

Fundamentals and Application of Environmental Isotopes in Chlorinated Solvent Investigations

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1 The Environmental Isotopes

1.1 Elements, nuclides, and isotopes

The nuclear structure of a nuclide is classically defined by its number of protons which defines the element, and the number of neutrons which defines the isotope of that element. The sum of protons and neutrons gives the atomic weight. Unstable isotopes or radioactive nuclides will decay with time, while stable isotopes do not. For example, hydrogen has three isotopes (^1H to ^3H) although only ^1H and ^2H are stable. ^3H is radioactive with a half-life of 12.4 years. Carbon has 11 isotopes (^8C to ^{18}C) although only ^{12}C and ^{13}C are stable. The others are radioactive with half-lives varying from 5730 years (^{14}C) to less than a millisecond.

1.2 Why "Environmental" isotopes?

Environmental isotopes are important to us. They are the naturally occurring isotopes of elements found in abundance in our environment: H, C, N, O, S, and Cl, etc. Stable isotopes of these elements serve as tracers of water, carbon, nutrient and solute cycling. As they are light elements, the relative mass differences between their isotopes are large, imparting measurable fractionations during physical and chemical reactions. For example, ^2H has 100% more mass than ^1H , whereas the two stable isotopes of bromine (^{81}Br and ^{79}Br) have a mass difference of only 2.5%. Radioactive environmental isotopes are also important. ^{14}C and ^3H , for example, are often applied to estimate the age or circulation of groundwater (Clark and Fritz, 1997).

1.3 Isotope ratios and delta (δ) notation

The variations in numbers of neutrons in an element provides for the different masses (atomic weights) of the element and the molecules of which they may be a part. For example, heavy water, $^2\text{H}_2^{16}\text{O}$, has a mass of 20 compared to normal water, $^1\text{H}_2^{16}\text{O}$, which has a mass of 18.

Stable isotopes are measured as the ratio of the two most abundant isotopes of a given element. For carbon it is the ratio of ^{13}C , with a terrestrial abundance of 1.11%, to common ^{12}C which represents 98.89% of terrestrial carbon. Thus the $^{13}\text{C}/^{12}\text{C}$ ratio is about 0.011.

Measuring an absolute isotope ratio requires rather sophisticated mass spectrometers. Rather than measuring a "true ratio", measuring its "apparent ratio" can be easily done by gas source mass spectrometry. To cancel the instrumental error due to operational variations in different labs and instruments, etc., a known reference can be measured on the same instrument at the same time (Clark and Fritz, 1997). The difference between the measured ratios of the sample and reference is expressed by the delta (δ) notation. Further, δ values are expressed as the parts per thousand or permil (‰) difference from the reference:

$$\delta^{13}\text{C}_{\text{sample}} = \left[\left(\frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{reference}}} \right) - 1 \right] \times 1000\text{‰ PDB}$$

Where PDB is the name of the reference used, in this case Pee Dee Belemnite, a carbonate formation. A δ -‰ value that is positive, say +5‰, signifies that the sample has 5 permil or 0.5% more ^{13}C than the reference, or is enriched by 5‰. Similarly, a sample that is depleted from the reference by this amount would be expressed as $\delta^{13}\text{C} = -5\text{‰ PDB}$.

The ratios for the other elements such as O, H, Cl, S or N are expressed in the same way relative to their specific standard. For oxygen and hydrogen isotopes, the accepted reference is Standard Mean Ocean Water (SMOW); for chlorine isotope, it is Standard Mean Ocean Chloride (SMOC); for sulfur isotope, it is the troilite (FeS) phase of the Canon Diablo meteorite (CDT); for nitrogen isotope, it is atmospheric nitrogen (AIR).

1.4 Isotope fractionation

When one of the above heavy isotopes is a part of a compound, its bond to adjacent atoms is slightly stronger than the equivalent bond of the lighter isotope when it is in the same position in another molecule of the same compound. When molecules of this compound enter into chemical or biologically mediated reactions, the molecules with the lighter isotopes react a little faster than the ones with the equivalent heavier isotopes. This means that as the reaction proceeds, the reactant that remains has a progressively higher content of the heavy isotope since the molecules containing light isotopes have reacted to form product faster than those containing heavier isotopes. Such process is called "isotope fractionation" (Urey, 1947). Fractionation processes will slightly modify the isotope ratio for any compounds containing target isotope such as carbon, but these variations are normally seen only at the fifth or sixth decimal place (Clark and Fritz, 1997).

