Dating of young ground water with CFCs, SF$_6$, $^3$H, and $^3$H/$^3$He: Principles and Examples

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U.S. Geological Survey, Office of Water Quality
Forensic Hydrology Workshop, Annapolis, MD
September 1, 2004
Selected Environmental Tracers
0-50 Year Timescale

- $^3$H, $^3$H/$^3$He
- $^{85}$Kr
- CFC-11, CFC-12, CFC-113
- SF$_6$
- Event Markers: $^3$H, $^{36}$Cl, $^{14}$C
- Age: time elapsed since recharge

Cook and Bohlke, 2000
Why measure environmental tracers in ground water?

- Estimate fractions of young water and the mean age of the young fraction in mixtures.
- Evaluate vulnerability to contamination.
- Estimate recharge rates.
- Calibrate models of groundwater flow.
- Estimate rates of geochemical and microbiological processes.
- Date historical records of contaminant loading to aquifers.
- Estimate remediation times.
Approach to “Dating” Young GW

- Collect water samples without contacting air.
- Minimize mixing effects by sampling monitoring wells with narrow screens.
- Analyze with high precision for CFCs, SF$_6$, $^3$H, $^3$H/$^3$He, and others (multi-tracer approach).
- **Age interpretation.** Evaluate multiple tracer data in context of models of groundwater flow.
- **Age is model dependent.**
Age Interpretation

- Comparison of simulated and observed tracer concentrations. **Lumped-parameter models.** (1) multiple tracers from the source, (2) a time series from the source, or (3) multiple tracers from multiple sources in the system. *Choose a model based on hydrogeology.*

- **Tracer plots.** Method of comparing simulated and observed multiple tracer data; recognizing cases of possible piston flow and binary mixing (dilution); elimination of some mixing models.

- **Flow-model calibration** and simulation of age. Use of age information to calibrate the model. (Reilly et al., 1994; Inverse modeling; UCODE)

- All “ages”, regardless of method, are **model dependent.**

- **Contradictions?** What’s wrong with the tracers? What’s wrong with the model?
Lumped Parameter Models

**QCFC**
http://www.iaea.org/programmes/rial/pci/isotopehydrology/

**USGS-CFC2004**
http://water.usgs.gov/lab/cfc

**TRACERMODEL1**
J.K. Böhlke, is a Microsoft Excel spreadsheet program.

**CFC**
IAEA Isotope Hydrology Laboratory Excel based program.

**FLOW (FLOWPC)**
Lumped-parameter models, FORTRAN, Maloszewski and Zuber (1996).

**TRACER**
EXCEL workbook (Bayari, 2002)
http://www.iamg.org/CGEditor/index.htm

**LUMPED**
Visual Basic (Ozyurt and Bayari, 2003)
http://www.iamg.org/CGEditor/index.htm
http://www.sukimyasilab.hacettepe.edu.tr/english/software.shtml

**BOXMODEL**
EXCEL workbook (Zoellmann, Kinzelbach & Aeschbach-Hertig)
http://www.baum.ethz.ch/ihw/boxmodel_en.html
http://water.usgs.gov/lab/cfc

See extensive bibliography
Tritium/Helium-3

- Half-life 12.3 years; decays to $^3\text{He}$.
- Atmospheric thermonuclear weapons testing from the 1950’s, and especially in the period 1962-1963
- Initial $^3\text{H}$ measured
- Terrigenic He sources
- Dispersion around bomb peak
- Confinement of $^3\text{He}$
Dating with $^3$H/$^3$He

Measured

$^3H_m$

$^4He_m = ^4He_{eq} + ^4He_{atm} + ^4He_{ter}$

$Ne_m = Ne_{eq} + Ne_{atm}$

$\delta^3He = \left( \frac{R}{R_a} - 1 \right) \cdot 100$

$^3He_m = ^3He_{eq} + ^3He_{atm} + ^3He_{ter} + ^3He_{tri}$
Some Definitions

\[ N_{atm} = (\text{He}/\text{Ne})_{atm} = 0.288 \text{ for air excess} \]
\[ R_{atm} = (\text{He}/\text{He})_{atm} = 1.384 \times 10^{-6} \text{ for air excess } (R_a) \]
\[ R_{ter} = (\text{He}/\text{He})_{ter} = 2 \times 10^{-6} \text{ for radiogenic helium } (R_{rad}) \]
\[ = 1 \times 10^{-5} \text{ for mantle helium } (R_{man}) \]

