

ISEF Virginia Beach, Virginia Workshop, September 9 - 10, 2003

Abstracts

Forensic Evaluation of Aircraft Deicing Fluids and Jet Fuel Components in Soil, Water and Air Compartments with Implications for Remediation or Surface Water and Groundwater Protection

Eric M. Cherry, Hull & Associates, Dublin, OH

The use of aircraft and pavement deicing fluids and intermittent releases of jet fuel can result in contamination of soil and water at airport facilities. These complex mixtures can break down in the subsurface environment resulting in the loss of parent compounds and formation of multiple degradation products that are not typically included on standard USEPA analyte lists. Therefore, false negative results may be obtained when trying to identify areas of soil or water contamination, and evaluating potential ecological and human health risk. The presence of these daughter compounds can present human health or ecological concerns if concentrations are sufficiently high, or can present operational or nuisance problems to potential receptors if impacted areas are exposed to ambient conditions even when present in concentrations below risk levels. Therefore, a forensic approach must be developed to identify the parent and daughter compounds, and subsequently evaluate potential risks.

Soil, water and air samples were collected from potentially impacted areas at a municipal airport, with subsequent analysis for VOCs, SVOCs, ammonia, aldehydes, glycols, and sulfur compounds. A total of 164 different compounds were detected in one or more of the sample media. The local geochemical and microbial environment appears to play a significant role in the formation of daughter products. A comparison of chemical concentrations to promulgated standards or risk-based target concentrations suggests that the greater proportion of allocation of risk is due to non-target list daughter compounds relative to the parent compounds evaluated by the standard target list approach. In situations where large volumes of soil are affected by these contaminants, a field screening protocol has been developed to differentiate between potentially contaminated soils and those that can be reused at the facility, thereby reducing potential remedial costs.

The approach presented here has broad implications for selecting appropriate chemical tests to determine if contaminated soils present a concern at civil or military aviation facilities.

Identifying the Source and Timing of Gasoline Spills: Forensic Analysis of the Gasoline Additives MTBE and TBA

James M. Davidson, P.G., Exponent, Boulder, CO

This session will review the available scientific knowledge regarding the use, occurrence & movement of the gasoline additive methyl tertiary butyl ether (MTBE). Because MTBE has several characteristics that differ from those of other gasoline compounds, it is often possible to use MTBE as an identifier of a spill's source or timing. Forensic analysis of MTBE, and its common companion compound tert butyl alcohol (TBA), can identify when multiple gasoline spills have occurred at a single site; this can aid in allocating responsibility among a series of site owners. Great care must be used when including TBA in such analysis as there are several distinctly different causes for subsurface TBA plumes; these causes will be reviewed. Although MTBE is usually indicative of a gasoline spill, there are several non-spill sources of MTBE that must be considered during forensic analysis.

Integration of Real Time, Continuous Data Streams into Groundwater Modeling and Neural Network Technologies

John E. Dustman, Summit Envirosolutions, St. Paul, MN

The combination of disparate and converging technologies presents exciting opportunities to enhance the use of science for environmental forensics. The evolving nature of the individual capabilities of the following technologies can be integrated into a powerful tool for environmental forensics purposes:

- Computer processing speeds
- Global Positioning Systems (GPS)
- Aerial and satellite imagery
- Chemical and physical parameter sensors
- Solar power
- Wireless telecommunications
- Supervisory Control and Data Acquisition (SCADA)
- Geographic Information Systems (GIS) software (RealFlow)
- Automated Neural Networks (ANN)
- Groundwater modeling software
- Database and internet programming (GEMS)
- Data visualization and rendering (VAR) software

Field applications of these technologies have been demonstrated at a petroleum/chemical storage facility, a municipal water supply wellfield, and a mine tailings disposal facility. This presentation will present the overall concepts of integrating these technologies with examples of actual field applications. In addition, this presentation will present a vision of the potential ramifications for forensic science of the ongoing advances of these technologies.

A Canary in the Kitchen: Determining Whether Contaminated Groundwater Represents an Indoor Air Health Hazard

William A. Duvel, Jr., Ph.D., P.E., and Robert J. Flatley ENSR, Westford, MA

Everyone knows canaries were formerly used in underground coal mining to detect the unseen hazard of methane gas accumulation. More recently there has been considerable interest in detecting the hidden potential health hazard resulting from the intrusion of solvent vapors off-gassing from contaminated groundwater into the living spaces of private homes and the work places of commercial establishments. A particularly vexing problem is determining whether and to what extent indoor air contaminants are present due to vapor intrusion from outside (i.e., from groundwater off-gases) or from other sources derived from materials and products used in the home or workplace. Using information from actual recent case studies, this paper describes the practical methods for differentiating between intrusive and non-intrusive gases.