2 Stable Isotope Analyses of Environmental Contaminants

2.1 Inorganic and organic contaminants

Stable isotope analysis has long been realized to be a valuable technique to investigate the sources and the subsurface behavior of inorganic contaminants, such as nitrate (Aravena et al., 1993). A combination of Elemental Analyzer-isotope ratio mass spectrometry (EA-IRMS) is often applied for isotope analysis of inorganic contaminants. The basis of IRMS is to bend a beam of charged molecules in a magnetic field into a spectrum of masses; the beam of charged molecules is usually generated by ionization of a gaseous sample.

Stable isotope analysis has also been applied to organic contaminants, such as trichloroethene (Poulson and Drever, 1999). By definition, all organic contaminants of environmental concern contain carbon, and hydrogen virtually, while many may also contain elements such as chlorine (e.g., chlorinated solvents), oxygen (e.g., gasoline additive MTBE), nitrogen (e.g., herbicides such as Atrazine), and/or sulfur (e.g., various pesticides). Using multiple stable isotope analyses of a single individual contaminant would provide additional discriminants to be used to investigate the sources and the subsurface behavior of an organic contaminant.

2.2 Gas chromatography-isotope ratio mass spectrometry

The ability to measure the isotopic composition of the organic contaminant itself has been facilitated by gas chromatography-isotope ratio mass spectrometry (GC-IRMS), which allows for the measurement of the isotopic composition of individual compounds within a complex mixture (Freeman et al., 1990; Hayes et al., 1990; Hilkert et al., 1999). GC-IRMS provides rapid, cost-effective analysis with four to five orders of magnitude more sensitivity than conventional labor-intensive "offline preparation then dual-inlet measurement" techniques.

The basic concept for the determination of the carbon isotopic composition of individual compounds, for example, is the same as for the bulk isotopic values in that the components are completely combusted to CO₂ and water and the isotopic composition of the resulting CO₂ determined. However, the big difference is that these values are determined in real time as the individual compounds elute from the GC column. These separated compounds pass through a combustion tube where they are combusted, the CO₂ and water pass through a separator, such as a "Nafion" tube to remove the water, and the CO₂ continues into the IRMS (Philp, 2002). Samples can readily be prepared for GC-IRMS analyses by a number of techniques including solvent extraction, direct injection of headspace gas, and rapid extraction from either gas or aqueous solution by solid-phase micro-extraction (SPME), purge and trap, etc. Preparation methods have been developed and improved to convert different sample compounds separated by GC to an appropriate gas (CO₂, H₂, N₂ and SO₂).

2.3 Compound-specific isotope analysis

Sample preparation and GC-IRMS techniques can permit compound-specific isotope analysis (CSIA) of contaminants in low-parts per billion (ppb) concentration ranges. The typical analytical uncertainty is $\pm 0.5\%$ for carbon, and within similar ranges for hydrogen, chlorine, nitrogen, sulfur. Recently, U.S. EPA has issued a guide for assessing biodegradation and source identification of organics using CSIA (Hunkeler et al., 2008). CSIA technique can variously be used to measure the isotopic composition of many types of contaminants, and CSIA has been applied to study the sources and behavior of subsurface contaminants including mono-aromatic hydrocarbons such as Benzene, Toluene, Ethyl-benzene, and Xylenes (BTEX) (Kelly et al., 1997), polycyclic aromatic hydrocarbons (Hammer et al., 1998; Wang et al., 2004), crude oils and other refined hydrocarbon products (Wang et al., 2001, 2003; Pond et al., 2002).

Unlike commonly used carbon and hydrogen isotope analyses, chlorine isotope analysis by traditional methods can't be carried out without upstream, lab-intensive, offline pretreatments to convert chlorinated compounds into a molecule containing a single chlorine atom, such as methyl chloride (CH_3Cl). After such conversion, the chlorine isotope ratio is determined using dual-inlet isotope ratio mass spectrometer. These complex sample preparation processes are disadvantages of conventional chlorine isotope methods although high-precision isotopic analysis ($\pm 0.1\%$) is achievable with these techniques.

