Chapter 6: Isotopes

Protium

Deuterium

Tritium

Proton
Electron
Neutron
What makes an isotope and what is the difference between radioactive and stable isotopes?

- **carbon-12**: 98.9%  
  6 protons  
  6 neutrons

- **carbon-13**: 1.1%  
  6 protons  
  7 neutrons

- **carbon-14**: <0.1%  
  6 protons  
  8 neutrons

[Source](http://wordpress.mrreid.org/2011/03/23/potassium-iodide-pills-are-radioactive/)
Radioactive Decay and Growth

The decay of a radioactive isotope is a first-order reaction and can be written:

\[ \frac{dN}{dt} = -\lambda N \]

Where \( N \) is the number of unchanged atoms at the time \( t \) and \( \lambda \) is the radioactive decay constant.

This equation can be rewritten as:

\[ N = N_0 e^{-\lambda t} \]

Where \( N_0 \) is the number of atoms present at \( t = 0 \). This is the basic form of the radioactive decay equation.
Half-life: the length of time that it takes for half of the atoms to spontaneously decay.

\[ t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda} \]

The radioactive decay equation can also be written in terms of activity.

\[ A = A_o e^{-\lambda t} \]

Where \( A \) is the activity at some time \( t \), and \( A_o \) is the activity at \( t = 0 \). Rearranging this equation and solving for \( t \) yields:

\[ t = \frac{1}{\lambda} \ln \left( \frac{A_o}{A} \right) \]
In practice, it is often easier to consider radioactive decay in terms of a radioactive parent and radioactive progeny (daughter).

**For any closed system, the number of progeny atoms plus the number of parent atoms remaining must equal the total number of parent atoms at the start. Solving for time considering these components yield the following equation:

\[ t = \frac{1}{\lambda} \ln[1 + (P/N)] \]

Where \( P \) = the number of progeny atoms produced.
The number of radioactive progeny can be determined from the following formula:

$$P = N_0(1 - e^{-\lambda t})$$

With the passing of time, the radioactive parent atoms will decline and the radioactive progeny will increase.
**Measurement of Radioactivity**

**becquerel (Bq)** is the basic measurement of radioactivity; 1Bq = 1.000 disintegrations per second.

**curies (Ci)** another commonly used measurement of radioactivity where; 1Ci = 3.700 x 10^{10} disintegrations per second. A **picocurie** is 1 x 10^{-12} curies.

**gray (Gy):** the unit used in the study of the chemical and biological effects of radiation. A dose of 1Gy deposits 1 joule of energy per kilogram of material.

**rad:** another often-used unit where 1Gy = 100 rad.
The biological effects of radiation are due to changes in the chemistry of the cells. These changes are caused by ionization, excitation, dissociation and atomic displacement due to the passage of the radiation through the cells.

The **sievert (Sy)** is the unit of radiation dosage used to measure the biological effects of radiation.

*In the past, the rem (roentgen equivalent man) was the commonly used unit, where 1 Sy = 100rem.*

The **relative biological effectiveness (RBE)** is a measure of the ability of various types of radiation to cause ionization in biological materials.

The dosage in sieverts is equal to the dosage in grays multiplied by the RBE.
Tritium dating

There are three isotopes of Hydrogen: $^1$H, $^2$H (deuterium), and $^3$H (tritium), with average terrestrial abundances (in atomic %) of $99.985$, $0.015$ and $<10^{-14}$ respectively.
Tritium (also designated as $^{3}\text{T}$) is radioactive and have a half-life of $t_{\frac{1}{2}} = 12.43$ years. This means it is used to date sample that are less than 50 years old.