Environmental Forensics Applications at DOD Sites

Fred E. Goetz, Ph.D., US Navy, Port Hueneme, CA

The focus of this presentation is to give an overview of how environmental forensics is used within the Navy environmental program.

PAHs as Forensic Source Identification Tools: The Good, the Bad, and the Ugly!”



Robert H. Haddad, Ph.D., Applied Geochemical Strategies, Inc.

Polycyclic aromatic hydrocarbons (PAHs) have received much attention in the environmental literature over the past 30 years. The reasons for this focus include the ubiquitous occurrence of these compounds in impacted sediments, especially in the vicinity of large urban areas and the fact that these large multi-ring organic compounds are associated with human and ecological toxicity. As national and international environmental concerns continue to focus on urban riverine and coastal environments, differentiating between the various natural and anthropogenic PAH sources becomes a critical issue in the determination and allocation of environmental liability associated with these sites. PAH sources can be characterized at several levels. An initial level might include differentiating between natural or background (e.g., forest fires) and anthropogenic (e.g., petroleum releases, automobile and diesel fuel combustion, etc.) inputs to a site. The next level would involve differentiating the anthropogenic inputs in terms of their mechanisms of production (e.g., PAHs derived high temperature reactions [pyrogenic] vs. those derived directly from more moderate temperature reactions associated with petroleum formation [petrogenic]). Finally, characterization between different sources of pyrogenic PAHs (e.g., manufactured gas plant residue vs. combustion of fuels and wood) is required. This final characterization has proven to be quite difficult in many cases. It requires one to be able to identify characteristics of what has been termed urban runoff and likely includes PAHs from atmospheric deposition of vehicle combustion, from wood burning, and/or from coal burning processes; fugitive oil from vehicles (e.g., crank case drippings, motor oil, spillage from fuel loading, etc.); etc. In essence whatever PAHs are likely to find their way onto urban streets and into storm sewers.

This lecture initially provides basic background information about PAHs; focusing on a discussion of their structures and physico-chemical properties. Various major PAH sources are then discussed and illustrated, including background sources, with a focus on the analytical methods currently being used and on the major chemical differences between the various sources. These two issues (sources and chemistry) are integrated into a discussion of PAH environmental fate and transport and on the appropriateness and robustness of various PAH ratios and statistical techniques that have been used or proposed for use in identifying PAH sources in the environment. Finally, two case studies are discussed to illustrate the concepts presented earlier in the lecture; one that focuses on source characterization of PAHs found in urban aquatic sediment and the other on PAHs associated with a manufactured gas plant.

Application and Challenges in Groundwater Modeling for Environmental Forensic Investigations

Brendan M. Harley, Sc.D., P.H., C.Eng., FIEI, CDM International, Cambridge, MA

Recent developments in the operational capabilities of groundwater models and display capabilities have enormously increased the effectiveness of using groundwater modeling in forensic investigations of environmental problems. This session will present the application of long-term transient modeling using fully 3-dimensional codes for groundwater flow and mass transport to provide a very effective tool to the skilled investigator

The case study will present how a complex modeling effort enabled the development of a comprehensive understanding of a commingled regional plume emanating from several facilities along an industrial corridor. The simulations included a release period of more than 50 years, and required the incorporation of both regional pumping for municipal water supply and varying local industrial pumping, both of which impacted the long-term migration of the various plumes. A significant decline in the regional water table over the 50-year period was also incorporated. This case illustrates the ability of a skilled modeler to narrow the location of possible past releases to a relatively small area of the site. Graphical display techniques to enable detailed viewing of the varying groundwater flow system and plume migration will be presented.

The workshop will also examine the causes of temporal variations observed in a series of water quality samples at a monitoring well. This is not an uncommon observation at many sites. While these variations are frequently referred to as “pulses” and attributed to changing source release rates, we have found that in many instances these fluctuations can be observed in the simulation of plumes from a source with a constant release rate. Variations in water quality at a monitoring well location can be caused by subtle shifts in the location of the contaminant plume due to temporal variations in the groundwater flowfield, and may not be due to variation in the source loading rate. This is a characteristic not widely understood nor accounted for in many studies.

