Hydrogeochemical Tracers in Groundwater

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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**

  Site water management

  - Direction of flow
  - Flow velocity/Residence time
  - Extent of mixing

    Understand dilution

  - Properties of flow matrix
    - Hydraulic conductivity
    - Hydrodynamic dispersion
    - Porosity

    Inputs to flow models, water management

- **Bio/Geochemical Aspects**
  - Reactions and in situ reaction rates

    Potential for in situ bioremediation (& quantification)

  - Sorption and cation exchange processes

    Attenuation of chemicals

  - Mineral precipitation/dissolution

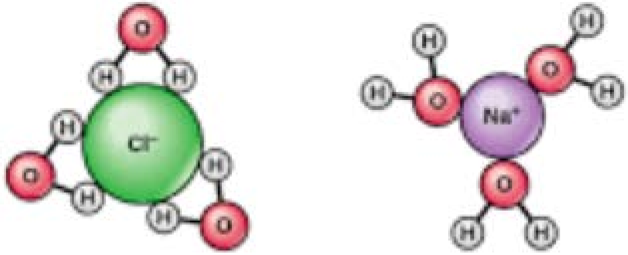
    Additions and loses of chemicals

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*

Clark, 2015

https://www.khanacademy.org/science/biology/water-acids-and-bases/hydrogen-bonding-in-water/a/water-as-a-solvent

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

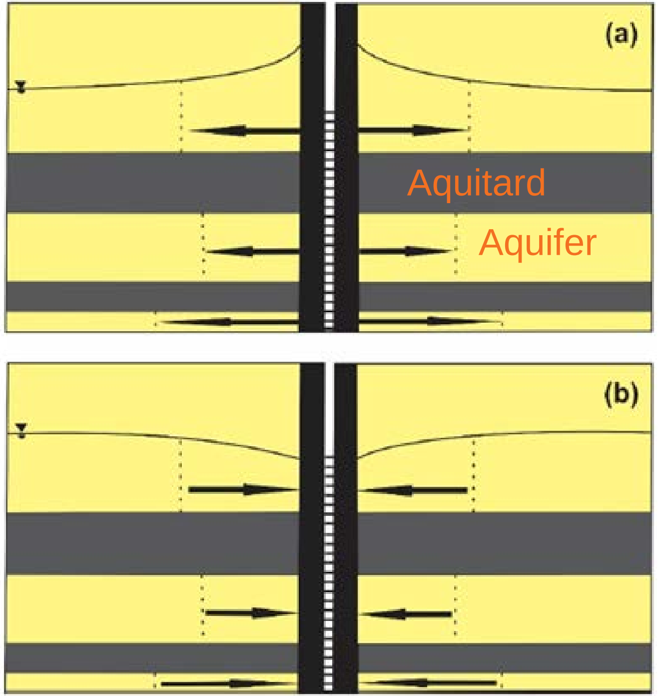
Salt Tracers

- 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

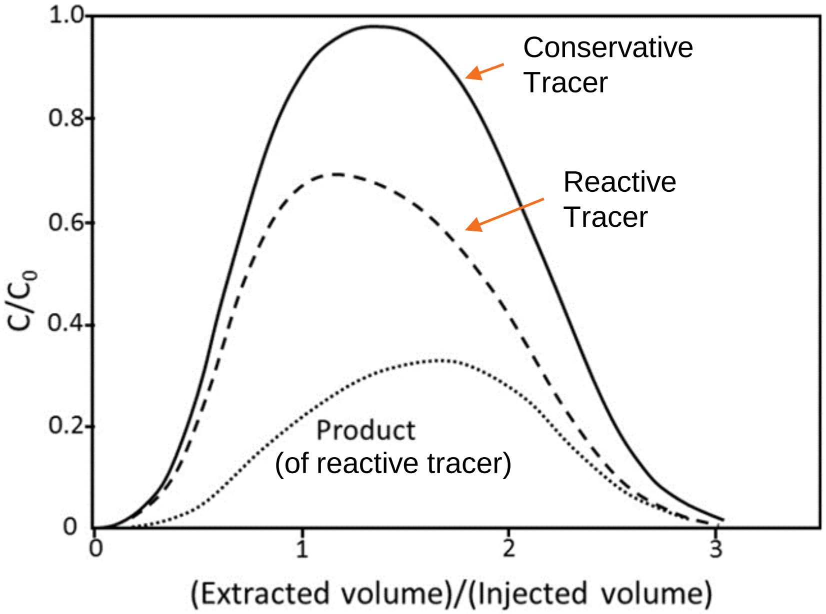
- Push-pull tests
  - Water labelled with conservative (Br) and reactive tracers (NO_3) is injected into a well
  - After a certain ‘reaction period’ the water is extracted
  - Conservative tracer provides dilution factor
  - Reactive tracer (and product) provide in-situ reaction rates

