Applications of Dissolved $N_2$ and Ar in Groundwater

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U.S. Geological Survey
Reston, VA
- $O_2$ unstable
- $N_2$ can be affected by NO$_3$ reduction
- Terrigenic source of He
- Most reliable are Ar, Ne, Kr, Xe
- Ar and $N_2$ solubilities from air are 3-5 orders of magnitude greater than that of remaining noble gases. Can be measured by gas chromatography.
Applications of N₂ – Ar Measurements in Groundwater

• Reconstruct recharge temperatures—
  ✓ $K_H$ calculation in dating with atmospheric gases such as CFCs and SF₆
  ✓ Paleoclimatic reconstruction (check $^{14}$C age)
• Reconstruct excess air—
  ✓ Function of recharge rate and hydrogeology
  ✓ Needed in dating with CFCs and esp. SF₆.
• Trace water sources through aquifers
• Recharge mechanism— Focused/diffuse recharge; rapid recharge; (altitude of recharge)
• Reconstruct initial nitrate in agricultural studies
BACKGROUND: N$_2$-Ar

- **Heaton, Vogel, Talma (early 1980s)**
  Paleorecharge temperatures, excess air, denitrification.

- **Don Fisher, USGS (1970s)**
  Developed GC method, field sampling device.

- **Current state at USGS**
  Dual column GC method, new sample collection, QA/QC procedures, software. Extensive use in agricultural studies, dating with CFCs and SF$_6$.
Bruce B. Hanshaw (the late), at Philip flowing well, Philip, South Dakota, 68°C, Madison aquifer, circa 1979; Bruce had a good sense of humor.
Sample Collection

- 160 cc glass bottle with septum stopper
- Filled without headspace under water
- Needle used to release fluid as stopper inserted
- Needle removed.
- Bottle weight measured empty and full.
CTR III / TCD
• Measures Ar, N₂, and O₂+Ar; O₂ determined by difference
• Thermal Conductivity Detector

CTR I / FID
• Separates all the gases
• Used only for CH₄ and CO₂
• CO₂ converted to CH₄ for measurement with FID

Schematic of analytical system
• Headspace equilibrated >24 hrs
• Water temp. measured in bottle immediately after injection
• All measurements made on same initial vol. of gas
• Two columns (each a double column; two detectors.
• Calibrated with known gas standards.
• QA/QC daily with water samples equilibrated in water baths at 9, 16, and 24 °C in same sample container.
Temperature of Standard Water - N₂/Ar Calculated Temperature

March 2004-July 2004

Water Standards
Blue = 9 °C
Yellow = 16 °C
Red = 24 °C

Deviation from calculated N₂/Ar temperature from standard water

Date of Analysis

USGS
http://water.usgs.gov/lab/cfc

The Reston Chlorofluorocarbon Laboratory (Internal Access)

Welcome

See extensive bibliography
Why Measure N$_2$ – Ar, when suites of noble gases can be measured?

- Relatively **high concentrations**; Waters can be analyzed by relatively simple GC methods.
- **In some cases, most of the information** obtained from noble gases can also be obtained from N$_2$-Ar.
- **Reconstruct amounts of denitrification.** Initial NO$_3$; Agricultural studies; fertilizers fate.
- **Cost effective.** Large numbers of samples can be collected and analyzed; potential for mapping flow in aquifers.
Limitations of $N_2$ – Ar data

- Only 2 independent measurements, but as many as 4 unknowns (Recharge temperature; Excess air; Altitude of recharge; Excess $N_2$).

- Gas fractionation? Need additional gases to even detect. Most applications of $N_2$ – Ar assume complete dissolution of excess air. This is an approximation, but considering the relatively high concentrations of $N_2$ and Ar in groundwater, appears to be a reasonable assumption.
Recharge Temperature - Excess Air

\[ N_2(\text{meas}) = N_2(\text{equil}) + N_2(\text{Ex air}) + N_2(\text{denit}) \]

\[ \text{Ar}(\text{meas}) = \text{Ar}(\text{equil}) + \text{Ar}(\text{Ex air}) \]

Aerobic waters
\[ N_2(\text{denit}) = 0 \]

Altitude of recharge assumed

Samples from wells in fractured rock in Virginia
RT 9 – 14 °C
3-10 cc/L excess air
Springs and wells from Blue Ridge Mountains of Virginia; Shenandoah National Park

Lewis Mountain Spring

Sampling from a Typical Spring Box and Weir
Springs and wells, Blue Ridge, VA

Comparison of excess air calculated from mass spectrometric He and Ne with excess air from GC N\textsubscript{2} -Ar

