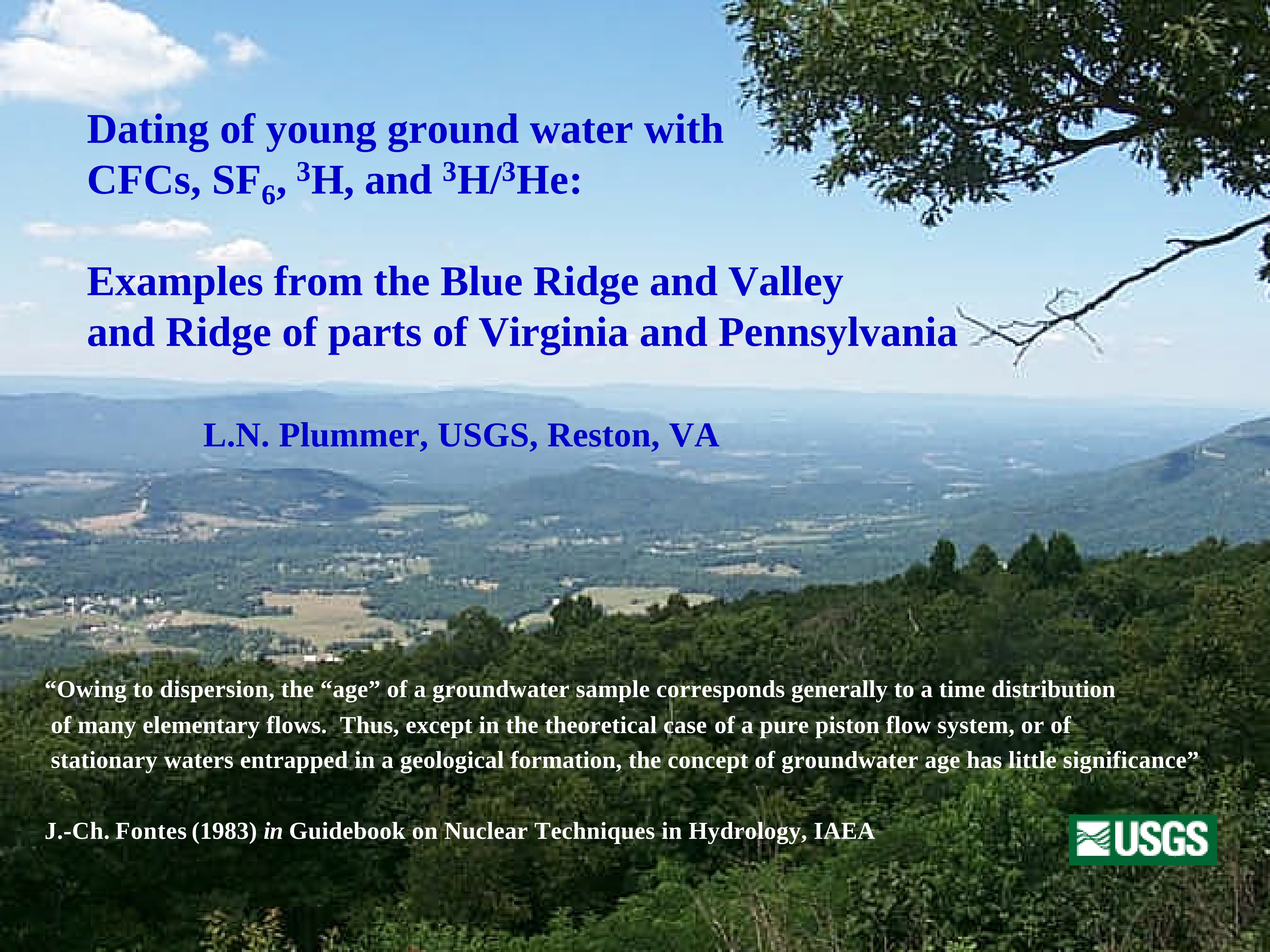


Dating of young ground water with CFCs, SF_6, ^3H, and $^3H/^3He$:

Examples from the Blue Ridge and Valley and Ridge of parts of Virginia and Pennsylvania

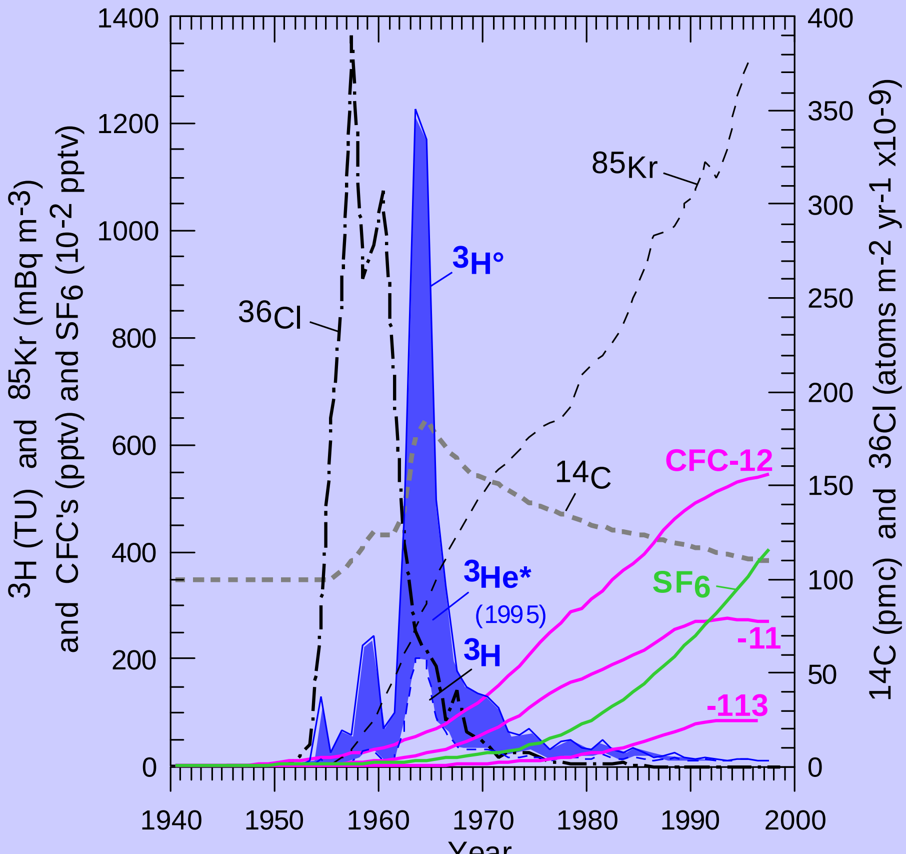
L.N. Plummer, USGS, Reston, VA

"Owing to dispersion, the "age" of a groundwater sample corresponds generally to a time distribution of many elementary flows. Thus, except in the theoretical case of a pure piston flow system, or of stationary waters entrapped in a geological formation, the concept of groundwater age has little significance"

J.-Ch. Fontes (1983) *in* Guidebook on Nuclear Techniques in Hydrology, IAEA

USGS

Selected Environmental Tracers
0-50 Year Timescale



Cook and Bohlke, 2000

- ^3H , $^3H/^3He$
- ^{85}Kr
- CFC-11, CFC-12, CFC-113
- SF_6
- Event Markers: ^3H, ^{36}Cl, ^{14}C
- Age: time elapsed since recharge

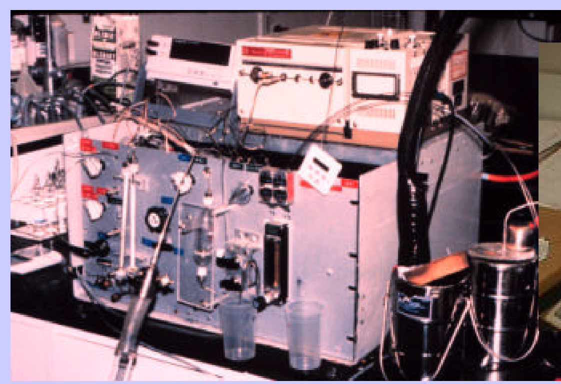
Why measure environmental tracers in ground water?

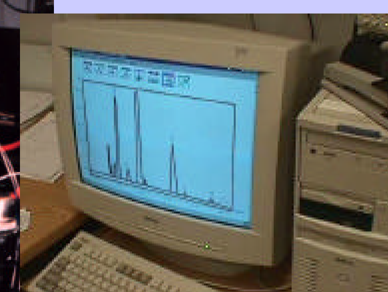
- Estimate fractions of young water and the mean age of the young fraction in mixtures.
- Evaluate vulnerability to contamination.
- Estimate recharge rates.
- Calibrate models of groundwater flow.
- Estimate rates of geochemical and microbiological processes.
- Retrieve historical records of contaminant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

USGS

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.





USGS

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.

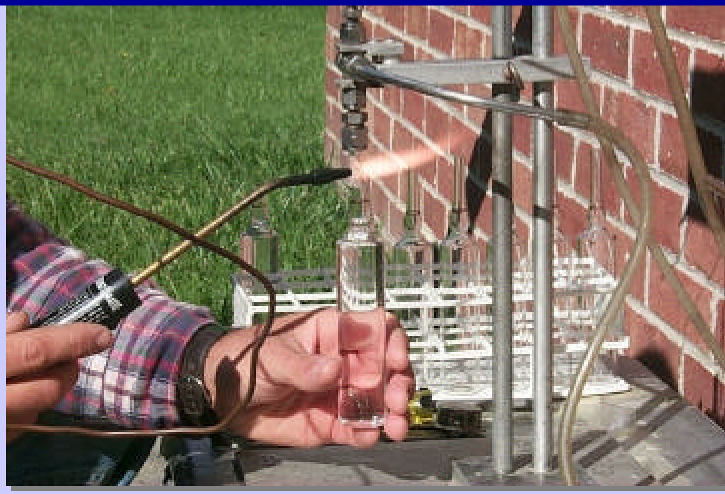
- Flow-model calibration and simulation of age.

- All "ages", regardless of method, are model dependent.

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

Chlorofluorocarbons

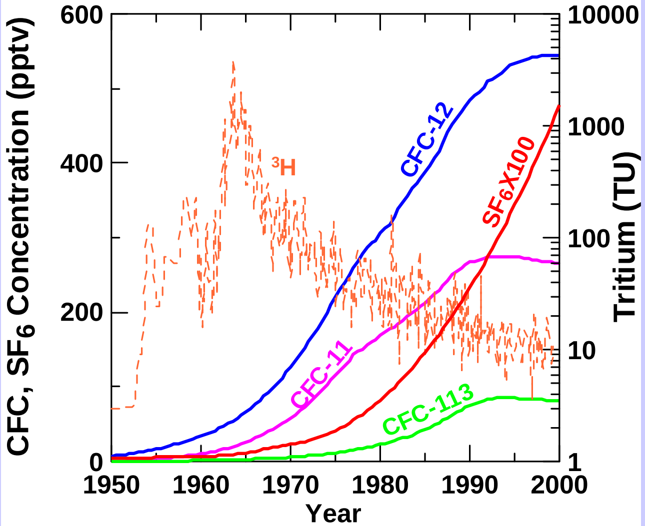


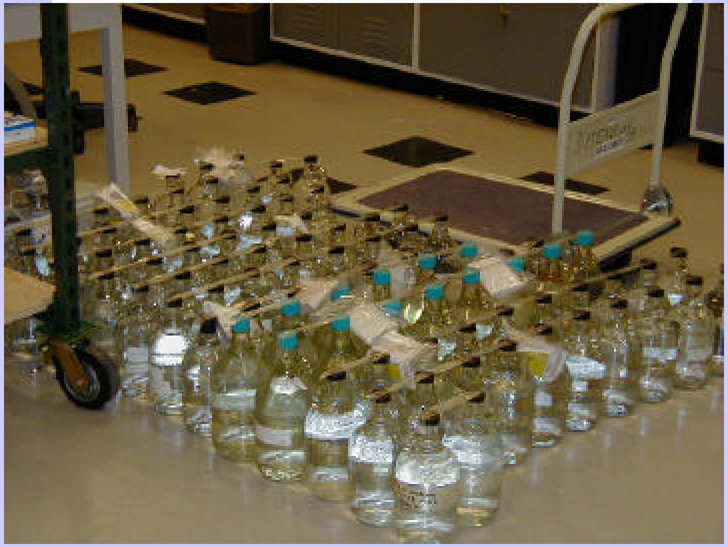
- CFC-12 (CF_2Cl_2), 1930
- CFC-11 ($CFCl_3$), 1936
- CFC-113 ($C_2F_3Cl_3$), 1944
- Input smooth, increasing until 1990s (dating range ~1950 to early 1990s).
- Stable in aerobic environments.
- In future- dual ages.
- Use of ratios.
- Can detect post 1940's water.
- Collection/analysis not overly labor intensive.
- Problems with contamination, degradation (anoxic), sorption?

