

Fingerprinting Water

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Introduction

In the past decade stable and other isotope analyses have become common in hydrologic and hydrogeologic investigations. Because surface water and groundwater can originate from a variety of sources (e.g., hot springs, precipitation, imported water, etc.) stable isotopes of oxygen and hydrogen are most useful in fingerprinting such sources.

Defining Isotopic Ratios

Isotopic ratios are used for fingerprinting sources utilizing a delta (δ) notation derived from the following equation:

$$\delta \text{ (isotope) in mils (‰)} = \left[\frac{R_{\text{(sample)}} - R_{\text{(standard)}}}{R_{\text{(standard)}}} \right] \times 1,000.$$

Where: $R_{\text{(sample)}}$ = the ratio of the first and second isotope such as oxygen-18/oxygen-16 ($^{18}\text{O}/^{16}\text{O}$), and
 $R_{\text{(standard)}}$ = the ratio of the isotopes used in international or other standards.

A δ value with a positive (+) sign corresponds to an increase of the more massive (“heavier”) isotope (i.e., ^{18}O) over the second (^{16}O) with respect to a standard, indicating that the sample is enriched with the heavier isotope. A minus (–) sign indicates a decrease of the heavier isotope with respect to the standard indicating that the sample has more of the lighter isotope.

Isotopic Fractionation

Fractionation or separation of naturally occurring oxygen and hydrogen isotopes in water occurs in the hydrologic cycle during evaporation and condensation. Isotopically light water molecules evaporate before heavy ones. As a result, surface water exposed to evaporation tends to be enriched in heavy isotopes relative to meteoric water and will have a less negative or more positive oxygen-18/oxygen-16 ($^{18}\text{O}/^{16}\text{O}$) ratio as indicated by the evaporative trend line on Figure 1. Oxygen isotope fractionation also occurs at different rates at different latitudes and climates because water vapor condensation is temperature-dependent. Therefore, the ratio of $^{18}\text{O}/^{16}\text{O}$ in rain and snow will change with latitude and elevation and also with seasons. The higher the latitude or the elevation, the more negative the $\delta^{18}\text{O}$ value; these vary from approximately 0 ‰ for Vienna Standard Mean Ocean Water (VSMOW), at the equator to about –50 to –55‰ VSMOW at the poles. VSMOW is the standard for $^{18}\text{O}/^{16}\text{O}$ established by the International Atomic Energy Agency and the National Institute of Standards and Technology.

Hydrogen (protium and deuterium) also fractionates from water in a similar manner and therefore, δD ($^2\text{H}/^1\text{H}$) ratios are directly proportional to $^{18}\text{O}/^{16}\text{O}$ fractionation. A plot of the $\delta^{18}\text{O}$ versus δD will show unique characteristics for water samples collected from different latitudes, climates, seasons, hydrologic basins, evaporative conditions, and thermal springs. In general, worldwide precipitation isotopic data plots along a straight line, known as the Global Meteoric Water Line (GMWL) as shown on Figure 1. The GMWL actually is an average for many worldwide local meteoric water lines each controlled by local climatic factors, including the vapor mass origin, secondary evaporation during rainfall, and seasonal precipitation. A local MWL based on $\delta^{18}\text{O}$ and δD in local precipitation can be compared with $\delta^{18}\text{O}$ and δD of local surface and groundwater. An example of local groundwater line is also shown on Figure 1. The average monthly and annual $\delta^{18}\text{O}$ and δD for local precipitation based on latitude, longitude, and elevation can be determined using a web-based calculator hosted by Purdue University.

Although the isotopic composition of water can be influenced by ion exchange reactions, sorption to aquifer materials, and biologic activity, it is generally unaffected by infiltration, recharge, and groundwater movement.

Sampling, Analysis, and Costs

Collection of local precipitation requires that the water sample be collected during the storm event to minimize evaporation. Isotopic signatures for precipitation may also be obtained from bottled water, if it can be shown that the bottled water is from a local surface water source.

Sampling surface and groundwater is less complicated. Generally, one 250 mL plastic container is sufficient for water collected from a well. Containers should be filled to the top, and tightly sealed to prevent leakage and evaporation. Preservatives are not required.

Most stable isotopes in substances are determined by isotope ratio mass spectrometry (IRMS) analysis in which a beam of charged ions is generated from the thermal ionization of a solid sample (known as a solid source) or by ionizing a gaseous sample (gas source). Solid source IRMS is used for elements with high atomic masses such as strontium, lead, and uranium. For most light elements (i.e., hydrogen, nitrogen, and oxygen) the analyzed material is converted to a gas prior to analysis. The isotopic concentrations are then measured as a ratio of the isotope to a common nuclide. In the case of gas source IRMS for water it is measured against VSMOW.