No evidence of gas fractionation

Largest deviations probably gas leaks in sample container.
Springs and Wells—Blue Ridge Mts., VA

- Springs—residuum and colluvium; 0-2 cc/L excess air [sand aquifers]
- Wells—fractured rock; 0-8 cc/L excess air [river floods; arroyos; fractured rock]
- Wide range of RT for springs;
- Narrow range of RT for wells
- Mean annual Temp about 7.8 °C
Springs and wells
Blue Ridge, VA

- Most springs have recharge temperatures near the water temperature (shallow)
- Seasonal dependence of RT (shallow recharge)
- A few springs warmed in circulation (deeper)
- Discharge from most wells warmed in ground (deeper)
- 3 samples cooled following a summer thunderstorm
CFC ages and NO$_3$: 40-yr record of NO$_3$ recharge rate.
Records increase in fertilizer application from the 1970’s.
20-35 % of applied fertilizer reached the aquifer.
Mean residence time of 20 yrs for gw discharge to local streams.

Böhlke and Denver (1995)
What to do about denitrification?

- **Aerobic samples; No denitrification**
  - Assume altitude of recharge and solve \( N_2 \) and \( Ar \) for \( T \) and Excess air

- **Anaerobic samples**
  - If Ne data available, solve \( N_2 \), \( Ar \), Ne for \( T \), Excess air and Excess \( N_2 \) (at assumed recharge altitude)
  - If no Ne data, determine an average \( T \) or excess air from other aerobic samples in the data set.

- **Can Probably ignore denitrification in most paleowaters**
Denitrification

All samples aerobic (3-8 mg/L O₂) except Sample A (in duplicate)

Average Recharge Temperature 14.3 ± 2.0

Average Excess Air 3.0 ± 1.1 cc STP/L

Sample A: 16 mg/L of N₂ from denitrification brings recharge temperature to 13.2 °C and excess air to 4.3 ccSTP/L
Paleoclimatic Reconstruction
Fontes-Garnier Model $^{14}$C Ages
Middle Potomac Aquifer

Chesapeake Bay Impact Crater (Eocene, some 40 million yrs ago)
Nitrogen-Argon Recharge Temperatures (Coastal Plain)

- Anaerobic, but initial NO$_3$ low in paleowaters
- Aeschbach-Hertig et al found 9 °C cooling in NGTs in Aquia aquifer just north of here in the Maryland Coastal Plain
Altitude of recharge dependence

- Assume altitude of recharge—
  - ± 500 m $\rightarrow$ ± 2.3 °C; ± 100 m $\rightarrow$ analytical uncertainty (± 0.5 °C)
  - Estimate from hydrologic conceptualization
- Reconstrcut using local lapse rate and (for deep UZ) temp-depth profile—
  - Calc. RT as function of altitude finding intersection with atmospheric lapse (Zuber et al.)
  - Calc. depth below land surface and RT using local thermal profiles.
Tracing Sources of Recharge to Ground-water Systems

- Stable isotopes
- Water comp.
- $^{14}$C data
- Dissolved gases
- RT, Ex Air
- Alt/depth of RC
- Focused/diffuse recharge
Recharge Temperatures across top of aquifer

Altitude of recharge assumed:
- 5000 feet (SW sources, NW, Abo Arroyo, NE zones)
- 6500 feet (NMF, EMF, Tijeras)
- 8000 feet (West Central zone)

• Mean Annual temp at Alb. 13.6 °C

• Large areas of the basin have recharge temperatures well above this.

• Warm recharge in NMF and NW zones found above cold RC of West Central zone
Paleowaters

- 15 to >30ka $^{14}$C yrs
- Depleted stable isotopes
- Recharge altitude assumed: 8,000 feet
- Both cold and warm recharge occurred. Cold=focused recharge or high alt. recharge. Warm=diffuse recharge through deep UZ

± 1500 feet alt. = ± 2.3 °C
Deep UZ
To about 900 feet
Direct infiltration
From rivers, arroyos
Combining Altitude – Temperature and Depth – Temperature Profiles with $N_2$-Ar Measurements

Lapse rate cooling

-0.55 °C/100m

Albuquerque
Alt. 1500 m, MAT 13.6 °C

Land Surface at Albuquerque

Temperature profile

5.5 °C/100m
Eastern Mountain Front Zone
Middle Rio Grande Basin, NM

Water temperature plotted at depth of water table below the land surface (EMF waters)

A. Lapse rate cooling, \(-0.55 \, ^\circ\text{C}/100\text{m}\)
C. Local geothermal warming, \(5.5 \, ^\circ\text{C}/100\text{m}\)

Albuquerque
Alt. 1500 m, MAT 13.6 \(^\circ\text{C}\)

Land Surface at Albuquerque

Water temperature plotted at depth of water table below the land surface (EMF waters)
A. Lapse rate cooling, -0.55 °C/100m
C. Local geothermal warming, 5.5 °C/100m

Calculated apparent recharge temperature for waters at solubility equilibrium along the temperature-depth profile, but at an assumed recharge altitude (1500 m) (Line D).