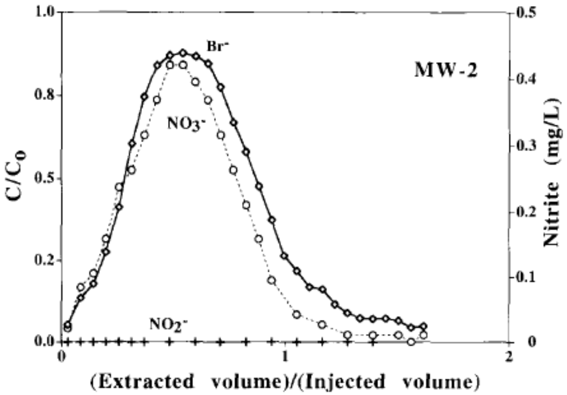


Istok, 1997

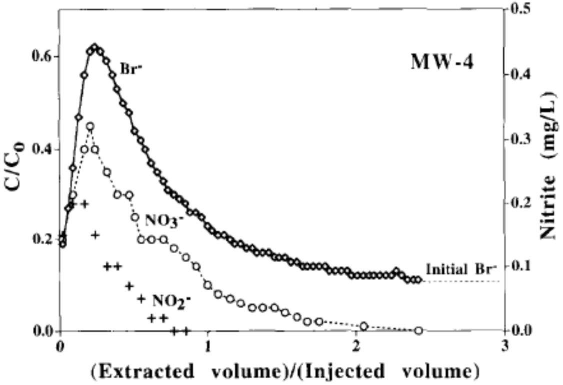
Example: Determine Biogeochemical Reaction Rates