Costs are relatively inexpensive, ranging from \$40 to \$50 per sample for University laboratories, to about \$55 to \$120 for commercial laboratories.

Additional Information Sources

On March 28, 2007, GRA will host a course on stable isotope use in groundwater. Course instructors will be Dr. Carol Kendall, U.S. Geological Survey and Dr. Jean Moran, Lawrence Livermore National Laboratory. A one-day symposium (March 29) will follow on uses of stable isotopes in groundwater hydrology; see announcements at www.grac.org.

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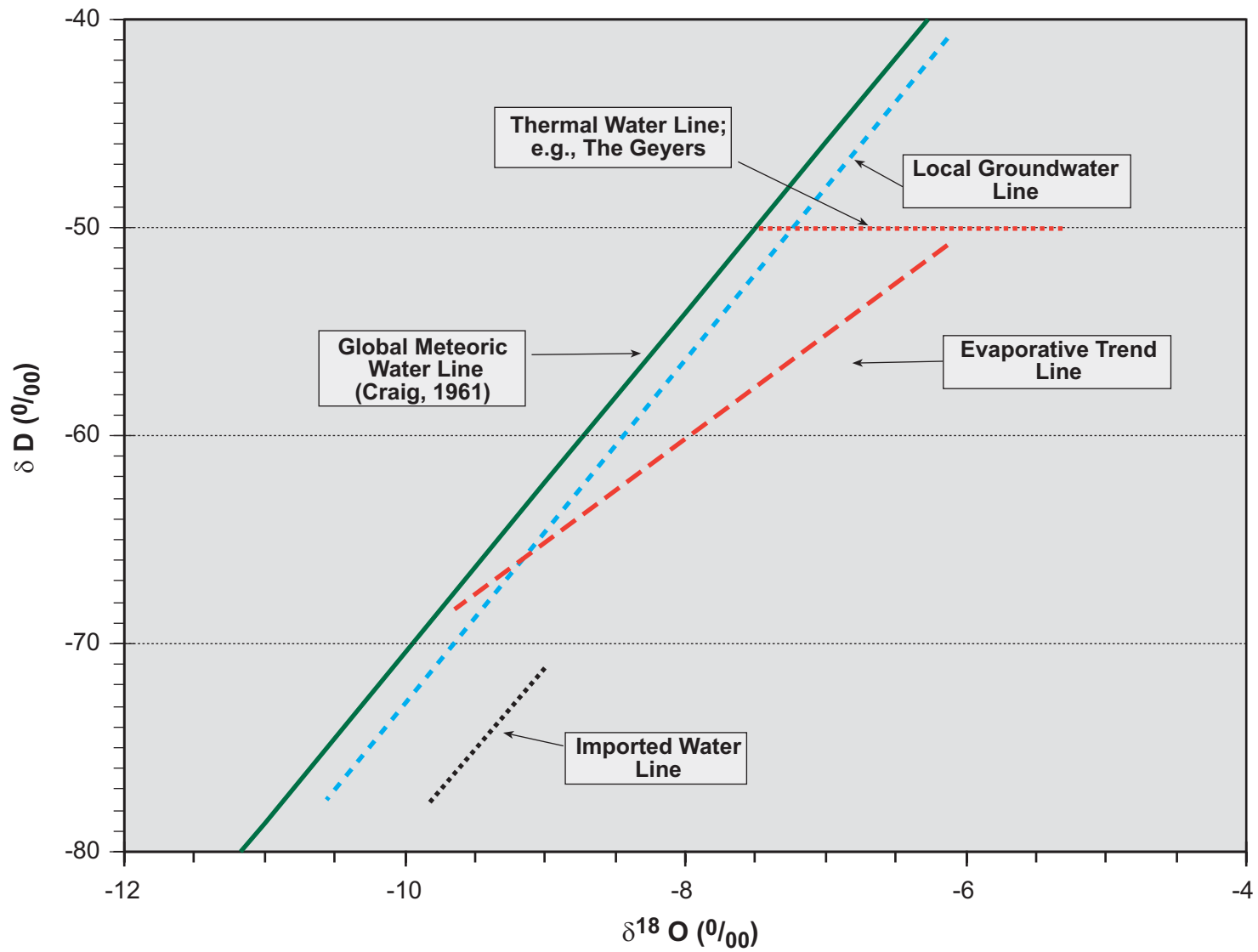


Figure 1