

Hydrogeochemical Tracers in Groundwater

Marcie Schabert, Tom Kotzer

SRK Consulting

SMA Environmental Forum

October, 2018

What is a Tracer?

- Used for
 - **Pathways:** track water movement through a system
 - **Identify:** distinguish between waters
 - **Fate:** determine hydraulic and Bio/Geochemical processes
- Tracers may be
 - **Natural:** pre-existing in system
 - **Artificial:** added to the system in order to investigate it
 - **Anthropogenic:** a by-product of a process, or accidental addition

Why Use Tracers?

- **Physical Aspects**

- Direction of flow
- Flow velocity/Residence time
- Extent of mixing of different water
- Properties of flow matrix
 - Hydraulic conductivity
 - Hydrodynamic dispersion
 - Porosity

- **Bio/Geochemical Aspects**

- Reactions (bio/geochemical)
- Sorption and cation exchange processes
- Mineral precipitation/dissolution

Why Use Tracers?

- **Physical Aspects**

- Direction of flow
- Flow velocity/Residence time
- Extent of mixing
- Properties of flow matrix
 - Hydraulic conductivity
 - Hydrodynamic dispersion
 - Porosity

Site water
management

Understand dilution

Inputs to flow
models, water
management

- **Bio/Geochemical Aspects**

- Reactions and in situ reaction rates
- Sorption and cation exchange processes
- Mineral precipitation/dissolution

Potential for in situ
bioremediation (&
quantification)

Attenuation of
chemicals

Additions and losses
of chemicals

Ideal Tracer

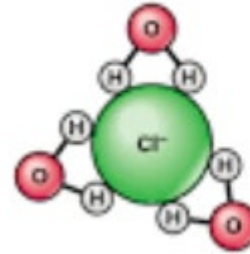
- **Non-toxic**
 - Environmental
 - Health & Safety
- **Transport Behavior**
 - Moves with water
 - Is chemically stable
 - Is not sorbed, exchanged, or filtered along flow path
- **Cost Considerations**
 - Tracer itself
 - Tracer application, sampling, and analysis
- **Analytical Considerations**
 - Does not quickly transform
 - Can be reliably detected at low concentrations
 - Is not already present at high concentrations

What kind of tracers are there?

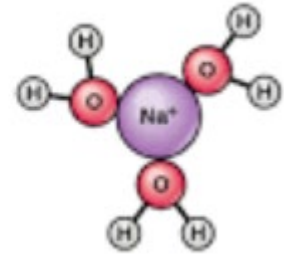
Salt Tracers

- Dissolve in water and separate into anion and cation components
 - Anions better tracers
 - Cations effected by sorption (transport is retarded)
- Low costs, reliable, and widely available analysis
 - Anions = IC, field ISE probe
 - Cations = ICP-MS

Negative Charge



Positive Charge



more soluble →
 $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$
 $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$
← *more sorption*

Salt Tracers

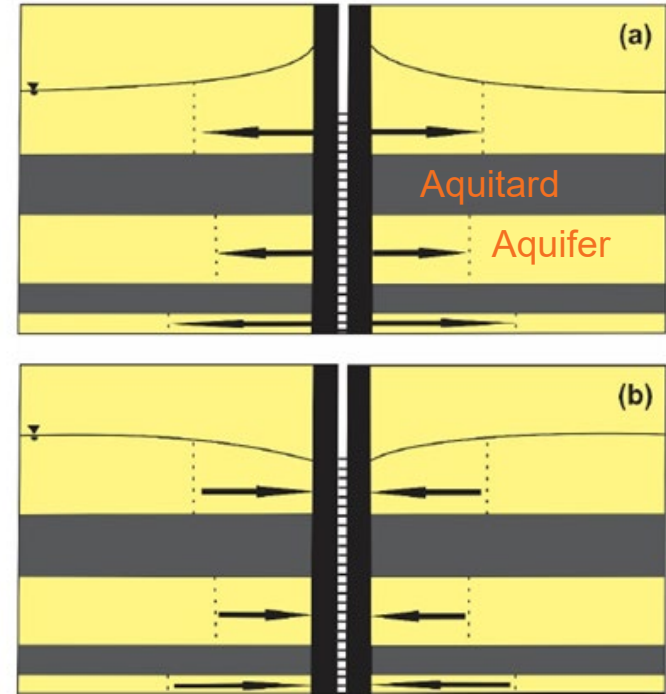
- Chloride (NaCl)
 - Inexpensive, readily available in bulk
 - Background Cl concentrations can be significant in some settings
 - Reduces resolution as tracer, or increases amount of tracer needed
 - Relatively high discharge limits for Cl
 - CCME long term guideline of 120 mg/L for Cl
- Bromide (KBr, NaBr)
 - Readily available in bulk
 - Background Br is generally low
 - Don't need much to alter water's Br signature
 - High resolution

