

Being an Ecological Detective:
Biogeochemical Methods to Assess
Watersheds

K. Limburg Lecture Notes
Watershed Ecology

Outline

1. What kind of assessments, and why?
2. Hydrograph separation
3. Isotopes and their use in hydrology & ecology

1. What kind of assessments, and why?

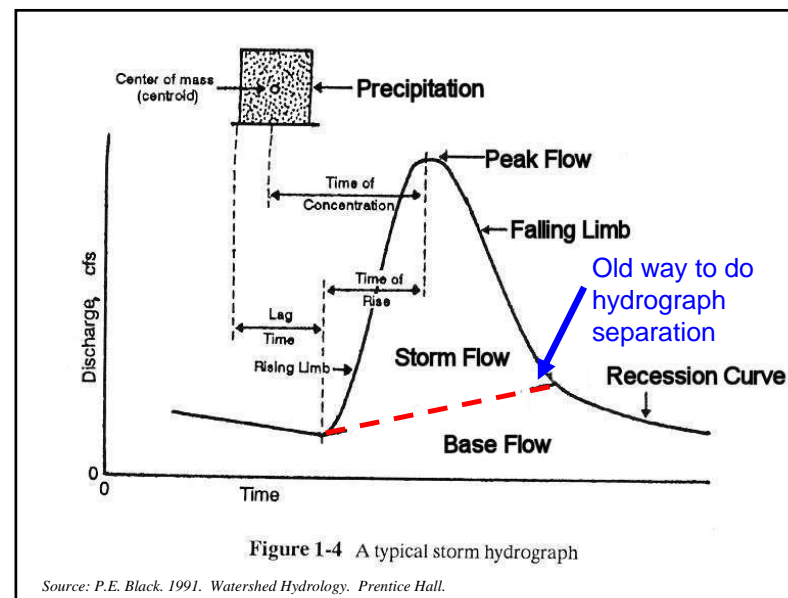
Many times, we cannot observe things directly that might be of interest, either because they aren't visible, or it would be impracticable.

Some examples:

1. What kind of assessments, and why?

- a. Source of water (rain, ground...)
- b. Sources of energy and matter flowing in food webs
- c. Transformation rates (biogeochemical processes)
- d. Track things that move around back to their origins (e.g., ivory) or through their lifetimes (fish)

Example of “parsing out different things” – hydrograph separation



Hydrometrics – the quantitative study of streamflow, snow, rain, water quality, etc.

Rather than simply “eyeball” a graph to estimate baseflow, we can track the contributions of “new” rainwater and “old” baseflow water if they start out with different concentrations of a chemical that we know is pretty unreactive – like chlorine (Cl) or bromine (Br)

How we do it: **end-member analysis**

End-member: the concentration or value of a tracer at one end of an expected gradient.

For example, the gradient could be rain water vs ground water, or it might even be fresh vs marine water.

The end-members would be the concentrations of the tracer at each end.

2. Hydrograph separation example.

Say we want to know the contribution of “new” rain water and “old” ground water to an observed hydrograph.

We know that the total flow, Q_t , should be equal to the sum of the flows of old (Q_o) and new (Q_n) water:

$$Q_t = Q_o + Q_n$$

If the new and old waters have different concentrations of a tracer in them, then the total amount of tracer is the sum of the new and old flows times their respective concentrations of tracer:

$$Q_t C_t = Q_o C_o + Q_n C_n$$

(units: Q = volume/time, C = mass/volume, so QC = mass/time)

We can re-write this expression to solve for either one of the water sources, old or new. Here's how we solve to get the new water flow:

$$Q_t C_t = Q_o C_o + Q_n C_n$$

Re-arrange:

$$Q_n C_n = Q_t C_t - Q_o C_o$$

We can also re-write Q_o in terms of Q_t and Q_n (to get rid of one of the unknowns) $\rightarrow Q_o = Q_t - Q_n$

$$Q_n C_n = Q_t C_t - (Q_t - Q_n) C_o$$
$$Q_n C_n + (Q_t - Q_n) C_o = Q_t C_t$$
$$Q_n C_n + Q_t C_o - Q_n C_o = Q_t C_t$$