Tritium is produced in the upper atmosphere by the bombardment of nitrogen with cosmic-ray produced neutrons.

$$\frac{14}{7}\text{N} + \frac{1}{1}\text{n} \rightarrow \frac{12}{6}\text{C} + \frac{3}{1}\text{T}$$

Tritium abundances are measured in several ways:

tritium unit (TU) = 1 tritium atom per $10^{18}$ hydrogen atoms,
dpm L$^{-1}$ = disintegrations per minute per liter, and
pCi L$^{-1}$ picocuries per liter (of water.)

$$1\text{TU} = 7.1\text{ dpm L}^{-1} = 3.25\text{ pCi L}^{-1}$$
From the onset of atmospheric testing of fusion bombs in 1952, until the signing of the Atmospheric Test Ban Treaty in 1963, bomb-produced tritium was the major source of tritium. Prior to the testing of fusion devices, the tritium content of precipitation was probably between 2 and 8TU. A peak of several thousand TU was recorded in northern hemisphere precipitation in 1963.

**Event dating** describes the marking of a specific period where the abundances of an isotope are uncharacteristically elevated or diminished. For example, groundwaters that were recharged between 1952 and 1963 will have a distinctive signature indicating an increase in $^3$H production.
Tritium decays through β- emission. This means that the parent material is $^3\text{H}$ and the progeny material is $^3\text{He}$.

Given $\lambda_T = 5.575 \times 10^{-2} \text{ y}^{-1}$, if through sampling ground water you find $^3\text{H} = 25\text{TU}$ and $^3\text{He} = 0.8\text{TU}$, what time has passed since that groundwater was recharged (at the surface)?

Recall: $t = 1/\lambda \cdot \ln[1 + (P/N)]$

$t = 17.937 \cdot \ln[1 + (0.8/25)] = 0.6 \text{ y}$
Carbon – 14 Dating

$^{14}\text{C}$ has been used for dating samples that are roughly 50,000 years old or younger (accelerator mass spectrometry ups the usage to 100,000 years). There are 3 isotopes of carbon: $^{12}\text{C}$, $^{13}\text{C}$, & $^{14}\text{C}$, with average terrestrial abundances of 98.90, 1.10, and $<10^{-10}$, respectively. $^{14}\text{C}$ is the only radioactive carbon isotope with a half-life of 5,730 years.
Tree-Ring Chronology

sample from living tree

sample from dead standing tree

sample from fallen tree

core

outer edge (newest growth towards bark)

common patterns

https://wikispaces.psu.edu/display/Biol110Sum/Antiquity+of+Life
In order to use $^{14}$C for geochronology, it is assumed that the atmosphere is in secular equilibrium with respect to $^{14}$C. Meaning that the rate at which $^{14}$C is produced by cosmic ray flux, is equal to the rate of decay of $^{14}$C so that the abundance in the atmosphere remains constant. However, for a variety of reasons, the abundance of $^{14}$C has not remained constant over time. These variations need to be accounted for when using this dating method.
U-Series Disequilibrium Methods of Dating

For a closed-system for a sufficiently long time, secular equilibrium will be achieved and the relative abundance of each isotope will be constant.

When the system enters disequilibrium due to separation of either parent or progeny, or subsequent decay, the reestablishment of equilibrium can be used as a dating method.

For example, when $^{234}$U decays to $^{230}$Th in sea water, the $^{230}$Th rapidly drops out of solution because, unlike uranium, thorium is very insoluble. In this case, the $^{230}$Th that accumulates in the sediments is said to be unsupported, as it is now separated from its parent isotope.
As we saw in the last example, $^{230}\text{Th}$ is unstable in the marine environment. In fact it has a mean residence time of about 300 years. Given that the addition and removal of U ($^{230}\text{Th}$’s parent) to the ocean is in balance, then $^{230}\text{Th}$ is produced at a constant rate. This means that as long as there has been no disruption to the sediment layers on the sea floor, the uppermost layer will represent present-day $^{230}\text{Th}$ deposition to the sediments.

$$\lambda_{^{230}\text{Th}} = 9.217 \times 10^{-6} \text{ y}^{-1}.$$  

$$t = 108,495 \ln\left(\frac{^{230}\text{Th}_{\text{initial}}}{^{230}\text{Th}_{\text{measured}}}\right)$$
Example 6-4

The $^{230}\text{Th}$ activity is measured for a marine sediment core. The top layer of the core has a $^{230}\text{Th}$ activity of 62dpm. At a depth of 1m, the $^{230}\text{Th}$ activity is 28dpm. Calculate the age of the sediment at a depth of 1m.

