noise intrusion during those hours. The Ldn has since gone on to be the most often referenced sound metric in setting community noise guidelines.



Source: Schultz, 1978

*Figure 2.* The Schultz curve

However, one size does not fit all when it comes to establishing appropriate community noise criteria. Each of these Federal agencies promulgate guidelines to regulate transportation noise sources, however they all use different noise metrics to do so. Thus, it can be difficult to determine a community's total noise exposure when multi-modes of transportation affect people simultaneously. This becomes even more problematic when it comes to funding necessary noise mitigation measures because the agency that makes the noise is responsible to control it.

# 3. USDOT TRANSPORTATION NOISE CRITERIA

## 3.1 FHWA Traffic Noise Criteria

The FHWA has promulgated traffic noise criteria to be used in all Federally-funded highway projects intended to identify community receptors impacted by traffic noise, thus warranting mitigation considerations. FHWA's *absolute* traffic noise abatement criteria, shown in Table 1, come from 23 CFR Part 772: *Procedures for Abatement of Highway Traffic Noise and Construction Noise* (USDOT, 2010). In addition, most State Transportation Agencies define a loud *relative increase* in traffic noise as an impact as well. The preferred noise metric is the loudest-hour Equivalent Sound Level (Leq), expressed in A-weighted decibels. Thus, a receptor is defined as being impacted by traffic noise if the future noise level "approaches" the FHWA noise abatement criteria within 1 or 2 dBA, or if the predicted future traffic noise level exceeds the existing traffic noise level by 10 to 15 dBA, depending in which state the project is located.

FHWA's traffic noise criteria differentiate between types of receptor land-use, or activity category, as well as whether the noise is evaluated inside or outside the building. For example, a Category B noise receptor, such as a residence or a multi-family residence, will be considered to be impacted by traffic noise if its future exterior traffic noise level is predicted to be 67 dBA Leq or more, or if it is expected to experience an increase of 10 to 15 dBA or more relative to existing traffic noise levels.

*Table 1*. FHWA traffic noise abatement criteria (NAC)

| **FHWA Activity Category** | **Traffic Noise Criteria Loudest-Hour Leq in dBA** | **Description of Activity Category (Land-Use)** |
|---|---|---|
| A | 57 (exterior) | Lands on which serenity and quiet are of extraordinary significance and serve an important public need and where the preservation of those qualities is essential if the area is to continue to serve its intended purposes. |
| B | 67 (exterior) | Residential. |
| C | 67 (exterior) | Active sport areas, amphitheaters, auditoriums, campgrounds, cemeteries, daycare centers, hospitals, libraries, medical facilities, parks, picnic areas, places of worship, playgrounds, public meeting rooms, public or nonprofit institutional structures, radio studios, recording studios, recreation areas, Section 4(f) sites, schools, television studios, trails, and trail crossings. |
| D | 52 (Interior) | Auditoriums, day care centers, hospitals, libraries, medical facilities, places of worship, public meeting rooms, public or nonprofit institutional structures, radio studios, recording studios, schools, and television studios. |
| E | 72 (Exterior) | Hotels, motels, offices, restaurants/bars, and other developed lands, properties or activities not included in Categories A-D or F. |
| F | None | Agriculture, airports, bus yards, emergency services, industrial, logging, maintenance facilities, manufacturing, mining, rail yards, retail facilities, shipyards, utilities (water resources, water treatment, electrical), and warehousing. |
| G | None | Undeveloped lands that are not permitted. |

Source: 23 CFR Part 772, Federal Highway Administration (USDOT, 2010)

## 3.2 FRA/FTA Rail/Transit Noise Criteria

The FRA and the FTA use the same approach to define community noise impacts from heavy or light rail operations. The basic goals of the noise criteria are to minimize the adverse noise impacts on the community and to identify areas where feasible and reasonable noise control may be necessary. FRA/FTA noise impact criteria are founded on the Schultz curve community reaction to absolute noise level, as well as on changes in noise levels using a relative increase scale. Although more rail noise is allowed in neighborhoods with high levels of existing noise, as existing noise levels increase, smaller increases in total noise exposure are allowed than in areas with lower existing noise levels.

FRA/FTA guidelines (USDOT, 2012; USDOT, 2006) define noise impacts for various land-use categories using different noise metrics, as shown in Table 2. For residential receptors (i.e. Category 2) adjoining the transit corridor, the Ldn noise descriptor is used due to the receptor's use for sleeping at night. For institutional and some commercial receptors (i.e. Category 3) involving daytime and evening uses, the Leq(h) noise descriptor is used for the noisiest hour of transit-related activity during which human activities may occur at these locations.

*Table 2*. FRA/FTA noise receptor land-use categories

| Land-Use Category | Applicable Noise Metric in dBA | Description of Land-Use Category |
|---|---|---|
| 1 | Outdoor $L_{eq}$(h) | Tracts of land where quiet are an essential element in their intended purpose. This category includes lands set aside for serenity and quiet, and such land-used as outdoor amphitheaters and concert pavilions, as well as National Historic Landmarks with significant outdoor use. Also included are recording studios and concert halls. |
| 2 | Outdoor $L_{dn}$ | Residences and buildings where people normally sleep. This category includes homes, hospitals, and hotels where a nighttime sensitivity to noise is assumed to be of utmost importance. |
| 3 | Outdoor $L_{eq}$(h) | Institutional land-uses with primary daytime and evening use. This category includes schools, libraries, theaters, and churches where it is important to avoid interference with such activities as speech, meditation, and concentration on reading material. Places of meditation or study associated with cemeteries, monuments, museums, campgrounds and recreational facilities can also be considered to be in this category. Certain historical sites and parks are also included. |

Source: Federal Railroad Administration (USDOT, 2012) and Federal Transit Administration (USDOT, 2006)

FRA/FTA noise impact criteria are based on a comparison of the existing outdoor noise levels (Leq(h) or Ldn depending on land-use category) and the future outdoor noise levels produced by the proposed project. It considers both *absolute* criteria, which is the noise generated solely by the transit noise source, and *relative increase* criteria, which gauges annoyance due to the change in the noise environment caused by the transit project. As shown in Figure 3, noise impact severity is categorized as “No Impact”, “Moderate Impact”, or “Severe Impact” as determined by comparing the project-generated noise exposure with respect to existing noise exposure at a given receptor’s location.

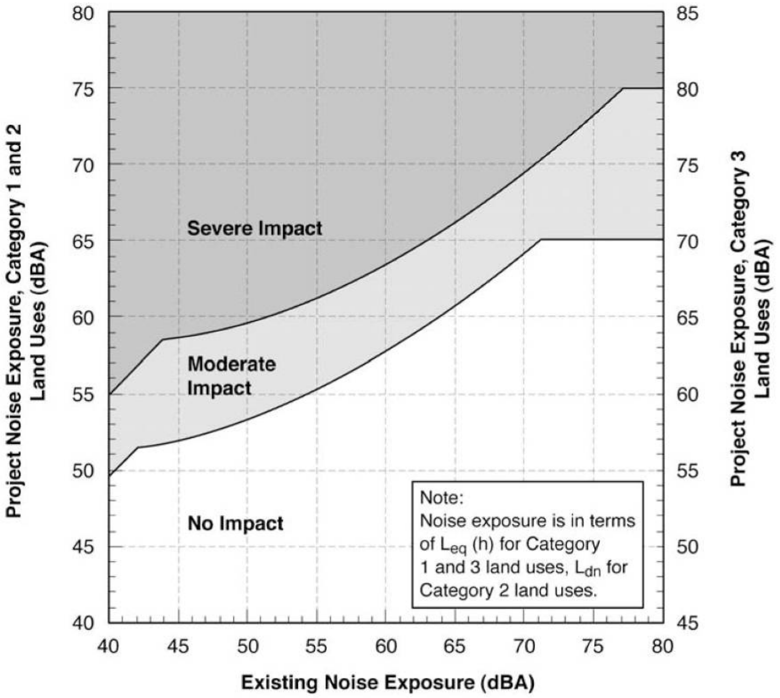


*Figure 3.* FRA/FTA rail/transit noise criteria

Source: Federal Railroad Administration (USDOT, 2012) and Federal Transit Administration (USDOT, 2006)

## 3.3 FAA Airport/Aircraft Noise Criteria

The FAA's community noise criteria, promulgated in 14 CFR Part 150: *Airport Noise Compatibility Planning* (USDOT, 1979) and shown in Table 3, is perhaps the most difficult to understand and to determine on a case by case basis. It is based on the exterior sound level considered to be conducive or compatible with the receptor's intended land-use. Land-uses of various kinds are recognized, each with its own noise criteria expressed in dBA Ldn when inbound and outbound flight operations are *averaged over a full year*. However, receptors can be exposed to louder levels of aircraft noise so long as certain noise control mitigation is incorporated into the buildings, thus providing for a lower interior noise level.

For example, to be eligible for noise mitigation consideration, a residence is defined to be impacted if it is exposed to aircraft noise levels exceeding 65 dBA Ldn. However, a residence exposed to 65 to 75 dBA Ldn can still be considered compatible so long as 25 decibels-worth of noise reduction is built into the structure.

*Table 3.* FAA aircraft noise land-use compatibility criteria

| Land-Use | Yearly Day-Night Average Sound Level Ldn in dBA | | | | | |
|---|---|---|---|---|---|---|
| | Below 65 | 65-70 | 70-75 | 75-80 | 80-85 | Over 85 |
| ***Residential*** | | | | | | |
| Residential, other than mobile homes and lodgings | Y | N(1) | N(1) | N | N | N |
| Mobile home parks | Y | N | N | N | N | N |
| Transient lodgings | Y | N(1) | N(1) | N(1) | N | N |
| ***Public Use*** | | | | | | |
| Schools | Y | N(1) | N(1) | N | N | N |
| Hospitals and nursing homes | Y | 25 | 30 | N | N | N |
| Churches, auditoriums, and concert halls | Y | 25 | 30 | N | N | N |
| Governmental services | Y | Y | 25 | 30 | N | N |
| Transportation | Y | Y | Y(2) | Y(3) | Y(4) | Y(4) |
| Parking | Y | Y | Y(2) | Y(3) | Y(4) | N |
| ***Commercial Use*** | | | | | | |
| Offices, business and professional | Y | Y | 25 | 30 | N | N |
| Wholesale and retail - building materials, hardware | Y | Y | Y(2) | Y(3) | Y(4) | N |
| Retail trade - general | Y | Y | 25 | 30 | N | N |
| Utilities | Y | Y | Y(2) | Y(3) | Y(4) | N |
| Communication | Y | Y | 25 | 30 | N | N |
| ***Manufacturing and Production*** | | | | | | |
| Manufacturing, general | Y | Y | Y(2) | Y(3) | Y(4) | N |
| Photographic and optical | Y | Y | 25 | 30 | N | N |
| Agriculture (except livestock) and forestry | Y | Y(6) | Y(7) | Y(8) | Y(8) | Y(8) |
| Livestock farming and breeding | Y | Y(6) | Y(7) | N | N | N |
| Mining and fishing, resource production, extraction | Y | Y | Y | Y | Y | Y |
| ***Recreational*** | | | | | | |
| Outdoor sports arenas and spectator sports | Y | Y(5) | Y(5) | N | N | N |
| Outdoor music shells, amphitheaters | Y | N | N | N | N | N |
| Nature exhibits and zoos | Y | Y | N | N | N | N |
| Amusements, parks, resorts and camps | Y | Y | Y | N | N | N |
| Golf courses, riding stables and water recreation | Y | Y | 25 | 30 | N | N |

Source: 14 CFR Part 150, Federal Aviation Administration (USDOT, 1979)

Notes: Y (Yes) = Land-use and related structures compatible without restrictions.
N (No) = Land-use and related structures are not compatible and should be prohibited.
OINR = Outside to Inside Noise Reduction for a building, measured in decibels (dB).
## = Land-use and related structures generally compatible; mitigation to achieve OINR of ## dB must be incorporated into design and construction of structure.
(1) Where the community determines that residential or school uses must be allowed, mitigation to achieve OINR of at least 25 dB and 30 dB should be incorporated into building codes.
(2) Mitigation to achieve OINR 25 dB must be incorporated into the design and construction of portions of these buildings where the public is received, office areas, and noise sensitive areas.
(3) Mitigation to achieve OINR of 30 dB must be incorporated into the design and construction of portions of these buildings where the public is received, office areas, and noise sensitive areas.
(4) Mitigation to achieve OINR 35 dB must be incorporated into the design and construction of portions of these buildings where the public is received, office areas, and noise sensitive areas.
(5) Land-use is compatible provided special sound reinforcement systems are installed.
(6) Residential buildings require an OINR of 25 dB.
(7) Residential buildings require an OINR of 30 dB.
(8) Residential buildings are not permitted.

# 4. NOISE CONTROL MITIGATION OPTIONS

The generation and propagation of transportation noise is a physical phenomenon which can therefore be measured, modeled, mitigated and controlled. In general, control options can be applied to the noise *source*, the *pathway*, or the *receiver*. The degree of noise reduction achieved is a function of the effectiveness of the controls, proper installation of the controls, the frequency range requiring attenuation, and the perception of the receivers. In general, a minimum noise reduction of 5 decibels is needed to provide perceptible benefits, and the practical limit of noise control is a reduction of about 25 decibels.

## 4.1 Source Controls

Noise controls applied at the source are usually the most effective option because they prevent unwanted noise from being generated in the first place. However, it is often impractical or impossible to materially affect the noise source without degrading or preventing the source from performing its intended purpose.

Examples of transportation noise sources control options would include the following:

- Establish quieter vehicle noise emission limits (e.g. Stage 3 aircraft)
- Require improved exhaust mufflers
- Prohibit use of particularly loud vehicles during certain times of day/night
- Provide alternative forms of quieter transportation (e.g. transit systems)

## 4.2 Pathway Controls

Noise can be effectively relocated, blocked or diverted along its propagation pathway. The most notable form of transportation pathway noise control is a noise wall or barrier. To be effective, noise barriers must be long- and tall-enough to completely block the line-of-sight between the noise source and the receivers; must be free of any holes or gaps; and must be built either very close to the noise source or to the receiver.

Noise barriers can be built of any solid mass material providing a surface density of at least 4 lbs/SF. Common noise barrier materials include wooden timbers, concrete, brick, steel or plastic panels, and earthen berms. If designed and built properly, a noise barrier can provide up to 15 decibels of noise reduction. However, the amount of noise reduction is greatest for receivers close to the barrier and is lessened with distance from the barrier. The unit cost for noise barriers can range from $20/SF to $50/SF depending on the material, anchoring system, and labor rates.

Note, trees do <u>not</u> provide appreciable noise reduction of transportation systems. While there is a psycho-acoustic benefit of not being able to see an offending noise source, trees planted simply as a vision barrier do nothing to reduce noise. It requires many hundreds of feet of fully mature conifer trees to provide a measureable noise reduction.

Examples of transportation noise pathway control options would include the following:

- Noise walls or barriers (often subject to cost-effectiveness criteria)
- Relocating the transportation system either underground or farther away
- Enclosing the noise source

## 4.3 Receiver Controls

Though typically not the first preference, on occasion noise control options can be applied to directly affect the receivers. This option can become attractive when there are only a few residences in need of noise reduction. Many public and private projects have resorted to receiver noise control measures when source and/or pathways control options are either infeasible or not sufficient.

One form of receiver noise control that does get implemented frequently is to enhance the soundproofing capabilities of people’s homes. This is often done around airports and where construction projects might take years to complete. Residential soundproofing consists of augmenting or replacing window and doors, installing AC systems, and reinforcing a “room of preference” (such as bedroom) with additional insulated gypboard walls and ceilings. When done correctly, noise levels inside the home can be reduced by 10 decibels relative to the unmitigated condition. Of course, soundproofing the houses only reduces noise infiltrating into the homes; it does nothing to reduce outdoor noise. From residential soundproofing programs implemented by FAA and FHWA, the cost to soundproof a single-family home would be approximately $30,000/home.

Examples of transportation noise receiver control options would include the following:

- Residential soundproofing
- Relocating the receiver farther away from the noise source
- Wearing hearing protection
- White noise sound masking systems
- Public outreach and education (increases people’s tolerance of noise)

Very rarely, and never with public money, monetary compensation can be offered to the aggrieved receiver in return for their signing waivers to stop complaining about the noise. This form of receiver noise control is jokingly referred to as “hush money”, but there are times when it is the only pragmatic solution. Specific details and dollar amounts are usually kept confidential.

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# EFFECT OF ENVIRONMENTAL VARIABLES ON VAPOR TRANSPORT

*West Coast Conference, March 2016*

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## ABSTRACT

Site characterization efforts at vapor intrusion (VI) sites typically include measurement of soil gas concentrations at various locations. The measured soil gas concentrations will exhibit some degree of temporal variability due to various environmental factors, including: 1) Air temperature; 2) Soil moisture; 3) Water infiltration; 4) Changes in groundwater level; 5) Barometric pressure; and 6) Surface winds. For sub-slab soil-gas, additional temporal variability may exist due to changes in building operations.

Environmental variables can be important to the extent that they affect soil gas concentrations in the vadose and rates of gas transport from the source of the vapors to overlying buildings. The effect of environmental variables on soil-gas concentrations of oxygen and carbon dioxide have long been of interest for agronomy, and an extensive literature exists in texts related to agronomy and soil science, but this information is largely unknown to VI practitioners. This paper summarizes over 100 years of published data on the effect of environmental variables on soil gas concentrations and transport rates. The six environmental variables listed above are discussed as they apply to VI sites containing volatile organic compounds (VOCs). Previously unpublished data on this topic also is included.

**Keywords:** vapor intrusion, gas transport, environmental factors, barometric pressure, variability

## 1. INTRODUCTION

For vapor intrusion (VI) to occur, there must be a subsurface source that gives rise to vapors in the vadose (unsaturated) zone, migration of these vapors to the buildings of interest, and movement of the vapors from the exterior to the interior of the building.

Site characterization efforts typically include measurement of soil gas concentrations at various locations. The results can be highly variable, with total variability comprised of spatial, temporal and measurement (sampling and analysis) elements.

The largest contributor to total variability tends to be spatial variability, which can be attributed to: i) the distribution of contaminants in the groundwater or soil that are the source of the vapors, and ii) variations in soil type or conditions that leads to varying rates of vapor transport through the vadose zone. It is not uncommon to observe spatial variabilities of three or four orders of magnitude in soil gas concentrations, which far exceeds measurement variability which

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is assumed to be no worse than ±50% to ±100%. For example, McHugh et al. (2007) reported that most field duplicates in their study had relative percent differences of <30%.

Measured soil gas concentrations also will exhibit some degree of temporal variability. For relatively new releases, the soil gas concentrations will change over time as steady-state conditions become established. Once steady-state is reached, temporal variability may occur due to various environmental factors, including:

1. Air temperature;
2. Soil moisture;
3. Water infiltration;
4. Changes in groundwater level;
5. Barometric pressure; and
6. Surface winds.

For indoor air and sub-slab soil-gas, additional temporal variability may exist due to changes in building operations which affect the rate of vapor intrusion across the building slab ($Q_{soil}$) and/or the rate of building ventilation ($Q_{bldg}$). For example, seasonal heating may result in higher rates of $Q_{soil}$ due to stack effects. Building-related factors are outside the scope of this paper.

Environmental variables can be important to the extent they affect soil gas concentrations in the vadose and rates of gas transport from the source of the vapors to the building of interest. In terms of gas transport, environmental variables may affect the rate of diffusion or induce advective (pressure-driven) transport. For an overview of how various variables are relevant to VI, readers are referred to Provoost, et al. (2011), USEPA (2004), and Tillman and Weaver (2006).

## 2. DISCUSSION

The effect of environmental variables on soil-gas concentrations of oxygen and carbon dioxide have long been of interest for agronomy and an extensive literature exists in texts related to agronomy and soil science. Soil gas measurements date back to the work of Boussingault and Lewy (1853), who made measurements at depths of 30 to 40 cm in various types of agricultural fields.

The general effects of environmental variables on soil gas concentrations, at least in the very shallow soil, have been known for about a century. Russell and Appleyard (1915) summarized the soil-gas literature to that point and reported the results of their own measurements and the effect of temperature, moisture, barometric pressure, etc. Jury, et al. (1991) in their textbook on soil physics drew heavily upon the work of Romell (1922) in discussing the effect of environmental variables. Nonetheless, the VI community is not sufficiently aware of such findings and therefore we think the following review will prove to be helpful for VI decision makers. The six environmental variables listed in the Introduction are discussed in turn below. The discussion is oriented towards VI sites containing volatile organic compounds (VOCs) dissolved in groundwater.

## 2.1 Effect of Air Temperature

The effect of temperature will depend on the soil type and the timeframe. Diurnal variations may extend from 0.3m in dry sand to 1m in rock (Florides and Kalogirou, 2004). In their work, they found a time lag of about five hours between maximum air and soil temperatures, with the daily variation below a depth of 0.25m to be "*nearly negligible*." Rutten, et al. (2010) measured soil temperature and moisture at two locations at depths of 2, 4, 8, 32, 64, and 100 cm every 15 minutes over an 11-week period. They found minimal variability in temperature at the 32 cm depth and deeper.

Above ground air temperature may vary by 50°C (80°F) or more over the course of a year at a given site and the effect of annual changes may extend to a depth of 10 to 20m. Any effect of air temperature will be most pronounced in the shallow soil layers. Bekele, et al. (2014) performed 12 consecutive monthly soil temperature measurements at four depths at a VI site in Adelaide. The maximum variability over the course of the study was about 4°C at 3m, 5°C at 2m, 8°C at 1m and 14°C at 10 cm. Higher soil temperatures were associated with lower soil moisture levels. The mean annual soil temperature was relatively constant as a function of depth, and varied by 1°C or less among the 1m, 2m, and 3m probes. This is consistent with USEPA (2001) guidance, which states that mean annual soil temperature is relatively stable at a depth below 1m.

Given the high heat capacity of water, the effect of air temperature on soil temperature should be inversely correlated with soil moisture content. The primary effect of increased soil temperature on vapor intrusion will be increased partitioning to the gas-phase. In the Bekele study, the highest soil-gas concentrations coincided with the highest soil temperatures and lowest soil moistures. Soil-gas concentrations varied by up to one order of magnitude over time, but at most locations the soil gas concentrations varied by only about a factor of two. Calculated emission fluxes also varied by about a factor of two. The predominant source of variability in soil gas concentrations was spatial variability, which exceeded four orders of magnitude.

In addition to Henry's Law constants, other physical parameters of interest that have a temperature dependence include vapor pressure, air diffusivity, water diffusivity, and water solubility. The relationship of temperature to water diffusivity is a direct, linear correlation whereas air diffusivity correlates with temperature to the 1.5 to 2 power (Lyman, et al., 1990). Most VOCs exhibit increased water solubility as water temperature increases, but compounds such as methane and 1,4-dichlorobenzene show the opposite trend. MEK (2-butanone) also has decreasing water solubility with increasing temperature in the typical range of soil temperature.

## 2.2 Effect of Soil Moisture

At most sites, the source of vapors is groundwater or soil contamination that has been in place for many years. This typically is long enough for steady-state conditions to have been reached. The time required is a function of the chemical's diffusivity in air and the transport distance (Devitt, et al., 1987).[1] It should be noted, however, that any perturbations to the system may result in a new or different steady-state to become established and that transition to the new steady-state will take time.

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[1] For a VOC with $D_i = 0.1$ $cm^2/s$, the predicted time to reach steady-state conditions is about 10 days for a 1m depth, 90 days for a 3m depth, and 1 year for a 6m depth, assuming a tortuosity of 3.

Under steady-state conditions, diffusion of VOCs will occur along a concentration-gradient that exists in the soil, with the highest soil gas concentrations present at the source of the vapors and the soil gas concentration generally decreasing linearly with distance as you move up the soil column towards the ground surface or building slab. The source of the vapors should be assumed to be the top of the capillary fringe as opposed to the depth to groundwater (Shen, et al., 2013a). There will be partitioning of contaminant mass between the gas-phase and the liquid-phase in the vadose zone, so higher levels of soil moisture will contain higher amounts of dissolved VOCs.

The rate of gaseous diffusion is dependent on the air-filled porosity of the soil, which in turn is influenced by the amount of soil moisture. The effective (air) diffusivity is proportional to the air-filled porosity to the 3.33 power (Millington and Quirk, 1961).

Changes in soil moisture will have two effects. One, the rate of gaseous diffusion will change. Two, the mass of a given VOC that has partitioned to the liquid phase will change. The effects will be reinforcing. So, for example, an increase in soil moisture from 10% to 11% will decrease the effective air diffusivity and result in additional partitioning to the liquid-phase, thereby decreasing soil-gas concentrations. The former effect is exponential whereas the latter effect is linear. The kinetics also differ, with changes in effective air diffusivity being instantaneous but partitioning dependent on the diffusivity in water for the given chemical. The time for partitioning to reach its final equilibrium will tend to be slow.

The relative importance of changes in partitioning versus changes in effective diffusivity will depend on what fraction of a given VOC in the vadose zone is present in the gas-phase (i.e., will depend on the Henry's Law constant). Figure 1 shows the predicted relative change in soil-gas concentration and effective diffusivity for tetrachloroethylene at 1,000 μg/m$^3$ in a typical silt loam soil as the moisture content varies up or down from 12%.

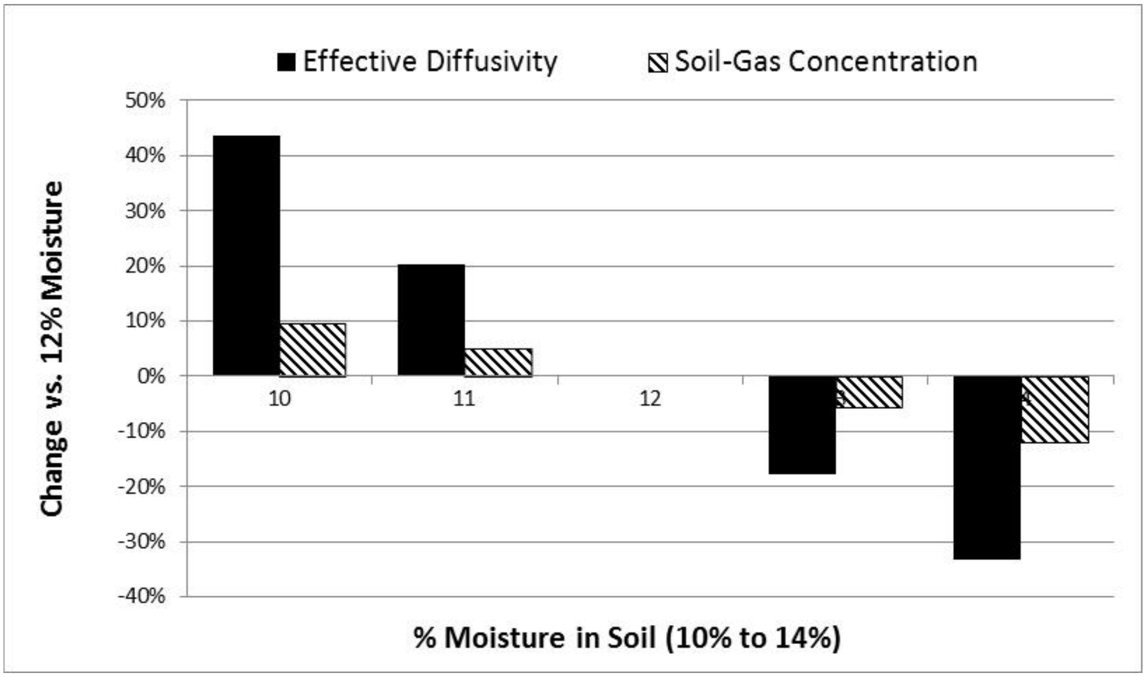

*Figure 1.* Relative effect of changes in soil moisture on effective diffusivity and soil-gas concentration

For the example shown in Figure 1, the primary effect of changes in soil moisture is to influence the rate of soil gas transport, rather than to affect the soil gas concentration at a given depth. The change in concentration will be more significant than the example above for VOCs, such as BTEX, with Henry's Law constants lower than that for PCE.

## 2.3 Effect of Water Infiltration

Infiltrating precipitation or other water will decrease the air-filled porosity of the soil. The magnitude of this effect will depend on the amount of water and the air-filled porosity of the soil. For a sandy soil, the air-filled porosity may be about 30%. If so, the top 1m of the vadose zone would have about 0.3 $m^3$ (300L) of air-filled space per $m^2$ of surface area. A rain event of 0.4 inches (1 cm) would decrease the air-filled porosity by about 3% if there was no run-off, all the water entered the soil and it remained in the top meter of soil. If this occurred on multiple consecutive days, it could have a large cumulative effect.

As the water infiltrates into the soil, the existing soil-gas is displaced. The displaced gas is either emitted from the ground or pushed downward thereby compressing the underlying soil gas. If the water infiltration rate is slow, all of the displaced gas will be emitted. Subsequent gas emissions will decrease due to the lower air-filled porosity (and due to mass transfer to the new water). So, the effect of water infiltration is to have a short-term spike in air emissions due to displacement followed by a period of lower than average gas emissions. This effect has been observed both experimentally and in the field (Eklund, 1992). For example, water was added to dry, sandy soil in a pilot-scale soil cell. Trace precipitation (0.01 in.) had no effect on measured emission fluxes, but rains of 0.4 in. reduced the emission flux by 90 to 95% and the reduction in emissions lasted for about eight days. This effect is shown in Figure 2.

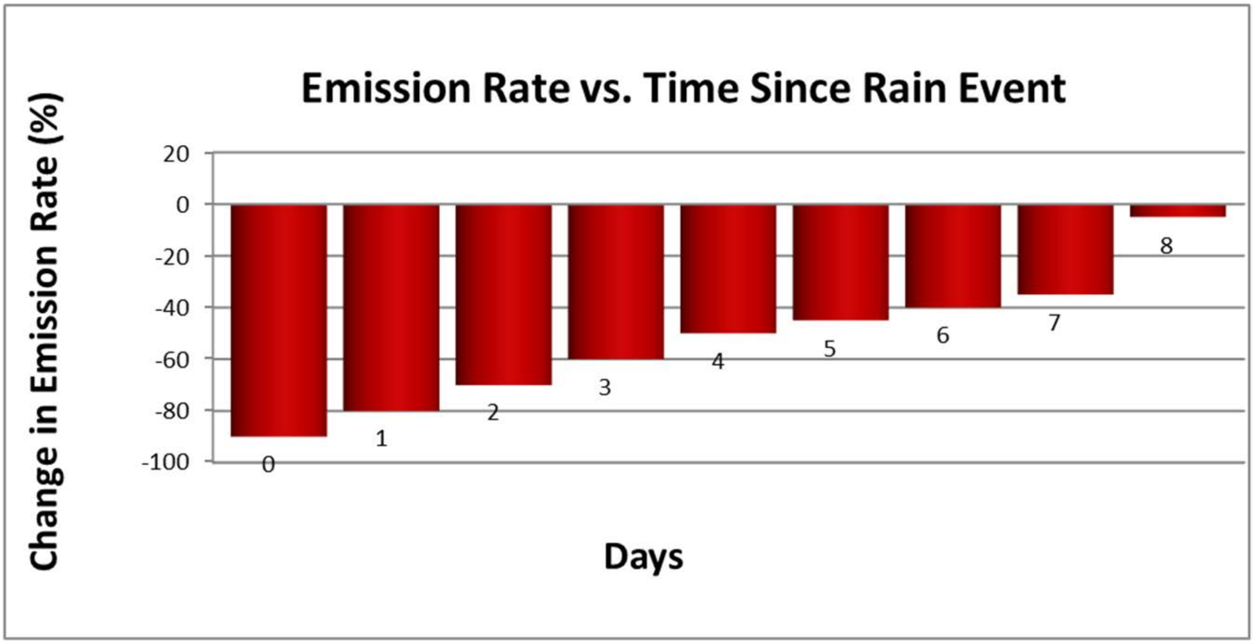

*Figure 2*. Relative effect of air emission flux after simulated rain event

The mathematical basis for the effect of rainfall events is described in Shen, et al. (2012). The authors suggest that rainfall will not have a significant effect at typical soil-gas sampling depths:

> "The rainfall effect on lower soil vapor concentration is much more modest. The depth of soil gas probes can be optimized by using such a model assuming that common rainfall patterns are known. For example, at a relatively dry site with rare rainfall events, soil gas probes at 1 m below the ground surface experience minimal change of soil moisture and the change of the vapor concentration right after rainfall is also minimal."

Any effect on sub-slab soil-gas presumably will be less, due to the "rain shadow" effect of the building slab. The building slab, and paved areas in general, can limit infiltration in some areas and any run-off can increase the amount of water reaching near-by unpaved areas. The type of ground cover also has an effect, with asphalt being much more water permeable than concrete.

High rates of infiltrating water can result in a fresh water lens atop the groundwater which acts as a barrier to volatilization. It has been noted that there is a poor correlation between groundwater concentrations and deep soil gas concentrations. For example, the 180 or so paired groundwater and deep soil gas values in EPA's database (USEPA, 2012a) have a correlation coefficient of only 0.14 (Shen, et al., 2013a). A fresh water lens is a possible reason for this poor agreement at some sites, but a more general cause is that groundwater wells are screened over a lengthy interval and the concentration of "bulk" groundwater samples may not be representative of the groundwater concentration at the boundary layer with the vadose zone. Shen, et al. (2013b) note that the capillary fringe acts as a large resistance to diffusion and cannot be assumed to be well-mixed with the underlying groundwater. Equilibrium partitioning based on Henry's Law may over-predict deep soil-gas concentrations by about two orders of magnitude, with the process controlled by liquid-phase diffusion of VOCs from the bulk liquid to the boundary layer (McHugh and McAlary, 2009).

## 2.4 Effect of Changes in Groundwater Elevation

Groundwater elevation may change over time at sites, especially those that have a wet and a dry season. Per Fick's 1st law, the rate of diffusion of a gas will depend on the concentration gradient, the effective diffusivity, and inversely on the transport distance. Changes in groundwater elevation can have an effect on all three of these variables and so there can be competing effects in play.

During the wet season, rises in groundwater elevation will reduce the distance between the source of vapors and the building slab, which will directly increase the rate of diffusive gas transport. At the same time, however, the soil in the vadose zone during the wet season will tend to have lower amounts of air-filled porosity, which will tend to decrease the rate of diffusive gas transport. In addition, with a falling water table there is increased surface area of contaminated groundwater as water trapped by capillary forces drains from large pores, thereby enhancing transfer of VOCs from groundwater to the gas phase (McHugh and McAlary, 2009). This serves to increase the concentration gradient and may be an important consideration at many sites. The overall result is that worst-case conditions are more likely to occur during the dry season or periods of falling groundwater elevation than during the wet season or periods of rising groundwater.

Falling groundwater levels can result in increased oxygen transport into the vadose zone and this may have implications for aerobic biodegradation of petroleum hydrocarbons.

Choi and Smith (2005) did a modeling study and found that water-table fluctuations of 0.1m could cause advective fluxes larger than those under atmospheric pressure changes of 300 Pa.

In one atypical case, rapidly rising groundwater at a riverfront site has led to high rates of pressure-driven gas transport and rates of vapor intrusion that posed a potentially acute hazard (ATSDR, 2010).

## 2.5 Effect of Barometric Pressure

Under typical conditions, the transport of soil gas through the vadose zone is controlled by diffusion, with advection only becoming important within about a meter of building envelopes. Diffusion is a relatively slow process. For example, for groundwater at a depth of 20 ft. below ground surface, it may take a year for vapors to diffuse to the surface. Pressure gradients can potentially result in much faster rates of gas transport. For example, a pressure gradient of 500 Pa (2” $H_2O$) over a 1m distance will result in a rate of advective transport that is about 30x higher than diffusive transport in soils with a permeability of $10^{-8}$ $cm^2$ (e.g., sandy soils); (Eklund, 2011).