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

USGS

Sulfur Hexafluoride



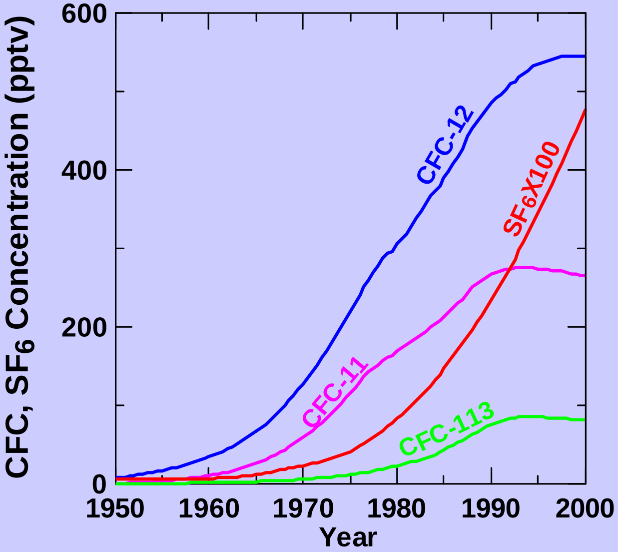


- Electrical insulator in high voltage switches
- First produced 1953
- Very low solubility in water.
- Does not degrade
- Terrigenic source
- Dating range: 1970-modern.
- Smooth input, increasing in air at 6%/yr; 5 pptv today.

USGS

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

USGS

Limitations

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

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

SF_6

- Terrigenic SF_6
- Mixing

CFCs

- Contamination
- Degradation
- Mixing

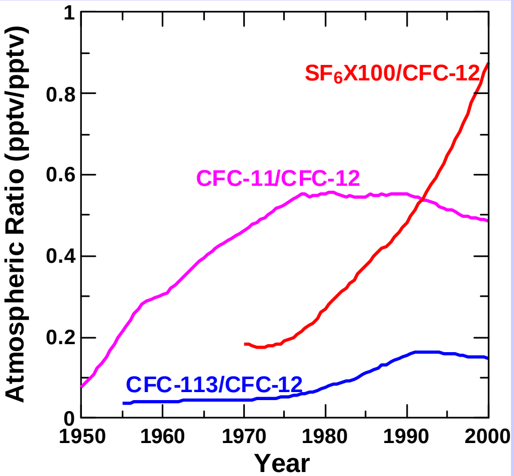
^{85}Kr

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

There is no perfect tracer. Multi-tracer approach recommended.

USGS

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.**

USGS

$^3H/^3He$ Age Applies to that of the Young Fraction in Simple Binary Mixtures

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

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

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

$t_{1/2}$ = 12.3 years

USGS

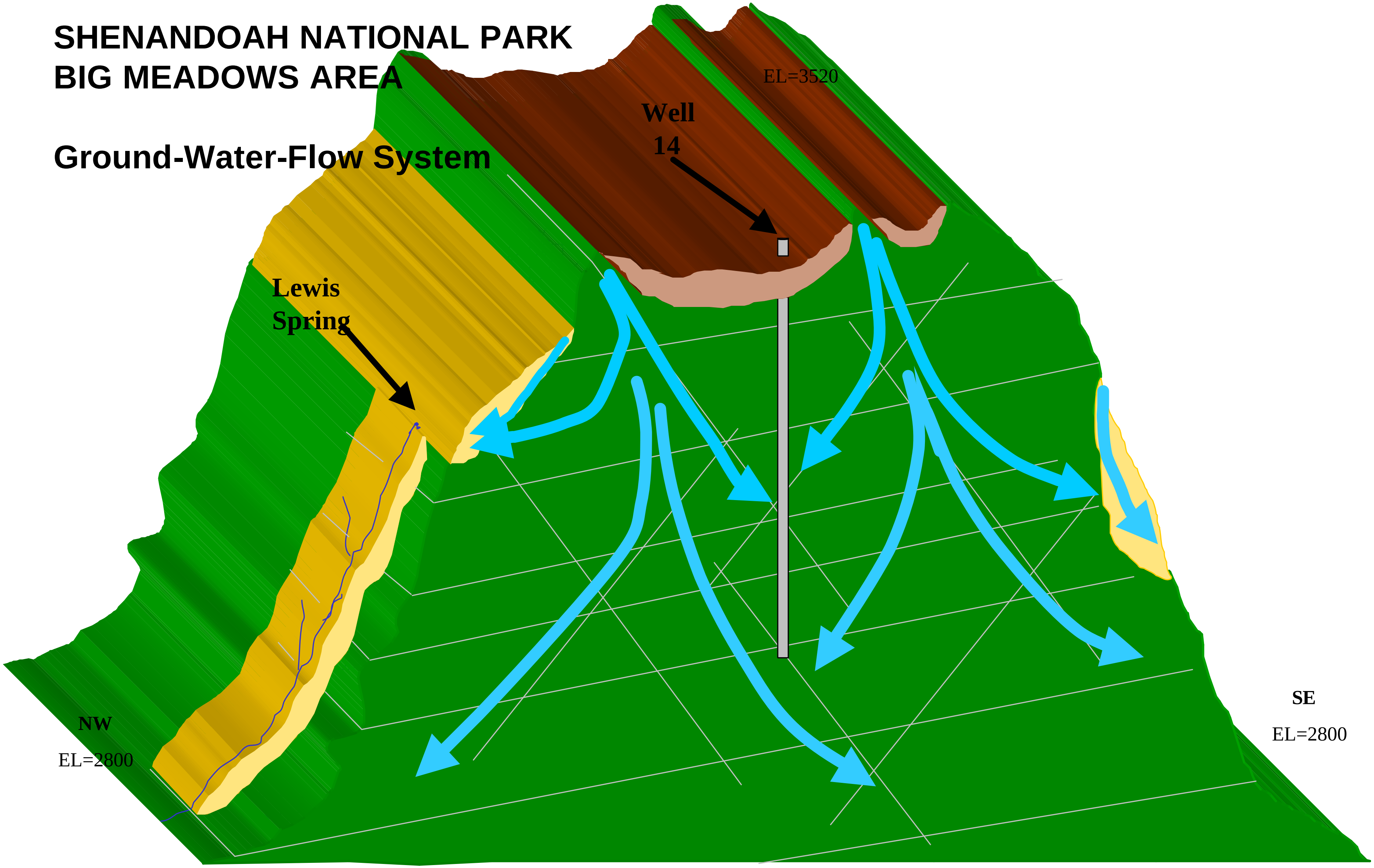
Blue Ridge Mountains of Virginia

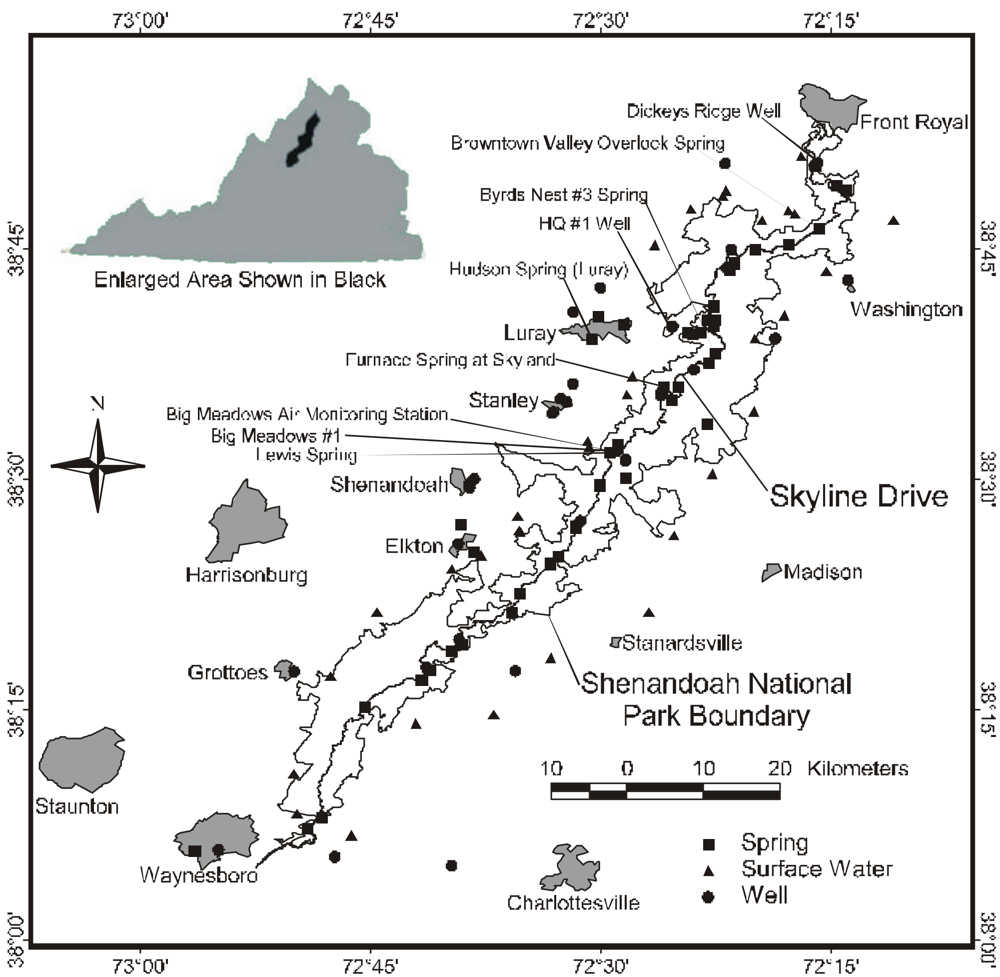
Plummer, L.N., Busenberg, E., Böhlke, J.K., Nelms, D.L., Michel, R.L., and Schlosser, P., 2001, Groundwater residence times in Shenandoah National Park, Blue Ridge Mountains, Virginia, USA: A multi-tracer approach. Chemical Geology, v. 179/1-4, p. 93-111.

- 800 km^2;elev. 170-1230 m
- Annual precipitation averaged 114 cm; mean annual temperature, 7.8 ^oC 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/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, $^3H/^3He$, SF_6, ^{35}S, stable isotopes, dissolved N_2, Ar.