\[ t = 108,495 \ln(62/28) = 86,246 \text{ y} \]

Rate = (sediment thickness / time) = 1m / 86,246 y = 1.16 cm / 1000 y.
$^{230}\text{Th} / ^{232}\text{Th}$ Sediment Dating

Uses the ratio of these two radioisotopes instead of just $^{230}\text{Th}$
More precise

\[ t = \frac{1}{\lambda} \ln \left( \frac{R_0}{R} \right) = 108,495 \ln \left( \frac{R_0}{R} \right) \]

Where……
\[ R = \frac{^{230}\text{Th}}{^{232}\text{Th}} \text{ measured} \]
\[ R_0 = \frac{^{230}\text{Th}}{^{232}\text{Th}} \text{ initial} \]

\[ R \text{ is also} = \left( \frac{^{230}\text{Th}}{^{232}\text{Th}} \right)^0 e^{-\lambda t} \]

So far the examples have been for ‘unsupported’ activity. We have assumed that parent and progeny are separated
Supported activity – case where a parent or grandparent gets stuck on the sediment particle with the progeny isotope scavenged from the water column

\[ ^{230}\text{Th} = \text{Thorium scavenged from the water column = unsupported activity} \]

\[ ^{230}\text{Th} = \text{Thorium produced from } ^{238}\text{U stuck on the particle = supported activity} \]

Total activity = \[ ^{230}\text{Th} + ^{230}\text{Th} \]
\[ ^{230}\text{Th} / ^{231}\text{Pa} \text{ Sediment Dating} \]

Very similar to the \(^{230}\text{Th} / ^{232}\text{Th}\) except the half life is shorter so, you can use it for somewhat faster accumulation rates.

**Activity and Sediment-Rate Relationships**

Radioactive decay is a first-order process (i.e. exponential decay)

If sedimentation is constant then the sedimentation rate \((a) = (\lambda / -2.303m)\)

![Graph showing exponential decay](image1)

![Log graph showing exponential decay](image2)

- \(m\) is the slope
Stable Isotopes
Do not spontaneously breakdown to form other isotopes

Table 6-6. Average terrestrial abundances of stable isotopes used in environmental studies*

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Average Terrestrial Abundance (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>(^1)H</td>
<td>99.985</td>
</tr>
<tr>
<td></td>
<td>(^2)H</td>
<td>0.015</td>
</tr>
<tr>
<td>Carbon</td>
<td>(^{12})C</td>
<td>98.9</td>
</tr>
<tr>
<td></td>
<td>(^{13})C</td>
<td>1.1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>(^{14})N</td>
<td>99.63</td>
</tr>
<tr>
<td></td>
<td>(^{15})N</td>
<td>0.37</td>
</tr>
<tr>
<td>Oxygen</td>
<td>(^{16})O</td>
<td>99.762</td>
</tr>
<tr>
<td></td>
<td>(^{17})O</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>(^{18})O</td>
<td>0.2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>(^{32})S</td>
<td>95.02</td>
</tr>
<tr>
<td></td>
<td>(^{33})S</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>(^{34})S</td>
<td>4.21</td>
</tr>
<tr>
<td></td>
<td>(^{16})subp(^{36})S</td>
<td>0.014</td>
</tr>
</tbody>
</table>


Don’t have to worry about accounting for decay, but you might have to worry about fractionation.
Stable isotopes are used in two ways

Fractionations
Source ID and mixing

**Isotopic Fractionation** – partitioning of isotopes during phase change or reactions. Partitioning is proportional to the masses of the isotopes

**Equilibrium Fractionation**

- Bi-directional reactions at equilibrium (like water vapor over water)
- Lighter isotopes in the gas phase (lighter isotopes = more kinetic energy)

**Kinetic Fractionation**

- Unidirectional reaction where product is isotopically lighter than the substrate

