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Abstracts

The Implications of Bioavailability in Determining Risk-Based Sediment Cleanup Standards: New Regulations and Perspectives

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Research has shown that the biological response of benthic organisms to divalent metals (Cd, Cu, Ni, Pb, Zn) differ across sediments. This variability is due to differences in the geochemistry (e.g., organic carbon, grain size distribution, pH, Eh, cation exchange capacity, AVS, temperature, and interstitial water content) among sites that control metal bioavailability. Bioavailability of a given metal may differ by as much as a 1000-fold among different sediment types. Careful sediment characterization is therefore a crucial step in assessing ecological risk because it helps define the extent of any remedial action.

In 1999, the U.S.EPA convened a meeting of their Scientific Advisory Board that considered the issue of sediment metal bioavailability. These deliberations led to an evolution in regulatory thinking and production of recent draft guidance. Specifically, the EPA advocated the use of the equilibrium partitioning approach (EqP) which focuses on the concentration of metals partitioned into sediment pore water rather than on bulk concentrations in sediment. The EqP approach is based on growing evidence that the most bioavailable fraction (that which relates directly to toxicity) of sediment-bound metals is within the aqueous phase – i.e., within sediment pore water. Indeed, geochemical interactions between surface water, suspended solids, bed sediments and mineralogy are integral components in controlling metal solubility, and consequently metal bioavailability in fluvial environments.

This paper describes the potential risk to benthic organisms accruing from historical waste stream discharges at 3 sites. The null hypothesis was that the ambient geochemical conditions of the river sediments would facilitate sequestration of divalent metals in insoluble mineral phases and that other inert forms would minimize metal solubility in the pore water.

In the Clark Fork River, the recipient of over 100 years of mining activity, a modified single tube core-freezing device was used to profile bed sediment (~65% cobbles and 35% gravel substrate), and a novel pore water sampler developed to collect interstitial water. In the sediment, the <63 μm fraction comprised <4% by weight yet contained approximately an order of magnitude higher metal concentrations compared to the 63 μm -2 mm fraction (constituting ~20% of the mass). However, on a mass basis the sand fraction contained 60% of the metals, compared to 40% in the clay/silt fraction in the gravels, while in point bars the distribution was ~50:50. The metals occur predominantly in sulfides frequently armored with an oxide rim, and other sparingly soluble phases that may explain the low pore water metal concentrations. These data demonstrate that

consideration of multiple particle size cutoffs is necessary to accurately characterize fluvial bed sediment metal conditions, and that the form of the metal is important in understanding metal solubility in the benthos.

In the Halls Brook Holding Area Pond (HBHAP) sapropel, As (3,000 mg/kg), and Cr (1,400 mg/kg), are sequestered by amorphous ferric hydroxide ($K_{d_{As}} = 560$; $K_{f_{Cr}} = 59,000$ L/kg), while Pb solubility is limited by $PbS_{(am)}$. Fillet As concentrations in detritivorous and omnivorous fish were similar in the HBHAP (1.19 mg/kg), and the adjacent unimpacted Phillips Pond (1.18 mg/kg). Cr and Pb in both HBHAP and Phillips Pond fish were below analytical detection limits, except for one (0.73 mg/kg Pb), in the HBHAP. The low sediment bioaccumulation factors for As, Cr, and Pb (6.5×10^{-4} , $< 1.1 \times 10^{-4}$, and 1.8×10^{-6} , respectively in HBHAP) suggest that the sediment acts to sequester metals, rendering them non-bioavailable due to precipitation of solids, and sorption to iron phases.

In the Quinnipiac River sediments nickel (Ni) solubility is constrained by NiS and NiO are thermodynamically stable in the shallow sediments and, therefore, will remain as stable phases indefinitely. In addition to precipitation of primary and secondary solids, aqueous Ni concentrations are controlled by adsorption to iron minerals such as amorphous ferric hydroxide ($Fe[OH]_3$), hematite (Fe_2O_3), and goethite ($FeOOH$).