Barometric pressure changes are known to cause gas movement in caves and other large subsurface voids. This is often called barometric pumping and has been observed in fractured rock to depths of 150 ft. (INEEL, 2003). Pressure differentials of 1,000 Pa have been reported (Scanlon, et al., 2002). The effect has also been seen in rock piles. Wels et al. (2003) reported high concentrations of oxygen in rock piles at a depth of 7m in conjunction with increasing barometric pressure, but the effect was largely attenuated at the 14m depth.

Researchers at DOE and elsewhere have sought to take advantage of such barometric pumping for mass removal of VOCs from the subsurface. To work, this process has to overcome one inherent limitation (Lowry, et al., 1996):

> “The daily oscillations in atmospheric pressure always return to a mean value. Over time, no net soil gas displacement occurs in a homogeneous medium due to barometrically-induced advective forces alone.”

Neeper and Stauffer (2005), however, found that over time there is very small one-way migration downwards into the soil column because the air density is slightly greater for air flow down into the ground than for air flow out of the ground.

Remediation systems that relied upon barometric pumping used one-way check valves to limit air flow into the subsurface and covers were added to the ground surface to further limit air infiltration. Such passive venting or bioventing systems were an active topic of research and discussion in the mid- to late 1990’s, but are no longer a topic of interest at remediation conferences presumably due to failure to live up to the initial promise.

For soils, the effect is much more muted than in fractured rock or rock piles. If the vadose zone has no low-permeability layers, there will be little or no measureable pressure difference due to barometric pressure changes (McHugh and McAlary, 2009).

Even under optimal conditions of a surface layer of clay atop a more permeable layer of sand or gravel, differential pressures of only up to 0.7 in. w.c. (175 Pa) are reported (Vernon and Arkell, 1998). This pressure differential would be expected to result in gas transport about one order of magnitude higher than the rate due to diffusion alone.

Relatively large effects of barometric pumping in the vadose zone have been predicted (Massmann and Farrier, 1992), but field data suggests that in typical soils, the effects of barometric pressure changes are minimal and only extend a short distance into the soil column. The consensus is that any such effect is limited to about one meter.

Tillman and Smith (2005), for example, found that barometric pressure changes could move soil gas 12.5 cm at a test site in New Jersey. Simulations suggested that changes in soil air permeability over five orders of magnitude would have no measurable effect on soil gas movement. The effect may be more pronounced at sites with relatively deep groundwater. If groundwater were at a 200m depth, the soil-gas movement would be as much as 1.4m. Neeper and Stauffer cite a figure of 1m for their numerical simulations.

Paw U, et al. (2004) also found the effect of barometric pressure to be limited to the top 1m. They measured pressure at multiple depths and found an exponential decrease in pressure changes with depth. There was a one-third reduction in the top 20cm of soil and the damping depth was about 70 cm. They caution that failure to compensate pressure sensors for temperature differences can result in potentially large errors in these types of field studies.

Schumacher, et al. (2007) made continuous soil-gas concentration measurements over a six week period at 12 sampling locations from 3 to 17 ft. bgs, while also measuring barometric pressure, wind speed, wind direction, soil temperature, and differential soil gas pressure. Observed trichloroethylene (TCE) concentrations varied by less than 27% (maximum) and 20% (average) for all of the probes. Meteorological variations “had little effect on soil gas concentrations even as shallow as 3’ bgs in sandy soil with no surface covering.” No rain events occurred during their study period.

Russell and Appleyard (1915) found an effect of rainfall and temperature with soil gas concentrations, but barometric pressure showed no consistent relationship. They conclude, “the influence of barometric pressure appears to be only minor and easily swamped by other factors.”

Bogner, et al. (1997) report that in a study of landfill cover soil:

> “Extensive continuous measurements of differential soil gas pressures on probes and chambers by the authors at the Mallard Lake site indicated that barometric pressure variations were minimal.”

If barometric pressure effects were significant, advective transport rates would far exceed diffusive transport rates, but the limited available data suggests that this is not the case. Choi, et al. (2002) measured emission fluxes of trichloroethylene (TCE) in the unsaturated zone under natural conditions and found that, “[f]or two of the three sampling events, the TCE gas-phase diffusion flux at land surface was significantly greater than the advection flux over the entire sampling period.” For the other sampling event, the average advection and diffusion fluxes were comparable in magnitude. Choi and Smith report that diffusion fluxes were always higher than advection fluxes by several orders of magnitude in their simulations. They found that soil moisture was the most significant environmental variable.

Patterson and Davis (2009) found that fluctuations in sub-slab to building differential pressures correlated well with semidiurnal decreases in barometric pressure. When the building was under ambient pressure conditions, “diffusion of VOC vapors through the concrete slab was the dominant vapor intrusion pathway. Also, no net flux of vapors from advective transport through cracks or gaps in the concrete slab as a result of the cyclical pressure changes within the building was observed." When the building was under reduced internal pressure, however, advective transport through cracks was significant.

Barometric pressure changes are assumed to be important at petroleum hydrocarbon sites as a mechanism to replenish oxygen and maintain a biodegradation zone. The available data, however, suggests that such effects are confined to very shallow soil layers. Lundegard, et al. (2008) flooded the subsurface beneath a house with nitrogen and measured the replenishment of oxygen over 90 days using in-situ, real-time sensors. They observed some effect from rainfall and surface winds, but "[a]ny effect of changes in barometric pressure with time is not obvious in the transient $O_2$ data."

## 2.6 Effect of Surface Winds

Surface winds blowing along the ground surface can induce negative pressure changes in the underlying soil due to Bernoulli's principle. The effect generally is relatively small, with the effect extending down to about 50 cm of depth (Flechard, et al., 2007). Nonetheless, the effects of surface wind and not barometric pumping were the main factor for advective soil gas flow over diurnal cycles based on a study of carbon dioxide in California soils (Lewicki, et al., 2003).

As mentioned above, the Lundegard study found an effect of wind speed, which occurred when the wind speed doubled over typical wind speed peaks. A more rapid $O_2$ response was seen for a day at two of their 16 sub-slab monitoring locations.

Luo, et al. (2009) collected data at 31 multi-depth monitoring locations for oxygen, total petroleum hydrocarbons (TPH), and differential pressure. They found a wind-induced lateral soil-gas pressure gradient of 0.1 Pa/m during one month. The estimated average linear soil-gas velocities were on the order of 0.1 to 10 cm per day.

## 2.7 Applicable Results from Other Studies at VI Sites

The variability of soil gas concentrations over time has implications for the extent of variability due to environmental factors. If environmental variables had a large effect, this would be reflected in field measurements over time. Field studies, however, tend to show relatively low variability. For example, Luo, et al. (2006) collected shallow soil gas samples at one location every 2.6 hours for 70 days and found that the concentrations were "relatively stable with time (<20% variation in TPH)." Furthermore, they note that "[m]ost of the 2 ft and 4 ft bgs $O_2$ sensors beneath the building (13 of 17) exhibited little change in $O_2$ concentration with time."

Swanson, et al. (2010) collected soil-gas samples every two weeks at four depths each from eight wells at a USEPA research site. They found that shallow soil-gas concentrations varied "by less than 3X over 12 months." Eklund (2010) reported that soil gas concentrations at a study site were reasonably stable over a two year period in both shallow and deep soil gas.

Indoor air concentrations at VI sites are dependent on soil gas concentrations plus additional variables related to building design and use. Therefore, indoor air measurements would be expected to show greater variability than soil gas measurements. Even so, these studies also tend to show only modest levels of variability.

USEPA (2012b) reported that the short-term variability in sub-slab and shallow soil gas measurements was "quite low (<2x)" based on semi-hourly observations over a period of a week.

Folkes, et al. (2009) report that “[u]p to 10 years of indoor air monitoring data in 45 unmitigated homes at the Redfield site indicate that 1,1-DCE concentrations typically vary be a factor of 2 to 3 about the annual average for each home.” Variations in soil gas concentrations and the effects of environmental factors presumably were smaller.

Steinmacher, et al. (2009) reviewed 3,453 indoor air samples collected from 1,333 homes at the Hill AFB site in Utah. They looked at eight variables related to temperature, precipitation, wind speed, and barometric pressure over different seasons and concluded, “[t]he contribution of meteorological variables to the seasonal fluctuations of TCE concentrations in indoor air appears to be negligible.” A statistical analysis showed a significant correlation for temperature and barometric pressure, but they found “less than 1% of the variability in TCE concentration level is related to these meteorological variables.”

Other researchers have looked for the effect of environmental factors on the measured ratio of indoor air to soil gas (i.e., attenuation coefficient [$\alpha$]). Yao, et al. (2013) report that they could not explain the large variations in $\alpha$ based upon most environmental factors. Song, et al. (2014) looked at stack and wind effects and found that they had little influence because $Q_{soil}$ and $Q_{bldg}$ were well correlated. For residential buildings, they found the 95th percentile $\alpha$ to be in the 0.001 to 0.003 range.

## 3. CONCLUSION

The vadose zone can be thought of as relatively stagnant in terms of air flow and vapor transport, which is one reason why subsurface contamination can persist for years after a release. Environmental factors have the potential to retard or speed up the rate of vapor transport in the vadose zone and are largely responsible for temporal variability at a given measurement location (after factoring out measurement variability). The effect of environmental variables, however, generally is relatively small. For typical soils, the effects are largely limited to the top one meter or less of the soil column. The results for various environmental variables are summarized in Table 1.

The implication is that if soil gas concentrations at a depth of 3 to 5 ft. bgs are zero, or are small relative to evaluation criterion, additional subsequent measurements are very unlikely to show a significant increase.

*Table 1*. Effect of environmental variables

| Variable | Effect for Typical Soils | Comments |
|---|---|---|
| Air temperature | Little diurnal variability below depth of about 0.3m. Annual soil temperatures stable below 1m bgs. | Rock or very dry soil may show diurnal effect to depths of about 1m. |
| Soil moisture | Increasing levels of soil moisture will reduce rates of diffusion via reduction in effective diffusivity and reduction in soil-gas concentration. | The most significant environmental variable at most sites. Changes in soil moisture levels will be most pronounced in the topmost soil layers. |
| Water infiltration | Can result in short-term spike in air emissions followed by reduced rates of gas transport. | One-time rain events of <1cm (<0.4 in.) will have minimal effects. |
| Changes in groundwater level | Falling groundwater levels result in worst-case conditions for vapor intrusion. | Some riverside sites may experience pressure-driven flow from rapid rises in groundwater level. |
| Barometric pressure (BP) | Any effect limited to top 1m of soil with an exponential decrease in pressure changes with depth.<br>Important mechanism for oxygen transport into soil column at petroleum hydrocarbon sites. | Sites with very deep groundwater will show more barometric pumping than sites with groundwater within 10 to 20m of ground surface.<br>Fractured rock sites may show BP-induced pressure effects at much greater depth than sites with typical soils. |
| Surface winds | Small effect down to about 0.5m depth. | Effect of surface winds exceeds effect of barometric pressure in field studies. |

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# SUBSURFACE ONE-DIMENSIONAL TRANSPORT OF DIOXIN BENEATH AN UNCONTROLLED DUMP SITE – A CASE STUDY

*West Coast Conference, March 2016*

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## ABSTRACT

Measurements of 17 dioxin and furan congener concentrations were made as successive layers of clayey glacial till were excavated at a former municipal and industrial dump site. The measurements demonstrate separation of 1,2,3,4,6,7,8-HpCDD, OCDD and 2,3,7,8-TCDD with increasing depth. The dioxin congener 2,3,7,8-TCDD penetrated the clay to depths exceeding two meters. Application of the advective-dispersive one-dimensional transport equation for a reactive solute resulted in a reasonable fit to subsurface concentration measurements. All boundary and material variables were treated as constants when best-fitting the measured congener concentration distributions. The congener specific retardation factors, $R_d$'s, and initial concentrations, $C_o$'s, were necessarily varied. $C_o$'s for respective congeners were selected to be an area average measured during the initial investigation. $R_d$'s were selected that resulted in the best visual fit of data to the transport equation. A good fit between the measured and calculated depth concentration distribution occurred when the ratio of $R_d$'s was approximately 6:1:4 for 1,2,3,4,6,7,8-HpCDD, 2,3,7,8-TCDD and OCDD respectively. These results differ insignificantly from corresponding ratios of octanol-water partitioning coefficients, approximately 10:1:10, that expectedly would be similar. The depth of 2,3,7,8-TCDD penetration was greater than anticipated. Uncertainties associated with estimating the advective-dispersive transport equation variables explain the difference between expectations and observations. Dioxin-like compounds other than 1,2,3,4,6,7,8-HpCDD, OCDD and 2,3,7,8-TCDD were not detected at reportable concentrations below the surface. The dioxin-like compounds measured at the dump site were those compounds with nonzero toxicity equivalency factors as identified in *Estimating Exposure to Dioxin-Like Compounds*, EPA/600/6-88/005B1.

**Keywords:** composite, soil, sample, dioxin, furan, transport, subsurface, groundwater

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# 1. INTRODUCTION

## 1.1 Site Location and History

Dioxin and furan measurements were made at the Krejci Dump Site during both the initial site characterization in 1996 and remediation in 2012 (BOR, 1996a; BOR, 1996b; BOR, 2002a; BOR, 2002b; NPS, 2012). The roughly 200,000 $m^2$ site is a former municipal and industrial dump and salvage located within the Cuyahoga Valley National Park in Summit County, Ohio, USA (41°16'17.63"N, 81°32'40.33"W). During the years of operation, from approximately 1950 to 1980, large volumes of solid and liquid waste materials were brought to the dump, where significant quantities of hazardous substances were released to the environment as a result of open dumping, spills, leaking containers, and burning. The United States purchased the land in 1980 for management by the Department of the Interior National Park Service (NPS). In 1987, it was determined that the Site constituted a threat to human health and the environment. In response to this determination, the U.S. Environmental Protection Agency (EPA) initiated an emergency removal in June 1987. In November 1988, the NPS completed the removal of wastes that had been staged by the EPA and also removed some unconsolidated wastes and contaminated soil. Large quantities of debris and contaminated soil remained. An extensive remedial investigation was performed during 1994 through 1996. Debris and soils containing unacceptable levels of contaminants were excavated and removed from the site between October 2005 and December 2011. Site restoration was completed in 2012.

## 1.2 Dioxin Contamination and Remediation

The remedial site investigation discovered unacceptable dioxin-like congener concentrations in surface soil within and adjacent to a 10 m to 20 m deep debris-filled ravine. A fire had purportedly smoldered in this ravine during most of the facilities approximately 30 years of operation. Seventeen discrete locations were investigated to determine dioxin and furan congener concentrations in 1996. The area contaminated with dioxin and furan was estimated to be approximately 44,000 $m^2$. Many other chemical contaminants, including organic solvents, were also found to be present[5].

Remediation goals were established for dioxin-like compounds and 33 other contaminants. It was determined that soil having a calculated 2,3,7,8 TCDD toxicity equivalency factor (TEQ) greater than 3 pg/g would be excavated and removed from the site (Blancato et al., 1988; BOR, 2002b) .

The initial remediation effort required removal of: 1) all debris; 2) visibly contaminated or altered soil; and 3) minimally, an additional 15 cm of soil where contaminants had been discovered to exceed remediation goals. This effort was followed by collection of 40-part composite soil samples in each of 11 approximately 4000 $m^2$ subareas of the site. The 11 subareas are outlined on Figure 1. Contour lines on this figure represent approximately 3 m elevation intervals and generally define the ravine location at the time of the remedial investigation. For each subarea, 40 equal volume specimens of surface soil were collected at approximately 10 m spaced nodes of a rectangular grid and combined to create a composite sample. The concentrations of 17 dioxin and furan congeners were measured for each sample. Following the initial remedial effort, only 2 of the 11 subareas achieved the TEQ goal of 3 pg/g.

Minimally 15 cm of soil was removed from the entire surface of the 9 failing subareas. Forty-part composite samples, one representing each subarea, were collected and analyzed for dioxin-like compounds. At the end of this second remediation effort, 5 of the original 11 subareas had achieved the 3 pg/g TEQ goal. All remaining failing subareas included a part of the ravine.

Again, minimally, 15 cm of soil was removed from the entire surface of the 5 remaining failing subareas. Each remaining subarea was further subdivided into four approximately 1000 $m^2$ "quarter-areas" to better focus the remaining remedial effort. Quarter-areas had unique alphanumeric identifiers as shown on Figure 1. Forty-part composite samples were created to represent individual quarter-areas by combining equal volume soil increments collected from node points of an approximately 5 m grid.

Subsequent episodes of sampling, analysis and excavation occurred in quarter-areas having calculated TEQ greater than 3 pg/g. The excavation, sampling and analysis sequence was iterated in each quarter-area until the calculated TEQ of the quarter-area composite sample was less than 3 pg/g. Each failure to achieve the desired TEQ resulted in minimally 15 cm of soil being removed from the entire failing quarter-area. Excavation as deep as 1.7 m was required to achieve the TEQ remediation goal following the initial removal effort.

## 1.3 Stratigraphy and Soil Characteristics

The site is located on a narrow ridge of glacial, glaciofluvial, and lacustrine sediments within the buried pre-glacial valley of the Cuyahoga River (41°16'18.11"N, 81°32'40.64"W). The ridge is approximately 30 m above adjacent valleys. Sediments are at least 60 m deep and consist of four basic glacial till units (BOR, 2002a). Only the upper two of these units are pertinent to this discussion and are described in the following two paragraphs. Dioxin contamination was located in and adjacent to a 5 to 20 meter deep ravine that had been filled with municipal and industrial waste mixed with other debris. A fire smoldered in the debris filled ravine for several decades when the dump was in operation. The ravine incised the upper till unit and cut deeply into the second unit. Ravine slopes in the area are typically 2H:1V. Precipitation permeated the waste and debris resulting in locally perched water, both within the debris and adjacent slopes. An unnatural perennial stream in the ravine was maintained by water slowly released from storage within the debris. The water stored in the waste and debris contained dissolved dioxins and furans and infiltrated the adjacent clay tills. This was the primary source of soil dioxin and furan contamination.

The uppermost unit consists of approximately 10 m of weathered, dense, homogenous, relatively stiff, yellow-brown clay with a few scattered pebbles and cobbles. Naturally occurring near surface soil is classified as Lean Clay (CL) with about 10 percent fine sand and about 90 percent medium-plasticity fines (fines are particles less than 0.075 mm in size.) (ASTM, 2011). Petrographic analyses revealed that the near surface clay minerals are composed of about 5 to 25 percent vermiculite, 5 to 25 percent illite/mica, and 5 to 20 percent kaolinite, and contain minor traces of mixed-layer minerals. In-situ dry unit mass is about 1680 kg/m, the measured particle average specific gravity is approximately 2.71, and soil porosity is approximately 0.38. Laboratory measurement of vertical hydraulic conductivities using intact core samples ranged from $2.8 \times 10^{-8}$ cm/s to $8.6 \times 10^{-8}$ cm/s. Significant high angle to vertical fractures were observed in nearby road cuts and later on the excavated ravine slopes. Six approximately 46-cm diameter single-ring surface infiltration tests were performed. Calculated hydraulic conductivities using measurements from these tests ranged between 7 x $10^{-6}$ cm/s and 6 x $10^{-5}$ cm/s [5].Twenty-one site-wide measurements of total organic carbon content, representing upper unit soil at a depth of about 0.3 m, ranged between 4.7 and 0.28 percent with an arithmetic mean of about 1 percent.

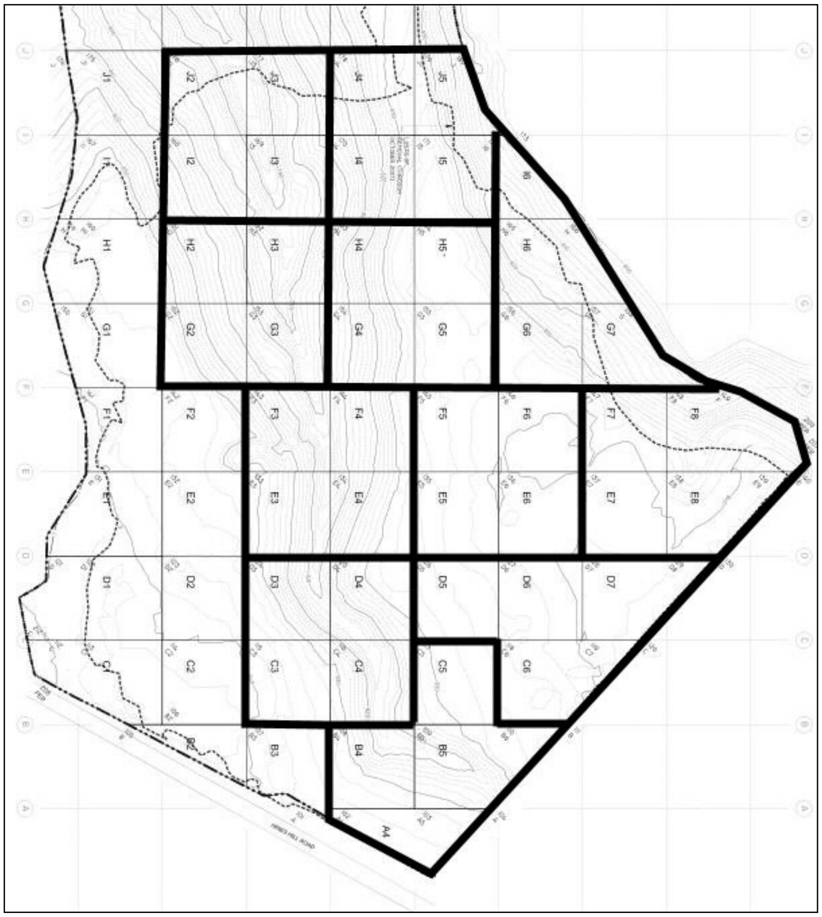

*Figure 1.* Limits of the Krejci Dump West Site: Eleven approximately 4000 $m^2$ remediation subareas (bold outline) and interior quarter-areas

The lower second unit is 20 m to 30 m of predominantly unweathered, dense, gray Lean Clay (CL) having approximately 95 percent fines, containing a few pebbles and cobbles, and having infrequent 0.7 m to 3 m thick zones of thinly laminated silts and clays of lacustrine origin. This unit also contains occasional lenses of silt or sand which are generally 0.3 m to 1 m thick. These lenses are expected to be isolated, discontinuous, and may not be oriented horizontally. Laboratory testing on intact core samples measured hydraulic conductivity of the gray clay ranging between 1.5 x $10^{-8}$ cm/s and 8.7 x $10^{-8}$ cm/s. This unit is highly erosive and contains infrequent vertical fractures. Vertical fractures were not observed in core samples or laboratory test specimens. Although infrequent, vertical fractures and other minor geologic details are expected to cause the unit to have an average vertical hydraulic conductivity much greater than the average laboratory measured values.

The approximately 5 m to 20 m deep ravine, in which the subject dioxin and furan contamination was found, completely incises the upper unit (yellow clay unit) and extends about 15 m into the lower unit (gray clay unit). Fourteen measurements of cation exchange capacity, representing both units at the site, ranged between 6.9 meq/100g and 15.1 meq/100g.

# 2. MATERIAL AND METHODS

The dioxin-like compound investigation plan and results are presented and discussed in several project reports (BOR, 1996a; BOR, 1996b; BOR, 2002a; BOR, 2002b; NPS, 2012). Surface dioxin-like compound measurements representing 17 locations were made during the 1996 site characterization. There were no subsurface measurements at that time. Seventeen congeners were evaluated. Dioxin-like compounds moved into the soil adjacent to the debris-filled ravine by mechanisms of advective transport and chemical diffusion. Initially all 17 dioxin and furan congeners were measured at quantifiable concentrations in ravine debris and soil. However, only three of these had reportable concentrations in subsurface soil following the second excavation effort. The remaining quantifiable congeners were 1,2,3,4,6,7,8 HpCDD, OCDD, and 2,3,7,8 TCDD and these are the focus of this paper. Concentrations were observed to decrease with depth for all three of these compounds. The concentration v. depth distribution for these three congeners would expectedly be described by the well-known “advective-dispersive” equation for reactive solutes.

The contaminant transport model for one-dimensional flow of a reactive solute is described by the “advective-dispersive” equation for reactive solutes (Freeze and Cherry, 1979).

$$\frac{\partial c}{\partial t} = \frac{D}{R_d}\frac{\partial^2 c}{x^2} - \frac{v_s}{R_d}\frac{\partial c}{\partial x}$$

Where:

$R_d$ is the “ retardation factor”; $R_d = \frac{v_c}{v_s}$;

$v_s$ = average interstitial seepage velocity;

$v_c$ = average velocity of the retarded solute;

$t$ = time elapsed;

$x$ = distance;

$c$ = concentration of organic solute in water;

D = hydrodynamic dispersion coefficient.

From this equation it is evident that the concentration variation with time and distance is completely described by the two ratios $D/R_d$ and $v_s/R_d$. Herein, values for these two ratios were determined that best-fit the equation to the concentration v. depth distribution for each of the three congeners.

$D/R_d$ and $v_s/R_d$ that best-fit the field data are derived for each of the three congeners. These estimates are then compared to similar ratios calculated using estimates of $v_s$, $R_d$ and $D$ derived from commonly used predictive mathematical expressions and information acquired during the remedial investigation such as soil density, specific gravity, hydraulic conductivity, and organic carbon content.

The retardation factor, $R_d$, is expected to be different for each congener. $R_d$ is subsequently identified using the terms $R_{d(HpCDD)}$, $R_{d(TCDD)}$, and $R_{d(OCDD)}$ when referring to 1,2,3,4,6,7,8 HpCDD; 2,3,7,8 TCDD and OCDD respectively.

An analytical solution to the advective-dispersive equation has been developed by Ogata and Banks (Ogata and Banks, 1961) and it is this solution that is best-fit to the field measurements in the next section.

$$\frac{c}{c_o} = \frac{1}{2}\{erfc(Z_1) + erfc(Z_2)erfc(Z_3)\}$$

Where:

$$Z_1 = \frac{x - v_{Rs}t}{2\sqrt{D_R t}}$$

$$Z_2 = \frac{v_{Rs}x}{D_R}$$

$$Z_3 = \frac{x + v_{Rs}t}{2\sqrt{D_R t}}$$

and

$$v_{Rs} = \frac{v_s}{R_d} \quad ; \quad D_R = \frac{D}{R_d}$$

The value of $c$ is the concentration at depth $x$ and time $t$. The variable $t$ is the time that has elapsed since the introduction of the contaminant at the surface. This solution to the advective-dispersive equation inherently assumes a constant contaminant source concentration $c_o$ and one-dimensional flow into a homogeneous, isotropic half-space of clean soil. The elapsed time ($t$) used for all calculations is 30 years. Arguably, $t$ could be 40 or even 50 years since the burning of chemicals that could create dioxins may have been ongoing before the 1960’s and most remediation measurements were acquired in 2010. However, it is difficult to establish when the source of dioxin was removed. Herein it is presumed that the source was removed in the late 1980’s when much of the bulk waste was removed from the valley.

The ratios $D/R_d$ and $v_s/R_d$, determined by the method just described, will be compared in the next section to ratios $D/R_d$ and $v_s/R_d$ calculated using a typical predictive approach. A hydraulic gradient of one is assumed for both calculations. The assumption of a hydraulic gradient of one is justifiable because the thick, clayey, glacial till is underlain by a sand layer. The sand layer acts to drain water from beneath the clayey till with water exiting the sand layer where it intersects adjacent valley side slopes. Also, the depth of perched water in the debris is small relative to the thickness of the clayey till layer. Under these conditions, the change in total hydraulic head is approximately equal to the change in elevation head. Consequently, a gradient equal to approximately one is reasonably expected.

# 3. RESULTS

## 3.1 Dioxin Congener Concentration v. Depth

Dioxin-like compounds moved into soils adjacent to the ravine by mechanisms of advective transport and diffusion. Of the 17 dioxin and furan congeners investigated, only three had reportable concentrations in subsurface soil following the second excavation effort. These were 1,2,3,4,6,7,8 HpCDD; 2,3,7,8 TCDD and OCDD. Concentrations were observed to decrease with depth. Ratios of measured concentrations to the measured surface concentrations following the second excavation effort were calculated and are presented on Figure 2. Individual quarter-areas are identified in the legends of these figures using alphanumeric quarter-area identifiers. The depth of the initial soil excavation was not measured, but observations suggest it varied between 0.5 m and 2 m. A depth of 1 m is used to represent the initial excavation on Figure 2 and the included graphs are shaded in this depth range to remind the reader that this depth is uncertain. It is also noteworthy that physical and chemical characteristics of the soil and debris removed by initial excavation were sometimes significantly different than unaltered native soil. Furthermore, the depositional characteristics of glacial tills cause them to be inhomogeneous and anisotropic. Regardless, all soil is treated as homogeneous and isotropic to simplify this analysis.

The solution to the advective-dispersive equation for one-dimensional flow of reactive solutes through soil, subject to reversible sorption reactions, was visually best-fit to each of the distributions. The average concentrations measured at the time of the remedial investigation were used to represent $C_o$ for each congener. These concentrations were 1015 pg/g, 11.7 pg/g and 12850 pg/g, for 1,2,3,4,6,7,8-HpCDD; 2,3,7,8-TCDD and OCDD respectively The best-fit relationships are shown on Figures 1, 2 and 3. All material variables in the equations were held constant for all calculations except that different $R_d$ and $C_o$ were selected to represent each congener. A good fit between the measured and calculated concentration distribution with depth occurred when the ratio of $R_d$'s was 6:1:4 for 1,2,3,4,6,7,8-HpCDD; 2,3,7,8-TCDD and OCDD respectively. A ratio of 10:1:10 would be expected if $R_d$ had varied in approximate proportion with octanol-water partitioning coefficients ($K_{ow}$). The reason for this expectation is discussed in the next section.

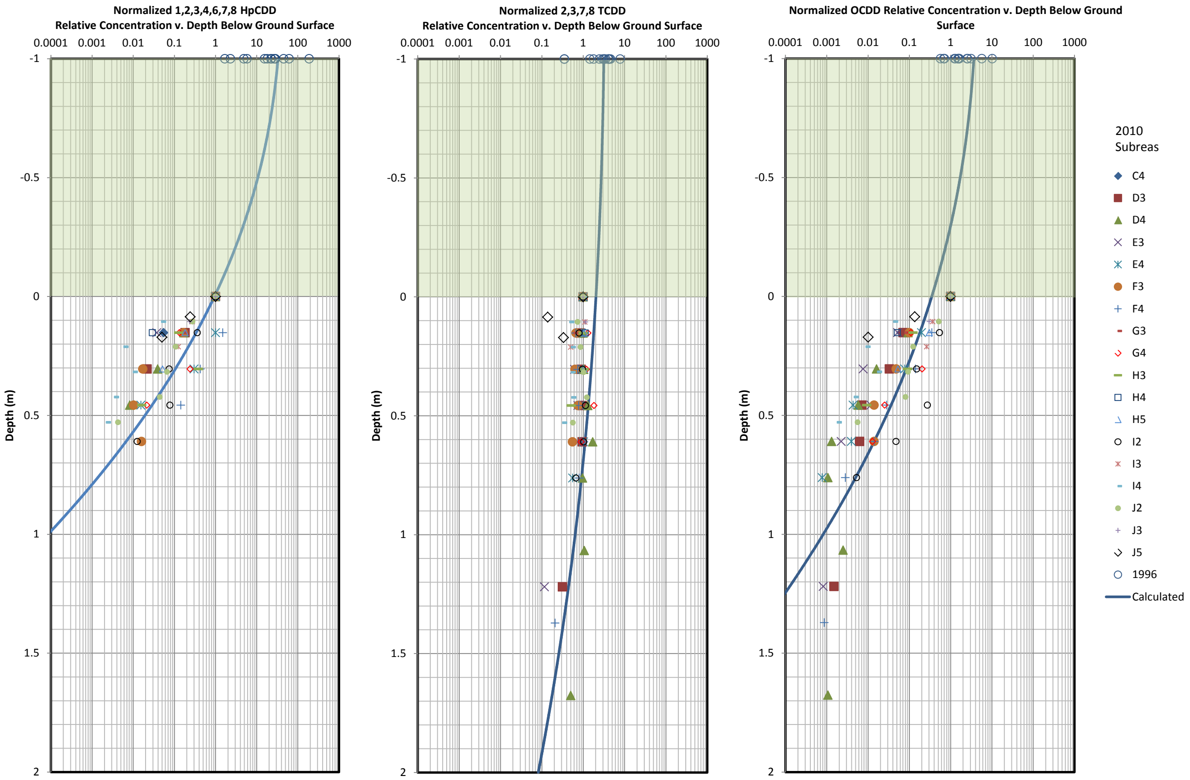

*Figure 2.* Relative concentration measurements v. depth with best-fit curve

The values used to visually best-fit the advective-dispersive equation to each congener, including the best-fit ratios of $D/R_d$ and $v_s/R_d$, are presented in Table 1.

*Table 1.* Values used to visually best-fit the advective-dispersive equation

| Variable | 1,2,3,4,6,7,8-HpCDD | 2,3,7,8 TCDD | OCDD |
|---|---|---|---|
| $R_d/R_{d(TCDD)}$ | 6 | 1 | 4 |
| $D/R_d$ $(m^2/s)$ | 8.17E-11 | 4.90E-10 | 1.23E-10 |
| $t$ $(sec)$ | 9.46E+08 | 9.46E+08 | 9.46E+08 |
| $v_s/R_d$ $(m/sec)$ | 1.67E-10 | 1.00E-09 | 2.50E-10 |
| $C_o$ $(g/g)$ | 1.02E-09 | 1.17E-11 | 1.29E-08 |

## 3.2 Derivation of $D/R_d$ and $v_s/R_d$ Ratios Using a Common Predictive Approach

Values for variables used in the advective-dispersive equation are estimated and compared to best-fit values presented and discussed in the previous section.

$R_d$ can be estimated for each congener for the condition of saturated flow using soil porosity ($n$), bulk density ($\rho_d$), and the compound partition coefficient ($K_d$).

$$R_d = [1 + K_d \frac{\rho_d}{n}]$$

$\rho_d$ = 1.650 g/cm$^3$ and $n$ = 0.38 were previously presented as results of the remedial investigation. $K_d$ is commonly calculated using the relationships:

$$K_d = K_{oc}(f)$$

$$logK_{oc} = A + B\ logK_{ow}$$

Where:

$A$ and $B$ are constants derived by previous study for sets of organic compounds and found in literature (Dragun, 1988). For this analysis, A= .088 and B=.909 (Hassett et al., 1983);

$K_{ow}$ is the octanol-water partitioning coefficient: use $log\ K_{ow}$ = 7 for TCDD and $log\ K_{ow}$ = 8 for OCDD and HpCDD; these values reflect one-significant-digit approximations of values commonly presented in literature (these values may be +/- 1) (USEPA, 1994);

$f$ is the fraction of soil mass that is organic carbon: the lowest value from remedial investigation report, $f$ = 0.0028, is thought to best represent the subsurface soil and used for this analysis.

The calculation results are:

$R_{d(TCDD)}$ = 75,000;

$R_{d(OCDD)} = R_{d(HpCDD)}$ = 750,000.

The average interstitial velocity, $v_s$, is the same for all three congeners since all three are subject to the same water flow rate; $v_s$ may be estimated by the equation.

$$v_s = \frac{ki}{n}$$

Where:

$k$ = hydraulic conductivity; measured during the remedial investigation to be in the range between $10^{-8}$ cm/sec and $10^{-4}$ cm/sec; the value $10^{-5}$, nearer the higher end of this range is selected since both field and laboratory measurements generally underestimate the effects of minor geologic details resulting in a bias toward low $k$ values;

$i$ = hydraulic gradient; a unit gradient is estimated for the site conditions that existed during dump operations and until debris removal was nearly complete;

$n$ = porosity; $n$ = 0.38 is estimated using the results of the remedial investigation.

The calculated value is: $v_s = 2.6 \times 10^{-5}$ cm/sec.

