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Forensic Environmental Geochemistry *Litigation Support Applications*

Definition & Applications

Forensic environmental geochemistry is the knowledgeable application of chemical speciation, reactions, relationships, and fate and transport characteristics to resolve or gain insight into questions related to the presence of contaminants in the environment. It is employed in litigation support or in resolving disputes between multiple parties. The main applications of forensic environmental geochemistry are 1) determining the source of contaminant releases, 2) dating the timing of releases, 3) assessing liability, 4) risk assessment, and 5) documenting natural attenuation processes.

In short, forensic environmental geochemistry is used to answer the basic questions:

- Whose contamination is it?
- When did it happen?
- Where and what is the source?

Aging

Chemicals undergo changes in the environment depending on the processes they endure. The rate of change will differ depending on the chemical and the associated environmental conditions. For a simple example, fresh gasoline has a considerable concentration of benzene and xylene in their aromatic compound composition (BTEX), but as the gasoline ages in the soil, micro-

organisms preferentially break down the benzene relative to the xylene. Therefore, a low concentration ratio of benzene relative to xylene may indicate a biodegraded (aged) fuel rather than a 'fresh' gasoline release. Additionally, additives as lead, lead scavengers, anti-knock compounds (ethylene dibromide, ethylene dichloride) and oxygenates (methanol, ethanol, MTBE) are used to determine the origin and timing of the release.

A similar analysis of concentration ratios, is used for evaluation of the aging of chlorinated chemicals such as tetrachloroethene (PCE). PCE ages (degrades) by a process called *reductive dehalogenation*. Under certain chemical conditions in the soil or groundwater, PCE with four chlorine atoms, will lose a chlorine. The resulting compound, trichloroethene (TCE), has three chlorine atoms. TCE is the daughter product of PCE, having evolved by the degradation of the pre-existing PCE. In this simple example, the concentration ratio of PCE to TCE indicates the relative age of a chlorinated solvent spill.

The examples above are simplified and show a single process influencing the aging of a chemical in the environment. Usually, multiple processes are influencing the changes a chemical undergoes. Experience and knowledge are critical to unraveling the puzzle.



Techniques using stable isotopes can also be used to help date a release or identify the source of the release. Typical isotopes used include carbon, lead, and chlorine. Recent advances in stable isotope geochemistry hold particular promise in using lead isotopes for distinguishing between various ages of older gasoline releases. New data also show the potential use of chlorine isotopes to distinguish between sources and dating of chlorinated solvent releases. Additionally, recent studies indicate the use of stable isotopes to distinguish between the natural (background) contribution of chemicals like perchlorate from the manmade contribution.

Hydrocarbon Fingerprinting

Hydrocarbon fingerprinting is used to identify fuel products and their crude oil origins. Various analytical techniques including, gas chromatography, mass spectrometry, and stable isotope analysis, may be combined

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to determine the type and distribution of specific compounds making up the hydrocarbon product. These compounds can include: paraffins, isoparaffins, aromatics, naphthalenes, polynuclear aromatics, olefins, and/or terpanes. An experienced geochemist can distinguish the type of fuel product or mixture and crude oil origin from the specific composition.

The use of hydrocarbon fingerprinting is shown in the following example of polynuclear aromatic hydrocarbons (PAHs) found in soil samples on an abandoned Town Gas site. Environmental geochemical evaluation found that the PAHs originated from several different sources; only one from on-site activities.

some PAH compounds are significantly carcinogenic, (2) PAHs tend to persist in the environment for many years, and (3) as combustion is a major generation mechanism, PAHs from numerous sources including fires, cars, trucks, trains, ships, and industry smokestacks, (as well as gas production on Town Gas sites) are found in the environment. Distinguishing how much of the PAHs found on the site (and which ones) were contributed from the gas generation activities were important to allocating clean-up costs between several responsible parties.

In this case, coal tar and fuel oil were burned on the site for many years to generate gas. The feedstock (coal tar and fuel oil) was brought to the Town Gas site by train. The train tracks ran up one side of the property.

Several data analysis techniques were used by our environmental geochemists including, statistical variance, geospatial distribution, reaction thermodynamics, and pattern recognition, to determine PAH contribution from the Town Gas manufacturing and other sources. The results led to a negotiated settlement in which the client (a Utility company) paid only part of the clean-up costs as some of the PAH contamination originated from other (offsite) sources.

Author's Biographical Sketch

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Dr. Kulla is a geochemist and hydrogeologist with over 23 years experience. She has conducted environmental site investigations, feasibility studies, and remediation of impacted properties. Dr. Kulla also provides litigation support and expert witness testimony.

Dr. Kulla has specialized expertise in the geochemical fate of contaminants and forensic geochemistry. She applies the science of stable isotope geochemistry, dating of transporting water masses, chemical tracer interpretation, organic fingerprinting compounds, and the interpretation of chemical reaction signatures to decipher the source, age, and transport history of chemical contaminants. She uses forensic geochemistry to delineate responsibility for contamination in soil and groundwater with multiple contaminants and sources. She also uses geochemistry to evaluate the timing of contaminants release and distribution, cost-effective remediation technologies, to defend and minimize client liabilities, and to document and justify natural attenuation as a remediation solution.



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PAHs are a common chemical group found on old Town Gas sites due to the combustion of the feedstock to produce gas. PAHs consist of two or more fused 'benzene' rings; up to six fused rings to make up the specific compound. From a technical standpoint, there are numerous problems with PAHs found on a property: (1)