The fractionations occur because the lighter isotope has more vibrational energy
Equilibrium fractionation

\[ \text{O}_2 \text{ Low } ^{18}\text{O}/^{16}\text{O} \text{ ratio} \]

\[ \text{O}_2 \text{ High } ^{18}\text{O}/^{16}\text{O} \text{ ratio} \]

\[ ^{16}\text{O} \text{ selectively in headspace} \]

Kinetic Fractionation

\[ \text{CaCO}_3 \text{ High } ^{13}\text{C}/^{12}\text{C} \text{ ratio} \]

\[ \text{CO}_2 \text{ Low } ^{13}\text{C}/^{12}\text{C} \text{ ratio} \]

\[ ^{12}\text{C} \text{ selectively reacted} \]
Fractionation Factor

Describes the partitioning of stable isotopes between two substances A and B

\[ \alpha = \frac{R_A}{R_B}, \]

where \( R \) is the ratio of the heavy to light isotope of the element.

Sometimes expressed as an enrichment factor (\( \varepsilon \)), which is:

\[ (1-\alpha) \times 1000 \]
The $\delta$ (delta notation)

$$\delta = \left[ \frac{R_{\text{samp}} - R_{\text{std}}}{R_{\text{std}}} \right] \times 1000$$

same as

$$\delta = \left[ \frac{R_{\text{samp}}}{R_{\text{std}}} - 1 \right] \times 1000$$

Units are per mil “‰”

Again $R$ is the ratio of the heavy to light isotope, and measured with a mass spectrometer.

$R_{\text{std}}$ is element specific…

### Table 6-7. Stable isotope ratios for standards *

<table>
<thead>
<tr>
<th>Element</th>
<th>Standard</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>V-SMOW</td>
<td>$\text{^2H}/\text{^1H} = 155.76 \times 10^{-6}$</td>
</tr>
<tr>
<td>Carbon</td>
<td>PDB</td>
<td>$\text{^13C}/\text{^12C} = 1123.75 \times 10^{-5}$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>V-SMOW</td>
<td>$\text{^18O}/\text{^16O} = 2005.2 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>PDB</td>
<td>$\text{^18O}/\text{^16O} = 2067.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>NBS-14</td>
<td>$\text{^15N}/\text{^14N} = 367.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>Sulfur</td>
<td>CDT</td>
<td>$\text{^34S}/\text{^32S} = 449.94 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

*Data from Kyser (1987).
Rearranging the del-notation equation and combining it with the fractionation Factor (\(\alpha\)) equation allows for calculation of the del value of one compartment if you know the del value of the other compartment and the \(\alpha\) value.

\[
\alpha = \frac{R_A}{R_B} = \frac{\delta_A + 1000}{\delta_B + 1000}
\]

Example 6-6: For the evaporation of water, the \(\alpha = 1.0092\). What is the \(\delta\) (oxygen) value for the water vapor in equilibrium with lake water having a \(d\) value of \(-5.0\text{‰}\)?

\[
\alpha_v = \frac{R_l}{R_v} = \frac{\delta_l + 1000}{\delta_v + 1000}
\]

Rearranging and solving for \(\delta_v\),

\[
\delta_v = \left[\frac{\delta_l + 1000}{\alpha_v}\right] - 1000 = \left[\frac{-5 + 1000}{1.0092}\right] - 1000 = -14.1\text{‰}
\]
Oxygen and Hydrogen Isotopes in Water

Used for ‘sourcing’ water

For hydrogen we consider $^1$H and $^2$H (deuterium; D)
For oxygen we consider $^{16}$O and $^{18}$O

$\delta$ values for O and H in water are zero for seawater

Water vapor in equilibrium with seawater at $25^\circ$C $\delta D = -69 \, \text{‰}$; $\delta^{18}O = -9.1 \, \text{‰}$

Water vapor in equilibrium with seawater at $10^\circ$C $\delta D = -84 \, \text{‰}$; $\delta^{18}O = -10.1 \, \text{‰}$

Temperature effects the fractionation from liquid to vapor phase for H and O. The temperature effect comes into play both latitude and altitude.