In addition a biological survey conducted concurrent with the pore water and sediment sampling event demonstrated that taxa richness (number of unique taxa) for two of the locations sampled (SD3-5 and SD3-OF) was higher than at the upgradient reference site. All locations sampled downstream of historical waste discharges had a higher proportion of sensitive taxa present than the upgradient reference site, suggesting that the downstream community is not impaired compared to the upstream community. The results of the bioassessment are in accord with the pore water and sediment chemistry, indicating that although elevated metals were detected in bulk sediments, the bioavailable portion does not pose a risk to the benthic macroinvertebrate community.

An Overview of Forensic Applications of Laser Ablation High Resolution ICP Mass Spectrometry (LA-ICPMS)

A. Mohamad Ghazi, Ph.D., Georgia State University, Atlanta, GA, U.S.A.

The purpose of this presentation is to provide a brief overview on the important role of Inductively Coupled Plasma Mass Spectrometry (ICPMS) as powerful analytical tool for trace elemental and isotopic analysis in wide range of media, in particular environmental and forensic applications. Improvements in the detection and quantification of trace and ultra-trace elements and their isotopic ratios are critical to the better understanding of their occurrence, transport, and fate in virtually all media. ICPMS technique offers the required detection limits for more than 80% of elements and also allows separate determination of various isotopes of each element. The latter capability permits the implementation of isotopic dilution techniques, thus greatly improving accuracy in analyses of complex environmental and biological samples. Isotopic discrimination is also advantageous in studies of the transport and ultimate fate of pollutants. In some instances, there is also the possibility of identifying a pollution source by subtle

variations in isotopic abundances (i.e., isotopic ratio analysis). Finally, since the chemical form of a trace element can affect its biological activity, it is often important to separately quantify the various specified ultra-trace elements. Therefore, ICP-MS has often been used in conjunction with various chromatographic or other species-selective sampling techniques for elemental speciation. The most recent development in this area has been the advent of high resolution magnetic sector (both single and multicollector) ICPMS instruments which has lead into significant improvement in detection limits and isotope ratio capability of these instruments. In terms of sample introduction method, the newest development in this area has been the application of laser ablation technique for analysis of solid samples. This presentation provides a detailed list of applications that has employed ICPMS and HR-ICPMS together with various sampling method. In terms of future development having direct impacts on the environmental forensic applications, in particular fingerprinting the source for hydrocarbon pollutants, a new multi-trace element procedure is being developed that are compound-specific. This technique involves comparison of data with an established database of trace metal profiles from various origins. Multivariate Statistics are used for establishing the database and for making the country-of-origin determination.

Environmental Forensics Applications at DOD Sites
Fred E. Goetz, Ph.D., US Navy, Port Hueneme, CA , U.S.A.

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

Overview of Forensics Data Analysis and Interpretation
Robert H. Haddad, Ph.D., Applied Geochemical Strategies, Inc., Arroyo Grande, CA, U.S.A.

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.

PAH Data as Forensic Source Identification Tools: The Good, the Bad, and the Ugly!

Robert H. Haddad, Ph.D., Applied Geochemical Strategies, Inc., Arroyo Grande, CA, U.S.A.

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 Forensics Investigations

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

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 modeller 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.

Vapor Intrusion Risk Pathway: Forensics to the Rescue?

Blayne Hartman, Ph.D., H & P Mobile Geochemistry, Solana Beach, CA, U.S.A.

Upward vapor intrusion into overlying structures has become a risk pathway of great concern to Federal EPA and State agencies. Current approaches to assess this risk pathway consist primarily of direct measurement of indoor air contamination or measurement of subsurface contamination and application of a predictive model. Both approaches have limitations that complicate the assessment of this risk pathway. Forensics could play a role in alleviating some of the uncertainty by allowing the source of indoor contamination to be determined. However, application of forensic methods have been limited to date and case histories are lacking. Whatever forensic methods are used will require enough data to distinguish background sources from subsurface sources. Conventional methods using Summa canisters are expensive and laborious, hence alternative sampling and analytical methods are required.

Forensic Analysis of Fugitive Methane Gas Emissions
Alan Jeffrey, Ph.D., ZymaX Forensics, San Luis Obispo, CA, U.S.A.

Methane gas seeping out of the ground is a widespread phenomenon. Marsh gas bubbling up in swampy areas is easily observed, and is a natural feature of this environment. In areas not adjacent to estuaries or swamps, methane seeps are less obvious, and may originate from human activities. Fugitive methane can pose levels of concern ranging from unpleasant smells at low concentrations to life-threatening explosions at high concentrations. Some fugitive methane sources, such as marsh gas, are natural; others, such as ruptured gas pipelines, anaerobic degradation of petroleum plumes, and landfill gas are anthropogenic and identifying the source may be important to mitigate the effects and assign responsibility.

