Dating of young ground water with CFCs, SF_6, ^3H, and $^3H/^3He$: Principles and Examples

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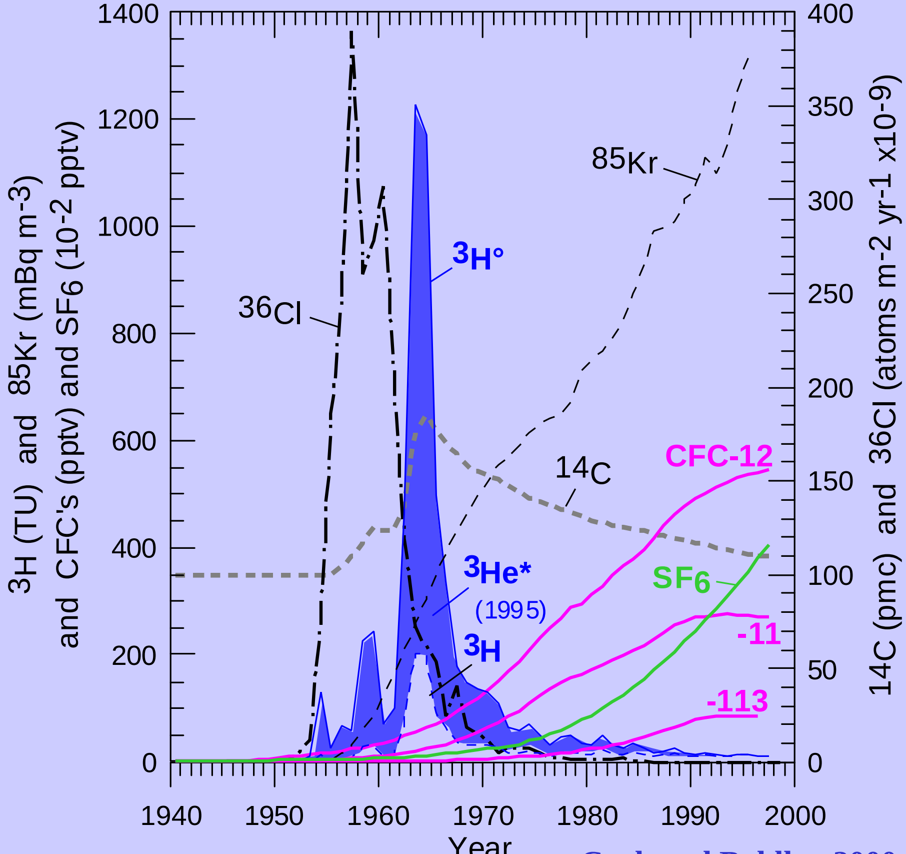
U.S. Geological Survey, Office of Water Quality
Forensic Hydrology Workshop, Annapolis, MD
September 1, 2004

Selected Environmental Tracers
0-50 Year Timescale



Cook and Bohlke, 2000

- ^{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

Why measure environmental tracers in ground water?

- Estimate fractions of young water and the <u>mean age of the young fraction in mixtures.</u>
- 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.

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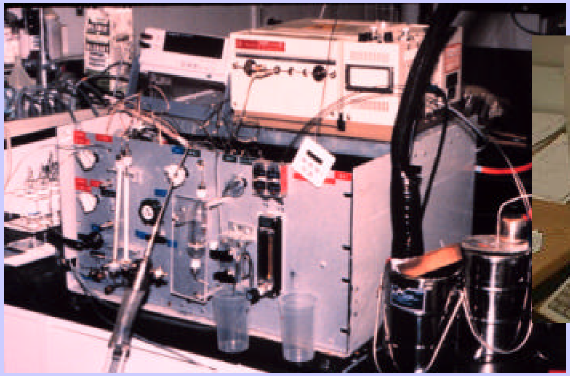
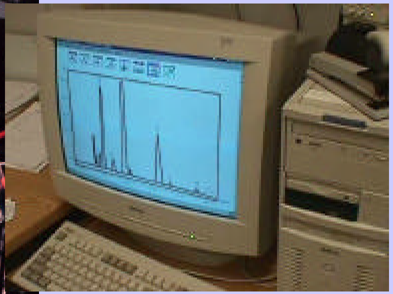
Approach to “Dating” Young GW

- Collect water samples without contacting air.
- Minimize mixing effects by sampling monitoring wells with narrow screens.
- Analyze with high precision for CFCs, SF_6, ^3H, $^3H/^3He$, 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?

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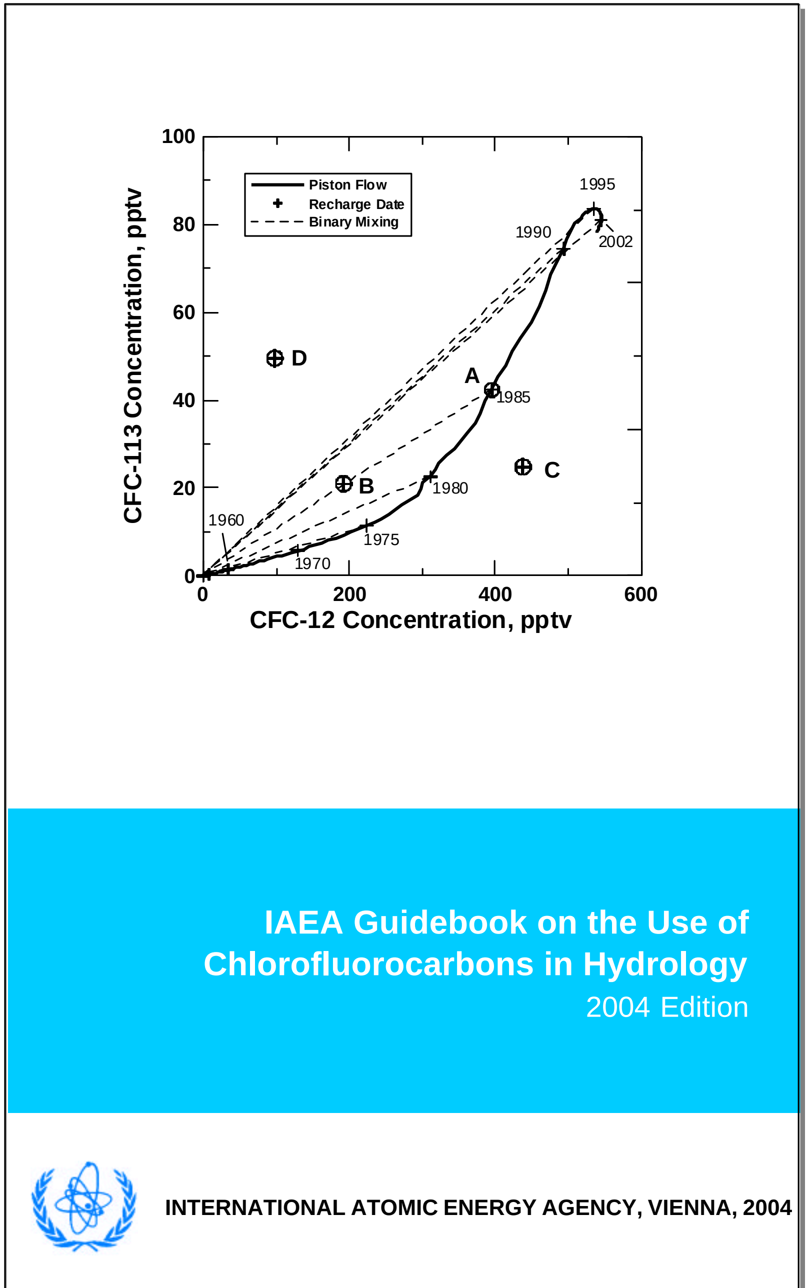

Lumped Parameter Models

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

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

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science for a changing world

The Reston Chlorofluorocarbon Laboratory (Internal Access)

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Welcome

See extensive bibliography

U.S. Department of the Interior · Geological Survey

Dating of young groundwater with CFCs, SF_6, ^3H, & $^3H/^3He$
PDF (3.07 MB) (June 2004)

Dating of Young Groundwater
PDF (5.29 MB) (November 2003)

Tritium/Helium-3

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

Dating with $^3H/^3He$

Measured

$$^3H_m$$

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

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

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

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

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Some Definitions

N_{atm} = $(He/Ne)_{atm}$ = 0.288 for air excess

R_{atm} = $(^3He/^4He)_{atm}$ = 1.384×10^{-6} for air excess (R_a)

R_{ter} = $(^3He/^4He)_{ter}$ = 2×10^{-8} for radiogenic helium (R_{rad})

= 1×10^{-5} for mantle helium (R_{man})

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

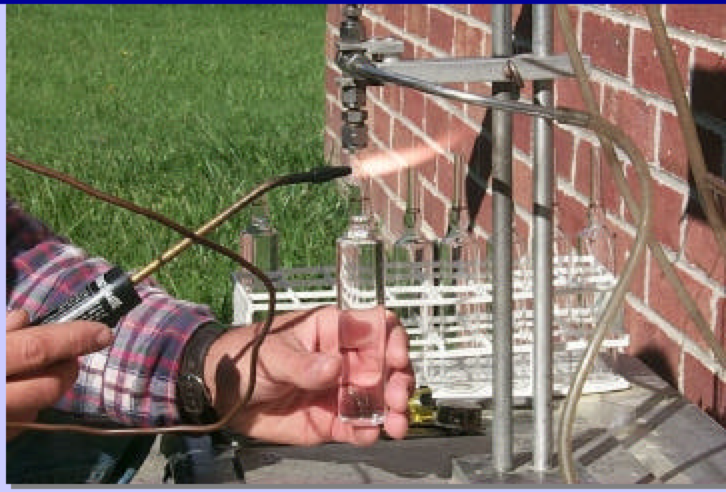
$$^4He_m = {}^4He_{eq} + N_{atm} \cdot Ne_{atm} + {}^4He_{ter}$$

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

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

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

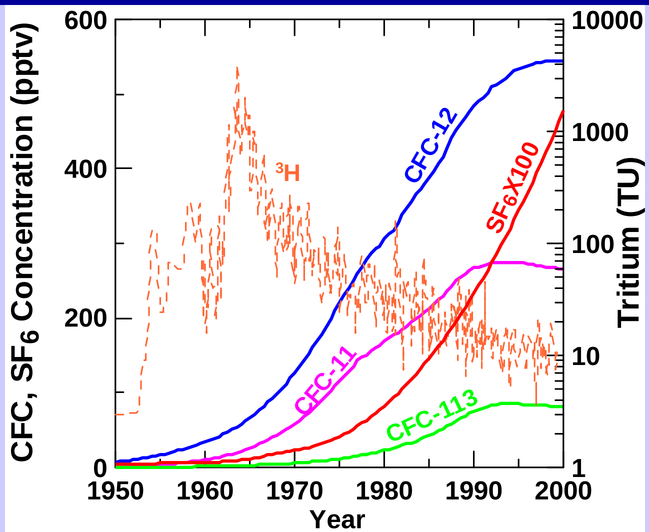
Chlorofluorocarbons

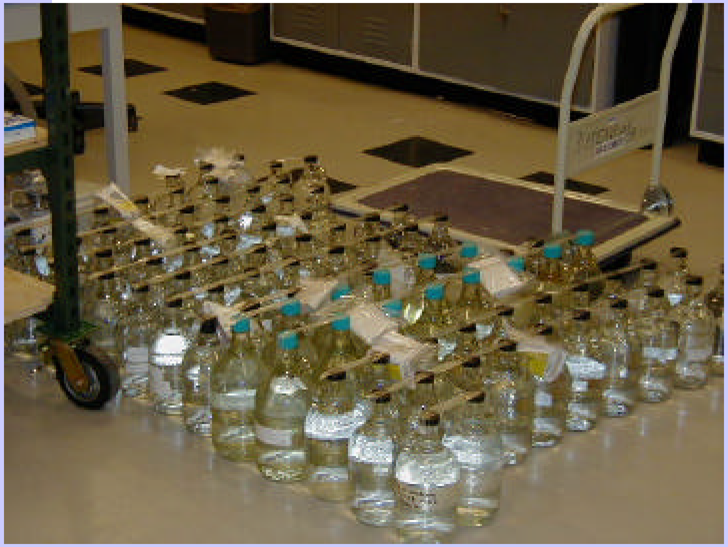


- CFC-12 (CF_2Cl_2), 1930
- CFC-11 ($CFCl_3$), 1936
- CFC-113 ($C_2F_3Cl_3$), 1944
- Input smooth, increasing until 1990s (dating range ~1950 to early 1990s).
- Stable in aerobic environments.
- In modern cases: dual ages.
- Use of ratios.
- Can detect post 1940's water.
- Collection/analysis not overly 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
- Terrigenic source
- Dating range: 1970-modern.
- Smooth input, increasing in air at 6%/yr; 5 pptv today.

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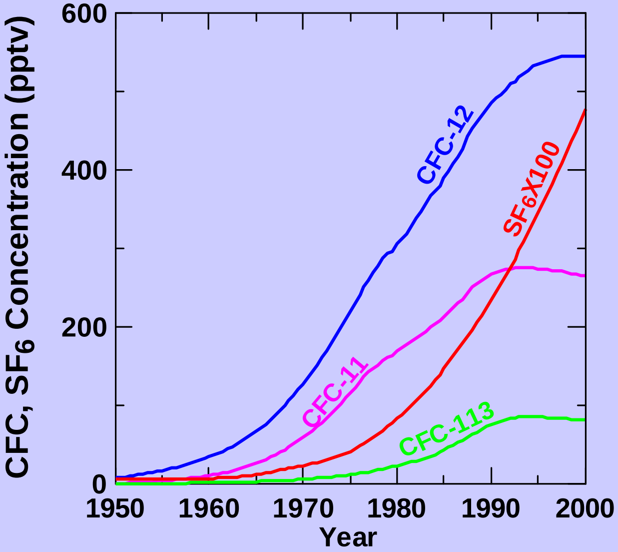
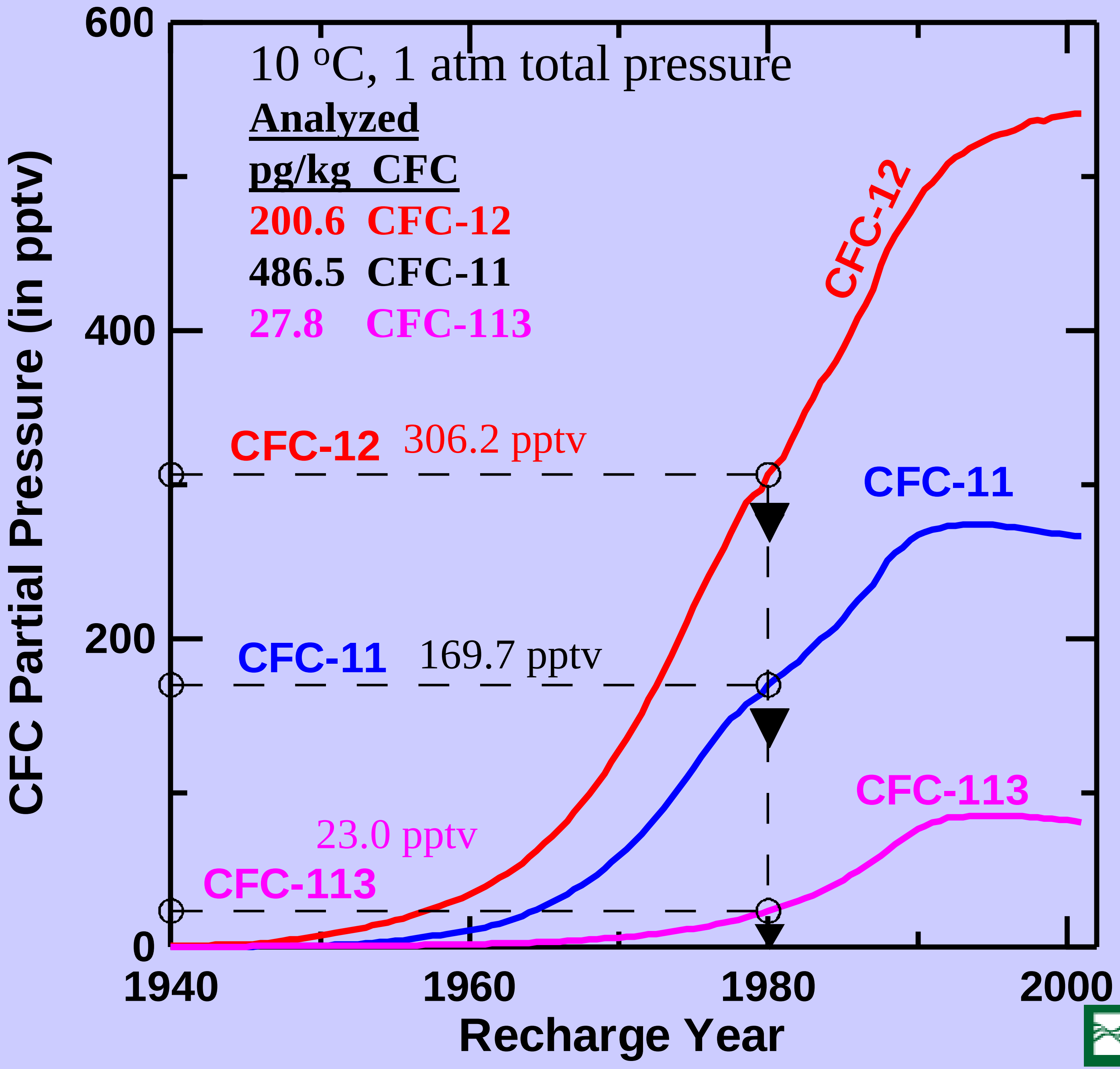
Dating with CFCs and SF_6

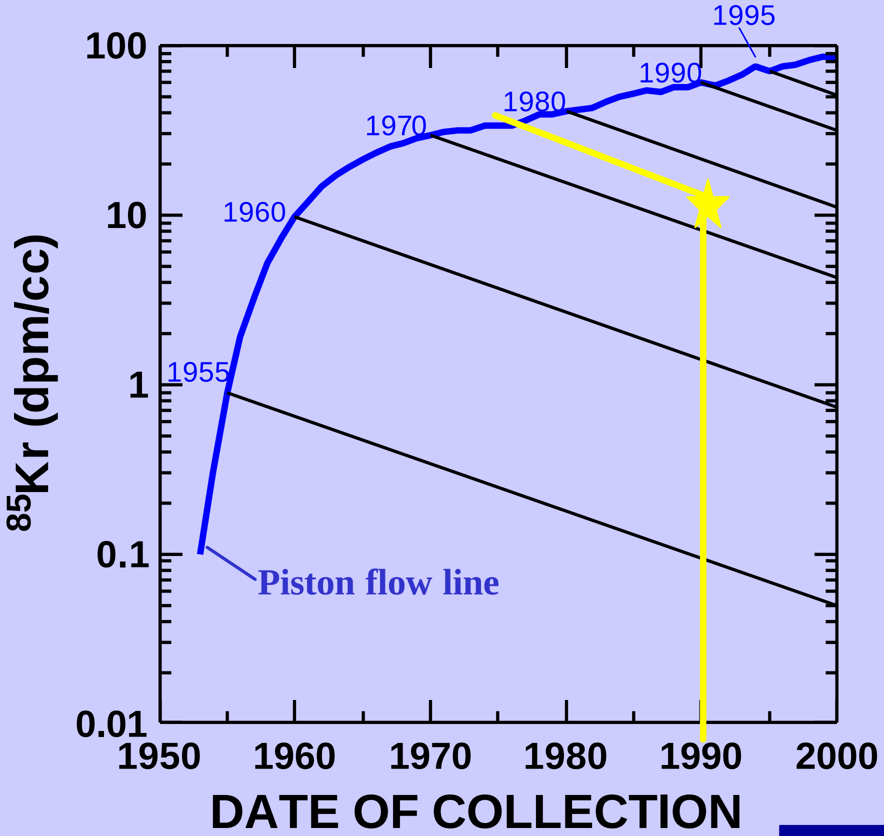
- **Henry's law solubility** $C_i = K_H \, x \, p_i$
- **Requirements:**



➢ 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
200.6 CFC-12
486.5 CFC-11
27.8 CFC-113
CFC-12
306.2 pptv
CFC-11
169.7 pptv
23.0 pptv
CFC-113
CFC-12
CFC-11
CFC-113
600
400
200
0
1940
1960
1980
2000
CFC Partial Pressure (in pptv)
Recharge Year

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.