This temperature effect on fractionation is what gives rise to different isotopic values In H and O for different areas of precipitation.
The process of fractionation during condensation

Start with water vapor that is isotopically light in H and O relative to seawater

As the vapor begins to condense out into clouds
   Initial droplets are rich in $^{18}$O and D
   Vapor becomes more depleted in $^{18}$O and D

As condensation continues-
   - Vapor becomes more depleted
   - Droplets in turn reflect lower $^{18}$O and D coming from source vapor

The change in isotopic value of both the vapor and liquid is a function of how much of the original vapor is left.

Described by a Rayleigh Distillation function
Rayleigh Distillation (or fractionation)

\[ \delta^{18}O_v = [\delta^{18}O_0 + 1000] f^{(a-1)} \]

vapor starting vapor fraction remaining

To relate the condensing liquid to the vapor

\[ \delta^{18}O_l = \alpha(\delta^{18}O_v + 1000) - 1000 \]
Rayleigh Fractionation in general

Consider a kinetic fractionation reaction where a substrate is being consumed by a reaction that fractionates. If the substrate is not replenished, then it will continue to get isotopically heavier over time.

A simple form of the Rayleigh fractionation curve can be used to describe

\[ \delta_{\text{time}} = -\varepsilon \ln(f) + \delta_{\text{initial}} \]

Substrate

At some time

enrichment factor

Fraction

Substrate remaining

Original substrate
Isotope fractionation of H and O in water (during condensation)

This process results in:

- rain early in a precip event is isotopically heavier than at the end of the event
- delta values of rain decreases from coastal to inland areas
- rain is isotopically lighter at the poles

The H and O isotopes in precipitation are related:

\[ \delta D = 8 \delta^{18}O + 10 \]  (excess of D relative to \( ^{18}O \); \( \delta \))

or

\[ \delta D = 8 \delta^{18}O + d \], where \( d \) is the D excess
\[ \delta D = 8 \delta^{18}O + 10 \]

Is the equation for the Global Meteoric Water Line

This has nothing to do with meteors

Figure 6-6. Plot of $\delta D$ versus $\delta^{18}O$ illustrating the mean global meteoric water line and local meteoric water lines. Other processes that affect the isotopic ratios - e.g., low-temperature water-rock exchange, geothermal exchange, and evaporation - are also illustrated. A and B are two water masses and the dashed line represents the possible isotopic compositions of water produced by mixing of these two end members. The diagram is modified from “Uses of Environmental Isotopes” by T. B. Coplen in REGIONAL GROUND WATER QUALITY edited by W. M. Alley, pp. 227-254. Copyright © 1993. This material is used by permission of John Wiley & Sons, Inc.
Different areas influenced by evaporation, water-rock interaction, etc. will cause a deviation in the D excess ($\delta$) relative to $^{18}$O in water.

It is the different $\delta$D values relative to the GMWL that allows you to ‘tag’ water masses.

With this tag you can examine contributions of different water sources to ground and surface waters.

Example: Snowmelt vs. direct precipitation.
Example 6-7: River flow below a dam is a mixture of water coming from the reservoir behind the dam and from a groundwater source.

River.....$\delta^{18}O = -3.6\%$, $\delta D = -44.6 \%$
Res..... $\delta^{18}O = -4.5\%$, $\delta D = -38 \%$
GW..... $\delta^{18}O = -3.0\%$, $\delta D = -49 \%$

What's the percentage contribution of each source?

This is a two-endmember mixing problem.

For D........$f_{GW} \delta D_{GW} + f_{res} \delta D_{res} = \delta D_{riv}$

For $^{18}O$... $f_{GW} \delta^{18}O_{GW} + f_{res} \delta^{18}O_{res} = \delta^{18}O_{riv}$

Also $f_{GW} + f_{RES} = 1$

$f_1 = 0.40\rightarrow$ GW supplies 40% of the water in the river

$f_2 = 0.60\rightarrow$ Reservoir supplies 60% of the water in the river
Climate Change

Because the fractionation of H and O in water changes with temp, isotopic measurements of ice-cores are used to estimate paleoclimate.

1) Isotopic composition of snow reflects air temp.