History and Evolution of Environmental Forensics

Paul T. Kosteki, Ph.D., ISEF, Amherst, MA

Environmental forensics has evolved over time into a discipline that attempts to solve environmental contamination questions through the use of analytical techniques and methods. It encompasses a wide variety of disciplines including analytical chemistry, geochemistry, atmospheric chemistry, environmental fate and transport assessment and is used in environmental litigation.

Environmental forensic techniques can be applied to the investigation of contaminated sites, determination of environmental liability, oil spill source identification, bacterial contamination and allocation of remedial costs. The techniques are used to answer the following questions:

- Who caused the contamination?
- When did the contamination occur?
- How did the contamination occur?
- Who could be the potentially responsible parties?
- How do you allocate remediation costs?
- What can be interpreted from the analyses?

This presentation will introduce the topics of the workshop and describe the activities and history of the International Society of Environmental Forensics (ISEF).

Overview of Historical Environmental Forensic Techniques: Aerial Photography, Artifact Sampling, Chemical Usage History, Commercial Formulations and Ratios, Scanning Electron Microscope, Microbiological/DNA

Robert Morrison, Ph.D., DPRA, Escondido, CA

This presentation shares information on the application of historical information combined with more traditional forensic techniques. Included in these more traditional techniques are aerial photo acquisition and interpretation, artifact sampling, the acquisition and use of chemical use information for contaminant source identification, the use of commercial formulation and ratio applications for source identification and cost allocation, scanning electron microscopy for trace metal speciation and opportunities for using microbiological techniques for source identification. A difference in data interpretation due to the presence or absence of signature additives, the use of molar ratios and surrogate chemicals and useful petroleum and chlorinated solvent ratios is summarized. The use of additives to chlorinated solvents and their reaction products (e.g., uninhibited TCA reacting with aluminum to form aluminum chloride to form aluminum chloride, 2, 2, 3, 3-tetrachlorobutane, 1, 1-dichloroethylene and hydrogen chloride) is summarized along with how this information is combined with historical information for source identification.

Overview of Data Analysis and Interpretation: Tracers and Surrogates, Associations, Ratio Evaluations Spatial and Temporal Relationships, Transport and Fate Modeling, and Mass Balance Methods

Brian L. Murphy, Ph.D., Exponent, Tampa, FL

This presentation provides a unified overview of data analysis and interpretation by noting that there are only four basic manipulations possible for concentration data. (1) Looking for tracers, which is simply the presence or absence of a substance. In some cases the tracers are surrogates indicating either the nearby or former presence of another substance. (2) Forming concentration ratios, or when many ratios are considered simultaneously, considering patterns. (3) Analyzing trends, for example in space or time. (4) Integrating concentrations in space or time to find total mass.

What is analyzed is as or more important than how. In this context site remediation programs condition thinking in ways that are not useful for forensics, by restricting what is measured (e.g. not isotopes or nonpriority pollutants) or by “coarse-grain” sampling. Some recent technologies are noted that provide “fine-grain” detail or that represent more powerful methods of data interpretation. Finally, this presentation emphasizes confidence limits or other measures of uncertainty as a necessary part of data analysis and interpretation.

The Use of Stable Carbon Isotopes to Estimate MTBE Plumes Impacting Ground Water

Gil Oudijk, Triassic Technology, Inc., Princeton, NJ

Methyl-tert-butyl ether (MTBE) is an oxygenate added to gasoline in the United States and elsewhere to boost the octane ratio and reduce tailpipe emissions. Because of its known usage time frame, the presence of MTBE can help estimate the age of gasoline releases to the environment. However, because of its recent ubiquitous presence, it can no longer be used to fingerprint or differentiate gasoline plumes in ground water. Compound-specific stable carbon isotope analysis has recently become a method for differentiating MTBE sources and plumes affecting ground water. Ground-water samples were collected from 20 monitoring wells located at two gasoline service stations in central New Jersey. The purpose of the sampling was to differentiate the dissolved gasoline plumes and possibly identify their sources. The ^{13}C values for each sample were calculated and the impacted area for each plume delineated.