To simplify subsequent analysis, $D$ will be assumed equal for each congener. This is a reasonable assumption since only an order of magnitude estimate of the value can be made under the best experimental conditions. Furthermore, all congeners are subject to the same flow velocity and congener molecules are all approximately the same size. The magnitude of $D$

depends on both molecular diffusion and mechanical dispersion. Herein, a typical value for nonreactive organic compounds, $D = 10^{-6}$ $cm^2/sec$, will be used.

The ratios $D/R_d$ and $v_s/R_d$ are calculated and presented in Table 2 with other variables used in the advective-dispersive equation to predict congener transport.

*Table 2.* Calculated ratios $D/R_d$ and $v_s/R_d$ and other predictive parameters

| Variable | 1,2,3,4,6,7,8-HpCDD | 2,3,7,8 TCDD | OCDD |
|---|---|---|---|
| $R_d/R_{d(TCDD)}$ | 10 | 1 | 10 |
| $D/R_d$ $(m^2/s)$ | 1.3E-12 | 1.3E-11 | 1.3E-12 |
| $t$ $(sec)$ | 9.46E+08 | 9.46E+08 | 9.46E+08 |
| $v_s/R_d$ $(m/sec)$ | 3.5E-11 | 3.5E-10 | 3.5E-11 |
| $C_o$ $(g/g)$ | 1.02E-09 | 1.17E-11 | 1.29E-08 |

The predicted curves for t = 30 years are presented as a dashed line on Figure 3 with the previously discussed normalized field data. It is evident that the predicted depth of dioxin movement is considerably less than measured at the site. Such error can be explained as resulting from large uncertainties in estimated values for problem variables. For example, the estimates of permeability coefficient, octanol water partitioning coefficient, and hydrodynamic dispersion are, at best, accurate only to plus or minus one order of magnitude.

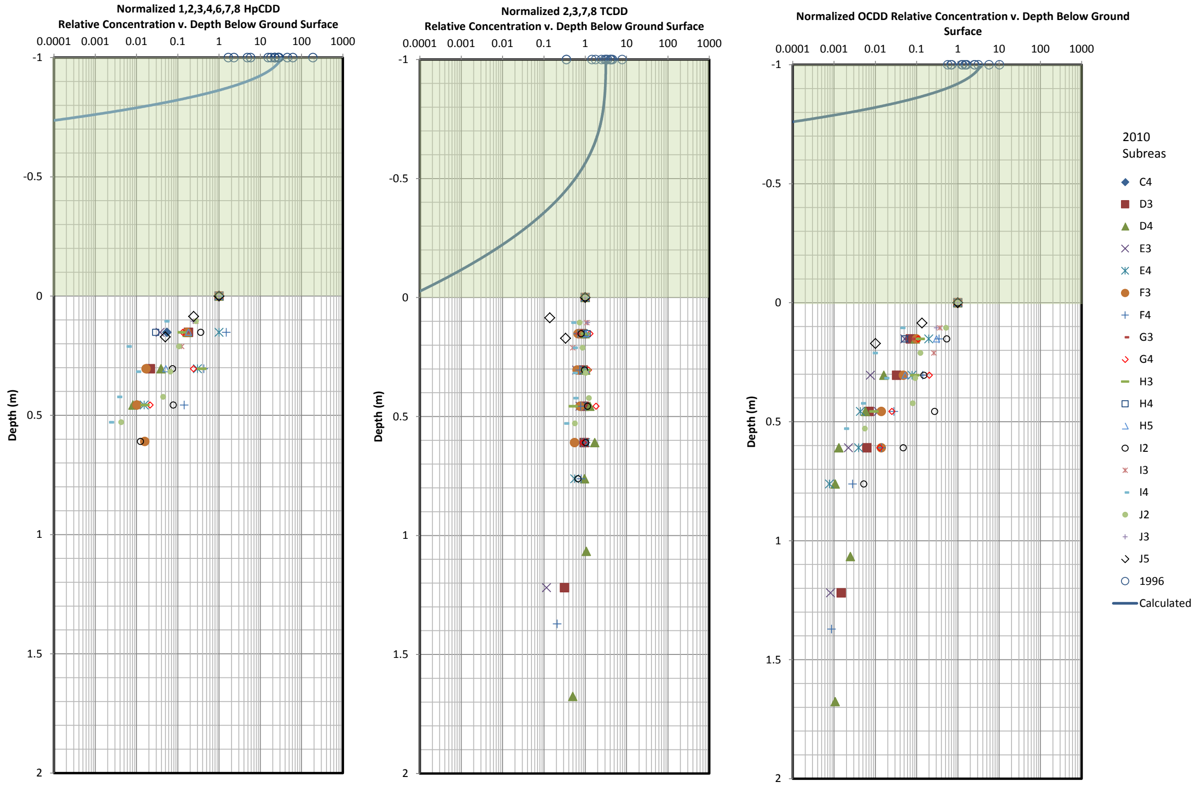

*Figure 3.* Relative concentration measurements v. depth with predicted curve

# 4. DISCUSSION/CONCLUSION

Measurements of 17 dioxin and furan congener concentrations were made as successive layers of clay soil were excavated at the Krejci Dump Site, a former municipal and industrial dump site located in the Cuyahoga Valley National Park, Ohio. The measurements demonstrate separation of 1,2,3,4,6,7,8-HpCDD, OCDD, and 2,3,7,8-TCDD with increasing depth. The dioxin congener 2,3,7,8-TCDD penetrated the clay to depths exceeding two meters. Application of the advective-dispersive one-dimensional transport equation for a reactive solute (transport equation) resulted in a reasonably good fit to subsurface concentration measurements. All boundary and material variables were treated as constants when best-fitting the measured congener concentration distributions. Only the congener specific retardation factors, $R_d$'s, and initial concentrations, $C_o$'s, were varied. $C_o$'s for respective congeners were selected to be the area average measured during the initial investigation. A good fit between the measured and calculated depth concentration distribution occurred when the ratio of $R_d$'s was approximately 6:1:4 for 1,2,3,4,6,7,8-HpCDD; 2,3,7,8-TCDD and OCDD respectively. These results are reasonably different than corresponding ratios of octanol-water partitioning coefficients, approximately 10:1:10, that expectedly would be similar. The depth of penetration of the three congeners was also greater than calculated using common estimates of problem variables.

The difference between observations and expectations are explained by considering the large uncertainties associated with estimating the advective-dispersive transport equation variables. The large difference between observed and predicted depth of dioxin transport serves as a reminder that the problem variables of the advective-dispersive equation must be carefully defined and the subsurface characteristics measured by laboratory tests and in field studies in order to have a reasonable chance of useful predictions. Even with such care, prediction uncertainty will still remain significant due to the general inability to accurately describe the minor geologic details and associated hydraulic conductivity that control subsurface water movement and contaminant transport.

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# EFFECTS OF FLOODING AND ELEVATED $CO_2$ LEVELS ON GAS EXCHANGE OF SAWTOOTH OAK (*QUERCUS ACUTISSIMA*) SAPLINGS

*West Coast Conference, March 2016*

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## ABSTRACT

The climate records in the Gulf Coast of Mexico region of the USA documented an increased $CO_2$ level, precipitation, extreme climatic events, and flooding. Recent flooding events in New Orleans induced by hurricanes Katrina and Rita demonstrated the urgent need for research addressing urban flooding and how urban trees cope with the stress. Understanding the responses of urban tree species subjected to flooding is crucial for management of the natural resources in general and urban forests in particular. The objective of this study was to assess the physiological responses of sawtooth oak (*Q. acutissima*) to flooding at different $CO_2$ settings/levels. Saplings of sawtooth oak were subjected to periodic flooding treatments consisting of a two-week flooding period (flooding cycle) followed by a three-week dry-down period (recovery cycle). Data on photosynthesis (Ps), stomatal conductance (Sc), and transpiration (Tr) were collected both for the flooding cycles and for the recovery cycles using a Licor-6400 Portable Photosynthesis System at different $CO_2$ settings/levels (400, 500, 600, 700, and 800ppm). Independent T-tests, paired T-tests, and two-way ANOVAs were used to analyze data with R software. The study found that photosynthesis, stomatal conductance and transpiration were affected by flooding treatments in May. However, the significant effects only occurred at lower $CO_2$ levels (<600 ppm). The results also indicated that elevated $CO_2$ levels caused lower stomatal conductance and reduced transpiration rates for the recovery cycle. How urban tree species respond to the effect of flooding and elevated $CO_2$ may influence the full range of ecological processes that operate in urban forest systems, including sapling survival.

**Keywords**: flooding, elevated $CO_{2,}$ urban forest, photosynthesis, transpiration, stomatal conductance

## 1. INTRODUCTION

The Intergovernmental Panel on Climate Change predicts that atmospheric $CO_2$ concentration will increase 50% by the middle of this century. Current projections are for concentrations to continue to rise to as much as 500–1000 ppm by the year 2100 (Edenhofer et al., 2014). Previous studies have indicated that the Gulf Coast region in the Southeastern USA, including Texas, Louisiana, Mississippi, Alabama, and Florida, currently, and will continue, experiencing climate

[§] Corresponding Author: Zhu H. Ning, Ph.D., Urban Forestry and Natural Resources Program, Agriculture Research and Extension Center, Southern University, P.O. Box 11686, Baton Rouge, LA 70813; zhu_ning@subr.edu change including increases in $CO_2$ level, temperature, precipitation, and extreme climatic events such as hurricanes, and that increased precipitation will result in flooding in many places (Burkett et al., 2001; Crowe and Quayle, 2000; Melilo et al., 2000; Muller and Grymes, 2000; Ning et al., 2003).

The urban forests of the Southeast region are susceptible to flooding for several reasons. The trend of urbanization and global change to clear vegetation and increase impervious surfaces affects hydrology of urban areas (Nagy and Lockaby, 2011). Urbanization also alters precipitation in what is called the "urban rainfall effect" (Shem and Shepherd, 2009). Changes in climate, including sea level rise, increased and/or severe hurricanes, salinity, and land subsidence also increase flood risk for the region, especially for the Louisiana floodplains and the coastal areas. For example, in the forests of Maurepas, LA, the most significant stressor appeared to be near continuous flooding with slow-moving, nutrient-poor water. Increased flooding with salinity resulted in mortality for the majority of trees across species (Hoeppner et al., 2008).

The Gulf Coast region of the U.S. is also rapidly urbanizing and experiencing increasing industrialization and land cover change (Wu et al., 2012; Gong and Wu, 2014). Urban forests as green infrastructure provide cities with many ecological benefits (Gong et al., 2011; Gong et al., 2013a). Tree growth, evapotranspiration, and biomass accumulation provide carbon storage, temperate regulation, shade, climate regulation, as well as other services (Chen et al., 2012; Nowak et al., 2013). The benefits that urban forests provide cities as green infrastructure are determined by the physiological functions of urban trees, which are influenced by environmental factors (Gong et al., 2011; Yang, 2012). Trees in urban environments face stress conditions induced by global climate change, including greenhouse gas emission, increased temperature, pollution, water stress, pests, and other disturbances (Gong et al., 2013b). The urban forests in the Gulf Coast region are especially vulnerable to global change in addition to other risks (Nagy and Lockaby, 2011). Therefore, it has become increasingly important to address this issue.

Flooding affects trees at every stage of their development, the effects including injury, changes in anatomy and physiology, growth form, etc. Most upland tree species respond to increased atmospheric $CO_2$ concentrations by increasing photosynthetic rate, which generally results in increased productivity (Curtis and Wang, 1998; Delucia et al., 1998; Norby et al., 1999). However, scant studies have been conducted on the responses of urban tree species to flooding and elevated $CO_2$. Sustainability of natural resources and ecosystem services, coupled with economic and ecological benefits, are highly dependent on the changing environment. The impacts of flooding and elevated $CO_2$ on economically and environmentally important urban tree species need to be adequately studied.

The objective of this study was to assess the physiological responses of the saplings of sawtooth oak (*Quercus acutissima*), a commonly planted urban oak species in the region, to flooding at different $CO_2$ settings (levels) by examining photosynthetic rate, stomatal conductance, and transpiration rate. The following hypotheses were tested: 1) there are significant differences for the physiological parameters between the saplings under flooding and control at the same $CO_2$ level; 2) there are significant differences for the physiological parameters of the saplings under flooding at different $CO_2$ levels; and 3) there are significant interactions between the effects of flooding and elevated $CO_2$ levels.

## 2. MATERIAL AND METHODS

The experiments were conducted in the greenhouse at Southern University (Baton Rouge, LA, USA; 30°53'N and 91°19'E). The five-year-old saplings of sawtooth oak were grown in 30 liter (8 gallon) containers in a controlled greenhouse environment under ambient $CO_2$ condition and temperature, as well as filtered sunlight. For periodic flooding treatments, 9 saplings/containers with an average height of 2.4 m (7.9 feet) were placed into four 450 liter (120 cubic foot) tubes filled with water. The soil surfaces in the containers were flooded with a water level of +2 cm (0.79 inches) above the soil surface. To simulate periodic flooding, tubs were filled with water for two weeks as the flooding cycle. During the flooding cycle, water was changed every three days to ensure that the $O_2$ content in the water was intact. Two weeks after the flooding, water was drained from the tubs for three weeks of dry-down period for the saplings to go through a recovery cycle. For control (not flooded) saplings, a set of 9 saplings/containers were placed on the benches adjacent to the flooded saplings/tubs.

Data was collected both in the flooding cycle and the recovery cycle. The LI-6400 portable photosynthesis system (LI-COR, Inc.) equipped with an artificial light source of 6400-02B Red/Blue and the broadleaf chamber was used to collect data on photosynthetic rate (Ps, μmol $CO_2$ $m^{-2}$ $s^{-1}$), stomatal conductance (Sc, mol $H_2O$ $m^{-2}$ $s^{-1}$) and transpiration rate (Tr, mmol $H_2O$ $m^{-2}$ $s^{-1}$). To test the effect of flooding at different $CO_2$ settings/levels, data was collected at 5 different $CO_2$ settings/levels – 400, 500, 600, 700, and 800 umol $CO_2$ $mol^{-1}$ (from the ambient level to its double level) with the constant light intensity (1000 umol $s^{-1}$ PAR). Three mature and fully expanded leaves of each plant were randomly selected from each sapling for data collection. Independent T-tests were first performed to test any significant difference on Ps, Sc, and Tr between the saplings under flooding treatment and under control at each $CO_2$ levels. The paired T-tests were conducted to test any significant difference on Ps, Sc, and Tr of the saplings under flooding treatment due to different sampling settings of the $CO_2$ levels. Two-way ANOVAs were used to detect interactions between flooding and $CO_2$ levels. All tests were conducted by using R software (Source: http://www.r-project.org/, last accessed on March 1st, 2015).

## 3. RESULTS

For the flooding cycle in May, comparison of the saplings under flooding and under control at the same $CO_2$ level, Ps, Sc, and Tr rates were generally lower for the saplings under flooding than those under control. There were significant differences on the Ps, Sc, and Tr rates between the saplings under flooding and under control at 400, 500 and 600 ppm (parts per million; $p=0.06$ for Tr rate at 600 ppm) $CO_2$ levels (Figure 1).

For the saplings under flooding, the Ps rate increased as the $CO_2$ level increased, and the Ps rates were significantly higher at 700 and 800ppm levels than that of 400, 500 and 600 ppm $CO_2$ levels. The Ps trend was opposite for the saplings under control; the Ps decreased when $CO_2$ settings were elevated. The Sc and Tr rates were not affected by the elevated $CO_2$ for those saplings under flooding. For the saplings under control, the Sc and Tr rates displayed a decreased trend as the $CO_2$ level elevated. However, it was not statistically significant. There were interactions between the effects of flooding and elevated $CO_2$ for all three physiological parameters (Table 1).

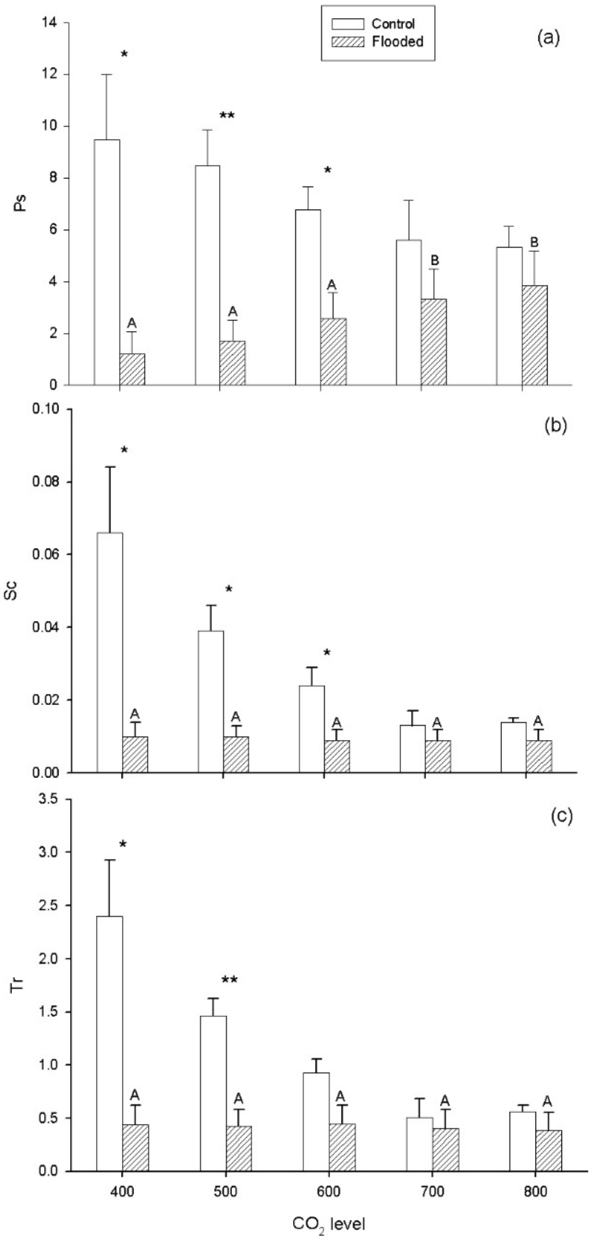

*Figure1*. Flooding cycle in May - The effects of flooding and elevated $CO_2$ levels (400ppm to 800ppm) on (a) photosynthetic rate (Ps, μmol $CO_2$ $m^{-2}$ $s^{-1}$), (b) stomatal conductance (Sc, mol $H_2O$ $m^{-2}$ $s^{-1}$) and (c) transpiration rate (Tr, mmol $H_2O$ $m^{-2}$ $s^{-1}$), with the independent T-tests between the saplings under control and under flooding treatment at each $CO_2$ levels ("*" denotes $p<0.05$ and "**" denotes $p<0.01$) and paired T-tests for the saplings under flooding treatment across all $CO_2$ levels (different "letters" denotes $p<0.05$)

For the recovery cycle in May, comparison of the flooded saplings to the control at the same $CO_2$ level, Ps rates were found to be generally lower for the flooded saplings than those of the control, and it was significantly lower at 500 and 600 ppm.  Sc and Tr rates were also generally lower for the flooded saplings than those of the control except at 700ppm, where Sc was higher for flooded, however, the differences were not statistically significant (Figure 2).

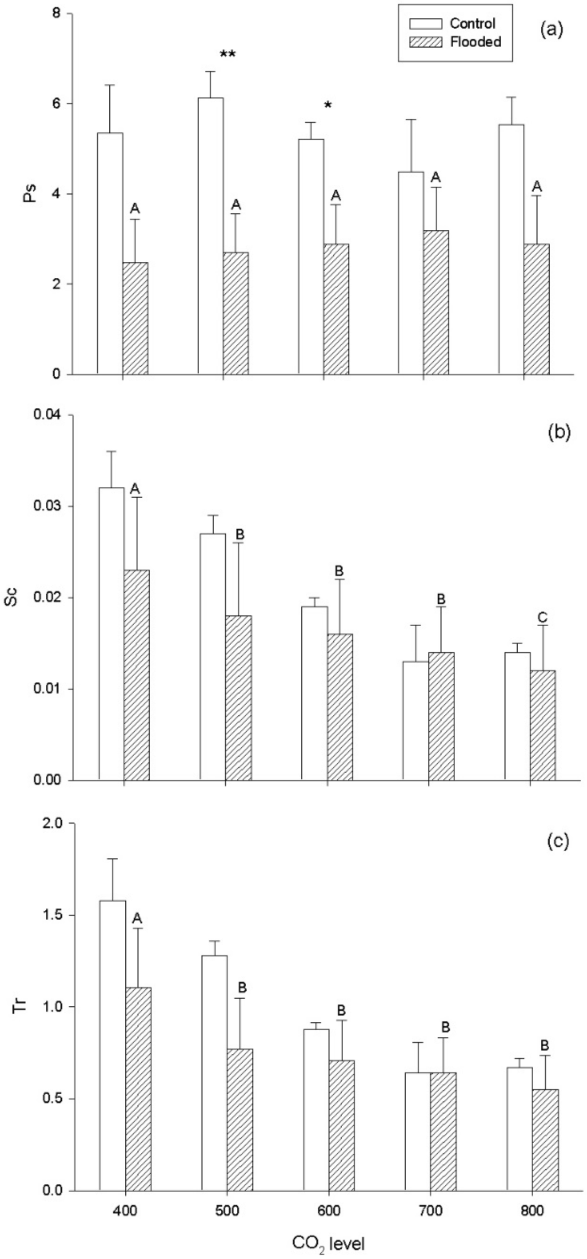

*Figure 2*. Recovery cycle in May - The effects of flooding and elevated $CO_2$ levels (400ppm to 800ppm) on (a) photosynthetic rate (Ps, µmol $CO_2$ $m^{-2}$ $s^{-1}$), (b) stomatal conductance (Sc, mol $H_2O$ $m^{-2}$ $s^{-1}$) and (c) transpiration rate (Tr, mmol $H_2O$ $m^{-2}$ $s^{-1}$), with the independent T-tests between the saplings under control and after flooding treatment at each $CO_2$ levels ("*" denotes $p<0.05$ and "**" denotes $p<0.01$) and paired T-tests for the saplings after flooding treatment across all the $CO_2$ levels (different "letters" denotes $p<0.05$)

*Table 1*. Flooding cycle - Means (±S.E.) and probability values of two way-ANOVA to compare the effects of flooding and different $CO_2$ levels (from 400ppm to 800ppm) on photosynthetic rate (Ps, μmol $CO_2$ $m^{-2}$ $s^{-1}$), stomatal conductance (Sc, mol $H_2O$ $m^{-2}$ $s^{-1}$) and transpiration rate (Tr, mmol $H_2O$ $m^{-2}$ $s^{-1}$)

| Var | Soil Flooding | | $CO_2$ level (μmol $CO_2$ $mol^{-1}$) | | | | | P-values | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Treatment | 400 | 500 | 600 | 700 | 800 | Flooding | $CO_2$ level | Interaction |
| Ps | 7.130±0.720 | 2.529±0.472 | 4.509±1.712 | 4.409±1.304 | 4.249±0.948 | 4.238±0.945 | 4.443±0.856 | <0.001** | 0.009** | 0.001** |
| Sc | 0.031±0.006 | 0.010±0.001 | 0.032±0.011 | 0.022±0.006 | 0.015±0.004 | 0.011±0.002 | 0.011±0.002 | <0.001** | <0.001** | <0.001** |
| Tr | 1.171±0.193 | 0.421±0.072 | 1.226±0.388 | 0.842±0.201 | 0.637±0.138 | 0.444±0.122 | 0.457±0.104 | <0.001** | <0.001** | <0.001** |

*Table 2*. Recovery cycle - Means (±S.E.) and probability values of two way-ANOVA to compare the effects of flooding and different $CO_2$ levels (from 400ppm to 800ppm) on photosynthetic rate (Ps, μmol $CO_2$ $m^{-2}$ $s^{-1}$), stomatal conductance (Sc, mol $H_2O$ $m^{-2}$ $s^{-1}$) and transpiration rate (Tr, mmol $H_2O$ $m^{-2}$ $s^{-1}$)

| Var | Soil Flooding | | $CO_2$ level (μmol $CO_2$ $mol^{-1}$) | | | | | P-values | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Treatment | 400 | 500 | 600 | 700 | 800 | Flooding | $CO_2$ level | Interaction |
| Ps | 5.341±0.347 | 2.821±0.408 | 3.433±0.816 | 3.837±0.769 | 3.654±0.679 | 3.616±0.742 | 3.766±0.821 | 0.150 | 0.734 | 0.573 |
| Sc | 0.021±0.002 | 0.017±0.003 | 0.026±0.005 | 0.021±0.005 | 0.017±0.004 | 0.014±0.004 | 0.013±0.003 | 0.276 | 0.039* | 0.382 |
| Tr | 1.008±0.099 | 0.755±0.108 | 1.263±0.232 | 0.940±0.195 | 0.764±0.144 | 0.641±0.134 | 0.590±0.122 | 0.155 | 0.009** | 0.276 |

There was also an obvious change in how elevated $CO_2$ settings affected the flooded saplings. As the $CO_2$ level elevated, there was no significant difference on the Ps rates, while the Sc and Tr rates at 400 ppm $CO_2$ level were significantly higher than at any other levels, and the lowest Sc occurred at 800ppm CO2 level. There was no interaction between the effects of flooding and elevated $CO_2$ on any parameters (Table 2).

# 4. DISCUSSION AND CONCLUSION

Climate change is making weather less predictable, rains more uncertain and heavy storm rainfalls more likely to happen (Muller and Grymes, 2000). High intensity rainfall can cause flooding when the city sewage system and drainage canals do not have the necessary capacity to drain away the amounts of rain falling (Khairy, 2003). The Southeastern region of the United States has rapidly urbanized, driven by economic and population growth. It is projected that the South will have the greatest absolute increase in population of any region in the U.S. from 2000-2030 (Nagy and Lockaby, 2011). Urbanization increases flooding risk by restricting where flood waters can flow, covering large parts of the pervious ground with roofs, roads and pavements, and obstructing sections of natural channels and building drains. Elevated $CO_2$ is also one of the major climate change risks for urban trees in the Gulf Coast region (Nagy and Lockaby, 2011). $CO_2$ plays several critical roles in plant physiological functions, including as a substrate for assimilation, influence on photorespiration and dark respiration, and as an environmental influence on stomata. In our study, we found that the three physiological parameters of the sawtooth oak saplings, including photosynthesis, stomatal conductance and transpiration, were affected by flooding and elevated $CO_2$ levels.

The effects of flooding on southeastern trees have been studied on a variety of species. Gravatt and Kirby (1998) found that flooding significantly reduced growth (leaf area, height, diameter, and biomass) of both broadleaf and conifer coastal species. According to a study on the seedlings of bald cypress, nuttall oak, and swamp chestnut oak after exposure to flood-hardening (Anderson and Reza Pezeshki, 2001), net photosynthesis was significantly decreased for oaks, but did not affect the bald cypress. However, the stomatal conductance of bald cypress increased during flooded treatments. In our study, we found that flooding significantly decreased Ps, Sc, and Tr of the sawtooth oak saplings in May.

Rising $CO_2$ concentrations have profound direct effects on the growth, physiology, and chemistry of plants. Studies on tree response to elevated $CO_2$ have found some common trends on photosynthesis rates among species. Generally, trees exhibit higher photosynthesis rates (Kim et al., 2015) when the $CO_2$ level is elevated. In our studies, we also found elevated $CO_2$ caused significant higher photosynthesis rates in May for the sawtooth oak saplings subjected to flooding.

The interactions between the effects of flooding and elevated $CO_2$ might have played a role in the Ps response of the saplings under flooding treatment. Elevated $CO_2$ levels might have helped the saplings under flooding by increasing their Ps rates.

Furthermore, elevated $CO_2$ may lead to lower stomatal conductance, reduced transpiration, and thereby, increased water efficiency (Ainsworth, 2008; Kim et al., 2015). In our study, we also found lower stomatal conductance and reduced transpiration rates caused by the elevated $CO_2$ levels in May, but only for the recovery cycle.

The Gulf Coast of Mexico region of the USA has been and will continue to be impacted by climate change. The climate records in the region documented an increased precipitation, extreme climatic events, and flooding (Crowe and Quayle, 2000; Muller and Grymes, 2000). Recent flooding events in New Orleans induced by hurricanes Katrina and Rita demonstrated the urgent need for research addressing urban flooding and how urban trees cope with the stress.

Understanding the responses of urban tree species subjected to flooding is crucial for management of the natural resources in general, and urban forests in particular. How urban tree species respond to the combined effect of flooding and elevated $CO_2$ may influence the full range of ecological processes that operate in urban forest systems, including sapling survival.

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# LIMITING SITE SOIL CHARACTERIZATION TO CONSEQUENTIAL CONTAMINATION

*West Coast Conference, March 2016*

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## ABSTRACT

Contamination in an abundance that is sufficient to threaten human health or the environment is herein termed consequential contamination. The most common approach to sample plan design inherently assumes that the absence of discovered contamination is sufficient evidence to conclude the absence of consequential contamination. This assumption is indefensible if it can be reasoned that consequential contamination might exist between sampling locations. Small areas of discontinuous contamination, e.g. hot spots, would reasonably be expected at uncontrolled dump and industrial sites, when defining the spatial limits of contamination at any site, and when determining the effectiveness of a cleanup that relies on excavation and removal of contaminated soil. In these instances, it is prudent that both soil characterization and rules for decision making minimally ensure greater than a 50 percent chance of responding to the reasonably conceivable smallest hot spot of consequential contamination. An approach to create, evaluate and defend sample plan designs for these and similar situations is described.

**Keywords:** composite, incremental, soil, sample, multi increment, number, many increments, contamination, hot spot

## 1. INTRODUCTION

Contamination in an abundance that is sufficient to cause the average concentration ($C_{ave}$) of a soil mass or a surface area to exceed a related risk-based limiting concentration or regulatory standard ($C_{index}$) is consequential contamination. A method is presented that calculates the minimum number of locations ($\underline{n}$) required to be represented by sampling when the reasonably smallest footprint of consequential contamination is present. Such a footprint is called a consequential hot spot. The value $\underline{n}$ is managed by the action concentration, $C_{act}$, which is a user selected value less than $C_{index}$ that, if equaled or exceeded, indicates the possible presence of consequential contamination. For example, if $C_{index}$ limits cancer risk to $10^{-5}$, the action concentration, $C_{act}$, may be selected as the concentration that would limit cancer risk to $10^{-6}$. Taking action when $C_{act}$ is exceeded provides a prescribed level of assurance the area average does not exceed $C_{index}$. It will be seen that selecting $C_{act}$ ten times lower than $C_{index}$ reduces $\underline{n}$ by an order of magnitude.

This approach focuses on providing reasonable assurance that hot spots inadvertently not represented in the sampling effort are inconsequential to decision making. Typically, in hot spot

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[§] Corresponding Author: Mark C. Gemperline, Ph.D., PE, President, MCG Geotechnical Engineering, Inc., 4817 S. Zang Way, Morrison, CO 80465; Tel: 303-973-2660; mcg_engineering@q.com scenarios, a large number of samples are needed to apply nonparametric statistical methods or statistical methods that are based on the Central Limit Theorem. The approach presented herein requires considerably fewer samples and provides a defensible level of confidence for the often presumed, yet seldom defensible, expectation that undiscovered contamination is inconsequential.

The number of locations that must be represented in a sampling effort depends on: 1) the remediation goal or regulatory concentration ($C_{index}$); 2) an action concentration ($C_{act}$) that, if equaled or exceeded, would indicate a possible exceedance of $C_{index}$; 3) the size of the smallest hot spot that can reasonably exist and also cause a soil mass or area average concentration to exceed $C_{index}$; and 4) the hypothesized contaminant distribution within such a hot spot. The method being presented has evolved over several decades as it has been used by the author for site assessments and to develop characterization and cleanup verification plans for uncontrolled dump sites, mine sites and industrial sites (Gemperline, 1999a; Gemperline, 1999b; Gemperline, 2010). Several example applications are presented and discussed.

## 2. MATERIAL AND METHODS

### 2.1 Background

The most common approach to sample plan design inherently assumes that the absence of discovered contamination is sufficient evidence to conclude the absence of consequential contamination. However, finding no contamination is insufficient to verify this supposition. This incorrect perception is generally based on an indefensible belief that common sense, judgment, experience, or incomplete technical argument is sufficient to support the decision.

Most sampling efforts are formulated to estimate the mean concentrations of contaminants of concern. Such estimates are required to perform quantitative risk assessments and for comparisons to remediation goals or regulatory limits. Commonly applied statistical methods rely on the Law of Large Numbers and Central Limit Theorem. Taken together, these constitutive rules of statistics guarantee that repeated measurements of contaminant mean concentration, with each measurement determined using the results of sampling at $\underline{n}$ random locations, will be normally distributed and centered on the true mean *if $\underline{n}$ is sufficiently large*. Unfortunately, it is impossible to know if a solitary consequential hot spot exists between sample collection locations in an otherwise clean area. Hence, in a single sampling event, there is no assurance that any assumed or derived $\underline{n}$ is sufficient.

This problem can be resolved by considering the nature of potentially unrepresented contamination and its associated effect on decision making. As will be discussed, both contaminant distribution and size of the smallest consequential hot spot can be reasonably hypothesized and used to make assertions regarding the adequacy of $\underline{n}$.

### 2.2 Extreme Hot Spot Example

The following example is presented to demonstrate fundamental aspects of the perception problem. Consider sampling a field suspected of containing buried explosive landmines. Needless to say, missing a single landmine is consequential. Suppose ten locations are sampled and each is found clean, i.e. no landmine. Concluding that the field contains no landmines would be inappropriate. The clarity of this conclusion is based on common sense recognition; 1) a landmine may remain undetected between sampling locations; and 2) there is an extreme human health risk associated with landmines. For these reasons it is simple to conclude that $\underline{n}$ must be larger than ten to enable a meaningful decision regarding the potential presence of a landmine.

Unlike this landmine example, most chemical hot spots are not explosive on contact. Furthermore, ill-effects may not be deadly, are often manifested only after numerous encounters over long time periods, and may not be correctly associated with consequential contamination encounters. Consequently, common sense does not always foster a clear understanding of the need for larger $\underline{n}$. A more theoretical understanding is therefore required, as demonstrated with the next example.

## 2.3 Typical Hot Spot Example

The following is a typical example of surface chemical soil contamination. It is applicable to both initial site characterization and cleanup verification.

A surface soil sampling program must be designed to acquire data needed to evaluate human carcinogenic risk caused by PCBs in a park setting. PCBs may have leaked or been dumped from transformers 30 years ago. The exposure area for use in human health risk assessment is established to be 5000 $m^2$. Furthermore, the exposure model assumes a person will encounter all locations within the exposure area with equal probability over a long period of time. Consequently, an estimate of the mean total PCB concentration will be used to represent the exposure concentration in risk calculations.

Total PCB exposure concentrations of 1.0 mg/kg and 0.10 mg/kg are calculated to present $10^{-5}$ and $10^{-6}$ carcinogenic human health risks respectively. The anticipated risk-based limiting concentration, $C_{index}$, is 1.0 mg/kg. To ensure this goal is attained, action will be taken to remediate the exposure area if it is discovered that the average concentration of $\underline{n}$ randomly selected surface soil locations equals or exceeds $C_{act}$ = 0.10 mg/kg. The problem is to determine the value of $\underline{n}$ that results in a 50 percent or greater chance that $C_{act}$ will be equaled or exceeded if the reasonably conceivable smallest footprint of consequential contamination is the only contamination present. Hereafter such contamination is termed the smallest consequential hot spot (*SCHS*).

The following rationale is used to select $\underline{n}$. First, it is reasonable to assume that the spilled or leaked transformer oil initially saturated the soil at the time of release resulting in a PCB soil concentration of about 100,000 mg/kg. Using an estimated five year half-life for PCBs, it is reasoned that the maximum concentration 30 years after release is about $C_{max}$= 1560 mg/kg.

