



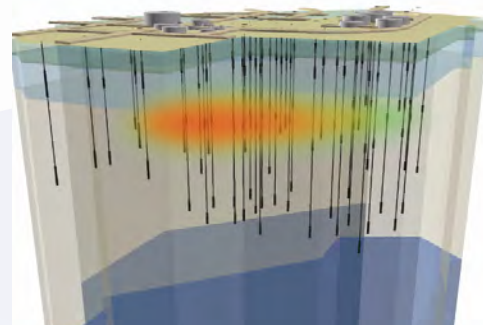
## In This Special Issue:

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## Carbon Isotope Method Distinguishes PCE Solvent Plumes

By Alan Jeffrey, PhD

DPRA Inc. and Zymax Forensics have developed and used a stable isotope technique to determine if PCE (a common dry cleaning solvent) plumes originate from a single or multiple sources. This involves measuring the carbon isotope ratio of PCE in groundwater or soil. Similar ratios in different plumes would indicate a similar source; different ratios would indicate different sources. DPRA presented the method and case studies using the method at a recent Groundwater Resources Association meeting in California on isotopic methods, and was well received.



Carbon isotope ratios have been used to identify likely manufacturers of PCE and differentiate multi-source plumes

### Case Study 1

PCE was present in substantial concentrations in soil and groundwater near a dry cleaning facility. The dry cleaner had multiple owners over a long period of time, and the main issue was whether the PCE was from one source, associated with a single owner, or from multiple releases, perhaps associated with several owners. The carbon isotope ratios were similar in all the soil and groundwater samples, and it was even possible to identify the manufacturer of the PCE. This suggested one source for the PCE, but raised another issue: whether a single source meant that the multiple owners used the same PCE supplier.

Groundwater flow was to the northeast, and the highest PCE hits were at the southern edge of the site. The owner suspected that PCE from one or more sources had migrated on to the site. The carbon isotope ratio analysis indicated the presence of the three distinct plumes. PCE in plumes A and B showed the largest isotopic difference, with PCE in plume C showing intermediate values. From the isotope ratios and groundwater flow direction, it was inferred that PCE in plume A and B were from different sources and plume C represented mixing of these plumes. This also provided isotopic fingerprints that could be used to identify possible offsite sources.

### Case Study 2

PCE was present in substantial concentrations in groundwater at a retail store site.

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Dr. Alan Jeffrey has a BS in Biochemistry, an MS in Organic Chemistry and a PhD in Oceanography. Dr. Jeffrey has over 20 years of US and international experience in environmental science and geochemistry. His expertise includes managing research projects, managing geochemical and environmental analytical laboratories; initiation and management of countrywide water monitoring program; QA/QC management of analytical laboratories; and setting up and managing a small environmental consulting company. At ZymaX Forensics, Dr Jeffrey has focused on the use of geochemical techniques to solve environmental problems, including sources of spilled hydrocarbon fuels, nitrates, and fugitive methane seeps. Dr. Jeffrey interacts with clients to determine the particular forensic issues at a site and sets up forensic analytical schemes to clarify these issues. He has prepared over 100 proprietary reports for clients that interpret analytical data, place data in the context of other site information, and answer questions such as the identity of spilled petroleum products, the similarity or difference in the products in separate plumes, and the time of release of the products.

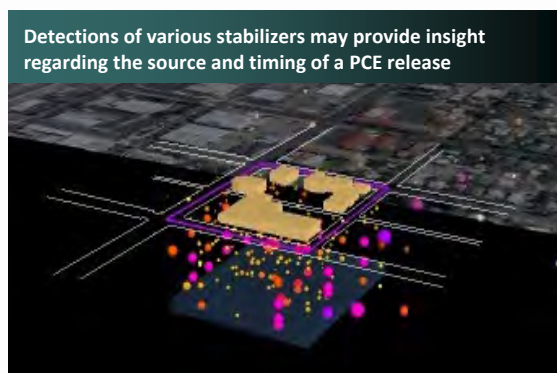
Dr. Jeffrey has served as an expert witness, has been deposed and testified at trial in litigation cases involving petroleum product spills, and is the author of fourteen publications on oceanography, petroleum geochemistry and environmental monitoring. He has conducted workshops in environmental forensics and has given numerous presentations at scientific meetings in USA, Europe and Asia.