Albuquerque
Alt. 1500 m, MAT 13.6 °C

Land Surface at Albuquerque

D. Apparent N₂-Ar RT along geothermal gradient
A. Lapse rate cooling, -0.55 °C/100m
B. Apparent N₂-Ar RT along lapse rate
C. Local geothermal warming, 5.5 °C/100m
D. Apparent N₂-Ar RT along geothermal gradient

Calculated apparent recharge temperature for waters at solubility equilibrium along the local atmospheric lapse rate, but at an assumed recharge altitude (1500 m) (Line B).
Calculate RT of ground-water samples at 1500 m. Extrapolate to apparent RT (line B), then to Lapse rate to estimate altitude of recharge and RT.
A. Lapse rate cooling, -0.55 °C/100m
B. Apparent N₂-Ar RT along lapse rate
C. Local geothermal warming, 5.5 °C/100m
D. Apparent N₂-Ar RT along geothermal gradient

Calculate RT of ground-water samples at 1500 m. Extrapolate to apparent RT (line D), then to temperature profile to estimate depth of recharge and RT.
A. Lapse rate cooling, -0.55 °C/100m
B. Apparent N2-Ar RT along lapse rate
C. Local geothermal warming, 5.5 °C/100m
D. Apparent N2-Ar RT along geothermal gradient

Eastern Mountain Front Zone
Middle Rio Grande Basin, NM

$\Delta^{14}C$ ages of 0-12ka

All calculations at reference Altitude of 1500 m; use lapse rate to find RT at other altitudes.

Land Surface at Albuquerque

Albuquerque
Alt. 1500 m, MAT 13.6 °C
A. Lapse rate cooling, -0.55 °C/100m
B. Apparent N₂-Ar RT along lapse rate
C. Local geothermal warming, 5.5 °C/100m
D. Apparent N₂-Ar RT along geothermal gradient
CONCLUSIONS

- RT determined by GC from N₂-Ar measurements in ground water typically ±0.5 °C on laboratory standards; best suited for aerobic or low nitrate waters where altitude of recharge is known.
- Large uncertainties in RT and Ex air can result if denitrification is significant.
- Possible to combine a local depth-temperature profile with N₂-Ar data to estimate depth of recharge below deep unsaturated zones in arid regions, but estimation of altitude of recharge from the local atmospheric lapse rate is poorly constrained.
- Most waters recharged along the Eastern Mountain Front of the MRGB, NM were recharge at depths of up to 150 meters below the land surface.
- Thousands of measurements of N₂-Ar in US groundwater have been made at the USGS over the past decade to estimate 1) recharge temperature for CFC/SF₆ dating studies, 2) agricultural denitrification studies, 3) paleo-temperature reconstruction, 4) tracing sources of water in aquifers, and 5) interpreting recharge mechanism.
Increasingly, geochemists and hydrologists are including measurements of concentrations of dissolved gases in hydrologic investigations. These include suites of noble gases (Ar, Ne, Kr, Xe, He) to study recharge conditions and deep groundwater circulation, gases that are indicators of microbial processes (O\textsubscript{2}, CH\textsubscript{4}, CO\textsubscript{2}, H\textsubscript{2}S, N\textsubscript{2}O, N\textsubscript{2}, etc.), and gases that can be used to interpret groundwater age (CFCs, SF\textsubscript{6}, \textsuperscript{4}He, \textsuperscript{85}Kr, \textsuperscript{39}Ar, \textsuperscript{81}Kr, etc.).

Thousands of measurements of N\textsubscript{2} and Ar in groundwater have been made at the USGS over the past decade to estimate 1) recharge temperature and excess air for CFC/SF\textsubscript{6} dating studies, 2) estimate quantities of denitrification in agricultural studies, 3) reconstruct paleo-environmental conditions, 4) identify and trace sources of water in aquifers, 5) interpret recharge mechanisms, and 6) estimate altitude or depth of recharge.