Fingerprinting Environmental Contaminants Using Non-Traditional Stable Isotope Analysis

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Environmental litigation involving complex sites and multiple contaminant sources requires increasingly sophisticated analyses to understand the contaminants’ origins. Stable isotope analyses have emerged as an increasingly available and reliable tool for these “fingerprinting” problems.

Fingerprinting is a common forensic approach for identifying sources of chemical mixtures in environmental samples. For example, specific patterns within the polycyclic aromatic hydrocarbon, alkanes, and petroleum biomarkers can be used to identify the source of a sample containing crude oil. However, some contaminants, especially metals, do not possess a well-defined composition or pattern, analogous to petroleum. Traditionally, in the absence of such a pattern, the ratio of the contaminant of concern with a known co-contaminant has been used to track a source. This approach, however, is of limited use in complicated sites with multiple sources. Stable isotopes, in some instances, can overcome some of these complications for fingerprinting at complex sites.

This article focuses on the state-of-art environmental forensics applications of “non-traditional” stable isotopes, which include common site contaminants such as mercury, chromium, lead, and chlorine in chlorinated compounds. We previously discussed the use of mercury stable isotopes, with an emphasis on potential environmental applications (Murray 2010). In six years since that was published, stable isotopes, and non-traditional stable isotopes in particular, have become more widely used in environmental investigations. While stable isotope analyses have been available for many years, the increased reliability and availability of commercial stable isotope analyses, allows for these techniques to be applied in litigation cases. Several new case studies are discussed here.
What are stable isotopes?

Isotopes are versions of an element, such as carbon, that weigh slightly more or less than the most common form (Figure 1). Some isotopes are radioactive—that is, they decay with time while others are stable. The relative amounts of the stable isotopes of an element vary in nature due to physical, chemical and biological processes. This leads to differing isotopic ratios of a specific element, which can be used for fingerprinting in analogous manner to petroleum hydrocarbons.

For many years, isotopes of the lighter elements have been routinely measured...hydrogen, oxygen, carbon, etc. However, thanks to recent advances in analytical methods, commercial laboratories are now available to measure isotopes of heavier elements like mercury, zinc and chromium, some of the so-called “non-traditional” stable isotopes (Figure 2, dashed boxes) (Mineralogical Society of America 2004, Baskaran 2011). These advances allow investigators to quantify very small differences in isotope abundances between samples.

In addition to technological advances in measurement, consistent standards and reference materials have improved the quality control of the isotope methods and allowed for direct comparison of data collected in multiple studies. Some non-traditional stable isotope elements, such as mercury and lead, have well-developed protocols and standards are available commercially from a variety of sources, while others are still being refined and have only limited availability.

The stable isotope fingerprint of an element develops due to physical, chemical and biological processes collectively described as “fractionation”. Fractionation may occur naturally in source material (e.g., the formation of an ore in the earth’s crust) or due to industrial processes such as retorting. In general, lighter isotopes are more reactive than heavy isotopes. As a result, the residual material becomes “heavier” as a reaction progresses while the products are “lighter”. Examples of natural processes known to result in isotope fractionation include evaporation, photochemical reactions and biological uptake. Fractionation may continue to occur after a contaminant is released to the environment and should be considered when interpreting stable isotope fingerprints.
How can non-traditional stable isotopes be used in environmental investigations? While the lighter, “traditional” stable isotopes such as carbon and nitrogen provide important information regarding environmental and ecological processes, which may influence the fate and transport of contamination, the non-traditional stable isotopes can be particularly useful in environmental investigations because they often represent the contaminant of concern. For example, non-traditional stable isotopes have been used to:

- Determine the source of metals contamination in sediments
- Identify the specific pool of environmental mercury, which affects a food chain
- Track chlorinated solvent plumes in groundwater
- Track atmospheric emissions from an industrial source.

As with most analyses in complex forensic investigations, stable isotope methods are best used in a multiple-lines-of-evidence approach. Even if all the methods are reliable and the data quality is good, the data have to be interpretable in a way that makes sense and is consistent with other site information, such as contaminant transport pathways. For example, the history of chemical use at a site should be consistent with the results from chemical fingerprinting.