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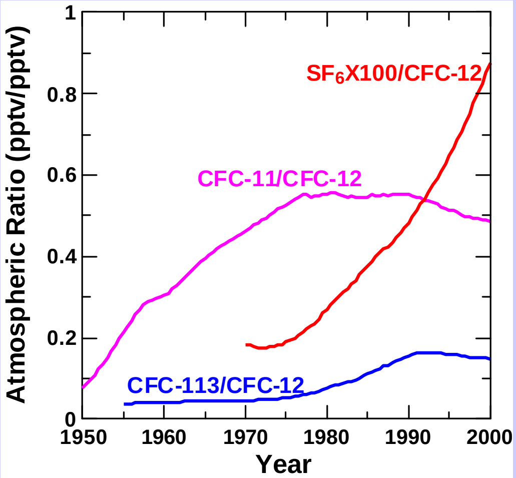
Tracer method of dating the young fraction in binary mixtures of young and old



- **CFC pptv ratio defines age of young fraction.**
- **% young water (pptv$_{(measured)}$ /pptv$_{(ratio\ year)}$) x 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:
($^{3}H^{o}/^{3}H_{m}$)

$$t = \frac{1}{l} \cdot \ln\left(1 + \frac{^{3}He_{tri}}{^{3}H_{m}}\right)$$

λ = decay constant = ln 2/$t_{1/2}$ = 0.05635 $year^{-1}$

$t_{1/2}$ = 12.3 years

Limitations

$^{3}H/^{3}He$

- Cost
- Terrigenic He
- Bubbles, Gas-stripping, confinement
- Mixing

SF_6

- Terrigenic SF_6
- Mixing

CFCs

- Contamination
- Degradation
- Mixing

^{85}Kr

- Very difficult collection and analysis
- No labs available to us

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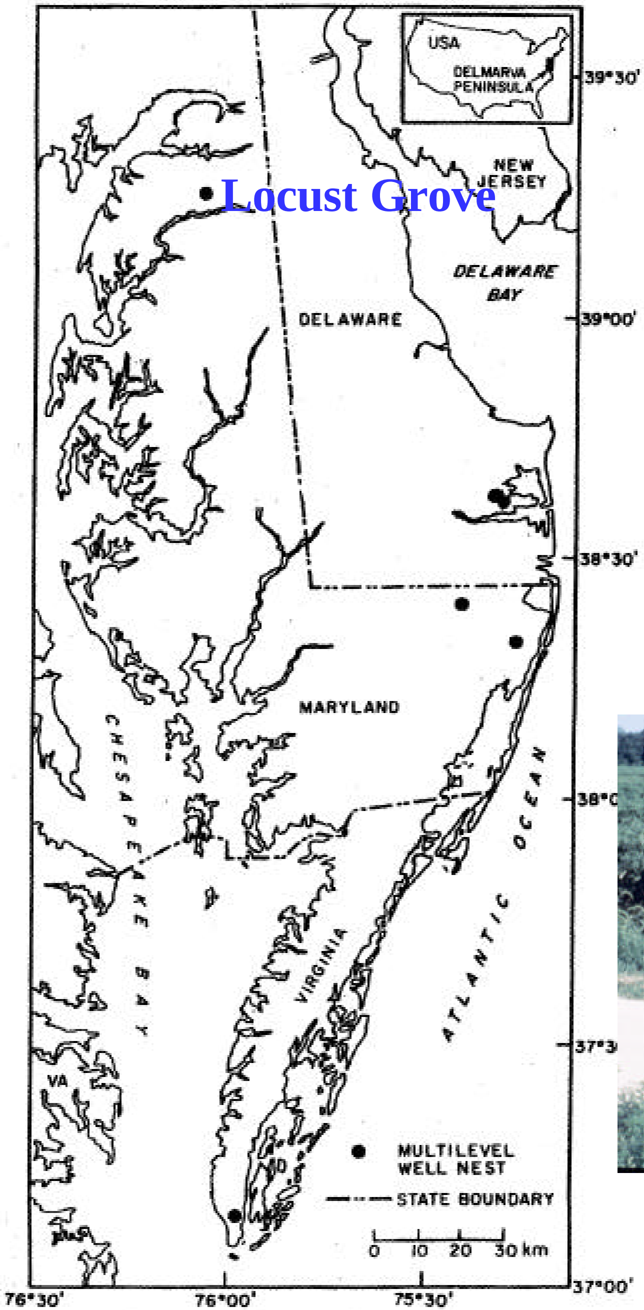
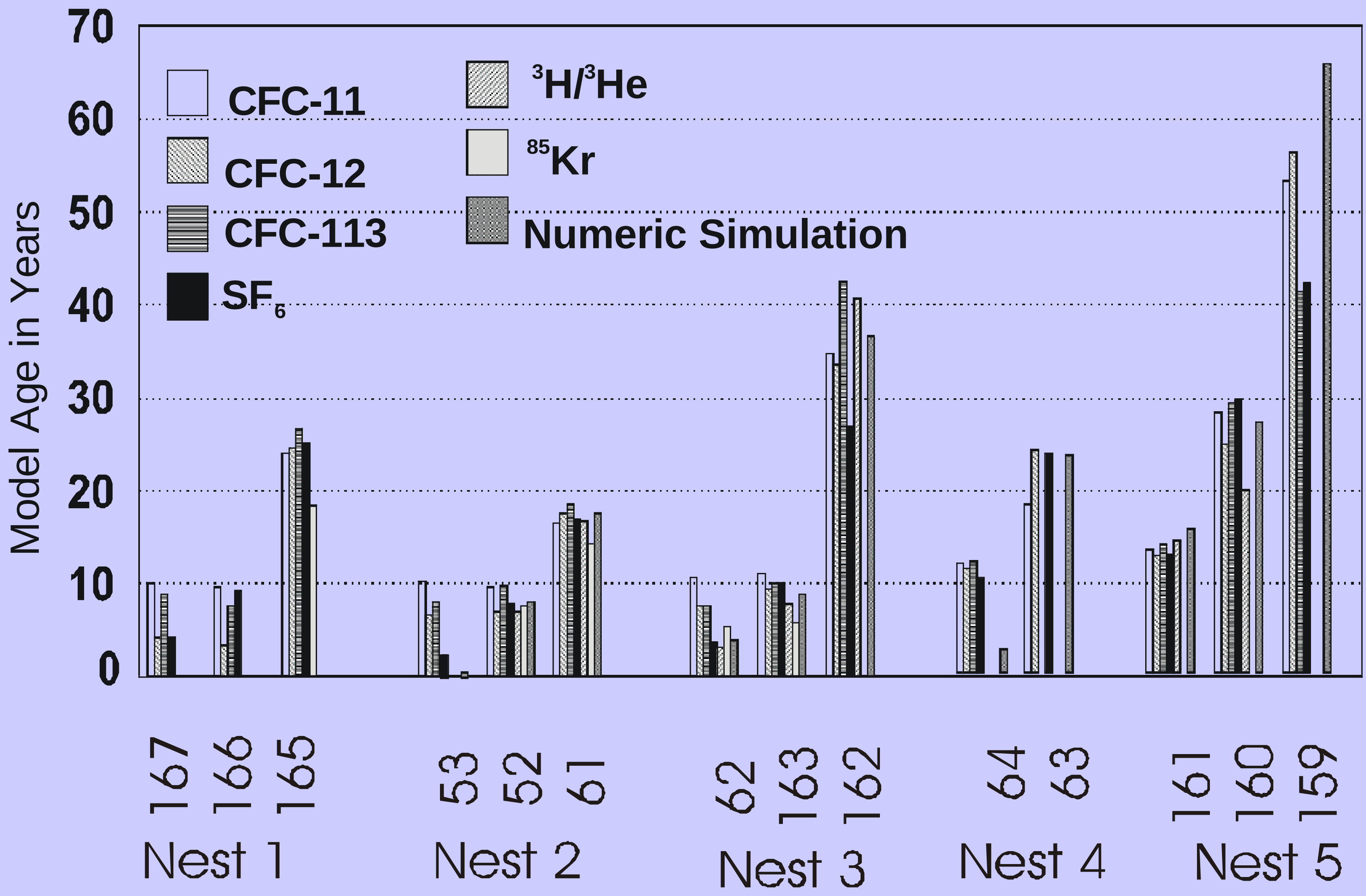
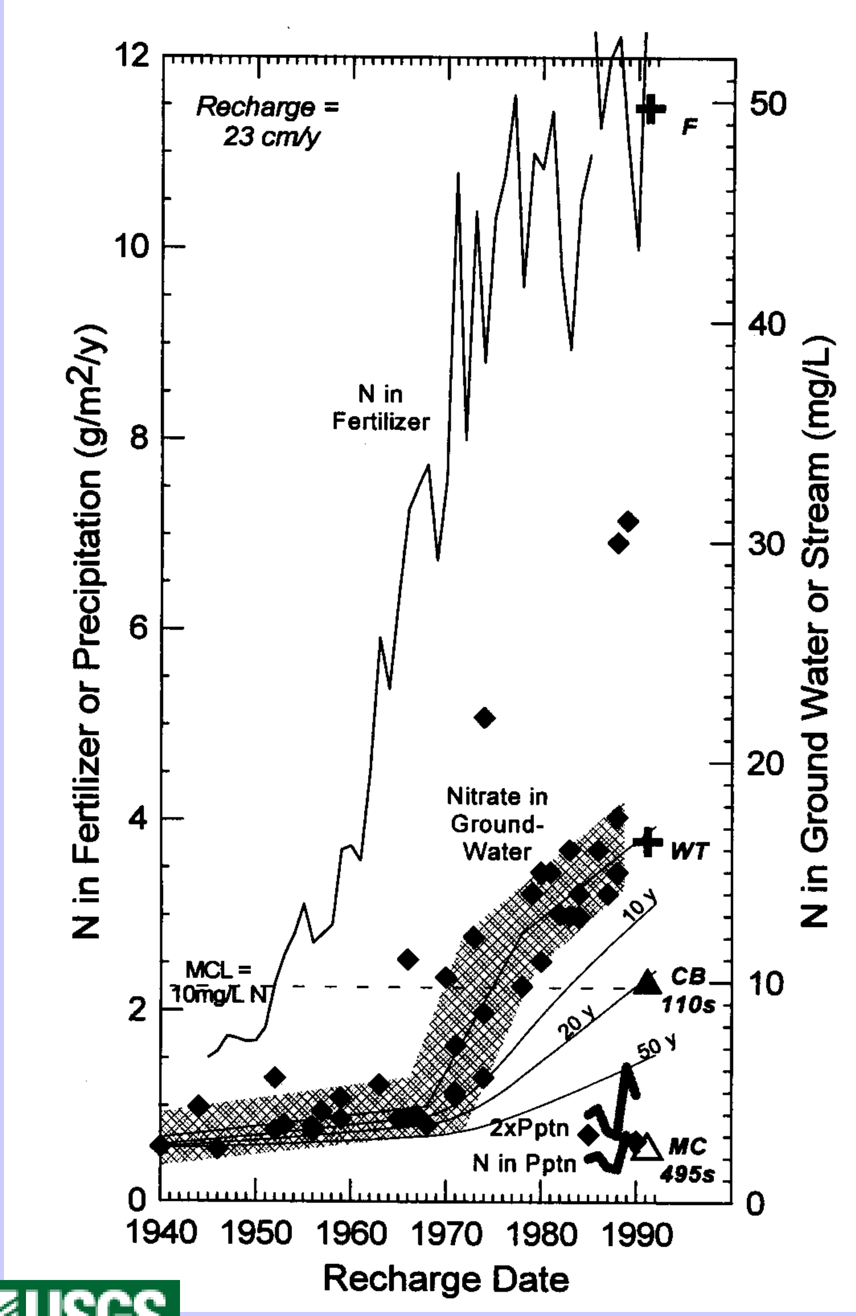
Delmarva Peninsula
Atlantic Coastal Plain





70
60
50
40
30
20
10
0
Model Age in Years
CFC-11
CFC-12
CFC-113
SF6
3H/3He
85Kr
Numeric Simulation
167
166
165
53
52
61
62
163
162
64
63
161
160
159
Nest 1
Nest 2
Nest 3
Nest 4
Nest 5



- •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)

USGS

Blue Ridge Mountains of Virginia

Plummer, L.N., Busenberg, E., Böhlke, J.K., Nelms, D.L., Michel, R.L., and Schlosser, P., 2001, Groundwater residence times in Shenandoah National Park, Blue Ridge Mountains, Virginia, USA: A multi-tracer approach. Chemical Geology, v. 179/1-4, p. 93-111.

Background

- **800 km^2;elev. 170-1230 m**
- **Annual precipitation averaged 114 cm; mean annual temperature, 7.8 ^{o}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.**

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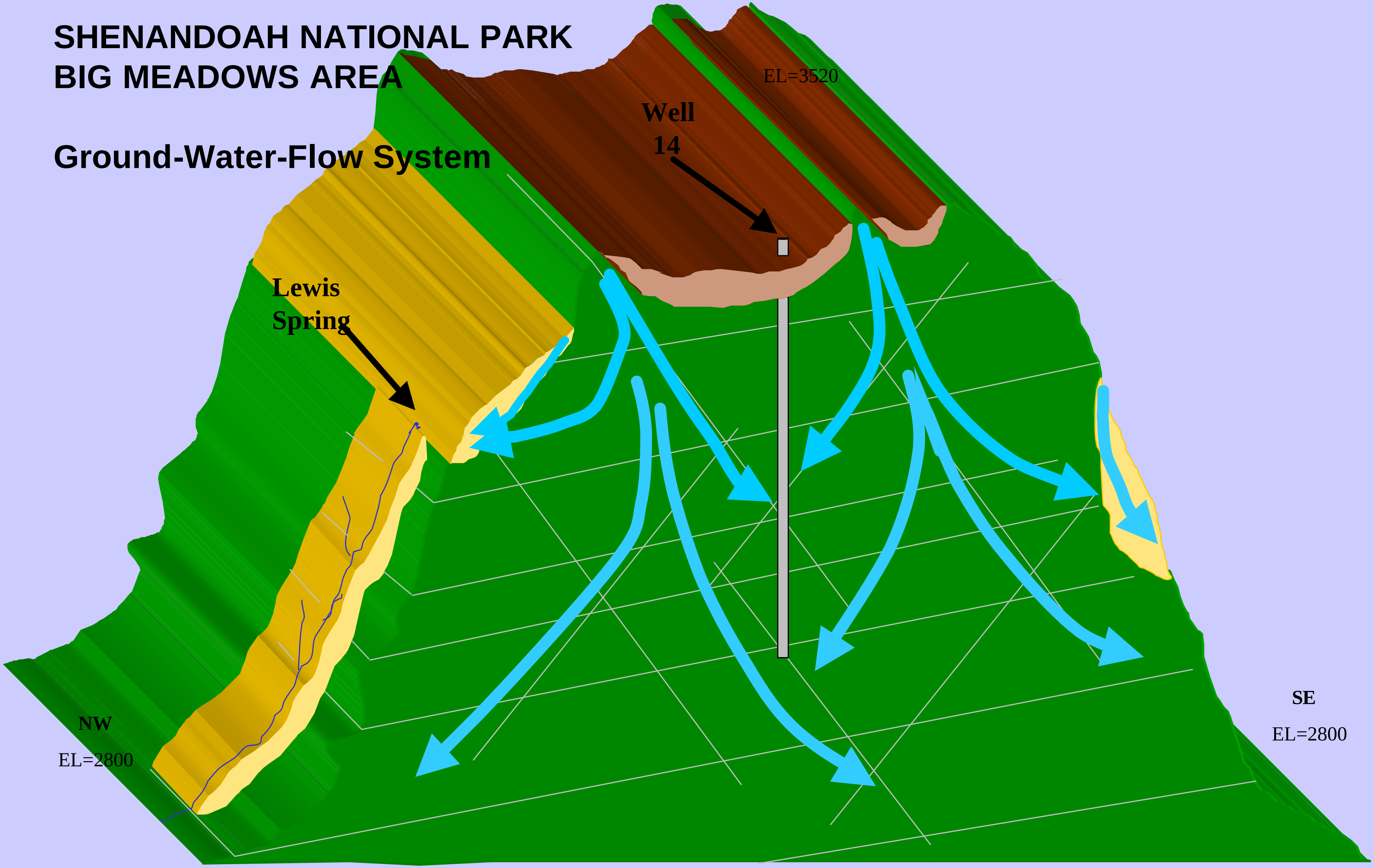
SHENANDOAH NATIONAL PARK
BIG MEADOWS AREA