SHENANDOAH NATIONAL PARK
BIG MEADOWS AREA

Ground-Water-Flow System

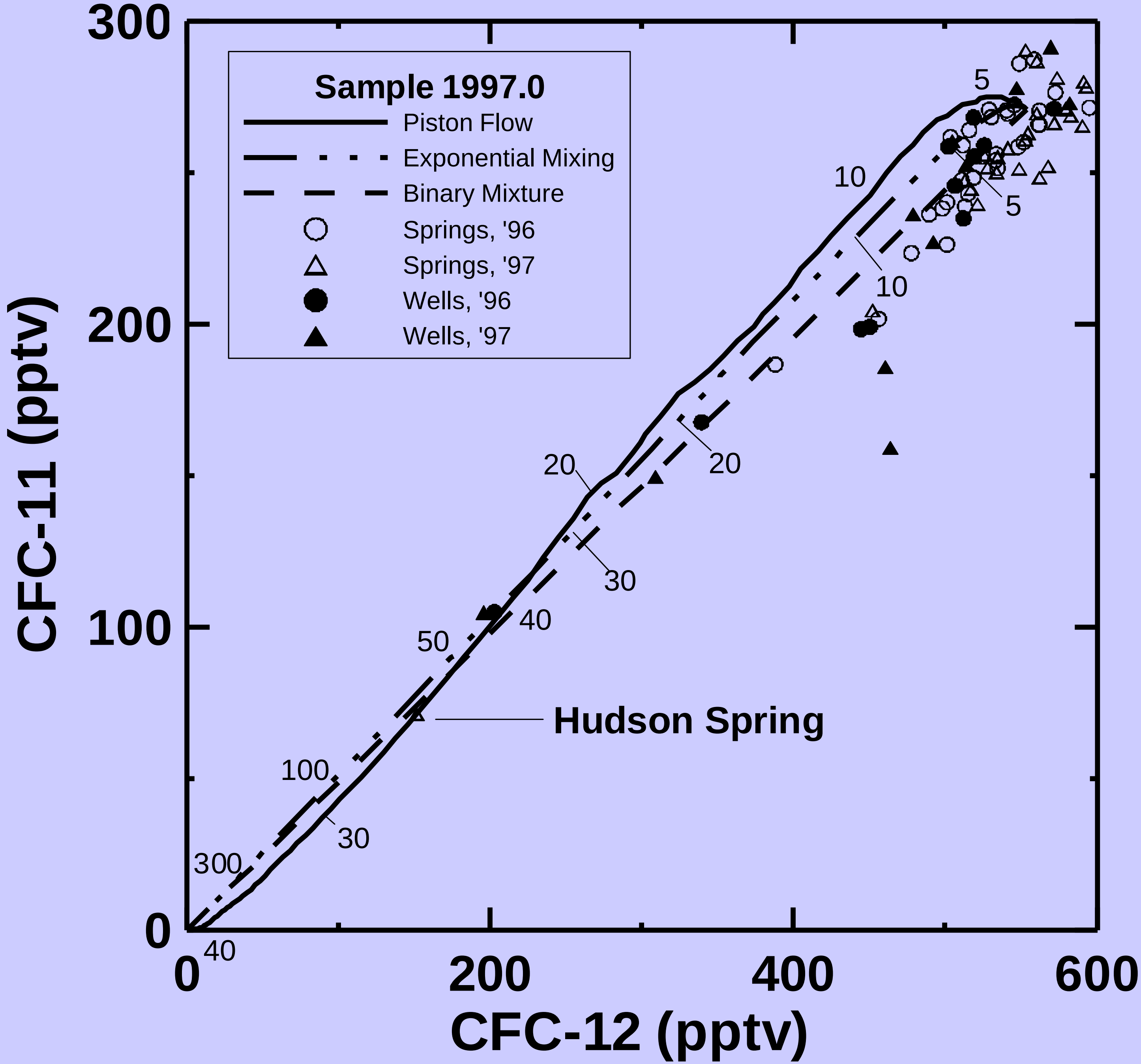




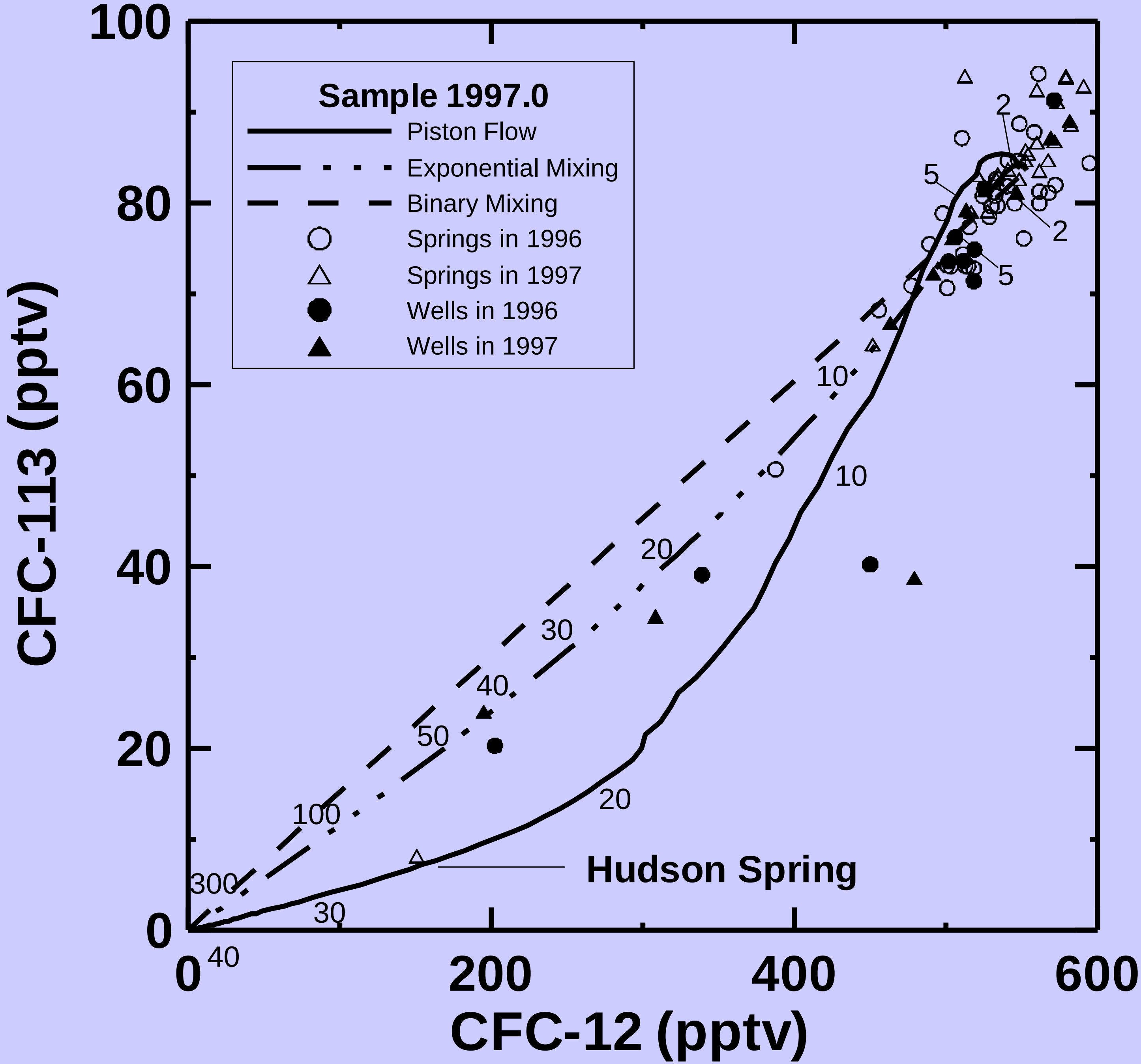
73°00'
72°45'
72°30'
72°15'
38°45'
38°30'
38°15'
38°00'
Enlarged Area Shown in Black
Dickeys Ridge Well
Front Royal
Browntown Valley Overlook Spring
Byrds Nest #3 Spring
HQ #1 Well
Hudson Spring (Luray)
Washington
Luray
Furnace Spring at Skyland
Stanley
Big Meadows Air Monitoring Station
Big Meadows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

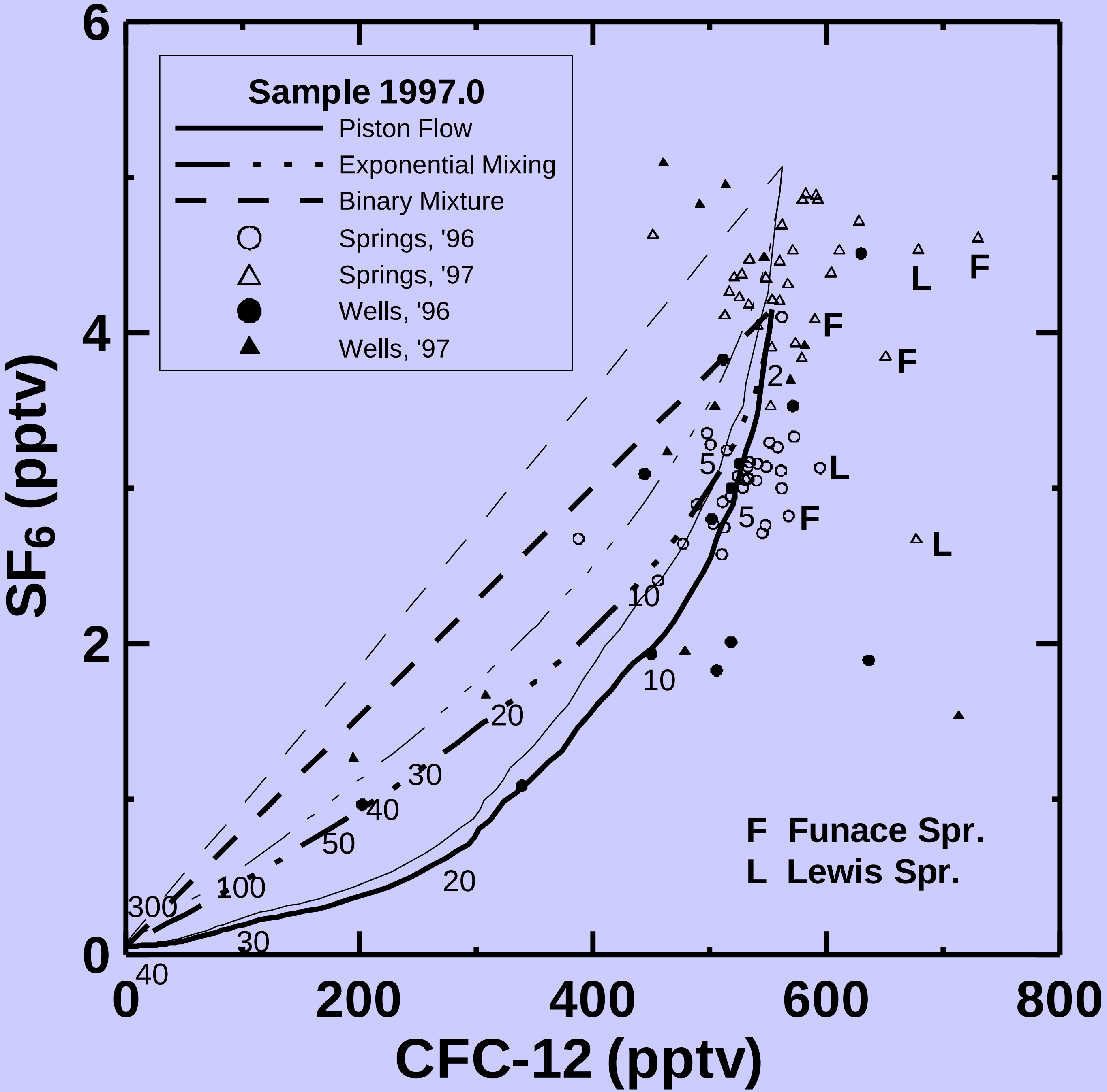
Lewis Mountain Spring

Sampling from a Typical
Spring Box and Weir

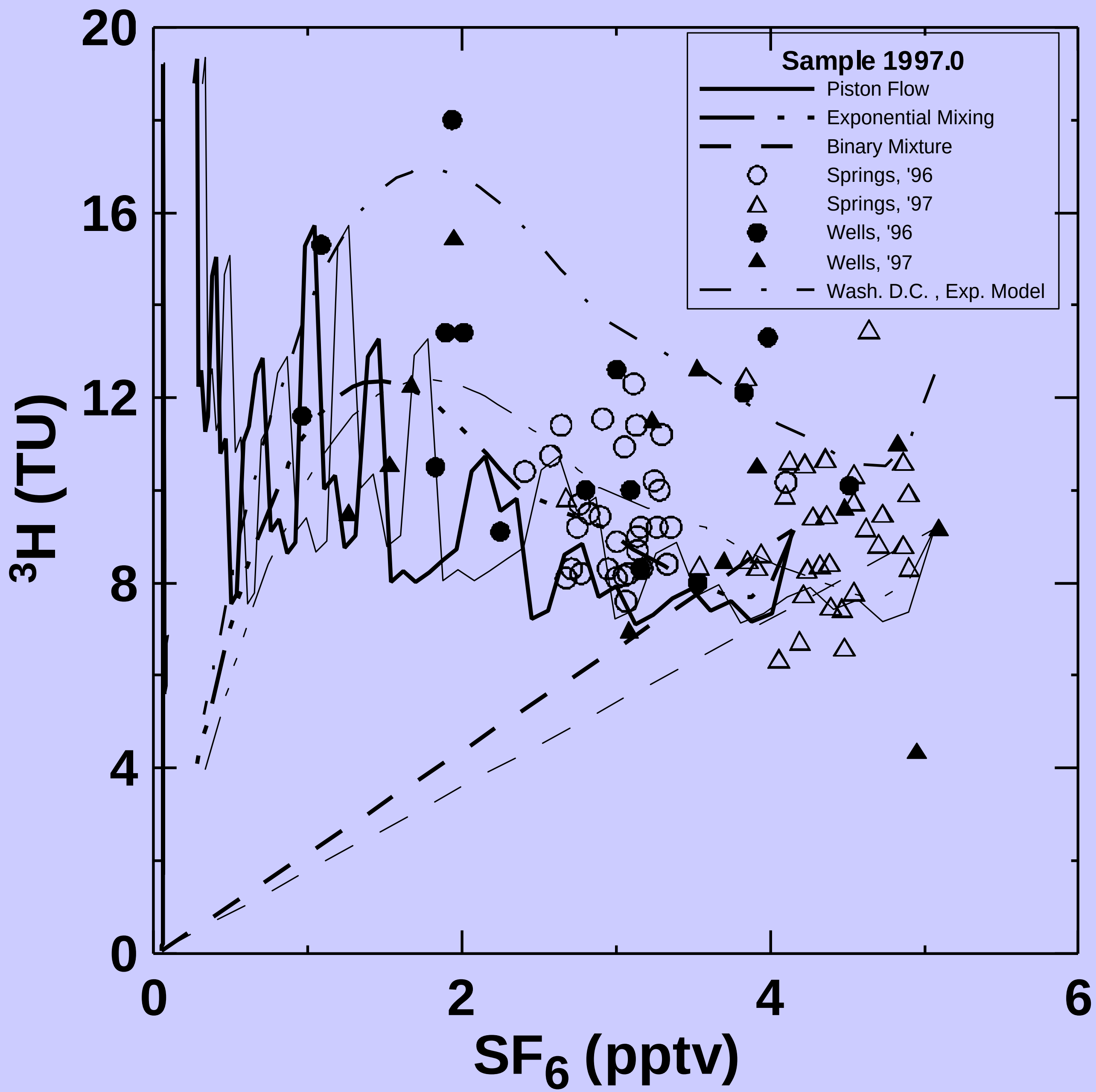


Sample 1997.0
Piston Flow
Exponential Mixing
Binary Mixture
Springs, '96
Springs, '97
Wells, '96
Wells, '97
Hudson Spring
CFC-11 (pptv)
CFC-12 (pptv)
300
200
100
0
200
400
600
5
10
5
10
20
20
30
40
50
100
30
300
40