$$Q_n C_n + Q_t C_o - Q_n C_o = Q_t C_t$$

Gather terms:

$$Q_n C_n - Q_n C_o = Q_t C_t - Q_t C_o$$

Gather more terms:

$$Q_n (C_n - C_o) = Q_t (C_t - C_o)$$

$$Q_n = Q_t \frac{(C_t - C_o)}{(C_n - C_o)}$$

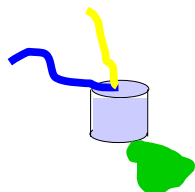
So now, we have a formula that lets us “back out” the amount of new rainwater that contributes to the hydrograph.

And if we know the amount of new water, we can easily determine the amount of old water, too.

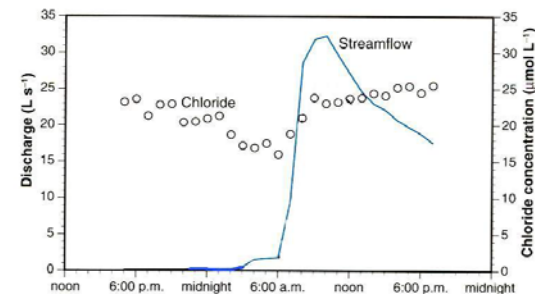
Why?

Because $Q_o = Q_t - Q_n$

In general, we can determine
 ...two sources with one tracer
 ...three sources with two tracers
 ...four sources with three tracers
 etc.

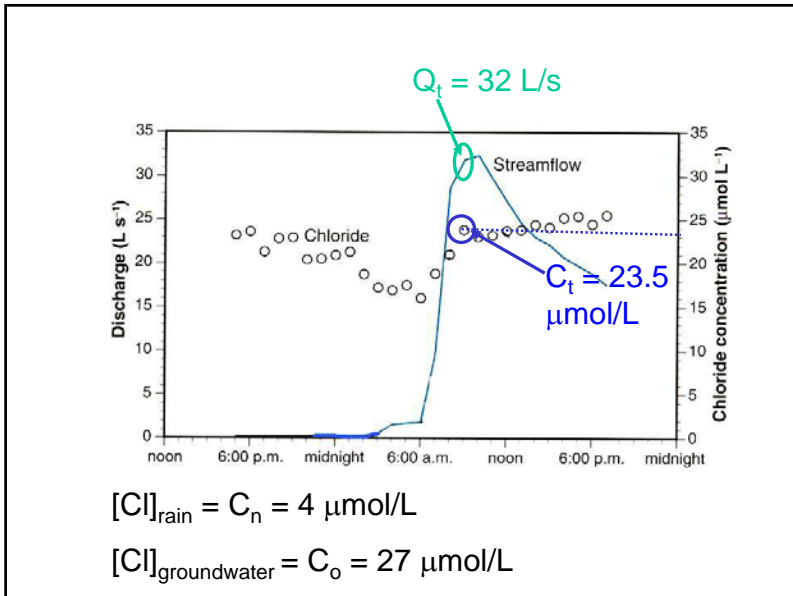


An example: Shaver Hollow catchment, Shenandoah National Park, Virginia*



$$[Cl]_{rain} = 4 \mu\text{mol/L}, [Cl]_{groundwater} = 27 \mu\text{mol/L}$$

Bazemore, D.E. 1993. M.Sc. Thesis, U. Virginia. Cited in Hornberger et al. 1998. Elements of Physical Hydrology. Johns Hopkins Press