- Istok et al., 1997 example





Aerobic Conditions

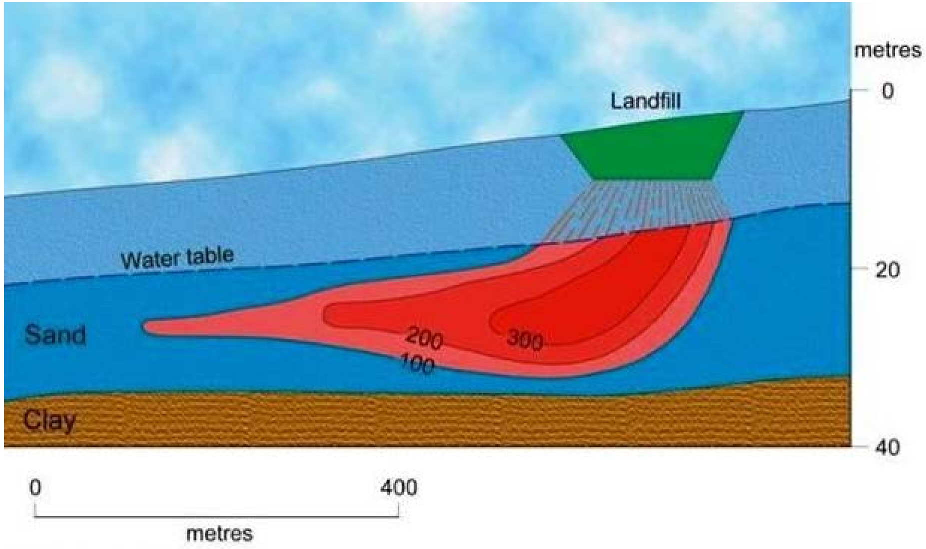


Anaerobic Conditions

Istok, 1997

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



Carpenter, 2012

What kind of tracers are there?
Dye Tracers

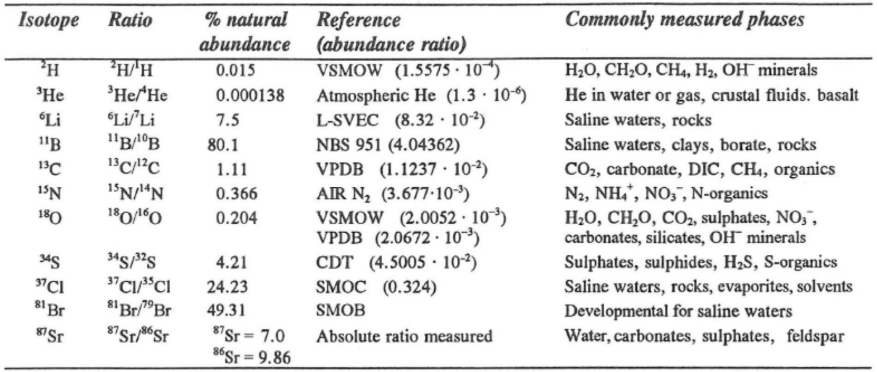
- Fluorescein
- Rhodamine
- Rhodamine WT

USGS, 2006

- **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



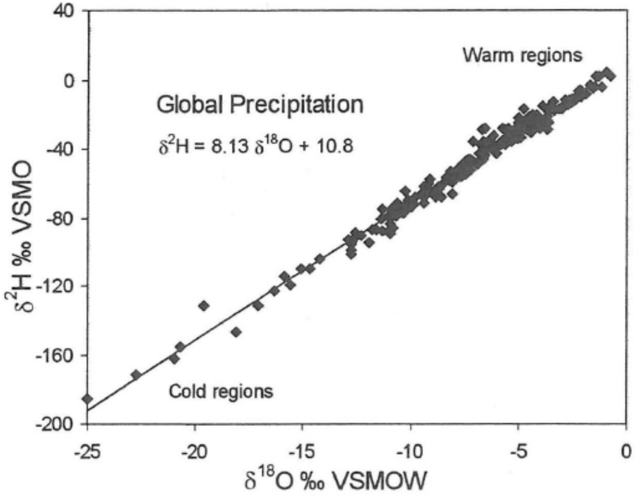
Isotope	*Ratio*	*% natural abundance*	*Reference (abundance ratio)*	*Commonly measured phases*
^{2}H	$^{2}H/^{1}H$	0.015	VSMOW $(1.5575 \cdot 10^{-4})$	H_2O, CH_2O, CH_4, H_2, OH^- minerals
^{3}He	$^{3}He/^{4}He$	0.000138	Atmospheric He $(1.3 \cdot 10^{-6})$	He in water or gas, crustal fluids. basalt
^{6}Li	$^{6}Li/^{7}Li$	7.5	L-SVEC $(8.32 \cdot 10^{-2})$	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 $(1.1237 \cdot 10^{-2})$	CO_2, carbonate, DIC, CH_4, organics
^{15}N	$^{15}N/^{14}N$	0.366	AIR N_2 $(3.677 \cdot 10^{-3})$	N_2, NH_4^+, NO_3^-, N-organics
^{18}O	$^{18}O/^{16}O$	0.204	VSMOW $(2.0052 \cdot 10^{-3})$ VPDB $(2.0672 \cdot 10^{-3})$	H_2O, CH_2O, CO_2, sulphates, NO_3^-, carbonates, silicates, OH^- minerals
^{34}S	$^{34}S/^{32}S$	4.21	CDT $(4.5005 \cdot 10^{-2})$	Sulphates, sulphides, H_2S, 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