The two principal processes that produce methane in soils and sediments are biological reduction of organic matter by bacteria at relatively shallow depths, and non-biological thermal decomposition of deeply buried organic matter. These produce hydrocarbon gases with distinct compositional and stable isotopic characteristic. However, fugitive hydrocarbon gas may be altered chemically and isotopically during migration to the surface, obscuring the source. This can often be resolved by analysis of the ^{14}C content of the methane. The use of the sequential analysis of hydrocarbon composition, stable isotope ratios, and ^{14}C content to identify the source of fugitive methane is illustrated in a flow chart. Case studies demonstrate how these techniques have been used.

PCB Fingerprinting
Glenn Johnson, Ph.D., University of Utah. Salt Lake City, UT, U.S.A.

Environmental forensics investigations of sites contaminated with polychlorinated biphenyls (PCBs) present a unique challenge. PCB source inference in environmental media requires a broad range of knowledge in a number of subdisciplines. In this presentation we will review PCB industrial use, PCB chemistry, analytical laboratory methods, and commonly encountered source / alteration patterns. The implications of these topics will be illustrated using PCB case studies conducted in a variety of different environmental media (air, water, sediment and biota). Finally, we will discuss the importance of data preparation, data analysis and data visualization in environmental forensics investigations involving PCBs.

Forensic Evaluation of Contamination by Solvents Originating from Coatings Used In Public Water Supply Storage and Distribution Facilities
Thomas M. Johnson, P. G., R.G., C.HG., LFR Levine Fricke, Emeryville, CA , U.S.A.

There has been a significant increase in the number of environmental litigation cases involving contamination of public water supply systems by volatile organic solvents (VOCs) and other hazardous chemicals. Forensic investigations have revealed that some public water supply systems likely have contributed to groundwater contamination through releases of solvents that were historically used in the coating and lining of water

system reservoirs and pipelines. In 1982, the California Department of Health Services notified public water systems throughout the state regarding possible contamination of public water supplies by VOCs from the use of coal-tar coatings and linings to protect and repair steel water supply reservoirs and pipelines. These coatings, which had been used since the early 1950s, contained up to 37% volatiles (primarily tetrachloroethene (PCE) and trichloroethene (TCE)). Water samples from recently coated reservoirs were found to contain up to 1,300 micrograms per liter (ug/l) PCE, and more than 100 ug/l PCE even after several months of reservoir usage.

In the early 1980s, PCE was also found to be leaching into water systems from vinyl coatings (containing up to 70% PCE) that were applied to asbestos-cement (AC) water distribution pipelines in the northeastern U.S. PCE concentrations exceeding 1,000 ug/l were found in water samples from vinyl-lined water pipelines in Massachusetts. In response, by 1984 manufacturers had replaced PCE and TCE in their coal tar and vinyl coatings products with petroleum-based solvents (primarily xylene and toluene).

The occurrence of PCE and TCE in water supply systems resulting from such coatings represents a significant potential historical source of groundwater contamination. Leakage from water supply and distribution facilities (typically estimated to be 5-10% annually) is a common and recurring problem. Calculations of mass flux indicate that these releases represent a significant possible source of VOC contamination of groundwater during the period from the late 1950s through the early 1980s. These releases likely contributed to the widespread low PCE and TCE concentrations (5-20 ug/l) found in groundwater in many large urban areas.

Molecular Microbiology Applications in Environmental Forensics: Terminal Restriction Fragment Patterns

Christopher L. Kitts, Ph.D., Environmental Biotechnology Institute, California Polytechnic State University, San Luis Obispo, CA, U.S.A.

Molecular tools devised by microbial ecologists now provide an opportunity to visualize bacterial community structure for use as an indicator of bulk functionality, and bio-potential in complex bacterial processes such as those taking place in soil and groundwater. This presentation focuses on one of these tools, Terminal Restriction Fragment (TRF) patterns; a.k.a. Terminal Restriction Fragment Polymorphisms (T-RFLP). The method is discussed and then two examples are explored where analysis of TRF data enhanced the understanding of environmental processes. Both examples stem from work on petroleum bioremediation at the Guadalupe Dunes, formerly a Unocal petroleum production facility. In both cases, information supplied by TRF data was used to bolster evidence of natural petroleum degradation and make predictions of future activity based on bacterial community structure as visualized by TRF patterns.