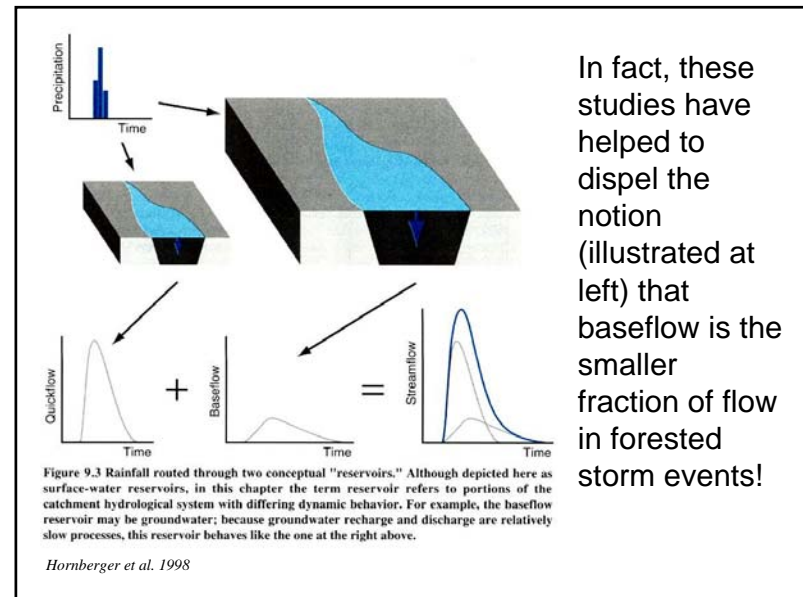
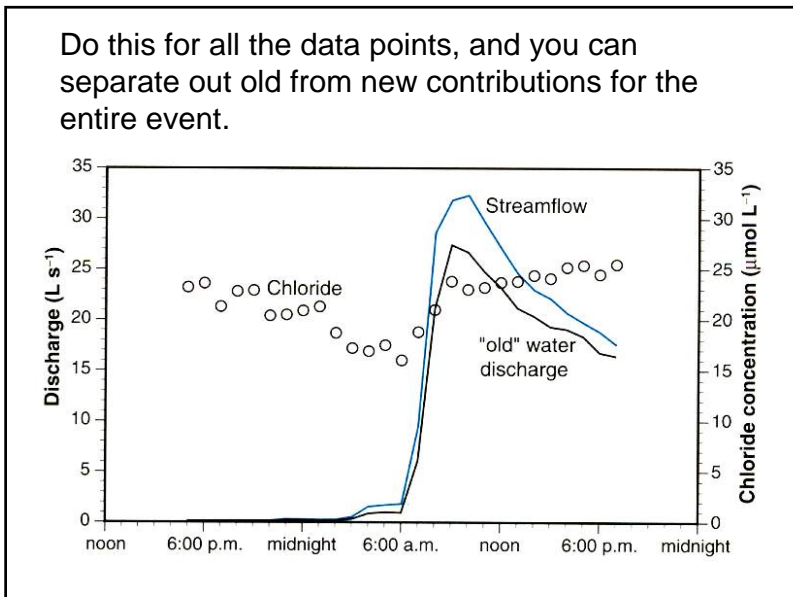
$$Q_n = Q_t \frac{(C_t - C_o)}{(C_n - C_o)}$$

All in units of $\mu\text{mol/L}$ – cancel out

$$Q_n = 32 \text{ L/s} \frac{(23.5 - 27)}{(4 - 27)}$$

$$Q_n = 32 \text{ L/s} (.13) \approx 4.15 \text{ L/s}$$

$$Q_o = Q_t - Q_n \rightarrow 32 - 4.15 = 27.85 \text{ L/s}$$



3. Isotopes and their use in assessment

(more fun with physics)

Atoms can be classified by their protons and neutrons.

Nuclide = an isotope-specific atom

Nuclides are defined by:

of protons (Z) which defines *element*

of neutrons (N) – defines the *isotope*

Atomic weight (A) = sum of Z + N

Denoted as ${}^A_Z Nu_N$

where Nu denotes the nuclide

Example:

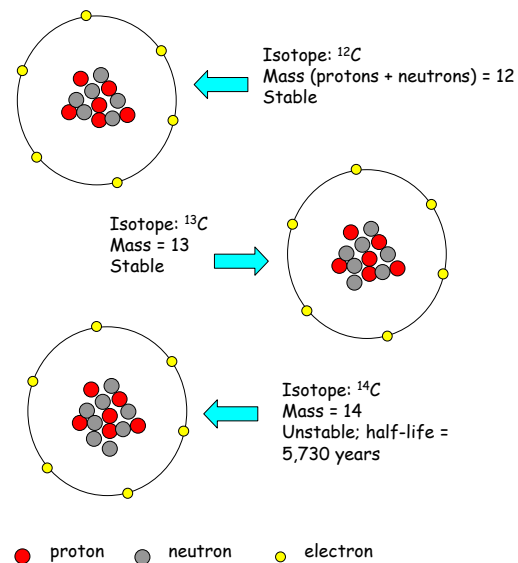
${}^{16}_8 O_8$ ← Most common form of oxygen