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
0
200
400
600
2
5
2
5
10
10
20
30
40
50
100
300
20
30
40



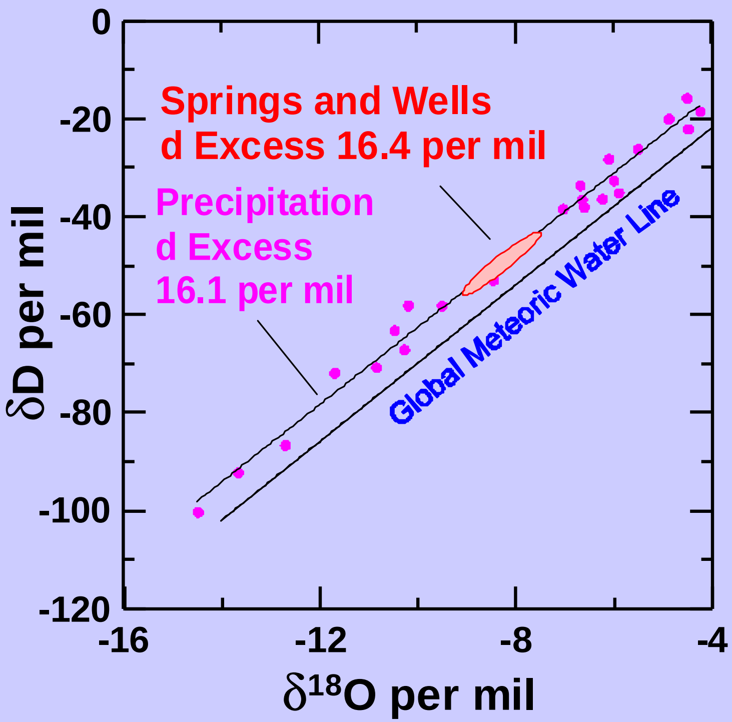
Sample 1997.0
Piston Flow
Exponential Mixing
Binary Mixture
Springs, '96
Springs, '97
Wells, '96
Wells, '97
F Funace Spr.
L Lewis Spr.
SF6 (pptv)
CFC-12 (pptv)
0
2
4
6
200
400
600
800

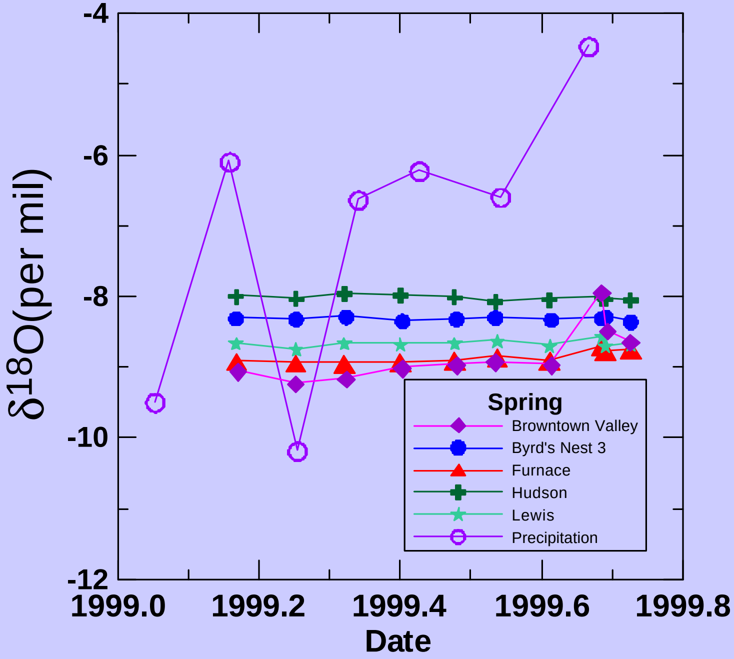


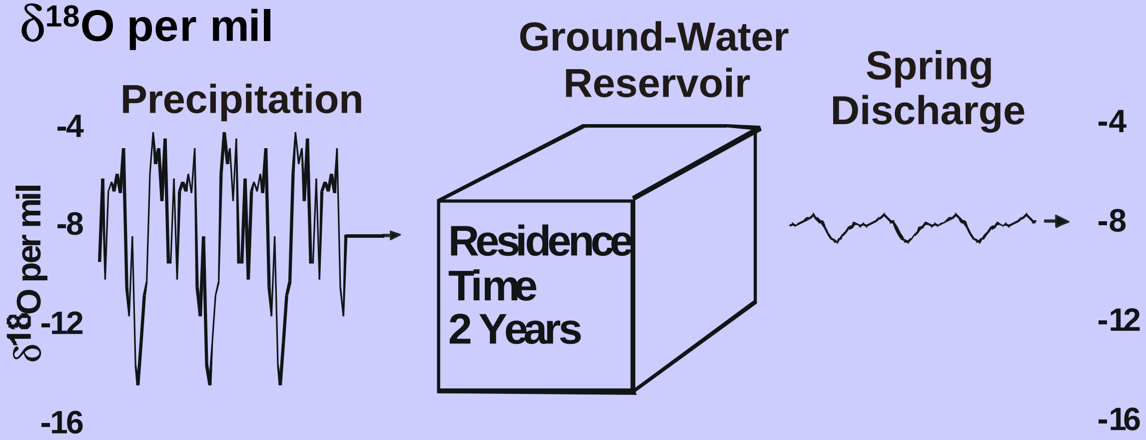
Two ^{3}H input functions:

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

Also 0-2 cc/L of excess air

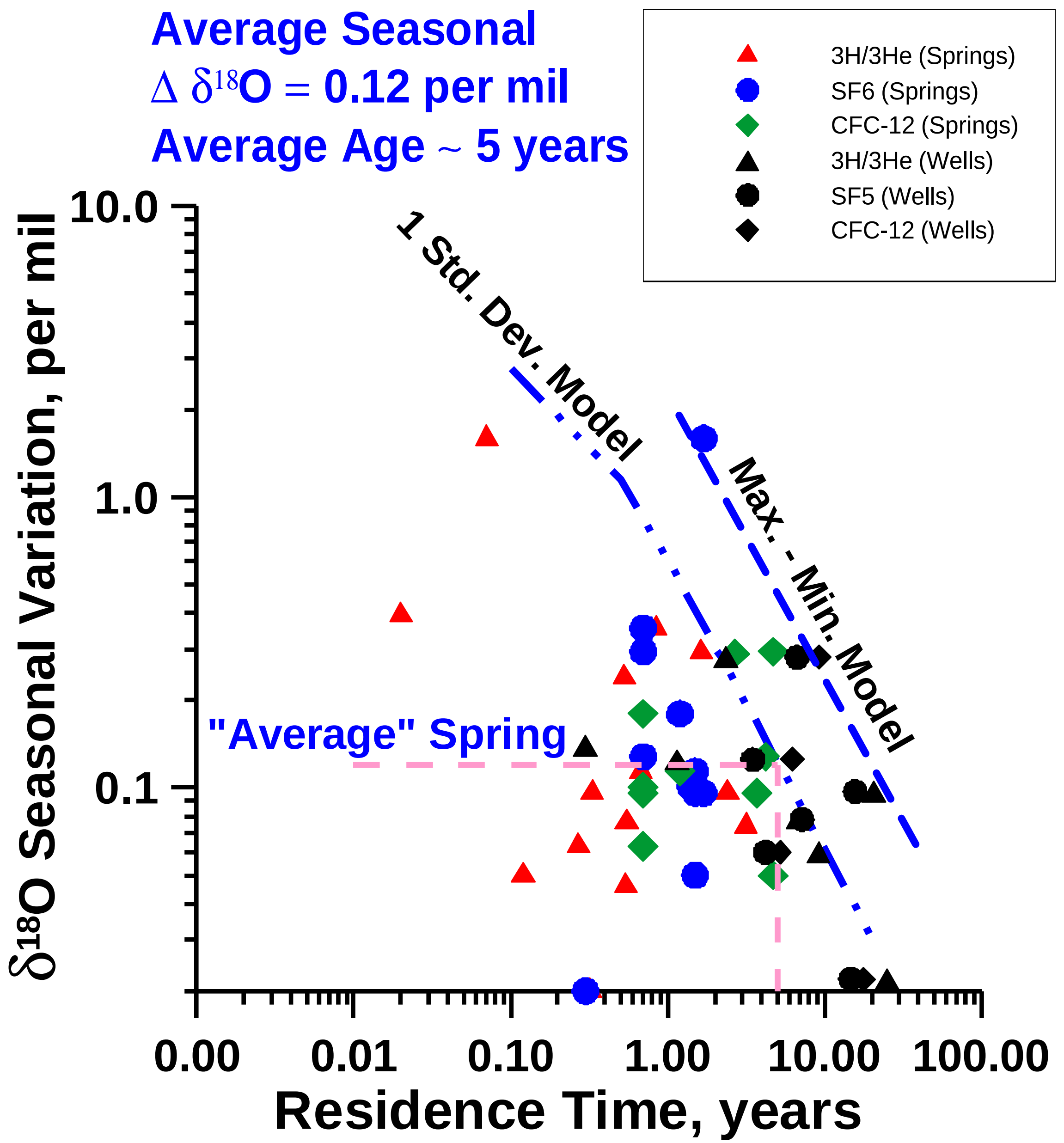






Average -8.2 per mil
Amplitude 9.6 per mil
Std. Dev. 2.8 per mil

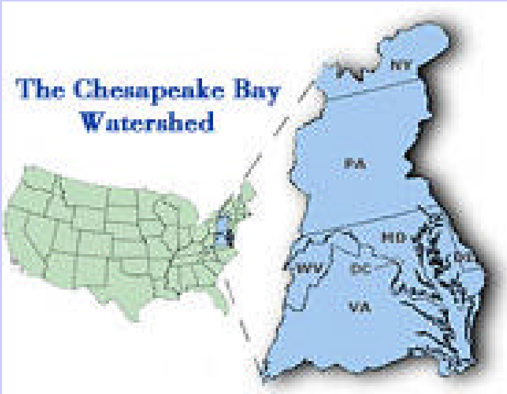
Average -8.2 per mil
Amplitude1.1 per mil
Std. Dev. 0.3 per mil



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

Conclusions from Blue Ridge (SNP)

- d ^{18}O **data: Mean residence time of 5 years. (Range 0-10 yrs.) Age includes uz travel time.**
- **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?**

