

ISEF Stresa, Italy Workshop, May 19-20, 2003

Abstracts

Microbiology and its Application to Environmental Forensics **Andrew Ball, Ph.D., University of Essex**

Analysis of soil micro-organisms has to date been ignored by the forensic scientific community. This is mainly due to limitations of traditional culturing techniques, which only allow around 1% of the organisms to be isolated and characterized. However the rapid growth of molecular biology has resulted in techniques that can circumvent the requirement to isolate and culture micro-organisms as a prerequisite to identification. Soil microbial diversity is now routinely characterized using simple molecular techniques based on amplified ribosomal RNA. Soil community profiles can be obtained using techniques such as Denaturing Gradient Gel Electrophoresis (DGGE) or Terminal- Restriction Fragment Length Polymorphism (T-RFLP). To date molecular analysis of microbial diversity and community composition has been used to analyze microbial populations in many diverse environments. The potential exists for such technologies to be used for forensic purposes. This paper describes these techniques and examines the results of one investigation of the forensic analysis of soils using these techniques. In this example soil community profiles were obtained using the T-RFLP fingerprinting method that uses fluorescent primer technology and semi-automated analysis techniques similar to those used in human DNA profiling in forensic laboratories. This example showed that a soil microbial DNA profile could be obtained from a small sample of soil from a sole of a shoe and from soil stains on clothing. The study also shows that the profiles obtained were representative of those found at the site of collection and could therefore be used as associate evidence to prove a link between suspects and crime scenes.

Advanced Forensic Techniques for Petroleum Hydrocarbons: The Exxon Valdez Experience

Gregory Douglas, Ph.D., Battelle

The defensible identification of spilled crude oils and petroleum products and their correlation to suspected source(s) is a critical part of most oil spill assessments. Quantitative chemical fingerprinting and subsequent statistical analyses of these data can provide a defensible means to differentiate among qualitatively similar oils and thereby identify the source(s) of spilled oil from the available candidate sources or, alternatively, determine that the source(s) has not been found. This presentation describes a methodology for correlating spilled oil to any number of candidate sources, while simultaneously addressing (1) the effects that weathering can have on the chemical fingerprinting data after the spill and (2) the laboratory precision of the data used in the correlation analysis. Case studies including the Exxon Valdez Oil Spill will be examined and used to demonstrate the applications of this approach.

Status of Environmental Legislation in the United States with an Emphasis on Natural Resource Damages

Allan Kanner, Esq., Allan Kanner & Associates, P.C.

There has been little contemporary action regarding the restoration and compensation for damages to natural resources. While the environmental administration relied on the Superfund regime to effectively remediate contaminated sites, the recalcitrance of polluters and the inability of governing agencies to effectively combat such resistance has actually caused an expansion of the chemical damage at most Superfund sites. The inclusion of natural resource damage actions in Superfund cases is becoming more routine in some jurisdictions and is expected to become far more so. But public lawsuits focusing on imminent and substantial endangerments to public health and the environment are not enough. To some

extent, the Supreme Court has circumscribed the effectiveness of public citizen suits. Private lawsuits enable the restitution of damages to public health and property values.

Use of Manual and Computer Controlled SEM Techniques for Characterization of Soil and Airborne Particulate

Stephen Kennedy, Ph.D., RJ Lee Group, Inc.

Materials consisting of individual particulate are commonly of interest in environmental forensics. Among the objectives of analyzing such material are to identify the source, assess its potential for adverse health effects, and to devise remediation or clean-up strategies. Such material can be characterized by bulk or particle-by-particle techniques. The bulk characterization can result in very precise compositional information. However, the complete characterization of basic units of material includes composition, size, and shape of individual components which bulk analytical methods cannot provide. Furthermore, the complete characterization of complex material adds the geometrical properties of orientation and packing of the individual components. The combination of the imaging (secondary and backscattered electron images) and compositional analysis (energy dispersive spectrometer) allows all five characteristics to be quantified.

In this session, the fundamentals of the scanning electron microscope (SEM) will be presented, followed by example applications. The applications include describing the signature of World Trade Center dust, characterizing nuisance dust, identifying the specific source(s) of an industrial dust, and two examples of source determination of heavy metals (arsenic and lead).

Data Validation in Addressing Potential Litigations Between Regulators and Responsible Parties: Italian Case Histories

Giovanni Longoni, ENSR Italia – S.r.l.

The validation of analytical data is important in all environmental measurements activities to assess the quality of the data generated and verify that method quality control requirements and project data are met. Data validation has been defined by USEPA as a systematic process comprising data editing, auditing, checking, verification, certification and review for comparing data to established criteria in order to assure that the data are adequate for their intended purpose in environmental decision-making.