Chemical diffusion and mechanical dispersion cause the contaminant distribution to vary between zero and $C_{max}$. For calculation simplicity, assume the hot spot is circular and that the concentration decreases linearly with distance from the center. The average concentration of such a hot spot is one third of the maximum concentration, about 520 mg/kg in this example. Using this information, the hot spot size that would cause the 5000 $m^2$ exposure area to have an average concentration of 1.0 mg/kg is calculated to be 9.6 $m^2$. This represents a reasonably conceivable smallest footprint for the *SCHS* because: 1) a hot spot with maximum concentration lower than $C_{max}$ must be larger than the *SCHS* if it is to cause an average exposure area concentration of 1.0 mg/kg; and 2) a hot spot smaller than the *SCHS* must have a maximum concentration greater than $C_{max}$ to cause an average exposure area concentration of 1.0 mg/kg and, based on the exponential decay model, this is not expected 30 years after the PCBs release.

It is desired to limit the chance of erroneously declaring the exposure area clean to less than 50 percent if the *SCHS* is present. In other words, the problem is to determine the value of $\underline{n}$ that results in a 50 percent or greater chance that $C_{act}$ will be equaled or exceeded if the *SCHS* is the only contamination present.

The number of samples required for application of methods that rely on the Central Limit Theorem of Statistics is exceptionally large. This is because a large number of the sampled locations must occur within the *SCHS* if it represents the only contamination present. For this example, 1/520 is the probability that a randomly selected location will fall within the footprint of the *SCHS*. This is the ratio of the hot spot area to the site area. The number of locations that occur within the hot spot when $\underline{n}$ random samples are collected has a binomial distribution. It is calculated that 20560 random sampling locations are needed for a 95 percent chance that 30 or more will occur within the *SCHS*. When the n is small, there is a good chance the hot spot will be missed altogether. For this example, when $\underline{n}$=30 there is about a 95 percent chance of completely missing the *SCHS*. This leads to the conclusion that it is unreasonable to represent a sufficient number of sample locations to ensure confident statistical inferences using methods that rely on a large number of these locations falling within the *SCHS*. A method that depends on a smaller number of sample locations is developed next.

It is desired to determine the value for $\underline{n}$ that will result in a 50 percent or greater chance that the average concentration of $\underline{n}$ randomly selected locations is greater than or equal to $C_{act}$ when the *SCHS* represents the distribution of site PCBs. The method is developed and examples given in subsequent sections. Application of the method results in the expectation that $\underline{n}$ = 392 locations will be sufficient to achieve this objective. The average total PCBs concentration of the 392 locations may be practically determined as the calculated average of eight independent composite sample measurements. For this example, each composite will be comprised of 49 equal-mass soil specimens (8 samples x 49 locations = 392 locations), collected at either randomly selected locations or at the nodes of 7x7 square grids. If grids are used, the node spacing of each grid will be the largest that results in at least 49 nodes within the exposure area.

A calculated average total PCBs concentration equal or exceeding 0.10 mg/kg would be an indication that consequential contamination, i.e. contamination that causes the mean concentration to equal or exceed 1.0 mg/kg, may be present. Therefore, action would be prudent if the average of the eight composite samples equals or exceeds 0.10 mg/kg.

## 2.4 Terminology, Application and Method Development

The method presented herein controls the risk of erroneously declaring an area or soil mass clean when the smallest footprint of consequential contamination, the *SCHS*, is present. It does this by selecting the number of sampling locations necessary to ensure a 50 percent or greater chance that the average concentration of the selected locations will exceed $C_{act}$ if the decision unit contamination distribution is characterized by the *SCHS*.

Herein the following terminology is used:

*Contaminant:* An analyte or compound; a risk normalized value that represents several analytes or compounds, such as TEQ for dioxin-like compounds; or an indicative measurement, such as gamma radiation.

*Area or Volume of Concern ($A_c$):* Typically the smallest exposure area or volume used in risk assessment and that is associated with the contaminant. This may also be the smallest area or volume used in the development of a regulatory limit for the contaminant.

*Consequential Contamination ($C_{index}$):* The lowest mean contaminant concentration within $A_c$ that presents an unacceptable risk to human health or the environment.

*Smallest Consequential Hot Spot (SCHS):* The reasonably smallest footprint of contamination that, if present within $A_C$, would cause $C_{index}$ to be equaled or exceeded. Sampling this hot spot sufficiently to support good decision making is what drives the sampling effort. A hypothesized distribution for contamination within the *SCHS* is used to determine the number of locations within $A_c$ that must be represented.

*Maximum Concentration ($C_{max}$):* Maximum concentration that can reasonably exist in $A_c$.

*Action Concentration ($C_{act}$):* The average concentration of the contaminant that has equal or better than 50 percent probability of exceedance when the *SCHS* is present and n random locations within $A_c$ are sampled.

*Number of Represented Locations (n):* The number of locations within $A_c$ that must be represented by sampling to provide at least a 50 percent chance that $C_{act}$ is exceeded when the *SCHS* is present.

*Average Concentration ($C_{ave}$):* The average concentration of contaminant at n random locations within $A_c$.

The minimum number of samples, *n*, and $C_{act}$ are most commonly determined given $C_{index}$ and an estimate of $C_{max}$. The following process is applied to each contaminant of concern and the largest *n* selected for sample plan design.

1. Determine $C_{index}$. Human or ecological risk assessment may be applied to establish the concentration for an exposure area, $A_c$, that results in unacceptable risk. $C_{index}$ often differ for surface and subsurface conditions and also for different exposure areas or subareas. The values for *n* will be accordingly different.
2. Determine the reasonable $C_{max}$ within $A_c$. Estimating $C_{max}$ requires a degree of understanding and modeling of contaminant release events. Technical understanding of fate and transport mechanisms may be applied to hypothesize a reasonable dispersion model from which $C_{max}$ may be calculated. Alternatively, a simple exponential decay model may be applied using 1) a published decay constant; 2) an estimate of the time since chemical release; and 3) a reasonable estimate of the maximum soil concentration at the time of the release. Maximum concentrations obtained by analysis of samples from within *Ac* would expectedly be lower than the true maximum since the true maximum occupies a very small soil volume and will likely be missed by sampling. Therefore, maximum concentrations obtained by analysis of samples from within $A_c$ should not be used to represent $C_{max}$. However, because such measurements are expectedly lower than $C_{max}$, they may aid in evaluating the adequacy of the hypothesized $C_{max}$.

3. Calculate the ratio of $C_{max}/C_{index}$.
4. Select an acceptable combination of $C_{act}/C_{index}$ and determine $\underline{n}$ from Table 1 or Equation 1. This is an iterative process that ends when an acceptable combination of $\underline{n}$ and $C_{act}/C_{index}$ is found. $C_{act}$ is the most reasonably altered variable. However, in some situations $C_{index}$ may be increased thereby accepting a greater human or ecological risk in exchange for lower $\underline{n}$, or to explain the benefit of reduced risk gained by using a larger $\underline{n}$. $C_{max}$ must not be altered unless the previous estimate is determined to be erroneous.
5. The value for $A_c$ is generally an exposure area or a volume of soil established by risk assessment and associated with $C_{index}$. [1]
6. Design the sampling plan to include soil collection at $\underline{n}$ random locations in $A_c$ and expect to take action if the calculated average of measured concentration exceeds $C_{act}$. Care should be taken to control errors introduced by sample collection, processing, and measurement to assure the contribution of these errors to decision-making uncertainty is less than that attributable to the process just described.

The values in Table 1 were generated by computer simulation of sampling events. Equation 1 fits the data in Table 1 limited to the significant digits used in the table and rounded to the nearest whole number. Table 1 and Equation 1 provide values that are sufficiently accurate for their intended use as presented in this paper. Uncertainty in this method is expected to be governed by uncertainty in the estimates of $C_{index}$ and $C_{max.}$ The uncertainty in the estimate of $C_{max}$ may not be as great as the uncertainty attributable to $C_{index}$ derived by risk assessment. Consequently, it is expected that method uncertainty will typically be governed by $C_{index}$ uncertainty.

*Table 1.* The value n that provides a greater than 50 percent chance that $C_{ave}/C_{index}$ exceeds $C_{act}/C_{index}$ in the presence of the smallest consequential hot spot (*SCHS*)

| | **$C_{act}/C_{index}$** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **0.95** | **0.9** | **0.8** | **0.7** | **0.6** | **0.5** | **0.4** | **0.3** | **0.2** | **0.1** | **0** |
| **$C_{max}$/ $C_{index}$** | **$\underline{n}$ That Provides Greater Than-50% Chance that $C_{ave}/C_{index}$ Exceeds $C_{act}/C_{index}$ in the Presence of the Smallest Consequential Hot Spot** | | | | | | | | | | |
| **1000000** | 2000000 | 970000 | 530000 | 400000 | 340000 | 310000 | 290000 | 270000 | 260000 | 250000 | 230000 |
| **100000** | 200000 | 97000 | 53000 | 40000 | 34000 | 31000 | 29000 | 27000 | 26000 | 25000 | 23000 |
| **10000** | 20000 | 9700 | 5300 | 4000 | 3400 | 3100 | 2900 | 2700 | 2600 | 2500 | 2300 |
| **1000** | 2000 | 970 | 530 | 400 | 340 | 310 | 290 | 270 | 260 | 250 | 230 |
| **100** | 200 | 97 | 53 | 40 | 34 | 31 | 29 | 27 | 26 | 25 | 23 |
| **10** | 20 | 10 | 5 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 2 |
| **3** | | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

$$n = \frac{C_{max}}{C_{index}}\left(0.764\left[\frac{-0.102}{LN\left(\frac{C_{act}}{C_{index}}\right)}\right]^{1.21} + 0.233\right) \qquad (1)$$

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[1] $A_c$ may be subdivided and a disproportionate risk assigned to the subdivided areas while ensuring the sum of risks remain unchanged. A different $C_{index}$ results for each subarea. This technique can help to justify the use of different sampling densities within subareas of $A_c$.

## 2.5 Sampling Design

A properly processed composite sample that is comprised of $\underline{n}$ specimens, collected from within $A_c$ from node locations of a randomly oriented grid or from random locations, is an effective and cost efficient method to represent large numbers of sampling locations. Replicate composite samples that cumulatively are comprised of a total of $\underline{n}$ specimens may be used rather than a single composite sample. Use of replicate composite samples reduces the effect of analytical uncertainty on decision making and sometimes is necessary to represent a large $\underline{n}$ with manageable sample mass. Appropriate processing, including homogenization and subsampling, is required to ensure that each test aliquot is representative of the composite sample mean contaminant concentration. Fundamental Error is described by Pierre Gy and may be used to help define the minimum mass of the field sample (Pitard, 1993). An iterative process of grinding the composite sample and subsampling is often necessary to maintain fundamental error when test aliquots are expected to be small.

To evaluate the effectiveness of composite sample processing, a field spike must be introduced to each sample and the recovery (*R*) and relative percent difference (*RPD*) of the spike in subsamples determined. The spike should be added to the field sample in a manner intended to mimic a single potentially contaminated field specimen. Composite sample homogeneity is generally considered sufficient if the error introduced to decision making by inhomogeneity is less than that introduced by the laboratory analytical methodology. Hence, proper homogenization and subsampling should result in *R* and *RPD* that are statistically indistinguishable from values measured at the bench in accordance with laboratory analytical procedures. To ensure this level of quality, the recovery of the field spike should be routinely 80 percent or greater. Likewise, the *RPD* of totally independent subsamples should routinely be less than 30 percent.

It is sometimes difficult to develop a homogenization and subsampling procedure that routinely achieves the field spike *R* and *RPD* limits of 80 percent and 30 percent respectively. However, a successful procedure that is tailored to soil type and condition is always achievable. As a word of caution, *RPD*'s often misleadingly achieve the 30 percent upper limit. This is because when processing is inadequate the spiked chemical remains predominantly as a hot spot in the sample and is missed in subsampling. Therefore, it is necessary to process the sample sufficiently to ensure that both *R* and *RPD* limits are routinely achieved. A pilot study is recommended to initially evaluate a proposed homogenization and subsampling procedure and it should be repeated whenever the soil physical characteristics change in a manner than may significantly affect the process. Furthermore, field spike *R* and the *RPD* of two subsamples should be evaluated for each sample. Corrective action must be taken to improve the homogenization process if *R* or *RPD* limits are not always achieved.

## 2.6 Historical Development of the Relationship Between $\underline{n}$, $C_{max}/C_{index}$ and $C_{act}/C_{index}$

The author developed the following relationship to establish a defensible reason to sample at $N$ locations during the remedial investigation of the Krejci Dump Site (Gemperline, 1993; Gemperline, 1994; BOR, 1994).

$$N = \frac{\log(\alpha)}{\log\left(1 - 3\frac{C_{index}}{C_{max}}\left(1 - \frac{C_d}{C_{max}}\right)^2\right)} \qquad (2)$$

$C_d$ is the reporting limit of the screening or laboratory procedure.

Equation 2 estimates the number of discrete samples ($N$) required to provide a 1- α probability that at least one sampling location is from within the detectable area of the *SCHS*. The equation is valid for conditions where $N$ decreases as $C_{max}$ approaches $C_{index}$. This condition is satisfied when $C_d/C_{index}$ is less than 4/9 (Gemperline, 1994). Application also requires that the detectable hot spot area must also be less than or equal to the Site area.

Equation 2 was developed to indicate the possible presence of the *SCHS* using field screening methods, primarily for the purpose of having a defensible reason for selecting $N$. However, there are several shortcomings to this approach. First, any quantifiable concentration would indicate the possible presence of the *SCHS*. Second, the rate of false positive decisions cannot be established or easily controlled. Third, $C_d$'s for field screening methods were often much higher than risk-based remediation goals and therefore they cannot be used to characterize large low concentration consequential hot spots. Fourth, the numbers of samples required to ensure one sampled location was from within the *SCHS* were sometimes very large. Finally, the smallest consequential hot spot may be discontinuous, so finding a discrete location with an elevated concentration may erroneously be interpreted as indicating a *SCHS* location.

A risk-based composite sampling methodology was developed to overcome the above problems. The approach uses low detection limit laboratory methods and requires a user selected action level, $C_{act}$. $C_{act}$ is both greater than the method quantitation limit and less than the concentration indicative of unacceptable risk, $C_{index}$. Furthermore, it combines specimens collected at $\underline{n}$ locations into a single composite sample. Consequently, rather than estimating the mean concentration for purposes of risk assessment by mathematically averaging discrete measurements, it used mechanical homogenization to create a uniform concentration representative of the mean. This approach helps alleviate the problems discussed in the previous paragraph. First, quantifiable concentrations exceeding $C_{act}$ , rather than the mere detection of contaminant, will indicate the possible presence of the *SCHS*. Second, the rate of false positive decisions can be controlled by adjusting the proximity of $C_{act}$ to $C_{index}$. Third, the use of analytical methods that have reporting limits less than $C_{act}$ would reasonably ensure characterization of large low concentration consequential hot spots. Fourth, the number of analytical samples is greatly reduced because the locations are not individually sampled and tested. Finally, the composite nature of the sample eliminates the possibility that measured contaminant concentration at a discrete location is misinterpreted as being unique.

The potential discontinuous nature of the *SCHS* is important because it helps to explain this methods indifference to random sampling and grid sampling. The selection of samples from the nodes of a randomly created grid is nearly as effective a design as random location selection for application of the concepts presented in this paper. Until now the *SCHS* has been portrayed as shown on Figure 1, a circle with the concentration decreasing with increasing distance from its center. Figures 1a, 1b and 1c all represent the same Site contaminant distribution. A truncated histogram depicting the site distribution is shown on Figure 1d.The contaminant concentration is portrayed as decreasing linearly from red to green, except for Figure 1c. On Figure 1c the contaminant concentration is portrayed as decreasing from red to blue.

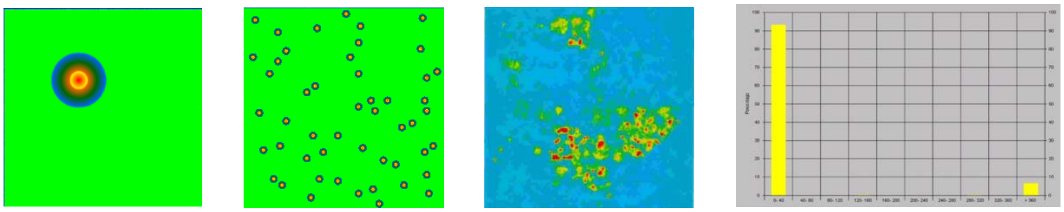
(a) (b) (c) (d)

*Figure 1. SCHS* a) Continuous, b) Discontinuous, c) Discontinuous, d) Truncated contaminant distribution

Grid sampling and random sampling are expected to be equally effective at characterizing randomly distributed contamination and contiguous contamination respectively. The nature of the *SCHS* distribution about the site is unknown. Hence, either grid or random sampling is applicable for the purposes of the method presented in this paper.

The relationship between $n$, $C_{index}$, $C_{act}$, and $C_{max}$ presented in Table 1 were determined by computer simulation of sampling events. The computer algorithm simulated an *SCHS* that is completely defined by $C_{max}/C_{index}$ with a distribution characterized as a circular hot spot with concentration decreasing linearly from its center. Five thousand computer simulated sampling events using increasingly larger $\underline{n}$ were performed to calculate $C_{ave}/C_{index}$ for each combination of $C_{max}/C_{index}$ and $C_{act}/C_{index}$. The lowest value of $\underline{n}$ that resulted in 50 percent or more $C_{ave}/C_{index}$ exceedances of $C_{act}/C_{index}$ were determined for each $C_{max}/C_{index}$. Equation 1 was fit to the results of computer simulations. Table 1 represents the values calculated using Equation 1, adjusted to indicate a maximum of two significant digits. Equation 1 and the values in Table 1 estimate $\underline{n}$ with sufficient accuracy for general application.

## 3. RESULTS

Three example applications of Table 1 are provided in this section. For simplicity, the contaminant of concern for all examples are PCBs. Examples 1 and 2 use the author's experiences at the Krejci Dump Site, a former municipal and industrial dump, to calculate $\underline{n}$ for site remediation and cleanup verification respectively. Example 3 describes selection of $\underline{n}$ applicable to either characterization or cleanup verification at a former power substation.

### 3.1 Example 1: Krejci Dump Site Remedial Investigation – 1990 Through 1996

An early version of the process just described, Risk-Based Composite Sampling, was applied to determine the number of sampling locations required to characterize surface soil (depth = 2 inches) at the Krejci Dump Site (BOR, 1994; Gemperline, 1993; Gemperline, 1994). The following applies Table 1 to select $\underline{n}$.

### *Background:*

The roughly 186,000 $m^2$ site is a former municipal and industrial dump and salvage located within the Cuyahoga Valley National Park in Summit County, Ohio, USA. The United States purchased the land in 1980 for management by the Department of the Interior National Park Service (NPS) and all dumping operations ceased. In 1987, it was determined that the Site constituted a threat to human health and the environment. In response to this determination, the U.S. Environmental Protection Agency (EPA) initiated an emergency removal beginning in June 1987. In November 1988, NPS completed the removal of wastes staged during the initial EPA activity, as well as the removal of some unconsolidated wastes and contaminated soil. Large quantities of debris and potentially contaminated soil remained. A remedial investigation and feasibility study ensued.

During the years of operation, from approximately 1950 to 1980, large volumes of solid and liquid waste materials were brought to the Krejci dump, where significant quantities of hazardous substances were released to the environment as a result of open dumping, spills, leaking containers, and burning. The operational history of the Site as well as testing of previously removed waste, soil, and debris showed that dump operations had resulted in PCBs released into the environment. These releases were very likely confined to the site. Operational characteristics of the dump suggested that PCBs contamination was the result of fluid releases from electrical equipment.

The Data Quality Objective (DQO) process was employed during the planning phase of the remedial investigation (Neptune et al., 1990). Conceptual models of possible worst-case contaminant distributions were developed at this early stage and cursory human health risk assessments using available information were performed to assist with the identification of data needs (BOR, 1994). The site was divided into 12 decision units. Each decision unit represents a unique exposure area for human health risk assessment. The DQO process revealed that the need to discover and represent PCB hot spots would likely drive both the site characterization and future cleanup efforts.

Table 1, and the process that utilizes it, postdates the Krejci remedial investigation. Never-the-less, an application of the process is demonstrated in the context of original remedial investigation planning. The ensuing plan is compared to the actual plan implemented during the remedial investigation.

### *Decision:*

It is desired to not erroneously declare decision units clean with respect to total PCBs if either the *SCHS* or a greater amount of PCBs contamination is present.

### *Study Boundaries:*

- $A_c$: Each decision unit represents an anticipated human health risk assessment exposure area for which an estimate of the mean concentration is desired. Hence, $A_c$'s are individual decision units.
- The human health risk associated with site contamination at the time of the remedial investigation, 1994, is the concern. Therefore, contaminant dispersion and attenuation that will lower maximum concentrations in the future will not be considered during development of the remedial investigation plan.
- Total PCBs concentrations, expressed in units of mg/kg, is the contaminant of concern.

- It is assumed that the surface expression of subsurface contamination has higher maximum concentration.

***Inputs:***

- $C_{index}$: A cursory risk assessment suggested total PCBs concentration equal or exceeding 20 mg/kg will present an unacceptable $10^{-5}$ carcinogentic risk to human health (BOR, 1994). Hence, $C_{index}$ = 20 mg/kg. The minimally acceptable average total PCB concentration is 20 mg/kg.
- $C_{max}$: Records indicated that PCBs from transformers may have been released at various unknown locations as late as 1980. Soil saturated with transformer oil containing PCBs are expected to exhibit a soil concentration of about 100,000 mg/kg total PCBs. Contemporary literature suggests an approximately 6 year half-life, therefore it is reasonable to expect that the maximum concentration in 1994, $C_{max}$, is about 20,000 mg/kg. A considerable amount of PCB contaminated soil had been removed from the Site during the initial removal actions by the EPA and NPS during 1987 and 1988. The soil maximum total PCBs concentration measured during that period was about 8000 mg/kg. It is expectedly less than the 20,000 because only a few soil measurements were made, and consequently, the true maximum was likely missed. Hence, and $C_{max}/C_{index}$ = 1000.
- $C_{act}$ : To help avoid an erroneous declaration that the $A_c$ average does not exceed $C_{index}$ it is decided that remedial action will be required if $C_{ave}$ exceeds 2.0 mg/kg. This value is the estimated concentration that would result in an acceptable $10^{-6}$ human carcinogenic risk. Hence, $C_{act}/C_{index}$ = 0.10.
- $C_{ave}$: The average concentration for each $A_c$ will be the numerical average of quadruplicate composite sample representations. Each composite will be comprised of $\underline{n}/4$ equal volume specimens collected from within $A_c$.

***Decision Rule:***

It will be concluded that unacceptable PCBs contamination may be present if $C_{ave}$ exceeds $C_{act}$.

***Limit on Decision Error:***

The probability of an erroneous declaration that the mean $A_c$ total PCBs concentration is less than $C_{index}$, when the SVHS or greater amounts of PCBs are present, is limited to less than 0.50.

***Design:***

From Table 1, $\underline{n}$ = 250 for the condition that $C_{act}/C_{index}$ = 0.10 and $C_{max}/C_{index}$ = 1000. Therefore, quadruplicate sets of 63-specimen composite samples will be created to represent each $A_c$ . The total number of locations represented at the site will be 3024 (12 decision units x 4 samples/unit x 63 specimens/sample).

***Outcome:***

A work plan for the Remedial Investigation and Feasibility Study (RI/FS) was developed during the period 1990 through 1993 and implemented during the summers of 1994 and 1995. The approach used at that time resulted in 2520 locations being represented in sampling. Quadruplicate and sometimes octuplicate sets of composite samples were created to represent each $A_c$. Altogether, 72 composite samples were collected, processed and tested. $C_{ave}$ exceeded $C_{act}$ in eight of the twelve $A_c$'s. Remedial action was implemented to address PCB contamination in the eight exceeding $A_c$'s.

In addition to composite samples, 85 discrete surface samples were concurrently collected throughout the site, analyzed, and used to calculate $A_c$ averages. Only four of these $A_c$ averages exceeded $C_{act}$. The observation that half as many of the $A_c$ averages indicated $C_{act}$ exceedance when calculated using discrete samples indicates that discrete samples often missed consequential contamination. This conclusion is also supported by the observation that the average $A_c$ total PCBs concentration calculated using composite samples exceeded the $A_c$ average calculated using discrete samples in all but one $A_c$.

## 3.2 Example 2: Krejci Dump Site Cleanup Verification – 2005 Through 2010

***Background:***

The Krejci Dump Site Remedial Action (RA) was initiated in 2005 following several years dedicated to completing the RIFS, CERCLA litigation, and planning. The Record of Decision required, among other things, that all debris and soils containing unacceptable levels of contaminants be excavated and disposed off-site at appropriately licensed or permitted facilities. Ecological and human health risk assessments had been performed as part of the feasibility study. Risk assessments established risk-based concentration limits for each of 33 identified site contaminants of concern, $C_{index}$. Action levels, $C_{act}$, were subsequently established as remediation goals for cleanup verification.

PCBs remediation was driven by the need to protect native omnivores. The ecological risk assessment used an approximately 1000 $m^2$ area to represent the home range of a native omnivore. Hence, the site was subdivided into 186 approximately 1000 $m^2$ decision units. Ecological risk assessment established that limiting decision unit mean total PCB's concentrations to less than 0.075 mg/kg will protect individual omnivores. It was also was concluded that limiting 4000 $m^2$ area mean total PCBs to 2.5 mg/kg will sufficiently protect omnivore populations.

The following design process utilizes Equation 1 to determine $\underline{n}$. It necessarily deviates from the actual design process since Table 1 and Equation 1 were developed after this design was complete.

***Decision:***

It is desired to not erroneously declare decision units clean with respect to total PCBs if either the *SCHS* or a greater amount of PCBs contamination is present. The first priority is to protect populations of omnivores and the second priority is to protect individual omnivores.

***Study Boundaries:***

- $A_c$: Each 1000 $m^2$ decision unit represents the approximate size of the home range for the omnivore. Hence, $A_c$'s are individual 1000 $m^2$ decision units. These will be called Tier 1 $A_c$'s. Each set of four adjacent Tier 1 $A_c$'s, approximately 4000 $m^2$, represents the area associated with omnivore populations. Therefore, each set of four adjacent Tier 1 $A_c$'s represents a Tier 2 $A_c$. Hence, every Tier 1 $A_c$ has four adjacent Tier 2 $A_c$'s, each having a corner of a corner of the Tier 1 $A_c$ at its center.
- The risk associated with site contamination at the time of remediation, 2005, is the concern. Therefore, contaminant dispersion and attenuation that will lower maximum concentrations in the future will not be considered during development of the cleanup verification plan.

- Total PCBs concentrations, expressed in units of mg/kg, is the contaminant of concern.
- It is assumed that subsurface contamination will decrease with depth and the maximum concentration will always be at the ground surface.

***Inputs:***

- $C_{index}$: Ecological risk assessment indicated that an Tier 2 $A_c$ average total PCBs concentration equal or exceeding 2.5 mg/kg would present an unacceptable risk to an omnivore population. Hence, $C_{index}$ = 2.5 mg/kg.
- $C_{max}$: As in the first example, $C_{max}$ was calculated by presuming exponential decay. In this instance, the shortest period for decay is estimated to be 2005-1975 = 30 years. Assuming an initial soil concentration of 100,000 mg/kg and a contemporary published half-life of 5 years, the maximum concentration of PCB was calculated to be $C_{max}$=1563 mg/kg.
- $C_{act}$ : $C_{act}$ is 0.075 mg/kg, the value which ecological risk assessment indicated would protect individual omnivores if not exceeded as an Tier 1 $A_c$ average.
- $C_{ave}$: The Tier 1 $A_c$ mean total PCBs concentration will be represented by analysis of a single composite sample comprised of $\underline{n}$ specimens. Therefore, Tier 1 $C_{ave}$ is the composite sample total PCBs concentration. The Tier 2 $C_{ave}$ will be the average of four adjacent Tier 1 $C_{ave}$.

***Decision Rule:***

Decisions will be made for each Tier 1 $A_c$. It will be concluded that remediation is necessary if two conditions coexist. First, the Tier 1 $C_{ave}$ equals or exceeds $C_{act}$. This will be called the Tier 1 decision. Second, an associated Tier 2 $C_{ave}$ equals or exceeds $C_{act}$. This will be called the Tier 2 decision. An exceedance will result in a minimum of 150 mm of soil being excavated from all Tier 2 $A_c$'s associated with the failing Tier 1 $A_c$ and the sampling, analysis and decision process repeated. This process will iterate until remediation is no longer indicated.

***Limit on Decision Error:***

It is desired to limit to less than 0.50 the probability of an erroneous declaration that an $A_c$ mean total PCBs concentration is less than $C_{index}$ when the *SCHS* or greater amounts of PCBs are present.

***Design:***

Equation 1 is used to calculate $\underline{n}$.

$$n = \frac{1563}{2.5}\left(0.764\left[\frac{-0.102}{LN\left(\frac{.075}{2.5}\right)}\right]^{1.21} + 0.233\right)$$

This yields, $\underline{n}$ = 152.

Hence, 152 specimens are required per Tier 2 $A_c$. Therefore, it was decided that each composite sample would be created by combining 40 specimens within each $A_c$. This results in a total of 160 specimens representing all combinations of 4 adjacent $A_c$'s.

This design and decision process provides a 50 percent or better chance that action will be taken to protect omnivore populations if an *SCHS* is present in the Tier 2 $A_c$. The decision to excavate soil throughout each Tier 2 $A_c$ when an exceedance occurs in a Tier 1 $A_c$ ensures that all potentially discontinuous *SCHS* contamination is addressed.

If the decision rule were reestablished with expressed intent to protect individual omnivores, $C_{index}$ must be 0.75 mg/kg, $C_{act}$ selected to be less than $C_{index}$, and $\underline{n}$ determined for each Tier 1 $A_c$. Then, remedial action would be required if $C_{ave}$ exceeds $C_{act}$ in a Tier 1 $A_c$. The determination of $\underline{n}$ is left as an exercise for the reader.

***Outcome:***

The plan implemented at the Krejci Dump Site for Cleanup Verification resulted in 40 specimen composite samples being created to represent each Tier 1 $A_{c.}$ Any Tier 1 $A_c$ exceeding 0.75 mg/kg total PCBs was excavated a minimum of 150 mm. This process of sampling, decision making and remediation was repeated until remediation was no longer indicated. Remediation began in 2005 and was completed in 2012.

## 3.3 Example 3: Power Substation

***Problem:***

The site of a former power substation is to be developed into ¼-acre residential lots. The substation operated between 1955 and 1975 and transformer oil containing PCB’s may have been released during this period. The most recent release would have been at least 40 years ago.

***Decision:***

It is desired to not erroneously declare any residential-size lot clean if PCBs are present in sufficient quantity to present an unacceptable risk to human health.

***Study Boundaries:***

For the purpose of site characterization, the site is subdivided into approximately ¼-acre areas to mimic future residential lots. Due to the low mobility of PCBs, the highest concentrations would expectedly be near surface soils. Therefore, the upper six inches of soil in each ¼- acre subarea represents $A_c$.

***Inputs:***

- $C_{index}$: The minimally acceptable average total PCB concentration is 2.0 mg/kg and represents a $10^{-5}$ human health risk.
- $C_{max}$: A reasonable maximum total PCBs concentration is estimated to be 390 mg/kg. This is determined by assuming exponential decay over a 40 year period, using a half-life of 5 years obtained from literature, and estimating soil concentration at the time of release to be 100,000 mg/kg. $C_{max}/C_{index} = 195$.

***Decision Rule:***

It will be concluded that unacceptable PCBs contamination may be present if the average total PCBs concentration, $C_{ave}$ exceeds $C_{act} = 0.2$ mg/kg. A residential-size lot having this average concentration is estimated to present a$10^{-6}$ carcinogenic risk. $C_{act}/C_{index} = 0.10$.

***Limit on Decision Error:***

The probability of erroneously declaring a residential-size lot clean when the *SCHS* is present must be less than 50 percent.

***Design:***

The approximate minimum number of specimens per sample, $\underline{n}$ = 49, is calculated using Equation 1.

$$n = \frac{390}{2.0}\left(0.764\left[\frac{-0.102}{LN\left(\frac{0.2}{2.0}\right)}\right]^{1.21} + 0.233\right)$$

Four 4 x 4 grids will be used to simplify specimen collection. Each ¼-acre subarea will be represented by quadruplicate composite samples comprised of specimens collected at the nodes of four independent 4 x 4 grids. Hence, each composite sample will be created by combining 16 equal mass soil specimens. The total number of locations represented in each residential-size lot is 94, acceptably more than the 49 needed. Each grid will have a random origin and orientation. Each specimen will represent the upper six inches of soil. $C_{ave}$ for each ¼-acre subarea will be calculated and compared to $C_{act}$ and the decision rule applied.

***Discussion:***

$C_{index}$ is the user controlled variable having the greatest impact on the required $\underline{n}$. For example, the same analysis using $C_{index}$ = 10 mg/kg results in $\underline{n}$ = 10; if $C_{index}$ = .25 mg/kg, $\underline{n}$ = 826.

The 4 x 4 grid is chosen because it is simple to establish in the field and in quadruplicate results in more than the minimum $\underline{n}$. The use of quadruplicate representations helps to minimize laboratory measurement uncertainties associated with imprecision.

Each composite sample will be field spiked with sufficient potassium nitrate, $KNO_3$, to cause the average composite concentration to be 50 mg/kg. It has been predetermined that that measurements of nitrate + nitrite as N for this $NO_3^-$ spike concentration is about 20 times greater than that of similar measurements on native site soil. The liquid volume of $KNO_3$ solution introduced to the sample as the spike will be approximately equal to the estimated volume of pore space in one in situ specimen volume. The intent is to mimic a contaminated specimen so that recovery and RPD will reflect the effectiveness of the homogenization process at the appropriate scale.

Prior to the start of sampling, a pilot study will be performed using site soil to evaluate the homogenization effectiveness of the proposed sample processing procedure. The procedure will be adjusted during this study to reasonably ensure that recovery of $NO_3^-$ (nitrogen as nitrate analysis) will routinely exceed 80 percent and the RPD of duplicates will routinely be less than 30 percent.

Recovery and RPD will be determined for independent duplicate aliquots obtained from each composite sample. Action will be taken to change the sample processing procedure if recovery is ever found to be less than 80 percent or RPD is ever greater than 30 percent.

## 4. DISCUSSION AND CONCLUSION

Contamination in an abundance that is sufficient to cause the average concentration of a soil mass or a surface area to exceed a remediation goal or regulatory standard is herein termed consequential contamination. The most common approach to sample plan design inherently assumes that the absence of discovered contamination is sufficient evidence to conclude the absence of consequential contamination. This assumption is indefensible if it can be reasoned that consequential contamination might exist between sampling locations. Small areas of discontinuous contamination, e.g. hot spots, would reasonably be expected at uncontrolled dump sites, when defining the spatial limits of contamination at any site, and when determining the effectiveness of a cleanup that relies on excavation and removal of contaminated soil. In these instances, it is prudent that both soil characterization and rules for decision making minimally ensure a greater than 50 percent chance of responding to the reasonably conceivable smallest hot spot of consequential contamination. An approach to create, evaluate and defend sample plan designs for these and similar situations is described and examples presented.

The method may be used to determine minimum sampling requirements for either composite sampling or discrete sampling. When composite samples are used, extreme care must be taken to ensure that sample processing results in every potential test aliquot representing the mean composition of the sample. Quality control should include a field spike that is introduced prior to sample processing and that mimics a single contaminated soil specimen. Inadequate composite processing is indicated by any failure to achieve 80 percent recovery, or any field spike RPD calculation indicating an exceedance of 30 percent.