\[ Ne_m = Ne_{eq} + Ne_{atm} \]

\[ ^4He_m = ^4He_{eq} + N_{atm} \cdot Ne_{atm} + ^4He_{ter} \]

\[ ^3He_m = R_{eq} \cdot ^4He_{eq} + R_{atm} \cdot N_{atm} \cdot Ne_{atm} + R_{ter} \cdot ^4He_{ter} + ^3He_{tri} \]

\[ ^3He_{tri} = ^4He_m \cdot (R_m - R_{ter}) - ^4He_{eq} \cdot (R_{eq} - R_{ter}) - N_{atm} \cdot (Ne_m - Ne_{eq}) \cdot (R_{atm} - R_{ter}) \]

\[ \tau = \frac{1}{\lambda} \cdot \ln \left( 1 + \frac{^3He_{tri}}{^3H_m} \right) \]
Chlorofluorocarbons

- CFC-12 (CF$_2$Cl$_2$), 1930
- CFC-11 (CFCl$_3$), 1936
- CFC-113 (C$_2$F$_3$Cl$_3$), 1944
- Input smooth, increasing until 1990s (dating range ~1950 to early 1990s).
- Stable in aerobic environments.
- In modern cases: dual ages.
- Use of ratios.
- Can detect post 1940’s water.
- Collection/analysis not overly labor intensive.
- Problems with contamination, degradation (anoxic), sorption?

New bottle method of collection.
See http://water.usgs.gov/lab/cfc
Sulfur Hexafluoride

- Electrical insulator in high voltage switches
- First produced 1953
- Very low solubility in water.
- Does not degrade
- Terrigenc source
- Smooth input, increasing in air at 6%/yr; 5 pptv today.
Dating with CFCs and SF₆

• Henry’s law solubility \( C_i = K_H \times p_i \)

• Requirements:

★ Gas–water equilibrium at recharge
★ Recharge temperature
★ Barometric pressure at recharge
★ Knowledge of atmospheric history of the gas
10 °C, 1 atm total pressure

**Analyzed**

pg/kg CFC

- **CFC-12**: 200.6
- **CFC-11**: 486.5
- **CFC-113**: 27.8

**CFC Partial Pressure (in pptv)**

- CFC-12: 306.2 pptv
- CFC-11: 169.7 pptv
- CFC-113: 23.0 pptv

1940 1960 1980 2000

**Recharge Year**

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[USGS logo]
Krypton-85

- Radioactive noble gas with a half-life of 10.76 years.
- $^{85}$Kr in the atmosphere has steadily increased since the mid-1950s.
- Interpreted age insensitive to recharge temperature, altitude, etc.
- Does not degrade.
- Atmosphere is only significant source.
- Although difficult to collect and analyze, even a few $^{85}$Kr can often help resolve questions.

Example: sample collected in 1990 had a Specific Activity of Kr-85 of 10 dpm/cc. This would have a Piston flow recharge date of about 1975.
Tracer method of dating the young fraction in binary mixtures of young and old

- CFC pptv ratio defines age of young fraction.
- \( \% \) young water \( \left( \frac{\text{pptv}_{\text{measured}}}{\text{pptv}_{\text{ratio year}}} \right) \times 100 \)

- Cannot date outside range for ratio.
- Cannot use if one of the CFCs in the selected ratio is “contaminated”, even if ratio is “in range”.
- Ratio-based age must be less than (younger than) apparent (piston flow) model ages for both CFCs in the ratio.
$^3$H/$^3$He Age Applies to that of the Young Fraction in Simple Binary Mixtures

$^3$H/$^3$He Age is based on an isotope ratio: 

$\left( ^3H^o/ ^3H_m \right)$

$$\tau = \frac{1}{\lambda} \cdot \ln \left( 1 + \frac{^3He_{tri}}{^3H_m} \right)$$