As biological degradation of MTBE proceeds, the carbon isotope ratio ($^{13}\text{C}/^{12}\text{C}$ expressed as ^{13}C) becomes heavier; petroleum-degrading bacteria preferentially assimilate the lighter ^{12}C isotope, thereby enriching the residual MTBE in the heavier ^{13}C isotope. The isotopic composition of MTBE at different locations demonstrated the varying degree to which MTBE had been altered by biodegradation. The ^{13}C values provided insight into the type of release and the magnitude of biodegradation. Two types of leaks occurred at the sites: a shallow piping leak and deeper leak from a tank system. ^{13}C values in the vicinity of the shallow leak were heavier revealing increased biodegradation in the soil, while ^{13}C values in the vicinity of the tank leak were lighter revealing the lack of biological degradation in non-aqueous phase liquid (NAPL) trapped beneath the water table.

Strategic Positioning in Litigation: Development and Presentation of Field Data Supporting Cost Recovery Associated with Faulty Design of a Landfill Gas Recovery System that Impacted Residential Dwellings: A Case Study

Michael J. Pierdinock, LSP, CHMM, Lightship Engineering, LLC, Plymouth, MA

Residential apartment buildings located at 1250 through 1260 Westford Street in Lowell, Massachusetts (the “Site”) are located directly adjacent to the City of Lowell landfill. The unlined landfill accepted industrial and solid waste from 1947 through the 1980’s. The elevation of the landfill increased to 180 feet above grade in 1978. A leachate collection system was installed at the landfill in 1981. In 1992 a landfill and methane gas recovery system was installed at the landfill that utilized the methane as a fuel source to generate electricity for retail sale.

In 1995 explosive levels of methane gas was detected in a crack in an indoor pool located at one of the apartments buildings at the Site. Nuisance odors (ie. landfill gas) was evident throughout the building. As a result of this condition the City of Lowell installed combustible gas alarms in the apartment buildings and installed an in-situ horizontal landfill gas recovery system to prevent or at least abate the migration of landfill gas into the buildings. The landfill gas collected by the in-situ horizontal landfill gas recovery system was discharged to the City of Lowell landfill gas recovery and electric generation facility located directly adjacent to the Site.

The migration of landfill gas to the apartment buildings resulted in a 50 to 60% vacancy rate. The owner, Mr. Natale Sergi, had lost several hundred thousand dollars of revenue as a result of the vacancies. Mr. Sergi also claimed that the City of Lowell had over assessed the value of the property by considering the site as “clean property.” The owner sought a reduction in property taxes reflecting the loss in assessed property value and reimbursement of lost revenue from the vacancies.

Based upon a review and analyses of historical project documents, and data generated from the field investigations conducted as part of the litigation, Michael J. Pierdinock developed professional opinions regarding the nature and extent of methane and other landfill gases at the Site and the method and cost to abate the migration of methane and other landfill gases onto the Site. The findings, conclusions and opinions are set forth below and were presented in Worcester Federal Court.

Investigating the Sources and Fates of Petroleum Hydrocarbons on the Molecular Level: Recent Developments with Comprehensive Two Dimensional Gas Chromatography

Christopher M. Reddy, Ph.D., Woods Hole Oceanographic Institute, Woods Hole, MA

To study the sources and fate of petroleum hydrocarbons in coastal marsh sediments, we have been using comprehensive two-dimensional gas chromatography with flame ionization detection (GC×GC/FID) to observe and compare weathering patterns from two diesel fuel spills that occurred ~30 years ago. GC×GC/FID is a powerful approach as it is capable of resolving the complex distribution of petroleum hydrocarbons in diesel fuel at a level that has never been previously attained. The barge Florida went aground near West Falmouth, Massachusetts and spilled ~700,000 liters of diesel fuel on September 16, 1969. Marsh sediments near Wild Harbor (about a one km away from the grounded barge) were severely impacted and a recent sediment core revealed that oil still persists at sediment depths of 8 to 20 cm. On October 9, 1974, the barge Bouchard 65 spilled an undetermined amount of its cargo in Buzzards Bay, Massachusetts and contaminated Winsor Cove, which is located about 4 km north of Wild Harbor. Recent analysis of sediments from Winsor Cove also revealed that large amounts of diesel fuel continue to persist. However, most of the oil is located in the top 2-cm of the sediment. GC×GC/FID analysis of extracts from both locations allowed for excellent resolution of the saturates, naphthoaromatics, and aromatics. The saturate regions from both locations were dramatically similar and showed that the n-alkanes were completely degraded but branched alkanes (i.e., pristane and phytane) continue to persist even though one-dimensional gas chromatography was not able to confidently detect them. However, the extracts from Winsor Cove were severely depleted in the aromatics compared to the extracts from Wild Harbor. We believe this difference is due to water-washing of the spilled oil in the surface sediments of Winsor Cove. The results from these studies confirm the persistent nature of diesel fuel in coastal marsh sediments.