${}^{18}_8 O_{10}$ ← “Heavy” oxygen isotope. Rare (0.2%)

Radioisotopes are those which are unstable and tend to decay to a more stable state (about 1700 identified)

Stable isotopes are just that – stable! (about 270 identified)

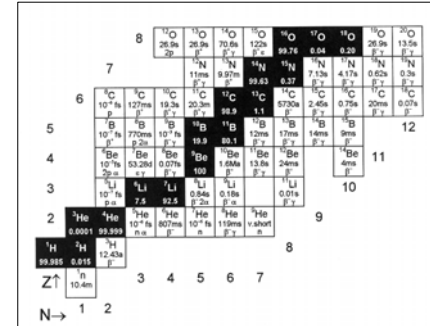
Stable isotope analysis is increasingly used in geology, hydrology, ecology, etc.



Nuclear binding energy occurs between *pairs* of neutrons and protons, so that stable nuclides with even numbers of N and Z predominate.

Nuclides with 2, 8, 20, 28, 50, 82, or 126 (“magic numbers”) of neutrons and/or protons are the most common.

This figure shows the nuclides of the light elements (from hydrogen to oxygen). The stable isotopes are shown in black, and their relative abundances (in %) are given below the element symbol.



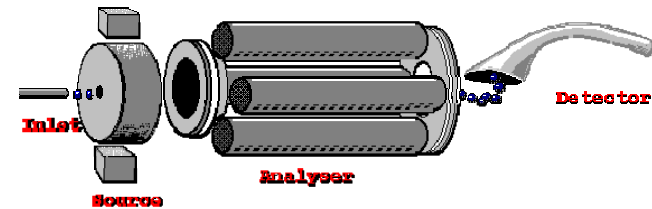
Clark, I., and P. Fritz. 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers.

We measure stable isotopes with a machine called a **mass spectrometer**



Photo: W.P. Patterson, Syracuse University

The basic mechanism is to pass an ion source through a magnetic field that separates out the ions according to their mass-to-charge ratios



This type of spectrometer is called a **quadrupole mass spectrometer**; the ions travel a flight path through a quadrupole (a 4-pole, electrically charged magnet – the long rods in the figure above).

We express stable isotope measurements as ratios of ratios (**delta values** or δ), and expressed in permille (‰):

For example, using oxygen again,

$$\delta^{18}\text{O}_{\text{sample}} = \left(\frac{\frac{^{18}\text{O}}{^{16}\text{O}}_{\text{sample}}}{\frac{^{18}\text{O}}{^{16}\text{O}}_{\text{reference}}} - 1 \right) \times 1000 \quad (\text{SMOW})$$

where **SMOW** stands for Standard Mean Ocean Water. (The current standard is Vienna SMOW or VSMOW, because the original SMOW ran out!)

δ values can be (+) or (-), being enriched or depleted in the heavy isotope relative to the lighter one

Other standards:

- ☞ PDB = Pee Dee belemnite (a carbonate rock from Texas). The standard for carbon (and also O in carbonates)
- ☞ Atmospheric nitrogen
- ☞ CDT = Cañon Diablo troilite for sulphur
- ☞ (hydrogen is also standardized to SMOW)

Isotope fractionation

Isotopes are electrochemically the same, i.e. they all undergo the same chemical reactions.

However, the slight differences in their masses results in some of the isotopes being preferentially used.

This process results in a “winnowing” or **fractionation** of the isotopes between reactant and product.

This is expressed by a fractionation factor, α , that is the ratio of isotope ratios of reactant and product:

$$\alpha = R_{\text{reactant}} / R_{\text{product}}$$

If you start a reaction and let it go only part way, there may be a large fractionation initially.