The number of locations that must be represented, $\underline{n}$, increases with increasing $C_{act}$ and decreasing $C_{index}$. $C_{index}$ is the user controlled variable having the greatest impact on the required $\underline{n}$. $C_{act}$ may be increased as needed to reduce the likelihood of an erroneous declaration that consequential contamination may be present.

PCBs are the only contaminant discussed in the examples presented herein. However, the method is applicable to any contaminant. Also, only sites of uncontrolled chemical releases are presented in examples. However, the method is applicable for other situations. It has been used to aid in the design of pilot studies, site assessments, radiological screening, compost evaluations, and truckload waste disposal compliance. The method may also have application in the food sampling industry where bacterial or chemical contamination expectedly occurs in hot spots.

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# TRICHLOROETHYLENE IN INDOOR AIR: TO-15 SUMMA DATA VS HAPSITE DATA

*East Coast Conference, October 2016*

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## ABSTRACT

How do Human Health Risk Assessment (HHRA) calculations based on validated 8 hour time-weighted summa canister data differ from HHRA calculations based on chemist-reviewed HAPSITE grab samples? Collection of time-weighted indoor air samples using summa canisters has been considered by many as a “gold standard” approach, and is currently the most commonly used technique for identifying indoor air impacts and informing associated HHRAs. The availability of canisters and the cost of the sampling and laboratory analysis often limit sampling frequency. Consequently, there are concerns about the representative nature of samples collected on monthly, quarterly, or even a semi-annual basis, given the potential temporal variability (per day, and day to day) in vapor intrusion impacted indoor air.

We compare and contrast air monitoring data collected over a one-year time period in multiple commercial buildings at a single site in the United States sampled with infrequent summa canisters against daily grab samples. Indoor air quality is characterized for trichloroethylene (TCE) for both types of data: 1) semi-annual 8 hour summa canister samples with Method TO-15 or equivalent laboratory analysis; and 2) daily 2 minute grab samples collected and analyzed with HAPSITE portable gas chromatograph with mass spectral detector (GC/MS). We outline the approaches taken and rationale behind collection of both datasets, the methods employed, and the interpretation of the results.

Will the variability of the analytical data for two simultaneous monitoring efforts show a similar story? The characteristics of the two data sets (range, central tendency, and 95% Upper Confidence Limit on the mean) are compared, and the variability of TCE concentrations and the associated implications for risk characterization, particularly for sensitive receptors, are analyzed and discussed. The utility of HAPSITE data for vapor intrusion investigation and risk assessment is discussed.

**Keywords**: indoor air, trichloroethylene, time-weighted, grab sample, risk assessment

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# 1. INTRODUCTION

To evaluate health risk from breathing volatile organic compounds (VOCs) in indoor air, contaminant concentrations must be characterized over the period of human exposure. The USEPA OSWER vapor intrusion guidance recommends ‘several rounds of sampling’ and ‘time-integrated sampling methods’ to ensure that the data is representative of reasonable maximum concentrations and the temporal variability is understood (USEPA, 2015a). Long duration sample collection methods are available, estimating average concentrations over several days or weeks (Odencrantz et al., 2009). However, estimates of continuous duration concentrations (24 h) may not be appropriate for assessing occupational exposure (8 h). Concentrations in commercial buildings may vary widely over the course of the diurnal cycle (Hartman, 2016 [In Press]), as ventilation requirements are only applicable when buildings are occupied (ANSI/ASHRAE, 2016). Lower ventilation rates generally increase levels of indoor air contaminants and associated health hazards (Shields, 2000; Sundell et al., 2011). Therefore, including concentrations captured during periods of minimal ventilation when buildings are unoccupied in the estimate of average exposure does not result in an accurate risk evaluation for an occupational scenario. Reconciling the available data collection methods with real-world exposure scenarios presents a challenge for accurate characterization of long-term commercial worker exposure.

The study site is a federal government research facility: Cold Regions Research and Engineering Laboratory (CRREL) Post, located in Hanover, New Hampshire. A comprehensive vapor intrusion investigation was initiated in 2010 and remains ongoing. Two different collection and analytical methods have been employed at the site, which supported a supplemental chronic human health risk assessment for post-mitigation (current) conditions at the facility. This assessment was a follow-up to a CERCLA-compliant baseline human health risk assessment. The facility includes multiple buildings, the largest of which is the Main Laboratory Building, a four-story structure, with about 100 employees typically present working both part-time and full time, primarily during a day time shift. This building houses several types of activities and the occupied spaces are offices, conference rooms, laboratories, cold rooms used for experimentation, maintenance rooms, workshops, and a cafeteria.

Starting in 2010, the investigations into indoor air at CRREL applied one of the leading approaches to collect data for the characterization of occupational exposure to VOCs in indoor air. This method entails the collection of time-weighted indoor air samples using evacuated passivated stainless steel canisters fitted with 8 h flow controllers and laboratory analysis with gas chromatography/mass spectrometry (GC/MS) by Method TO-15 (USEPA, 1999; USEPA, 2015a). This collection and analysis method is referred to as “8 h TWA TO-15” for the rest of the paper. Collection of whole air using steel canisters is one of the more expensive sampling methods (Camel and Caude, 1995). Cost is a key consideration for developing sampling programs, which aim to find representative results with the minimum number of samples (Schneider, 1999). Consequently, long-term programs utilizing steel canisters typically sample once every 3, 6, or 12 months (Folkes et al., 2009), which do not capture variability between sampling rounds and may miss important short term variations, such as those associated with changes in atmospheric pressure (USEPA, 2012; Holton et al., 2013; Johnston and Gibson, 2014).

An alternative approach to 8 h TWA TO-15 is collecting and analyzing a series of short duration field samples with a portable GC/MS. This approach was initiated at CRREL in 2012, and allows for very short sample collection and analysis times (one minute grab sample analyzed per 10 minute period). This sampling and analysis method is referred to as “grab portable GC/MS” throughout this paper. The rapid on-site collection and analysis allows a higher sampling density and frequency than 8 h TWA TO-15, resulting in an improved understanding of the site (USEPA, 2002). Low detection limits (typically around 1 ug/m$^3$) are also achievable. The portable GS/MS has been used successfully to collect data when the goal is to investigate the underlying source of VOCs, such as consumer products in a home (Gorder and Dettenmaier, 2011). Use of Portable GS/MS for long-term monitoring is still uncommon, but appears to be increasing in frequency, as it has great potential to improve site-specific understanding of temporal and spatial variability of concentrations (Holton et al., 2013; Hartman, 2016 [In Press]).

In this study, data was collected using both 8 h TWA TO-15 and grab portable GC/MS methods in parallel, and parallel indoor air occupational health risk assessments have been performed using the results. Risk assessments aim to quantify the risk of cancer or other adverse effects from exposure to potentially toxic substances, thereby providing a scientific basis to inform environmental risk management decisions (NRC, 1983; NRC, 2009). The typical risk assessment framework is conducted in four phases: 1) hazard identification, 2) dose response, 3) exposure assessment, and 4) risk characterization (USEPA, 1989). In the fourth step, hazard quotients (HQ) and excess lifetime cancer risks (ELCR) are calculated and compared to reference levels identified by USEPA to assess the need for mitigation or remediation (USEPA, 1989).

This study focuses on one halogenated solvent known to have been released at the site and impacting the main laboratory building through vapor intrusion: trichloroethylene (TCE). Characterizing indoor air exposure effectively is particularly important for TCE, due to the complexity of evaluating risk and hazard for this chemical (Chiu et al., 2006). Risk assessments typically evaluate chronic health effects by combining conservative estimates of average concentrations for the period of long-term exposure with unit cancer risk probabilities and chronic reference concentrations (RfCs) (USEPA, 1989). However, TCE is unique in that the chronic RfC (2 ug/m$^3$) is based on two different endpoints (immune system and developmental effects) (USEPA, 2011). The chronic TCE threshold for occupational exposure to indoor air associated with target HQ=1 (8.8 µg/m$^3$) is calculated assuming an 8 hour exposure for 5 workdays each week (USEPA, 2016b). The traditional chronic risk assessment does not address questions about short-term TCE concentration excursions above the occupational exposure threshold and the likelihood of developmental effects occurring.

There are various positions taken on the assessment of acute exposure to TCE during the gestational period, with some guidance suggesting that a single exposure of a developmental toxicant during the critical period may cause an adverse effect (implying a maximum indoor air concentration be used to evaluate non-cancer hazard) (USEPA, 1989). However, none of the USEPA guidance published concurrent with the 2011 revision of the inhalation RfC for TCE addressed the issue of quantifying acute exposure directly (USEPA, 2015b; USEPA, 2016a). Therefore, it is uncertain for situations where an average exposure is less than the threshold (8.8 ug/m$^3$), whether the frequency and magnitude of individual TCE concentrations (or clusters of concentrations) greater than the threshold might impact the likelihood of an adverse developmental effect. Conducting daily grab portable GC/MS monitoring may help to account for this unknown by providing valuable information on short-term variability, which can inform short-term mitigation decisions.

The purpose of this study is to compare two datasets collected in parallel by two different sampling/analytical methods (8 h TWA TO-15 and grab portable GC/MS), and the associated parallel risk assessment results, to identify strengths and weaknesses of each method and inform an opinion concerning the utility of portable GC/MS indoor air data in the human health risk assessment process. Some of the major sources of uncertainty and limitations are also discussed.

## 2. MATERIAL AND METHODS

The dataset selected for this study is limited to data collected following mitigation activities, including deployment of Healthmate® air filtration units, which remove VOCs directly from indoor air, and installation of sub-slab depressurization systems (SSDS) that limit the potential for VOCs in subsurface soil gas to migrate into indoor air. The sampling program was planned and conducted using industry best practice for each method of sampling and analysis.

### 2.1 Sampling and Analysis

Sampling was performed in the Main Laboratory Building of the CRREL Post located in Hanover, New Hampshire. Data was collected at ten exposure areas within the Main Laboratory Building, which is approximately 4,700 $m^2$. This facility is positioned on the side of a hill, creating a partial basement (southeast) and partial slab-on-grade (northwest) scenario. The exposure areas are defined by the geographic location, the level of the building, and the area as defined by specific structures on the lowest levels of the building (sub-basement in the west area and one large room in the basement in the north area). The West and North areas have fully operational SSDS in place. The south area is defined as the remaining space in the building. Exposure areas are: North B, North 1, North 2, South B, South 1, South 2, West SB, West B, West 1, and West 2 as illustrated in Figure 1.

*Figure 1*. Main Lab: 10 exposure areas. The West areas are approximately 850 $m^2$, the North areas are approximately 700 $m^2$, and the South areas are approximately 3,100 $m^2$

Analytical data has been evaluated for indoor air collected in steel canisters and analyzed by Method TO-15, and collected and analyzed with portable GC/MS over 11 months between October 2, 2014 and August 20, 2015.

*Method 1 – 8 h TWA TO-15*: The evacuated steel canisters used in this study were SUMMA® canisters, equipped with 8-hour flow controllers. Whole air canister sampling is the most commonly used method for air sampling (Wu, 2009), and the simplest (Camel and Caude, 1995). All indoor air samples were collected in the breathing zone (approximately 4 ft above floor level). The canisters were analyzed in an off-site laboratory using USEPA Method TO-15, which is one of the most commonly applied indoor air VOC analytical methods used to monitor individuals in the workplace (Wang and Austin, 2006a; Wang and Austin, 2006b). Collection of 8 h TWA TO-15 samples and subsequent analysis in a fixed laboratory followed USEPA protocol (USEPA, 1999), and project-specific QA/QC procedures.

*Method 2 – Grab Portable GC/MS*: The Portable GC/MS used in this study is called a Hazardous Air Pollutants on Site (HAPSITE) (Inficon, Syracuse, NY, USA), which was run in the selected ion monitoring (SIM) mode for TCE only. Samples were collected using grab methodology, over one minute intervals. All samples were collected in the breathing zone. Collection and analysis of grab portable GC/MS samples followed USEPA protocol (USEPA, 2004), and project-specific QA/QC procedures.

Meteorological conditions were recorded at the time of sampling, including the temperature and pressure. Additional meteorological data including temperature, wind speed, pressure, and precipitation has been collated as recorded at Lebanon Airport (The Weather Company© LLC, 2016). The Lebanon meteorological covariates were evaluated for correlation with detected TCE concentrations using regression modelling and analysis of variance (ANOVA) in R (R Core

Team, 2016). Regression diagnostics were performed and found to improve with log-transformation of the detected results. Therefore, log-transformation of detected concentrations was conducted prior to statistical evaluation of covariates.

## 2.2 Evaluation of Data Sets

Each sample was allocated to a specific exposure area based on the building, floor, and room number of the collection point. Any samples not representative of the breathing zone, not meeting QA/QC protocols, or impacted by a current known release of TCE in the building, were removed from the dataset.

Field duplicate samples collected as part of the quality assurance plan were resolved prior to statistical evaluation. For 8 h TWA TO-15 data a detected concentration in a field duplicate was averaged with the corresponding detected concentration in the field sample. In cases where only the field sample or field duplicate had a detected concentration, the detected result was selected. If results from the field sample and the field duplicate were below the limit of detection, then the lower detection limit was selected. Results obtained by the portable GC/MS required an additional resolution step because in several cases, multiple samples were collected at one location per day. These results were averaged following the same process, after resolution of field duplicates to obtain one sample per sample location per day. For the purpose of statistics used to prepare the figures, detection limits for non-detect compounds were used as surrogates for detected results.

The processed data was used in the calculation of summary statistics per exposure area. Several statistics were calculated for each dataset: the maximum, minimum, and mean detected concentration, the frequency of detection, the standard error, range of reporting limits for non-detects and the mean calculated using detection limits of non-detect results as a surrogate for detected concentrations. Statistics are compared per area. The processed 8 h TWA TO-15 and grab portable GC/MS data were also evaluated with respect to relationships with meteorological conditions.

## 2.3 Risk Characterization

Although the nature of the samples (time-weighted composites (8 h TWA TO-15) vs one-minute grab samples (grab portable GC/MS)) is different, both data sets are evaluated in the Human Health Risk Assessment (HHRA) for occupational inhalation exposure using the same methodology. The risk assessment was conducted using USEPA methodology (USEPA, 1989) and other relevant guidance documents (USEPA, 2015a; USEPA, 2014; US DoD, 2009).

The first stage of risk assessment is hazard identification, which entails identifying the specific hazard to be addressed. This has been partly discussed within the Sampling and Analysis and Evaluation of Data Sets sections. Ten exposure points were defined, and the data was collected and evaluated as discussed. To complete the hazard identification step, the maximum concentrations were compared to the USEPA ambient air regional screening level (RSL) for a worker scenario based on non-carcinogenic effects with a target HQ of 0.1 (the standard screening level approach to account for potential cumulative effects from multiple compounds): 0.88 ug/m$^3$ (USEPA, 2016b). This initial screening value is also protective of carcinogenic effects associated with a cancer risk of $1x10^{-6}$ (3.0 ug/$m^3$). Exposure points with at least one maximum value > 0.88 ug/$m^3$ were carried through the risk assessment.

The second stage of risk assessment is dose response, which entails the collation of chemical-specific information specific to TCE. The toxicity values from IRIS represent the current values at the time of publication, updated in 2011 (USEPA, 2011; USEPA, 2016a). The chronic inhalation RfC for TCE is 2 µg/$m^3$. The inhalation URF for TCE is 4.1 $x10^{-6}$ (µg/$m^3$)$^{-1}$.

The third stage of risk assessment is exposure assessment, which entails the collation of exposure information specific to the selected receptors, which are indoor workers in a northern temperate climate. The majority of exposure assumptions were obtained from USEPA (2014). Also included in stage three is the calculation of exposure point concentrations (EPC). EPCs were calculated for each exposure area with at least one detection > 0.88 µg/$m^3$. If no detections were > 0.88 µg/$m^3$, risk was considered negligible for the area and no EPCs were calculated. EPC calculations select the lower of the recommended 95% UCL calculated with ProUCL software (ProUCL 5.0) (USEPA, 2013) and the maximum detected result.

The EPC and the exposure information are combined into an average daily exposure (ADE) (Equation 1), which averages the chronic daily exposure concentration over the exposure period (USEPA, 2009; note ADE as used here, is referred to as “exposure concentration” in Equation 8 within USEPA, 2009). ADE in µg/$m^3$ is calculated according to the following equation:

$$ADE = (EPC * ED * EF * ET) / (AT * CF) \qquad (1)$$

where EPC is the concentration of TCE in air per exposure area (µg/$m^3$); ED exposure duration (25 years); EF exposure frequency (250 days/year); ET exposure time (8 hours/day); AT averaging time (for carcinogens, AT = 70 years * 365 days per year; for noncarcinogens, AT = ED * 365 days per year); and CF conversion factor (24 hours/day).

The fourth stage of risk assessment is risk characterization, which entails the combination of the dose response and exposure assessment steps to calculate risks. Both cancer risk and non-cancer hazard have been calculated. Cancer risk is expressed as excess lifetime cancer risk (ELCR) (Equation 2). ELCR is the product of the ADE and potency of a carcinogenic substance: unit risk factor (URF). Non-cancer hazard is expressed as a hazard index (HI) (Equation 3). The HI is the quotient of the chronic ADE and the potency of the non-cancer substance: RfC.

The risk assessment equations are:

$$ELCR = ADE * URF \qquad (2)$$

$$HQ = ADE / RfC \qquad (3)$$

## 3. RESULTS

Between October 2, 2014 and August 20, 2015, 3813 indoor air samples were collected by grab portable GC/MS in 10 exposure areas within the Main Laboratory Building and the associated data were selected for use in this study. During the same timeframe, 41 indoor air samples were collected by 8 h TWA TO-15 and selected for use. Portable GC/MS samples were collected during each work day between October 3rd and August 12th. 8 h TWA TO-15 samples were collected during two sampling events on March 12 and August 20. The number of samples is higher for both methods than the recommended number of VOC samples to characterize indoor air in large office buildings (USEPA, 2003). Figure 2 shows the large difference in quantity of data available between the non-baseline 8 h TWA TO-15 and grab portable GC/MS datasets in the Main Laboratory Building. The maximum TCE concentrations and the range of TCE concentrations were highest in the South area, where no SSDS system is operating.

The range of detected concentrations is greater for the portable GC/MS data than for the 8 h TWA TO-15 data. EPCs were calculated for all 10 exposure areas for the portable GC/MS dataset. EPCs were only calculated for 5 of the 10 exposure areas for the 8 h TWA TO-15 data, as maximum concentrations in the remaining 5 areas were < 0.88 µg/m$^3$, indicating negligible risk. The EPCs are similar, but overall slightly higher for portable GC/MS data. The comparison between the ranges of the two data sets is shown on Figure 3. Table 1 provides a comparison of the summary statistics and calculated EPCs.

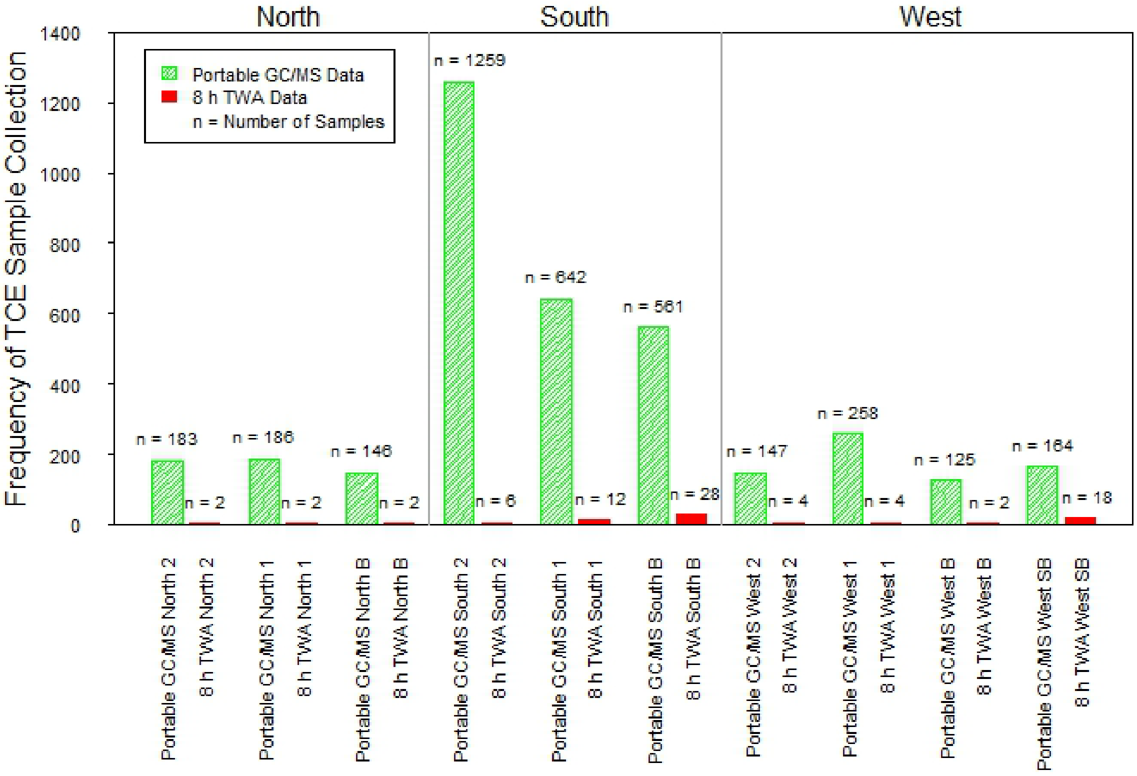

*Figure 2.* Sample frequency per exposure area

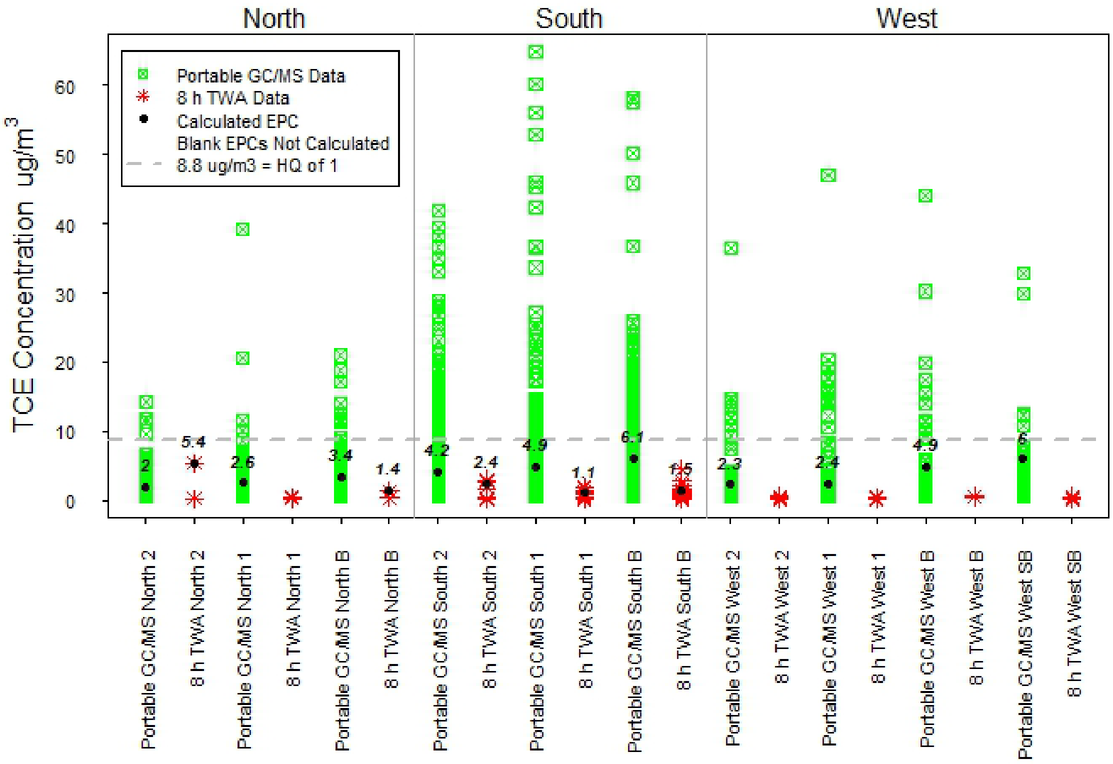

*Figure 3.* Comparison of processed data and calculated EPCs per exposure area

*Table 1.* TCE summary statistics for both datasets per exposure area (µg/m$^3$): J indicates detected value is estimated; -- indicates no EPC calculated due to negligible risk

| Exposure Area | Sample Method | Frequency of Detection | Minimum Detected | Maximum Detected | Mean Detected | Calculated EPC |
|---|---|---|---|---|---|---|
| North - Basement | 8 h TWA TO-15 | 2 / 2 | 0.36 J | 1.3 | 0.8 | 1.3 |
| | Grab Portable GC/MS | 135 / 151 | 0.54 | 21 | 3.2 | 3.4 |
| North - Level 1 | 8 h TWA TO-15 | 1 / 2 | 0.53 J | 0.53 J | 0.5 | -- |
| | Grab Portable GC/MS | 154 / 193 | 0.59 | 39 J | 2.6 | 2.6 |
| North - Level 2 | 8 h TWA TO-15 | 2 / 2 | 0.22 J | 5.4 | 2.8 | 5.4 |
| | Grab Portable GC/MS | 148 / 191 | 0.54 | 14 | 2.1 | 2.0 |
| South - Basement | 8 h TWA TO-15 | 28 / 28 | 0.15 J | 4.5 | 1.1 | 1.5 |
| | Grab Portable GC/MS | 488 / 574 | 0.54 | 58 J | 5.6 | 6.1 |
| South - Level 1 | 8 h TWA TO-15 | 12 / 12 | 0.18 J | 2.0 | 0.8 | 1.1 |
| | Grab Portable GC/MS | 522 / 667 | 0.54 | 65 | 4.6 | 4.9 |
| South - Level 2 | 8 h TWA TO-15 | 6 / 6 | 0.12 J | 3.0 | 1.4 | 2.4 |
| | Grab Portable GC/MS | 1164 / 1335 | 0.54 | 42 | 4.5 | 4.2 |
| West - Sub-Basement | 8 h TWA TO-15 | 18 / 18 | 0.13 J | 0.54 J | 0.3 | -- |
| | Grab Portable GC/MS | 111 / 169 | 0.55 | 33 | 2.7 | 2.5 |
| West - Basement | 8 h TWA TO-15 | 2 / 2 | 0.48 J | 0.59 | 0.5 | -- |
| | Grab Portable GC/MS | 73 / 125 | 0.55 | 44 | 4.1 | 4.9 |
| West - Level 1 | 8 h TWA TO-15 | 4 / 4 | 0.20 J | 0.42 J | 0.3 | -- |
| | Grab Portable GC/MS | 102 / 259 | 0.54 | 47 | 4.0 | 2.4 |
| West - Level 2 | 8 h TWA | 4 / 4 | 0.17 J | 0.64 | 0.34 | -- |
| | Grab Portable GC/MS | 55 / 149 | 0.56 | 36 J | 3.8 | 2.3 |

South 1, the area with the highest grab portable GC/MS detected concentration of TCE in indoor air (64.8 µg/m$^3$), had an EPC of less than 8.8 µg/m$^3$ (concentration associated HQ = 1 for chronic exposure). Approximately 10% of the detected concentrations (63 out of 667 samples) were above 8.8 µg/m$^3$. Due to multiple sample collection within one area per day, individual concentrations were above 8.8 µg/m$^3$ for 45 days out of the total exposure period. The maximum detected result is about 7 times higher than the level associated with an HQ of 1. The maximum TCE concentrations and the range of TCE concentrations were lower in the Main Laboratory North Area and West Area where fully operational SSDSs were in place.

As illustrated in Figure 4, the standard error is generally much larger for the 8 h TWA TO-15 data, indicating that the 8 h TWA TO-15 means (though similar to the grab portable GC/MS means) provide a much less accurate representation of the mean than do the grab GC/MS TO-15 data.

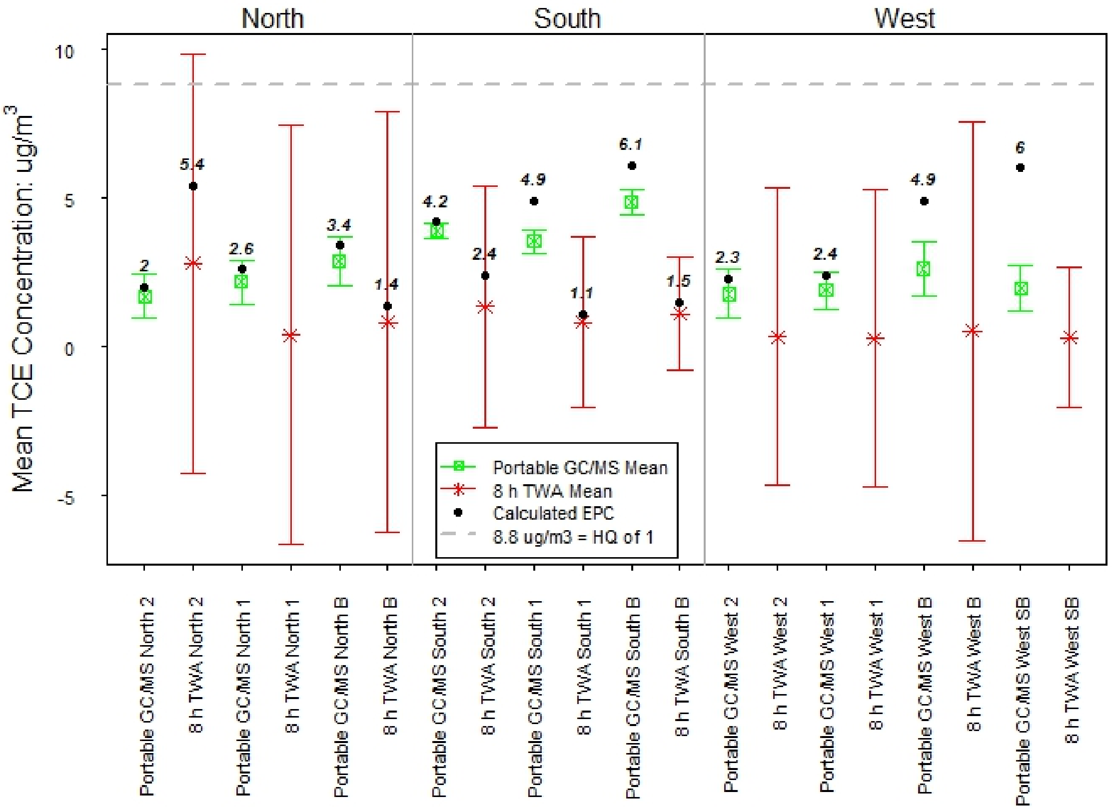

*Figure 4.* Comparison of means with standard error and EPCs per exposure area

As illustrated in Figure 5, the results of the linear regression show that a relationship exists between two meterological covariates and TCE concentration: 1) TCE concentration increases as outdoor pressure drops, and 2) TCE concentration increases as outdoor temperature increases. The same relationships between TCE concentration and meterological covariates is present in both parallel datasets. The relationship appears visually more pronounced in the 8 h TWA TO-15, but due to the amount of data collected by the grab portable GC/MS data, the grab dataset is more accurate and more statistically significant.

This test statistic (F Value) evaluates whether the reduction in variance is significant (representing a real relationship in the data), or may be explained by sampling variability, indicating that no relationship exists. The probability that this decision is wrong (Type I error) is very small for both relationships in both datasets ($P < 0.001$). The probablity of rejecting the null hypothesis incorrectly (Type II error) is very low for both meterological covariates in the grab portable GC/MS data: $< 2.2\text{x}10^{-16}$. The relationship was slightly less significant using the 8 h TWA TO-15 data, with F values of $8 \text{ x } 10^{-6}$ for the relationship of both covariates to TCE concentration. A graph of the sample results for the grab portable GC/MS data over time is shown on Figure 6.

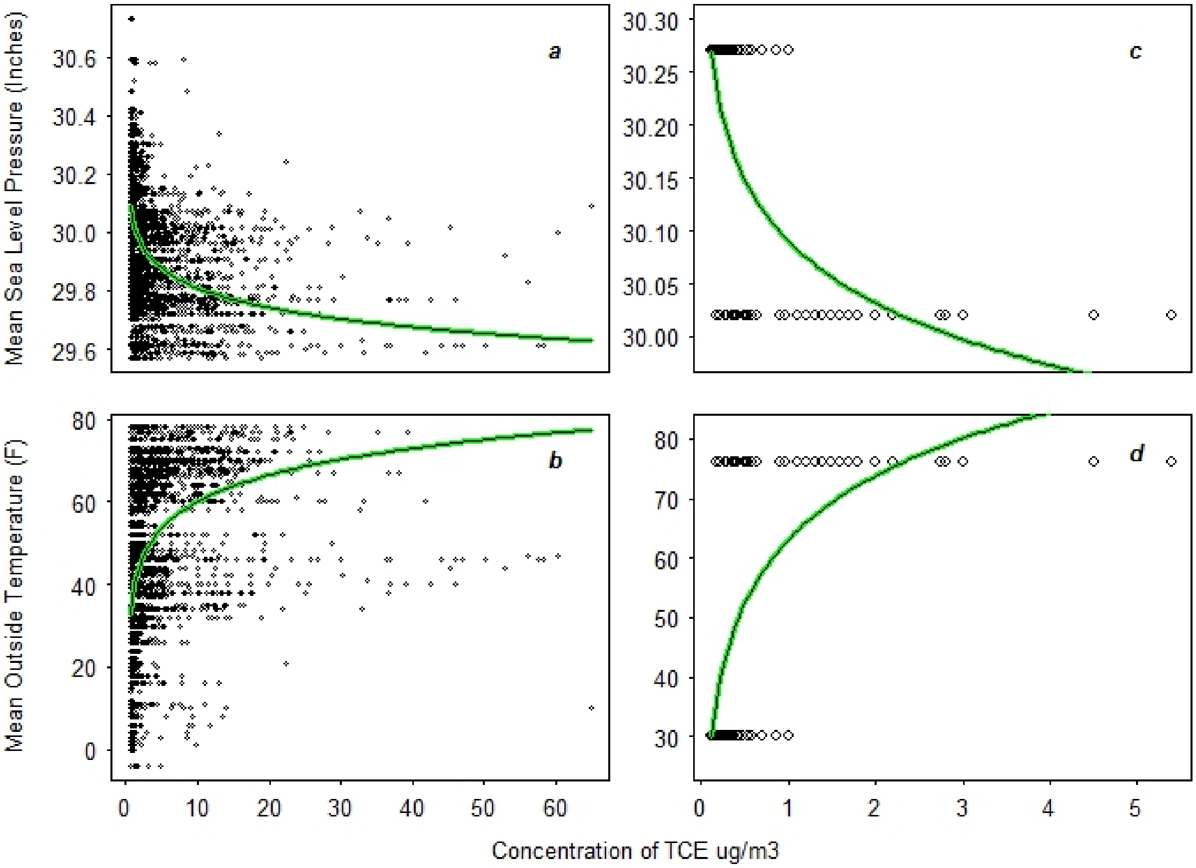

*Figure 5.* Relationship to meteorological conditions: a) shows the relationship of mean sea level pressure to grab portable GC/MS data, b) shows the relationship of mean outdoor temperature to grab portable GC/MS data, c) shows the relationship of mean sea level pressure to 8 h TWA TO-15 data, and d) shows the relationship of mean outdoor temperature to portable 8 h TWA TO-15

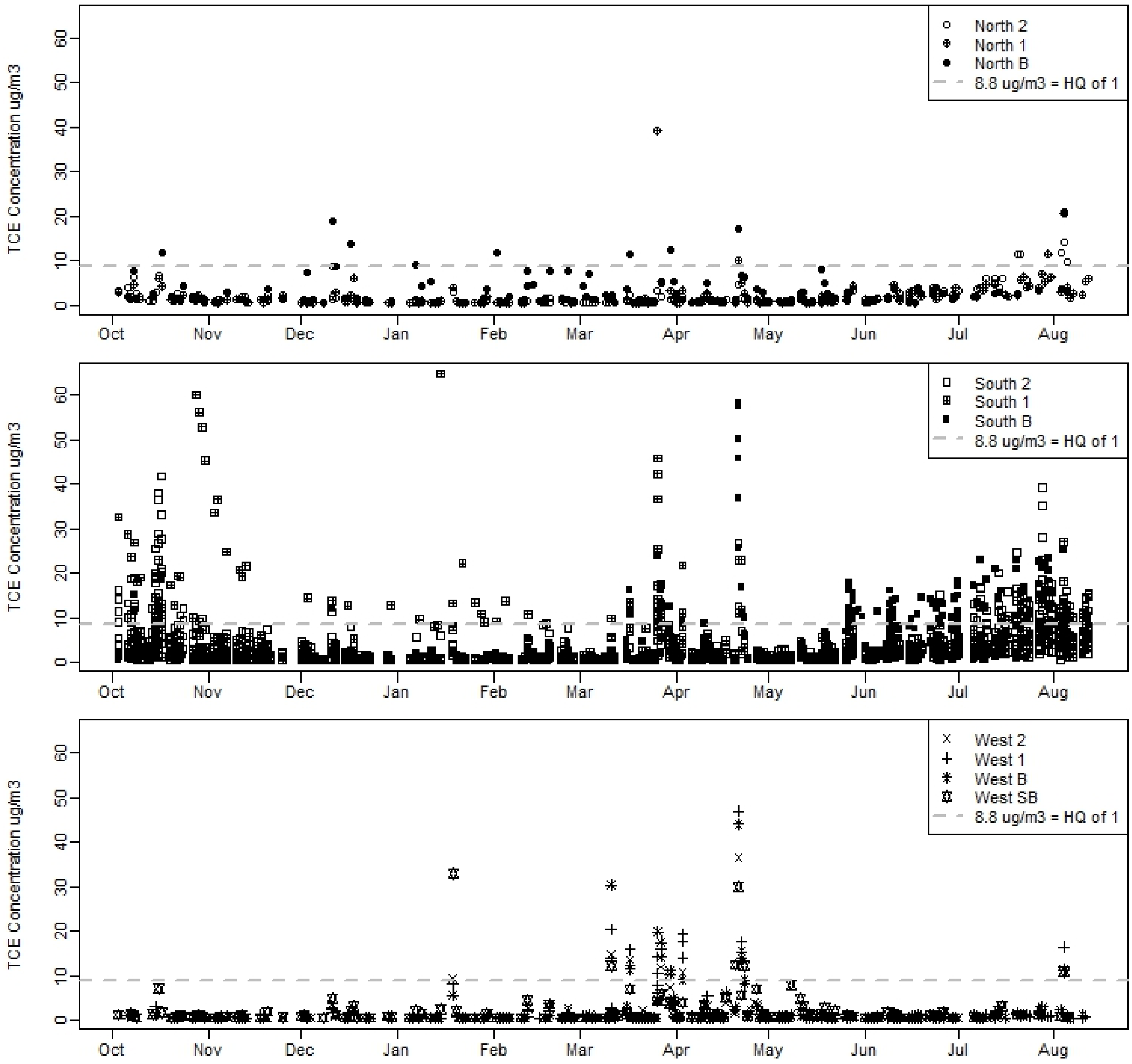

*Figure 6.* Detected and non-detect portable GC/MS concentrations over time

A comparison of the results for the parallel post-mitigation risk assessments based on the EPCs shown in Table 1 for grab portable GC/MS and 8 h TWA TO-15 is shown in Table 2. Each potential ELCR calculated for the inhalation of TCE from the indoor air pathway is within or below the USEPA cancer risk range of 1x10$^{-6}$ to 1x10$^{-4}$. Each HQ is below the USEPA threshold of 1.

