Application of Environmental Tracers to Interpretation of Groundwater Age and Flow at the Leetown Science Center, WV

Niel Plummer¹, Phil Sibrell², Jerry Casile¹,
Andy Hunt³, Ed Busenberg¹, Peter Schlosser⁴

¹ USGS, NRP, Reston, VA
² USGS, LSC, Leetown, WV
³ USGS, Denver, CO
⁴ Lamont-Doherty Earth Observatory, Palisades, NY

Objectives– What can measurements of a suite of environmental tracers in groundwater at the LSC tell us about?

• Groundwater age and relation to discharge, volume of the water supply, and sustainability issues.

• Groundwater age distribution, transient flow from springs.

• Amounts of anthropogenic halogenated VOCs at and near LSC.

• Tracing directions of groundwater flow using VOCs and stable isotope data.

• Is there old water in well and spring discharge at the LSC?
Environmental Tracers and Isotopes Measured

- Chlorofluorocarbons (CFC-11, CFC-12, CFC-113)
- Sulfur Hexafluoride ($\text{SF}_6$)
- Tritium ($^3\text{H}$)
- Noble Gases ($^4\text{He}$, $\text{Ne}$, $\text{Ar}$, $\text{Kr}$, $\text{Xe}$; $^3\text{He}$); $^3\text{H}/^3\text{He}$ age
- Permanent Gases ($\text{N}_2$, $\text{Ar}$)
- Halogenated VOCs (PCE, Chloroform, TCE, etc.)
- Inorganic Water chemistry
- Stable Isotopes of Water
- Age: time elapsed since RC
- Age is an interpretation
Samples Collected

- 2004, 2006. Initial sampling during Kozar study. (CFCs and $^3$H/$^3$He).
- 2008. Sampling of LSC springs and wells.
- 2009. Sampling of LSC springs, wells (comparison tests: $^3$H/$^3$He), 21 domestic wells and 10 local surface water sites.

2. **Dating Old Groundwater**: With “calibrated” helium-4 accumulation rate. Timescale about tens to hundreds of thousands of years. Measure helium-4, use tritium/helium-3 ages to determine the helium-4 accumulation rate.
Tritium/Helium-3 age is age of the young fraction in binary mixtures of old and young

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

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

\( \lambda \) is the decay constant (0.05626 yr\(^{-1}\))

\( \lambda = \ln 2 / 12.32 \), where 12.32 is the half-life of tritium.

The tritium/helium-3 age is based on an isotope ratio that is hardly affected by dilution with old water.

The tritium/helium-3 age is the time it takes the initial tritium from precipitation to decay to the measured tritium concentration.

Tritium/helium-3 dating re-constructs the initial tritium concentration from measurements. (Only dating tool we have like this; but expensive).
Red arrows denote sample time and average $^{3}H/^{3}He$ age obtained at Balch, Gray, and Bell Springs.
Average $^3\text{H}/^3\text{He}$ ages in yrs

Sample Year

2008 | 2009
--- | ---
O Old, >30 yrs | 3.4 | 4.3
Y Young, <1 yrs | 5.8 | 6.7

Y

O

O

USDA Sulfur well
USDA Fault well
USDA Domestic well

Balch Spring
Ballfield well

Stable well B
Stable well C

New and Old Dodson well
Bell Spring

Average

3
H/
He

ages in yrs

Sample Year

2008 | 2009
--- | ---
O Old, >30 yrs | 3.4 | 4.3
Y Young, <1 yrs | 5.8 | 6.7

Y

O
Finding the “age” of old water at LSC from radiogenic $^4\text{He}$

- Calculate $^4\text{He}_{\text{rad}}$ from Helium isotope mass balance: $^4\text{He}_{\text{rad}} = ^4\text{He}_{\text{tot}} - ^4\text{He}_{\text{eq}} - ^4\text{He}_{\text{ex}}$
- Determine $F_{\text{old}}$ (from CFCs or $^3\text{H}$)
- Re-construct amount of $^4\text{He}_{\text{rad}}$ in old fraction, $^4\text{He}_{\text{rad(old)}} = ^4\text{He}_{\text{rad}} / F_{\text{old}}$
- Calculate the $^4\text{He}$ age of the old fraction from the calibrated $^4\text{He}$ accumulation rate, $A_{^4\text{He}} \ (2 \times 10^{-9}\text{ccSTP/g/yr})$,

\[ \text{Age} = ^4\text{He}_{\text{rad(old)}} / A_{^4\text{He}} \]
$^4$He accumulates in groundwater with age.