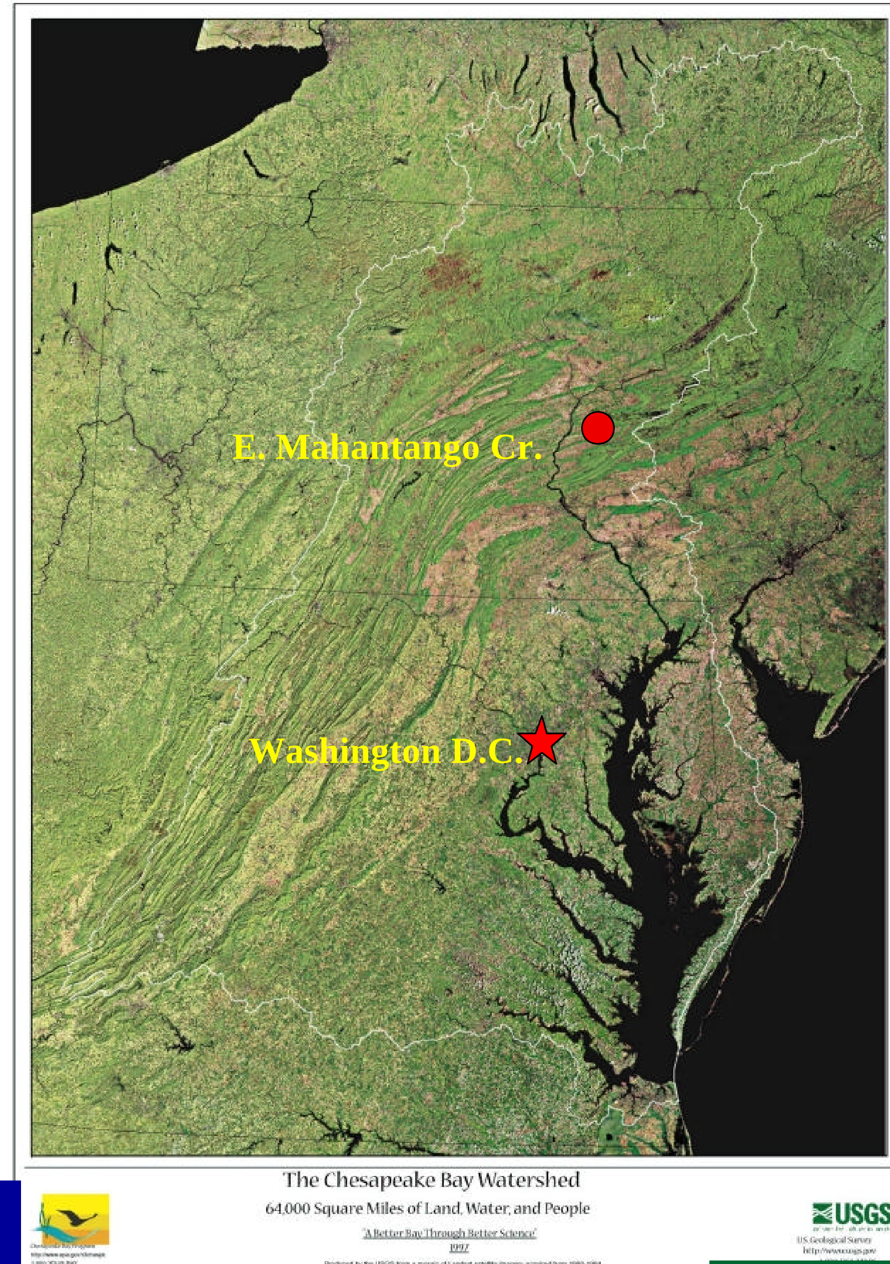


Chesapeake Bay Watershed

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.

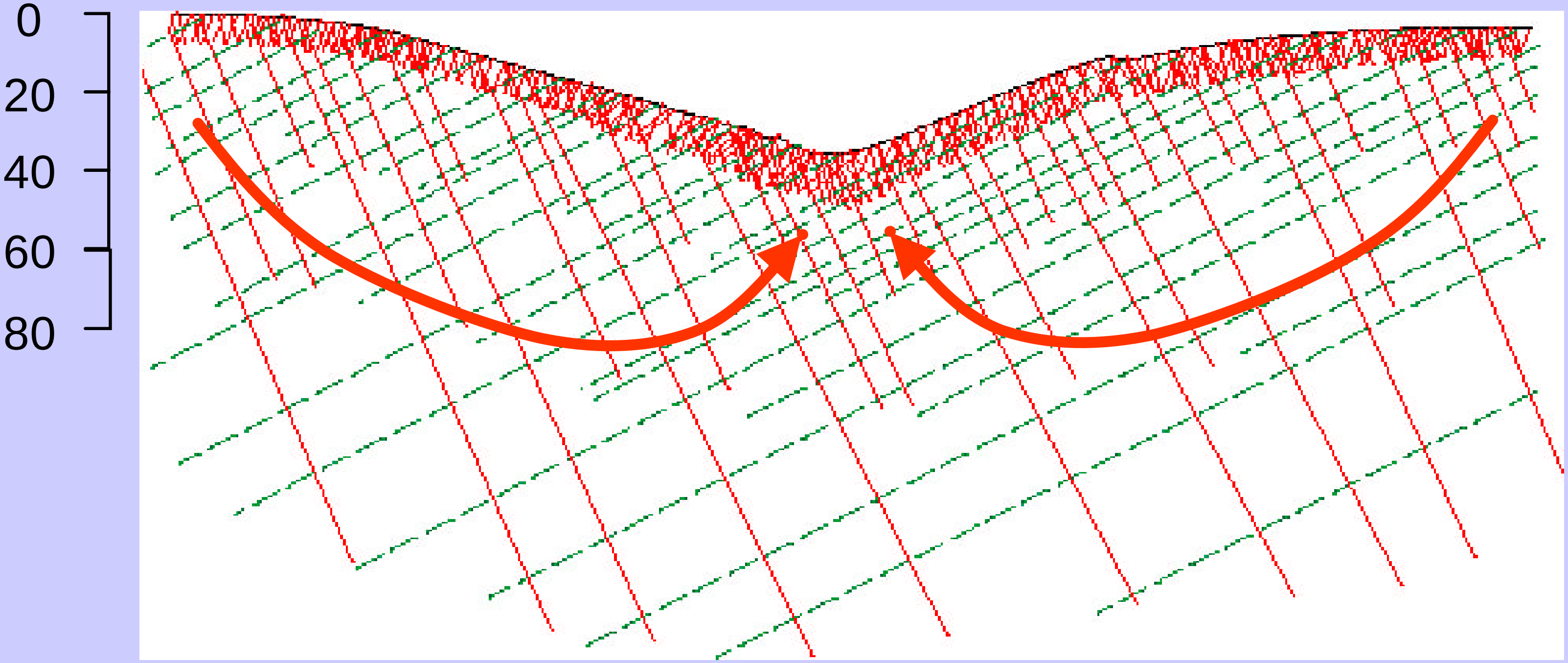
Assess lag time between changes at the land surface and the response in the base-flow component of groundwater discharge to the bay.



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

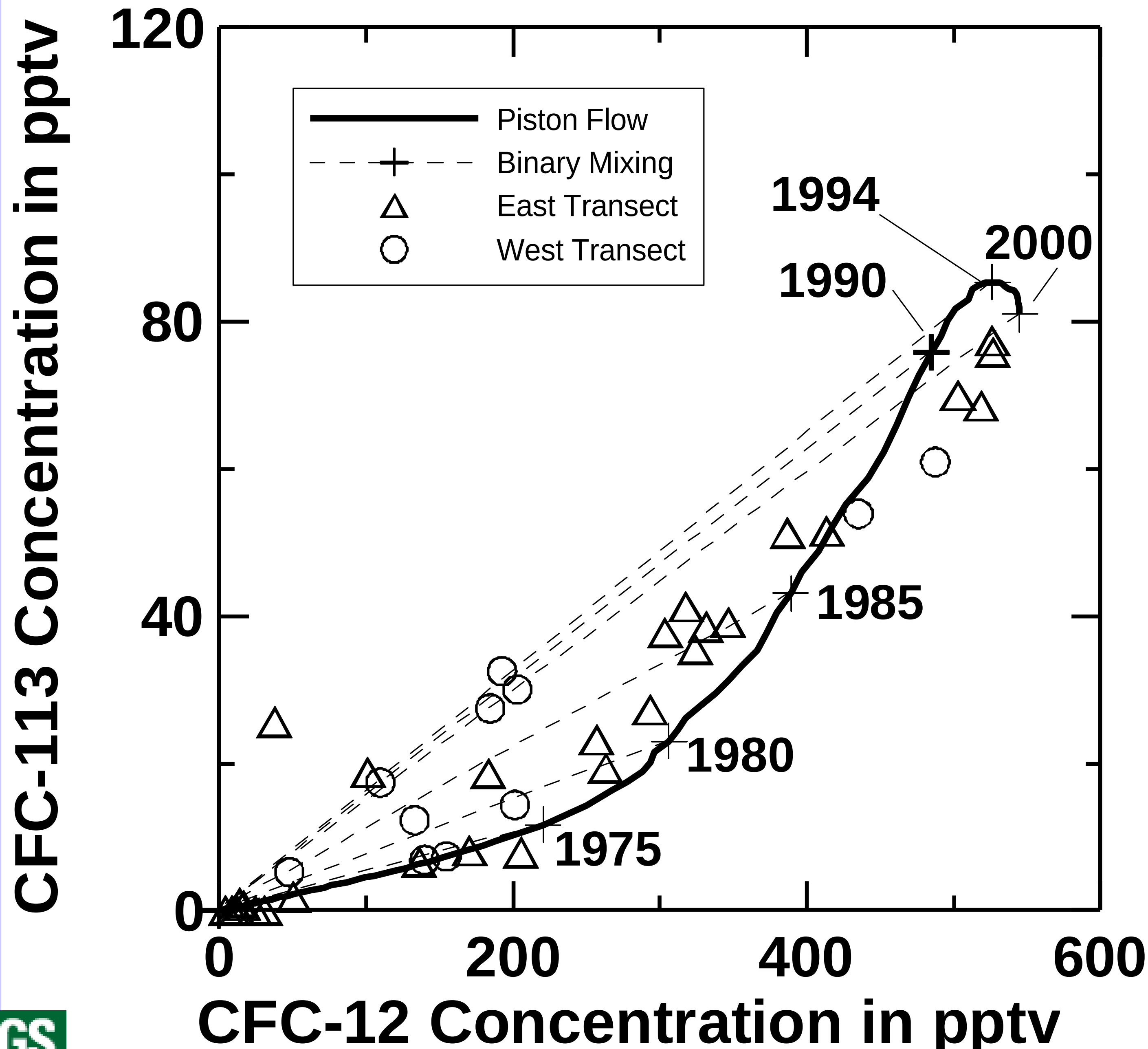
Layered fracture density model

(Gburek, Folmar, and Urban (1998)



Burton et al. 2002

USGS



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

East Piezometer Transect

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

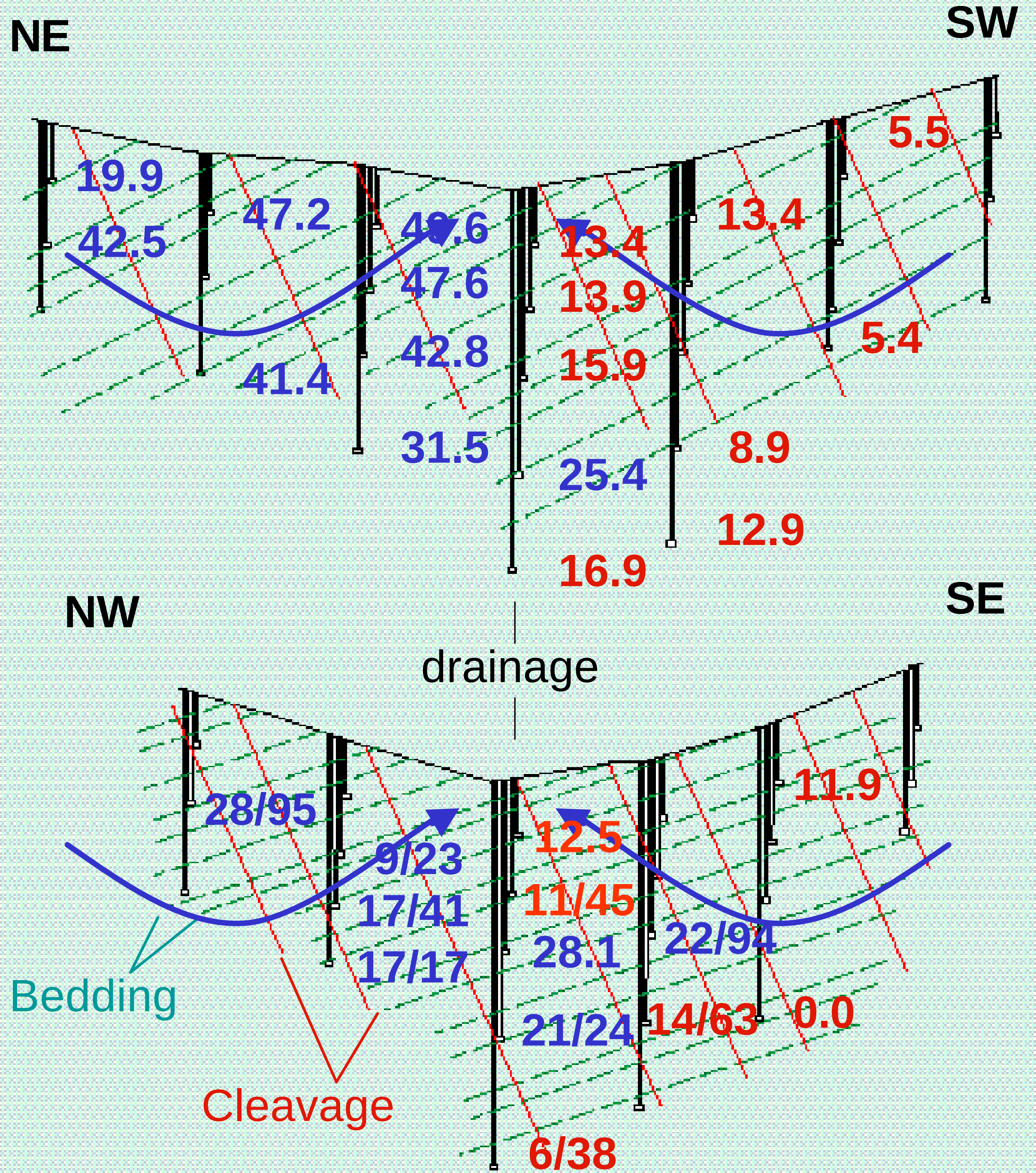
..than those underneath and SW of stream