*Table 2.* Risk assessment results **(**-- indicates no EPC calculated and no risk calculation performed due to negligible risk)

| | ELCR | | HQ | |
|---|---|---|---|---|
| Exposure Area | 8 h TWA TO-15 | Grab Portable GC/MS | 8 h TWA TO-15 | Grab Portable GC/MS |
| North - Basement | 4E-07 | 1E-06 | 0.1 | 0.4 |
| North - Level 1 | -- | 9E-07 | -- | 0.3 |
| North - Level 2 | 2E-06 | 7E-07 | 0.6 | 0.2 |
| South - Basement | 5E-07 | 2E-06 | 0.2 | 0.7 |
| South - Level 1 | 4E-07 | 2E-06 | 0.1 | 0.6 |
| South - Level 2 | 8E-07 | 1E-06 | 0.3 | 0.5 |
| West - Sub-Basement | -- | 8E-07 | -- | 0.3 |
| West - Basement | -- | 2E-06 | -- | 0.6 |
| West - Level 1 | -- | 8E-07 | -- | 0.3 |
| West - Level 2 | -- | 8E-07 | -- | 0.3 |

# 4. DISCUSSION/CONCLUSION

The daily grab portable GC/MS sampling and analysis method was selected (i) to provide information about short-term indoor air variability due to the unknowns regarding the potential adverse effects of acute exposure to TCE, and (ii) to confirm the effectiveness of SSDS and Healthmate® air filtration units. The data was used to inform short-term mitigation decisions, including providing filtration systems in offices, moving workers into areas with lower potential exposures, and providing guidance about limiting exposure. The data was also published within the facility to inform workers about potential risks and provide strategies within workers' control for mitigating such risks (e.g., limiting on-site work hours).

The availability of the on-site portable GC/MS made daily sampling possible, increasing the temporal and spatial coverage of the data. This led to some notable differences in the dataset: 1) the grab portable GC/MS had a much larger number of samples, which showed more variability and higher maximum concentrations, 2) smaller standard error for the grab portable GC/MS data, and 3) the grab portable GC/MS had a substantial fraction of data points above the TCE air concentration associated with chronic HQ=1 (8.8 µg/m$^3$), whereas there were no 8 h TWA TO-15 concentrations above 8.8 µg/m$^3$.

The greater temporal and spatial coverage improves our understanding of the range of detected concentrations on days between the 8 h TWA TO-15 sampling events, providing a more comprehensive estimate of representative concentrations than the use of 8 h TWA TO-15 alone. The greater number of sampling events provides a greater understanding of concentration variation over a longer period of time (days, months or years), corresponding to meteorological conditions or building operations. The smaller standard error for the portable GC/MS data indicated that the grab portable GC/MS means provided a more accurate representation of the mean.

Despite clear differences, the two datasets also had several similarities: 1) the means calculated both using only detected concentrations, and using detection limits as surrogates for non-detect concentrations were similar between the two datasets, 2) the calculated EPCs were similar between the two datasets, 3) the meteorological correlations show the same trends, and 4) the associated risk assessment showed the same results (risk and hazard below CERCLA limits).

The grab portable GC/MS provides a snapshot of concentrations at a given time (1 minute), which is a limitation for assessment of a worker exposed over 8 h, as the variation within the 8 h period is not captured, as it is within the 8 h TWA TO-15. Although some evidence suggests that grab samples may correlate well with longer duration weighted samples, particularly at lower concentrations (Fitzgerald, 2016; Johnston and Gibson, 2014), we would encourage further work to study the level of correlation and explore the factors influencing variation over the course of an 8 h work day. Since the grab portable GC/MS data does not undergo the same validation process as lab-generated data, it would likely improve the option of the regulatory community if the validation process were more standardized.

The major limitation for 8 h TWA TO-15 is that it misses long stretches of time between sampling events that could show important variations with potential consequences for human health. This is particularly important with respect to TCE, which may have adverse effects over a short duration interval. Within this study, the grab portable GC/MS showed a spike in mid-April, but no 8 h TWA TO-15 sampling round was conducted at this time.

The limitations of the 8 h TWA TO-15 method has important implications for managing occupational exposure and risk reduction. Over the course of investigation at the site, during two consecutive summers, the increased spatial and temporal resolution of the grab portable GC/MS clearly identified areas that required short-term mitigation of risk. High frequency sampling helped identify problems as they occurred, rather than after the fact. It also helped identify when it was safe for people to return to the affected workspace. This problem was not identified with infrequent lab-based 8 h TWA TO-15 sampling. We now understand that higher short-term and somewhat higher average exposures may occur at times when they are invisible using the “gold standard” sampling method. That has serious implications for environmental health when short-term health effects may be of concern.

The relationship of vapor intrusion-driven concentrations to a drop in pressure is well established (Robinson et al., 1997). However, the relationship to outdoor temperature was unexpected. It is commonly expected that winter heating conditions produce the highest vapor intrusion risk (Johnston and Gibson, 2014), yet this information suggests that heated conditions (winter) produced the lowest concentrations. It is not possible to draw conclusions based on one study, particularly as background sources and building contamination are known confounding variables at this site, yet these results recommend further consideration.

The utility of on-site grab portable GC/MS to identify indoor air sources and support vapor intrusion evaluations is well established (Beckley et al., 2013; Beckley et al., 2014; Johnston and Gibson, 2014; Holton et al., 2013). It is the opinion of the authors of this paper that both types of data can provide an acceptable basis for evaluating health risk providing the sampling program is sufficient and well informed based on the assumed exposure, the data follow adequate validation procedures, and the limitations of the selected method are understood and considered within the assessment. In this study we’ve shown that the broader understanding of the indoor air environment provides an adequate foundation for a health protective risk assessment or a valuable augmentation to the traditional 8 h TWA TO-15 based chronic health evaluation.

The ELCR calculated for inhalation of TCE in indoor air was at the lower end or below the USEPA cancer risk range of $1 \times 10^{-6}$ to $1 \times 10^{-4}$ for both the results generated by grab portable

GC/MS and 8 h TWA TO-15. The HQs calculated for both parallel assessments were below the USEPA threshold of 1. The results provide a measure of confidence in the overall conclusions of each risk assessment, provided the underlying assumptions and methods are valid.

It is still uncertain for situations where the 95% UCL on the mean is less than 8.8 $\mu g/m^3$ whether the frequency and magnitude of individual TCE concentrations (or clusters of concentrations) greater than 8.8 $\mu g/m^3$ might impact the likelihood of an adverse developmental effect. However, daily monitoring with portable GC/MS allows employers to make short-term health-protective decisions based on available information.

For context, the RSL used for initial screening comparison in this evaluation is 0.88 $\mu g/m^3$. This is below: the WHO air concentration based on the cancer endpoint (2.3 $\mu g/m^3$) (WHO, 2010), well below the 8 h Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) of 535,000 $\mu g/m^3$, the 10 h National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) of 134,250 $\mu g/m^3$ (CDC, 2016), and the 8 h American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) of 53,700 $\mu g/m^3$ as referenced by OSHA (OSHA, 2016).

The nature of comparing results from a grab portable GC/MS sampling program to results collected by 8 h TWA TO-15 is likely to lead to an unbalanced study design. However, it is noted that it would improve the comparison of the two datasets if the study were balanced. Further study is recommended to identify impacts of HealthMate® air filtration devices, fluctuations in the groundwater concentration, sub-slab soil vapor concentrations, and outdoor air concentrations, correlations to sub-surface pressure differentials, and further evaluate the variability within the 8 h TWA vs 1 minute grab samples.

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# EVALUATION OF HYDROPHOBICITY AND PHYSICAL QUALITY IN A PETROLEUM-CONTAMINATED SOIL WITH PLANTED MAIZE INOCULATED WITH *P. INDICA*

*West Coast Conference, March 2016*

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## ABSTRACT

Degradation of hydrophobic petroleum compounds may improve water adsorption and holding capacity in contaminated soils. There is little information regarding effects of phytoremediation on hydraulic properties and quality indices of petroleum-contaminated soils, particularly when plants with an endophytic fungus are involved. In this study, a rhizobox experiment was conducted to evaluate the effect of maize roots inoculated with endophyte fungus, *Piriformospora indica*, on water repellency, physical quality index (S-index) and surface fractal dimension of a petroleum-contaminated soil after a 64-day phytoremediation. The rhizoboxes were subdivided into four compartments of increasing distance from the roots of the experimental plants. Results showed that the inoculation with *P. indica* promoted plant growth. The inoculated plant roots strongly increased the microbiological activities of soil, however, this effect decreased with distance from the root surface. The total degradation of petroleum hydrocarbons was 35–40% of the initial TPH concentration in the root compartments of rhizoboxes with non-inoculated plants and up to 50% in those of inoculated plants. The results also showed that the behavior of water adsorption and retention in soil changed as it was affected by rhizodegradation of petroleum contaminants. Results revealed that water repellency and surface fractal dimension of soil decreased with decreasing total petroleum hydrocarbons (TPH) in soil. Although the lowest amount of TPH was in the root compartment, the lowest hydrophobicity was observed in the compartment next to it. It seems that hydrophobic exudate of roots caused higher water repellency in the root compartment as compared with the near root compartment. Also, the elimination of petroleum compounds in the root compartment of both inoculated and non-inoculated treatments improved the physical quality of soil from poor category to very good, and plant available water (PAW = $\theta_{fc} - \theta_{pwp}$) increased with decreasing petroleum contaminants in soil.

**Keywords:** rhizobox, phytoremediation, endophyte, water repellency

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# 1. INTRODUCTION

Remediation of contaminated soil is measured using a baseline concentration of total petroleum hydrocarbons (TPH), frequently set at 10,000 mg/kg (1%). Although this concentration of TPH is believed to minimize toxicity to humans and reduce the substantial threat of oil discharge into the navigable waters, it does not address toxicity to other organisms or deleterious impacts on overall soil quality. Therefore, consideration of other aspects of soil properties such as soil quality, water adsorption, and retention by soil may be essential to determine the success of remediation methods.

Plant roots play a crucial role in providing soil conditions to stimulate and promote degradation and remediation of contaminants like petroleum hydrocarbons by rhizospheric microbial communities. Plant roots can create conditions in the surrounding soil under which the degradation of petroleum hydrocarbons is greatly accelerated (Phillips et al., 2012). Hence, the use of plants and the associated microorganisms, including endophyte, has recently been considered as a more promising green technology for soil remediation (Weyens et al., 2009).

Endophytes are bacterial or fungal endosymbionts of plants that spend at least part of their life cycle in plants and increase the host plant's tolerance to biotic and abiotic stresses. Based on work by Kumar et al. (2009) showing that maize is a suitable host plant, and on our preliminary tests, we selected the fungus, *Piriformospora indica*. *P. indica* (*Sebacinales*, *Basidiomycota*) is a cultivable root-colonizing endophytic fungus that has been found to promote growth, biomass production and tolerance of inoculated plants to various stresses. There are not many reports on the effects of *P. indica* on remediation of petroleum contaminated soils, especially when considering soil quality and water adsorption and retention after remediation. Therefore, the main objective of this study was to assess the effect of association of maize and endophyte fungus, *P. indica*, on remediation of petroleum contaminated soil, and physical quality and water repellency of petroleum-contaminated soil.

# 2. MATERIAL AND METHODS

## 2.1 Soil Sampling and Characteristics

The contaminated soil was collected from a landfill near the Shahid Hasheminejad Gas Refinery Complex at Sarakhs in northeastern Iran (36° 34' N; 60° 49' E). Three soil samples (from 0 to 30 cm depth) from each location were bulked, thoroughly mixed, air-dried and sieved through a mesh of 2 mm size. The pollution was due to the application of diesel-contaminated sewage sludge produced by the refinery. The concentration of total petroleum hydrocarbons (TPH) averaged 21.6 mg $g^{-1}$ in the collected soil. Some other physical and chemical characteristics of the sieved soils are given in Table 1.

*Table 1*. Physical and chemical characteristics (mean ± standard error, n = 3) of the soil collected for this study

| Parameter | Unit | Value |
|---|---|---|
| Texture | --- | Loamy Sand |
| pH | --- | 7.4±0.1 |
| EC | dS $m^{-1}$ | 1.25±0.05 |
| Total organic C | % | 2.95±0.2 |
| Total N | mg $kg^{-1}$ | 200±10.3 |
| TPH | g $kg^{-1}$ | 21.6±0.2 |

## 2.2 Experimental Descriptions

Fifteen rhizoboxes (200×200×100 mm) were constructed for the experiment. Using nylon mesh of 25µm pore size, each rhizobox was subdivided into seven adjacent compartments: a middle compartment for planting (named ‘root’ compartment, even in the case of the plant-free treatment, for simplicity), and three lateral compartments on both sides (‘near root’, ‘near bulk soil’ and ‘bulk soil’ with increasing distance from the ‘root’ compartment). Schematic diagram and dimensions of used rhizotron is shown in Figure 1. All compartments were filled with air-dried contaminated soil, layer by layer, using the same filling procedure in all cases.

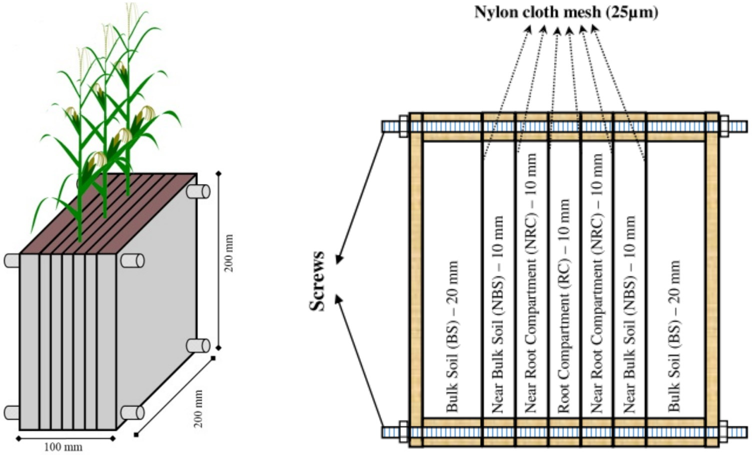

*Figure 1.* Schematic diagram and dimensions of the rhizoboxes used in the experiment

The fungal strain of *P. indica* used in this study was obtained from the Leibniz Institute DSMZ-German Collection of Microorganisms and Cell Cultures (DSM 11827). Complex medium in two steps (solid and liquid) was used to obtain large quantities of active spores of *P. indica*. The composition of the solid medium was composed of glucose (20 g $l^{-1}$), peptone (2 g $l^{-1}$), yeast extract (1 g $l^{-1}$), Hy-Casamino Acid (1 g $l^{-1}$), salt solution (50 ml $l^{-1}$), microelement solution (1 ml $l^{-1}$) and agar (15 g $l^{-1}$). Salt solution consisted of $NaNO_3$ (120 g $l^{-1}$), KCl (10.4 g $l^{-1}$), $MgSO_4.7H_2O$ (10.4 g $l^{-1}$), and $KH_2PO_4$ (30.4 g $l^{-1}$), and microelement solution of $MnCl_2.4H_2O$ (6 g $l^{-1}$), $H_3BO_3$ (1.5 g $l^{-1}$), $ZnSO_4$ (2.65 g $l^{-1}$), KI (0.75 g $l^{-1}$), and $Na_2MoO_4.2H_2O$ (2.4 mg $l^{-1}$). The composition of the liquid medium was the same as that of the solid medium, except that it did not contain agar. Germinated maize (*Zea mays* L. cv. SC704) seedlings were inoculated with *P. indica* inoculums and were then planted according to the experimental design at 1 cm depth into the ‘root’ compartments of the rhizoboxes and grown for 64 days. The rhizoboxes have been placed in a glasshouse (temperature 28±4°C, day/night cycle 13/11 h, and a 48±7% relative humidity) in a randomized array. Soil moisture was kept approximately constant (near 70% field capacity) by periodical watering in order to replace consumed water. No pesticides were applied and weeds were removed manually.

Sixty-four days after transplantation the rhizoboxes were dismantled, all plants harvested and soil samples were taken from the centre of all compartments. Shoots and roots were then separated, washed and dried at 60 °C for 48 hours and weighed. Microbial numbers, soil microbial respiration, dehydrogenase activity, water-soluble phenols and total petroleum hydrocarbons were determined in all samples of each rhizobox's compartments as described by Soleimani et al. (2010). Soxhlet was used to extract petroleum hydrocarbons from homogenized soil samples (10 g) in a 1:1 (v/v) mixture of HPLC-grade dichloromethane and n-hexane (125 ml) (Christopher et al., 1988). The extracts were sequentially purified and cleaned up using silica gel 60 (0.063–0.200 mm, Merck) to adsorb the polar compounds. The residues obtained (and weighed) after evaporation of the solvents in a rotary evaporator were considered as total petroleum hydrocarbons (TPH) according to USEPA (1998).

Also, undisturbed samples were taken from all compartments of the rhizoboxes to measure water repellency, physical quality index (S-index) and surface fractal dimension of the petroleum-contaminated soil after a 64-day phytoremediation. Figure 2 shows how undisturbed samples were taken from the rhizoboxes.

*Figure 2.* Undisturbed soil sampling from the rhizobox's compartments

Water retention curves were obtained by determining water contents at increasing suctions (0, 10, 30, 50, 100, 300, 500, 800 and 1500 kPa) and fitting the model proposed by van Genuchten (1980) to the experimental points. The S-index was determined from the fitted model curve using the following equation:

$$S = \frac{d\theta}{d(\ln h)} = -n(\theta_s - \theta_r).\left[1 + \frac{1}{m}\right]^{-(1+m)} \tag{1}$$

where m and n are the dimensionless shape parameters of the van Genuchten model curve (1980), $\theta_s$ is the saturated gravimetric soil water content and $\theta_r$ is the residual gravimetric soil water content.

Intrinsic sorptivity test was used to calculate soil water repellency using equation 2:

$$R = 1.95\frac{S_E}{S_W} \tag{2}$$

where $S_E$ and $S_W$ are the sorptivity of a 95% ethanol solution and distilled water, respectively. The infiltration device which was used to measure the sorptivity of soil was the same as described by Hallett and Young (1999).

Also, the surface fractal dimension of soil ($D_s$) was calculated using equation 3:

$$D_s = 3 + c \tag{3}$$

where c is a logarithmic relation between soil water content at pressure 33 and 1500 kPa.

## 2.3 Statistical Analysis

The data was analyzed using analysis of variance (ANOVA) in combination with the t-test and post-hoc analysis of Least Significant Differences. All statistical analyses were performed by means of the statistical software package SAS-Version 9.1.3 (SAS Institute, 2005).

# 3. RESULTS AND DISCUSSION

Based on the microscopic analyses, 64 ± 13% of the roots of inoculated plants were colonized by *P. indica*, while no colonization was observed in non-inoculated plants. Figure 3 shows typical images of chlamydospores and hyphae colonizing infected roots. The inoculated plants were clearly larger and greener than the non-inoculated in the entire experiment. The results of visual inspection were confirmed by the biomass and SPAD measurements at the end of the experiment. The total harvested biomass of roots and shoots was 40% larger in plants that had been inoculated than in the non-inoculated plants. With an average height of about 35 cm, inoculated plants were also an average of 1.4 times higher than non-inoculated plants, and a 4 unit higher SPAD index indicated that the leaves of the inoculated plants had significantly more leaf chlorophyll than the non-inoculated plants. Thus, we believe that rather general effects on the host plant such as improved nutrient supply to the roots and increased plant hormone levels were involved in the growth-enhancing effect observed in our study. Such effects have been reported for other endophyte-host plant combinations (Sirrenberg et al., 2007; Kuldau and Bacon, 2008; Kumar et al., 2011). In the root compartment of the planted soils, total bacterial counts were 30-40 times higher and the counts of petroleum-degraders were 140-200 times higher than the respective counts in the plant-free soil, with the upper end of these ranges showing an inoculated plant effect (Table 2). Although the counts of both total and petroleum-degrading bacteria significantly decreased with increasing distance from the root compartments, they were still higher in the 'bulk soil compartments' of the planted rhizoboxes than in the plant-free controls. At least in a qualitative sense, soil respiration, dehydrogenase activity and water-soluble phenols all showed similar patterns of treatment effects as the bacterial counts (Table 3).

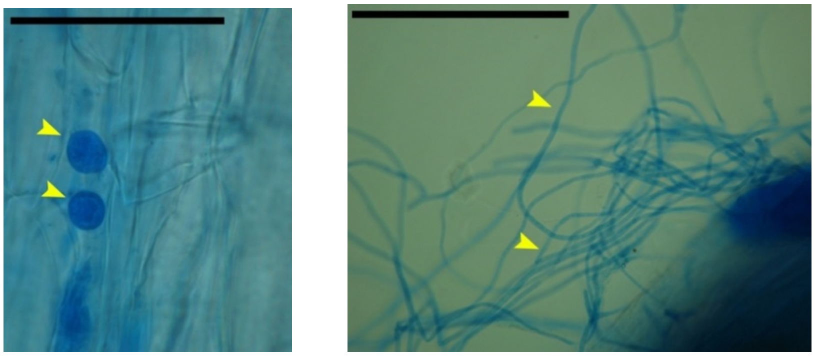

*Figure 3.* Colonization of maize roots with *P. indica*. The yellow arrows point at chlamydospores and hyphae (length of black bar = 100 µm)

*Table 2.* The total bacterial and petroleum-degrading bacterial counts of soil in the compartments of the rhizoboxes with no-plants, plants without inoculation and plants with *P. indica*

| **Compartments** | **Total Bacterial Counts (× $10^6$ CFU $g^{-1}$),** | | | **Petroleum-degrading Bacterial Counts (× $10^3$ CFU $g^{-1}$)** | | |
|---|---|---|---|---|---|---|
| | No-Plant | *- P. indica* | *+ P. indica* | No-Plant | *- P. indica* | *+ P. indica* |
| Root | 0.4±0.2c | 20.0±4.6a | 22.7±5.7a | 0.5±0.3g | 70.0±10.0b | 100.0±10.0a |
| Near-Root | 0.8±0.3c | 8.7±2.1b | 11.3±3.8b | 0.3±0.1g | 51.7±7.6c | 73.3±5.8b |
| Near-Bulk Soil | 0.5±0.2c | 2.8±1.9c | 2.5±1.3c | 0.5±0.1g | 16.3±5.5de | 23.3±4.5d |
| Bulk Soil | 0.6±0.1c | 1.1±0.7c | 1.4±0.6c | 0.6±0.2g | 6.2±2.3g | 10.7±3.8ef |

*Table 3.* Microbial respiration, water-soluble phenols content, dehydrogenase activity of soil in the compartments of the rhizoboxes with no-plants, plants without inoculation and plants with *P. indica*

| **Compartments** | **Microbial Respiration (mg CO2-C $kg^{-1}$ $day^{-1}$)** | | | **Water-soluble Phenols (µg vanillic acid $g^{-1}$ dry soil)** | | | **Dehydrogenase Activity (µg TPF $g^{-1}$ dry soil)** | | |
|---|---|---|---|---|---|---|---|---|---|
| | No-Plant | *- P. indica* | *+ P. indica* | No-Plant | *- P. indica* | *+ P. indica* | No-Plant | *- P. indica* | *+ P. indica* |
| Root | 45.4±5.9e | 95.4±4.9ab | 102.5±8.6a | 6.3±0.9f | 8.4±0.4bc | 9.9±0.7a | 544±26e | 643±26cd | 794±29a |
| Near-Root | 47.9±5.4de | 91.8±7.6b | 98.9±5.3ab | 6.4±1.0f | 8.0±0.5cde | 9.2±0.6ab | 525±37e | 607±30d | 778±23b |
| Near-Bulk Soil | 50.4±8.8e | 75.4±3.8c | 79.3±6.7c | 6.2±0.8f | 7.2±0.4def | 8.5±0.6bc | 514±44e | 528±41e | 674±34c |
| Bulk Soil | 56.8±2.8d | 75.0±4.7c | 77.5±5.4c | 6.4±1.0f | 6.9±0.3ef | 8.1±0.7bcd | 531±22e | 516±26e | 545±22e |

Also, soil dehydrogenase activity and water-soluble phenols showed clear plant and distance-to-root effects. The same basic pattern of treatment effects as on the microbial and biochemical soil parameters presented before can also be seen in the degradation of the contaminating petroleum hydrocarbons. The presence of maize roots in the root compartment further increased the decline in TPH, especially in the root compartment itself and the compartment next to it, while it had only a small (with inoculation) or no significant (without inoculation) additional effect on TPH in the other two compartments (Figure 4).

In all compartments, the additional decrease in TPH that was attributable to the presence of maize roots in the soil was almost twice as large for plants inoculated with *P. indica* than for non-inoculated plants. As a result, the total degradation of petroleum hydrocarbons amounted to 35 – 40 % of the initial TPH concentration in the root compartments of rhizoboxes with non-inoculated plants and to even 50% in those of inoculated plants. The endophyte effect on TPH elimination may thus simply have been due to enhanced root exudation and turnover resulting from boosted plant growth. It is also possible through the stimulation of microbial activity via root exudation. Cheema et al. (2009) and Lee et al. (2008) reported that the production of phenolic compounds tended to be enhanced in petroleum-contaminated soil. Moreover, Lee et al. (2008) found that this production of phenolic compounds was closely related to root turnover.

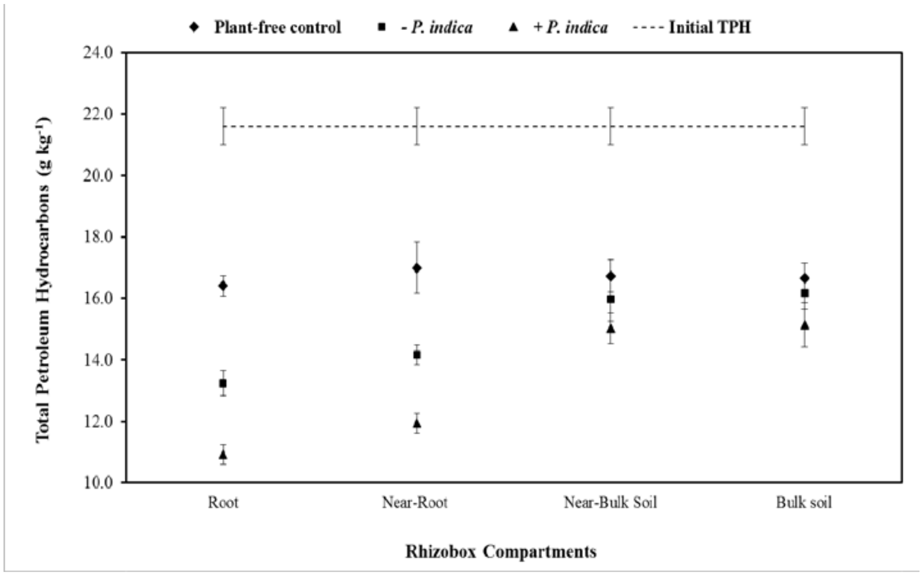

*Figure 4.* Total petroleum hydrocarbons in the compartments of the rhizoboxes with no plants (◆), plants without inoculation (■) and plants with *P. indica* inoculation (▲)

Thus, more root and microbiological activities in the planted treatments further increased the decline in TPH, particularly in the vicinity of roots in *P. indica*-inoculated treatment. The results also showed that the behavior of water adsorption and retention in soil changed as affected by rhizodegradation of petroleum contaminants. Results revealed that water repellency and surface fractal dimension of soil decreased with decreasing total petroleum hydrocarbons (TPH) in soil (Figure 5). Although the lowest amount of TPH was in the root compartment, the lowest hydrophobicity was observed in the compartment next to it. It seems that hydrophobic exudates of roots caused higher water repellency in the root compartment as compared with near the root compartment. Also, the elimination of petroleum compounds in the root compartment of both inoculated and non-inoculated treatments improved physical quality of soil from poor category to very good according to Dexter and Czyż (2007), and plant available water (PAW = $\theta_{fc} - \theta_{pwp}$) increased with decreasing petroleum contaminants in soil (Table 4). It is also shown in Figure 6 that the presence of plant roots in the root compartment increased the water content ratio in the low tensions and decreased it in the high tensions.

*Table 4.* Plant available water (PAW = $\theta_{fc} - \theta_{pwp}$) of soil in the compartments of the rhizoboxes with no-plants, plants without inoculation and plants with *P. indica*

| **Treatments** | **Compartments** | | | |
|---|---|---|---|---|
| | Root | Near-Root | Near-Bulk Soil | Bulk Soil |
| No-Plant | 12.07e | 12.87de | 14.37cd | 13.67de |
| - *P. indica* | 17.00b | 18.43ab | 14.30cd | 12.3de |
| + *P. indica* | 13.53de | 16.33bc | 19.83a | 19.53a |

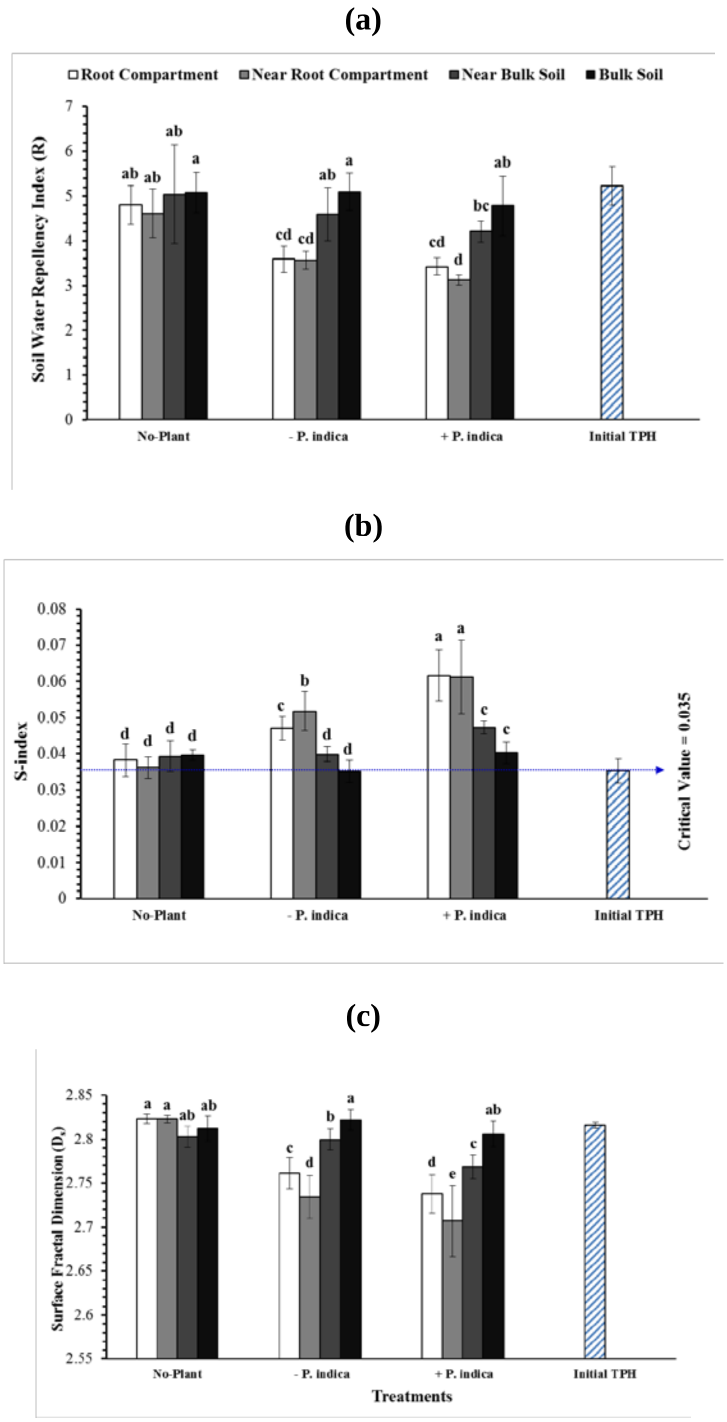

*Figure 5.* (a) Water repellency (R), (b) S-index and (c) surface fractal dimension (Ds) of soil in the compartments of the rhizoboxes with no-plants, plants without inoculation and plants with *P. indica*

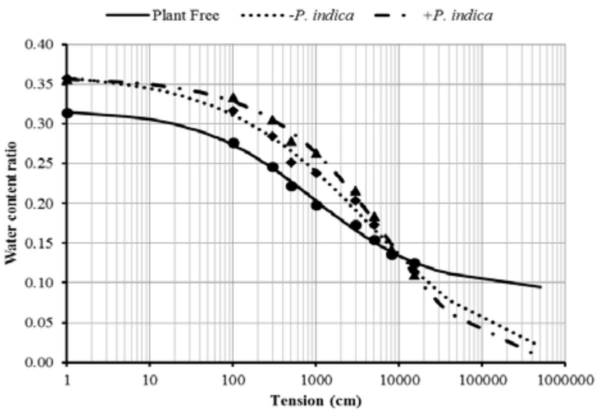

*Figure 6.* Soil Water Characteristic Curve in root compartments with no plants (plant free), plants without inoculation (- *P. indica*) and plants with *P. indica* inoculation (+ *P. indica*)

## 4. CONCLUSION

The results of this study showed that *Piriformospora indicia* could increase the ability of maize to grow in petroleum contaminated soil and to enhance phytostimulated elimination of petroleum hydrocarbons in contaminated soil. Inoculated plants had more roots, which enhanced root exudation and microbiological activities in soil, particularly in the vicinity of the roots, and it can consider as the main reason for elimination of petroleum hydrocarbons. Also, removal of hydrophobic petroleum compounds could increase the available water content (AWC) in soil and improve physical quality and water repellency of the contaminated soil.

