



ENVIRONMENTAL TOOL BOX



New Isotope Technique for Chlorinated Solvent Releases

In This Issue

- New Isotope Technique for Chlorinated Solvent Releases
- Stable Isotope Laboratory at ZymaX Forensics
- Environmental Tracers, Identifying the Sources of Nitrate Contamination in Groundwater
- Groundwater Resources Association (GRA) Isotope Course and Symposium

ZymaX Forensics

71 Zaca Lane, Ste 110
San Luis Obispo, CA 93401
Tel. (805) 544-4696
www.zymaxforensics.com

We at DPRA/Zymax Forensics are pleased to announce that following our establishment as the first commercial company to offer Compound Specific Isotope Analysis (CSIA), we have successfully completed our first project using this advanced forensic technique.

CSIA was used to measure the carbon isotope ratios of the chlorinated solvents, PCE, TCE, and DCE in soil and groundwater at a dry cleaner site that was the focus of litigation. We were able to demonstrate that the PCE, which was the major component in the soils and groundwater, had the same carbon isotopic signature in all the samples. This indicated that the PCE released on the site was produced by the same manufacturer, and by comparison with published isotope data on the small number of US producers, the manufacturer was identified. Work is ongoing to document the source of the PCE used by various operators of the dry cleaner.

The reproducibility of the CSIA is excellent, and reliable data can be obtained on soil and groundwater samples with concentrations in the low ppb range. CSIA of chlorinated solvents can also provide evidence of the time sequence of multiple releases at a site. The principle behind this is that in older releases, biodegradation may have changed the isotope ratio of the chlorinated solvent, so the oldest release may be the most altered from the fresh solvent.

We intend to expand our capabilities in the CSIA field to:

- Chlorine isotope ratios in chlorinated solvents for situations where carbon isotope ratios alone do not provide conclusive results.
- Carbon isotope ratios of dissolved BTEX compounds and MTBE. This can distinguish different releases of gasoline and MTBE-containing unleaded gasoline, and can monitor the efficiency of gasoline and MTBE remediation either by natural attenuation or in situ accelerated degradation.
- Carbon isotope ratios of polyaromatic hydrocarbons (PAHs). This can distinguish different sources of creosote or Manufactured Gas Plant residues.

DPRA/Zymax Forensics has already offered for a number of years, carbon and hydrogen isotopic analysis of individual hydrocarbons in natural gas samples. Typically methane, ethane, propane, butanes, pentanes, and carbon dioxide are separated and carbon and hydrogen isotope ratios measured. This is important in determining the source of fugitive methane that may seep out of surface soils or accumulate in residential basements. Isotope ratios can distinguish biogenic gas, such as marsh gas or landfill gas, from petroleum gas, such as fuel gas from ruptured gas lines or gas that has migrated from underground reservoirs. Isotope ratios have also been used in gas and petroleum exploration, as they can distinguish different producing reservoirs, correlate reservoirs in different fields, and give information on the maturity of natural gas accumulations. ■

Stable Isotope Laboratory at ZymaX Forensics

ZymaX Stable Isotope Laboratory is a laboratory with a long history and good reputation in the stable isotope community. It was established by Dr. Ian Kaplan in 1980 as a department of Global Geochemistry Corporation in Canoga Park. Since then, it has been dedicated to the development of cutting-edge techniques in stable isotope analysis and providing quality service for our clients around the world. In recent years, the laboratory has been updated with one of the most advanced isotope ratio mass spectrometers (IRMS), Micromass IsoPrime, which is coupled to several peripherals, including EuroVector EA (Elemental Analyzer) and Agilent 6980N GC (Gas Chromatography). This configuration allows fast on-line analysis of various stable isotopes (C, N, H, O and S) in both inorganic and organic materials. In addition, the laboratory is equipped with four vacuum lines designed for off-line preparation of samples that cannot be accomplished using online methods.

Being a part of the DPRA family now, ZymaX Forensics has been given tremendous opportunities for growth. In January 2006, Dr. Shaoneng (River) He joined ZymaX as the new manager of the isotope lab. Dr. He has more than 14 years of experience in stable isotope geochemistry, and extensive experience setting up a new stable isotope lab and developing analytical methods. He has successfully developed methods for compound specific isotope analysis of organic compounds, specifically chlorinated solvents. ZymaX Isotope Lab will continue to work on developing new analytical methods for isotope analysis to serve the environmental industry, and DPRA will provide all possible resources to support such growth.