Ground-Water-Flow System



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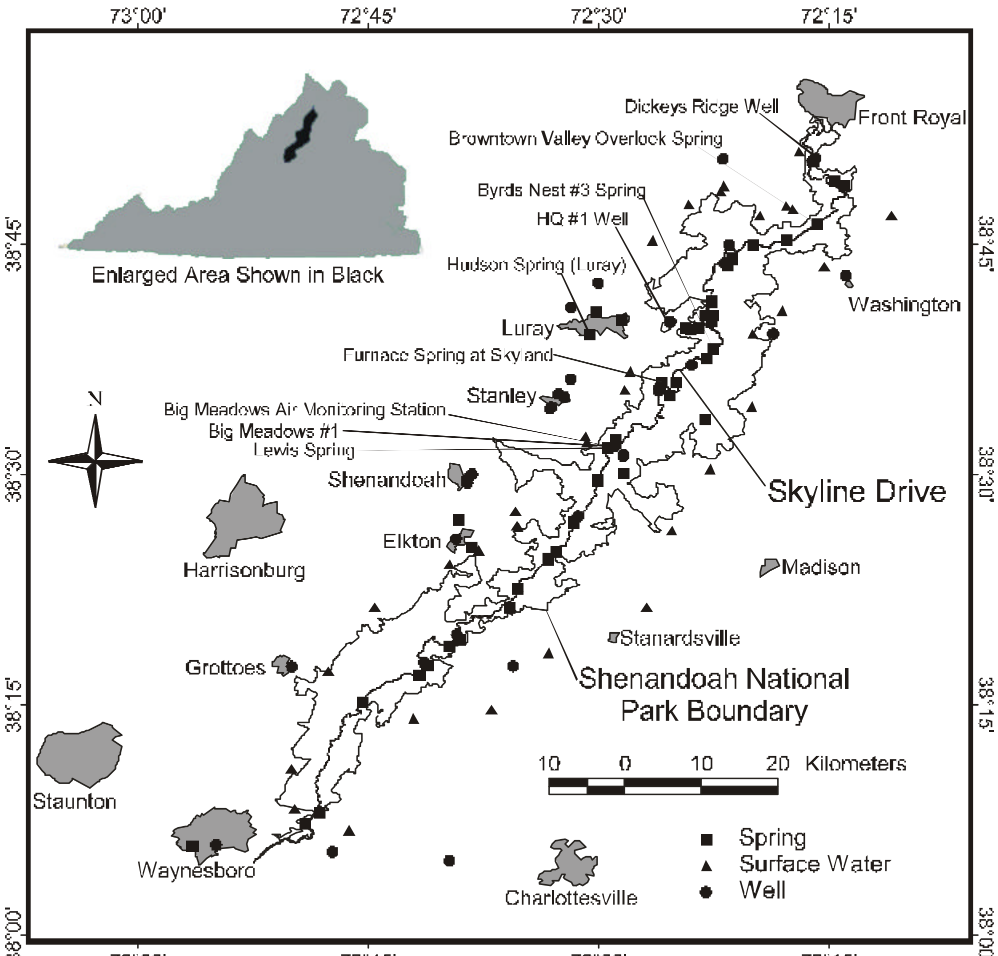
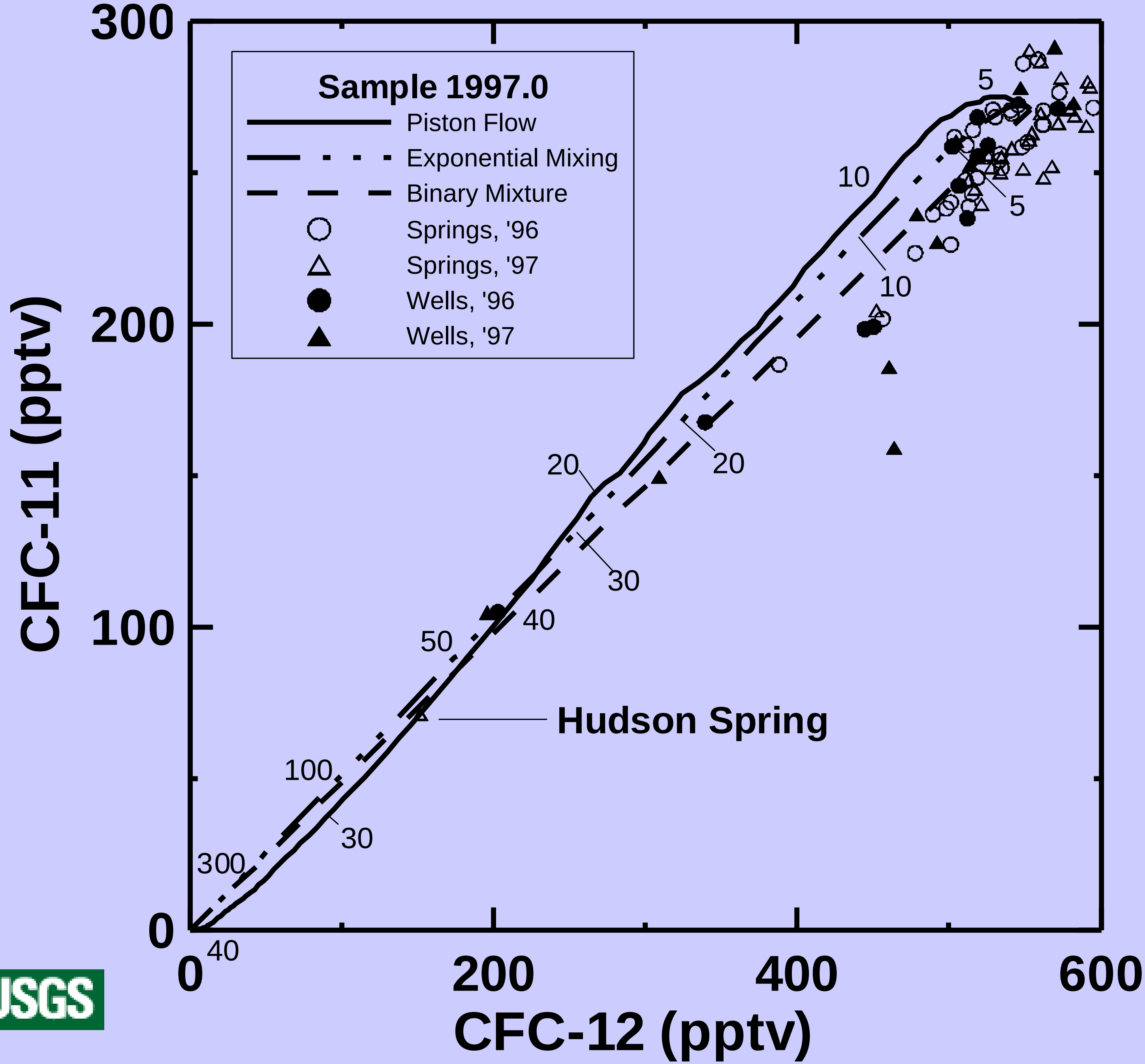
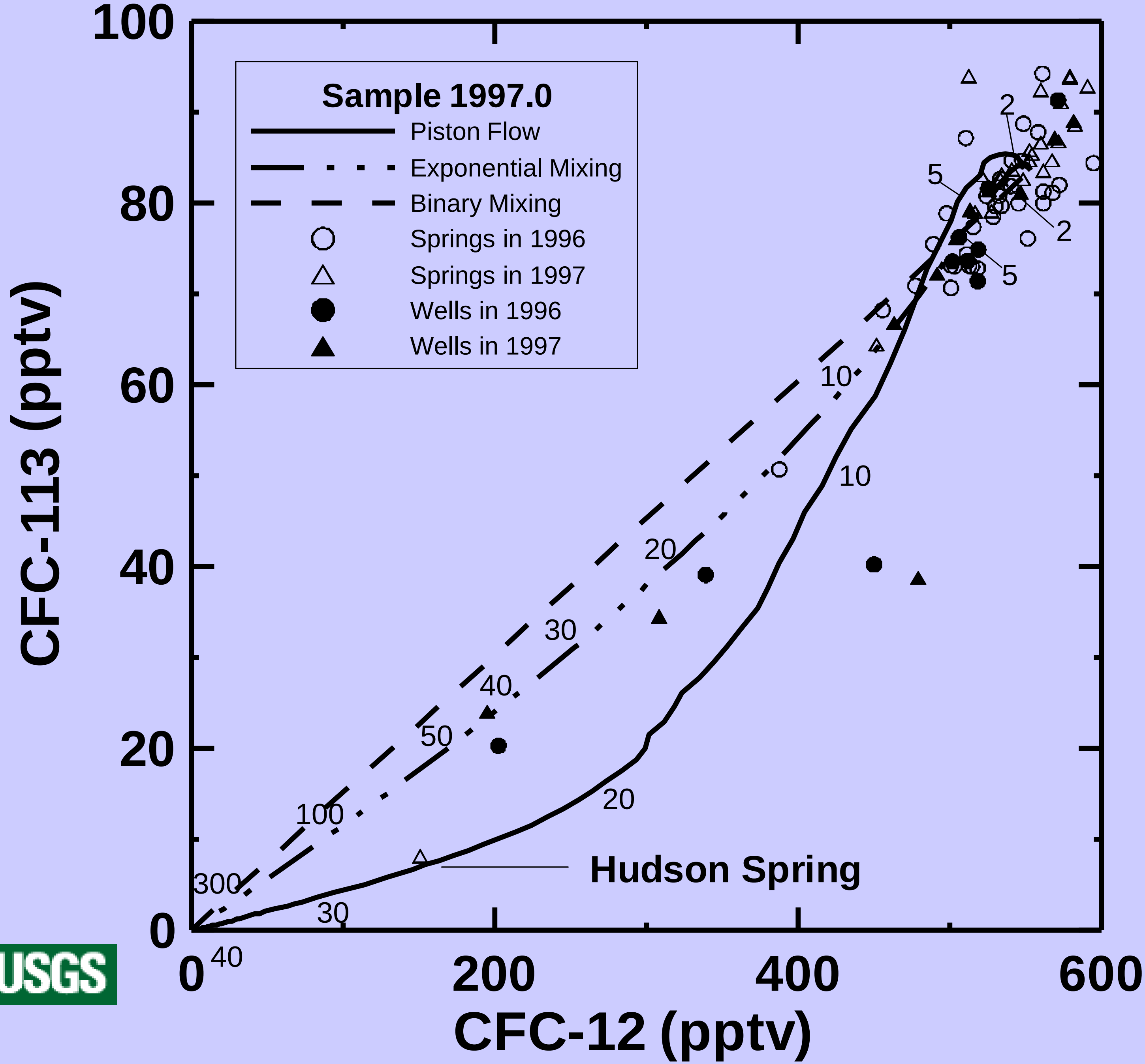


73°00'
72°45'
72°30'
72°15'
38°45'
38°30'
38°15'
38°00'
Enlarged Area Shown in Black
Dickeys Ridge Well
Front Royal
Browntown Valley Overlook Spring
Byrds Nest #3 Spring
HQ #1 Well
Hudson Spring (Luray)
Washington
Luray
Furnace Spring at Skyland
Stanley
Big Meadows Air Monitoring Station
Big Meadows #1
Lewis Spring
Shenandoah
Skyline Drive
Harrisonburg
Elkton
Madison
Stanardsville
Grottoes
Shenandoah National
Park Boundary
10 0 10 20 Kilometers
Staunton
Waynesboro
Charlottesville
Spring
Surface Water
Well
N

Lewis Mountain Spring

Sampling from a Typical
Spring Box and Weir


Sample 1997.0
Piston Flow
Exponential Mixing
Binary Mixture
Springs, '96
Springs, '97
Wells, '96
Wells, '97
Hudson Spring
CFC-11 (pptv)
CFC-12 (pptv)
0
100
200
300
400
600
5
10
20
30
40
50
100
300



Sample 1997.0
Piston Flow
Exponential Mixing
Binary Mixing
Springs in 1996
Springs in 1997
Wells in 1996
Wells in 1997
Hudson Spring
CFC-113 (pptv)
CFC-12 (pptv)
0
20
40
60
80
100
200
400
600
300
100
50
40
30
20
10
5
2
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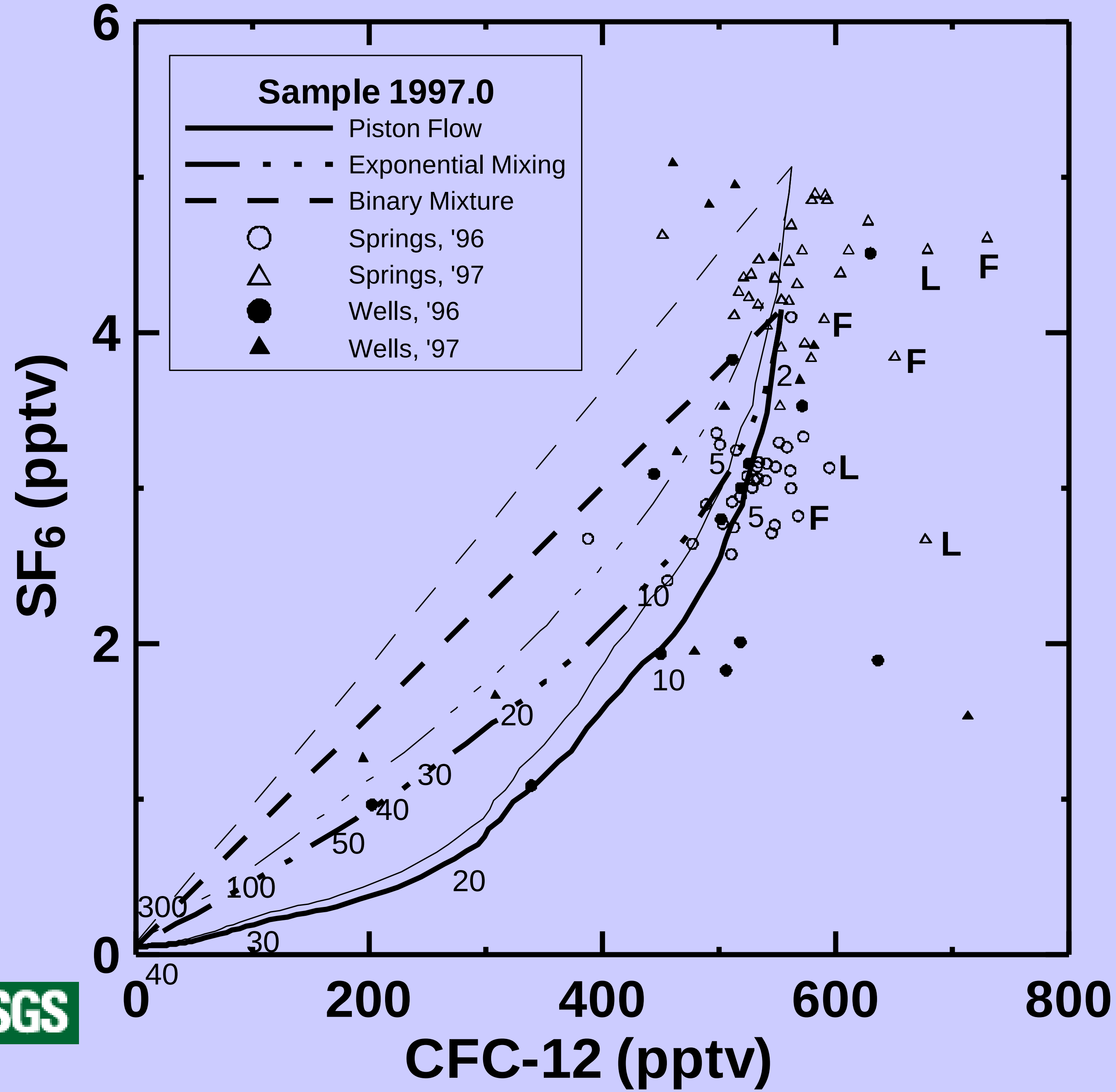

Sample 1997.0
Piston Flow
Exponential Mixing
Binary Mixture
Springs, '96
Springs, '97
Wells, '96
Wells, '97
SF6 (pptv)
CFC-12 (pptv)
0
2
4
6
0
200
400
600
800
300
100
50
40
30
20
10
5
2
30
40
20
10
5
L
F

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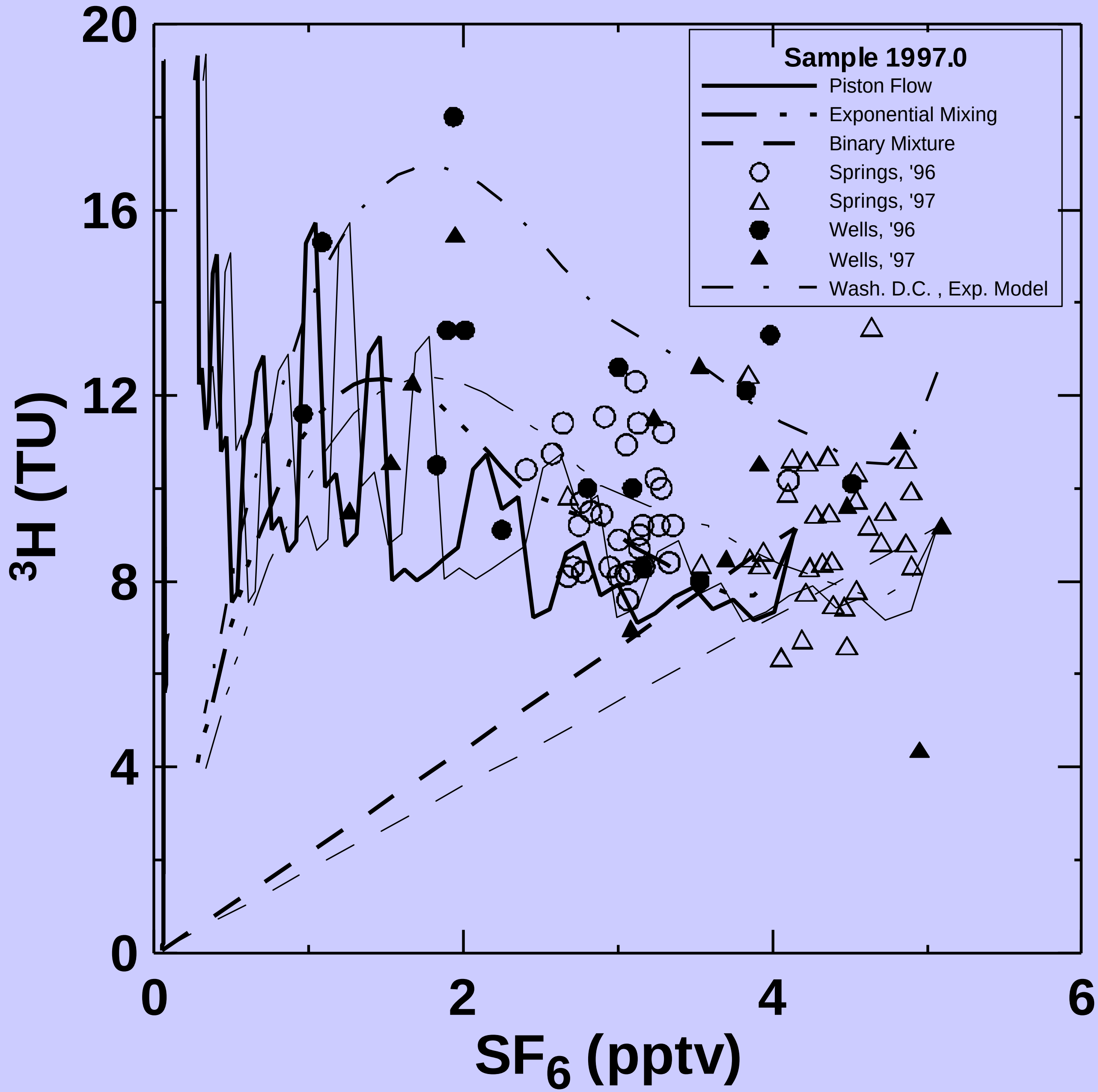

Two ^3H input functions:

- Wash. DC (upper)
- Wash. DC scaled to SNP (lower)

Also 0-2 cc/L of excess air

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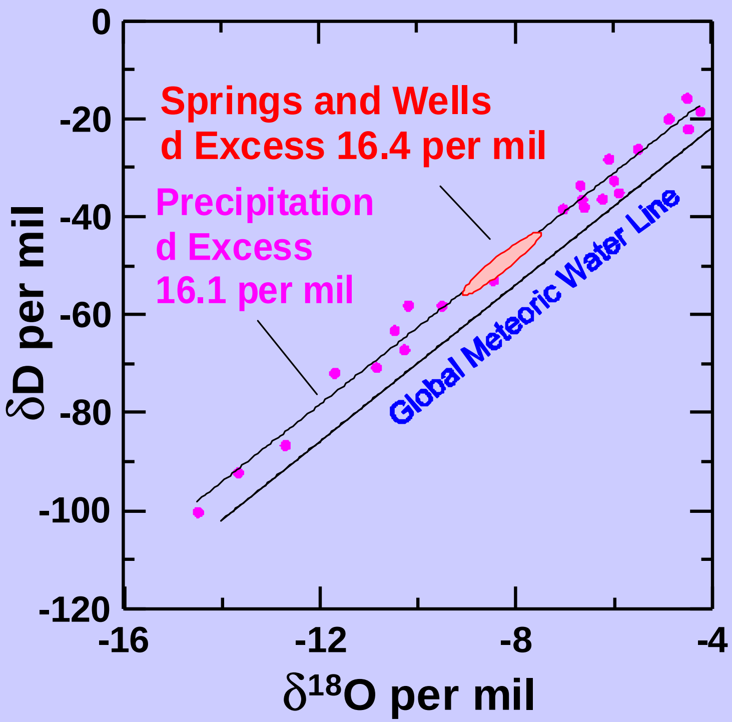