For litigation cases, the specific analytical method being used needs to be reliable and meet the Daubert criterion of being “widely accepted”. The use of non-traditional stable isotopes has been challenged by the courts in the case of the City of Pomona v. SWM North America (2014). In this case, the City of Pomona (City) sued a maker of nitrate fertilizer for contaminating the City’s groundwater with perchlorate (a chemical that consists of one chlorine atom surrounded by four oxygen atoms). The expert for the City used both oxygen and chlorine stable isotope
ratios to conclude that the nitrate fertilizer was the source of the perchlorate. However, the District judge excluded the opinion under Daubert, citing the lack of an EPA method, the lack of another lab running the same analysis, and the lack of some samples in the reference data base against which the chlorine stable isotope results were being compared. Under appeal, the 9th Circuit reversed this Daubert exclusion, finding that an EPA method is not required for admissibility, and that the issues of verification and reference samples are a matter of weight of evidence, not admissibility.

Examples of Source Identification Using Non-Traditional Stable Isotopes

Exponent has used non-traditional stable isotopes in a variety of projects both within and outside the United States to investigate the sources of contaminants at affected sites. Two examples of how stable isotopes were used to determine the source of contamination to sediments and soils are described below.

Mercury in River Sediments

Exponent was retained to evaluate and provide expert testimony regarding the extent of mercury sediment contamination associated with a former mercury cell chlor-alkali plant that operated for over a 40-year period in an estuarine area with multiple other potential mercury sources. Exponent reviewed available site history and conducted a thorough analysis of the sediment geochemistry. Traditional measurements such as mercury concentrations and cesium-137 and lead-210 dating of sediment cores were combined with cutting-edge mercury stable isotope data to determine whether the chlor-alkali plant was the sole source of mercury to river sediments. The analysis revealed three distinct mercury pools—the contamination from the chlor-alkali plant, background (e.g., atmospheric deposition or diffuse urban runoff) mercury in sediments considered “uncontaminated,” and a third, unidentified, source. (Figure 3) The stable isotope ratios in contaminated sediments fall on a line between the unidentified source and background samples, indicating a mix of these two sources.

Figure 3. Mercury stable isotope ratios from contaminated downstream river sediments (black diamonds), the chlor alkali plant (orange circles), an unidentified source (purple squares), and uncontaminated sediments that contain mercury related to regional background (green triangles).
Lead in Residential Soils

Lead isotopes can be useful at mining sites because the isotope fingerprint is very uniform for a single geologic ore body. They are less useful for assessing contributions at industrial sites because the lead could have come from many different ore bodies with a wide range of isotope ratios. Picher, Oklahoma, is the location of the Tar Creek Superfund site, where lead and zinc were mined for approximately 60 years, and piles of mine waste, called “chat”, were left scattered around town. Exponent used the results of a USGS lead stable isotope study to identify the sources of lead in residential yards. When lead stable isotope ratios were plotted, the chat (mine waste) samples clustered in a small group, but leaded paint samples collected from peeling exterior paint showed a much wider range, consistent with the idea that the lead added to the paint likely came from many sources. Residential soil samples had ratios that showed a mixture of mine waste and leaded paint.

Looking Forward

Non-traditional stable isotopes, particularly mercury and lead, have gained wide acceptance in scientific and litigation circles, while others are still emerging. Advances in the interpretation of isotope data are also being made, especially for mercury. The recognition that fractionation of even mercury isotopes is a unique signature for precipitation makes it possible in some cases to distinguish atmospheric deposition from anthropogenic sources. Additionally, new methods, which examine both non-traditional and traditional stable isotopes in specific compounds are being developed, and are increasingly widely used. Not every project can benefit from application of stable isotope measurements, however, these techniques, when properly applied, represent powerful new tools for environmental forensics. As one tool in an increasingly diverse toolbox, the stable isotope techniques should be applied within a framework that relies on multiple lines of evidence to develop strong conclusions in environmental investigations. Other lines of evidence, including spatial analysis of chemical concentrations, investigations of fate and transport processes at the site, and historical documentation of site usage, can be used with stable isotope analyses to provide a more complete evaluation of potential contaminant sources and their relative contribution.

References

Murray, KJ, Henry, B, and Bigham, G. Tracking Sources of Mercury Contamination Using Stable Isotopes. Exponent Environmental Forensics Notes, Volume 8, 2010.
SQM NORTH AMERICA CORPORATION v. CITY OF POMONA, CALIFORNIA, 135 S. Ct. 870, 190 L. Ed. 2d 703 (U.S. 2014).