2) Colder air = more negative $\delta D$ and $\delta^{18}O$

3) Warmer air = less negative $\delta D$ and $\delta^{18}O$

4) Works the same in both hemispheres

5) Once snow is packed into glacier, ice stratigraphy not disturbed, paleothermometer locked into place

Ice ages can confound this approach to some extent because by locking up a bunch of ocean water into glaciers, the overall $\delta D$ and $\delta^{18}O$ of all water gets less negative. This effect is small relative to the temp effect.
When records from both hemispheres agree, it is a global climate change.

When the disagree, it is a local climate change.
Pleistocene ice ages

Present

LGM ~20,000 years ago

sea level -130 m

benthic foram $\delta^{18}O$

LGM

ICE

SEA

more ice

Carbon

Can we use $\delta^{13}C$ to detect Fossil fuel contributions to Atmospheric $CO_2$?
DIC in aqueous systems

There are isotopic fractionations associated with each step of the carbonate buffering system. *Recall from Chapter 3 that the dominant carbonate species is pH dependent.*

\[
\begin{align*}
\text{CO}_2 \text{ gas} & \sim \text{CO}_2 \text{ aq} \\
\text{CO}_2 \text{ aq} & \rightarrow \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \rightarrow \text{HCO}_3^- \\
\text{HCO}_3^- & \rightarrow \text{CO}_3^{2-} \\
\text{CO}_3^{2-} & \rightarrow \text{CaCO}_3
\end{align*}
\]
Table 6-8. Fractionation factors for carbonate species relative to gaseous CO$_2$*

<table>
<thead>
<tr>
<th>DIC species</th>
<th>$%$ heavier than CO$_2$ gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ aq</td>
<td>1.04</td>
</tr>
<tr>
<td>H$_2$CO$_3$</td>
<td>-0.8</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>8.0</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>6.7</td>
</tr>
<tr>
<td>CaCO$_3$ (s)</td>
<td>9.8</td>
</tr>
</tbody>
</table>

*From Deines et al. (1974). T in Kelvin

Figure 6-10. Isotopic fractionation factors, relative to CO$_2$ gas, for carbonate species as a function of temperature. Deines et al. (1974).
Using Equations in Table 6-8

**Example 6-8:** CaCO$_3$ is ppt in water in equilibrium with the atm. What is the $\delta^{13}$C for the carbonate at 25ºC.

\[
\text{CaCO}_3 \text{ relative to CO}_2^g: \quad 1000\ln\alpha = -3.63 + 1.194 \times 10^6/T^2
\]

\[
= 9.8 \ldots \text{calcite is } 9.8\% \text{ heavier than CO}_2^g
\]

CO$_2^g = -7\%$, so calcite is 2.8%.

**Example 6-9:** Bicarb in ocean dominate DIC. What is the $\delta^{13}$C for DIC in the ocean at 10ºC.

\[
\text{HCO}_3^- \text{ relative to CO}_2^g: \quad 1000\ln\alpha = -4.54 + 1.099 \times 10^6/T^2
\]

\[
= 9.18 \ldots \text{bicarb is } 9.18\% \text{ heavier than CO}_2^g
\]

Bicarb dominates DIC so …

CO$_2^g = -7\%$, therefore ocean $\delta^{13}$ DIC = 2.8%.
Methane hydrates, biogenic in origin
\[ \delta^{13}C \text{ average of about } -65 \% \text{ (range -40 to -100\%)} \]
Carbon isotopes – food webs, paleo or otherwise.

C3 plants (deciduous trees) – $\delta^{13}\text{C} = -15\%\text{o}$

C4 plants (grasses, marsh, corn…) – $\delta^{13}\text{C} = -30\%\text{o}$

plankton – $\delta^{13}\text{C} = -22\%\text{o}$

Small trophic fractionation …about 1 \%\text{o}
Nitrogen

Stable isotopes of N and O used to trace sources of nitrogen pollution usually in the form of $\text{NO}_3^-$ or $\text{NH}_3$

$\delta^{15}\text{N}$ can be substantially altered by biological processes

Nitrates in surface and groundwater

\[ \text{Fertilizer } \delta^{15}\text{N} = 0 \text{‰} \qquad \text{Manure } \delta^{15}\text{N} = 15 \text{‰} \pm 10\text{‰} \]

In theory you can use $^{15}\text{N}$ to distinguish sources. In practice, it’s difficult……

Nitrate is reactive in surface and groundwaters undergoing denitrification.