# Age Dating PCE Releases at a Dry Cleaner Site

By Robert Morrison, PhD

Numerous forensic techniques are available to age date the release of PCE (perchloroethylene) at a dry cleaning site and includes advanced analytical techniques (stable isotope analysis, identification of stabilizing compounds), molar ratio analysis of PCE and its degradation products and the presence of surrogate compounds detected with PCE that are indicative of an activity with a unique time of operation. The majority of these techniques require the proper selection and chemical analysis of environmental samples as well as a detailed knowledge (if available) of the historical use of equipment and services offered. For example, in the early 1980s, 1,1,1-trichloroethane (TCA) was introduced as a solvent for use for leather cleaning, although it was suspected that it was unstable and caused equipment corrosion. The presence of TCA and PCE, for example, in the subsurface along with the knowledge of when a dry cleaner offered leather cleaning may provide a means to bracket when a release(s) occurred.



Detections of various stabilizers may provide insight regarding the source and timing of a PCE release

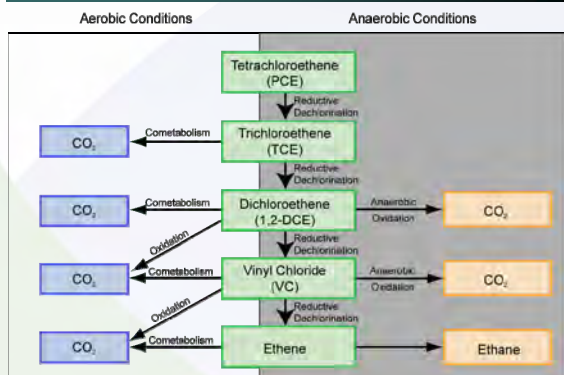
such as decabromodiphenyl oxide, organo-phosphates and phosphated ethers were commonly used.

The presence of solvents used by dry cleaners in the environmental samples can similarly be employed for age dating. Carbon tetrachloride was the primary dry cleaning solvent from the 1920s until the early 1950s. By the 1960s, PCE surpassed carbon tetrachloride for use in dry cleaning operations. The presence of non PCE solvents in environmental samples can often provide evidence regarding when releases occurred or overlapped the discharge of PCE. For example, non-PCE solvents and their date of introduction includes dipropylene glycol tertiary-butyl ether (RYNEX late 1990s), decameethylcyclotrasiloxane (GreenEarth™ late 1990s) or petroleum hydrocarbons along with hydrofluoroethane and / or perfluorocarbons (Pure Dry 2000).

Chemical stabilizers (used to minimize corrosion) and impurities may also provide insight regarding the source and timing of a PCE release. For example, the use of reclaimed PCE by a particular owner and its subsequent release into the subsurface may typically contain impurities such as methyl ethyl ketone, toluene, TCA, and butylated hydroxytoluene (a color inhibitor added to some reclaimed PCE). The use of non-reclaimed PCE (99.9% pure), in contrast, would only contain other chlorinated solvents.

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Molar ratio analysis of PCE and its degradation byproducts is one of the forensic methods used to age date a release



Other dry cleaner services may be associated with a particular owner/tenant or time frame that can be used to age date a release. For example, a dry cleaner may have also offered garment-treating services, such as waterproofing, flame retardants, stain repellants and fabric conditioners. TCA, for example, was used along with petroleum naphtha as a carrying agent for stain retardants on fabrics while flame retardant chemicals



**Dr. Robert Morrison** has a B.S. in Geology, a M.S. in Environmental Studies, a M.S. in Environmental Engineering, and a Ph.D. in Soil Physics from the University of Wisconsin at Madison. He has been working for over 35 years in the environmental field on issues related to soil and groundwater contamination. Dr. Morrison specializes in the forensic review and interpretation of scientific data for the purpose of identifying the source and age of a contaminant release and manages DPRA's environmental forensic practice group. Dr. Morrison is credited for coining the term "environmental forensics" and with Drs. Zhendi Wang (Environment Canada), Brian Murphy (Exponent), Paul Philp (University of Oklahoma), Cout Sandau (Trium, Inc.) and Steve Mudge (University of Wales) founded the International Network of Environmental Forensics (INEF) dedicated to this science, and authored the first textbooks on this subject.