..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

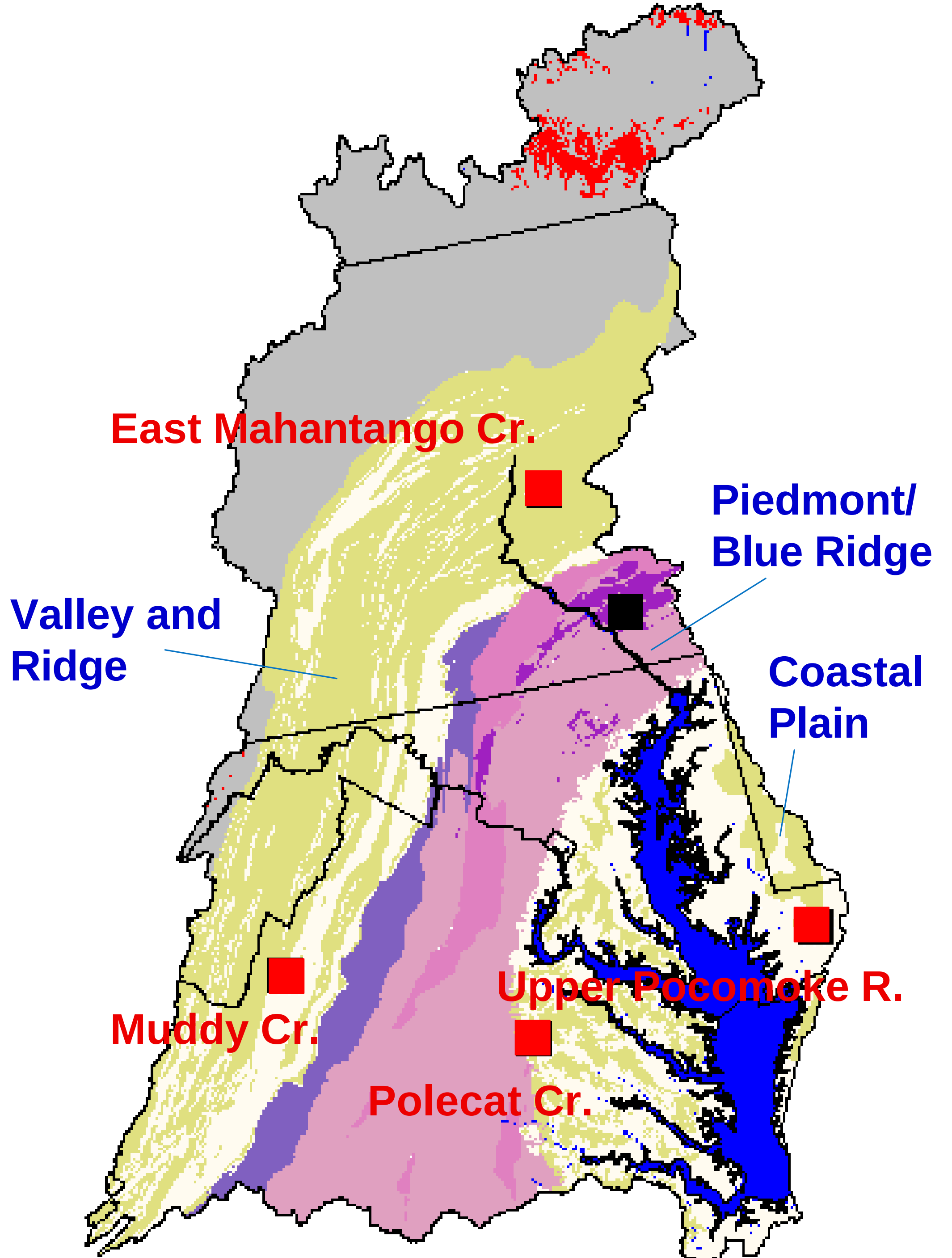
…and younger to SE

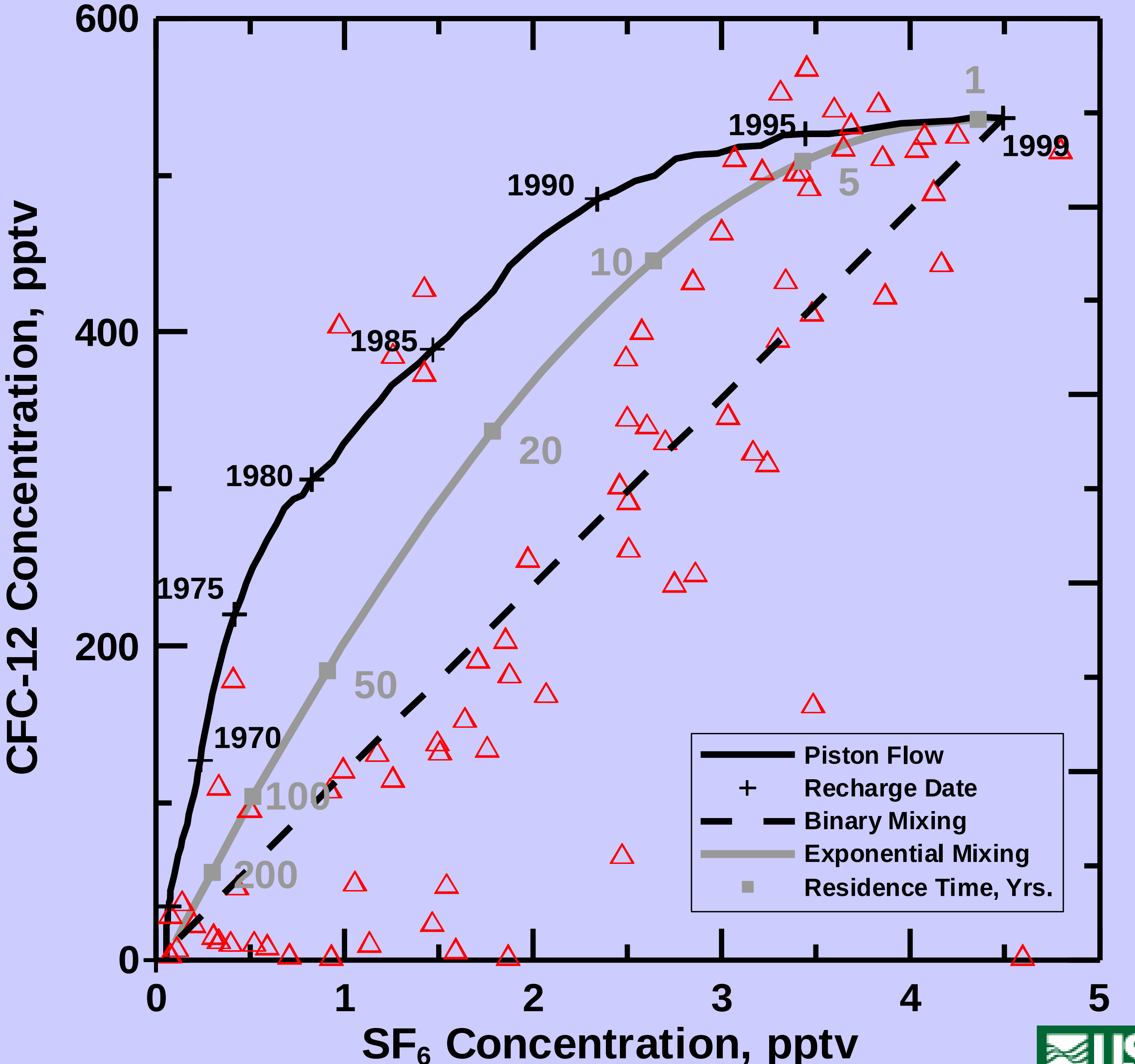


Burton et al. 2002

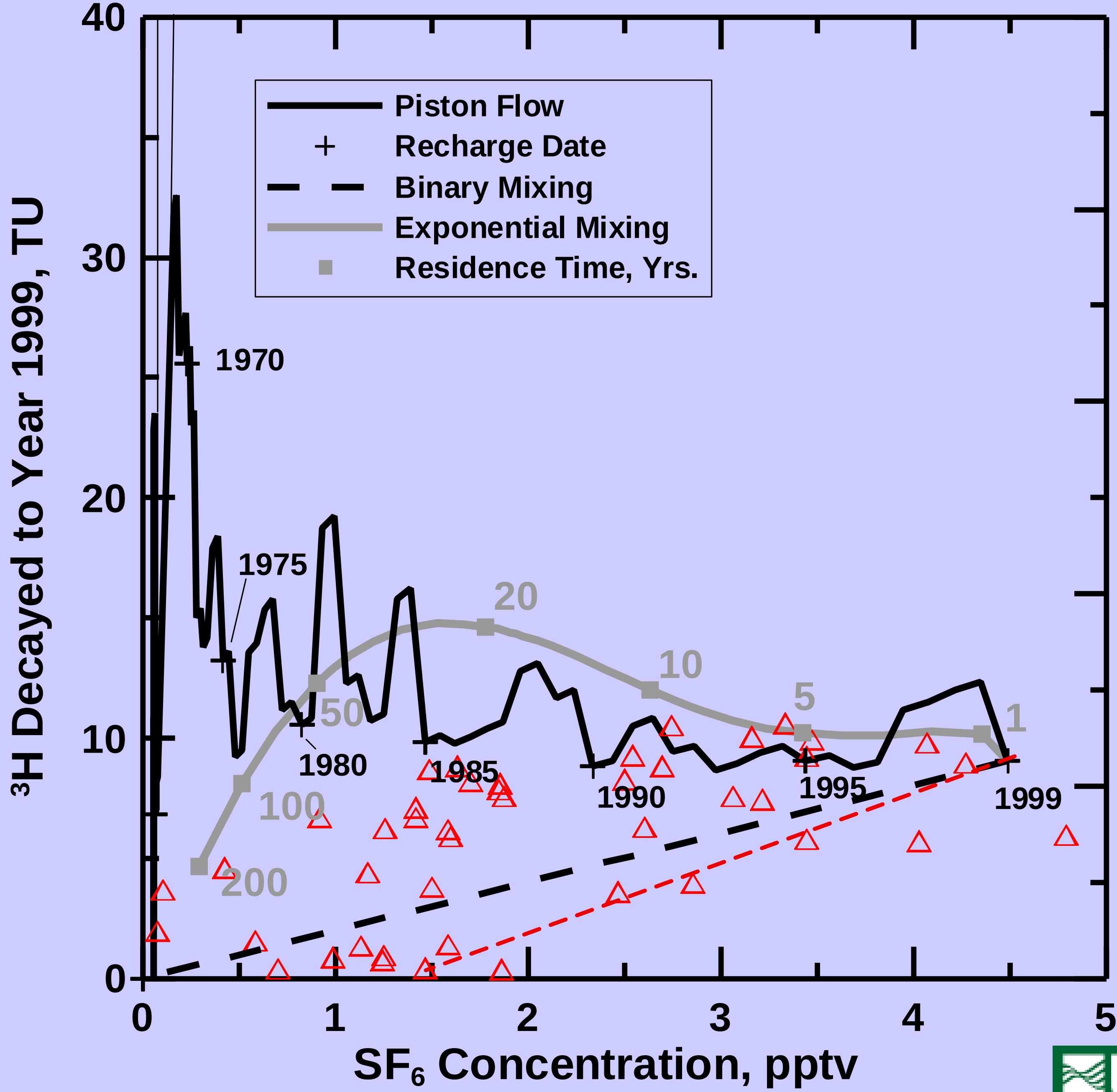
USGS Chesapeake Bay watershed nutrient study