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# ASSESSING SOIL PRODUCTIVITY INDEX FOR A SOLID WASTE MANAGEMENT SITE (NORTHERN CONTRA COSTA COUNTY, CALIFORNIA)

*West Coast Conference, March 2016*

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## ABSTRACT

Soil productivity index (SPI) is an important tool for evaluating land use and soil management practices for a variety of ecosystems. The aim of this project was to assess the SPI for 29 hectares of a solid waste management site located in northern Contra Costa County, California. The site is impacted with a variety of contaminants including total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs), and heavy metals, and is highly saline. Specifically, we compared the SPIs of the impacted sites with those of clean soils located nearby. For the purposes of analysis, we separated the contaminated areas into three components: high (HC), medium (MC), and low (LC) TPH concentrations in soil. One clean soil location (NC) was selected adjacent to the contaminated site for comparison. The SPI was assessed using 7 physical, chemical and biological soil properties (referred to as "indicators") and analyzed as follows: 1) identification of the minimum data set (MDS) of the indicators, 2) interpretation of the indicators using principal component analysis (PCA), and 3) integration of all indicator scores into one SPI value. The data showed that soil salinity and sodicity (sodium adsorption ratio, SAR, and exchangeable sodium percentage, ESP), and soil organic carbon (SOC) concentration, were the most discriminating and key indicators for SPI assessment. The results imply that the long-term influence of depositing petroleum hydrocarbons and other contaminants into this solid waste management site had major negative impacts on soil structural stability and plant nutritional status.

**Keywords:** productivity index, petroleum contaminants, waste management, assessment

## 1. INTRODUCTION

Currently, evaluation of soil productivity (soil quality) is carried out using new methods and tools, mostly related to plant growth factors (Burger, 1996; Kiniry et al., 1983; Gale et al., 1991; Milner et al., 1996). These methods of assessment should be sensitive to biological, chemical, and physical soil indicators in order to best evaluate decisions with respect to managing crop residues (e.g., for biofuels or for the application of animal manures (Karlen et al., 2008) or landfill with respect to industrial contaminants such as petroleum hydrocarbons, Hajabbasi et al., 2016). In order to develop a soil productivity index (SPI), the important issue is to examine key

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soil and agronomic characteristics, e.g., organic matter content, EC, and pH, and then integrate these into a single parameter that could be used as an indicator of overall soil productivity – an idea that has already been developed for some agricultural systems (Doran and Parkin, 1996).

Many studies (Fu et al., 1997) have reported suitable and quantifiable indices that are superior to the use of descriptive qualifiers for evaluating soil productivity (Milner, 1996). Kiniry et al. (1983) introduced an index by integrating the relationship between plant productivity and soil parameters. Pierce et al. (1983) developed it further by proposing that yield is a function of root activity and development, which in turn is controlled by soil environment. According to Gale et al. (1991), SPI shows the direct influences of soil properties, and therefore, can be used for a wide range of land management sites. Assessing soil quality is a matter of measuring the current state of an indicator and comparing the results with known or desired values (Karlen et al., 1997). Manley et al. (1995) used this tool to find the response of C and N to grazing, and to evaluate the sustainability of different rangeland systems. Soil organic matter, porosity, and infiltration rate are other important indicators for forest ecosystems (Doran et al., 1996; Elliot et al., 1999). Here, we have developed an SPI that integrates 19 soil agronomical properties (7 of which are presented here) that have been measured for a solid waste management site impacted with petroleum hydrocarbons, heavy metals and other contaminants.

## 2. METHODS AND MATERIALS

The 29-ha study area is located at Bay Point, California. The site was originally used for discharging industrial wastewater containing carbon black, metals and other compounds. Four distinct sampling areas (Figure 1) were measured that differed substantially with respect to the level of contamination by total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH). These are: HC (i.e., 42,000 mg TPH /kg and 993 mg PAH /kg), MC (3950 mg TPH /kg and 241 mg PAH /kg) and LC (1750 mg TPH /kg and 67 mg PAH/kg). A control site with no measurable contamination (NC) was also used for comparison. Two sampling points from each location and two replications from each point yielded a total of 32 sampling points (8*2*2). Analysis of the mineral soil includes salinity- and sodicity-associated parameters, i.e., EC, SAR and ESP, as well as cation exchange capacity (CEC), pH, organic matter, and sodium content.

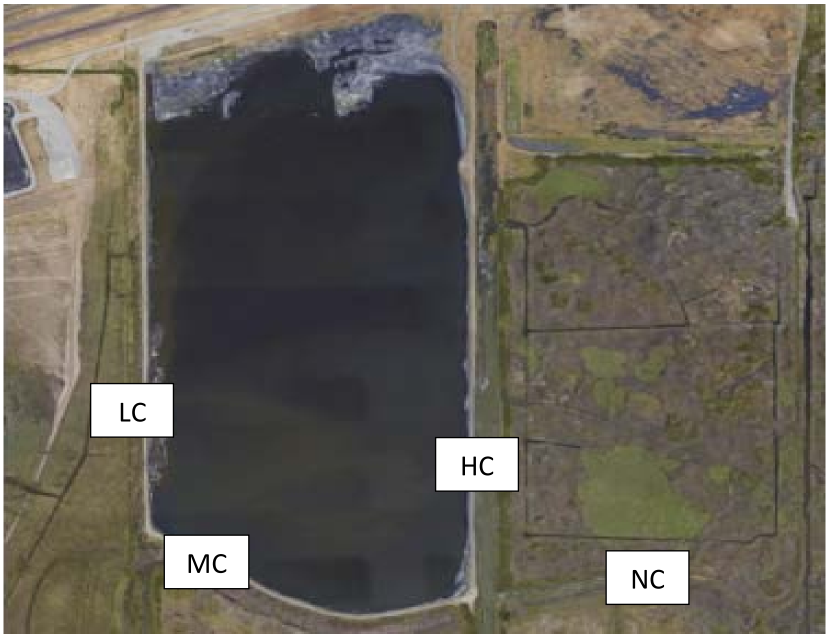

*Figure 1.* Selected sampling points of the study site. HC, MC, LC and NC are high, medium, low and no TPH contamination, respectively

## 2.1 Statistical Approach

In this approach, each soil parameter was first assigned a unit-less score ranging from 0 to 1 by employing linear scoring functions (Andrews et al., 2002). Soil indicators were then grouped into three mathematical algorithm functions, i.e., 'more is better' (e.g., OM, N, and CEC), 'less is better' (e.g., Na, SAR and ESP), and 'optimum values' (e.g., pH and EC). The 'optimum' means that the parameter has a positive influence up to a certain level beyond which the influence could be considered detrimental (Fernandes et al., 2011), For example, the pH of our study site ranged from to 5.8–7.3; pHs > 7.3 were scored as 'less is better', while pHs < 5.8 were scored as 'more is better' (see also Lal and Mukherjee, 2014).

The final principal component analysis, PCA-based soil productivity equation, is as follows:

$$\text{SPI} = \sum_{i=1}^{n} \frac{Si}{n}$$

where SPI is the soil productivity index, Si is the score given to each indicator, and n is the number of properties included in the minimum data set (MDS). According to Marzaioli et al. (2010), the SPI is then divided into three grades: SPI <0.55 was regarded as low soil quality; 0.55 < SPI < 0.70 was regarded as intermediate soil quality; and SPI > 0.70 as high soil quality.

The index values for each soil property measured on the Shell Pond plots are summed to give a total SPI:

$$\text{Total SPI} = \sum \text{each soil property index}$$

The maximum value of the total SPI is 7 and then total SPI expressed as a percentage of the maximum possible value of the total SPI for the measured soil properties:

$$\text{SPI, \%} = (\text{total each SPI} / \text{maximum possible total SPI for properties}) \times 100$$

## 2.2 Statistical Analysis

One-way analysis of variance (ANOVA) was performed to assess the effect of change in petroleum hydrocarbon content on soil physicochemical properties of pH, EC, OM, Na, SAR, ESP, and CEC (SAS, 2005). The separation of means among different treatments was made using the least significant difference test at 0.05 levels of probability (Tukey's test). Principal component analysis was also used in order to select the most appropriate soil productivity indicators (XLSTAT, 2015).

# 3. RESULTS

Results for the seven soil indicators selected to obtain the minimum data set (MDS) are presented in a one-way analysis of variance (ANOVA) in Table 1. There were significant differences in pH, EC, OM, Na, SAR, ESP, and CEC ($P < 0.05$) among the sites with different levels of TPH contamination (i.e., LC, MC, HC and NC), but no significant difference between replicates (e.g., LC1 vs LC2). As an important productivity indicator, pH affects almost all other soil physical, chemical and biological characteristics (Smith and Doran, 1996). It also influences soil nutritional behavior and therefore the productivity and yield of the crops (Ketterings et al., 2005). The proper soil pH for a variety of species range between 6.0 to 7.5 which depends on the tolerance of each crop (Patriquin et al., 1993): for example, legumes, and barley, have an optimum pH range of 6.5 to 7.0, whereas oats can tolerate a pH as low as 5.5 (Ketterings et al., 2005). The overall pH values of the study site are near neutral; the pH of the sites MC1 and NC2 are somewhat low (5.8 and 5.9), but not critically so.

Plant productivity is highly dependent on the organic matter content (OM) of the soil (Bauer and Black, 1994). High OM improves soil physical, chemical and biological properties of the soil environment and therefore productivity. High productivity itself, in turn, increases OM content.

*Table 1.* Amounts of pH, organic matter (OM), electrical conductivity (EC), sodium adsorption ratio (SAR), exchangeable sodium percentage (ESP), cation exchange capacity (CEC) and percentage Na element in composing CEC

| Sites | pH | OM (%) | EC (dS/m) | SAR | ESP | CEC (meq/g) | %Na |
|---|---|---|---|---|---|---|---|
| LC1 | 7.1ab | 1.03c | 2.00bc | 77.8a | 55.4a | 25.3abc | 48.8a |
| LC2 | 7.3a | 0.98c | 3.33b | 91.0a | 55.3a | 33.2a | 46.6a |
| MC1 | 5.8c | 1.10c | 2.16bc | 85.1a | 58.5a | 27.2ab | 47.8a |
| MC2 | 6.0bc | 2.36bc | 2.55bc | 100.2a | 60.0a | 33.6a | 51.4a |
| HC1 | 6.3abc | 15.20a | 8.59a | 92.0a | 57.2a | 36.5a | 49.0a |
| HC2 | 7.1ab | 2.00bc | 4.13b | 53.9b | 44.6b | 26.5ab | 36.5b |
| NC1 | 6.0bc | 2.35bc | 0.33c | 7.1c | 11.1c | 15c | 8.0c |
| NC2 | 5.9c | 5.25b | 0.37c | 2.6c | 3.7d | 19cb | 2.5c |

Values in each column with similar letters are not significantly (LSD, $P < 0.05$).

The amounts of OM in soils are in the low to medium range for almost all sites (Table 1). However, the HC1 site (which used to be the dumping point for the carbon black) has a very high OM content.

The NC2 site also has a greater amount of OM, most likely due to an enhanced plant establishment and therefore higher levels of decomposed roots and shoots at the site. Soil organic matter has been shown to be an important factor in forest ecosystem productivity (Paul, 1991). Organic matter leads to better water retention, greater structural stability and better nutrient cycling, and may also be a good source of nitrogen and phosphorus as well (Bauer and Black, 1994).

High potential evaporation and poor infiltration characteristics of the impacted sites result in substantial increases in salinity (EC values range from 2.0 to 8.6 dS/m, Table 1). Electrical conductivity which resembles the amount of salt in soil is an important factor affecting soil properties through which crop productivity will be influenced (Maas and Hoffman, 1977). EC affects soil productivity by impacting the uptake of nutrients necessary for plant growth (Adviento-Borbe et al., 2006). When salts accumulate in soil, they have several effects, both on plant growth and soil structure; salts diminish plant growth and productivity by lowering osmotic potential, and by inducing nutrient deficiencies (e.g., $Na^+$ competitively inhibits the uptake of nutrient cations such as $Ca^{2+}$ and $Mg^{2+}$).

The deposition of petroleum compounds into the soil resulted in an increase in CEC (Table 1). High CEC *can* enhance plant growth by increasing nutrient availability, which could increase soil productivity. Liang et al. (2006) reported that black carbon (BC) enhanced plant growth by increasing CEC. However, although CEC was higher in the impacted sites, nearly 50% of the cations were sodium ions, and therefore not likely to have beneficial effects on SPI. The data show that SAR was increased substantially in the impacted sites (Table 1), which not only disperses soil aggregates (aggregates will be dispersed into separated particles if $Na^+$ occupies more than 15% of the CEC sites on clays surface; Gawel, 2009), but also lowers soil hydraulic conductance (Arienzo et al., 2012).

For preparing the MDS, the fifth run of the principal component analysis (PCA) was used with Eigen values more than 1, the lowest variability and the highest cumulative variability (Table 2). The seven soil productivity indicators were arranged by different components, such as salinity or soil structural characteristics. The highly weighted loadings were arranged from high to low under each PCA. Within each PCA, indicators with values within 10% of the highest value were selected for the MDS. In order to minimize the redundancy among the data, a Pearson correlation test was used for the soil parameters (Andrews and Carroll, 2001). The first principal component (PCA1) explained almost 49% of the variance (Table 3). Sodium was the greatest contributor (0.98) to PCA1, given the highest factor loading (Table 3), so it was selected first as the most important index. Besides Na, SAR (0.95), ESP (0.94), and CEC (0.94) also had highly weighted factor loadings (Table 3).

There was more than an 80% correlation between Na and SAR, ESP, and CEC. The $Na^+$ component was identified as the “soil dispersion factor.” The second principal component (PCA2) explained 23% of the variance (Table 3). Organic matter was identified as the “soil aggregating factor” because it had a positive loading for OM (0.81). Under PCA4, only pH had a high factor loading (0.87) and accounted for 8.4% of the variance. Hence, Na, EC, OM, pH, SAR, ESP and CEC were the final indicators selected to calculate SPI. OM is commonly considered as a soil productivity indicator for its function in soil structural stability, fertility and microbial activity (Ontl et al., 2015).

*Table 2.* Eigen values, variability and cumulative variability for the principal component (PCA) for the seven runs of the analysis

| | PCA1 | PCA2 | PCA3 | PCA4 | PCA5 |
|---|---|---|---|---|---|
| Eigen value | 12.244 | 5.754 | 2.568 | 2.111 | 1.746 |
| Variability (%) | 48.975 | 23.015 | 10.271 | 8.443 | 6.984 |
| Cumulative % | 48.975 | 71.991 | 82.261 | 90.704 | 97.689 |

*Table 3.* Factor loadings for the principal component (PCA) for the first five runs of the analysis

| | PCA1 | PCA2 | PCA4 |
|---|---|---|---|
| pH | 0.398 | -0.002 | 0.866 |
| EC | 0.792 | 0.570 | -0.017 |
| OM | 0.467 | 0.812 | -0.165 |
| Na | 0.977 | -0.176 | -0.059 |
| SAR | 0.951 | -0.298 | -0.076 |
| ESP | 0.944 | -0.263 | -0.034 |
| CEC | 0.937 | -0.021 | -0.083 |

## 3.1 Indicator Scoring

Soil was considered productive if its index is equal to or greater than that of the non-contaminated site (NC); inversely it was low if the index is lower than that of NC. According to Karlen et al. (1997, 2008) three standard scoring functions were defined as: 1) more is better (with the values of 0-1), 2) optimum (with the values of 0-1-0), and 3) more is worse (with the values of 1-0). The values for each soil productivity indicator were then converted into some unitless scores ranging from 0 to 1. After deciding the shape of the anticipated response (“more is better” or “less is better”), the limits or threshold values were given for each indicator (Karlen and Stott, 1994). In the study, a “more is better” curve was applied to pH, because pH values were around 7 in all soils. A “less is better” curve was applied to total salt content because high salt content has an inhibitory effect on plant growth and soil organisms. A “more is better” curve was applied to total nitrogen and soil organic matter. From the PCA, SPI was determined using Eq. (3), by dividing the percentage of variation in the data set explained by each PCA that contributed to the indicated variables by the total percentage of variation explained by all PCAs with Eigenvalues >1 (Table 4). Finally, calculated SPI values (mean of two reps), and associated agronomic and macronutrients as the soil property threshold values, and interpretation were in the following order: NC (2.45) >HC (1.58) >LC (1.76) >MC (1.07). The percentage of each value with respect to the largest amount (NC2) of SPI (%SPI) is also showing that the soil productivity index of all impacted sites is at least half of the non-contaminated soil. The SPI values are between 40 to 60% lower in the impacted compared to the non-impacted site.

*Table 4.* The sum of soil quality indices for individual parameter, total quality index TPI and proportional deviation %SPI of the samples

| Site | pH | EC | OM | Na | SPI | %SPI |
|---|---|---|---|---|---|---|
| LC | 1.00 | 0.82 | 0.15 | 0.00 | 1.97 | 78.0 |
| LC | 0.88 | 0.67 | 0.00 | 0.00 | 1.55 | 61.3 |
| MC | 0.00 | 0.80 | 0.16 | 0.00 | 0.96 | 38.0 |
| MC | 0.22 | 0.76 | 0.19 | 0.00 | 1.17 | 46.3 |
| HC | 0.40 | 0.00 | 1.00 | 0.00 | 1.40 | 55.4 |
| HC | 1.00 | 0.59 | 0.17 | 0.00 | 1.76 | 60.0 |
| NC | 0.22 | 1.00 | 0.19 | 0.97 | 2.36 | 93.3 |
| NC | 0.16 | 1.00 | 0.37 | 1.00 | 2.53 | 100.0 |

## 4. DISCUSSION/CONCLUSIONS

The soil productivity index (SPI) model is a measure of soil productivity based on agronomical characteristics. The basic assumption of the SPI model is that plant growth is a function of nutrient bioavailability, which in turn is controlled by the soil environment and its constituents. The assessment and effectiveness of the SPI model for each of the four sampling points (HC, MC, LC and NC) was determined. Several years of adding petroleum hydrocarbons (and other contaminants including heavy metals) to the impacted sites caused a lowering of SPI. The sites with higher growth potential (NC) were shown to have higher calculated SPI values compared to the impacted sites. The results of this study indicated that the SPI model accurately characterized soil productivity at the solid waste management site.

## 5. ACKNOWLEDGEMENTS:

We thank Isfahan University of Technology for the funding provided to MAH who carried out this research as a visiting scholar at UC Berkeley. Funding for this research was provided by UC Berkeley fund number 51719.

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# SOURCES, CHEMISTRY AND TOXICOLOGICAL RISK CONSIDERATIONS OF AMINES FOUND IN THE ENVIRONMENT

*East Coast Conference, October 2016*

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## ABSTRACT

The amines are a very diverse family of environmentally and physiologically important aromatic and aliphatic nitrogen-containing compounds which include ethylamines, ethanolamines, methylamines, piperidine, aniline, amino acids, and catecholamines (e.g., epinephrine, norepinephrine, dopamine). From an environmental and an industrial perspective, the anilines, ethanolamines, and the ethylated or methylated amines (e.g., monomethyl-, dimethyl-, and trimethyl-) represent the most commonly encountered and chemically important members of the chemical class. Amines are of toxicological interest primarily based upon the irritant and sensitization properties at some exposure concentrations, potential organ toxicity for some representatives, and what often are very low odor thresholds in air. Tumorigenic potential generally is limited to the nitrosamines and some anilines. This paper describes the important sources of environmental amines, as well as their relevant physical and chemical properties. Also described is the range of toxicological properties for individual substances or groups of amines, and how those properties typically are addressed in a risk assessment context related to potential industrial or environmental exposure circumstances. A summary of health-based cleanup goals and contemporary recommended exposure limits for various applicable exposure scenarios is presented as well.

**Keywords:** amines, air, groundwater, risk, human exposure, environmental behavior

## 1. INTRODUCTION

Amine compounds are a large class of important nitrogen-based derivatives of ammonia in which one hydrogen atom is replaced with an alkyl (aliphatic) or aryl (aromatic) group, and like ammonia, are considered weak bases. Amines are classified according to the number of carbon atoms that are bonded directly to the nitrogen atom (i.e., primary, secondary, tertiary) and basicity is their most important chemical property. The alkylated amines are slightly stronger bases than ammonia, while aromatic amines are less basic.

Amines often come from biological sources in the environment including plants such as tobacco and *Chenopodium vulvaria* (notchweed or “stinking goosefoot”), decomposing organisms, fungi, and flowers (Bouchereau et al., 2000; Sintermann and Neftel, 2015). Seabirds and migratory

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[§] Corresponding Author: Michele Garber, Hazardous Substance & Waste Management Research, Inc., 2976 Wellington Circle West, Tallahassee, FL 32309; Tel: 850-681-6894; mgarber@hswmr.com wildlife urine and feces also contribute to amines in the environment as do pharmaceuticals and other industrial processes. Amines are widely used in dyes, cosmetics, agricultural pesticides, antioxidants in polymers and motor fuels (NJDHSS, 2002). Capture and storage facilities for carbon dioxide ($CO_2$) can be a source of environmental amines or amine degradation products from the amine solvents used in the $CO_2$ removal process (Gjernes et al., 2013; Krzemien et al., 2013; Gentry et al., 2014). Amines also are broadly used in the production of emulsifiers, detergents, solubilizers, absorbents, cosmetics, and textiles. They are also formed via biodegradation of proteins and nitrogen-containing compounds in domestic wastewater (Ma et al., 2012). There are hundreds of biogenic, as well as synthesized, amine compounds that can be evaluated; however, this discussion focuses principally on the simple alkylated amines, ethanolamines, aniline, and to some extent, the nitrosamines and nitramines.

A generally accepted principle in the discipline of toxicology is that the simple presence of an agent (e.g., an amine compound) is not sufficient to assess exposure, nor are characteristics such as odor sufficient for identification of toxicologically relevant exposure conditions. From a risk management perspective, the source of a potential exposure must be identified with sufficient certainty so that its potential impact on a population can be properly assessed. This is especially true for common substances, or for common odors with multiple potential sources. It is equally important to consider other parameters which may be specific to each potentially exposed individual and which may affect that person’s response to a particular exposure event. This is an important component of the standard risk assessment paradigm that is employed by U.S. EPA, the National Academy of Sciences, the World Health Organization and other relevant environmental and public health agencies not only in the United States, but worldwide. All of these aspects contribute to the reasonable and appropriate environmental evaluation of amines.

## 2. TYPES OF AMINES

### 2.1 Aliphatic Amines

The aliphatic amines are nonaromatic (non-ringed) compounds that may be straight-chain or branched molecules with relatively low molecular weight and good water solubility; however, as molecular weight increases, the associated solubility decreases. Their solubility allows them to stay in solution and travel with groundwater or surface water rather than to partition to the soil, sediment or biotic phases. Ethylamine is highly flammable and thus represents a strong fire hazard with a strong ammonia-like odor and low odor threshold of less than one ppm (parts per million; Amoore and Hautala, 1983). Diethylamine is a colorless, low viscosity liquid also with a pungent, fishy or ammonia-type odor with a slightly lower odor threshold of 0.13 ppm, much lower than health-based regulatory values set by Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Safety and Health (NIOSH), and/or the American Conference of Governmental Industrial Hygienists (ACGIH) (DEN, 1999; NIOSH, 2007; see Table 1). Burning of diethylamine can form toxic fumes of nitrogen oxides (CDC, 2015a). Triethylamine, a colorless, volatile liquid with a vapor pressure of 54 mm Hg and a strong ammonia to fish-like odor, is also highly flammable and will give off toxic fumes (or gases) in a fire as well (CDC, 2015b). The largest use of triethylamine in the 1990’s, when 20 million pounds per year were produced, was as a catalyst to cure the resin systems incorporated into sand cores for foundry molds. It reportedly enters the environment mainly from emissions and effluents released during its production and use (Tice, 1998). The odor threshold for triethylamine is reported to be 0.48 ppm, similar to that observed for the other two ethylamines (Amoore and Hautula, 1983).

The methylamines are similar in properties to the ethylamines and their occupational exposure guidelines and odor thresholds are listed in Table 1 as well. Methylamine is a colorless gas with a strong ammonia-like odor and at low concentrations exhibits a fishy odor with a reported odor threshold of 3.2 ppm (Amoore and Hautala, 1983). It was presented as a candidate for testing by the National Toxicology Program (NTP) due to: 1) potential for occupational exposures based on high production volume; 2) evidence of occupational exposures based on TLV and other literature documentation; 3) universal potential for general population exposures based on endogenous and exogenous occurrence in many consumed products and environmental media; and, 4) lack of chronic toxicity data (TRI, 1996). Dimethylamine is a colorless liquid or gas with a pungent, fishy odor at low airborne concentrations, compared with an ammonia-like odor at higher air concentrations (in the range of 100 to 500 ppm; USEPA, 1990). Dimethylamine is naturally occurring and is widespread in many ecosystems (USEPA, 1990), has been reported to be present at 1 to 7 ppm in some fresh vegetables such as corn, kale, lettuce and peas (Ripley et al., 1982; Neurath et al., 1977), and occurs in cigarette smoke at concentrations of approximately 100 ppm (HSDB, 2008). Dimethylamine has a tenfold lower reported odor threshold than methylamine at 0.34 ppm (Amoore and Hautala, 1983). Trimethylamine, a colorless gas or liquid with strong fishy odor, is widely distributed in the environment as a result of its formation during the decay of organic matter in plants, animals, fish, sewage and animal waste (NJDHSS, 2003b; HSDB, 2009). The most probable and common routes of human exposure to trimethylamine are inhalation of tobacco smoke and ingestion of food in which this compound occurs (HSDB, 2009). Trimethylamine has an even lower odor threshold than the other methylamines of 0.00044 ppm, which is also much lower than any occupational exposure value (Amoore and Hautala, 1983).

Ethanolamines, such as mono-, di- and tri-, are gas “sweetening” agents (e.g., used for amine scrubbing or acid gas removal processes), and are found in detergents or cleaner formulations. Monoethanolamine (MEA) is an amino alcohol, produced commercially by aminating ethylene oxide with ammonia. That process results in replacement of one hydrogen of ammonia with an ethanol group. MEA is widely used in cosmetics as a pH adjuster, buffering agent, and surfactant, and is used in making soaps and detergents, inks, dyes, and rubber (NJDHSS, 2002; CIR, 2012). Industrial uses include the manufacture of emulsifiers and dispersing agents for textile specialties, agricultural chemicals, waxes, mineral or vegetable oils, paraffin, polishes, cutting oils, petroleum demulsifiers, and cement additives (DOW, 2003). In addition, MEA is an intermediate for resins, plasticizers, and rubber chemicals, and can be used as a lubricant, humectant and surfactant (CIR, 2012). It has an ammonia-like odor, with a very low vapor pressure of 0.404 mm Hg, and a high boiling point of $171^{o}$ C (equivalent to $340^{o}$ F), which indicate that significant exposure via inhalation is highly improbable under any reasonable set of environmental circumstances (TCEQ, 2015). Further, MEA can occur naturally in the environment, as it is an important degradation product of phospholipids in mammal and bacterial cell membranes. MEA has a reported odor threshold of 2.6 ppm (Amoore and Hautala, 1983). Diethanolamine, a colorless powder or liquid with a slight ammonia-like odor, is used in a number of consumer products such as cosmetics, shampoos, and pharmaceuticals and is also used as an intermediate in the rubber chemicals industry, as a humectant and softening agent, and as an emulsifier and dispersing agent in various agricultural chemicals (USEPA, 2000).

Diethanolamine, like MEA, has a low vapor pressure of 0.577 mm Hg (USEPA, 2000) with a much lower odor threshold of 0.27 ppm (Amoore and Hautala, 1983). Triethanolamine is a clear, colorless, viscous liquid with a slight ammonia-like odor and low vapor pressure like the two other ethanolamines previously described, but there is no reported odor threshold. The National Cancer Institute nominated triethanolamine for study because of its widespread use in cosmetics and many other consumer products, its high potential for worker exposure, and its potential to convert into the carcinogenic nitrosamine, N-nitrosodiethanolamine (NTP, 1999).

Nitrosamines and nitramines can be formed during the process involving amine-based $CO_2$ capture technologies. Nitrosamines are very water soluble, with negligible soil adsorption and high leaching potential. They are formed during industrial processes such as rubber manufacturing, leather tanning, metal casting, and food processing. They are found in sewage and N-nitrosodimethylamine (NDMA) has been formed during water treatment processes, and in chlorinated swimming pools and hot tubs. NMDA is highly mobile in soil, with potential to leach into groundwater. It has a faint odor; however, no odor threshold has been established (USEPA, 2014). Nitrosamines can be formed when secondary and tertiary amines react with nitrogen oxides in the atmosphere, while nitramines can be formed from all three classes of amines (i.e., primary, secondary, and tertiary). Concentrations of nitrosamines in circulating/waste solvent have been reported to range from 1.6 mg/L to 215 mg/L (SEPA, 2015). Nitramines are more stable in the environment than nitrosamines, allowing greater potential for atmospheric accumulation with formation depending on environmental conditions, as well as the types of amines present (Sorensen et al., 2013). The primary anthropogenic source of nitramines to the environment is weapons manufacturing activities and military sites, as well as ammunition factories (Poste et al., 2014).

## 2.2 Aromatic Amines

Aromatic amines are weaker bases than alkylamines and more polar than alkanes, but less polar than alcohols. They have diminished solubility in water when compared to the alcohols and good solubility in many organic solvents. Aniline, the simplest aromatic amine, is a clear, slightly yellow oily liquid that turns brown when exposed to air (Teaf et al., 2016). It has a fishy odor which allows for adequate warning for acute exposures. The reported odor threshold for aniline is 1.1 ppm (Amoore and Hautala, 1983). Aniline is a parent amine raw material used in the chemical industry for the synthesis of many compounds, including dyes, rubber accelerators, antioxidants, drugs, photographic chemicals, isocyanates, herbicides, and fungicides (ATSDR, 2014). Exposure is most likely to occur in occupational settings for those working with aniline. People living near contaminated sites conceivably could experience exposure through food or drinking water. However, airborne exposures to aniline are unlikely under any reasonable set of circumstances, given a vapor pressure at ambient temperature reported to be 0.67 mm Hg (USEPA, 2000; ATSDR, 2014).

# 3. TOXICOLOGICAL PROPERTIES

Odors represent a potential indication of exposure, and the ease with which a chemical is detected by smell has implications which may be indicative of potential exposure levels. A very low detection threshold imparts a toxicological characteristic known as “good warning properties” to substances such as the amines. The alkylated amines are primarily irritants and have sensitizing properties. In most cases, health-based criteria are much higher than the odor threshold values, allowing warning properties to prevent unwanted or potentially dangerous exposures (see Table 1). Alkyl amines can irritate the nose, throat, and lungs causing coughing, wheezing, and/or shortness of breath, as well as burning eyes and skin, together with the potential for organ toxicity. One major concern for alkylated amines is the toxicity of their degradation products, such as nitrosamines and nitramines.

Repeated exposures to ethylamine may damage the liver, kidneys, and heart and can irritate the lungs, though there is no evidence that ethylamine causes cancer in animals (NJDHSS, 2003a). Inhalation of diethylamine can cause sore throat, cough, and shortness of breath. Symptoms of lung edema may occur a few hours following a high level exposure (CDC, 2015a). Exposure to triethylamine can result in the same types of symptoms as ethylamine and diethylamine, in addition to headache, dizziness, and nausea (CDC, 2015b). The eyes are the most sensitive organ to triethylamine exposure and may involve complaints of seeing “blue haze” or having “smoky vision” (NIH, 2016). Human health studies are lacking for triethylamine as no information is available on the reproductive, developmental, or carcinogenic effects of triethylamine in humans (OEHHA, 2002; NIH, 2016). The acceptable occupational exposure limit for long term exposure to triethylamine of 0.5 ppm, as adopted in 2015, is much lower than for the other two ethylamines values that were established in 2013 (see Table 1; ACGIH, 2001). The more recent value is close to the reported odor threshold for trimethylamine.

Methylamine liquid and vapor are highly irritating to the eyes following short-term exposure and prolonged exposure may irritate both the skin and eyes (CDC, 1978). Acute exposure to airborne methylamine may cause bronchitis and high levels of exposure may affect the liver (NJDHSS, 2004). All reported effects of dimethylamine in humans are related to the compound’s irritant properties (USEPA, 1990). Inhalation of concentrations greater than 100 ppm may cause irritation of the lungs, nose, throat, and eyes, as well as coughing or sneezing (USEPA, 1990; NJDHSS, 2001). Dimethylamine may cause temporary corneal edema when absorbed into the tissue of the eye from the atmosphere. Such corneal effects may give rise to a perception of “blue haze” or “fog” around lights. However, the effect is transient and has no known residual effect (Grant, 1986). Corneal edema also has been noted in animal studies, but only at an air concentration of 1,000 ppm or higher (Steinhagen et al., 1982). In experimental animals, the irritation concentration-response curve for rats indicates that a 10 minute exposure at 600 ppm would be expected to elicit a 51% decrease in respiratory rate, though concentrations of 600, 1,000 or 2,500 ppm produced no mortality (Steinhagen et al., 1982). While chronic exposure to dimethylamine at levels on the order of 175 ppm for 12 months may result in nonspecific reduced body weight gains (Buckley et al., 1985), these observations have no relevance to acute, short-term exposure at or around the odor threshold in air. Trimethylamine can be toxic by inhalation and sufficient concentrations can irritate the nose and throat, as well as the lungs, causing coughing and/or shortness of breath (NJDHHS, 2003b). Acceptable occupational exposure limits for long term exposure to these three methylamines range from 5 ppm (ACGIH TLV) to 10 ppm (NIOSH REL; see Table 1).

In general, ethanolamines have a low degree of acute toxicity (Gentry et al., 2014). Workplace exposure limits for MEA are set at 3 ppm for OSHA PEL and ACGIH TLV averaged over an 8-hour work shift, while the NIOSH REL is 3 ppm averaged over a 10-hour work shift (see Table 1). These limits are only protective for air exposures and don’t reflect potential occupational exposure through skin contact (NJDHSS, 2002), though the latter route is not of environmental significance. MEA poses risks similar to those of the other amines in that direct dermal exposure may cause burns, damage to the eyes, and may irritate skin, while inhalation exposure may irritate the lungs and throat of some persons (NJDHSS, 2002; Santa Cruz, 2009). In the case of MEA, like triethylamine, the odor threshold reported is close to the reported health-based occupational exposure values. There is no published carcinogenicity data regarding MEA, though mutagenic studies have been largely negative (CIR, 2012; TCEQ, 2015), suggesting that cancer risks are unlikely. Again, irritation of the nose and throat after inhalation, and irritation of the skin following dermal exposure, are acute effects of diethanolamine. However, there is no information available regarding chronic effects of diethanolamine exposure in humans, while animal studies have reported effects on the liver, kidney, blood, and CNS following chronic oral exposure. EPA has not classified diethanolamine for carcinogenicity (USEPA, 2000). Similar acute symptoms are seen with triethanolamine exposure. The eyes, skin, and respiratory system are the organs affected most dramatically (OSHA, 2004). Triethanolamine was not mutagenic in any of the *in vitro* or *in vivo* short-term tests performed by NTP and dermal carcinogenicity studies were inconclusive (NTP, 1999).