Salt Tracers

- Lithium (LiOH, LiCl)
- Fluoride (NaF)
- Iodide (KI)
- Suffer from one or more of the following:
 - High Cost
 - Low Discharge Limits
 - Retardation (non conservative flow)
 - Potentially damaging to biota
- Benefits:
 - Generally very low background levels
 - Low detection limits
- Reactive (non-conservative tracers) can also be used:
 - NaNO_3
 - Na_2SO_4
- Used to determine in-situ reaction rates of nitrate, sulphate

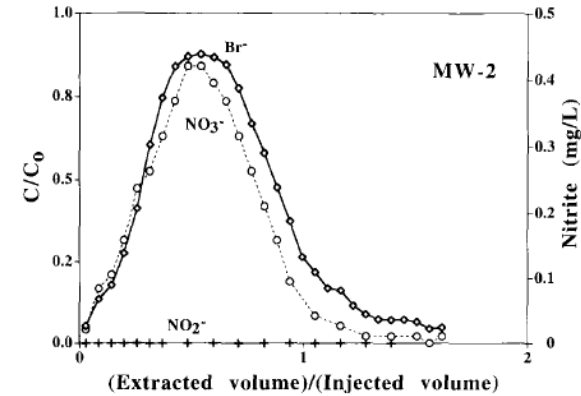
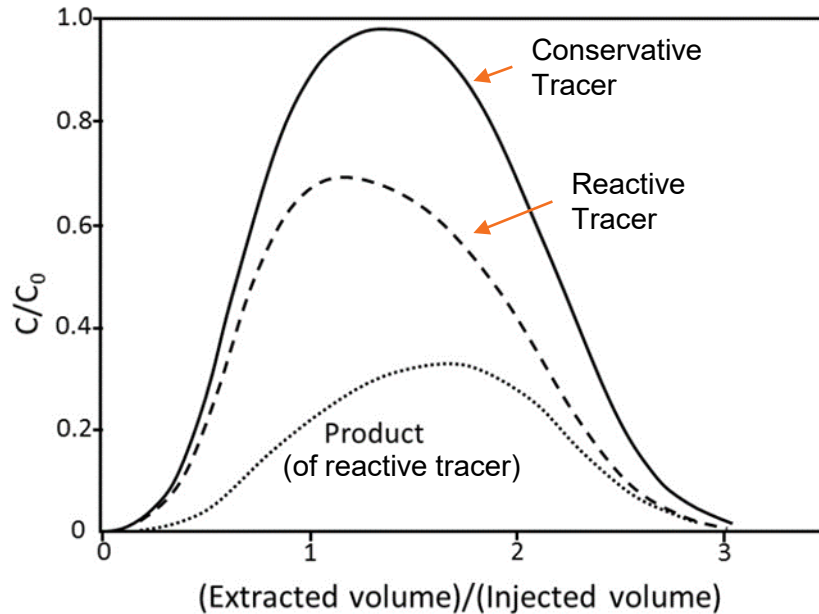
Example: Determine Bio/Geochemical Reaction Rates

- Push-pull tests
 - Water labelled with conservative (Br) and reactive tracers (NO_3) is injected into a well
 - After a certain 'reaction period' the water is extracted
 - Conservative tracer provides dilution factor
 - Reactive tracer (and product) provide in-situ reaction rates