Environmental Forensics: Using Science to Reconstruct Contamination Events and Determine Liability

Paul T. KostECKi, Ph.D., ISEF, Amherst, MA, U.S.A.

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).

Techniques in Perchlorate Source Identification and Release Reconstruction

Peter M. Mesard, P.E., C.E.G., C.Hg., Exponent – Failure Analysis Associates, Inc., Oakland, CA, U.S.A.

The development by the State of California of an analytical technique to detect the perchlorate ion at low part-per-billion levels has led to the recent discovery of its widespread presence in groundwater. This development, along with the ongoing re-evaluation of perchlorate toxicity, has created a need to better understand the sources and behavior of perchlorate in the environment.

In many locations, the specific source of a perchlorate release that has affected a specific well may be obvious. However, in other locations—such as the San Gabriel Valley, and the South San Francisco Bay Area, California—there are multiple potential sources in the same area, and the precise sources and timing of specific releases that affect specific receptors (e.g., municipal or domestic wells) may be difficult to ascertain.

Like most other applications of environmental forensics, there is no single technique, or “silver bullet,” that will allow one to definitively link a specific perchlorate source to a specific detection at all locations. However, as more information on the various formulations and uses of perchlorate becomes known, a number of tools and techniques are emerging that, used in conjunction with one another, may allow the

identification of different and distinct sources responsible for the presence of perchlorate in a water supply. These tools include:

- Applying the chemistry and environmental behavior of the perchlorate ion and its various associated cations to site-specific conditions (e.g., soil types, groundwater conditions, etc.),
- Differentiating the origins of various perchlorate salts,
- Differentiating perchlorate sources based on different manufacturing processes:
 - Documenting the presence of perchlorate as a trace compound in various products,
 - Documenting the presence of characteristic trace compounds and impurities in various perchlorate-containing products,
- Identifying specific uses and applications of perchlorate, in addition to its well-known use as an oxidizer for propellants and explosives—based on primary references (there are numerous misidentified or technically unsupported uses cited in the literature),
- Establishing milestones in the development and use of perchlorate in its various applications, and
- Developing site-specific timelines for the introduction and use of perchlorate.

Relating historical site-specific uses to established perchlorate development and application milestones, and to local geologic and hydrogeologic conditions, in many cases, may help in linking specific sources to specific receptors.

1,4-Dioxane and Other Solvent Stabilizer Compounds in the Environment

Thomas K. G. Mohr, R.G., Santa Clara Valley Water District. San Jose, CA, U.S.A.

Since the release of the author's Solvent Stabilizers White Paper, dozens of solvent release sites have come under close scrutiny by regulatory agencies for the presence of 1,4-dioxane. 1,4-dioxane is a Lewis base added to methyl chloroform (1,1,1-trichloroethane, or, TCA) to inhibit reactions with aluminum. While present in industrial grade TCA in relatively small volumes, 1,4-dioxane gets concentrated in vapor degreasing wastes due to its higher boiling point. Consequently, the degreaser wastes that have been released to soil and groundwater often contain elevated concentrations of 1,4-dioxane and other solvent stabilizers. 1,4-dioxane is extremely hydrophilic; its infinite miscibility renders it a poor candidate for air stripping. It also has a low affinity for sorption to organic matter and is thus not easily removed by carbon adsorption. Groundwater from solvent release sites treated by conventional pump and treat

technologies has been found to contain 1,4-dioxane. ReInjection of treated groundwater from which 1,4-dioxane has not been adequately removed has resulted in shut down of domestic and municipal supply wells.