Nitramines are generally more stable than nitrosamines in the environment, a feature which increases the potential for long term exposure (Sorensen et al., 2013). There are only a few studies regarding health effects of aliphatic nitramines, but due to structural similarities to nitrosamines there has been interest in their potential mutagenicity and carcinogenicity (NIPH, 2011). Some aliphatic nitramines have been found to be mutagenic in bacterial assays (NIPH, 2011); however, nitramines appear to be less potent than nitrosamines in carcinogenicity studies. Nitrosamines are practically nontoxic to fish and invertebrates in aquatic acute toxicity tests. They have moderate acute toxicity to animals and humans. However, approximately 90% of nitrosamines are thought to be carcinogenic including NDMA, currently only used in research, which is regulated as a carcinogen. The environmental toxicity of many individual nitrosamines is not well understood (SEPA, 2015), and Wagner et al. (2014) have suggested regulating these compounds not as a class, but as individual compounds based on the wide range of responses in mutagenicity and genotoxicity studies.

Some aromatic amines have tumorigenic capacity such as urinary bladder cancer. Toxicology of aniline compounds are dependent on: mode of action, type of substituents (chloro-, methyl- etc.), number of substituents (mono-, di-, etc.), and position (*ortho-*, *meta-*, *para-*). The most common symptoms of acute aniline intoxication in occupational exposures are cyanosis, lacrimation, tremors, tachypnea, lethargy, methemoglobinemia, sulfhemoglobinemia and Heinz body formation. Methemoglobinemia, which compromises the oxygen carrying capacity of blood, is characteristic of aniline exposure (ATSDR, 2002). Because of its fat solubility, aniline in liquid form can penetrate intact skin. Moderate exposure to aniline by any route may cause cyanosis, but headache, weakness, irritability, drowsiness, dyspnea, and unconsciousness may occur following oxygen deficiency. Aniline ingestion can cause enlargement of the spleen, hemosiderosis, and marrow hyperplasia. Chronic aniline poisoning at low levels is controversial though some CNS symptoms have been suggested. Severe acute toxic effects may occur at about 100 ppm in air, with symptoms appearing first at approximately 10 ppm (Teaf et al., 2015). The TLV set by ACGIH is 2 ppm, and the OSHA PEL is 5 ppm (Table 1). Both of these precautionary values carry a “skin” notation, acknowledging the possibility of significant dermal absorption potential. Carcinogenicity of aniline to humans is not clear, since it is only mildly carcinogenic to rats, and is not carcinogenic in mice. This may be due to interspecies metabolic differences. Industrially important exposures to aniline are evaluated by measurements of urinary aniline, aniline released from hemoglobin in the blood, or urinary *p*-aminophenol (Teaf et al., 2015).

## 4. AMINES IN THE ENVIRONMENT

Post combustion capture (PCC) and storage of $CO_2$ is a well-known and important mitigation technology used to reduce anthropogenic $CO_2$ emissions, and the most advanced and widely accepted technology is chemical absorption with aqueous amine solvents. Use of aqueous amines as solvents in PCC technology has caused some concern regarding potential human exposures to these amines and their degradation products following release to the atmosphere, which can result in what has been termed "summer smog" (Pehnt and Henkel, 2009). Aqueous amine solutions are the most common solvents used for PCC processes, and 30% monoethanolamine (MEA) is the industry standard (Reynolds et al., 2012), with advantages related to a high reaction rate and the capability to remove trace $CO_2$ levels (Veltman et al., 2010). Morken et al. (2014) measured atmospheric emissions, reporting main MEA degradation products to be amides, amino acids, and other amines. The authors also reported low parts per billion (ppb) levels of MEA, and below detection levels of nitrosamines and nitramines. Human and environmental impacts of substituting $CO_2$ emissions with amine solvent and degradation products is incompletely understood (Reynolds et al., 2012). Solvent combustion (degradation and evaporation), solvent management (corrosion, foaming, and reclaiming) and environmental management (solid and aqueous waste and emissions) are all important issues when dealing with PCC technology (Pehnt and Henkel, 2009; Reynolds et al., 2012). In those processes, heat is required in the stripper unit in order to regenerate the MEA solvent, resulting in a high energy penalty (Pehnt and Henkel, 2009; Luis, 2016). Net effects of commercial scale PCC are expected to exhibit mild human and environmental impacts, but some ecotoxicity in possible (Luis, 2016). Veltman et al. (2010) showed that emissions from MEA result in a 10-fold increase in adverse freshwater conditions due to the volatility of MEA, while human toxicity was not increased.

Interest regarding levels of amines in ambient air is lacking due to limited availability of published emissions data, likely due to the analytical challenge of detecting amines at ambient levels in the environment (Poste et al., 2014). One group in the U.S. has established promising techniques to characterize real-time emissions (Ge et al., 2014), while others acknowledge that further work is required to develop reliable methods that can measure nitrosamines in the ambient air over a sufficient period of time to determine likely impacts of the carbon capture process (SEPA, 2015). There are limited data available for amines in surface waters however most reported concentrations are often below detection limits (BDL) (Poste et al., 2014). Sites influenced by human activity generally have some of the highest concentrations of amines in surface waters (Poste et al., 2014).

In groundwater, the principal concern is exposure to nitrosamines and secondary amines. High levels of NDMA can be found at rocket engine test facilities. There is little data available regarding the environmental fate of nitrosamines and nitramines. One study showed that nitrosamines are highly susceptible to photolytic degradation while nitramines appear to be photolytically stable. The study authors intend to perform other studies on soil adsorption and biodegradation to better determine how these chemicals behave in the environment (Sorensen et al., 2013). As of March 2011, NDMA had been detected in 1,787 out of 17,900 samples obtained from public water systems monitored as part of the unregulated contaminant monitoring rule (UCMR; USEPA, 2014).

## 5. AMINE GUIDELINES

Table 1 compares the occupational exposure guidelines to the reported odor detection thresholds (Amoore and Hautula, 1983) for each of the chemicals previously discussed. Nearly every chemical in the table has an odor threshold much lower than its occupational exposure value, allowing for adequate warning of possible exposure. In most cases, except for triethylamine where the reported value by ACGIH, as adopted in 2015, is much lower than the OSHA value reported in the final rule in June of 1993, each of the agencies is in close agreement. For temporal comparison, the NIOSH RELs were originally published in September 2005 with the most recent version in September 2007 with only minor technical changes. In addition to the listed odor threshold values, Verschueren et al. (1983) listed the 100% recognition values for several of these amines that are the concentrations at which all members of an odor panel recognize the odor. For ethylamine, triethylamine, methylamine, dimethylamine, trimethylamine and monoethanolamine these values were 0.8, 0.3, 3, 6, 4, and 5 ppm, respectively (see Table 1).

*Table 1*. Occupational exposure values for select amines and reported odor thresholds

| Chemical | ACGIH-TLV (ppm) | OSHA-PEL (ppm) | NIOSH-REL (ppm) | DFG-MAK (ppm) | Carcinogenic Category | Reported Odor Threshold (ppm; 100% recognition) |
|---|---|---|---|---|---|---|
| Ethylamine | 5 | 10 | 10 | 5 | NL | 0.95 (0.8) |
| Diethylamine | 5 | 25 | 10 | 2 | TLV-A4 | 0.13 |
| Triethylamine | 0.5 | 25 | NL | 1 | TLV-A4 | 0.48 (0.3) |
| Methylamine | 5 | 10 | 10 | 10 | NL | 3.2 (3) |
| Dimethylamine | 5 | 10 | 10 | 2 | TLV-A4 | 0.34 (6) |
| Trimethylamine | 5 | NL | 10 | 2 | NL | 0.00044 (4) |
| Monethanolamine | 3 | 3 | 3 | 0.2 | NL | 2.6 (5) |
| Diethanolamine | 0.2 IFV | NL | 3 | NL | IARC-2B<br>MAK-3B<br>TLV-A3 | 0.27 |
| Triethanolamine | 5 | NL | NL | 5 I | IARC-3 | NL |
| Aniline | 2 | 5 | NL | 2 | EPA-B2<br>TLV-A3 | 1.1 |

IFV-measured as inhalable fraction and vapor; I-measured as inhalable fraction of aerosol; NL-not listed; MAK-Federal Republic of Germany maximum concentrations values at the workplace. Source: ACGIH, 2016; Amoore and Hautala, 1983; Verschueren, 1983.

For three of the above listed amines USEPA has established Regional Screening Levels (RSLs) in air. Those values are 0.73 ug/m$^3$, 0.021 ug/m$^3$, and 0.1 ug/m$^3$ for triethylamine, diethanolamine, and aniline, respectively (0.00018, 0.000005, 0.000026 ppm; USEPA, 2016). These residential values are believed to be without significant health risk, and are based on continuous chronic exposures over a lifetime.

## 6. AMINES IN RISK ASSESSMENT

Odor substances released from a source are only important to odor pollution if they are dispersed to the surrounding area (Yuwono and Lammers, 2004). Techniques used to detect odor emissions often are the most important challenges when dealing with odor pollution (Yuwono and Lammers, 2004). Odor issues often can overshadow health risk considerations of many of the amines, wherein people may perceive an odor as a human health concern. People detect and perceive odors in different ways and some may be more sensitive to odor than others. Individual sensitivity can vary significantly based on differences in sensory and physical responses experienced by individuals who inhale the same compounds (Yuwono and Lammers, 2004). Studies have found that symptoms reported following most odor detections are the result of nontoxicologically significant odor-related mechanisms because the low odor thresholds will provide an effective toxicological margin of safety (Shusterman, 1992). Because there are many chemicals that may have similar odors, it is imperative that local sources of odors be identified in order to determine possible exposure quantities. In most cases, perception of the odor is much different than the actual toxicity of the chemical; thus, site-specific circumstances should be taken into account when performing a risk assessment that deals with potential odor-causing chemicals.

## 7. CONCLUSION

Perceived odors in humans may cause issues related to psychological responses in individuals that are not always toxicologically significant in terms of human health. Psychological differences among individuals can lead to subjective and highly variable results in olfactometry, so researchers are focusing on objective measures via odor detection instrumentation, rather than the human sensory system (Yuwono and Lammers, 2004). When assessing risk to human health actual chemical exposure needs to be determined before casting aspersions toward health effects of odors that can be detected, in many cases, at levels well below levels that are cause for health concern. Emissions of amines from future PCC facilities will represent a new potential external source of amines to the air and surface water. However, due to numerous and widespread natural sources of amines in the environment, it will be difficult to quantitate the source in many instances. One risk of adverse environmental or health effects of amines is not from the amines themselves, but from potentially toxic compounds that may form through reactions with other atmospheric chemicals and degradation in the environment. This is of lesser concern with respect to substances exhibiting low vapor pressure and/or a high boiling point.

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# RESIDUAL EFFECTS OF BURNING ON SOME SOIL CHEMICAL AND PHYSICAL PROPERTIES IN FEREYDAN PASTURES

*West Coast Conference, March 2016*

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## ABSTRACT

Among various destruction factors affecting forests and grasslands, especially in arid and semi-arid regions, fire is considered dangerous and results in different physical, chemical and biological changes on soil properties depending on the conditions. This study aimed to evaluate the residual effects of burning on some soil chemical properties in Fereydan pastures. The experiment was conducted in a completely randomized design with unequal replicates. Soil texture, organic matter contents, soluble potassium, calcium and magnesium, available iron, manganese and zinc were measured using standard methods. The results showed that fire had a significant effect on some of the measured soil chemical properties. Soil organic matter content, soluble potassium, calcium and magnesium, available phosphorus, iron, and manganese were increased due to firing. Mean comparisons showed that soil organic matter increased from 2.10 in the unburned to 4.12% in the burned soil. The soluble potassium, calcium and magnesium increased from 0.45, 6.42 and 1.19 in the unburned to 0.95, 9.91 and 2.22 meq/l in the burned soil, respectively. The available phosphorus, iron and manganese were increased from 31.30, 18.22 and 37.29 in the unburned to 34.17, 20.39 and 55.64 mg/kg soil in the burned soil. The overall impact of burning on soil chemical properties was greater in the first year after the fire and the effect decreased with time.

**Key words:** arid and semi-arid, fire, time, grasslands, completely randomized design

## 1. INTRODUCTION

Fire is one of the natural destruction factors that occurs in most ecosystems. It is also a tool used by humans to manage a wide range of natural ecosystems around the world. For example, it can produce a variety of effects on soil, water, riparian biota, and components of the wetland ecosystems (Neary et al., 2005). Rangelands are a component of the natural and dynamic earth ecosystems that constitute the largest area of land (Sharifi and Imani, 2006). Rangelands can be defined as lands where livestock are grazed extensively on native vegetation, and where the rainfall is too low or erratic for agricultural cropping (Myers et al., 2004). Fire effect on the nutrients of an ecosystem depends on the type and frequency of fire, the available fuel load, time and season of the burn, vegetation type, and topography and weather conditions of the site after

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[§] Corresponding Author: M. A. Hajabbasi, Department of Soil Science, College of Agriculture, Isfahan University of Technology, Isfahan 84156-83111, Iran; Tel: +98 31 33913477; hajabbas@cc.iut.ac.ir fire (Kumar et al., 2013). Fire scientists, land managers, and fire fighters personnel need to assess the effects of fire on these components, and the balance of overall benefits and costs associated with the use of fire in ecosystem management (Neary et al., 2005). Fires in forests and pastures of Iran that have different climates and vegetation occur most often by humans and are intentional. According to available statistics, between 1991 and 1997, more than 3000 fire events occurred, which affected 13700 acres of land natural resources (Unnamed, 2012). This study aimed to evaluate the residual effects of fire on soil physical and chemical properties in the Fereydan pastures (Central Zagros, Iran). Figure 1 shows two of these grassland fires, adjacent to the un-fired part.

*Figure 1.* Fire in the grasslands of Iran (Isfahan Province, Fereydan pastures)

Many physical, chemical, mineralogical, and biological soil properties can be affected by forest fires (Certini, 2005). Soil texture is based on the relative proportion of different-sized inorganic constituents that are found in the 0.08 inch (less than 2 mm) mineral fraction of the mineral soil (DeBano et al., 1998). The components of soil texture (sand, silt, and clay) have high temperature thresholds and are not usually affected by fire unless they are subjected to high temperatures at the mineral soil surface. The most sensitive component of soil texture is clay, which begins changing at soil temperatures of about 752 °F (400 °C) when clay hydration and clay lattice structures begin to collapse. At temperatures of 1,292 to 1,472 °F (700 to 800 °C), the complete destruction of the internal clay structure could happen. However, silt and sand mainly quartz grains have a high melting point (1,414 °C). Quartz materials at the soil surface only under intense heating become fused. When fusion does occur, soil texture becomes more coarse and erodible (Neary et al., 2005).

Chemical changes in soil after fire are more important because changes in nutrient cycle and soil organic matter can alter the productivity of the ecosystem (Verma and Jayakumar, 2012). Fires exert multiple levels of effects on the earth system through regulating nutrient cycling in ecosystems and emitting climate-forcing gases and aerosols into the atmosphere (Zhao et al. 2012). In low intensity fires, combustion of litter and soil organic matter increase plant available nutrients, which results in rapid growth of herbaceous plants and a significant increase in plant storage of nutrients. Whereas high intensity fires can result in complete loss of soil organic matter, volatilization of N, P, S, K, death of microbes, etc. (Verma and Jayakumar, 2012). Most studies on the effects of fire on soil chemical quality have been focused on evaluating changes in organic matter and available macronutrients (e.g. Carballas, 1997; Couto-Vázquez and González-Prieto, 2006; Úbeda et al., 2006). On the contrary, fewer studies have evaluated post-fire effects on soil micronutrients and results are sometimes contradictory. Soil available micronutrients often increase after fire as extractable Mn and Zn, extractable Fe and B contents, and extractable Cu. However, lower levels of extractable Co, Fe and B, and Cu have also been reported, probably due to variations in fire intensity, precipitation regime and type of vegetation and soil (Gómez-Rey et al., 2013). As a general rule, the total amounts of chemical elements are never increased by fire. The total amounts of different chemical elements on a particular burned site most likely decrease, although in some cases may remain the same (for example, elements with high temperature thresholds such as Mg and Ca). The fire, however, does change the form of different elements and in many cases makes them more available for plants and other biological organisms (Neary et al., 2005).

## 2. MATERIAL AND METHODS

Fereydan, the study area located at central Zagros of Iran within 49º 52´ and 50º 51´E longitudes and 32º 31´ and 33º 21´ N latitudes (Figure 2). The average elevation above sea level was 2760 m, mean annual precipitation and temperature was 450 mm and 4.9 ºC respectively. Pastures of this region are burned each year for various reasons. Therefore, in this study it was decided that the information related to the years 2008 to 2012 should be used to select sampling locations. For this purpose, by using available information of the years 2008 to 2011, 10 stations per year and for 2012 due to the low number of fire occurrences, five stations were selected. In each station, one point as fire treatment and one point as a control section were chosen. To minimize the environmental and spatial variabilities impacts on soil characteristics, In choosing the location for the treatment and control at each station we tried the measuring points were selected as are close together as possible Soil samples were taken from the A horizon (0–5 cm depth), and for each point, three random samples were taken and mixed and then a composite sample was prepared from it.

Soil texture was determined after removing the OM and Fe-oxides H2O2 and oxalate solution (0.1 M) at room temperature by hydrometer method (Ge and Bauder, 1986). Soil organic matter was measured by Walkley-Black method (Walkley and Black 1934). Soluble K was determined by flame photometry (Sparks et al. 1996), and $Ca^{2+}$ and $Mg^{2+}$ were measured by EDTA titrimetry (Soil Survey Staff, 2009). Available Fe, Mn, and Zn were measured by DTPA extraction method (Liang and Karamanos, 1993). The experiment was conducted in a completely randomized design with unequal replicates.

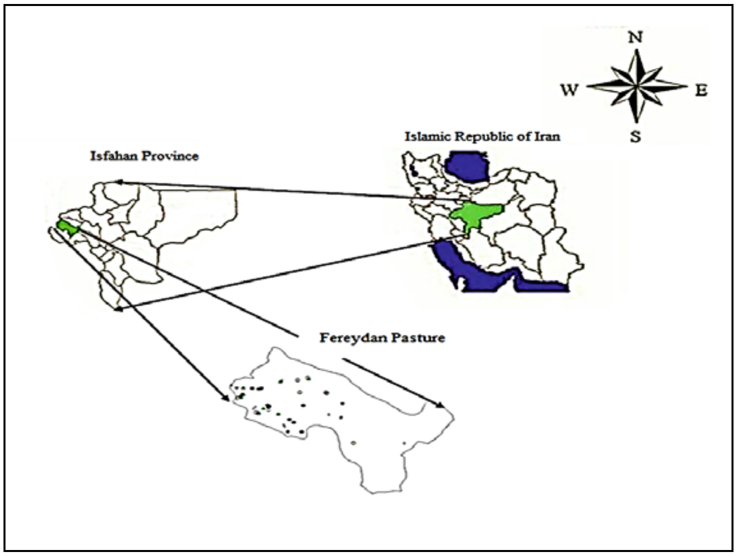

*Figure 2*. Study area and location of sampling points

# 3. RESULTS

Variation range of percentages soil-forming particles including sand, silt and clay were 14.2-73.8, 15.24-58.9 and 0.13-26.4 respectively in burned areas, and in unburned areas 2.6-60.6, 10.7-92 and 2.4-33.2 respectively. The minimum and maximum percentages of organic matter in unburned areas were 0.07 and 6.42, and 1.58 and 10.19 in burned areas, respectively. The results showed that fire significantly affected the measured soil chemical properties, but not much effect was seen on soil texture (Table 1), which is similar to the results of Granged et al. (2011) (Table 1).

Granged et al. (2011) reported that the sand content increased slightly from 41.9±3.7% (pre-fire conditions) to 52.7±5.7% (immediately after fire), and a strong reduction was observed in the proportion of clay, which decreased from 19.5±3.2% (pre-fire conditions) to 10.8±1.6% (immediately after fire). Average values of silt content decreased between 38.6±5.6% (pre-fire conditions) and 32.7±9.1% (3-years after fire), but no significant differences were observed between groups.

ANOVA showed no significant effect of fire on soil phosphorus.

*Table 1*. The analysis of variance of soil physical and chemical properties

| Sources variation | DF | Mean square | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | %OM | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Fe^{2+}$ | $Mn^{2+}$ | $Zn^{2+}$ | %Sand | %Silt | %Clay |
| Fire | 1 | $96.28^{**}$ | $6.34^{**}$ | $302.54^{**}$ | $33.51^{**}$ | $105.34^{*}$ | $18903^{**}$ | $6.54^{**}$ | $235.9^{ns}$ | $270.99^{ns}$ | $1.23^{ns}$ |
| Year | 4 | $4.65^{ns}$ | $0.47^{ns}$ | $4.24^{ns}$ | $3.19^{**}$ | $134.16^{**}$ | $2350.7^{*}$ | $1.04^{**}$ | $62.26^{ns}$ | $71.70^{ns}$ | $41.58^{ns}$ |
| Fire × Year | 4 | $5.02^{ns}$ | $0.46^{ns}$ | $14.52^{*}$ | $5.52^{**}$ | $4.04^{ns}$ | $2237.7^{ns}$ | $0.16^{ns}$ | $65.07^{ns}$ | $46.47^{ns}$ | $3.23^{ns}$ |
| Error | 80 | 2.76 | 0.21 | 4.67 | 0.67 | 26.03 | 986.46 | 0.35 | 254.14 | 179.23 | 51.25 |
| C.V | | 51.93 | 65.00 | 26.49 | 48.01 | 25.46 | 73.89 | 52.16 | 39.49 | 30.83 | 42.53 |

(*) and (**) indicated significant effect on the level of 5 and 1 percent respectively and ($ns$) indicates non-significant

In general, fire may lead to a coarser soil texture which is due to eroding silt and clay. Figure 3 shows that out of 45 locations for 23 sites, soil texture class has been changed. This change could also be due to various fire induced processes like increasing erosion and deposition in the burned places.

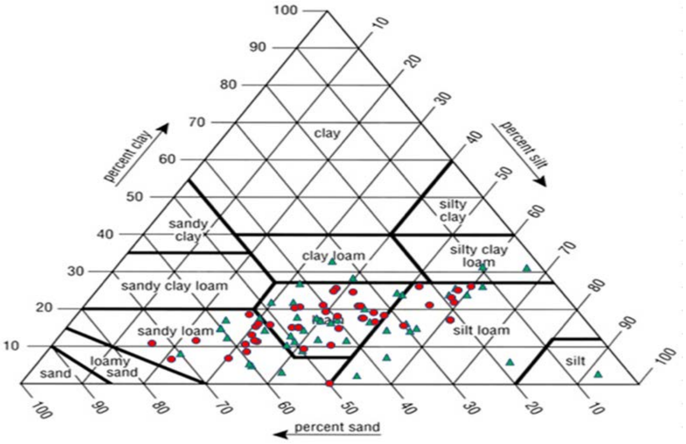

*Figure 3*. Soil texture class distribution in the studied sites, ▲before and ●after the fire

Nutrient availability in the soil can be increased by the translocation of nutrients downward into the soil during a fire. This occurs because steep temperature gradients are produced in the upper soil layers during the combustion of the litter and humus on the soil surface (DeBano, 1991). The behavior of micronutrients, such as Fe, Mn, Cu, Zn, B, and Mo, with respect to fire is not well known, but is useful to understand its effect on the post-fire recovery of soils and plants (Verma and Jayakumar, 2012).

Mean comparison showed that the main effect of fire on soil organic matter was statistically significant (Table 2). Organic matter content of the soil in the burned area was increased. The increase in the samples related to 2008, 2010, and 2012 were significant, and the samples related to 2009 and 2011 were not significant (Figure 4).

*Table 2*. The mean comparison of fire effect on soil properties

| Treatment | Soil properties | | | | | | |
|---|---|---|---|---|---|---|---|
| | OM | $K^{+}$ | $Ca^{2+}$ | $Mg^{2+}$ | $Fe^{2+}$ | $Mn^{2+}$ | $Zn^{2+}$ |
| | % | (meq.$l^{-1}$) | (meq.$l^{-1}$) | (meq.$l^{-1}$) | (mg.$kg^{-1}$) | (mg.$kg^{-1}$) | (mg.$kg^{-1}$) |
| Unburned | $2.10^{b}$ | $0.45^{b}$ | $6.42^{b}$ | $1.19^{b}$ | $18.22^{a}$ | $29.37^{b}$ | $0.87^{b}$ |
| Burned | $7.08^{a}$ | $0.95^{a}$ | $9.91^{a}$ | $2.22^{a}$ | $20.39^{a}$ | $55.64^{a}$ | $1.39^{a}$ |
| LSD | 0.70 | 0.19 | 0.91 | 0.34 | 2.14 | 13.17 | 0.25 |

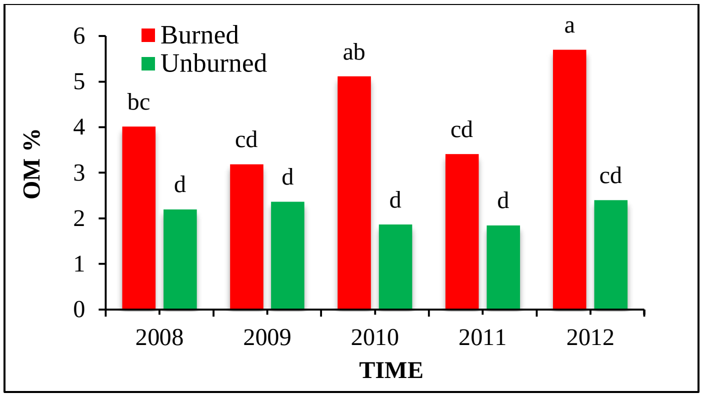

*Figure 4*. The interaction of fire and time on organic matter

Low-intensity fires increased soil nutrients, and positively affected regrowth of plants. However, wildfire causes loss of organic matter, evaporation of nitrogen, potassium, sulfur and phosphorus as well as the death of microorganisms. The average amounts of calcium and magnesium in the unburned area was 6.42 and 1.19 (meq.l$^{-1}$), respectively, and in the burned area was 9.91 and 2.22 (meq.l$^{-1}$) liter (Table 2). Figure 5A shows a reduction in the amount of calcium in the soil solution over time between burned and unburned areas. This process was observed also for magnesium in the soil solution (Figure 5B). Two months after the fire, the amount of calcium and magnesium soluble was increased in the burned area (Alauzis et al., 2004).

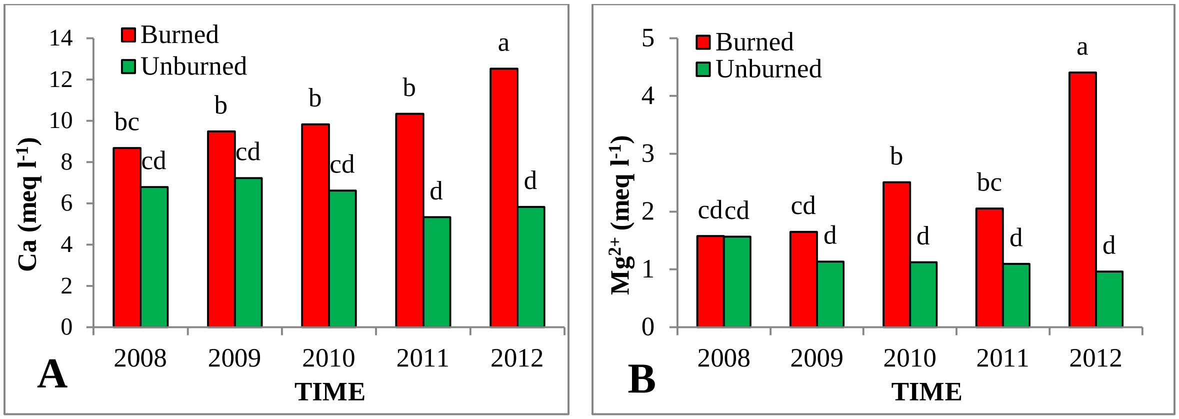

*Figure 5*. The interaction of fire and time on (A): calcium and (B): magnesium

By fire, the availability of nutrients, including potassium in the soil surface, increased (Table 2). This increase derived through the combustion of organic materials, burning herbs and turning them into ash. However, availability of potassium will have a direct relationship with the fire intensity. Some nutrient dynamics are more sensitive to fire than others. The concentration of potassium, calcium, and magnesium ions in the soil can increase or be unaffected by fires whereas nitrogen and sulphur often decrease. The pattern of changes in the amount of soluble potassium affected by fire was similar to calcium and magnesium. In the other words, rainfall and the subsequent leaching and also potassium uptake by plant species after the fire caused these decreases (Figure 6). Several researchers reported a significant increase of potassium levels in the burned area (Ekinci, 2006; Parlak, 2011; Hernández et al., 1997).

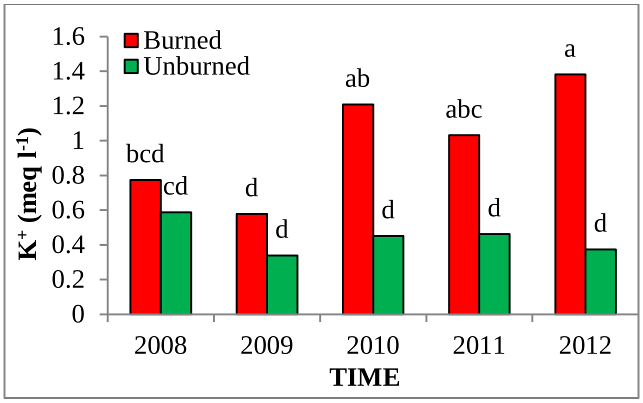

*Figure 6*. The interaction of fire and time on potassium

In short term periods, fire increased the soil micronutrients and stimulates plant growth. The main effect of fire on available Zinc, Iron and Manganese was significant (Table 2). In Figures 7A and 7C, it was observed that the difference between the amount of Zinc and Manganese in burned and unburned soils in 2012 was higher than the other years. Immediately after the fire, due to lack of rainfall and also absence of vegetation that consume release elements, the available amount of these elements in the soil surface will be increased. Garcia-Marco and González-Prieto (2008), Close et al. (2011) and Stankov Jovanovic et al. (2011) reported an increase in the availability of soil Zinc, Iron and Manganese due to fires.

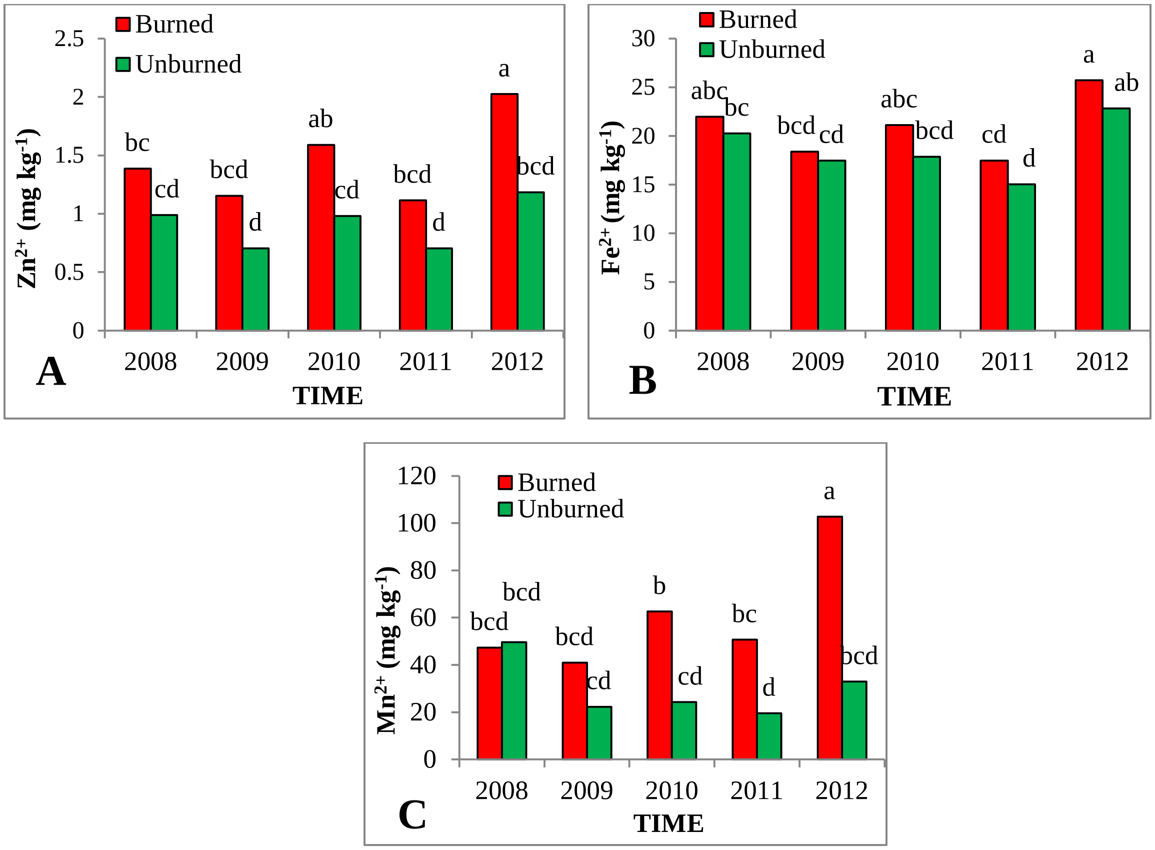

*Figure 7*. The interaction of fire and time on (A): zinc, (B): iron and (C): manganese

# 4. DISCUSSION

In the final analysis, we concluded that fire plays an important role in the management of the mentioned ecosystems. Burning increased the availability of most plant nutrients. Fires typically resulted in the reduction of organic soil nutrient pool sizes, increase soil nutrient turnover rates, and redistribute nutrients through the soil profile.

Fire intensity most likely determined post-fire soil nutrient dynamics. High intensity fires generally decreased nutrient pools more than low intensity fires and can have many other post-fire impacts that lower site productivity. Nutrient pools in the organic soil horizons are more likely to be impacted by fires than those in the mineral horizons.

Fire altered several physical soil properties, such as soil structure, texture, porosity, wettability, infiltration rates, and water holding capacity. The extent of fire effects on these soil physical properties depends on fire intensity, fire severity, and fire frequency. Intense burns may have detrimental effects on soil physical properties by consuming soil organic matter. Since soil organic matter holds sand, silt, and clay particles into aggregates, a loss of soil organic matter results in a loss of soil structure. Intense fires may also permanently alter soil texture by aggregating clay particles into stable sand-sized particles, making the soil texture more coarse and erodible. Therefore, we suggest that the influences of fire intensity and spatial heterogeneity should be fully considered in the future, and the setup of sampling plots should be based on the field survey and analysis. Finally, factors such as soil, vegetation, and climate should be taken into consideration in result analysis so as to achieve a more complete and accurate understanding of fire disturbances, and provide a theoretical basis for the restoration of forest ecosystems and sustainable forest management.

# 5. ACKNOWLEDGMENT

The authors would like to thank Isfahan University of Technology for the financial support of this thesis. We also thank the office of Agricultural Research (Soil Branch) at Fereydoonshahr, Isfahan.

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# INDEX