But when the reaction has used up all the starting material, the product should have all the isotopes, and therefore not show any fractionation.

Physicochemical fractionation: involves chemical transformations or changes of state.

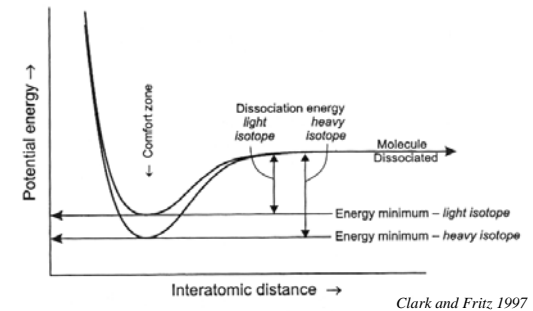
Examples include: water changing from liquid to vapor, biogeochemical transformations (digesting the protein in your dinner, for instance)

Diffusive fractionation: occurs when atoms or molecules diffuse across a concentration gradient.

Example: gas diffusing through another medium (oxygen diffusing into water)

Fractionation is due to the differences in the strengths of the bonds made by heavy and light isotopes:

a heavier isotope of an element has a stronger bond than a lighter one, and it takes more energy to break it apart (dissociate) and form a new bond with another atom.



SOMETIMES THE EXTRA NEUTRON MAKES A DIFFERENCE. IT'S HARDER TO PUSH THE HEAVY MOLECULES UP AN ENERGY HILL ...



M. Fogel and B. Fry, Woods Hole Stable Isotope Workshop, 1986

... SO THAT PRODUCTS HAVE MORE OF THE LIGHT ISOTOPE AND LESS OF THE HEAVY ISOTOPE. WE CALL THIS...

ISOTOPE DISCRIMINATION



M. Fogel and B. Fry, Woods Hole Stable Isotope Workshop, 1986

Isotopes of H and O in the water cycle.

Water can take on at least three isotopic forms: H_2^{16}O , $2\text{H}_2^{16}\text{O}$, and H_2^{18}O .

In the water cycle, condensation (the formation of liquid water from water vapor) transfers the heavier isotopes of hydrogen and oxygen into the liquid phase, leaving more of the lighter isotopes in the vapor phase.

Conversely, in the process of evaporation, the lighter isotopes “go first,” so that the vapor is isotopically lighter, and the remaining water becomes isotopically heavier (as more of the lighter isotopes evaporate away).

Isotopic “rainout”

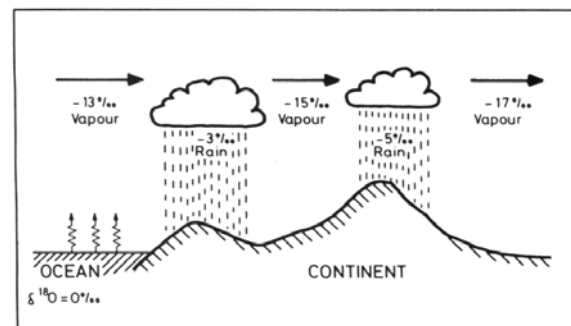


Fig. 3. Schematic ^{18}O fractionation in the atmospheric water cycle
(Source: Siegenthaler, 1979)

Fractionation of the isotopes in water is also a function of temperature.

This has been demonstrated repeatedly, and is due to the effect of temperature on the bond strength or dissociation energy.

Empirically, the relationship of the isotopic fractionation factor (expressed as $1000 \times$ the natural log of α) to temperature (T) is:

$$10^3 \ln(\alpha) = a (10^6 T^{-2}) + b (10^3 T^{-1}) + c .$$

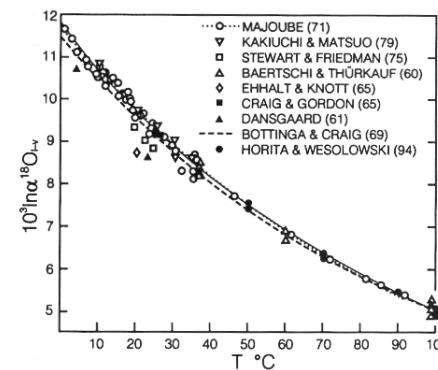


Fig. 1-7 Comparison of fractionation factors for ^{18}O in water-vapour exchange from various workers. Regression of these data (solid line) gives $10^3 \ln \alpha^{18}\text{O}_{v-w} = -7.685 + 6.7123 (10^3/T) - 1.6664 (10^6/T^2) + 0.35041 (10^9/T^3)$. Reprinted from Horita and Wesoloski (1994) with permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.