1,4-dioxane is usually the most mobile among organic contaminants at solvent release sites. In several instances, the footprint of the 1,4-dioxane plume is many times larger than the plume of TCA and its daughter products. As regulators, water suppliers, and remedial project managers begin to address this challenging contaminant, there is debate in the toxicological community about how harmful 1,4-dioxane is to human health. In the absence of a federal MCL, the states have independently developed advisory drinking water action levels, ranging from 3 ug/L in California to 85 ug/L in Michigan. Discovery of 1,4-dioxane at solvent release sites also raises questions for other uses of 1,4-dioxane that may contaminate groundwater. In several locations, presence of 1,4-dioxane in plumes that today are dominated by trichloroethylene has led to the assumption that 1,4-dioxane was added to TCE. Closer examination usually bears out that TCE is not the source of 1,4-dioxane in any appreciable quantities. TCE itself usually has a stabilizer package made of small quantities of four or more compounds, with most combinations drawn from a list of more than fifty stabilizers, some of which may warrant our attention.

This presentation profiles the major degreasing solvents and their stabilizers, and identifies candidates for consideration in site investigations, as well as those that pose little risk. Laboratory methods for analysis of stabilizer compounds, and the subsurface behavior, biodegradability, treatability, and toxicology of solvent stabilizer compounds are briefly introduced in this presentation, and case histories are contrasted. An update on the occurrence of 1,4-dioxane at solvent release sites in California and nationwide is provided. The potential application of solvent stabilizer compounds to identify sources of solvent contamination is examined and availability of information and documentation needed to make a case based on solvent stabilizers is discussed. The preferred stabilizer packages used by the major solvent manufacturers are profiled, and the potential for detecting these compounds is reviewed.

Overview of Historical Environmental Forensic Techniques: Aerial Photography, Artifact Sampling, Chemical Usage History, Commercial Formulations, Ratios, Scanning Electron Microscopy, and Microbiological DNA
Robert Morrison, Ph.D., DPRA, Inc., San Marcos, CA, U.S.A.

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.

Geochemistry and Source Speciation of Hexavalent Chromium in a California Aquifer

William E. Motzer, Ph.D., R.G., Todd Engineers, Emeryville, CA, U.S.A.

In 2002, the Soquel Creek Water District (SCWD) south of Santa Cruz, California, commissioned a drinking water source assessment and protection (DWSAP) study of six water supply wells screened in the Aromas Red Sands Aquifer (Aromas Aquifer). A component of the DWSAP was a focused assessment of potential hexavalent chromium [Cr(VI)] sources. Sampling of SCWD Aromas Aquifer well water confirmed Cr(VI) detections at concentrations ranging from 6 to 38 parts per billion (ppb). Cr(VI) also occurs regionally in the Aromas Aquifer as evidenced by low ppb detections in groundwater supply wells of other surrounding area water purveyors. While concentrations were below the maximum contamination level (MCL) for total chromium of 50 ppb, concerns about public health impacts from Cr(VI) in drinking water were raised during public meetings. The purpose of the focused Cr(VI) evaluation was to determine whether Cr(VI) detections resulted from anthropogenic (man-made) releases or from naturally occurring chromium in Aromas Formation sediments.

A detailed inventory of all historical possible contaminant activities (PCAs) compiled for the DWSAP did not suggest the presence of anthropogenic sources of Cr(VI). However, the evaluation found abundant evidence for naturally occurring chromium-bearing minerals in the Aromas Formation. Environmental conditions in Aromas Aquifer water tend to favor Cr(VI) production from dissolved trivalent chromium because the Aromas Aquifer waters are well oxygenated, generally have alkaline pH value ranges (greater than 7.0), and formation sediments are predominantly quartz-rich with low ferrous iron and aluminum oxides. Given these conditions, natural sources are believed to be the origin of Cr(VI) detected in the Aromas Aquifer.

Overview of Forensic Application of Statistical Methods in Environmental Forensic Investigations

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

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.

**Isotope Applications for Contaminant Source Identification and Allocation:
Theory to Practice**

Julie Sueker, Ph.D., P.H., P.E., Blasland, Bouck and Lee, Inc., Golden, CO, U.S.A.

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.

**Overview of Forensic Analytical Methods: Geochemical Testing Techniques for
Petroleum Hydrocarbons and Related Contaminants - GC, GC/MS, GC-IRMS**
Allen D. Uhler, Ph.D., Battelle Memorial Institute, Duxbury, MA, U.S.A.