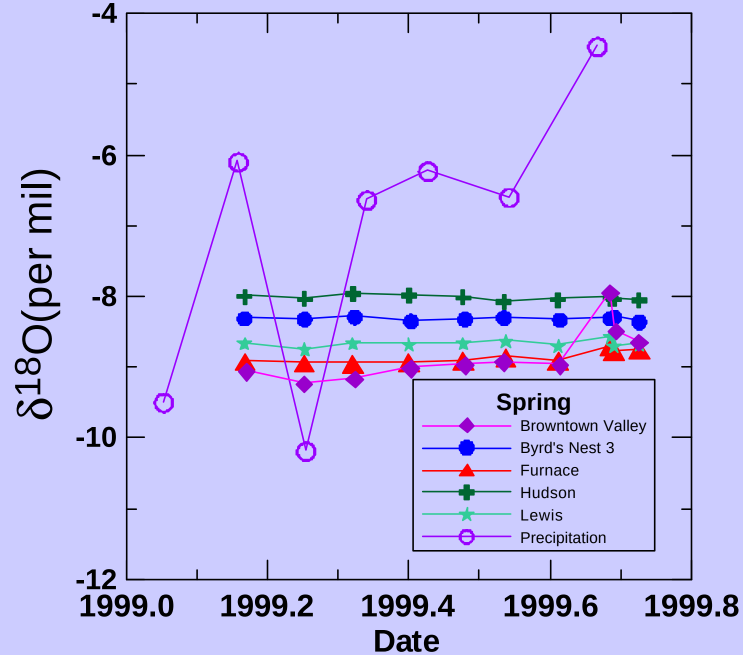

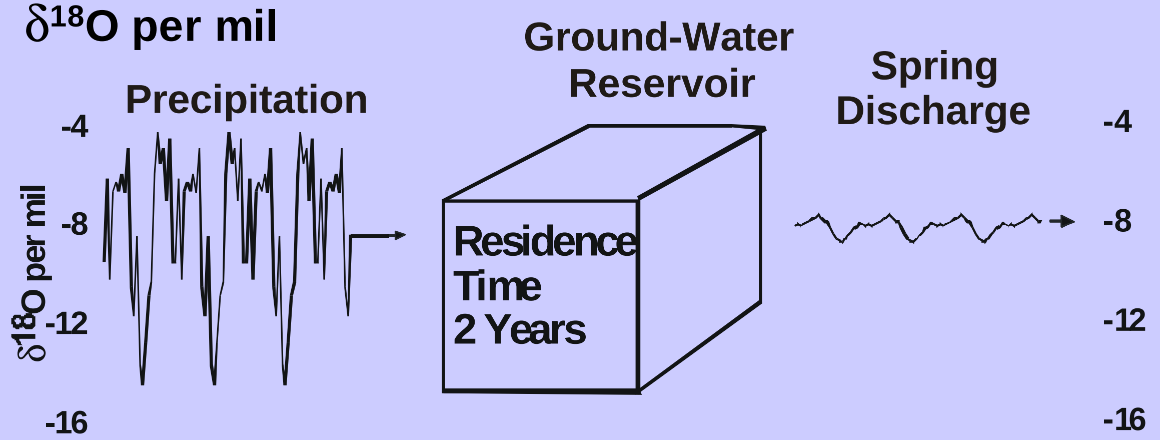

Average -8.2 per mil
Amplitude 9.6 per mil
Std. Dev. 2.8 per mil

Average -8.2 per mil
Amplitude1.1 per mil
Std. Dev. 0.3 per mil

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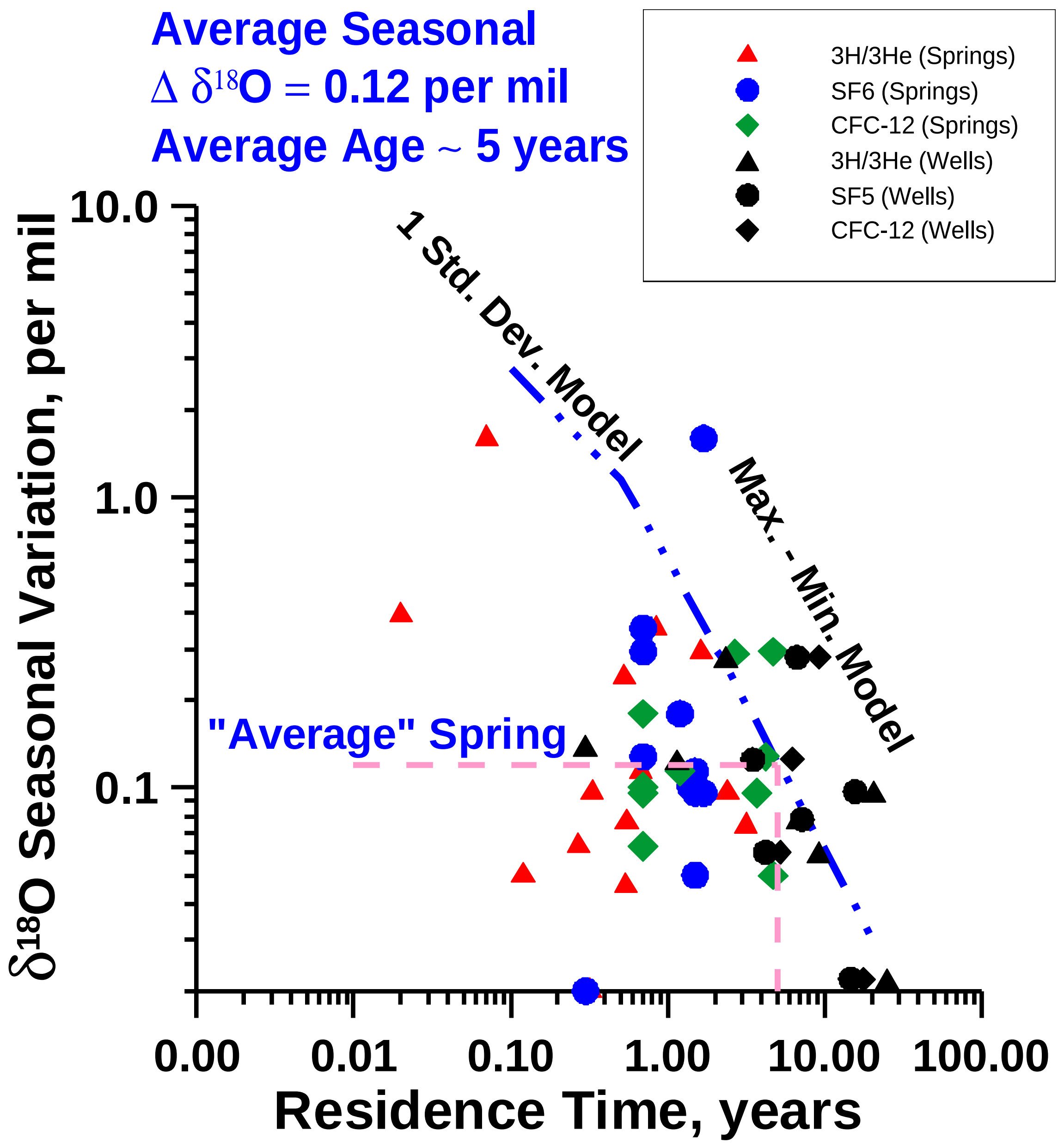

Average Seasonal
Δ δ18O = 0.12 per mil
Average Age ~ 5 years
3H/3He (Springs)
SF6 (Springs)
CFC-12 (Springs)
3H/3He (Wells)
SF5 (Wells)
CFC-12 (Wells)
1 Std. Dev. Model
Max. - Min. Model
"Average" Spring
10.0
1.0
0.1
δ18O Seasonal Variation, per mil
0.00
0.01
0.10
1.00
10.00
100.00
Residence Time, years
USGS

Conclusions from Blue Ridge (SNP)

- d ^{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 $^3H/^3He$ biased young (0-2 yrs, most 0)
- Water from wells have ages of 0 to 25 yrs. $^3H/^3He$ 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?

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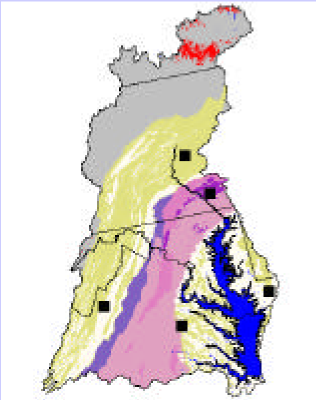
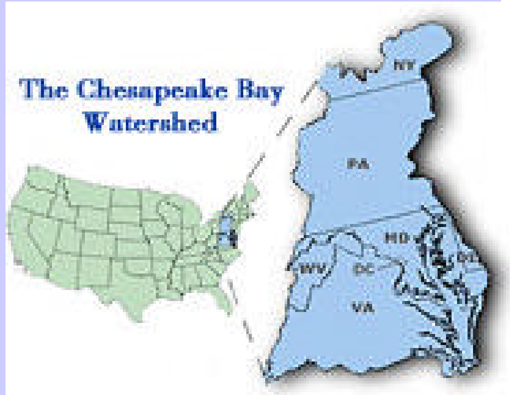




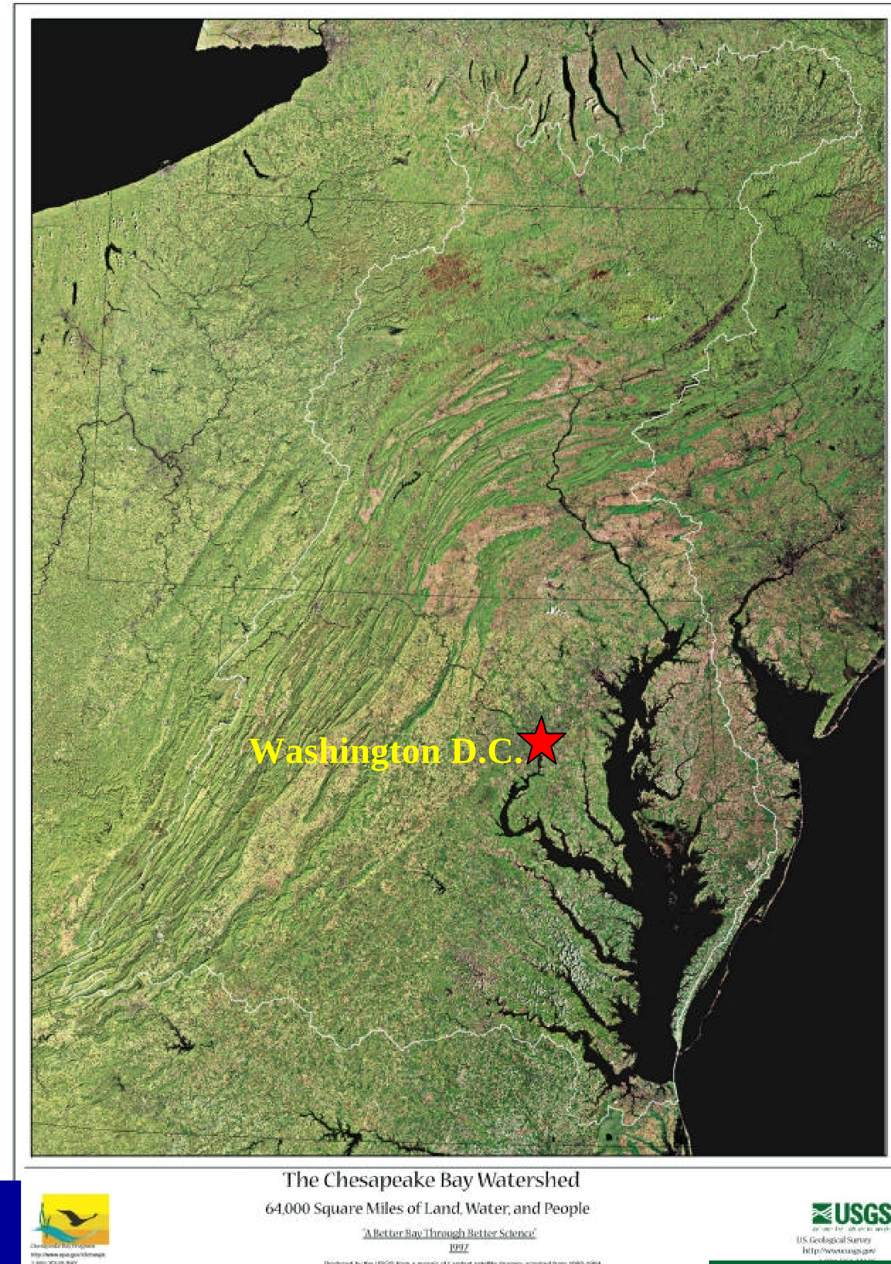
Chesapeake Bay Watershed

Region of 165,000 km^2 over parts of NY, PA, MD, DE, VA, and WV.

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

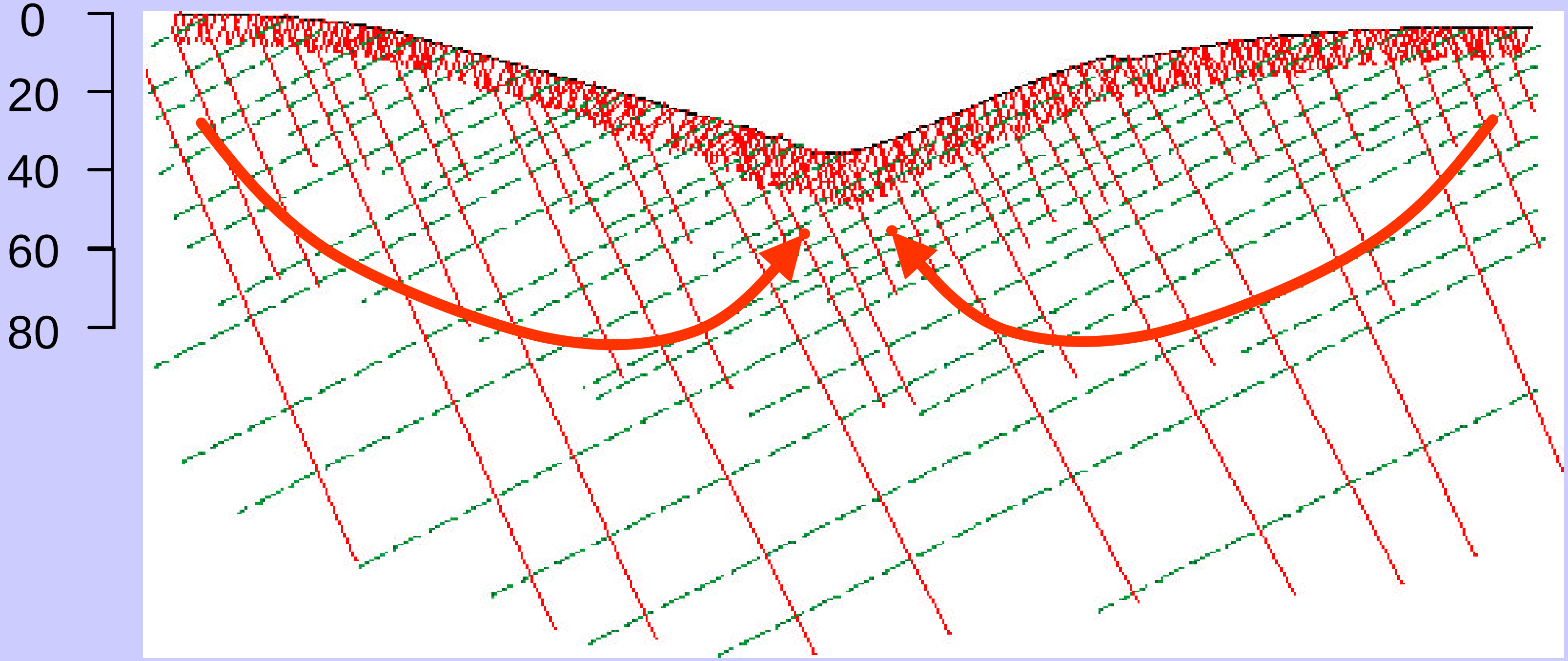
Assess lag time between changes at the land surface and the response in the base-flow component of groundwater discharge to the bay.

Lindsey and others, 2003, USGS WRIR 03-4035, http://pa.water.usgs.gov/reports/wrir03-4035.pdf

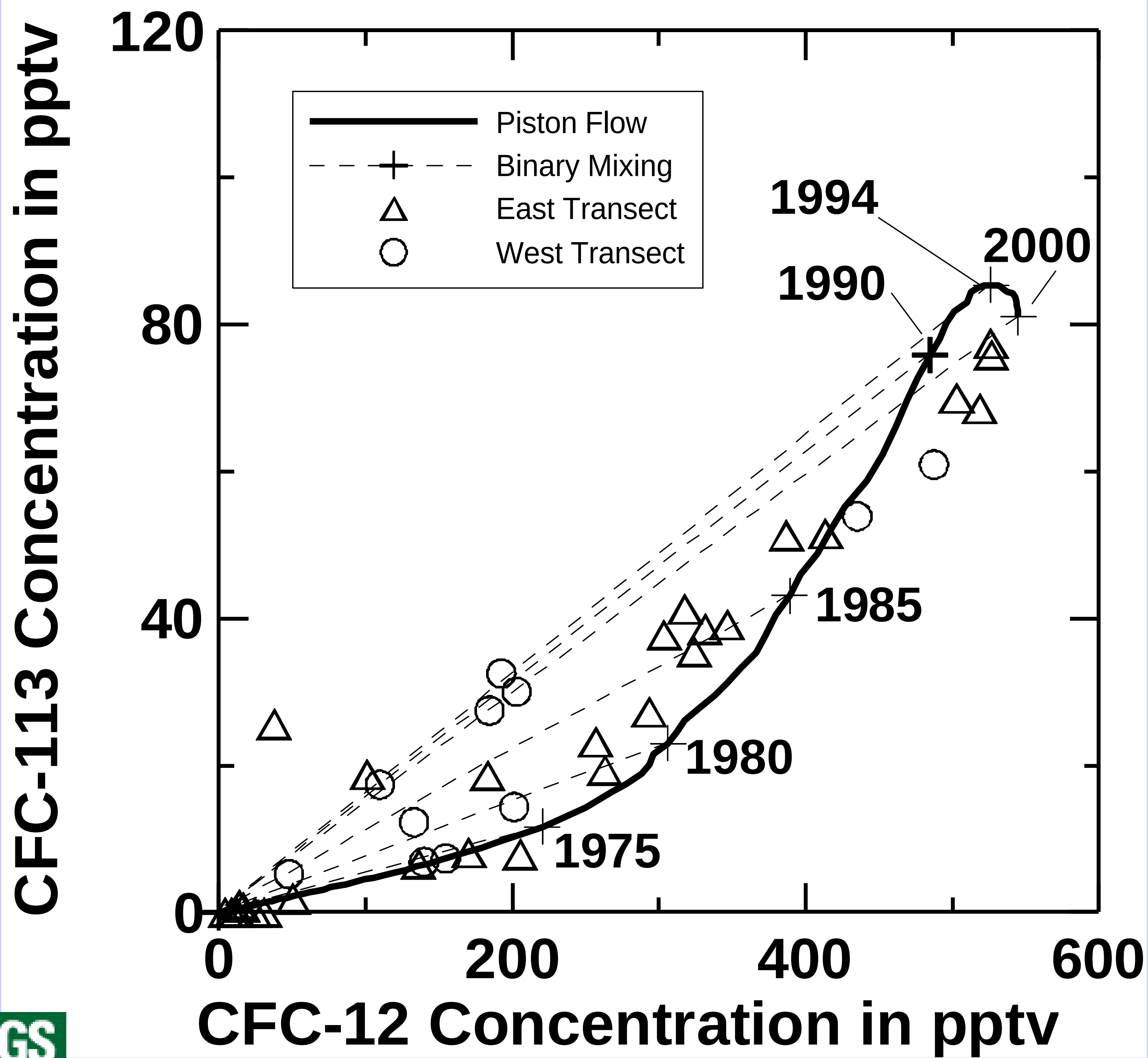


Layered fracture density model

(Gburek, Folmar, and Urban (1998)



Burton et al. 2002



CFC-113 Concentration in pptv
CFC-12 Concentration in pptv
Piston Flow
Binary Mixing
East Transect
West Transect
1975
1980
1985
1990
1994
2000
0
40
80
120
0
200
400
600

East Piezometer Transect

--Preferred CFC-12 ages NE of stream are older...