As denitrification converts nitrate to $\text{N}_2$, the residual nitrate becomes isotopically heavier. So a fertilizer source of nitrate that has undergone some denitrification will start to look isotopically like the manure nitrate.

A way to constrain this problem is to also measure $\delta^{18}\text{O}$ in nitrate

\[ \text{Fertilizer } \delta^{18}\text{O} = +23 \text{‰} \text{ (oxygen in nitrate comes from air)} \]
\[ \text{Manure } \delta^{18}\text{O} = -10\text{‰} \text{ (oxygen in nitrate comes mostly from water)} \]
During denitrification, both O and N are fractionated but their fractionations relative to each other are predictable.

Red circles = measurements

Draw the predicted fractionation lines for each end-member (blue lines). Note they have the same slope.

Draw a line through the measured GW sample (the mixture) that is perpendicular to the fractionation slopes (dashed line).

Now you can either do a mixing calc to determine fraction of each source, or Amount of A = C-B / A-C

The ‘lever law’...just like torque in physics.

Figure 6-12. Determination of the relative importance of nitrate sources to a groundwater system. Two sources for nitrates are fertilizer and manure. Both are undergoing denitrification. A and B represent each source at a particular stage in the denitrification process. C is the isotopic composition of the nitrate in the groundwater due to simple mixing. In this example, approximately 60% of the nitrate is contributed by the fertilizer.
**NH₄⁺ and NO₃⁻ in rain**

Sources of NOₓ = 65% from fossil fuel
Sources of NH₄⁺ = bacterial breakdown of organic matter and animal/human waste

Volatilized NH₄⁺ is extremely isotopically light (30-40‰ lighter than waste)

Global NO₂ pollution
Sulfur

Big isotopic difference between sulfides and sulfates

Sulfate reduction (microbial) has a big fractionation, as does microbial sulfide oxidation

Is the sulfide produced during sulfate reduction isotopically lighter or heavier than the sulfate?

What’s the major source of sulfate on the planet?

Burning fossil fuels…
Mixing

Binary mixing

\[ \delta_{\text{mix}} = \delta_A f_A + \delta_B (1-f_A) \]

If the two sources have unequal concentrations of the element of interest, the mixing equation must be weighted to reflect that:

\[ \delta_{\text{mix}} = \delta_A f_A (A/M) + \delta_B (1-f_A)(B/M) \]

…..where A, B, and M are the concentrations of source A, B, and the mixture with respect to the element of interest.
Mixing with more than two end members

Figure 6-14. Plot of PO$_4^{3-}$ versus NO$_3^-$ in water samples from feedlot runoff (M), cultivated fields (F), uncontaminated groundwater (G), and contaminated well water (W). The sample of contaminated well water falls within the triangle defined by compositions M, G, and F, indicating that this sample is a mixture of these three compositions. The relative proportions of each end member can be determined by applying the lever rule (see Example 6-11).
Paleothermometry – *using carbonates*

\[ \delta^{18}O \text{ in carbonate} \]

Fractionation factor governing water (oxygen) equilibration with CaCO3 is temperature dependent

\[ t \, (^{\circ}C) = 16.9 - 4.14(\delta^{18}O_{\text{calcite}} - \delta^{18}O_{\text{water}}) + 0.13(\delta^{18}O_{\text{calcite}} - \delta^{18}O_{\text{water}})^2 \]

Due to large and seasonal variations in freshwater oxygen isotopes, only oceanic carbonate organisms work.

Lots of other assumptions and corrections so the tool is used as a relative indicator of paleotemperature.
Last Homework Assignment!!!!!

Chapter 6: 1, 9, 11, 20, 21, 25, 30, 38, 43a (assume $^{230}$Th unsupported), 47 & 48a

Due: April 29th