Dr. Morrison has served on the editorial boards of *Ground Water*, *Groundwater Monitoring Review and Remediation* and was Editor in Chief of the *Journal of Environmental Forensics* for many years. He is the author of *Environmental Forensics: Principles and Applications* and *Environmental Forensics: A Glossary of Terms* published by CRC Press, Boca Raton, Florida and is co-author with Dr. Brian Murphy of *Introduction to Environmental Forensics* published by Academic Press, Oxford England. Dr. Morrison has worked as an expert witness and confidential consultant for the United States Department of Justice, the EPA and numerous law firms. Dr. Morrison has offered deposition and court testimony in over 50 cases. In his capacity as an expert witness and confidential consultant, Dr. Morrison has provided testimony in numerous cases, some with claims in the billions of dollars.



# In Situ Thermal Remediation of DNAPLs

By Greg J. Smith P.E., P.G.

## Introduction

A family of chemicals known as dense non-aqueous phase liquids (DNAPL) that includes industrial degreasing solvents such as perchloroethene (used in industrial and dry cleaning operations), trichloroethene and 1,1,1-trichloroethane (industrial degreasing solvents), and residuals from the late 19<sup>th</sup> and 20<sup>th</sup> century town gas and coking operations, coal and oil tars have represented some of the greatest challenges in environmental restoration. The reasons for the challenges in cleaning up this family of compounds are 1) relatively low aqueous solubilities; 2) these compounds are denser than water and tend to migrate under gravity contrary to prevailing hydraulic gradients; and 3) these compounds diffuse into the aquifer matrix and have the potential of being a source of groundwater contamination after removal of the DNAPL itself.

Thermal remediation system targeting sub-slab DNAPL



A variety of studies have been conducted on the utility of source removal with conflicting and outdated information being presented. Lawrence Livermore National Laboratories performed studies in the mid-1990s that recommended focusing on source removal as having the greatest benefit. A National Academy of Sciences Study (Fountain, et al., 2004) published in 2004 questions the effectiveness of source treatment. However, some outdated information is presented on treatment technologies including in situ electrical resistance heating stating that there was limited information on applications below the water table, yet the first application of this technology below the water table occurred in 1999 and was documented in an U.S. EPA report. Further, the study over-simplifies the mechanisms of clean up in situ thermal remediation methods stating that it is only effective for compounds with boiling points less than that of water, ignoring scientific principles such as Raoult's Law. More recent work (Smith, 2008) shows that reductive

An example of an electrical resistance heating installation



dehalogenation (biotic and abiotic) and increases in partial pressures of dissolved gas such as CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>S in groundwater during in situ thermal treatment play major roles in DNAPL cleanup.

## In Situ Thermal Treatment Methods

In situ thermal methods have demonstrated themselves to be the most effective means of source removal (EPA, 2006). In situ thermal methods include steam injection, electrical resistance heating, and thermal conductive heating. Currently there are 4 main practitioners of these technologies; with some others performing limited commercial work.

From this, it is believed that more than 100 sites have been treated using in situ thermal methods, with electrical resistance technologies being the most widely accepted in the marketplace, likely numbering in excess of 80 sites at the time of writing this article. The reason for ERH's popularity is that it can and has been successfully applied beneath working factories and has been proven effective for depths of up to 130 ft deep.

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<sup>1</sup>Fountain, J.C., L.M. Abriola, L.M. Alvarez-Cohen, M.J. Baedecker, D.E. Ellis, T.C. Harmon, N.J. Hayden, P.K. Kitandis, J.A. Mintz, J.M. Phelan, F. A. Pope, T.C. Sale, B.E. Sleep, J.L. Wilson, J.S. Young, and K.L. Yuracko, Yahsgs (2004) Contaminants in the Subsurface: Source Zone Assessment and Treatment. National Academies Press, Washington, DC.