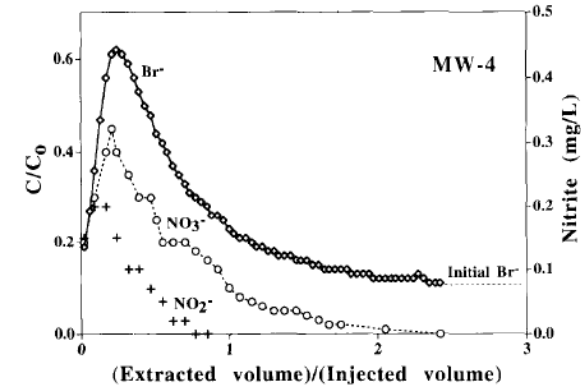


Example: Determine Biogeochemical Reaction Rates

- Istok et al., 1997 example



Aerobic
Conditions

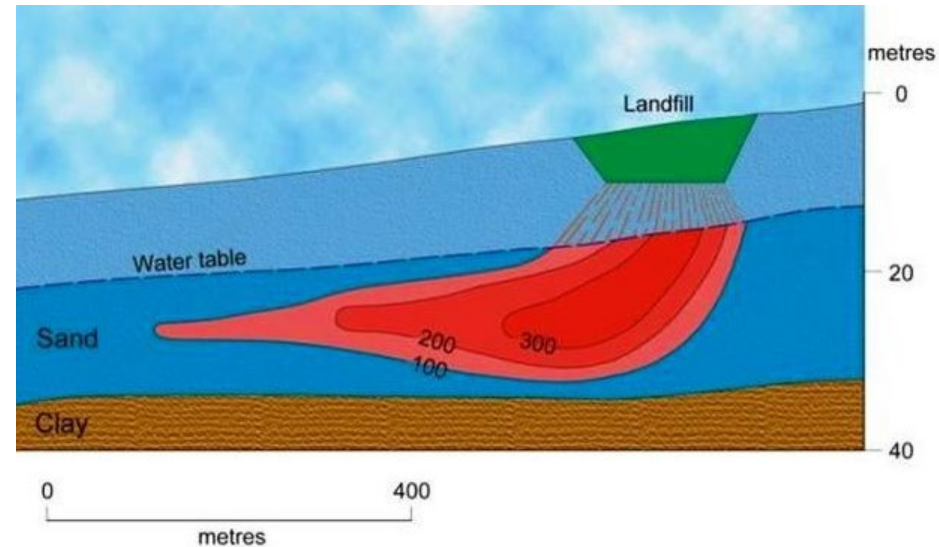


Anaerobic
Conditions

What kind of tracers are there?

In-Situ Physio-Chemical Tracers

- Use **existing differences** between waters to track movement and/or mixing
- Differences in:
 - Concentration of a particular solute
 - Conductivity
 - Temperature



What kind of tracers are there?

Dye Tracers

- Fluorescein
- Rhodamine
- Rhodamine WT



- **Visual tracer**
- **Portable detection** methods available (Fluorometer)
 - Very reliable
 - Low detection levels
- **Non-conservative:** All tracer dyes suffer retardation to some extent, depending on the setting
 - Can be an advantage if goal is to trace adsorbing organics
 - Rhodamine WT least effected by sorption

What kind of tracers are there?

Isotope Tracers

- **Isotope** = same number of protons, but different number of neutrons
- **Different masses** of isotopes mean they participate in reactions and physical processes differently

— Fractionation

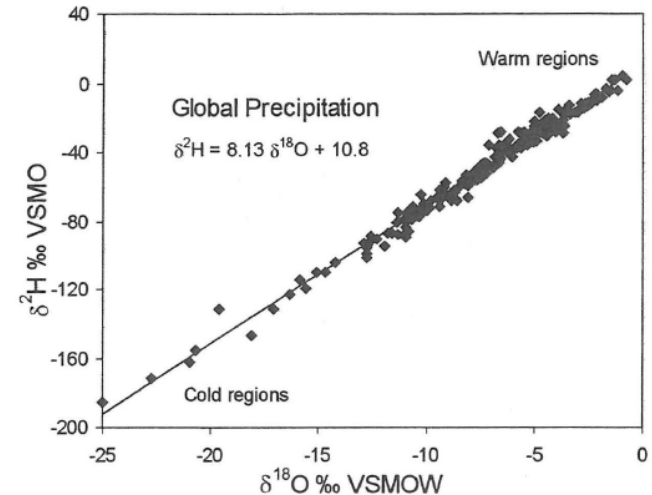
- Reported as 'permil' (‰), relative to a standard

