



Tracking Sources of Mercury Contamination Using Stable Isotopes

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Many elements occur in nature as mixtures of stable isotopes. For example, carbon 12 (¹²C) isotope is the most common form of carbon (99 percent of all carbon) and has 6 neutrons in the carbon atom. The ¹³C isotope (1 percent of all carbon) has one extra neutron (7) and is therefore “heavier” than ¹²C. Stable isotope techniques (for example, determination of the ratio of ¹³C/¹²C) have been applied to examining ecological relationships such as food webs, tracing and tracking the degradation of organic contaminants, and detecting organic contaminants as they degrade, as well as to identification of the sources of hydrocarbons and other organic compounds such as trichlorethylene (TCE).

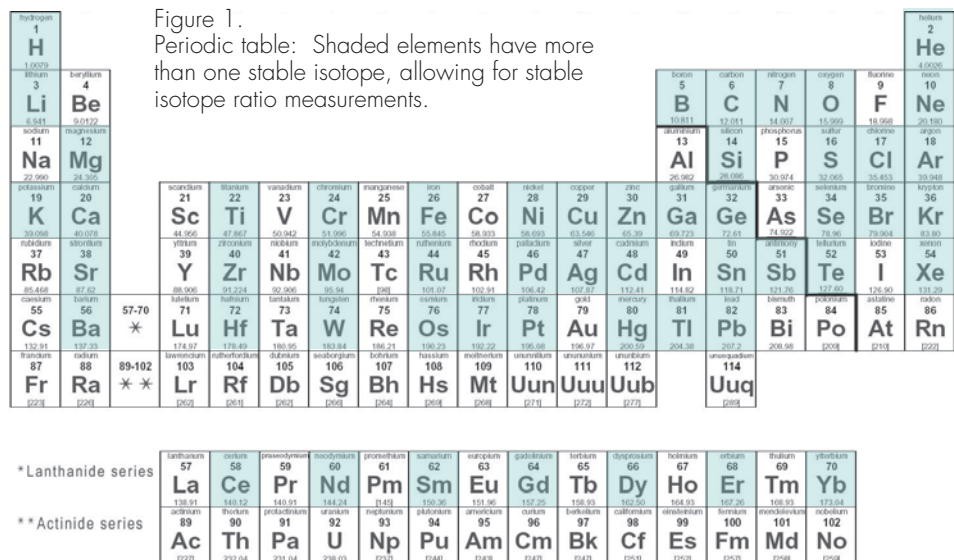
Most forensic applications rely on the use of “conventional” stable isotopes (stable isotopes for carbon, hydrogen, oxygen, nitrogen, and sulfur) to determine sources of contamination. However, recent advances in the analytical methods for stable isotopes have resulted in better detection of metal isotopes and the ability to analyze for a wider variety of elements (Figure 1). With the ability to detect particular ratios of stable isotopes of a metal, it is now

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possible to gain information about the sources and the environmental fate of a single metallic contaminant. In this issue, we discuss some of the advances in stable isotope techniques for mercury, a contaminant of concern in many food webs, and one of the key chemicals of concern for human exposure.

Introduction to Stable Isotopes

Isotopes are chemical forms of the same element and are either “stable” or “radioactive.” Stable isotopes are forms of the same element that differ in that they contain additional neutrons in the nucleus of the atom. They do not decay and change into other elements as do radioactive isotopes. The small differences in mass can be measured using sensitive mass spectrometers, and the amounts of each isotope in a sample can be quantified. Unlike radioactive elements, where the element is lost as the isotope decays and becomes another element (such as uranium decaying to lead), stable isotopes do not decay and thus persist as the original element in the environment.

Mercury Stable Isotopes

There are seven different stable isotopes of mercury (^{196}Hg , ^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg , ^{202}Hg , and ^{204}Hg) with ^{202}Hg being the most abundant (29.86 percent). Because mercury has multiple stable isotopes, the relative amounts of each isotope can provide a fingerprint of a particular source. To identify the isotopic fingerprint in an environmental sample, the value “ δ ” is calculated using the equation:

$$\delta^{xxx} = \left[\left(\frac{R_{xxx}}{R_{\text{STANDARD}}} \right) - 1 \right] \times 1000$$

where R is the ratio of mercury isotope XXX to ^{198}Hg .

The value δ (pronounced “dell”) is reported in parts per thousand (‰), where a value of 0 ‰ means that the sample is identical to the standard; a negative number indicates that the sample is lighter and a positive number indicates that the sample is heavier than the standard. While the atoms of a particular stable isotope do not change, the overall isotopic makeup of an element within a given environmental system can change with time, as a result of a process called fractionation. In general, isotopes react based on mass, with lighter isotopes being more reactive than heavier isotopes, resulting in stable isotope fingerprints that show a trend proportional to each isotope’s mass. However, some elements, including