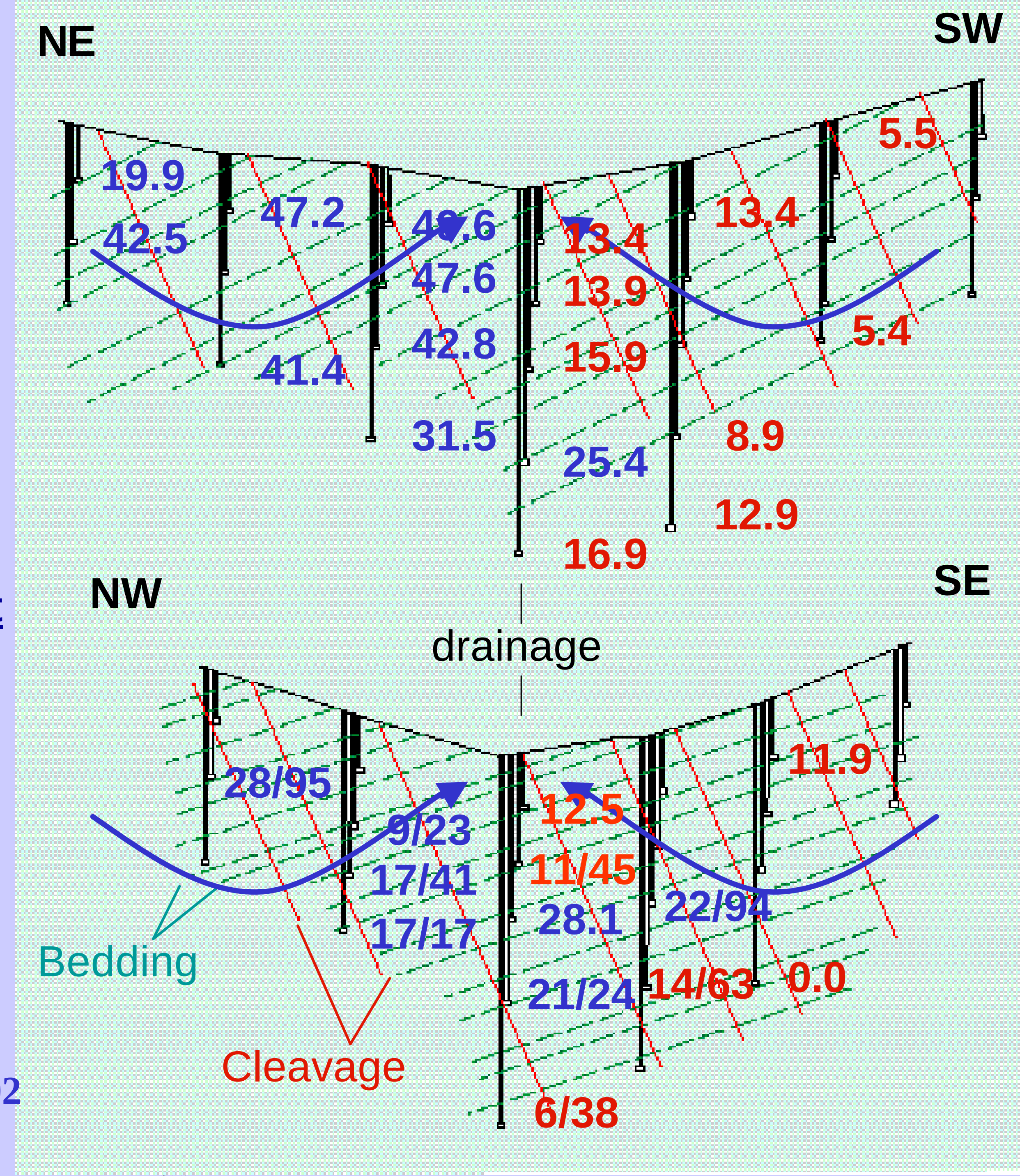
..than those underneath and SW of stream

..although these ages are really mixture ages!

West Piezometer Transect

--Ages are even more mixed, but % of young water (2nd #) shows older waters generally prevailing to NW

…and younger to SE



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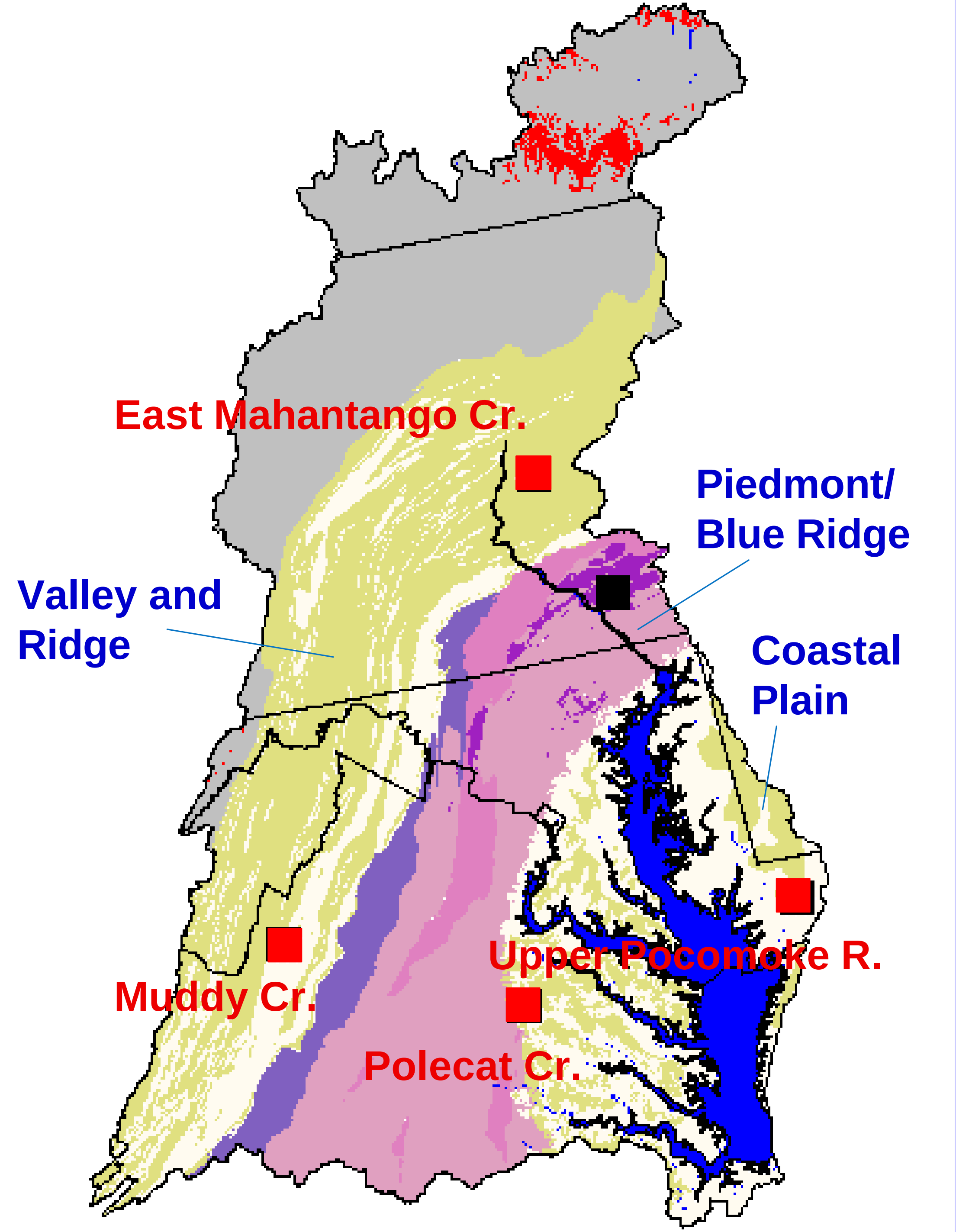
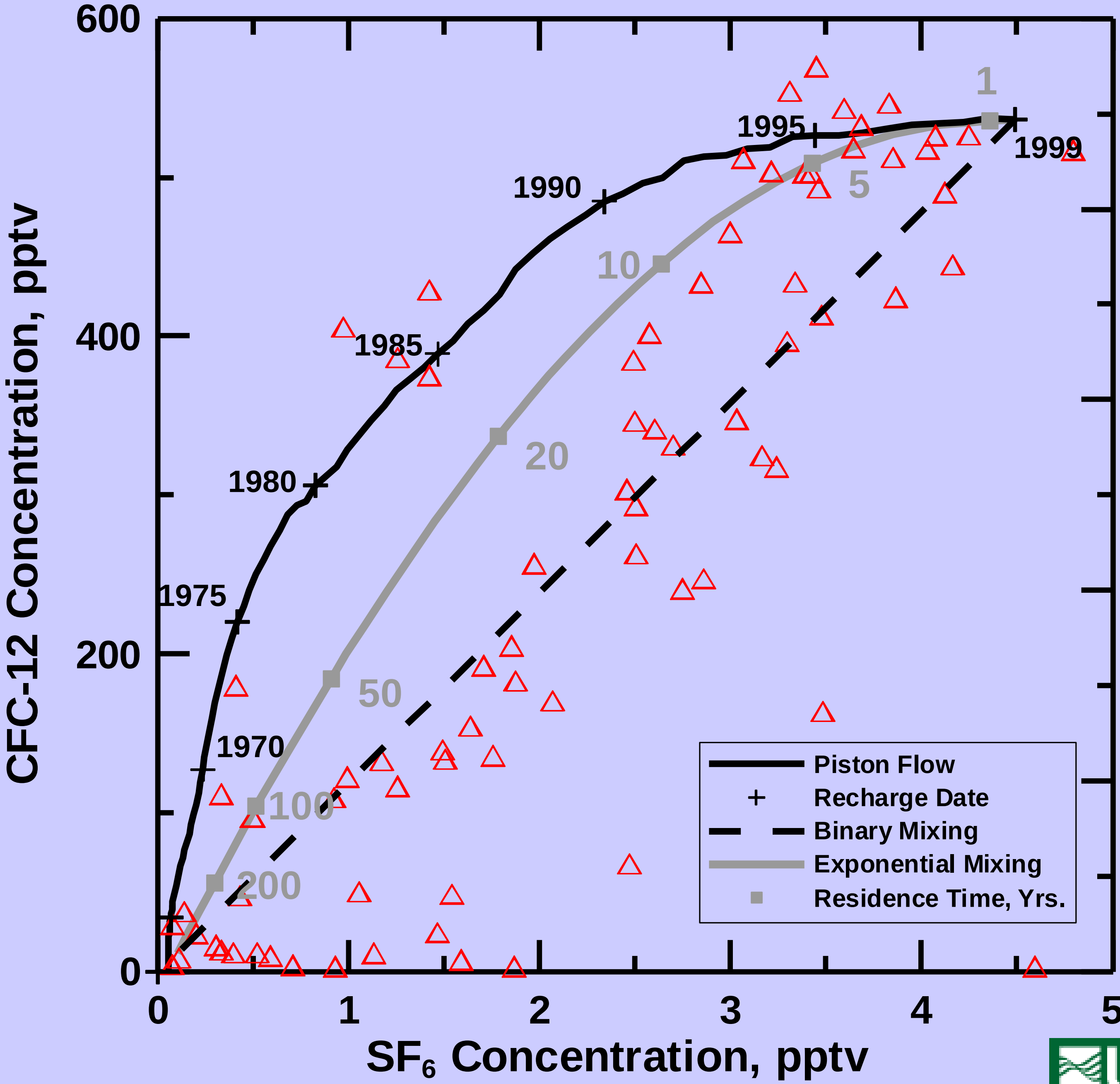
Burton et al. 2002

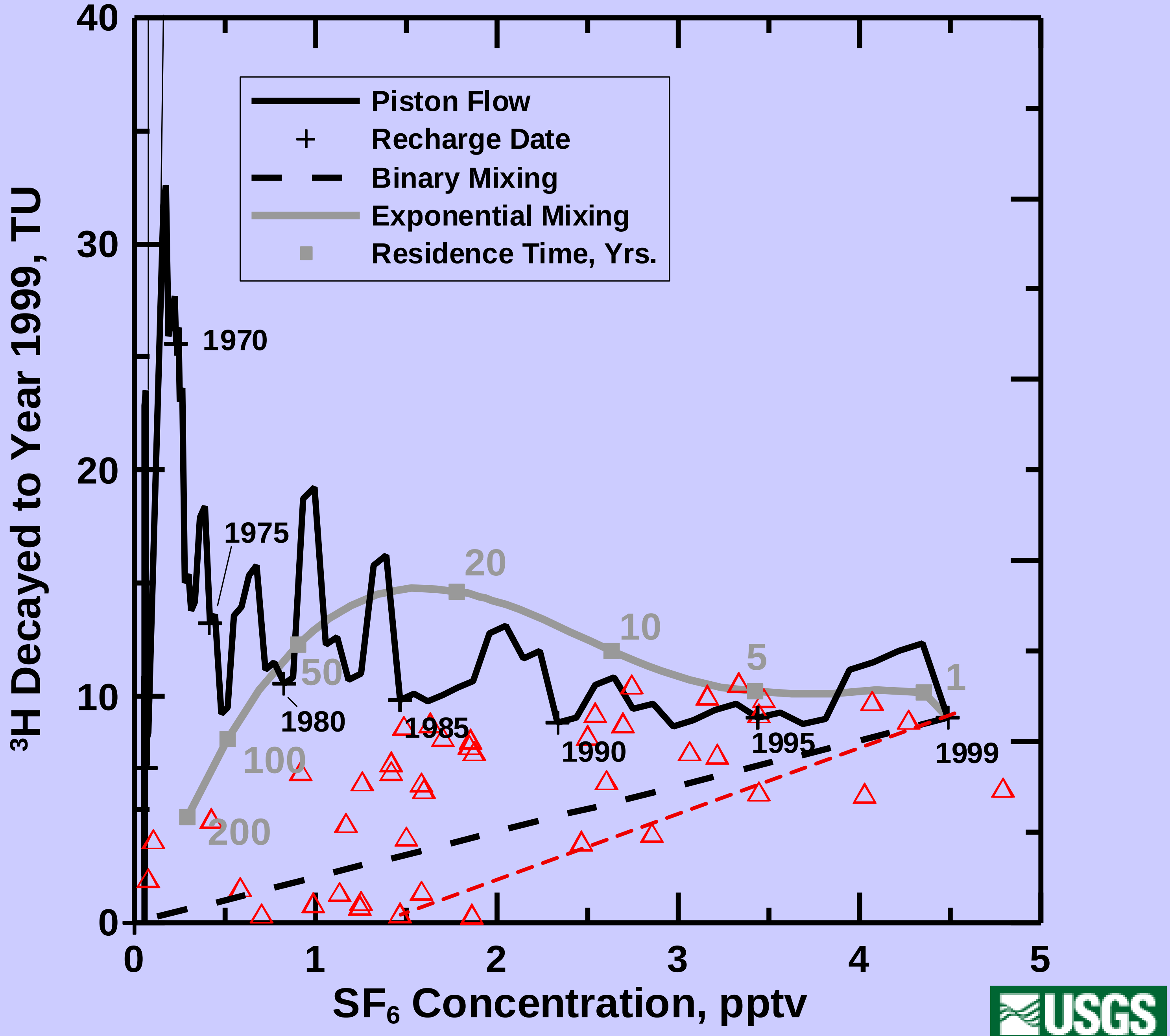
USGS Chesapeake Bay watershed nutrient study

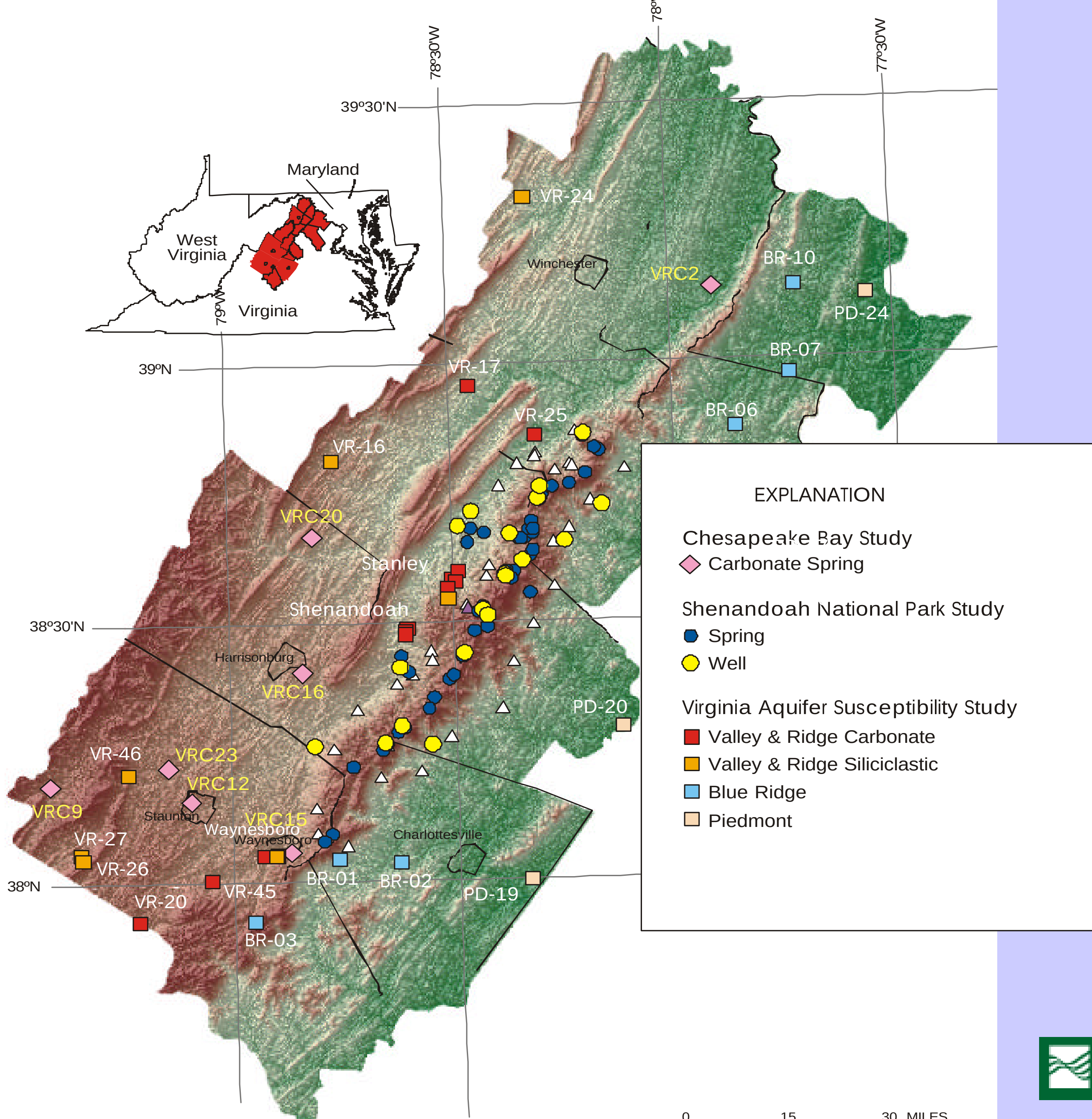
- SF_6 vs ^3H, CFCs
- Monitoring wells, springs from watersheds