<sup>2</sup>Smith, G.J. (2008). *Symbiotic Effects of Biodegradation During Electrical Resistance Heating*. Proceedings of the Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 19-22, 2008, Monterey, California

<sup>3</sup>U.S. EPA (2006). In June 2006, U.S. EPA sponsored a 2 day meeting at Tufts University in Massachusetts bringing together vendors/practitioners performing in situ treatment methods for source removal including chemical oxidation, surfactant flooding, enhanced biodegradation, chemical reduction, and in situ thermal. This was a free-wheeling series of discussions on the successes of individual technologies and how technologies may be combined.



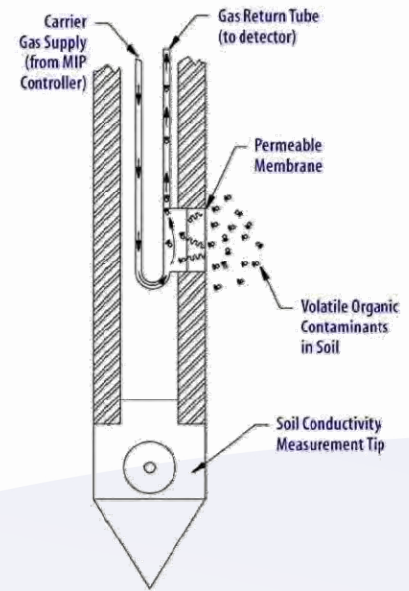
**Greg J. Smith, P.E., P.G.** is a Senior Hydrogeologist at DPRA with more than 20 successful DNAPL site closures in his resume of work starting with the industry's first in 1999 at the former AT&T Skokie Works in Illinois where regulatory standards were reached. Mr. Smith has also employed other remediation technologies, including in situ biodegradation, permeable reactive barriers, as well as conventional recovery methods including groundwater pump and treat and soil vapor extraction. Mr. Smith has worked with researchers at the University of Southern California at Los Angeles, University of Illinois at Chicago and Argonne National Laboratory performing stable isotope surveys (<sup>87</sup>Sr/<sup>86</sup>Sr, <sup>37</sup>Cl and <sup>14</sup>C) to determine fate and transport of contaminant plumes in groundwater in California, Missouri, Illinois and South Carolina. Mr. Smith has provided expert witness testimony on the fate and transport of chlorinated solvents in federal court in Michigan. He has published more than 20 articles on various aspects of soil and groundwater remediation, including a chapter on *Coupled Electrokinetics – Thermal Desorption*, in a book entitled: Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater, and co-authored the Encyclopedic Dictionary of Hydrogeology.



# What is an MIP?

MIP is an acronym for a Membrane Interface Probe which provides a means to identify the presence of dense non-aqueous phase liquids (DNAPLs) in the soil and groundwater using a direct push technology. An advantage using MIP technology is that a large number of borings can be quickly gathered and plotted to provide a three-dimensional portrayal of the DNAPL in the subsurface under real time conditions.

A MIP fits onto a conventional direct push rig, such as a Geoprobe, which is then pushed into the area of inquiry (see diagram to right). No drill cuttings are produced with this technology. The tip of the Geoprobe has a membrane that is permeable to volatile organic compounds (VOCs) along with a heating element that heats (120° F) and volatilizes compounds in the immediate vicinity of the probe tip. The volatilized VOCs pass through the membrane, where a carrier gas then transports them through sealed tubing to multiple detectors in the cab of the direct push vehicle. Detectors that can be used include a flame ionization detector (FID), an electron capture detector (ECD) and a photo-ionization detector (PID). The results from the FID, PID or ECD detectors can be combined with soil conductivity measurements to provide additional confirmation regarding the presence of a DNAPL. Daily costs using this technology are about \$3000 to \$4500; depending on the soil type and other site specific conditions, up to 300 vertical feet can be evaluated in a day.



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Mr. Hone has been an Associate Geologist with DPR since 2006 and received his B.S. in Geophysics from the University of California at Riverside. Since entering the environmental field in 2004, he has managed expert witness and litigation support projects, forensic site assessments, and remedial activities. He has utilized forensic techniques such as carbon isotope ratio analysis, interactive geo-spatial models, and aerial photography interpretation to investigate several chlorinated solvent, hydrocarbon, and nutrient releases. Mr. Hone's particular expertise is developing Geographical Information System (GIS) models and trial graphics to provide clients and juries with simplified concepts of otherwise complex geologic and hydrogeologic scenarios.

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