| <i>Isotope</i> | <i>Ratio</i> | <i>% natural abundance</i> | <i>Reference (abundance ratio)</i> | <i>Commonly measured phases</i> |
|------------------|------------------------------------|---|---|--|
| ² H | ² H/ ¹ H | 0.015 | VSMOW (1.5575 · 10 ⁻⁴) | H ₂ O, CH ₂ O, CH ₄ , H ₂ , OH ⁻ minerals |
| ³ He | ³ He/ ⁴ He | 0.000138 | Atmospheric He (1.3 · 10 ⁻⁶) | He in water or gas, crustal fluids, basalt |
| ⁶ Li | ⁶ Li/ ⁷ Li | 7.5 | L-SVEC (8.32 · 10 ⁻²) | Saline waters, rocks |
| ¹¹ B | ¹¹ B/ ¹⁰ B | 80.1 | NBS 951 (4.04362) | Saline waters, clays, borate, rocks |
| ¹³ C | ¹³ C/ ¹² C | 1.11 | VPDB (1.1237 · 10 ⁻²) | CO ₂ , carbonate, DIC, CH ₄ , organics |
| ¹⁵ N | ¹⁵ N/ ¹⁴ N | 0.366 | AIR N ₂ (3.677 · 10 ⁻³) | N ₂ , NH ₄ ⁺ , NO ₃ ⁻ , N-organics |
| ¹⁸ O | ¹⁸ O/ ¹⁶ O | 0.204 | VSMOW (2.0052 · 10 ⁻³) VPDB (2.0672 · 10 ⁻³) | H ₂ O, CH ₂ O, CO ₂ , sulphates, NO ₃ ⁻ , carbonates, silicates, OH ⁻ minerals |
| ³⁴ S | ³⁴ S/ ³² S | 4.21 | CDT (4.5005 · 10 ⁻²) | Sulphates, sulphides, H ₂ S, S-organics |
| ³⁷ Cl | ³⁷ Cl/ ³⁵ Cl | 24.23 | SMOC (0.324) | Saline waters, rocks, evaporites, solvents |
| ⁸¹ Br | ⁸¹ Br/ ⁷⁹ Br | 49.31 | SMOB | Developmental for saline waters |
| ⁸⁷ Sr | ⁸⁷ Sr/ ⁸⁶ Sr | ⁸⁷ Sr = 7.0 ⁸⁶ Sr = 9.86 | Absolute ratio measured | Water, carbonates, sulphates, feldspar |

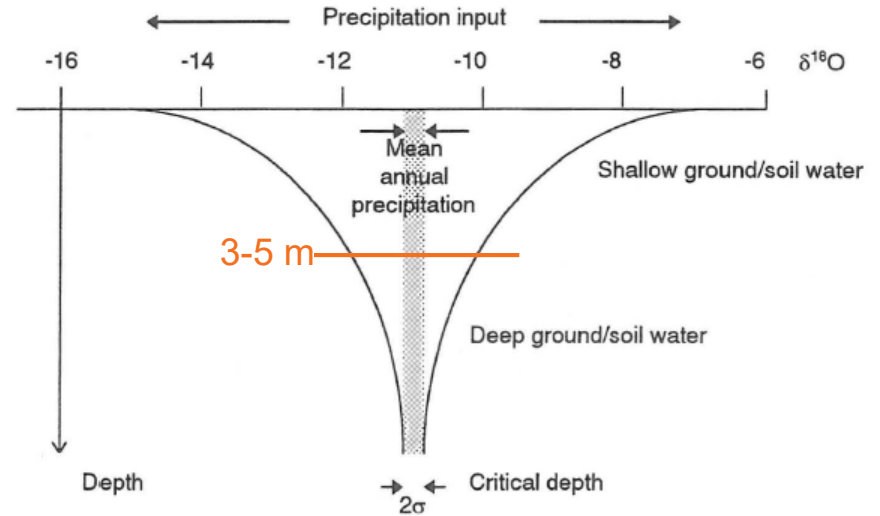
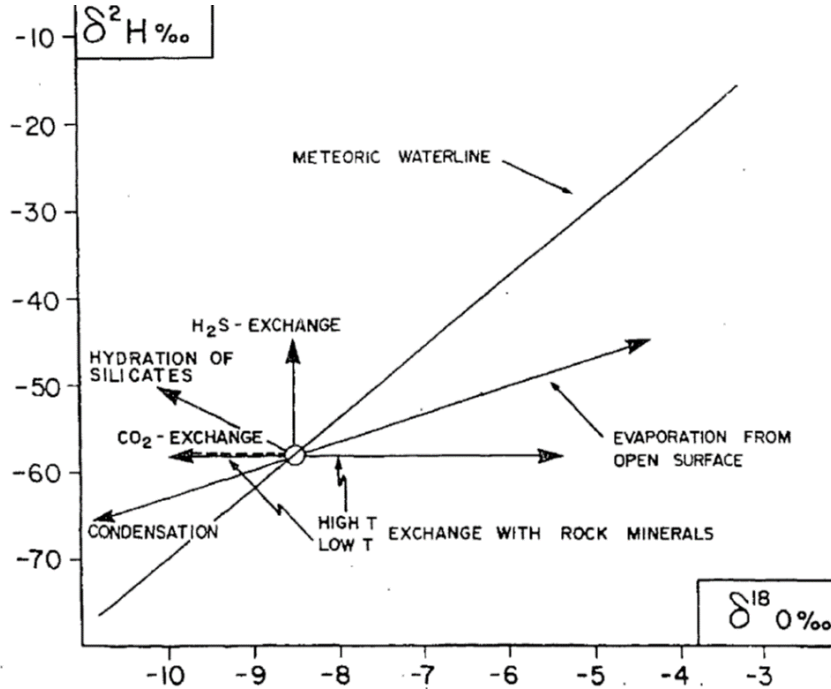
$$\delta^{18}\text{O}_{\text{sample}} = \left(\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{reference}}} - 1 \right) \cdot 1000 \text{‰ VSMOW}$$