The focus of most environmental forensics investigations includes identifying the nature (type or types) of chemical contamination found at a site, and determining the source or sources of that contamination. In such circumstances, the site investigator can use advanced chemical characterization tools to meet these goals. Without doubt the most common types of complex contamination encountered by site investigators are petroleum hydrocarbons. Hydrocarbon contamination can take many forms—for example as crude oil and its many refined derivatives; as coal-, coal/oil- or oil-tars; as runoff from combustion processes (e.g. urban runoff); and as many forms of

petrochemical wastes. Historically, the process of measuring, identifying and differentiating among types and sources of hydrocarbon contamination has been termed 'hydrocarbon fingerprinting'. The workhorse technology for 'hydrocarbon fingerprinting' has been, and remains, adaptations of gas chromatography.

This presentation will be a brief overview of advanced analytical techniques used for the measurement and identification of hydrocarbon contaminants in environmental media. The advances in chromatographic analysis of hydrocarbons made over the last decade will be discussed. Topics featured will include selection of appropriate chemical analyses for hydrocarbon fingerprinting; recommendations for target compound in an advanced hydrocarbon measurement program for environmental forensics investigations; understanding the role of environmental alteration (weathering) of hydrocarbons during interpretation of advanced analytical data; the role of petroleum biomarkers in environmental forensics investigations; and the need to integrate sophisticated analytical chemistry information with other important investigative information including site history, the implications of regulatory history affecting the site, and the hydrogeologic setting of the study area as it pertains to the fate and behavior of hydrocarbons at the site.

Biological Methods In Environmental Forensics: Tools For Impact and Risk Assessment

Josep Vives-Rego, Ph.D., Departament de Microbiologia, Facultat de Biologia, Universitat de Barcelona, Barcelona, Spain

This presentation reviews some biological tools used to estimated risks and impacts in environmental forensics and its complementary value when associated to chemical analysis and geology as well as its limitations. Ecotoxicity tests are relatively rapid tests that allow detecting the presence of toxicity in waters and the ecotoxicity potential of wastes. Also, a number of bio indicators and biomarkers may be used to monitor the recovery or the environmental damage that takes place in a specific ecosystem. The macro invertebrates indexes and more global studies of impact are a complex but deep manner of assessing the environmental damages produced by pollution sources or the recovery of the environment after remediation actions. These tools are of tremendous help in: i) the identification of the nature, extent and biological effects of pollution sources; ii) the final interpretation of chemical analysis and iii) the assessment of the efficiency in remediation actuations. Finally the interpretation of the results in forensics terms and the double way problem of communication between scientific and juridical experts are addressed.

Forensic Interpretation of Typical Petroleum Hydrocarbon and Oxygenate Analytical Data

Dawn A. Zemo, R.G., C.E.G., Zemo & Associates LLC, San Francisco, CA, U.S.A.

Many excellent forensic tools are available to answer questions about crude oil or product identification and age dating; these tools are most effective when samples can

be collected specifically for forensic analyses. However, questions about “what”, “whose”, “where” or “when” often arise during litigation subsequent to site characterization or remediation, when it is not possible to collect additional samples for forensic purposes. In these cases, the likelihood of successfully identifying products or age-dating releases will be limited by the existing site data, which were probably generated to satisfy regulatory requirements at the lowest cost. The robustness of a forensic interpretation based on these data will depend on, and be challenged in, several key areas including: 1) analytical factors, such as methods, analytes, interferences, detection limits, and data precision and accuracy; 2) site-specific surface and subsurface factors that influence fate (weathering) and transport; and 3) factors that influence data trends over time (for groundwater concentrations and product thickness). This presentation provides examples of how each of these factors can influence forensic interpretations.

For historical sites, the data set will typically consist of BTEX, TPH and possibly MTBE concentrations and chromatograms. In general, these types of analyses are of limited utility for use in forensic work because so little compositional detail of the petroleum is reported. This presentation shows that the forensic investigator should not take even these routine data at face value due to a myriad of analytical factors. The TPH chromatogram can be helpful in forensic work. The site physical setting and site hydrogeology are critical factors that influence forensic interpretations because of their influence on both petroleum weathering and transport. It is imperative not to confuse weathering and age. The development of a smear zone can be a key forensic tool, and it has significant impact on interpreting trends in groundwater monitoring results. Attempting to answer forensic questions using characterization or monitoring data typically available at historical petroleum release sites can be very challenging, and successful interpretations must accommodate these many factors.