600
400
200
0
0
1
2
3
4
5
CFC-12 Concentration, pptv
SF6 Concentration, pptv
1970
1975
1980
1985
1990
1995
1999
1
5
10
20
50
100
200
Piston Flow
Recharge Date
Binary Mixing
Exponential Mixing
Residence Time, Yrs.
USGS


Piston Flow
Recharge Date
Binary Mixing
Exponential Mixing
Residence Time, Yrs.
1970
1975
1980
1985
1990
1995
1999
20
10
5
1
50
100
200
0
10
20
30
40
0
1
2
3
4
5
^3H Decayed to Year 1999, TU
SF_6 Concentration, pptv
USGS



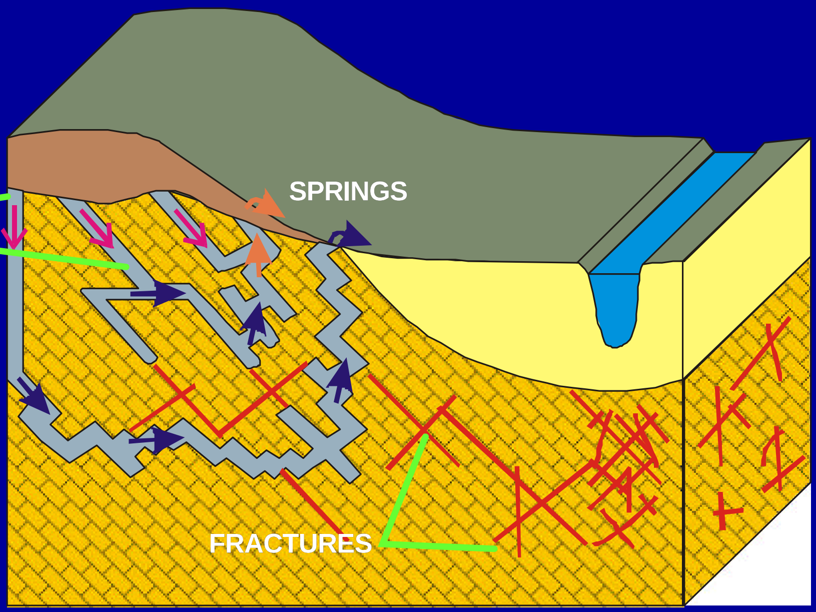
78°30'W
78°
77°30'W
39°30'N
39°N
38°30'N
38°N
79°W
Maryland
West Virginia
Virginia
VR-24
Winchester
VRC2
BR-10
PD-24
BR-07
VR-17
BR-06
VR-25
VR-16
VRC20
Stanley
Shenandoah
Harrisonburg
VRC16
PD-20
VR-46
VRC23
VRC12
VRC9
Staunton
VRC15
Waynesboro
VR-27
VR-26
Charlottesville
BR-01
BR-02
PD-19
VR-45
VR-20
BR-03
EXPLANATION
Chesapeake Bay Study
Carbonate Spring
Shenandoah National Park Study
Spring
Well
Virginia Aquifer Susceptibility Study
Valley & Ridge Carbonate
Valley & Ridge Siliciclastic
Blue Ridge
Piedmont
0 15 30 MILES

Hydrogeology of Carbonate Terranes of the Valley & Ridge Province

Soil & Regolith

Alluvium

Limestone



Younger Ground Water

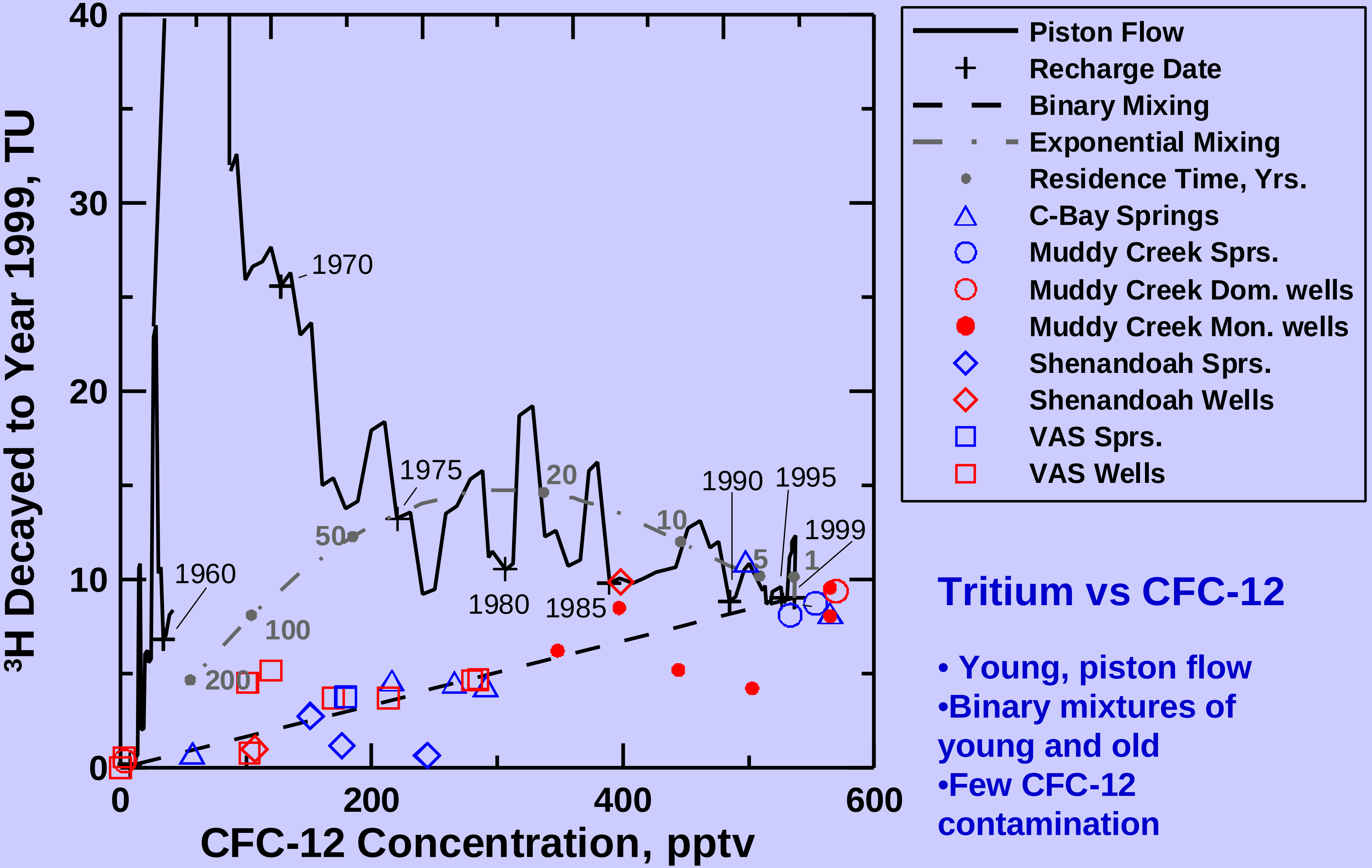
Older Ground Water

Mixture of Younger and Older Ground Water

Modified from Brahana and others, 1986

NOT TO SCALE

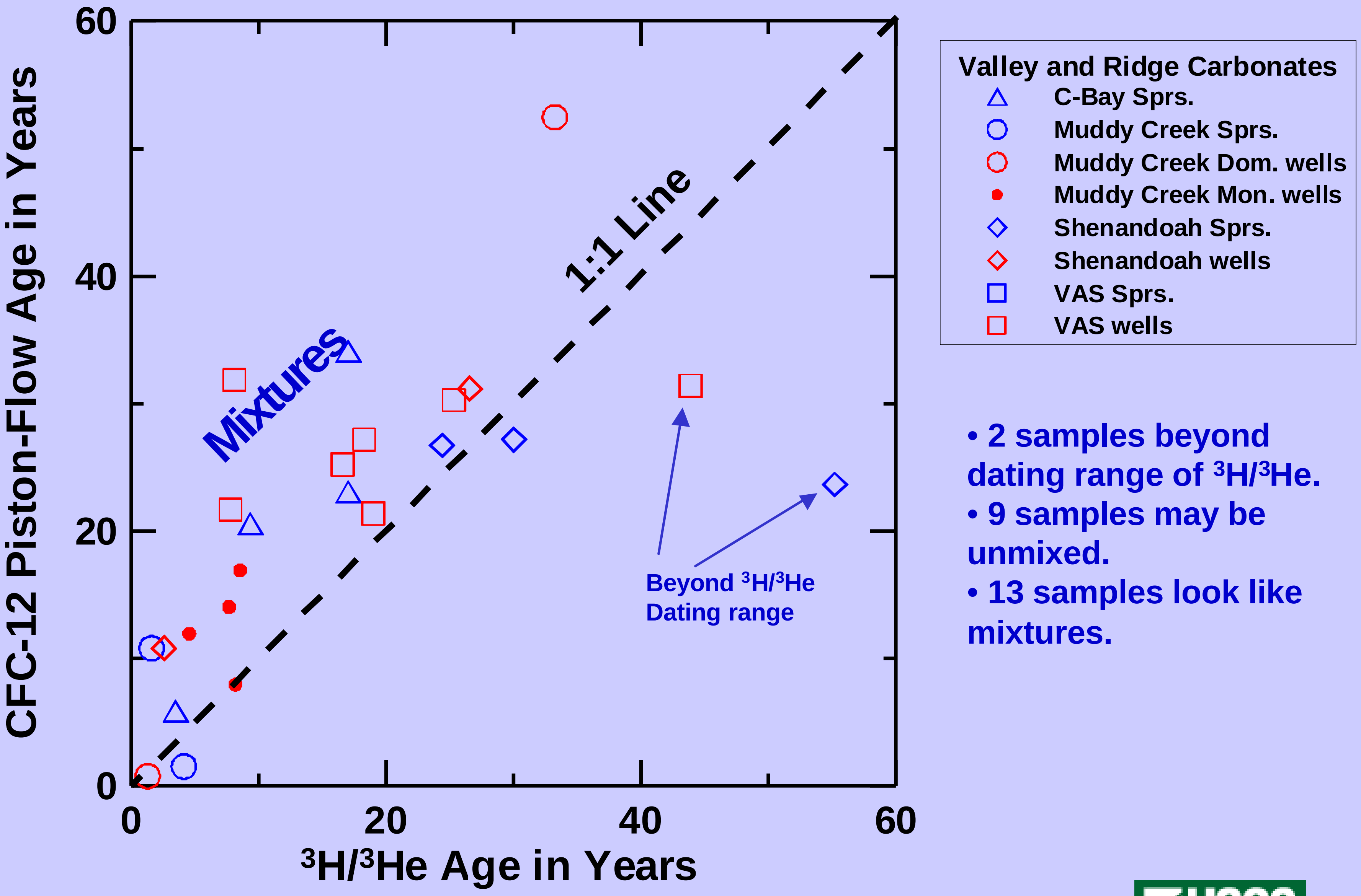
Blue Hole Spr., VA



Tritium vs CFC-12

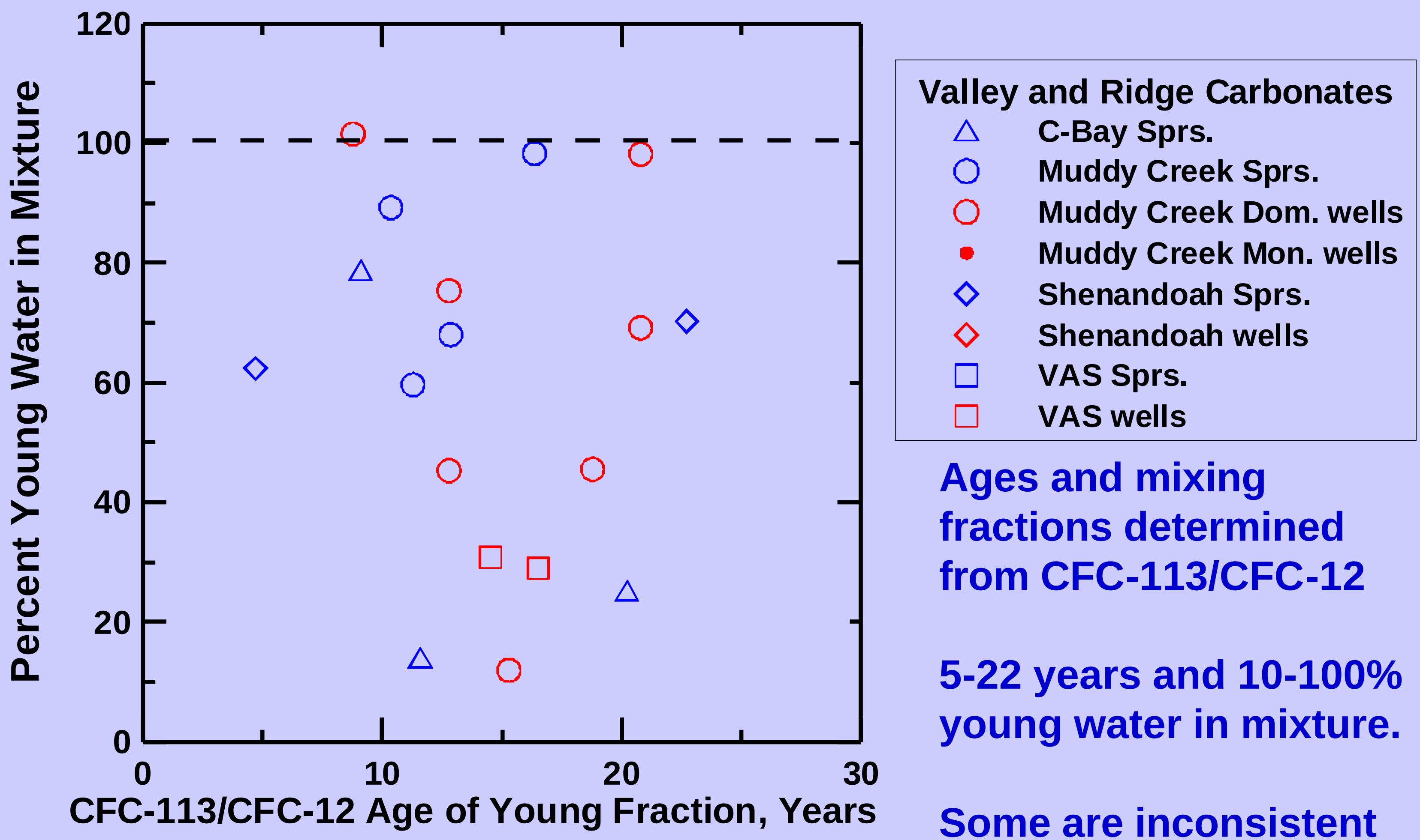
- Young, piston flow
- Binary mixtures of young and old
- Few CFC-12 contamination

USGS



- 2 samples beyond dating range of $^3H/^3He$.
- 9 samples may be unmixed.
- 13 samples look like mixtures.

USGS

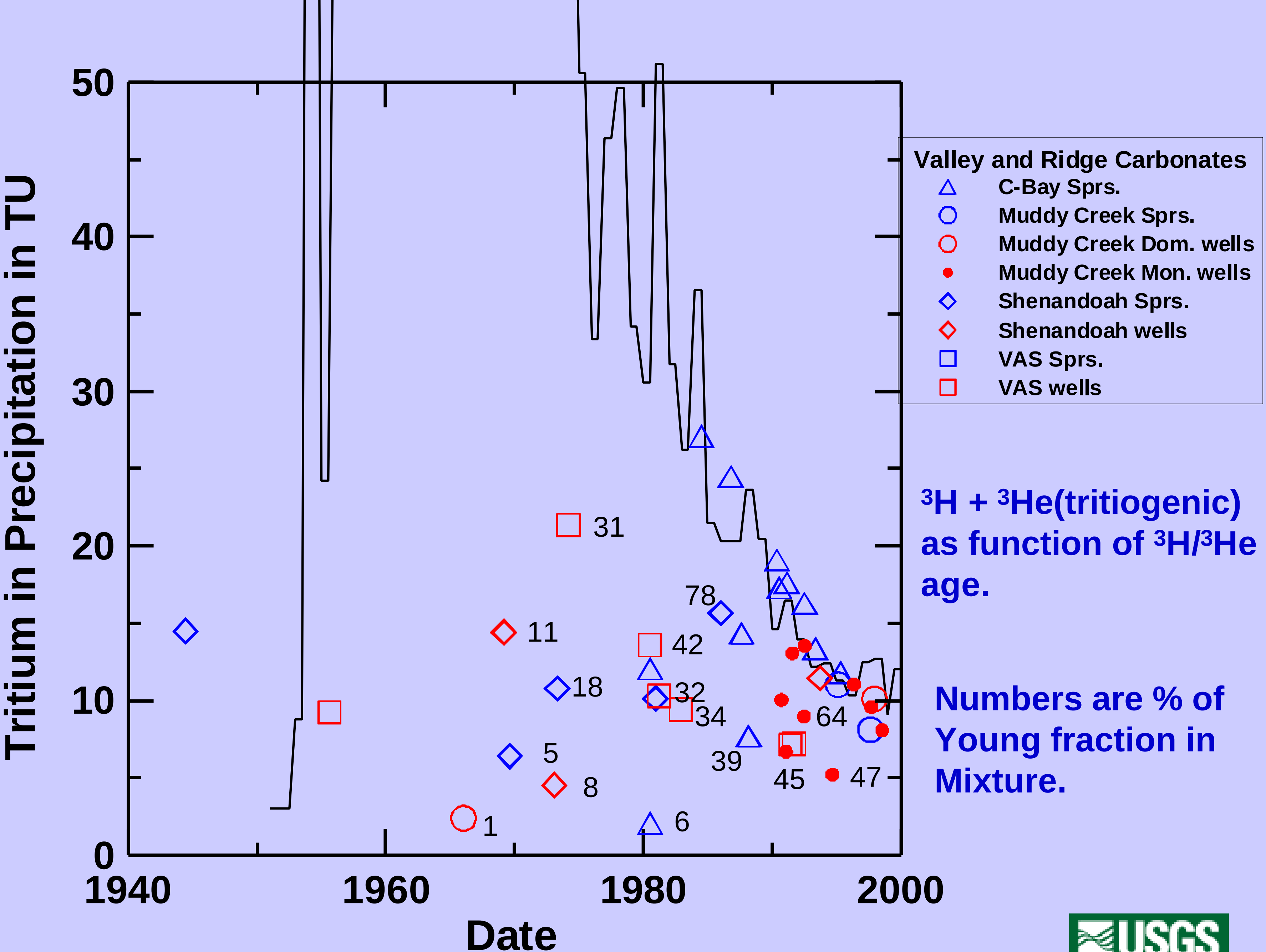


Ages and mixing fractions determined from CFC-113/CFC-12

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

Some are inconsistent with ^3H (CFC contam.)