Isotope Tracers

- δD and $\delta^{18}O$ of water
 - **Conservative:** Is part of the water molecule
 - **Inexpensive & Easy:** widely available analysis, few storage and collection considerations
 - IAEA monitoring network (worldwide precipitation monitoring dataset) →
 - Used to understand
 - contributions to system from precipitation
 - timing of recharge
 - Transformation processes (evaporation, condensation, sublimation)
 - **Deuterium oxide (D_2O)** – artificial tracer to modify isotopic composition of water



Isotope Tracers



Isotope Tracers

- Tritium (^3H)
 - **Conservative:** Is part of the water molecule
 - **Radioactive:** half-life (12.34 yrs) useful for aging groundwaters
 - **Anthropogenic input:** thermonuclear testing bomb pulse (1950s – 1980s)
 - IAEA monitoring network (worldwide precipitation monitoring dataset)

For continental regions:

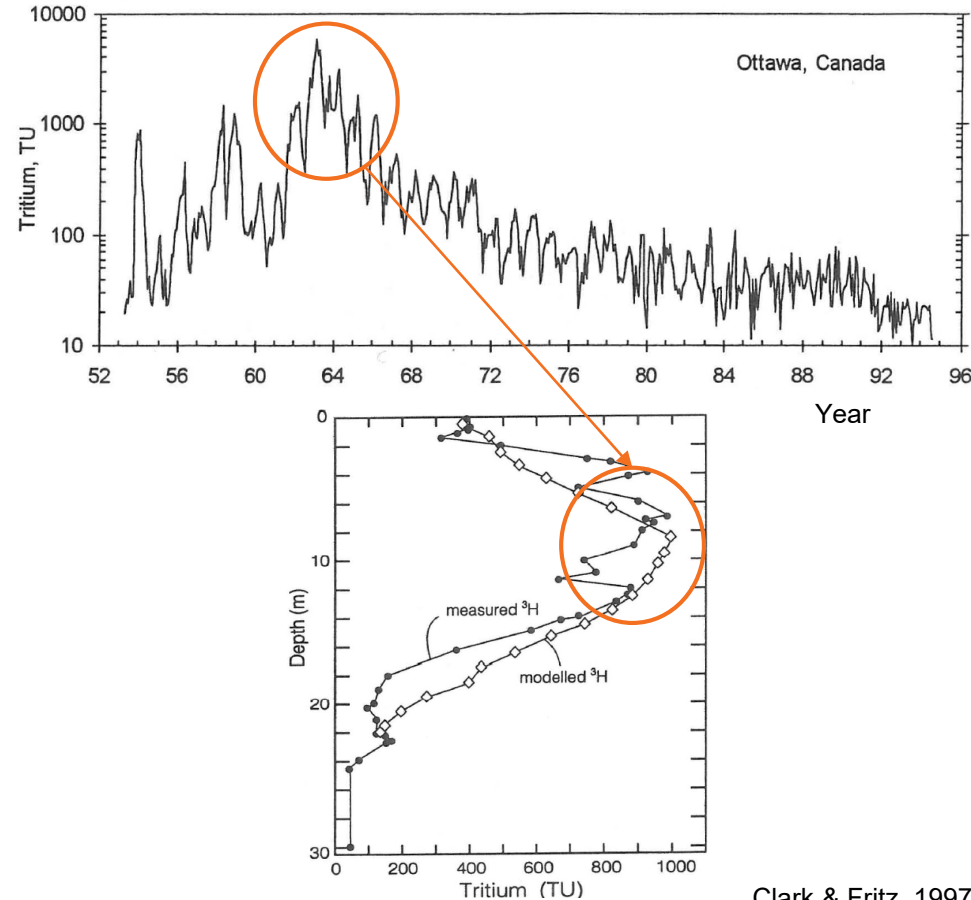
| | |
|--------------|--|
| <0.8 TU | Submodern — recharged prior to 1952 |
| 0.8 to ~4 TU | Mixture between submodern and recent recharge |
| 5 to 15 TU | Modern (<5 to 10 yr) |
| 15 to 30 TU | Some "bomb" ^3H present |
| >30 TU | Considerable component of recharge from 1960s or 1970s |
| >50 TU | Dominantly the 1960s recharge |