Clark and Fritz 1997

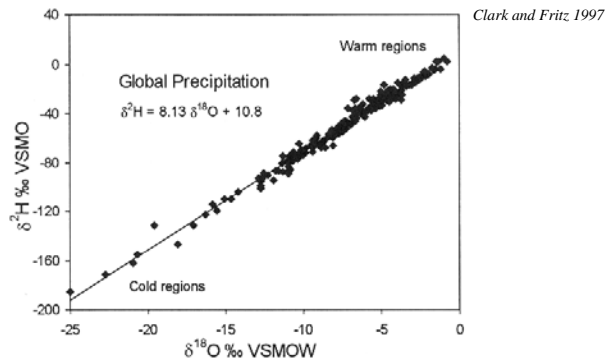
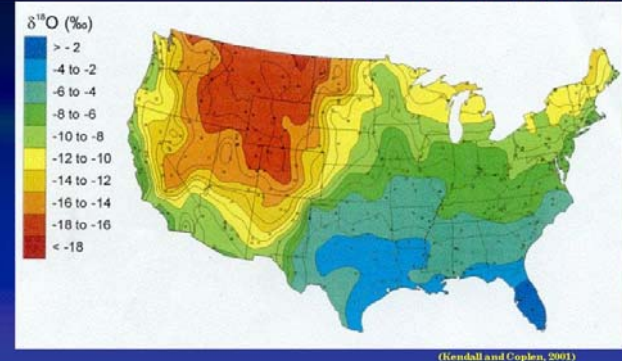


Fig. 2-1 The meteoric relationship for ^{18}O and ^2H in precipitation. Data are weighted average annual values for precipitation monitored at stations in the IAEA global network, compiled in Rozanski et al. (1993).

On a global scale, H and O stable isotopes are in steady state and their relationship is called the *global meteoric water line*. Deviations from this line can help to identify sources of water.

Surface Water Isotopic Concentrations in the USA



Values are depleted at higher latitudes, and also from “rainout” effects from mountain ranges.

Stable isotopes in ecology.

Ecologists have taken advantage of the differences in stable isotopic ratios of several light elements (H, C, N, and O) and also some of the heavier elements (for example S and Sr) to help unravel a variety of questions.

Examples include:

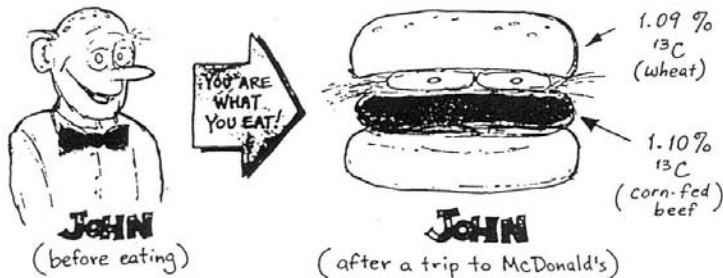
- sources of organic matter “flowing” through food webs
- migration of organisms from one place to another as determined by the “environmental tag” they carry from the source area
- sources of water used by plants
- assignment of organisms into trophic levels in the food web.

IN FACT, YOU WOULD NOT BE ABLE TO DISCRIMINATE BETWEEN ^{12}C AND ^{13}C , BUT FANCY MACHINES LIKE THE MASS SPECTROMETER IN THIS ROOM CAN, AND SO CAN PLANTS. PLANTS DISCRIMINATE AGAINST ^{13}C WHEN THEY TAKE UP CO_2 FROM THE AIR DURING PHOTOSYNTHESIS.