Data verification and validation are two key steps in an environmental data collection project life cycle as they determine whether sampling and analytical activities were performed in accordance with the planned approach; they also document the known quality of the data and specific concerns associated with data points or sets.

Data validation can be very useful in projects that involve regulatory agencies supervision and field duplicate samples collection. Split samples analysis quite often presents variances that can potentially lead to arguments, discussions and litigations. Case studies are presented which demonstrate how data validation can be used to address specific requests from regulatory agencies and address potential litigation between responsible parties and regulators. A general overview on data quality/data validation systems and on the Italian soil and groundwater analysis regulatory and technical framework is also presented.

Pointing the Finger - Using Multivariate Statistics to Identify the Source of Contamination

Stephen Mudge, Ph.D., University of Wales – Bangor

It is often the case that scientists need to be able to identify the source of contamination both in terms of accidental releases and when releases have been made purposefully. In pointing the finger, scientists

have access to several chemical compounds that may occur in discharges and may enable absolute identification of source. These include a range of technological (non-natural) organic materials such as chlorinated solvents. However, in several instances the source is more difficult to identify as the compounds occur naturally or are discharged from a series of potential points. Examples of this include metals and sewage derived materials. In this case, the discharges contain a range of lipids and other organic compounds which although any one might not be specific to a source, the suite may provide a signature. A method of identifying the sources unambiguously, therefore, is through the use of multivariate statistics incorporating these signatures. This presentation identifies and discusses Principal Component Analysis (PCA) and Partial Least Squares (PLS) as methods by which can be used to identify the sources. PCA has been used in several cases to identify compounds that are co-varying and sites which are affected by such discharges. This is usually accomplished in a qualitative manner and PLS extends this in a quantitative fashion such that source partitioning can be conducted. This presentation will outline the approach of these two techniques and several examples will be given which enable users to extract information from environmental data.

Forensic Techniques for Age Dating and Source Identification of Chlorinated Solvents

Brian L. Murphy, Ph.D., Exponent

This presentation deals with two chlorinated solvent problems. The first is age dating a 1,1,1-trichloroethane plume based on the concentration of the hydrolysis daughter product 1,1-dichloroethylene. Two age dating methods are outlined, one based on laboratory hydrolysis rate data and the other based on time-series field data. The focus throughout is on quantifying the uncertainty in estimates. The second problem is identification of chlorinated ethylene sources in a multi-source situation based on spatial ratio changes between parent and daughter products. This problem is illustrated with a case study from the Tutu wellfield in St. Thomas, V.I.

Shell Chemistry as a Record of Metal Contamination in the Marine Environment: A Laser Ablation Study

William Perkins, Ph.D., University of Wales

The oceans have been the ultimate 'sink' for anthropogenic metal contamination since humans began to extract and process earth materials. The oceans have been used to 'dilute and disperse' contamination from human activities. There are many geochemical techniques which allow us to measure the accumulated elemental concentrations in the marine system and to examine long-term changes in such concentrations. These methods have typically involved a wide variety of sample media, both organic and inorganic. The challenge is to develop techniques which can provide the end user with information about when contamination took place, where this contamination has traveled and who was responsible.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a technique which has the potential to measure very low levels of chemical elements in solid samples with good spatial resolution. The development of this technique is reviewed from early crude systems, which used infrared lasers, to modern high spatial resolution systems which use ultra-violet lasers. Instrument calibration and sample preparation are discussed to illustrate the relative simplicity of this technique when compared to other 'high spatial resolution' trace element analysis methods.

The application of LA-ICP-MS to marine pollution studies is demonstrated by the analysis of the carbonate shells of marine, and freshwater, molluscs. These shells preserve a record of their environment which can be 'read' using the laser. An understanding of the potential and limitations of the technique is provided by reference to specific examples. The examples will demonstrate that it is possible to determine the timing and location of pollution incidents.

Recent work combining laser ablation with ICP-MS and the use of isotopic studies has begun to address the question of identifying the pollution source. This is well illustrated by the use of lead isotopes in a

marine setting in southern France. The potential of future developments in laser systems and analytical instruments is described.

Graphical Presentation, Admissibility and Challenges to Environmental Forensic Techniques in Litigation: Case Studies

Paul D. Phillips, Partner/Holland & Hart LLP

This presentation by a practicing environmental attorney will analyze and offer answers to a series of key questions revolving around the Courtroom presentation of complex environmental disputes. These include: Why good graphics can be critical in the Courtroom; what constitutes effective (and ineffective) Courtroom graphics; examples and case studies of powerful Courtroom graphics, with special emphasis on petroleum hydrocarbons, simplifying the presentation and use of massive data sets, virtual reality, models, and 3-dimensional exhibits; when graphics should (and should not) be used; working with experts to develop effective graphics; avoiding problems with showing the graphics (admissibility); when in the process should graphics be considered; understanding the Courtroom audience; traps and pitfall for the unwary.