For coastal and low latitude regions:

| | |
|--------------|--|
| <0.8 TU | Submodern — recharged prior to 1952 |
| 0.8 to ~2 TU | Mixture between submodern and recent recharge |
| 2 to 8 | Modern (<5 to 10 yr) |
| 10 to 20 | Residual "bomb" ^3H present |
| >20 TU | Considerable component of recharge from 1960s or 1970s |

Age Dating of Waters: Modern Groundwater

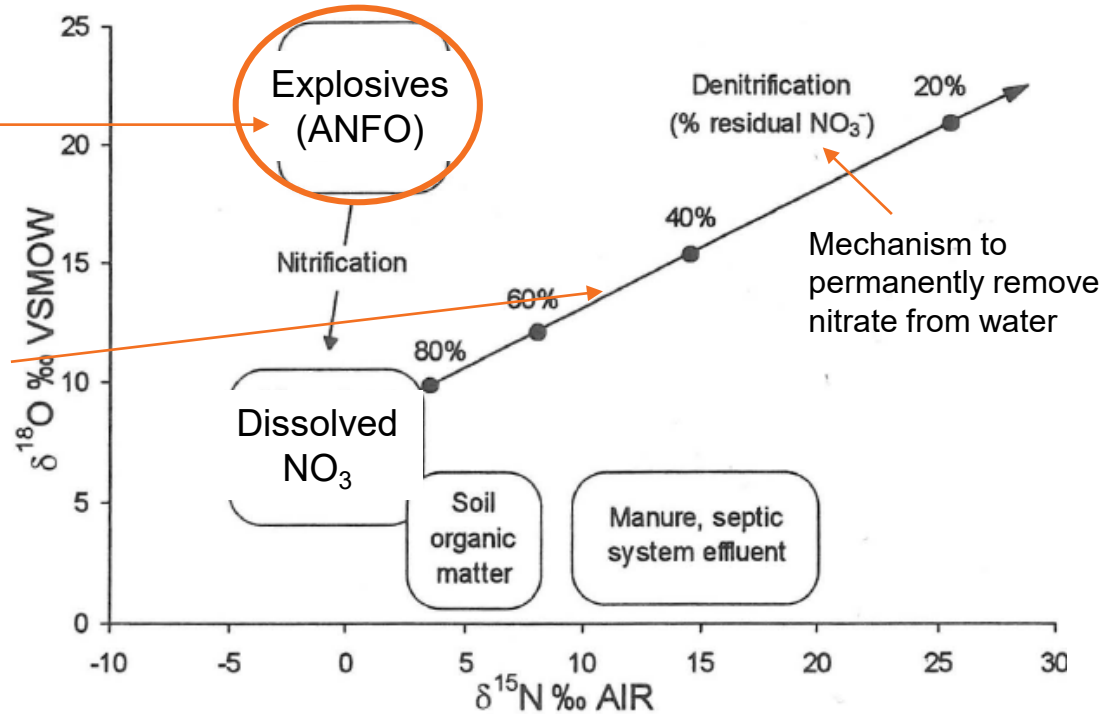
- Tritium (^3H)
 - Pre-bomb water (recharged before 1950) is tritium free
 - 1951 to 1976 large inputs from Thermonuclear bomb testing
 - Modern precipitation ~ 10 TU
 - If bomb peak can be identified, can calculate vertical water velocity
 - Decay product (He^3) can also be used to aid in dating of young waters