$\lambda =$ decay constant $= \ln 2/t_{1/2} = 0.05635 \text{ year}^{-1}$

$t_{1/2} = 12.3 \text{ years}$
Limitations

$^3$H/$^3$He
- Cost
- Terrigenic He
- Bubbles, Gas-stripping, confinement
- Mixing

$\text{SF}_6$
- Terrigenic $\text{SF}_6$
- Mixing

CFCs
- Contamination
- Degradation
- Mixing

$^{85}\text{Kr}$
- Very difficult collection and analysis
- No labs available to us
Delmarva Peninsula
Atlantic Coastal Plain

Locust Grove
Model Age in Years

- CFC-11
- CFC-12
- CFC-113
- \(^3\)H/\(^3\)He
- \(^{85}\)Kr
- Numeric Simulation
- \(\text{SF}_6\)

Nest 1: 167, 166, 165
Nest 2: 53, 52, 61
Nest 3: 62, 163, 162
Nest 4: 64, 63
Nest 5: 161, 160, 159
• 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)
Blue Ridge Mountains of Virginia


Background

- 800 km²; elev. 170-1230 m
- Annual precipitation averaged 114 cm; mean annual temperature, 7.8 °C in high altitude, central part.
- Precambrian to Cambrian fractured crystalline rocks, metabasalts with thin cover of colluvium and residuum.
- Two largest springs have maximum discharges of 20 and 11 l/sec. Most with max. discharge of < 2 l/sec.
- In drought, sprs. about 10% of max.
- wells produce < 6 l/sec, and typically < 1 l/sec.
- 34 springs, 15 wells: 1996 (wet season), 1997 (dry season).
- Shallow recharge through residuum and colluvium recharge fracture system which has low storage.
- CFCS, $^3$H/$^3$He, SF$_6$, $^{35}$S, stable isotopes, dissolved N$_2$, Ar.
SHENANDOAH NATIONAL PARK
BIG MEADOWS AREA

Ground-Water-Flow System

Lewis Spring

Well 14

EL=2800

NW

EL=2800

SE

EL=2800
Lewis Mountain Spring

Sampling from a Typical Spring Box and Weir
Sample 1997.0

- **Piston Flow**
- **Exponential Mixing**
- **Binary Mixing**

- **Springs in 1996**
- **Springs in 1997**
- **Wells in 1996**
- **Wells in 1997**

**Hudson Spring**
Sample 1997.0

- **Piston Flow**
- **Exponential Mixing**
- **Binary Mixture**

- **Springs, '96**
- **Springs, '97**
- **Wells, '96**
- **Wells, '97**

Graph showing the relationship between SF$_6$ (pptv) and CFC-12 (pptv).
Two $^3$H input functions:
- Wash. DC (upper)
- Wash. DC scaled to SNP (lower)

Also 0-2 cc/L of excess air
Precipitation

Ground-Water Reservoir

Spring Discharge

Average -8.2 per mil
Amplitude 9.6 per mil
Std. Dev. 2.8 per mil

Average -8.2 per mil
Amplitude 1.1 per mil
Std. Dev. 0.3 per mil

δD per mil

δ¹⁸O per mil

Precipitation d Excess 16.1 per mil

Springs and Wells d Excess 16.4 per mil

Global Meteoric Water Line

δ¹⁸O (per mil)

δD per mil

Precipitation

Residence Time
2 Years

Spring Discharge

1999.0 1999.2 1999.4 1999.6 1999.8

Date

Precipitation

-16 -14 -12 -10 -8 -6 -4 -2 0 2 4 6 8 10 12 14 16

δD per mil

δ¹⁸O (per mil)

-160 -140 -120 -100 -80 -60 -40 -20 0 20 40 60 80 100 120 140 160

δ¹⁸O per mil

-16 -12 -8 -4 0 4 8 12 16

Ground-Water Reservoir

Spring

Byrd's Nest 3
Furnace
Hudson
Lewis
Precipitation

Springtown Valley

USGS
Average Seasonal
$\Delta \delta^{18}O = 0.12$ per mil
Average Age $\sim 5$ years
Conclusions from Blue Ridge (SNP)