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

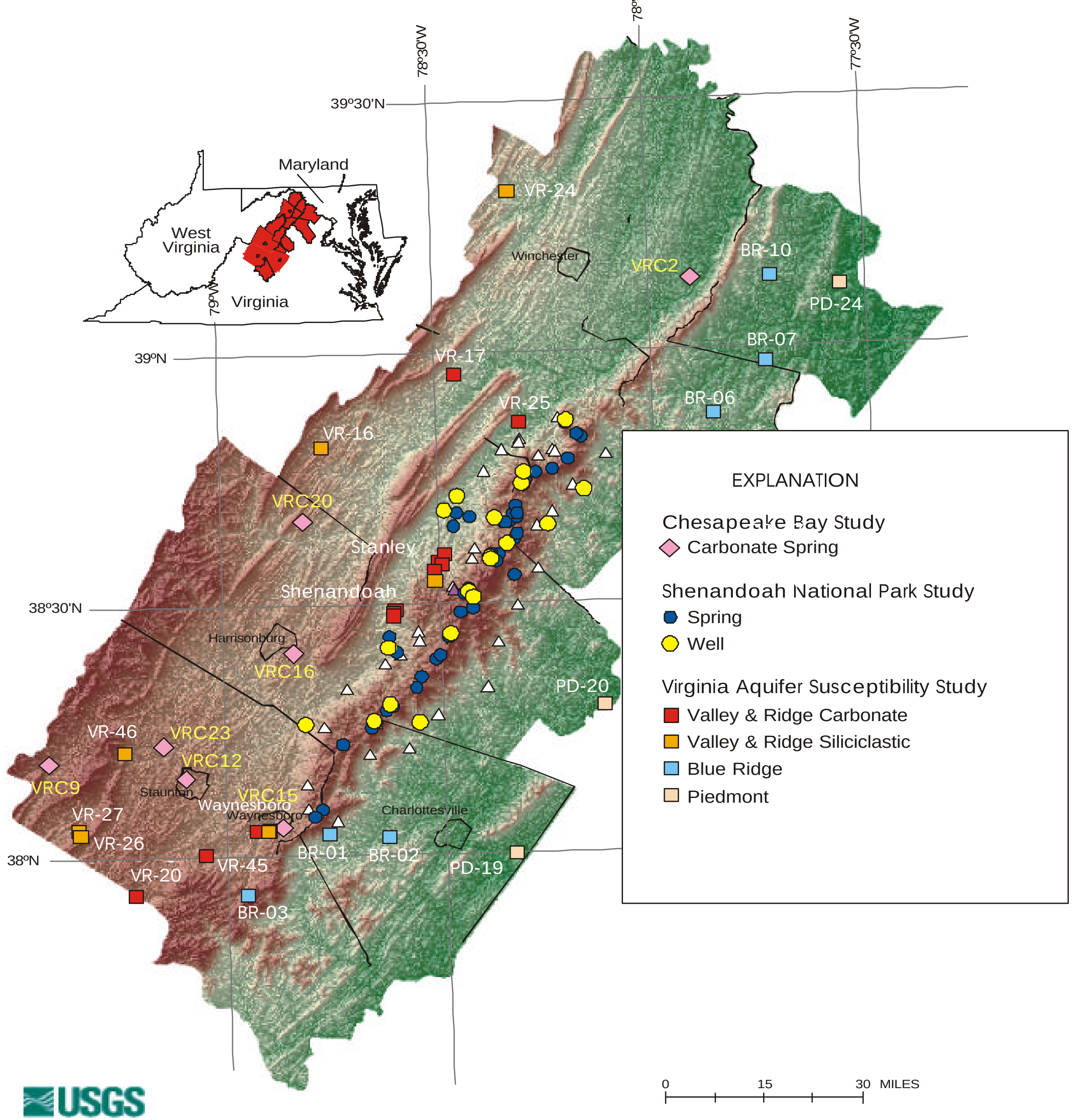




CFC-12 Concentration, pptv
SF6 Concentration, pptv
0
200
400
600
0
1
2
3
4
5
1970
1975
1980
1985
1990
1995
1999
1
5
10
20
50
100
200
Piston Flow
Recharge Date
Binary Mixing
Exponential Mixing
Residence Time, Yrs.
USGS



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



Maryland
West Virginia
Virginia
79°W
78°W
78°30'W
77°30'W
39°30'N
39°N
38°30'N
38°N
VR-24
Winchester
VRC2
BR-10
PD-24
BR-07
VR-17
VR-25
BR-06
VR-16
VRC20
Stanley
Shenandoah
Harrisonburg
VRC16
PD-20
VR-46
VRC23
VRC12
VRC9
Staunton
VRC15
Waynesboro
Charlottesville
VR-27
VR-26
VR-45
BR-01
BR-02
PD-19
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
USGS

Hydrogeology of Carbonate Terranes of the Valley & Ridge Province

Soil & Regolith

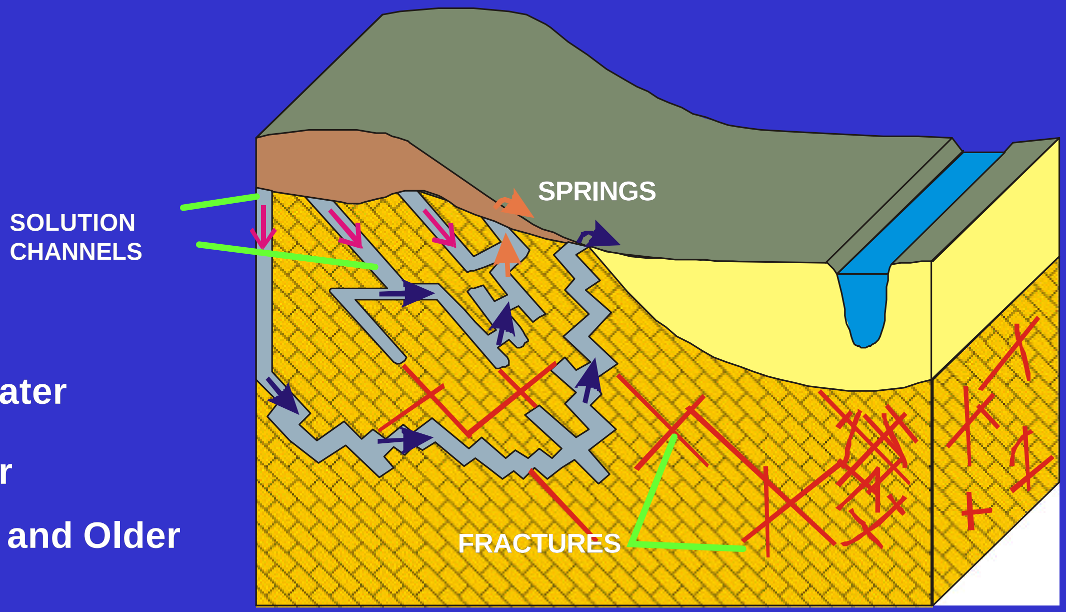
Alluvium

Limestone

Younger Ground Water

Older Ground Water

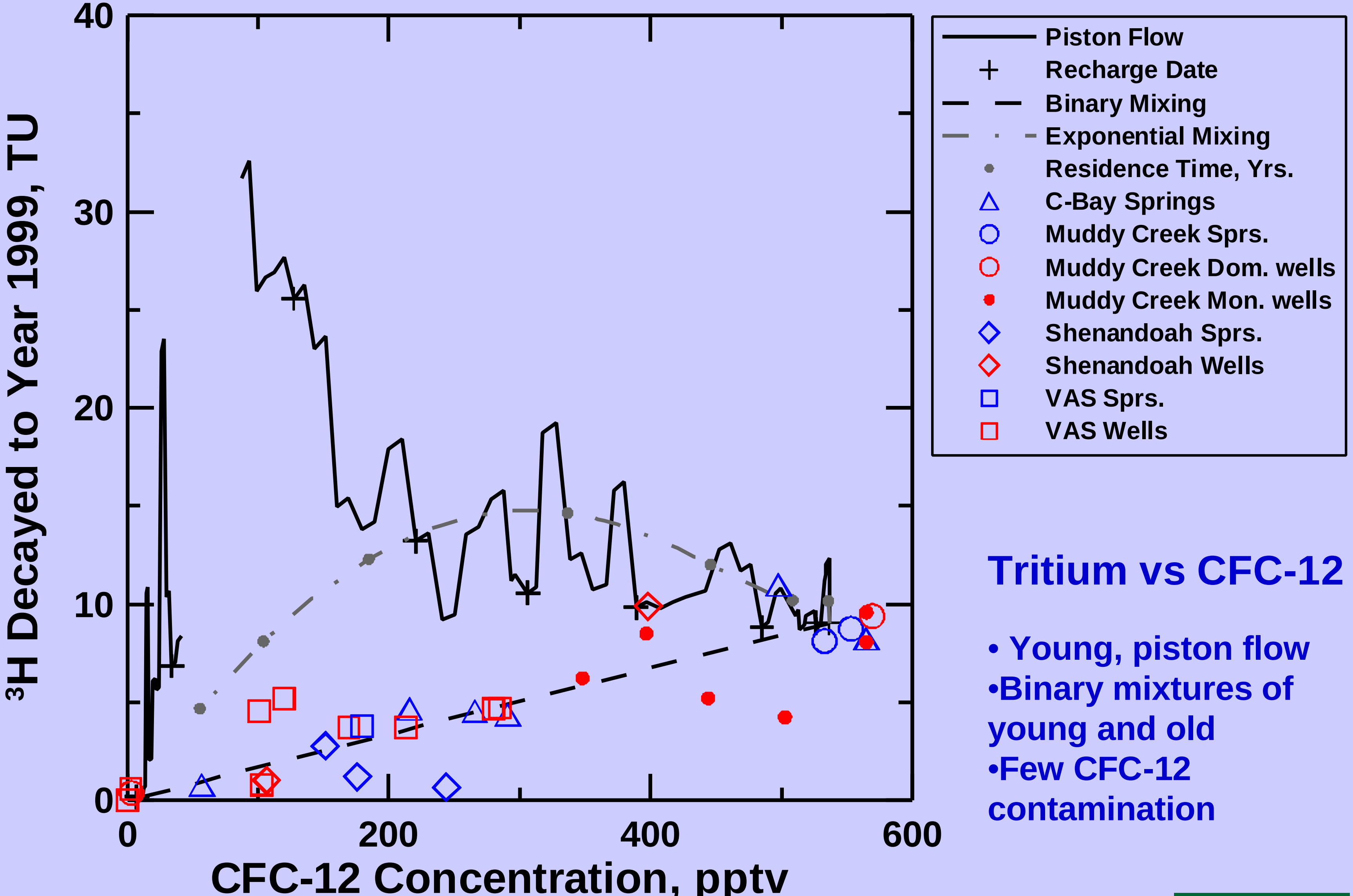
Mixture of Younger and Older Ground Water