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

Clark & Fritz, 1997

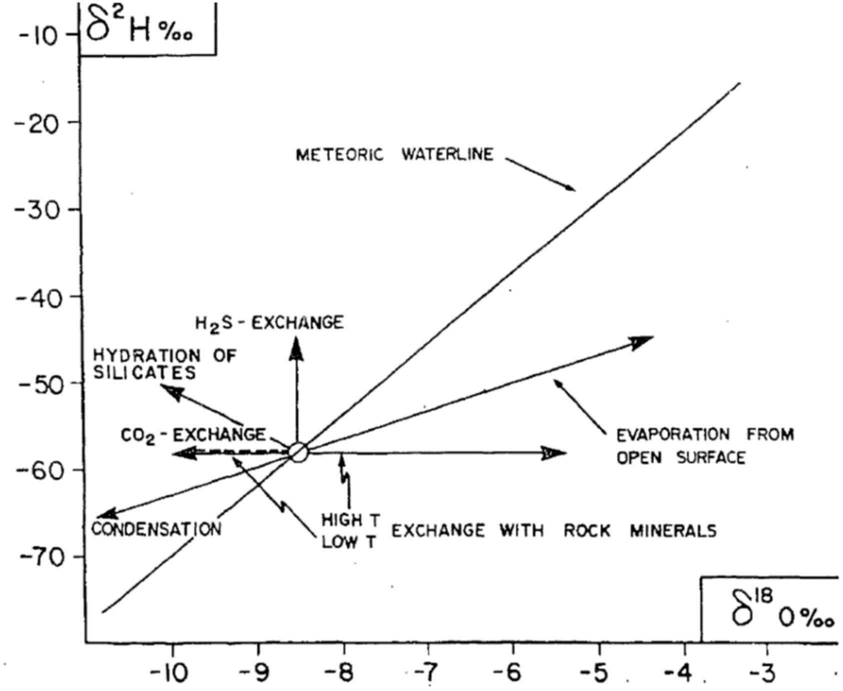
Isotope Tracers

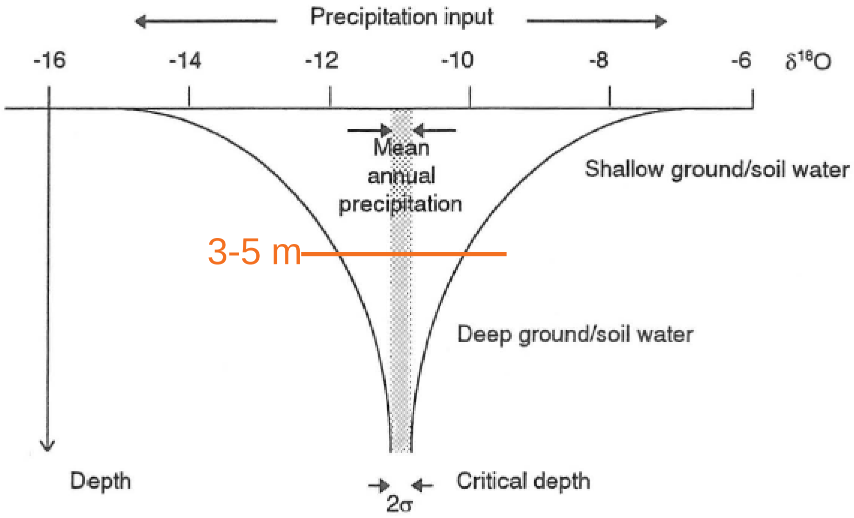
- δD and $\delta^{18}O$ of water
  - **Conservative**: Is part of the water molecule
  - **Inexpensive & Easy**: widely available analysis, few storage and collection considerations
  - IAEA monitoring network (worldwide precipitation monitoring dataset)
  - Used to understand
    - contributions to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