Overview of Forensic Applications of Statistical Methods in Environmental Forensic Investigations

Shahrokh Rouhani, Ph.D., P.E., NewFields, Inc., Atlanta, GA

Forensic investigations are driven by site-specific data, which usually display a high degree of variability. Often, only part of these variations can be explained by deterministic models. Under such conditions, statistical methods, supported by site knowledge, provide reliable quantitative tools to address forensic questions. The statistical tools range from simple exploratory methods to complex multivariate and spatial analyses. The choice of the appropriate tool depends on the specific forensic question posed. Arbitrary application of a given statistical method does not necessarily yield defensible forensic evidence. Through a case study, the applications of a number of statistical techniques are presented. For this purpose, soil dioxin data from an industrial facility are used. The main question evolves around the origin of detected dioxins, i.e. site-related versus background sources. This question is addressed through the use of simple methods, such as box and probability plots, as well as the principal component analysis. The results include signature profiles for site-related and background dioxins.

**Mono- and Polycyclic Aromatic Hydrocarbons in Source Identification/
Differentiation of Hydrocarbon Contamination**
Ted C. Sauer, Ph.D., BBL, Inc., New Bedford, MA

This presentation will review the state-of-the-art of hydrocarbon fingerprinting with emphasis on uses of alkylated mono-aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in identifying and differentiating sources of released hydrocarbons in the environment. Aromatic hydrocarbons from both pyrogenic (e.g., creosote) and petrogenic (e.g., fuel oils) origins will be discussed.

Practical Groundwater Forensics
Michael Gregory Sklash, Ph.D., The Dragun Corporation, Farmington Hills, MI

Typically, people rely on a single investigative technique to address a groundwater forensics problem. This presentation discusses the use of complementary and independent investigative techniques to solve practical groundwater forensics problems. When complementary and independent data are available, such as physical hydrogeology, environmental isotopes, and chemical fingerprints, each individual approach can be used to constrain and/or verify the others. This results in a more powerful argument for your conclusions.

To demonstrate this approach, we focus on the combined use of physical hydrogeology, environmental isotopes, and chemical fingerprints at a multi-aquifer landfill site. We used this approach to interpret the complex hydrogeology, delineate the maximum possible extent of groundwater impact, determine who was impacted by contaminated groundwater and who was not, and to identify groundwater contaminated from other sources.

**Isotope Applications for Contaminant Source Identification and Allocation:
Theory to Practice**
Julie Sueker, Ph.D., P.H., P.E., Blasland, Bouck and Lee, Golden, CO

Isotope applications are gaining acceptance for use in surface water and groundwater investigations, complementing traditional geochemistry and physical hydrology techniques. Recent developments in analytical methodologies and in the understanding of isotope dynamics now allow the use of isotopes to investigate sources and fate of common groundwater contaminants such as chlorinated solvents and petroleum hydrocarbons. Degradation of chlorinated solvents and some petroleum hydrocarbons impart unique isotopic signatures on both the original contaminant and the degradation product or products that provide verification of degradation. Contaminants with unique isotopic signatures may facilitate determination of contaminant source(s) in complex plumes, especially with recent advances in

compound-specific isotopic analyses. Inclusion of isotopic data in allocation models may contribute to the robustness and reliability of the allocation modeling process.

This workshop presentation will begin with an introduction of the basic concepts of isotope dynamics that are required for understanding the behaviour of isotopes in the environment. This “boot camp” portion of the presentation will include information regarding isotopic abundances, isotopic fractionation, Rayleigh distillation model, isotopic mixing models, and isotopic decay. The remainder of the presentation will include theoretical and case study applications of isotopes for identifying contaminant source(s) and fate in the environment.

Assessing the Timing of Historical Mercury Releases from Residential Gas Regulators

Jay A. Vandeven, Environ Corp., Arlington, VA

The timing of historical mercury releases from residential gas regulators was examined through the development of a predictive model and measured data. The nature and scope of mercury contamination in homes from this source are discussed. Two different modeling approaches are presented and the merits of each are outlined. Modeling results were used to assess the causes and timing of mercury releases.