USGS



^3H + ^3He(tritiogenic) as function of $^3H/^3He$ age.

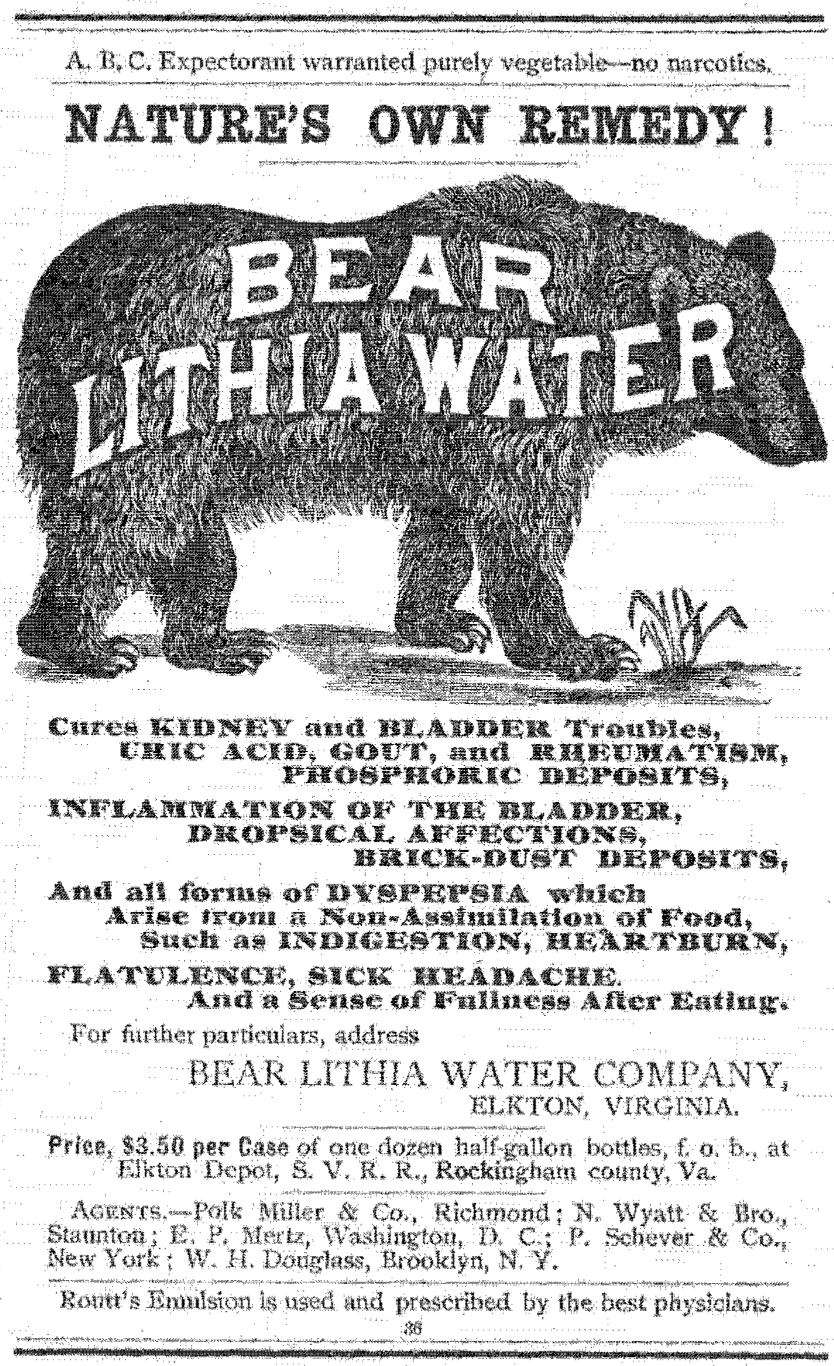
Numbers are % of Young fraction in Mixture.

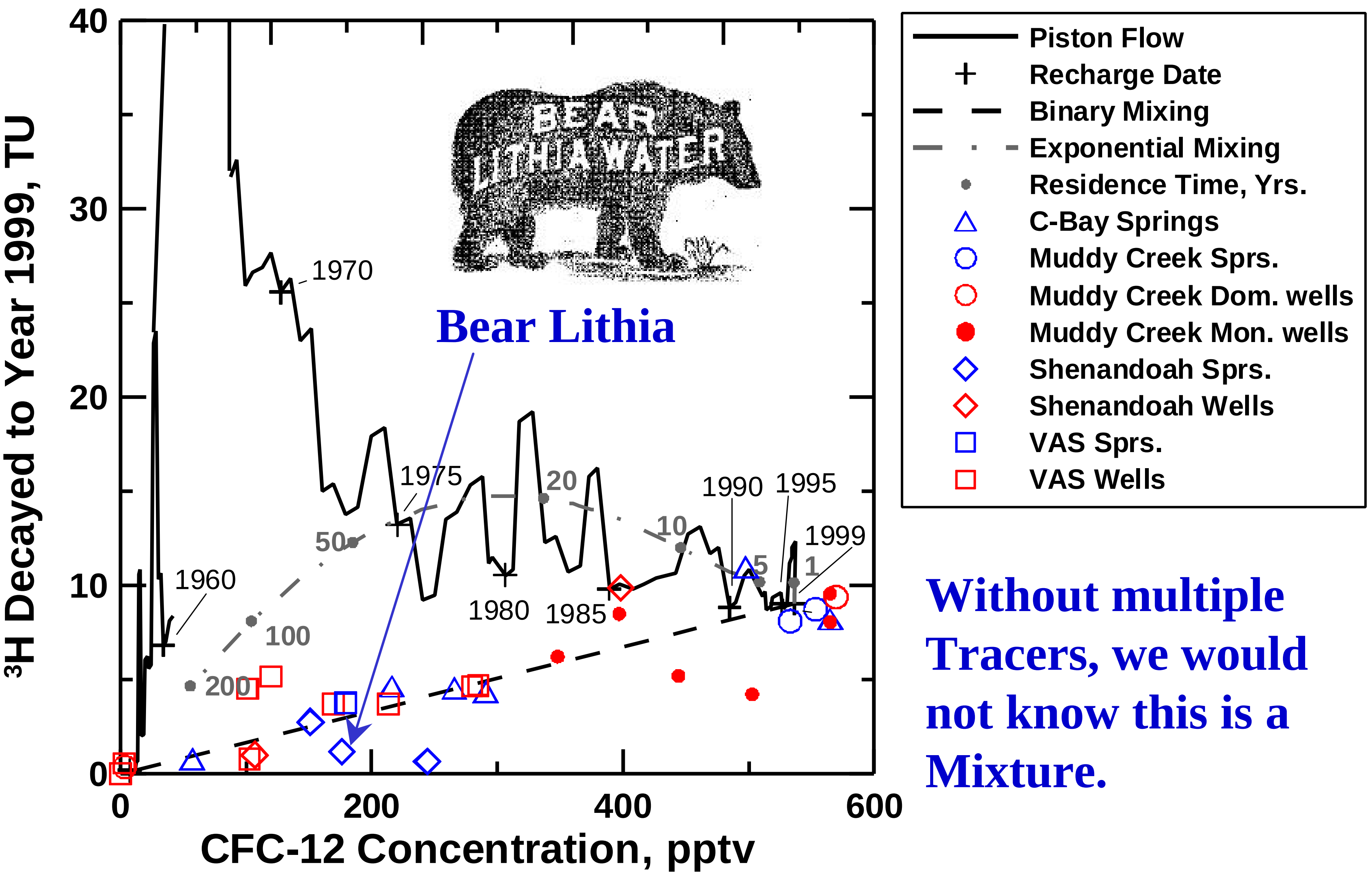
Bear Lithia Spring (9/2/99)

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



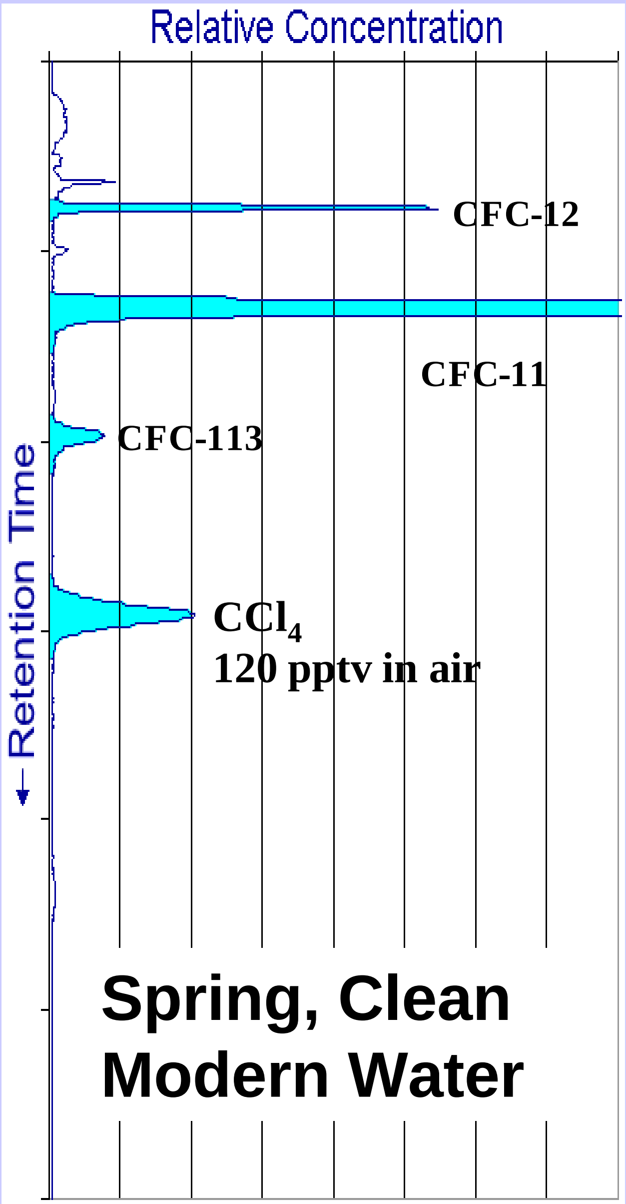


Without multiple Tracers, we would not know this is a Mixture.

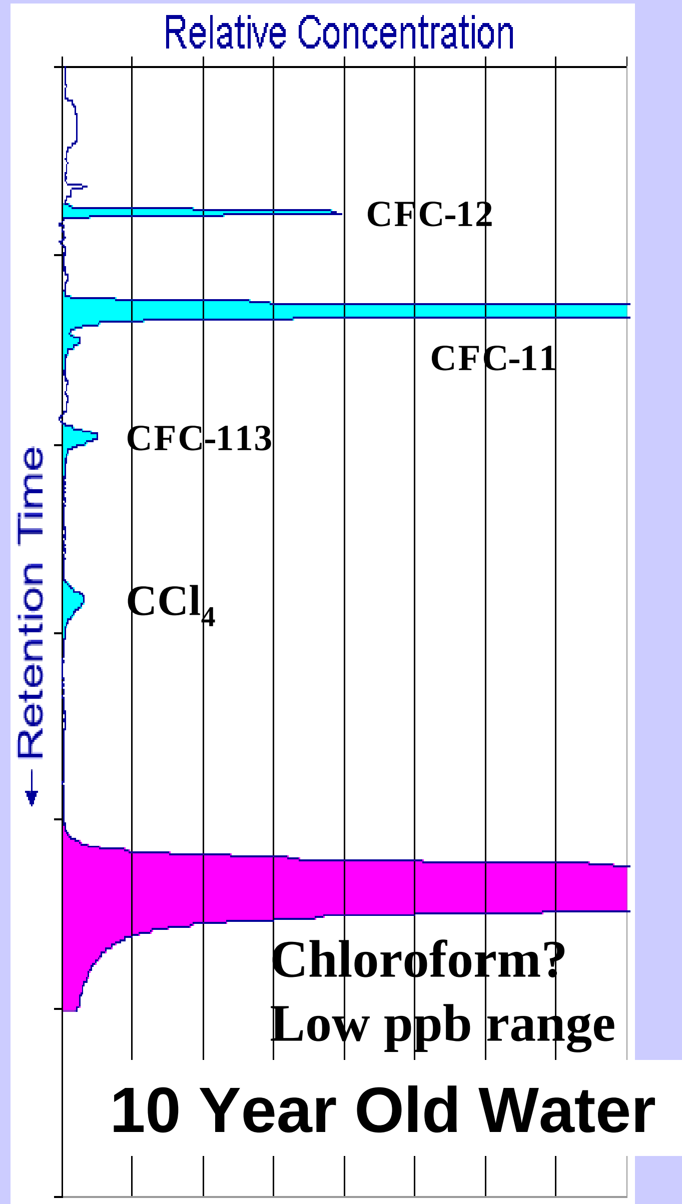
GC-ECD Chromatograms

- Analysis by GC-ECD: Purge and trap gas chromatography with electron-capture detector.
- Detects halogenated VOCs (examples: CFCs, CCl_4, 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