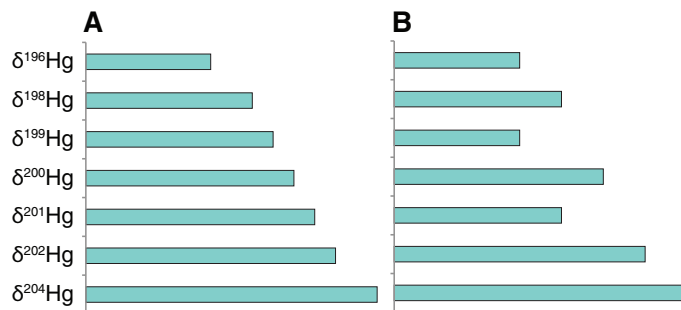


Figure 2. Example of stable isotope profiles showing a mercury sample that has undergone mass dependent fractionation only (A) and a sample that has undergone both mass dependent and mass independent fractionation (B). These samples would have the same values for $\delta^{200}\text{Hg}$, but different values for $\delta^{199}\text{Hg}$, allowing them to be differentiated using stable isotopes.

mercury, also undergo fractionation that is independent of mass, resulting in isotopic profiles that differ between even and odd isotopes (Figure 2).

An example of an application of mercury stable isotope analysis is the determination of the mercury contribution to a water body from a specific industrial source. In this situation, it may not be possible to simply examine sediments for elevated concentrations of mercury, because mercury could have come from other point and non-point sources over time. Traditionally, one approach to determining the mercury from the industrial source is to look for a co-contaminant, not present from other sources. The ratio of the mercury to co-contaminant is used to delineate the extent of contamination. Alternatively, the stable isotope ratio can be used, even in the absence of a co-contaminant. By using ratios based on odd and even isotopes, mercury sources can be tracked down. It is less likely that both the odd and even δ values from different sources will be identical, and the contribution of contamination from a single source can be determined.

One scenario where this could be applied is a case of a mercury spill from a known source in an area of urban background. Because the area is not pristine, using only the total mercury content of the sediment could result in an unclear mapping of the contaminant plume and an over- or under-estimation of the contribution from the new source. In this case, the stable isotope ratios may be used to identify the “new” mercury from background mercury (Figure 3). This method is especially useful if the stable isotope composition of the source mercury is known. The same approach could be used in other forensic situations, including cases of human exposure.

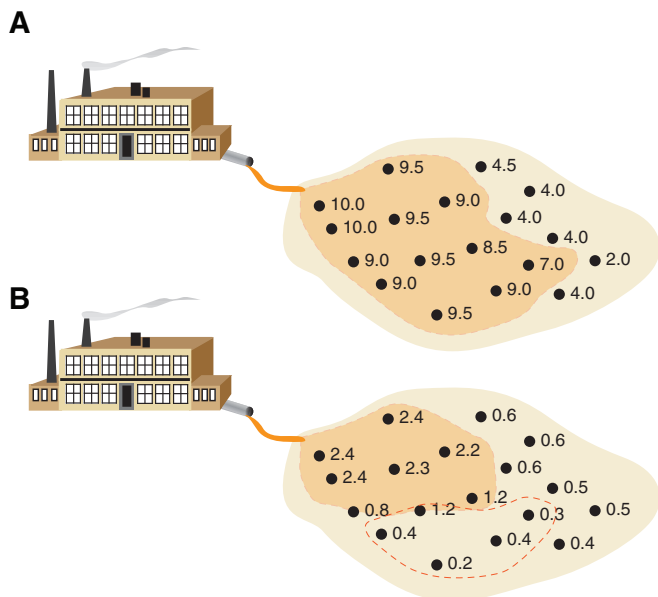


Figure 3. Comparison of mapping total mercury (ppm) (A) and $\delta^{198}\text{Hg}$ values (%) (B) for sediment samples from a contaminated lake. Note that elevated total mercury concentrations indicate a plume that is larger than that indicated by the isotope measurements, where some high-mercury samples are attributable to a different source with a distinct isotope value.

Applications of Stable Isotopes beyond Mercury

Stable isotopes have been used for forensic investigations of several other metals, including lead and chromium. For example, lead (Pb) has four stable, naturally occurring isotopes: ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb , with ^{208}Pb being the most abundant (52.4%). Lead from lead paint dust has a different signature than lead from leaded gasoline, and this signature can be used to determine the source of lead to soils or human exposure. Additionally, because the gasoline lead additive ratios are well known and changed from the 1960s to 1990s, these ratios can provide a way to date soil and sediment horizons.

Another example is chromium, which is also a priority pollutant metal. Naturally occurring chromium (Cr) is composed of three stable isotopes: ^{52}Cr , ^{53}Cr , and ^{54}Cr , with ^{52}Cr being the most abundant (83.789%). The environmental hazard from chromium is lessened as chromium(VI) is reduced to chromium(III), a process mediated by bacteria in the environment. Because the bacterial reduction is known to preferentially reduce lighter isotopes, as chromium(VI) is reduced to chromium(III), the remaining chromium(VI) gets heavier and the chromium(III) gets lighter. By monitoring changes in the stable isotope ratio of chromium(VI), it is possible to determine whether reduction (and therefore bioremediation) is occurring, even

without knowing the total concentrations of chromium in the system.

Applying stable isotope ratio measurements requires a significant amount of knowledge of the potential sources in a given environment, and currently has the potential to be most useful on well-characterized sites, especially for the exclusion of potential sources. However, as more laboratories develop the capability to measure metal isotopes and more literature is published regarding environmental fractionation, it is expected that stable isotope fingerprinting will be more widely applied.



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