Isotope Tracers

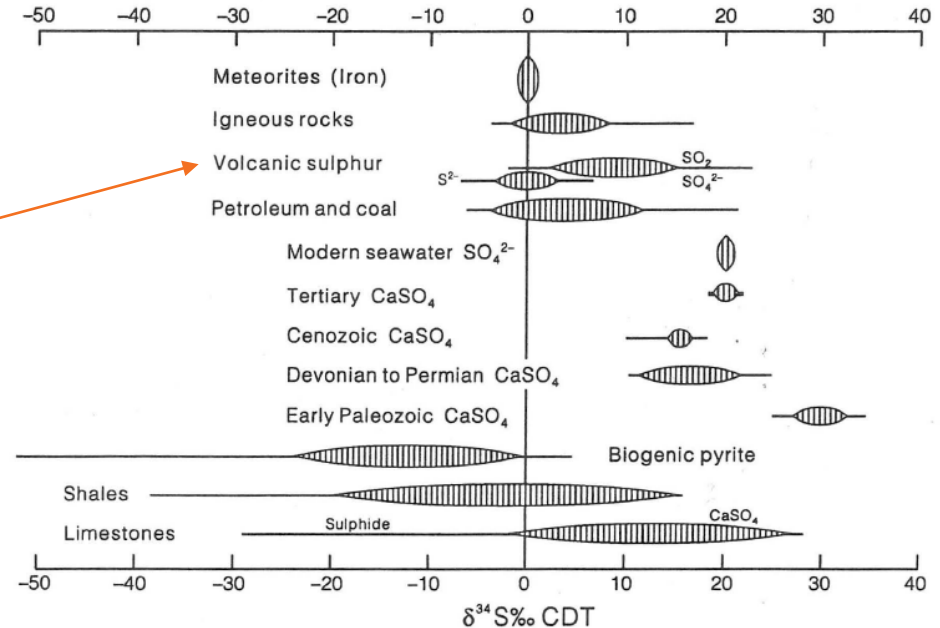
- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of Nitrate
 - Anthropogenic (explosives)
 - Distinct isotopic signature
 - Mining: generally no other significant sources of nitrate
 - Amount of enrichment related to of denitrification
 - Determine initial nitrate concentrations

$$\delta^{15}\text{N} = \delta^{15}\text{N}_{\text{initial}} + {}^{15}\varepsilon(\ln([\text{NO}_3^-]))$$



Isotope Tracers

- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of Sulphate
 - $\delta^{34}\text{S}$ alone can be used to distinguish between different sulphur sources (e.g. volcanic sulphur)
 - Through time
 - Sources
 - $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ together can be diagnostic of sources and age of dissolved sulphate



Take Home Message: Know your Goal

- Think about the question you are trying to answer, then look for an appropriate tracer
- Different options for tracers
- Different reasons for using tracers
 - Need to pick tracer appropriate for settings and purpose
- Just because you can measure it, doesn't necessarily mean you should

References

- Carpenter, P. J., Ding, A. & Cheng, L. (2012) Identifying Groundwater Contamination Using Resistivity Surveys at a Landfill near Maoming, China. *Nature Education Knowledge* 3(7):20
- Clark, I., 2015. *Groundwater geochemistry and isotopes*. CRC press.
- Clark, I.D. and Fritz, P., 1997. *Environmental isotopes in hydrology*. CRC press.
- Granger, J., Sigman, D.M., Lehmann, M.F. and Tortell, P.D., 2008. Nitrogen and oxygen isotope fractionation during dissimilatory nitrate reduction by denitrifying bacteria. *Limnology and Oceanography*, 53(6), pp.2533-2545.
- Istok, J.D., Humphrey, M.D., Schroth, M.H., Hyman, M.R. and O'Reilly, K.T., 1997. Single-well, "push-pull" test for in situ determination of microbial activities. *Groundwater*, 35(4), pp.619-631.
- Solvent Properties of Water
<https://www.khanacademy.org/science/biology/water-acids-and-bases/hydrogen-bonding-in-water/a/water-as-a-solvent>
Date Accessed: 10/15/2018
- USGS, Use of Dyre Tracing to Determine Groundwater Movement to Mammoth Crystal Springs, Sylvan Pass Area, Yellowstone National Park, Wyoming. Scientific Investigations Report 2006-5126. Lawrence E. Spangler and David D. Susong