This Radiogenic $^4$He accumulation rate is about 1,000 times greater than that expected from U-Th decay. Probably release from fluid inclusions.
Initial tritium in Leetown Science Center groundwater samples

Samples of Springs and wells at LSC

Not much evidence for mixing
Leetown Sites - Terrigenic Helium

**Legend**

- **Leetown_WV_Waters**
  - $10^8$ He4, ccSTP/g
  - 0.09 - 1.00
  - 1.01 - 3.00
  - 3.01 - 5.00
  - 5.01 - 7.00
  - 7.01 - 2000.00

- **Geology_Faults**
- **WV_Jeff_Roads**
- **EWV_Streams**
- **LSC_Boundary**

**Study Area Location**

- **1,000, $^4$He age, yrs.**
- **Very young water (low terrigenic $^4$He)**

- **1,000 Om**
- **33 Om**
- **7,800 Om**
- **36 Oc**
- **3,400 Cc**
- **500 Obrr**
Groundwater Volume

\[ V = \text{Discharge} \times \text{Age} \quad [V=(V/t) \times t] \]

Assumptions

• Groundwater flow at steady state
• Discharge constant, \( V/t \)
• Age distribution in discharge constant
• Mean age, \( t \), is constant
• \( V \) = volume of reservoir contributing to spring discharge
• Major event: Discharge increases, Age decreases, but \( V \) can still increase as the system of conduits and fractures fills to the land surface.

<table>
<thead>
<tr>
<th>Spring</th>
<th>Age range in years</th>
<th>Estimated discharge in cfs</th>
<th>Reservoir volume, millions of ft(^3)</th>
<th>Est. total thickness in ft of circular water zone</th>
<th>Diameter in miles of catchment zone</th>
<th>Area of catchment zone mi(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gray</td>
<td>2.1-6.5</td>
<td>1.1-2.7</td>
<td>90-500</td>
<td>2.5-7.5</td>
<td>1.2-1.8</td>
<td>1.1-2.6</td>
</tr>
<tr>
<td>Blue</td>
<td>4.8-5.3</td>
<td>0.13</td>
<td>20-22</td>
<td>5.5-6.0</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Bell</td>
<td>1.4-6.4</td>
<td>1.8-2.0</td>
<td>90-400</td>
<td>2-7</td>
<td>1.5-1.6</td>
<td>1.8-2.1</td>
</tr>
<tr>
<td>Balch</td>
<td>2.2-8.5</td>
<td>0.45</td>
<td>30-120</td>
<td>3-10</td>
<td>0.7-0.8</td>
<td>0.4-0.5</td>
</tr>
</tbody>
</table>

Assuming rule of thumb, 1 cfs=1 mi\(^2\)

\[ r = \left( \frac{V}{(Th \times \pi)} \right)^{1/2} \]

Find \( Th \) so that ratio of catchment area (mi\(^2\)) to discharge (cfs) = 1.0

If catchment were a circle

Cumulative thickness (Th) of water zone

Opequon Creek watershed area of Kozar model about 20 square miles.
Estimate the volume of water in the Hopewell Run watershed

Area of Hopewell Run watershed = 10 mi² (Jones and Deike, 1981)
Recharge = Discharge = 16.5 in./yr (Kozar, 2007) (normal climate)
Average discharge from watershed = 383 x 10⁶ ft³/yr = 12.1 cfs
Mean age of discharge 4-6 years (this study), use 5 yrs below.