- $\delta^{18}$O data: Mean residence time of 5 years. (Range 0-10 yrs.)
- Ages based on CFCs and SF$_6$ young; generally consistent with stable isotope data; do not include uz travel time.
- Ages based on $^3$H/$^3$He biased young (0-2 yrs, most 0)
- Water from wells have ages of 0 to 25 yrs. $^3$H/$^3$He dating works well for these (and applies to the young fraction).
- Some wells discharge mixtures; ratios of CFCs can define age of young fraction and percent young water in mixture.
- Excess CFCs-- Anthropogenic sources? Evidence of shallow recharge?
Chesapeake Bay Watershed

Region of 165,000 km² over parts of NY, PA, MD, DE, VA, and WV.

Evaluate residence times and nitrate transport in groundwater discharging to streams in the watershed.

Assess lag time between changes at the land surface and the response in the base-flow component of groundwater discharge to the bay.

Layered fracture density model
(Gburek, Folmar, and Urban (1998))

Burton et al. 2002
The graph shows the CFC-113 Concentration in pptv against CFC-12 Concentration in pptv. The data points are labeled with years from 1975 to 2000. The graph includes three lines: Piston Flow, Binary Mixing, and Transects. The Transects are further divided into East and West Transect markers.
East Piezometer Transect
--Preferred CFC-12 ages NE of stream are older...
..than those underneath and SW of stream
..although these ages are really mixture ages!

West Piezometer Transect
--Ages are even more mixed, but % of young water (2\textsuperscript{nd} #) shows older waters generally prevailing to NW
...and younger to SE

Burton et al. 2002
USGS Chesapeake Bay watershed nutrient study

- SF$_6$ vs $^3$H, CFCs
- Monitoring wells, springs from watersheds
Hydrogeology of Carbonate Terranes of the Valley & Ridge Province

Soil & Regolith
Alluvium
Limestone
Younger Ground Water
Older Ground Water
Mixture of Younger and Older Ground Water

Modified from Brahana and others, 1986

NOT TO SCALE

Blue Hole Spr., VA
Piston Flow
Recharge Date
Binary Mixing
Exponential Mixing
Residence Time, Yrs.
C-Bay Springs
Muddy Creek Sprs.
Muddy Creek Dom. wells
Muddy Creek Mon. wells
Shenandoah Sprs.
Shenandoah Wells
VAS Sprs.
VAS Wells

Tritium vs CFC-12
- Young, piston flow
- Binary mixtures of young and old
- Few CFC-12 contamination
Valley and Ridge Carbonates

C-Bay Sprs.
Muddy Creek Sprs.
Muddy Creek Dom. wells
Muddy Creek Mon. wells
Shenandoah Sprs.
Shenandoah wells
VAS Sprs.
VAS wells

Mixtures

- 2 samples beyond dating range of $^{3}\text{H}/^{3}\text{He}$.
- 9 samples may be unmixed.
- 13 samples look like mixtures.
Ages and mixing fractions determined from CFC-113/CFC-12

5-22 years and 10-100% young water in mixture.

Some are inconsistent with $^3$H (CFC contam.)
Valley and Ridge Carbonates

- C-Bay Sprs.
- Muddy Creek Sprs.
- Muddy Creek Dom. wells
- Muddy Creek Mon. wells
- Shenandoah Sprs.
- Shenandoah wells
- VAS Sprs.
- VAS wells

$3^\text{H} + 3^\text{He}$ (tritiogenic) as function of $3^\text{H}/3^\text{He}$ age.

Numbers are % of Young fraction in Mixture.
Bear Lithia Spring (9/2/99)

Piston-Flow Ages
CFC-11  27.2 yrs
CFC-12  27.2 yrs
CFC-113 >Modern (100 pptv)
$^{3}H/^{3}He$  30.0 yrs

Agreement in ages suggests
Piston flow (30 yrs in pipe flow).