Recently, simple online methods for compound-specific chlorine isotope analysis have substantially expanded the application range of CSIA in this area. Shouakar-Stash et al., (2006) carried out CSIA analyzing chlorinated solvents for their chlorine isotopes. This method does not involve time-consuming, offline chemical conversion process; however, a special GC-IRMS configuration is required. Sakaguchi-Soder et al., (2007) presented a simple, quick and sensitive CSIA method for chlorine isotope of chlorinated solvents by conventional quadrupole GC-MS. The chlorine isotope ratios of target compounds such as PCE and TCE are calculated from the peak areas of selected molecular ions and fragment ions of the substances, using a set of unique mathematical equations. The precision of the method was demonstrated to be better than $\pm 0.5\%$. This CSIA can be performed with sufficient accuracy using conventional quadrupole GC-MS especially when significant fractionation takes place during the biotic and abiotic remediations, which involve dechlorination process.

3 Stable Isotopes in Chlorinated Solvent Investigations

3.1 Chlorinated solvents

Chlorinated solvents, such as tetrachloroethylene (PCE) and trichloroethene (TCE), are the most frequently detected contaminants in groundwater due to their widespread use since early 1940s. These compounds are designed as priority pollutants by the U.S. EPA and are known or suspected to be carcinogenic or mutagenic in humans. Spills, leaks and improper disposal of these compounds have resulted in soil and water contamination to varying degrees. Their concentration in groundwater can range from non-detectable to the solubility limit (Mackay and Cherry, 1989). Chlorinated solvents are dense non-aqueous phase liquids and they tend to persist for extended periods of time in groundwater systems (van Warmerdam et al., 1995). In many cases, source of the chlorinated solvent plume is unknown.

As a rapidly emerging analytical method, especially in environmental sciences, CSIA has an array of applications for chlorinated solvents. The molecular isotopic signature (^{13}C , ^{37}Cl and ^2H) of chlorinated solvents acquired by CSIA can be used to: 1) trace their sources on a local to global scale, serving as an ideal tool in "environmental forensics"; 2) identify, characterize and quantify biotic and abiotic transformation reactions, help achieve site closure in some cases (Hunkeler et al., 1999; Pirkle, 2006).

3.2 CSIA data may distinguish different chlorinated solvent sources

The use of stable isotopes to differentiate manufacturers of chlorinated solvents has been proposed as a means to distinguish sources contributing to a co-mingled groundwater plume (Morrison, 1999). CSIA may 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 altered the isotope ratio of the target component so the oldest release may be the most altered from the fresh one.

The low abundance of ^{37}Cl isotope fraction in chlorinated solvents is bound more tightly to carbon than are ^{35}Cl atoms (Bartholomew et al., 1954). The difference in bond strength results in chlorine isotope fractionation due to temperature and pressure differences during the manufacturing of the chlorinated solvents (Tanaka and Rye, 1991). For example, the isotopic range of ACE grade TCE (>99.5% TCE) is: $\delta^{13}\text{C}=-48.0$ to -27.8‰ , $\delta^{37}\text{Cl}=-2.54$ to $+4.08\text{‰}$, $\delta^2\text{H}=-30$ to $+530\text{‰}$ (Poulson and Drever, 1999). In one case, the isotopic ratios for $^{13}\text{C}/^{12}\text{C}$ and $^{37}\text{Cl}/^{35}\text{Cl}$ were used to distinguish among three chlorinated solvent manufacturers (van Warner et al., 1995). Each measured chlorinated solvent showed a significant range in $\delta^{37}\text{Cl}$ and $\delta^{13}\text{C}$ values. In a similar application, ^{13}C and ^{37}Cl were used to discriminate between two different pure phase chlorinated solvent batches obtained from various manufacturers using CSIA (Beneteau et al., 1996).

Shouakar-Stash et al. (2003) have characterized selected chlorinated solvents in terms of their hydrogen, carbon and chlorine isotopic composition. They have noted that $\delta^2\text{H}$ for a range of manufactured TCE varied between $+466.9\text{‰}$ and $+681.9\text{‰}$ due to the dehydrochlorination reactions used in the industrial production of TCE, whereas TCE generated as a dechlorination (a degradation pathways) product of PCE was significantly depleted, $\delta^2\text{H} < -300\text{‰}$, a result of H atom incorporation from the environmental water. This suggests that $\delta^2\text{H}$ of certain chlorinated solvents such as TCE may be a powerful means of distinguishing between degradation products and manufactured solvents. The combination of carbon, chlorine and hydrogen isotopic data in addition to concentration will no doubt significantly enhance the ability to unravel the source of contaminants at complex sites (Hunkeler et al., 2005).