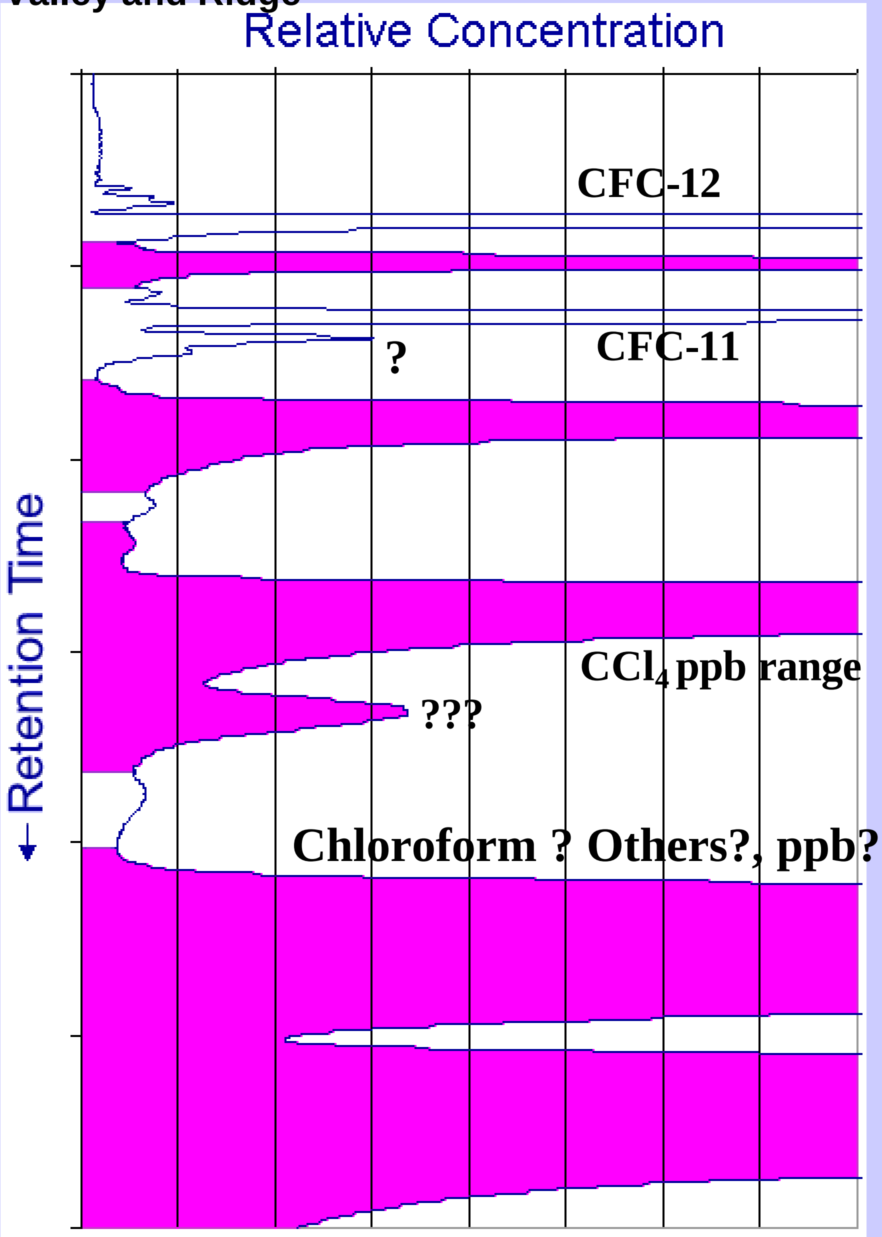


Spring
Yorktown, VA
Drinking Water

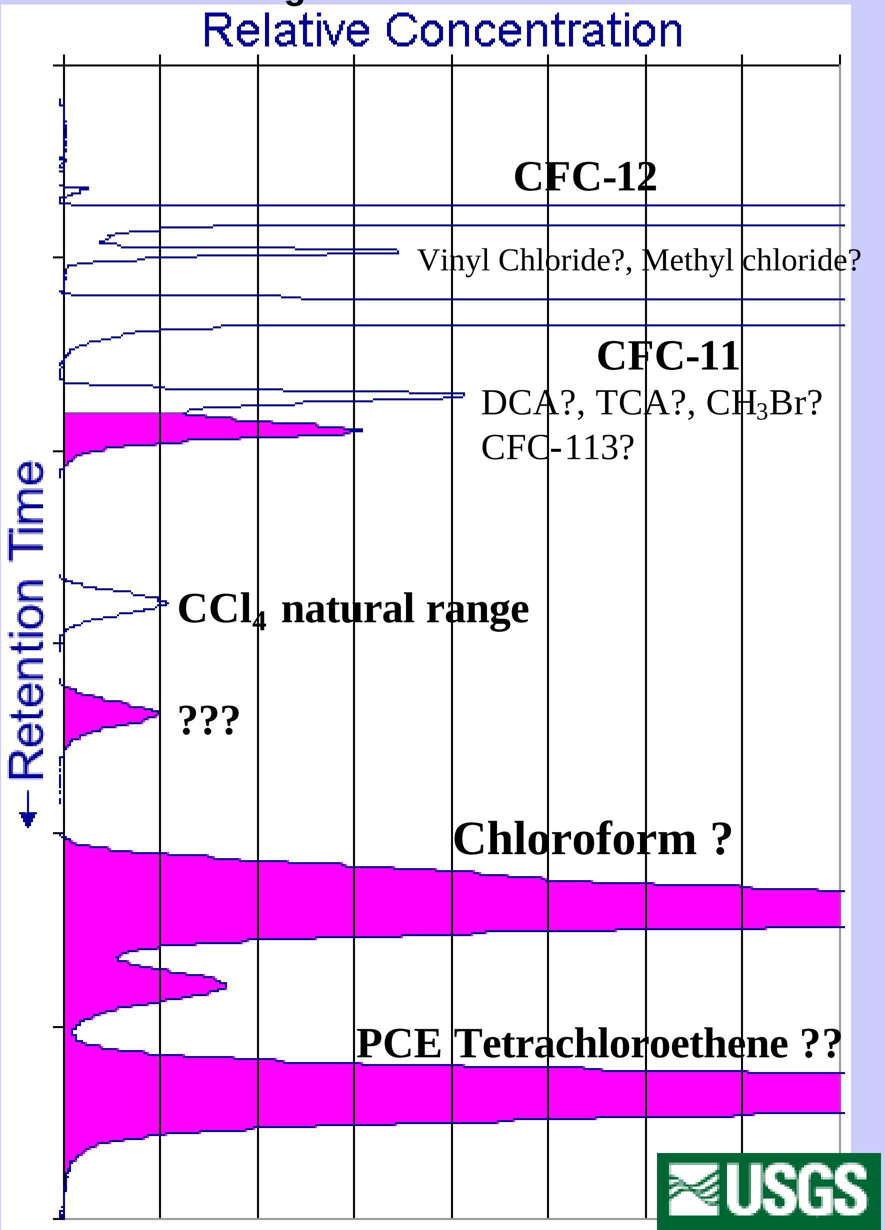


A Town well in VA
Drinking Water Well
Depth: 190 meters
Valley and Ridge

Vulnerable, fingerprints
of sources of contamination

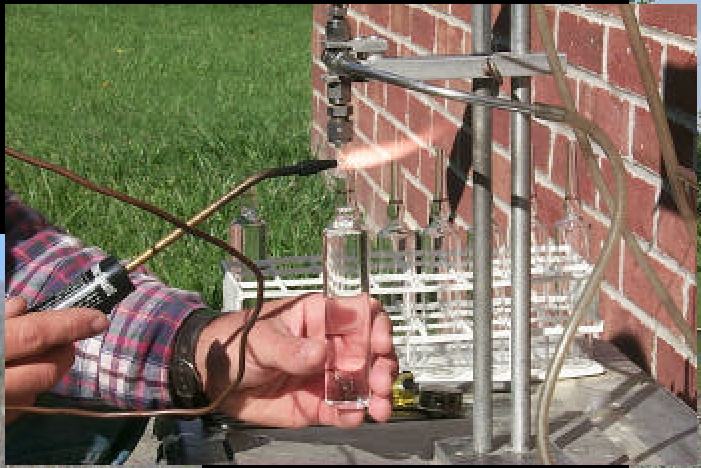


A Town well in VA
Drinking Water Well
Depth: 115 meters
Blue Ridge



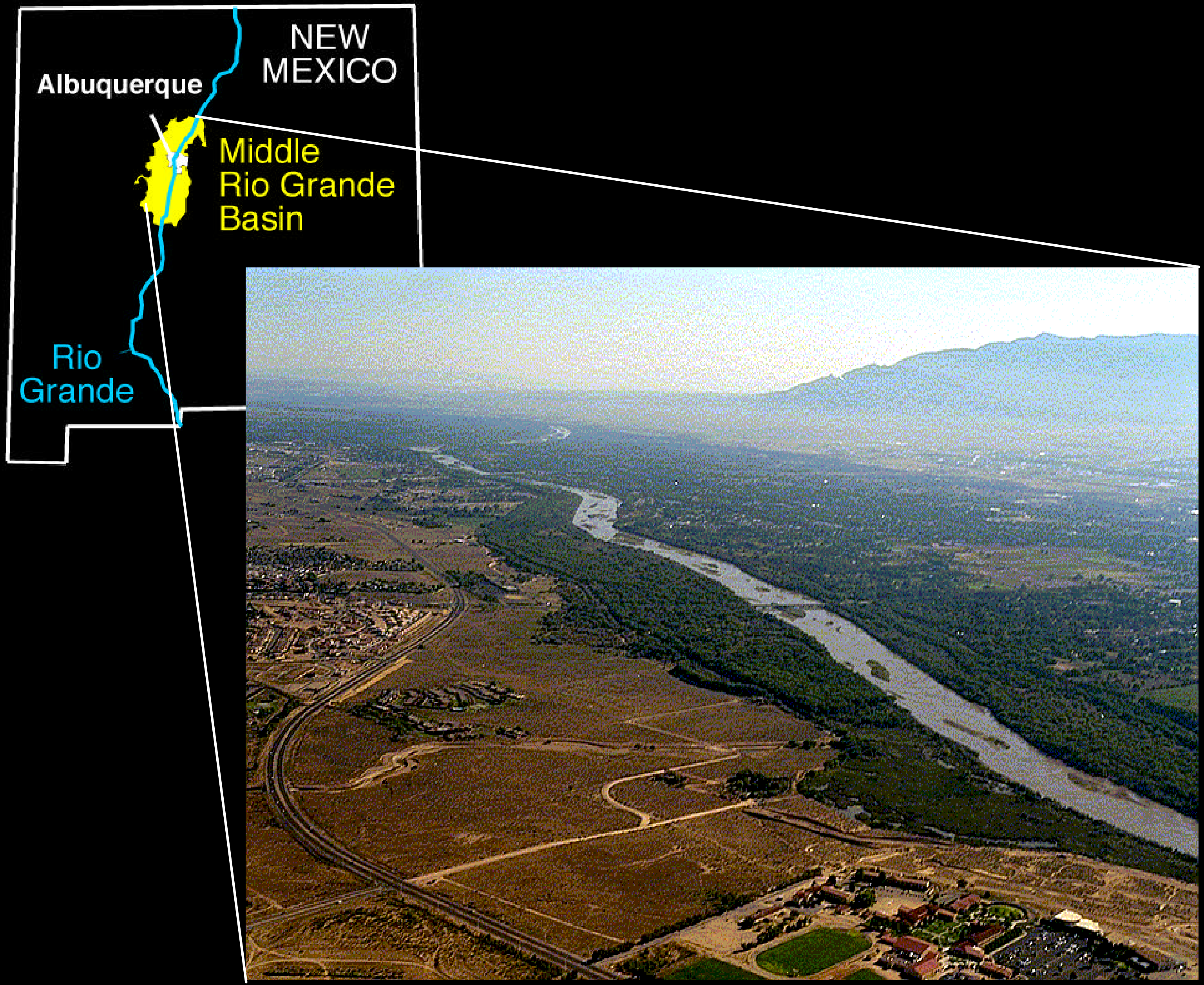
Aquifer Susceptibility in Virginia, 1998-2000

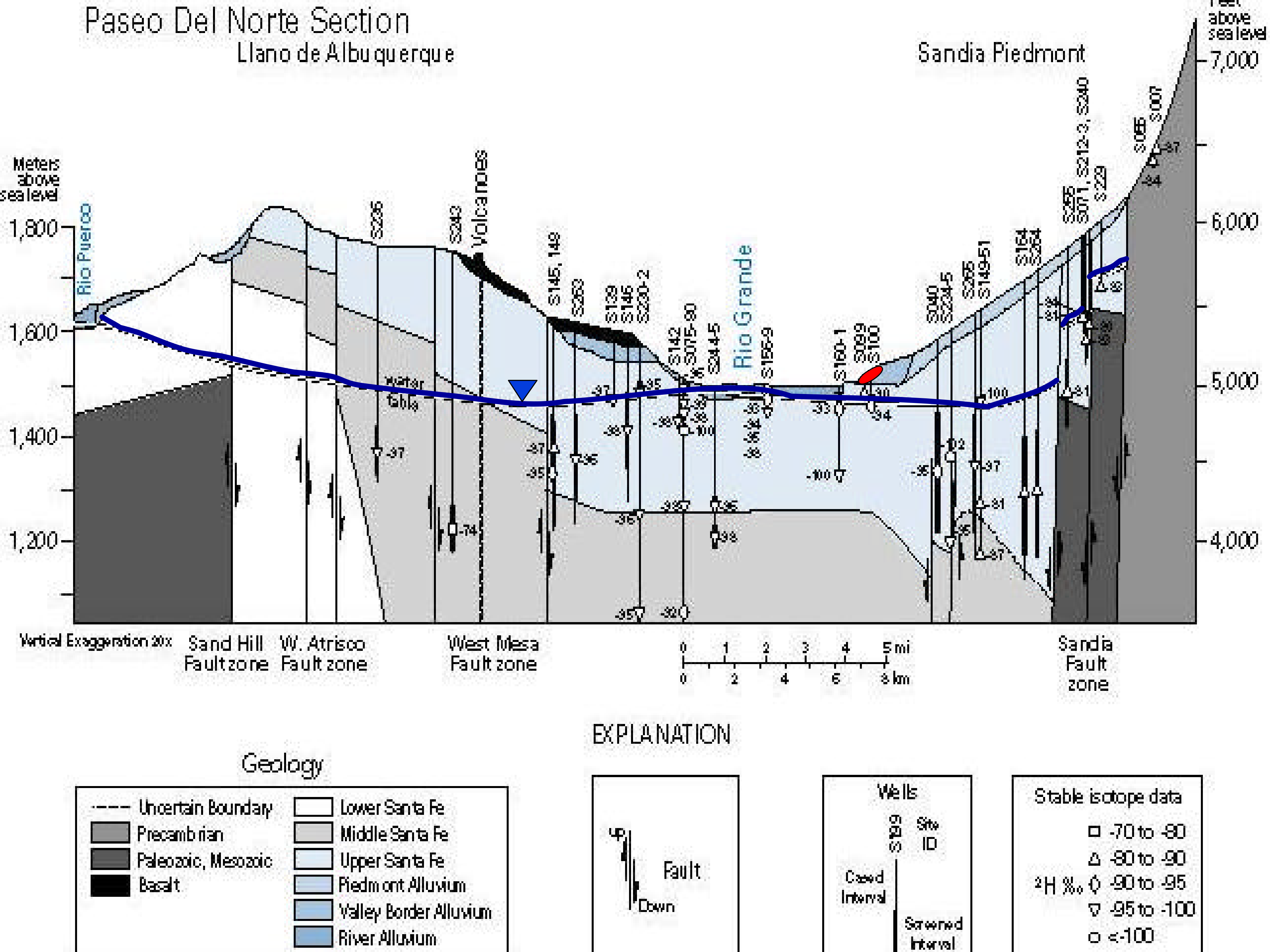
Nelms, D.L. and others,
2003, USGS
WRIR 03-4278



http://water.usgs.gov/pubs/of/2003/ofr03-246/ofr03-246.htm

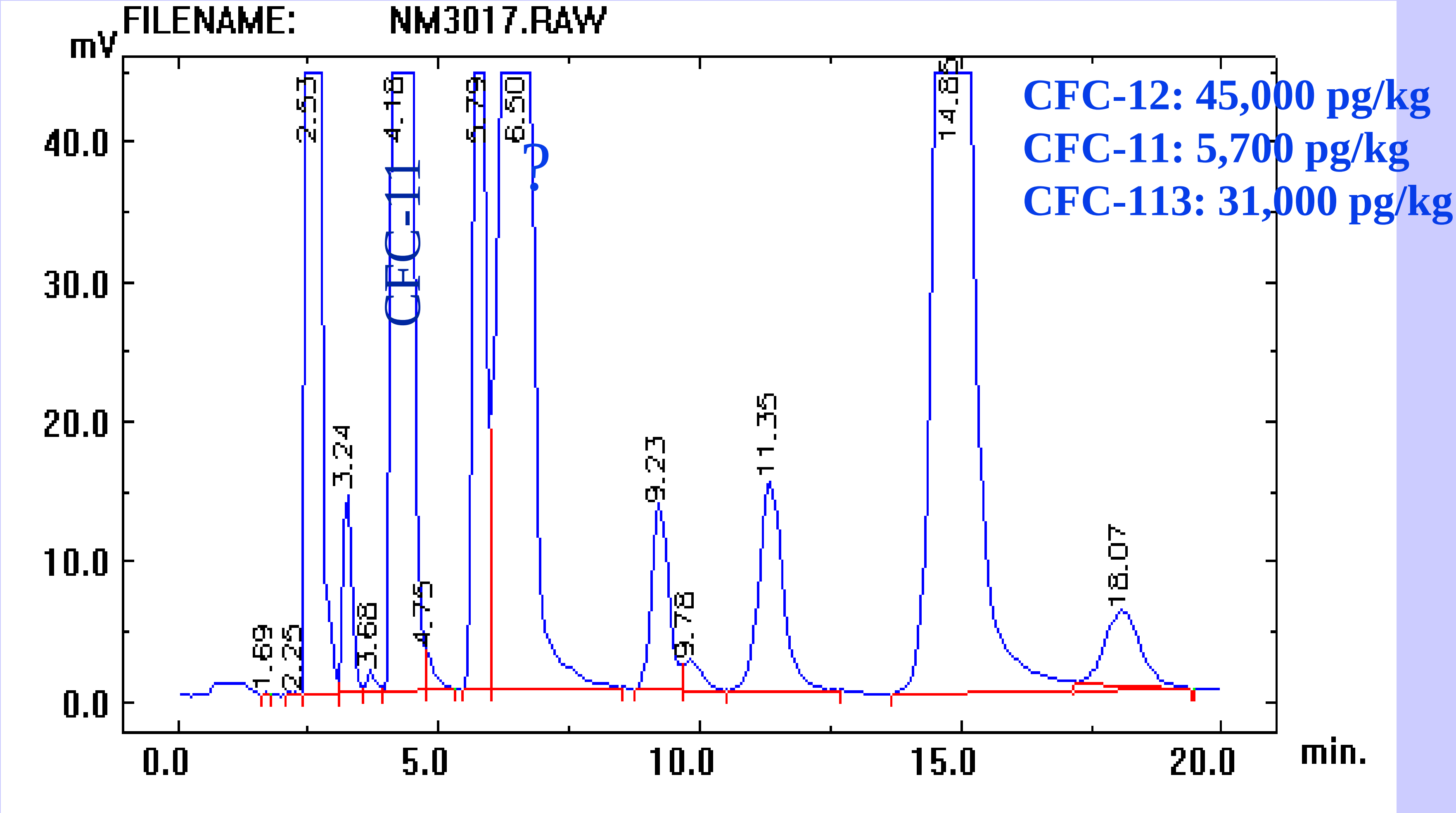
USGS
science for a changing world


NEW
MEXICO
Albuquerque
Middle
Rio Grande
Basin
Rio
Grande



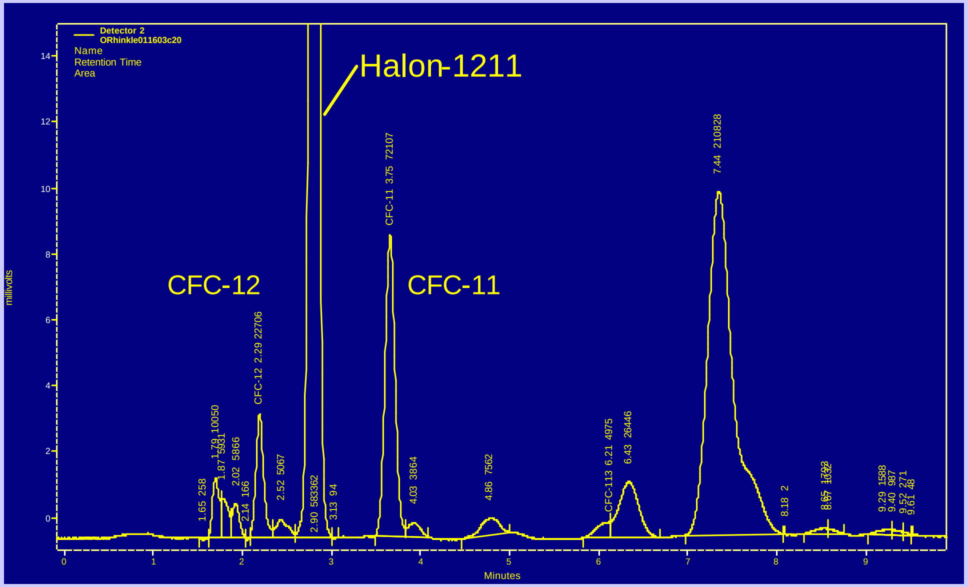
Paseo Del Norte Section
Llano de Albuquerque
Sandia Piedmont
Meters above sea level
Feet above sea level
1,800
1,600
1,400
1,200
7,000
6,000
5,000
4,000
Rio Puerco
Volcanoes
Rio Grande
water table
Vertical Exaggeration 20x
Sand Hill Fault zone
W. Atrisco Fault zone
West Mesa Fault zone
Sandia Fault zone
0 1 2 3 4 5 mi
0 2 4 6 8 km
EXPLANATION
Geology
Uncertain Boundary
Precambrian
Paleozoic, Mesozoic
Basalt
Lower Santa Fe
Middle Santa Fe
Upper Santa Fe
Piedmont Alluvium
Valley Border Alluvium
River Alluvium
Up
Fault
Down
Wells
Site ID
Cased Interval
Screened Interval
Stable isotope data
²H ‰
-70 to -80
-80 to -90
-90 to -95
-95 to -100
<-100

LALF-9, 6/29/96

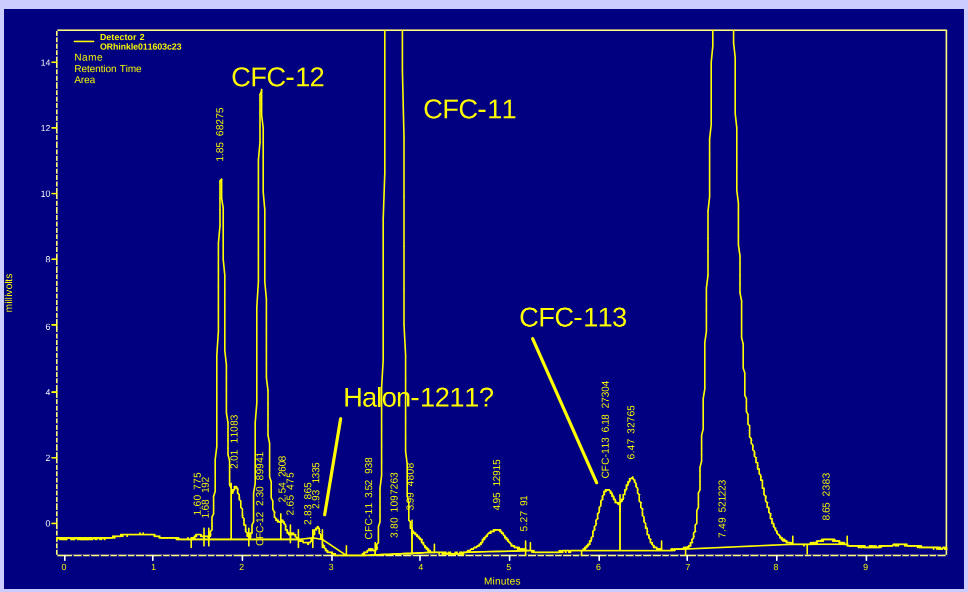


TD 233 ft, Screen 10 ft, 146 feet water above top of open interval


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 $^3H/^3He$ 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.

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<u>CONCLUSIONS (cont.)</u>

- **Dating with ratios can be very useful. Demonstrate cases of piston flow and binary mixing, but can be affected by contamination. (^3H/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 <u>low-level</u> VOC detections to identify and trace sources.**

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CONCLUSIONS (cont.)

"… 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.

USGS

Thanks

- **Chesapeake Bay Study.** Scott Phillips, Bruce Lindsey, Gary Spieran, 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.**

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