Major Contradiction:
Tritium = 1.2 ± 0.2 TU
1969.6 water would contained
about 130 TU; decays to 25 TU
Without multiple Tracers, we would not know this is a Mixture.
GC-ECD Chromatograms

- Analysis by GC-ECD: Purge and trap gas chromatography with electron-capture detector.
- Detects halogenated VOCs (examples: CFCs, CCl₄, Halons, TCE, TCA, etc.
- Traditional analysis: GC-MS < 0.1 ug/L (= 100 ng/L = 100,000 pg/L)
- GC-ECD: < 1 pg/L (= 5 orders of magnitude below normal reporting levels)
Shenandoah National Park Spring Drinking Water Modern Clean Water

Spring Yorktown, VA Drinking Water

Relative Concentration

Retention Time

CFC-12
CFC-11
CFC-113
CCl$_4$
120 pptv in air

Chloroform?
Low ppb range

10 Year Old Water
A Town well in VA
Drinking Water Well
Depth: 190 meters
Valley and Ridge

Vulnerable, fingerprints of sources of contamination

A Town well in VA
Drinking Water Well
Depth: 115 meters
Blue Ridge

Relative Concentration

CCl₄ ppb range

Chloroform ? Others?, ppb?

CFC-12

CFC-11

CFC-113?

CCl₄ natural range

Vinyl Chloride?, Methyl chloride?

DCA?, TCA?, CH₃Br?

CFC-113?

Chloroform ?

PCE Tetrachloroethene ??
Aquifer Susceptibility in Virginia, 1998-2000

Nelms, D.L. and others, 2003, USGS WRIR 03-4278

LALF-9, 6/29/96

TD 233 ft, Screen 10 ft, 146 feet water above top of open interval

CFC-12: 45,000 pg/kg
CFC-11: 5,700 pg/kg
CFC-113: 31,000 pg/kg
Halon 1211
Drilling Tracer
**Well MW-N3D.** Large Halon peak. CFC-11 and CFC-12 indicate mid- to late 1970s. Since CFCs came with Halon, water is older than 1970s, but cannot be dated further with CFCs because of contamination with drilling air. Possible mixture of old water and water contaminated with drilling air. Without the Halon data, we would have interpreted a CFC age that is too young.

**Well MW-N4D.** Trace or no Halon present. CFC data probably unaffected by drilling air. CFC data suggest a modern age for the water. Without the Halon data, we would not know that the CFCs are valid in this sample.
CONCLUSIONS

• Dating with environmental tracers can help answer the “When?” in forensic hydrology.

• Use of multiple tracers and “tracer plots” can help to eliminate some mixing models, and refine estimates of mean tracer age.

• To a first approximation, the ages and mixing fractions of many samples from karst or fractured rock can be interpreted using a simple binary mixing model.

• Young ages in Blue Ridge. Mixtures from wells.

• About half of the $^3$H/$^3$He samples from the Valley and Ridge karst have initial tritium consistent with piston flow (0-15 yrs, unmixed). Rest are mixtures of 0-25 yrs (apparent age) mixed with old (pre-bomb) water.
CONCLUSIONS (cont.)

• Dating with ratios can be very useful. Demonstrate cases of piston flow and binary mixing, but can be affected by contamination. ($^3$H/CFC-12, CFC-113/CFC-12, SF$_6$/CFC-12)

• Most ground water from fractured rock or karstic aquifers is vulnerable to contamination.

• Should include tracers in well drilling.

• Use of patterns in low-level VOC detections to identify and trace sources.
“… the concept of groundwater age has little significance” (Fontes, 1983).

Investigation of multiple environmental tracers in groundwater systems can often help to refine interpretation of age, and refine conceptualization of ground-water flow.
Thanks

- Chesapeake Bay Study. Scott Phillips, Bruce Lindsey, Gary Spierah, Mike Focazio, J.K. Bohlke, Bill Burton, Colleen Donnelly, Ed Busenberg.

- Virginia Aquifer Susceptibility Study. Dave Nelms and George Harlow.

- Shenandoah National Park Study. Ed Busenberg, Dave Nelms, Jerry Casile, Julian Wayland, Wandee Kirkland, Stephanie Shapiro, Brian Norton.

- Reston Chlorofluorocarbon Laboratory.

- Noble Gas Laboratory of Lamont-Doherty Earth Observatory, Columbia University.