The following summary lists major isotope analyses provided by ZymaX Stable Isotope Laboratory:

Organic Materials:

- Compound specific $\delta^{13}\text{C}$ analysis of chlorinated solvents in waters and soils;
- $\delta^{13}\text{C}$ analysis of natural gases (C1 to C5) and δD analysis of methane (C1);
- $\delta^{13}\text{C}$, δD , $\delta^{34}\text{S}$, $\delta^{15}\text{N}$ analysis of crude, fuel, kerogen, extract and fractions;

Aqueous samples:

- $\delta^{18}\text{O}$ and δD analysis of waters;
- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ analysis of dissolved nitrate;
- $\delta^{15}\text{N}$ analysis of dissolved ammonium;
- $\delta^{13}\text{C}$ analysis of dissolved carbon (DIC);
- $\delta^{34}\text{S}$ analysis of dissolved sulfate and sulfide;

Other samples:

- $\delta^{34}\text{S}$ analysis of H_2S gas;
- $\delta^{13}\text{C}$ analysis of CO_2 gas;
- $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, δD , $\delta^{34}\text{S}$ and $\delta^{15}\text{N}$ analysis of bulk materials (organic and inorganic) and pure minerals;

ZymaX Isotope Lab is also able to provide many other types of analysis, for example, compound specific isotope analysis of organic compounds other than chlorinated solvents. ZymaX can provide advice on setting up projects, sample locations, collecting samples, selecting analytical schemes, and interpreting results. Detailed interpretive reports can be prepared in most cases upon request. For more details about our isotope lab, please visit:

<http://www.zymaxforensics.com/index.htm>, or contact Dr. He at (805)544-4696 EXT 108 and riverhe@zymaxusa.com.

For general information about ZymaX Forensics, please contact Dr. Alan Jeffrey at (805)544-4696 EXT 104. ■

Environmental Tracers: Identifying the Sources of Nitrate Contamination in Groundwater

By Alan Jeffrey, Isaac Kaplan, Dachun Zhang, Shan-Tan Lu, and Jesper Nielsen, from *Contaminated Soil Sediment and Water*, June 2002, 34-35.

Background

Nitrate contamination of groundwater supplies is an increasing concern as urban areas continue to expand into rural areas. Farming, intensive livestock operations, septic sewage systems, and other practices in rural areas release organic and inorganic nitrogen into the environment, which ultimately show up in the groundwater as dissolved nitrate.

Elevated nitrate concentration in drinking water is a known health concern. Concentrations above 10 mg-N/L can cause methemoglobinemia, a form of anemia, in infants, and the public drinking water Maximum Contaminant Level for nitrate is established at the 10 mg-N/L level. Carcinogenic nitrosamine compounds may be formed in humans from ingested nitrates. Elevated nitrate concentrations are also a concern for the health of aquatic biota, and most water quality guidelines limit organic and inorganic nitrogen to 1 mg/L.

If elevated concentrations of nitrate are discovered in a groundwater aquifer, an immediate concern is to identify the source to limit future nitrogen inputs. The most common sources of groundwater nitrate are:

1. synthetic nitrogen fertilizers
2. animal waste
3. human septic waste.

Fortunately, the three sources can often be distinguished by differences in their stable nitrogen isotope ratios.

Stable Isotope Ratios - Explanation

Many elements exist as two or more stable isotopes. For example, all nitrogen atoms have 7 protons and 7 electrons. The number of protons and electrons defines the way nitrogen reacts chemically. Most nitrogen atoms also have 7 neutrons and have an assigned atomic weight of 14 (^{14}N). However, a small number, around 1 in every 270, has 8 neutrons and has an atomic weight of 15 (^{15}N). This difference in mass does not affect the way it reacts chemically. However, because ^{15}N has a greater mass, the ^{15}N isotope forms a stronger bond with other elements and may react at a reduced rate in physical, chemical and biological reactions. If a nitrogen-containing compound undergoes a reaction process where ^{14}N reacts faster than ^{15}N , then the product of the reaction will be enriched in ^{14}N , whereas the residual unreacted compound will be enriched in ^{15}N . This is what happens when nitrogen passes through the food chain in animals (and humans).

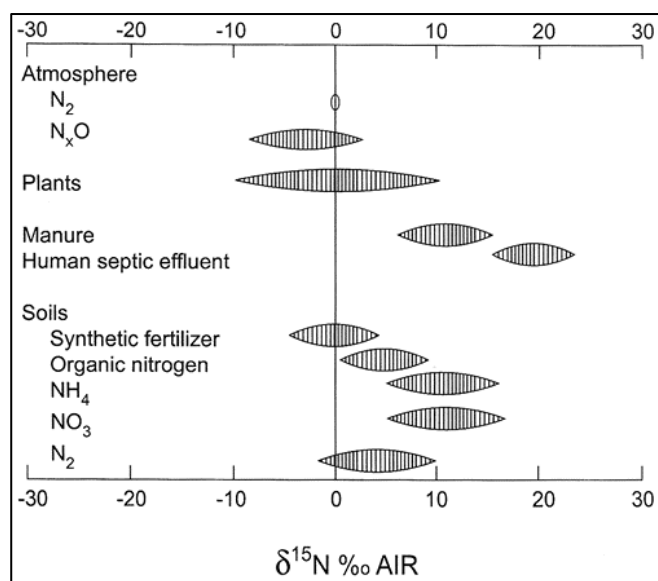
In the food cycle, nitrogen compounds are assimilated with little change in the relative amounts of ^{14}N and ^{15}N , and