Clark & Fritz, 1997

Isotope Tracers

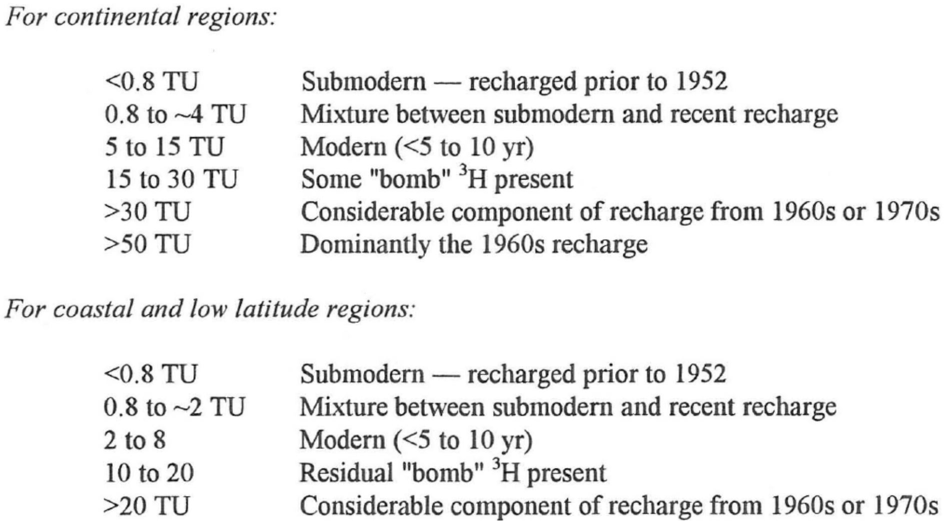




Clark & Fritz, 1997

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

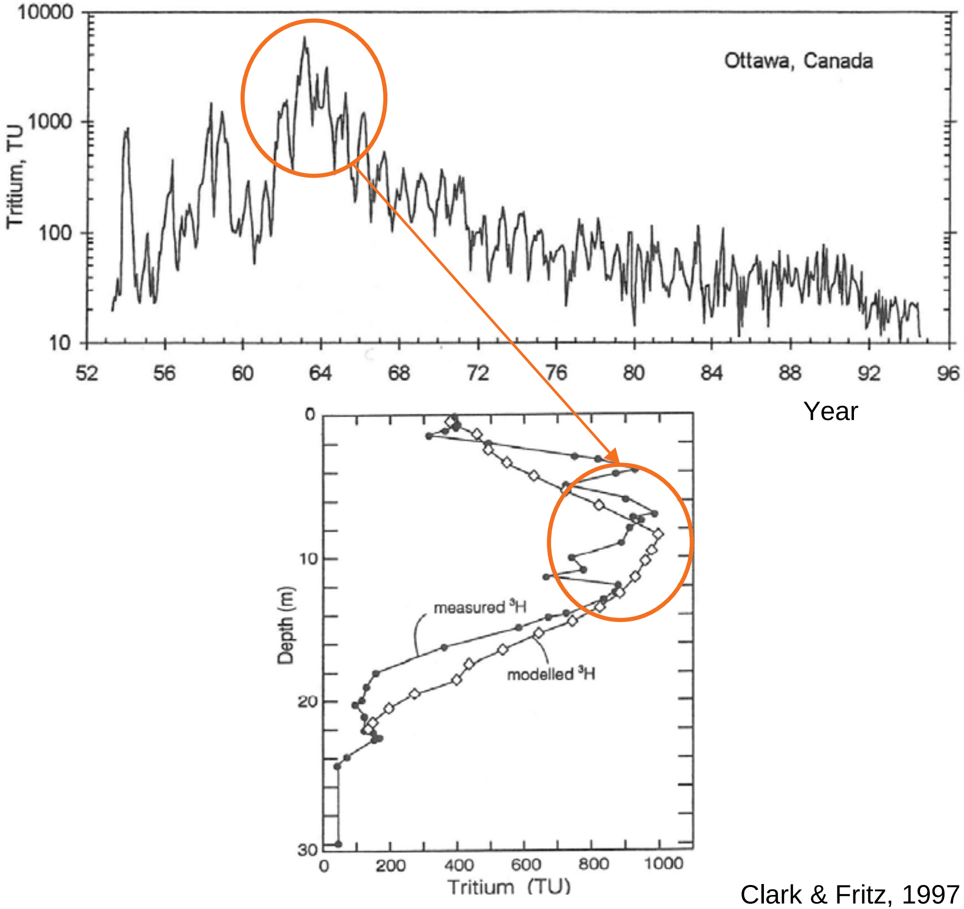
For coastal and low latitude regions:

<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

Clark & Fritz, 1997

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

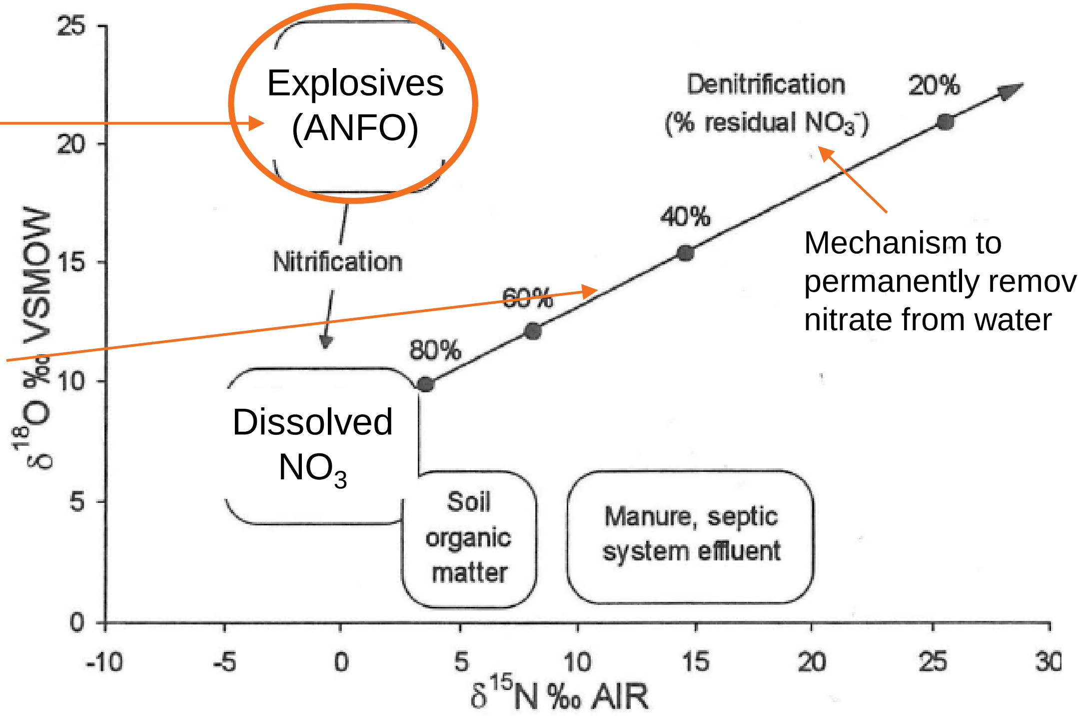


Clark & Fritz, 1997

Isotope Tracers

- $\delta^{15}N$ and $\delta^{18}O$ 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

$$\delta^{15}\mathrm{N} = \delta^{15}\mathrm{N}_{\mathrm{initial}} + {}^{15}\varepsilon\left(\ln\left(\left[\mathrm{NO_3^-}\right]\right)\right)$$



Explosives (ANFO)

Dissolved NO_3

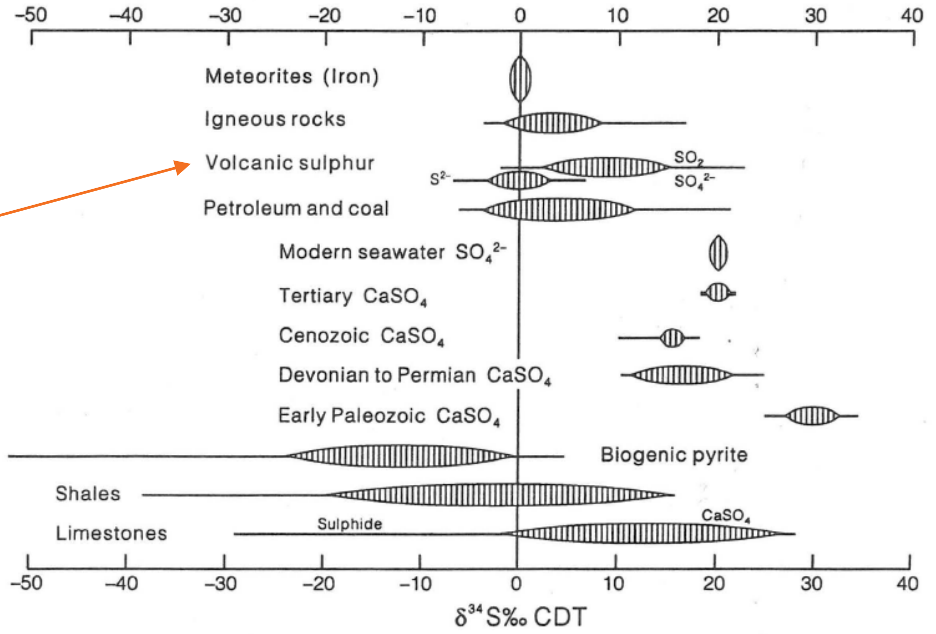
Mechanism to permanently remove nitrate from water

Granger et al., 2008

Clark & Fritz, 1997

Isotope Tracers

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



Clark & Fritz, 1997

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

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