Environmental Tracers in Hydrogeology: Powerful yet Underutilized Tools
Overview and Case Study

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Outline

• Environmental Tracers in Hydrogeology
• Dating Young Groundwater
  - Tritium ($^3$H)
  - $^3$H/$^3$He
  - CFCs, SF$_6$
• Dating Old Groundwater
  - Radiocarbon ($^{14}$C)
  - Helium-4 ($^4$He)
• Case Study
  - Geothermal Exploration in Yukon
Environmental Tracers

What are environmental tracers?
- Chemically inert trace substances (e.g., transient or radioactive) which are present in the water cycle and allow physical processes to be studied in aquatic systems

Environmental Tracers in Hydrogeology
- Stable Isotopes: Oxygen-18 ($^{18}$O), Deuterium($^2$H)
- Radioisotopes: $^3$H, $^{14}$C, $^{85}$Kr, $^{81}$Kr, $^{37}$Ar, $^{39}$Ar, $^{222}$Rn
- Noble Gases: He, Ne, Ar, Kr, Xe
- Transient Atmospheric Trace Gases: CFCs (CFC-11, CFC-12, CFC-113), SF$_6$
- Others...
Dating Young Groundwater

• Young Groundwater: mean residence time less than about 50 to 60 years
• Potential application of dating methods:
  - Aquifer vulnerability studies
  - Wellhead and aquifer protection plans
  - Contaminated site assessments
  - Geothermal assessments (geothermometry)
  - Quantification of groundwater mixing
  - Calibration/verification of numerical models
  - Determination of recharge rate
  - Many others...
• Several available methods; relatively inexpensive
Tritium ($^3$H)

Atmospheric Input Function

Half-life: $\tau_{1/2} = 4,500$ days

1 TU (Tritium unit): $^3$H/$^1$H = $10^{-18}$

(= 0.118 Bq/L = 3.19 pCi/L)

Natural background: ~5 TU

Concentration in modern precipitation: ~10 TU
Dating Groundwater Using Tritium

• Sample contains tritium ’ residence time <60 years
• Sample does not contain any tritium (detection limit!) ’ residence time >60 years
• “Classic” dating method: comparison of measured tritium concentration with decay-corrected local atmospheric input function (often non-unique)
Tritium/Helium-3 Method

\[ ^{3}\text{H} \rightarrow ^{3}\text{He} \]

\[ \tau_{1/2} = 12.3 \text{ yr} \]

\[ \tau = \frac{1}{\lambda} \cdot \ln \left( 1 + \frac{[^{3}\text{He}_{\text{tri}}]}{[^{3}\text{H}]} \right) \]

Residence Time ("Age")
Chlorofluorocarbons (CFCs) and Sulfur Hexafluoride (SF$_6$)

- Transient, atmospheric trace gases
- Man-made (small amount of natural SF$_6$)
- Inert gases
- CFCs are “ozone killers”
- SF$_6$ is the most potent greenhouse gas and has a very long atmospheric lifetime
Groundwater dating by CFCs, SF$_6$

Sampling

Analysis

“Age“ calculation
Dating Old Groundwater

• Radiocarbon ($^{14}$C)
  - Dating range: ~1,000 to 45,000 years
  - AMS technology has reduced required sample size to about 1 L (depending on HCO$_3^-$ concentration)

• Helium-4 ($^4$He)
  - Produced by the decay of U and Th
  - Accumulates in groundwater as a function of residence time on timescales of hundreds to thousands of years, and U/Th concentration in aquifer matrix
  - Usually use as a qualitative dating tool because $^4$He accumulation rate is unknown and difficult to determine
Helium Reservoirs

- Helium isotope ratio is characteristic for helium source
- High isotope ratios often indicate deep fluid circulation
- Use as geothermal exploration tool?

\[
{^{3}\text{He}}/{^{4}\text{He}} = 1.4 \times 10^{-6}
\]

\[
{^{3}\text{He}}/{^{4}\text{He}} = 10^{-5}
\]
Case Study
Geothermal Exploration, Yukon
Ground Reconnaissance

- Preliminary geological mapping
- Documentation of surface features
- Water sampling and flow estimates
- Temperature and other field parameter measurements
Thermal Water Analysis

- Field: pH, temperature, electrical conductivity
- Lab: alkalinity (total, HCO₃, CO₃, OH), hardness, F, Cl, NO₂, NO₃, SO₄, dissolved metals
- Environmental isotopes: ¹⁸O, ²H, ³H, ¹⁴C, He-Xe
Helium Isotopes: Thermal Springs in Yukon

- **Mantle-derived helium**
- **Air-saturated water**
- **Maximum shift by accumulation of tritiogenic $^3$He**
- **Mixing line between air-saturated water and crustal helium**
- **Accumulation of mantle helium and/or tritiogenic $^3$He**
- **Accumulation of crustal helium (increasing residence time)**
Geothermometer

• Estimate of subsurface temperature

• Assumptions:
  - Dissolved ions in equilibrium with reservoir rocks
  - Chemical equilibrium is mainly temperature-controlled
  - Fast conduit from reservoir to surface without time for chemical re-equilibration

• Most common geothermometer methods are based on Na-K-Ca ion ratios and Si concentration
Water Dating with $^3$H and $^{14}$C

- Tritium concentration was below detection limit (<0.8 TU)
  - Residence time >60 years
  - No significant admixture of young, shallow groundwater

- Radiocarbon concentration was very low (2.24 pmc)
  - Conventional radiocarbon age is ~30,000 years
  - Large residence time indicates long, deep flow path of thermal water
  - No significant admixture of young, shallow groundwater

- Thermal water has not been significantly diluted with shallow, cold groundwater
- Geothermometer temperatures are probably representative of subsurface reservoir temperatures
Summary and Conclusions

- Groundwater dating can provide significant information regarding the dynamics of groundwater systems (residence time, recharge rate, flow regime, etc.)
- This information can be useful for a large range of hydrogeological projects (aquifer vulnerability, contaminated sites, groundwater resource assessments, sustainability studies, geothermal assessments, etc.)
- Methods are widely underutilized in practical hydrogeology (high costs, unavailability of labs, long sample turnaround, lack of knowledge and experience)
- Opportunity for innovation...
THANKS FOR YOUR ATTENTION

Questions?