plants and soil microorganisms that can use atmospheric nitrogen or can metabolize nitrogen from man-made ammonium nitrate fertilizer, retain only a small enrichment of ^{15}N over the starting $^{15}\text{N}/^{14}\text{N}$ ratio in N_2 or NH_4NO_3 .

However, metabolic processes involved in protein breakdown result in a preferential release of ^{14}N -enriched products and retention of ^{15}N -enriched cellular chemicals. Herbivores further enrich their tissues in ^{15}N and each consumer up the food chain eats nitrogen progressively enriched in ^{15}N . The body mass and excreted waste of carnivores at the top of the food chain, including humans, are most enriched in ^{15}N .

Source Identification

Because of difficulties in measuring the precise concentration of the minor isotope ^{15}N , early studies (circa 1950) proposed the use of isotope ratios (i.e. $^{15}\text{N}/^{14}\text{N}$, also expressed as $\delta^{15}\text{N}$) to measure the enrichment or depletion of a particular isotope. $\delta^{15}\text{N}$ values are conventionally expressed in parts per thousand (‰) deviation from the ratio in an internationally assigned standard, and can be measured with a precision of ± 0.15 ‰. By convention, atmospheric N_2 has been adopted as the international standard for nitrogen isotope ratios, and is given a $\delta^{15}\text{N}$ value of 0 ‰. The nitrogen in synthetic nitrogen fertilizer is derived from atmospheric N_2 by high temperature catalytic reaction with hydrogen to form ammonia, which is subsequently oxidized to nitrate. This process results in very little change in the original atmospheric nitrogen isotope ratio. So ammonia and nitrate derived from such a fertilizer source has a $\delta^{15}\text{N}$ value close to 0 ‰, the value of atmospheric N_2 (Figure 1). Nitrate derived from sewage sources can have values greater than $+20$ ‰ signifying a ^{15}N enrichment of 2% over the original $^{15}\text{N}/^{14}\text{N}$ ratio in starting N_2 . This is significantly different from the fertilizer nitrogen isotopic value.



Whereas it is generally straightforward to differentiate the waste released by herbivores from that of carnivores, waste from animals in the food chain that consume both plant and animal protein, such as free-ranging poultry and hogs, may

have intermediate values. This may be useful in cases where it is important to distinguish nitrate derived from different livestock animal waste. Also, nitrogen in the environment is involved in a large number of reactions as it cycles through the food chain. In particular, dissolved nitrate can undergo denitrification under anaerobic conditions to N_2O and N_2 by bacteria in the soil. In this process, the products (N_2O and N_2) are enriched in ^{14}N , while the residual nitrate is enriched in ^{15}N . This could lead to nitrate derived from a fertilizer input having $\delta^{15}N$ values close to sewage nitrogen. Usually there are other indicators that can differentiate bacterial denitrification from sewage or septic tank contributions, and a more detailed study will identify this and allow the actual source of the nitrate to be determined.

References

Environmental Isotopes in Hydrogeology, Clark, I. and P. Fritz, Lewis Publishers, Boca Raton, FL, 1997. ■

Groundwater Resources Association (GRA) Isotope Course and Symposium

GRA has announced a course and symposium on isotope methods in groundwater investigations on March 28 and 29, 2007 in Concord, CA.. The course will be conducted by Dr. Carol Kendall (USGS) and Dr. Jean Moran (Lawrence Livermore Lab), two of the leading investigators in the field. The symposium will feature both novel research studies and survey papers on topics such as:

- Surface Water – Groundwater Interaction
- Contaminant Transport and Geochemical Evolution of Groundwater
- Aquifer Vulnerability and Water Residence Time

DPRA/Zymax Forensics is represented on the symposium editorial committee, and is one of the symposium exhibitors. The deadline for submitting abstracts of papers and posters to the symposium is January 26, 2007. We encourage you to attend the symposium and meet the DPRA/Zymax Forensics representatives.

More information is available at
<http://www.grac.org/isotope.asp>