\[ V = \text{Discharge} \times \text{Age} \quad [V=(V/t) \times t] \]

\[ V = \text{Volume of water in the reservoir} = 383 \times 10^6 \text{ ft}^3/\text{yr} \times 5 \text{ yrs} \]
\[ = 1.92 \times 10^9 \text{ ft}^3; \quad = 54.2 \times 10^6 \text{ m}^3 \text{ water in storage} \]

Median withdrawal at LSC = 1,473 gpm (Kozar et al., 2007)
\[ = 2.93 \times 10^6 \text{ m}^3/\text{yr.} \quad (= 3.3 \text{ cfs}) \]

Annual withdrawal from storage = \[(2.93/54.2)\times100 = 5.4\%\]
An important question is how much water can be withdrawn sustainably, without significantly impacting stream flow, spring discharge, and local water levels in wells.

Link spring did not flow during our study. Owens Farm spring did not flow in 2008, but did on 5/14/09 when we sampled. Even if there is more water at the LSC than previously thought (because the water is older than previously thought), it is not known how much water can be withdrawn sustainably (either normal climatic conditions or drought). The situation is further complicated if demand for water increases.

A transient flow model could help evaluate sustainable utilization of the groundwater resource.
Transient flow: Landscape near maximum saturation; 7 March, 2010

Saturated landscape following abrupt melting of snow from Period III near the intersection of US 340 and US 50, Clark Co., Virginia, on 7 March, 2010.

Gray Spring, LSC, Discharge

Mean Monthly Precipitation at Winchester, inches

Relative Discharge (Gage height, in Feet)

DATE

2008 2009 2010 2011

I Drying
II wet-summer
III wet-winter
IV Drying

USGS
Gray Spring, LSC, Water Temperature

### Mean Monthly Precipitation at Winchester, inches

### Water Temperature, °C

- **I**: Drying
- **II**: wet-summer
- **III**: wet-winter
- **IV**: Drying
Excess air and recharge temperature of Gray Spring discharge, 2008-2010

Excess Air, ccSTP/kg water

Plot showing amount of excess air dissolved in discharge from Gray Spring (red dashed line) between October 2008 and October 2010 compared to the amount and timing of precipitation at Winchester, Virginia. The error bars represent one standard deviation of replicate samples.

Recharge Temperature, °C

Plot comparing N$_2$-Ar recharge temperature in discharge from Gray Spring (red dashed line) in relation to monthly precipitation at Winchester, Virginia between October 2008 and October 2010. The error bars represent one standard deviation of replicate samples.
Gray Spring

Concentration in pptv

Monthly Precipitation in inches at Winchester

CFC-11
CFC-12
CFC-113

Modern

\[^{3}H/^{4}He\] "age" of Gray Spr discharge = 6.2 yrs on 9/21/2009
Old fraction in Gray Spring >25 yrs, based on $^4\text{He}$ accumulation rate of $2 \times 10^{-9}$ ccSTP/g/yr
Gas chromatography with an electron-capture detector is capable of detecting some halogenated VOCs at concentrations as much as 3 orders of magnitude below detections with GC-MS.

Examples: chlorofluorocarbons, (CFC-11, CFC-12, CFC-113, CFC-114), trichloroethylene (TCE), tetrachloroethylene (PCE), carbon tetrachloride, and many others.
Measurement with Electron-Capture Detector

A small radioactive source containing $^{63}$Ni ionizes the molecules of the nitrogen carrier gas, and a potential difference creates a small current. This current is reduced when an electronegative substance (such as a halocarbon) is introduced. The reduction in current is a measure of the concentration of the electronegative substance. The detection limit (threshold) varies greatly according to the substances to be analyzed.
LSC Chromatograms: Detections of Halogenated VOCs

Balch Spring on 10/16/08

- CFC-12
- CFC-11
- CH₃I
- CCl₄
- Chloroform
- PCE
- Methyl Chloroform

Bell Spring on 10/16/08

- CFC-12
- CFC-11
- CFC-113
- CCl₃
- Chloroform
- TCE
- cis-1,2-Dichloroethylene
- Methyl Chloroform
- 1,1-Dichloroethane?
LSC Chromatograms: Detections of Halogenated VOCs