Stable Isotopes and Biomarkers in Forensic Geochemistry

R. Paul Philp, Ph.D., University of Oklahoma

Traditional methods for correlating spilled products in the environment with suspected sources have used gas chromatography and gas chromatography - mass spectrometry to fingerprint the products. However in many cases this provides ambiguous or misleading results since many products have very similar fingerprints. The use of the stable carbon and hydrogen isotopes of individual compounds in these complex mixtures provides a way of discriminating refined products derived from different sources. In this paper it is proposed to illustrate this relatively novel approach for the correlation of gasolines and other refined products and also incorporate novel biomarkers from the GCMS analyses wherever possible to support these correlations.

In addition MTBE and TBA are two compounds that can be studied by this approach. It is possible to discriminate MTBE from different sources and perhaps more importantly use the isotopes to demonstrate the onset of natural attenuation. Isotope values can be determined at MTBE concentrations down to 1 ppb or less make it an extremely powerful analytical tool. Again it is proposed to demonstrate this approach with various examples.

Overview Of Environmental Legislation In The European Union Impacting On Management Of Contaminated Sites

Francesca F. Quercia, APAT

A brief overview of coming EU environmental legislation impacting on management of contaminated sites is presented. Relevant policy areas are environmental liability, water resources (groundwater) protection, soil protection. Common developments build on experience from mature legislation in several Member States and contaminated land management programs carried out in the last two/three decades. Positions resulted after the activity of several of EU Concerted Actions and networks in the field of risk assessment and risk management of contaminated sites, are given as expert contribute to policy development.

Overview of Petroleum Hydrocarbon Chemistry and Environmental Forensics

Ileana Rhodes, Ph.D., Shell Global Solutions, USA Incorporated

This workshop will describe hydrocarbon chemistry, commonly used techniques for measurement of hydrocarbons and oxygenates in environmental media, and related data analysis for fingerprinting the hydrocarbons ranging from the simple to the more advanced methods. Actual environmental forensic

case studies will be used to illustrate the capabilities and limitations of the different techniques and approaches.

Spatial Statistical Tools for Environmental Forensics at Multiple-Source Impacted Sites

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Many industrial sites are impacted by multiple sources and releases that can be attributed to different operators. Defining the liability of each operator is a common litigation and forensic issue. These problems, however, are complicated by unclear site history, co-mingled contaminations, heterogeneous impacted media, as well as complex source-specific fingerprints. Statistical techniques, supported by site knowledge, provide reliable quantitative tools to address such forensic questions. Through a case study, three groups of statistical and geostatistical techniques are presented. These are: (a) principal component analysis; (b) statistical comparison of spatially segregated datasets; and (c) variogram analysis. The main issue of concern is defining the relative liability of tank operators at a petroleum terminal where multiple groundwater plumes exist. For this purpose, a series of null hypotheses based on the site knowledge are developed. The statistical methods are then used to assess the validity of these hypotheses. As demonstrated, statistical analyses are powerful tools if used in a confirmatory manner. Appropriate application of statistical tools can convert a hypothesis into defensible evidence.

Application of Groundwater Contaminant Transport Modeling in Environmental Forensic Investigations: Tucson Airport Superfund Site

Daniel B. Stephens, Ph.D., Daniel B. Stephens & Associates, Inc.

Starting in the mid 1980's, several environmental cases were filed at the Tucson International Airport Superfund Site in Arizona, USA. The cases involved primarily the organic solvent TCE which migrated nearly five miles from a missile manufacturing facility to a municipal well field. The one-mile wide plume underlies numerous other potential sources of contamination.

The site is located in an alluvial basin with a semi-arid climate. Following extensive groundwater development, the depth to groundwater gradually increased through time. Contaminants released from the sites migrated downward through sand, caliche, and clay, and began to migrate laterally within a complex geologic system wherein flow paths changed as the regional water table declined.

A suite of numerical models was used to reconstruct the travel time, pathways and TCE concentrations in soil, the shallow groundwater, and the regional aquifer system. One model was a multiphase flow simulator of DNAPL movement. A second model simulated horizontal flow and transport through a time varying domain with complex physical properties determined from core samples, slug tests, and pumping tests scaled appropriately for the model grid and interpolated using indicator kriging. A third model was developed to simulate groundwater flow and TCE transport in the regional aquifer. This model relied on mass input from the shallow groundwater zone.

A detailed evaluation of simulation results was conducted using an extensive monitor well network with nearly 10 years of data. Time series analyses of chemical constituents showed a progression of contaminant migration that could be verified using travel time calculations based on Darcy's law. The evaluation also included identification of key geochemical parameters which served as fingerprints of source areas. These tools and the models were combined to interpret the nature and extent of contamination attributable to key sources, as well as the timing of historical impacts to municipal wells.