WHEN FORENSIC ISOTOPIC ANALYSIS Goes Bad

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Using isotopic data for forensic applications in hydrology ranks among the best new scientific developments for hydrologists. Nevertheless, to put this science in perspective, here are my "Top 5 Forensic Isotopic Flops" or "How forensic isotopic hydrologic analysis can go bad." Isotopic analyses are in general expensive, require extended time for sampling and analysis, often can be performed only a single time on a given project, and frequently yield results so late that resampling cannot be done before project completion. In other words, the work must be done correctly the first time to have an impact. When isotopic assessment works, it is a powerful independent approach, but when it fails, it can be an expensive lesson and even a setback to the acceptance of this new approach to hydrologic investigations.

1. Use of the terms "fingerprint" or "DNA-like analysis" to describe isotopic results in a legal or regulatory setting

Unlike human fingerprints or genetic matches that are individually unique, identical isotopic values are found frequently and are certainly non-unique. The usefulness of an isotopic analysis derives from its context, such as the hydrologic setting, time frame, correlative chemical data, or other supportive isotopic data. Overstating the certainty of a forensic isotopic analysis is not only unscientific and potentially a disappointment for an uninitiated client, but it also can lead to serious legal challenges to the credibility of a report or even to testimony in a legal proceeding. Data have uncertainty and associated error: this is acceptable and appropriate to acknowledge. Careless claims related to accuracy, on the other hand, can cause results to be dismissed.

2. Using the wrong isotopic system for the application

A report containing numerous deuterium and oxygen values clustered at one point on the Meteoric Water Line may have value in some circumstances, or it may mean you have chosen the wrong isotopic system for your investigation. Forensic isotope investigations generally depend on the following types of evidence:
1) isotopes that identify the water itself;
2) isotopic values of a solute that is the specific contaminant of interest;
3) isotopic information about co-migrating chemically conservative solute species;
4) isotopic values for a solute that is reactive and thus provide information about processes along a flow path; and
5) the radioactive solute or water itself that yields time-related information.

The point is to choose the system or suite of isotopic analyses that will specifically address the problem at hand. It is easy to waste analytical budget and project time on isotopic analyses that are commonly used, easy to understand, and of scientific interest, but if they are not directly applicable to the objectives of the study, the results may be too imprecise, marginally correlative, or even irrelevant.

3. Sampling error: trouble from the start

Know the most likely error sources for your system. A sample that was improperly collected or preserved will never yield useful data. If the protocols are unfamiliar, discuss them with other professionals or with personnel at the isotope lab. Although the U.S. Environmental Protection Agency does not issue guidelines for holding times or methods of analysis for isotopic samples, there are essential sampling and preservation procedures that, if ignored, will cause the forensic isotopic analysis to go bad.

Consider: When sampling for $\delta^{34}S$, don't use sample bottles that were pre-acidified or even prewashed with sulfuric acid. Watch for CO_2 loss or gain in radiocarbon analysis. Tritium hidden in air or drilling fluids of newly constructed wells will yield

false results. Microorganisms can modify stable isotopic values both in situ and in improperly preserved samples. Soaps or detergents used to clean equipment or bottles can affect boron isotopic analysis. Some analytes require field-filtered samples; others are compromised by the filtering process. Many such errors are discovered by accident and the anecdotal stories are illuminating.

4. Detection limits, precision, sufficient mass, and other uncertainties in life

The chemical concentrations of dissolved elements often fall below the detection limit of a specific instrument and thus cannot be quantified. Similarly, for some radioactive isotopes the measurement may yield insufficient counts or decays to be quantified. In contrast, stable isotopes are generally reported as ratios of predominant nuclides, then compared to the appropriate internationally accepted standard. The concern is not detection limit but resolution. For example, is the change in the ratio different enough between samples to be resolved by the selected mass spectrometer? The resolving power of a particular mass spectrometer is known ahead of time and can be provided by the laboratory, but determining whether the samples being collected are different enough to be distinguished may require preliminary sampling. A set of results in which the precision of the instrument is less than the spread of the sample values can provide useful information, but usually does not. In such cases the work fails to answer questions even though an impressive table of data may be generated.

Failure to collect sufficient sample volume to provide the needed mass for an isotopic analysis is a related issue. Every isotopic analysis has a mass requirement for reliable results. It may be impractical to collect the hundreds of liters of water needed for a specific method in cases where concentrations are low or instruments are low-resolution. Results can easily go bad if they are imprecise, statistically unquantifiable, or are uncertain due to insufficient mass.

5. Failure to effectively communicate the meaning and value of the isotopic assessment

The concepts and terminology surrounding isotopic measurements and interpretation are unique and generally not intuitive even to technical people. If the clients, regulators, or managers who receive the results of a forensic study are not given sufficient explanation to recognize the value of the work, the effort has failed. Many reports languish without impact or utility because definitions and procedures are inadequately communicated and described. Terms associated with isotopic analysis—such as *correction factors*, *deltas*, *Rayleigh processes*, *fractionation factors*, *machine bias*, *SMOW*, *becquerel*, *bomb pulses*, *TUs*, *per mil*, *TIMS*, *TAMS*, *cosmogenic* and *hyperbolic mixing*—are foreign and cryptic to all but a narrow segment of the scientific community. The most carefully planned and executed forensic isotopic project will generally not be understood without a significant tutorial effort.

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Too many of my own reports have become simply an appendix to other studies, or worse, an obscure scientific document because the client or audience was ill-prepared to understand the definitions or grasp the significance of the forensic data. Isotopic language is more like mathematics than a scientific discipline: it can be thought of as being in need of prerequisites, theorems, and example problems before the value of the work can be deciphered. If the preliminary tutorial groundwork is not provided, then poor communication results, second chances are rare, and the brilliant forensic isotopic hydrologic analysis has been wasted.

Finally, generating a reliable and useful forensic isotopic analysis for hydrologic applications and minimizing the probability that it will go bad is much like parenting. If you recognize who is the responsible adult, pay attention, make sure the homework is done, exert discipline, and communicate effectively, the results will usually be good.

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