M. Fogel and B. Fry, Woods Hole Stable Isotope Workshop, 1986

THESE PLANTS ARE LABELED BY THEIR ^{13}C CONTENTS. PEOPLE WHO EAT CORN HAVE MORE ^{13}C THAN PEOPLE WHO EAT WHEAT. WHY? BECAUSE AS FAR AS PEOPLE AND STABLE ISOTOPES GO, YOU ARE WHAT YOU EAT.



M. Fogel and B. Fry, Woods Hole Stable Isotope Workshop, 1986

Stable isotope ratios of plant carbon usually have a huge fractionation from the source (atmospheric CO_2), but animals that feed on the plants don't fractionate very much ($\sim 1 \text{ ‰}$)

So, if an animal has a choice of plants it can feed on, and the plants have very different $\delta^{13}\text{C}$ values, you can often determine the source of C that the animal **assimilated**.

Example:

Terrestrial plants: $\delta^{13}\text{C} \approx -28 \text{ ‰}$

Marine plankton: $\delta^{13}\text{C} \approx -20 \text{ ‰}$

If a fish has a $\delta^{13}\text{C}$ of -22 ‰ , how much of its source diet was terrestrial (decomposed leaf litter) vs marine plankton?

$\% \text{ C from marine plankton} =$

$$\frac{\delta^{13}\text{C}_{\text{fish}} - \delta^{13}\text{C}_{\text{terr. plant}}}{\delta^{13}\text{C}_{\text{mar. pl.}} - \delta^{13}\text{C}_{\text{terr. plant}}}$$

$\% \text{ C from marine plankton} =$

$$\frac{(-22) - (-28)}{(-20) - (-28)} = \frac{6}{8} = 75\%$$

Note how similar this is to our example of hydrochemical separation with chlorine. Here, we assume that the "Q's" are proportional to the $\delta^{13}\text{C}$'s.

N isotopes fractionate more than C as proteins are digested. Can be used to help determine what trophic level an organism feeds on

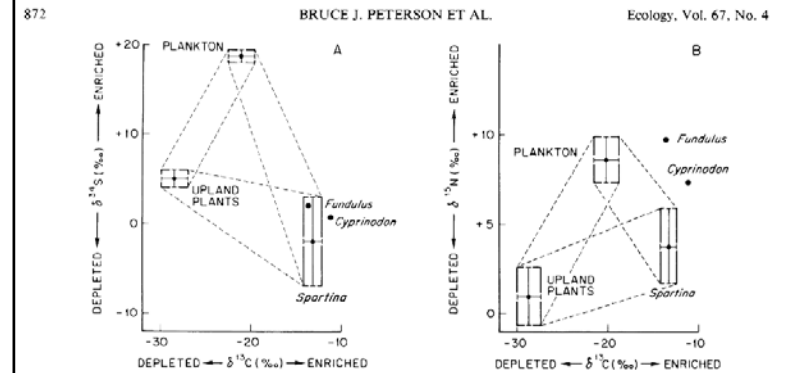
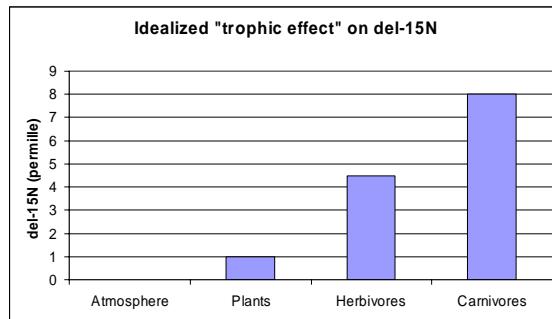


FIG. 7. A comparison of the isotopic compositions of *Fundulus heteroclitus* and *Cyprinodon variegatus*. The values for the producers are from Peterson et al. (1985).

Ecologists often construct “stable isotope maps” that show how organisms assimilate organic matter

Can sometimes get C, N, S, etc from different sources

Wrap-up.

Tracers can be chemically inert or chemically reactive – therefore, we need to know how they work in order to understand them as tracers

End-member analysis can be a powerful “detective tool” to separate out sources, be they hydrologic, biological, geologic, etc.

New applications are being thought up all the time!