Since early 2007, compound-specific carbon, hydrogen, and chlorine isotope analysis have been established in our lab to measure the isotope ratios of the chlorinated solvents in soil and groundwater at more than 10 dry cleaner sites that are the focus of litigation (Presentation by Wang Y., 2009). At a site in Los Angeles, 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. At another site in New York, carbon, chlorine and hydrogen isotope ratios of PCE, TCE and cis-DCE were measured in groundwater samples. The carbon and chlorine isotope ratios indicate that the chlorinated solvents at the site have at least three sources represented by two PCE plumes and one TCE plume. The hydrogen isotope ratios of TCE further indicate that the TCE in the above TCE plume has not migrated into adjacent wells (Presentation by Wang Y., 2009).

3.3 CSIA data may guide remediation decision and help achieve site closure

Whilst carbon, hydrogen, and chlorine isotopes are now being used in a fairly regular and systematic manner for evaluating the origin of chlorinated solvents and the correlation of these contaminants with their suspected sources, there are a number of other potential applications in environmental chemistry based on changes in isotopic compositions. The most important application for their isotopic values, in addition to source correlations, would be monitoring the rate and/or extent of degradation of individual compounds in the environment (Philp 2002; Murry and Morrison, 2002).

A promising means for mitigating chlorinated solvent contamination in soil and groundwater is in situ bioremediation, in which microbes convert chlorinated solvents to environmentally benign products such as CO₂, chloride and biomass. One of the most severe limitations of in situ bioremediation is the difficulty of proving that it works. Demonstration of natural attenuation for the volatile chlorinated solvents is particularly difficult due to their slow biodegradation rates. Also these contaminants are mobile and concentrations changing at the monitoring wells do not necessary reflect changes in concentration resulting from degradation (Philp, 2002). The changes in concentration at specific water wells may simply reflect movement of the samples within the plume, or physical processes such as adsorption, mixing, and dispersion, etc.

Because biodegradation cause significant isotopic fractionation between residual chlorinated solvents and their degradation products, isotope ratios can provide evidence that in situ bioremediation is occurring in situations where chemical measurements alone may provide insufficient or ambiguous data. Sturchio et al. (1998) reported stable isotope ratios of chlorine in TCE in groundwater from an aerobic aquifer beneath an extensively contaminated industrial site in western Kentucky. Variations in the concentrations and chlorine isotope ratios of TCE are consistent with those expected from natural attenuation. They demonstrated that stable chlorine isotope ratios provide a powerful tool for evaluating the effectiveness of natural attenuation. Isotopic measurements support partial natural attenuation of TCE, which is consistent with the available hydrogeologic data and the history of activities at this site.

Isotopic enrichment occurs to the parent compound during the sequential degradation processes such as the well known biodegradation of PCE to ethane. In general it has been found (Lollar et al., 1999; Bloom et al., 2000; Slater et al., 2001) that the enrichment factors increase with each step in the sequence from PCE to TCE (-2 to -5.5‰), TCE to cis-DCE (-7.1 to -13.8‰), cis-DCE to vinyl chloride (-15.1 to -20.4‰), and vinyl chloride to ethane (-22.4 to -24.1‰). The fact that enrichment factors fall into distinct ranges allows one to estimate the relative extent of degradation of a chlorinated ethane. The consistent observation of isotopic fractionation during reductive dechlorination suggests that CSIA is a useful tool to identify the occurrence of biodegradation (Pirkle, 2006).

Hunkeler et al. (2005) have used stable carbon isotope analysis in conjunction with concentration data to clarify and confirm the active degradation pathways at a former waste solvent disposal site where at least 14 different chlorinated hydrocarbons were present in groundwater. One of several issues which were resolved using carbon isotopic data was the observation of TCE at down gradient locations with $\delta^{13}\text{C}$ in the range of -41.0 to -45‰ which is well below the range of values known for pure-phase industrial TCE which has been determined in the range -24.3 to -31.0‰ (Hunkeler et al., 2004). Although PCE was not a major contaminant at the site, it was present with $\delta^{13}\text{C}$ in the range -28.3 to -30.5‰. Enrichment factors for degradation of PCE to TCE (-2 to -5.5‰) suggest that the observed TCE was not a degradation product of PCE.

As we have discussed above, more and more laboratory and field studies have demonstrated that the incorporation of CSIA constraints into remediation project may guide remediation decision and help achieve site closure. The isotopic data provided by CSIA can be used to unambiguously determine that biodegradation of chlorinated solvents is occurring; may be able to identify the process of degradation as aerobic or anaerobic; and in some cases determine the rate and extent of degradation; and may become a powerful predictive tool for assessing the extent and duration of contaminant plumes (Pirkle, 2006), thus CSIA may significantly decrease monitoring and remediation costs.

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