Gray Spring on 10/16/08

- CFC-12
- CFC-113
- CCl₄
- Chloroform
- Methyl Chloroform

USDA Domestic well on 10/23/08

- CFC-12
- CFC-113
- CCl₄
- Chloroform
- Methyl Chloroform
- 1,1-Dichloroethane
• Reston VA tap water is chlorinated.
• Samples from springs and wells at LSC were obtained prior to chlorination. We have not intentionally analyzed chlorinated water from LSC.
• Water from Gray and Balch springs and from USDA DW well much lower in halogenated VOCs than Reston tap water.
• VOCs from Bell well below MCLs. They just make good hydrologic tracers.
Max. PCE from urban air peaked at about 1,000 pg/L in 1970.
Leetown, WV - Chloroform

Elevated Chloroform

Legend

Leetown_WV_Waters
Chloroform
- 0.00 - 25000.00
- 25000.01 - 80000.00
- 80000.01 - 150000.00
- 150000.01 - 1000000.00
- 1000000.01 - 2200000.00

Geology_Faults

WV_Jeff_Roads

EWW_Streams

LSC_Boundary

Study Area Location
Leetown, WV - VOC, No Chloroform

Legend
- Leetown_WV_Waters
  - 0.41
- 1_1DCE / TDVOC
- cis1_2DCE / TDVOC
- PCE / TDVOC
- Me_Chlm / TDVOC
- Geology_Faults
- WV_Jeff_Roads
- EWV_Streams
- LSC_Boundary

Study Area Location
Excess CFC

Landfill
Modern Air-Water Equilibrium contains 800-1,000 pg/L PCE. Orange and Brown samples exceed; have anthropogenic source
Leetown Sites - Recharge Temperature

Legend

- **Leetown_WV_Waters**
  - Recharge Temp, °C
    - 6.26 - 8.00
    - 8.01 - 10.00
    - 10.01 - 11.00
    - 11.01 - 12.00
    - 12.01 - 20.00

- Geology_Faults
- WV_Jeff_Roads
- EWV_Streams
- LSC_Boundary

**MAT = 11.9°C**

Study Area Location
\[ \delta^2 H = 8 \delta^{18} O + 10 \]

\[ \delta^2 H = 8 \delta^{18} O + 14.38 \]
Summary and Conclusions

- At LSC, SF$_6$, $^3$H/$^3$He ages and $^4$He accumulation ages are in reasonable agreement, and confirm young water in vicinity of LSC. Springs and wells at LSC age range of 0-7 yrs; probably shallow circulation, most around 3-5 yrs.
- $^3$H/$^3$He ages at Gray, Balch, and Bell springs correlated with SPI and show transient in age distribution from 2004-2009.
- Monthly samples from Gray Spr. show transient flow in response to major precipitation events: (1) lag of about 2-3 months, (2) SF$_6$ shows age range of 0-5 yrs, between high and low flow (transient evidence in other gases, recharge temp, excess air).
- The accumulation rate of $^4$He in the Great Valley carbonates is on the order of $2 \times 10^{-9}$ ccSTP/g/yr. Combined with $^4$He measurements, shows old water in some domestic wells, particularly in area W and SW of LSC. Old water may be associated primarily with the Martinsburg Shale. Some domestic wells have $^4$He accumulation ages of more than 1,000 yrs (but $^4$He accum. rate uncertain in Martinsburg shale). Old water in carbonates may be about 40 yrs or so.
- Can combine age with discharge to estimate volume of water in spring catchment and for the watershed; need for a transient flow model.
- Halogenated VOC concentrations very low, but useful in tracing flow at LSC.
- Balch Spr. had warm recharge temperature (2008 sampling) and evaporated signal in stable isotopes, and may contain a fraction of water from the reservoirs.
Springs at or near the Leetown Science Center