Modified from Brahana and others, 1986

NOT TO SCALE

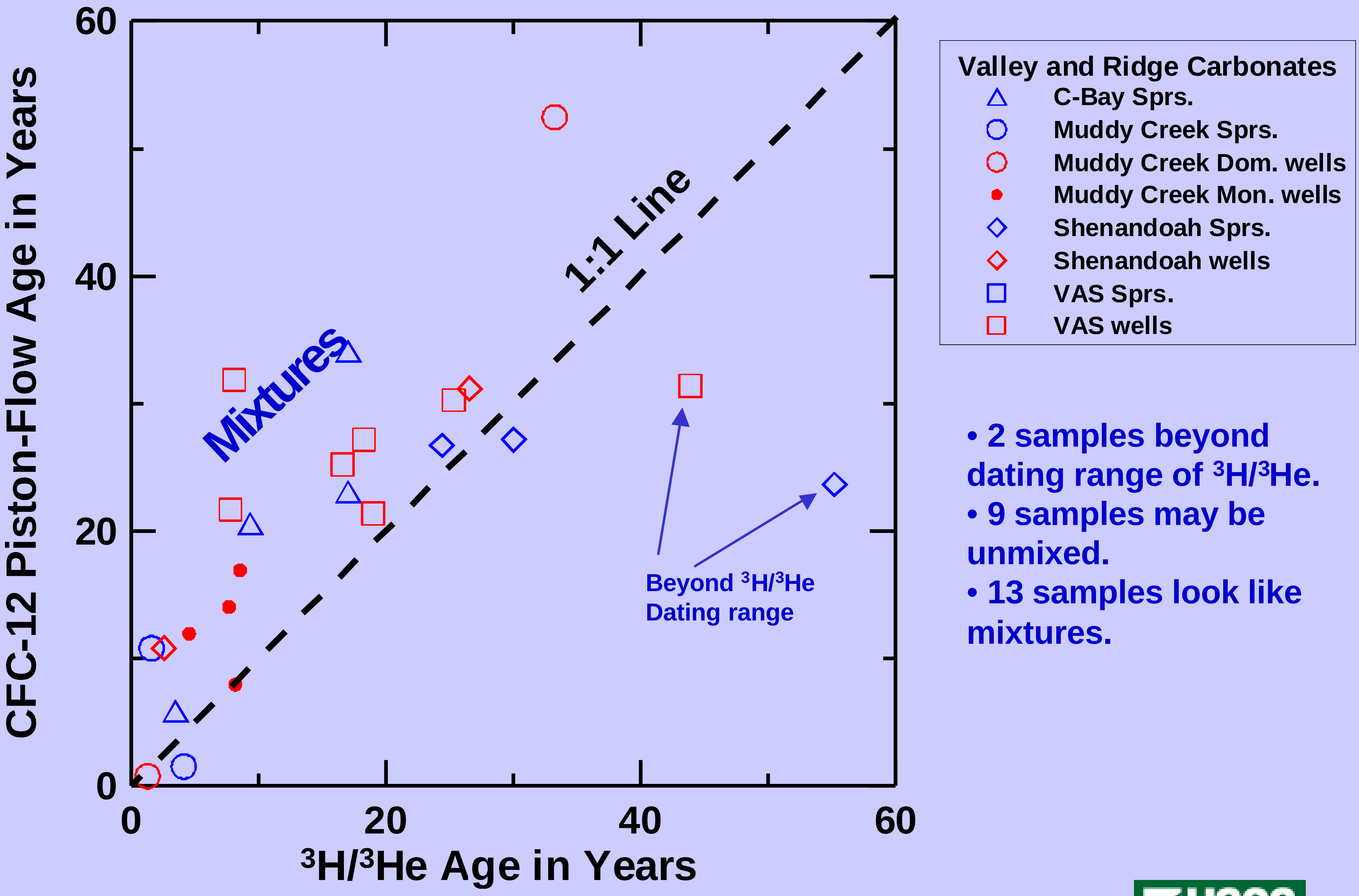
USGS



Tritium vs CFC-12

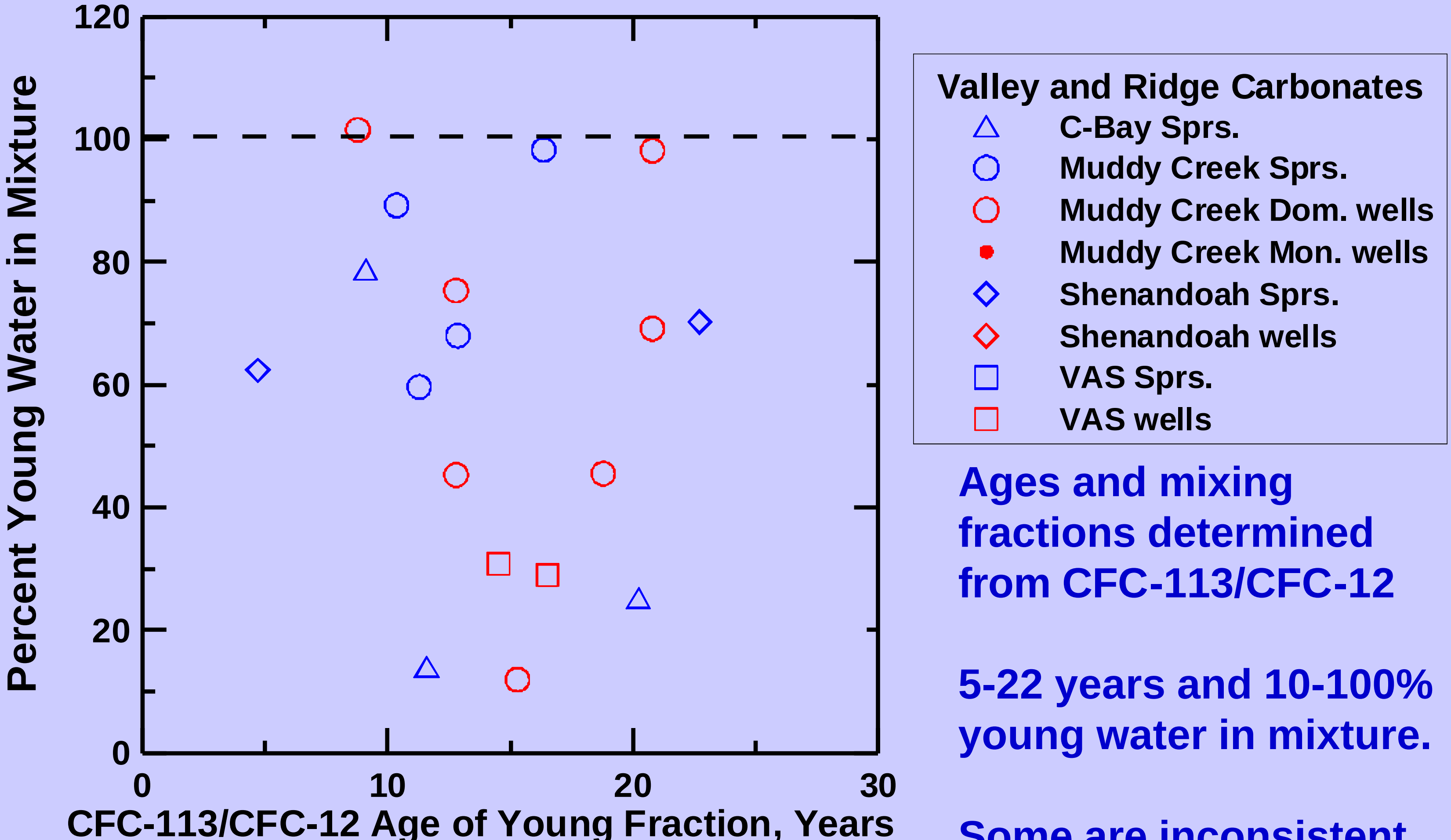
- Young, piston flow
- Binary mixtures of young and old
- Few CFC-12 contamination

USGS



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

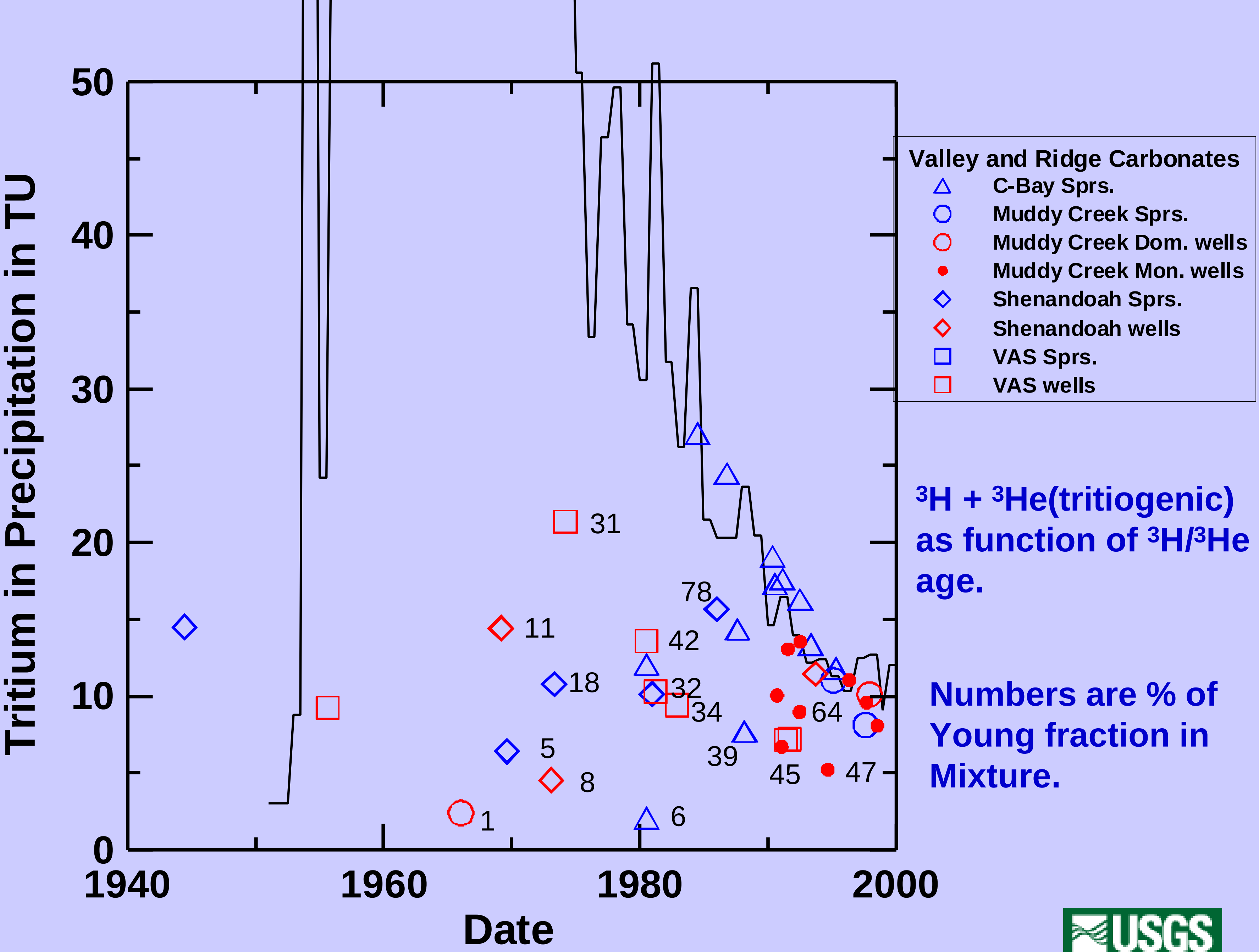
USGS



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

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

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



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

Numbers are % of Young fraction in Mixture.

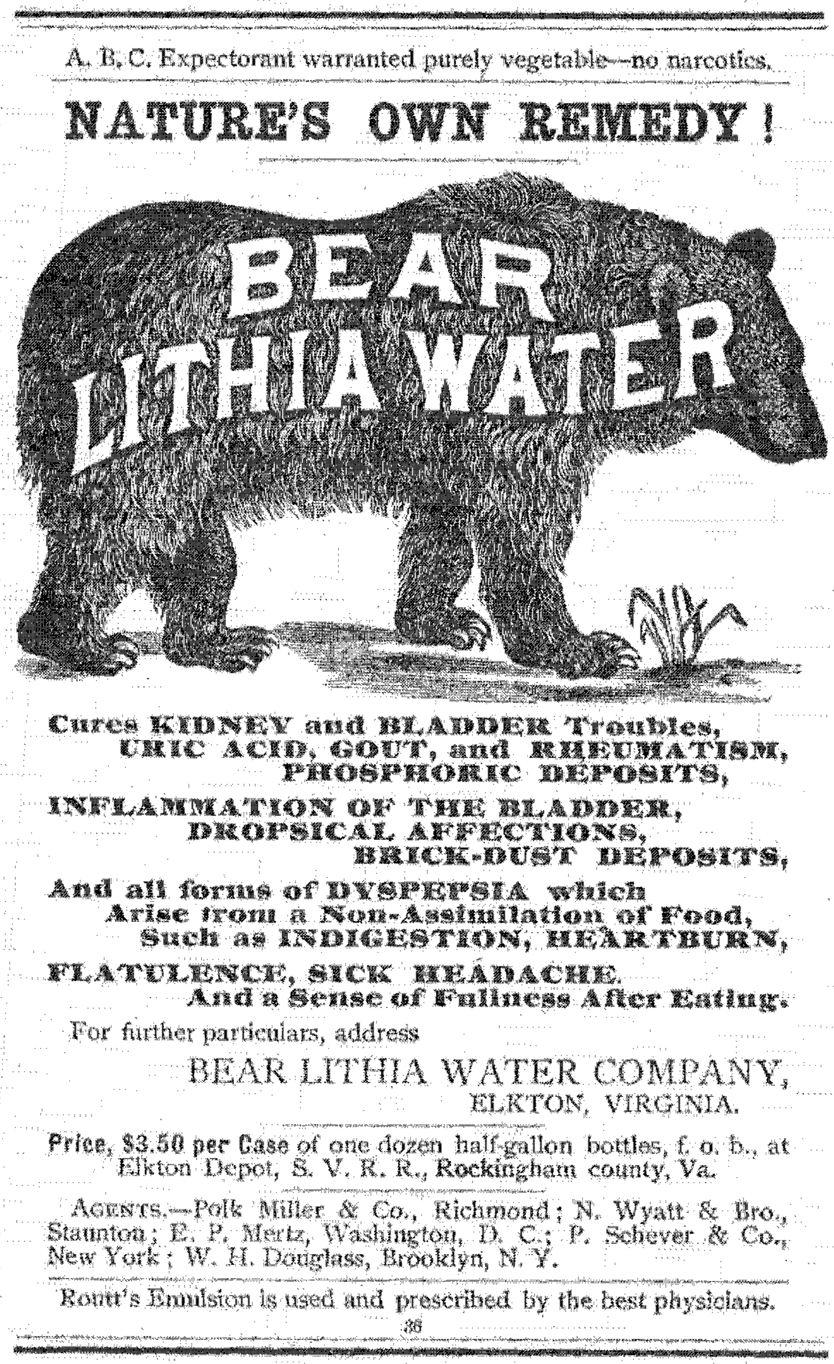
USGS

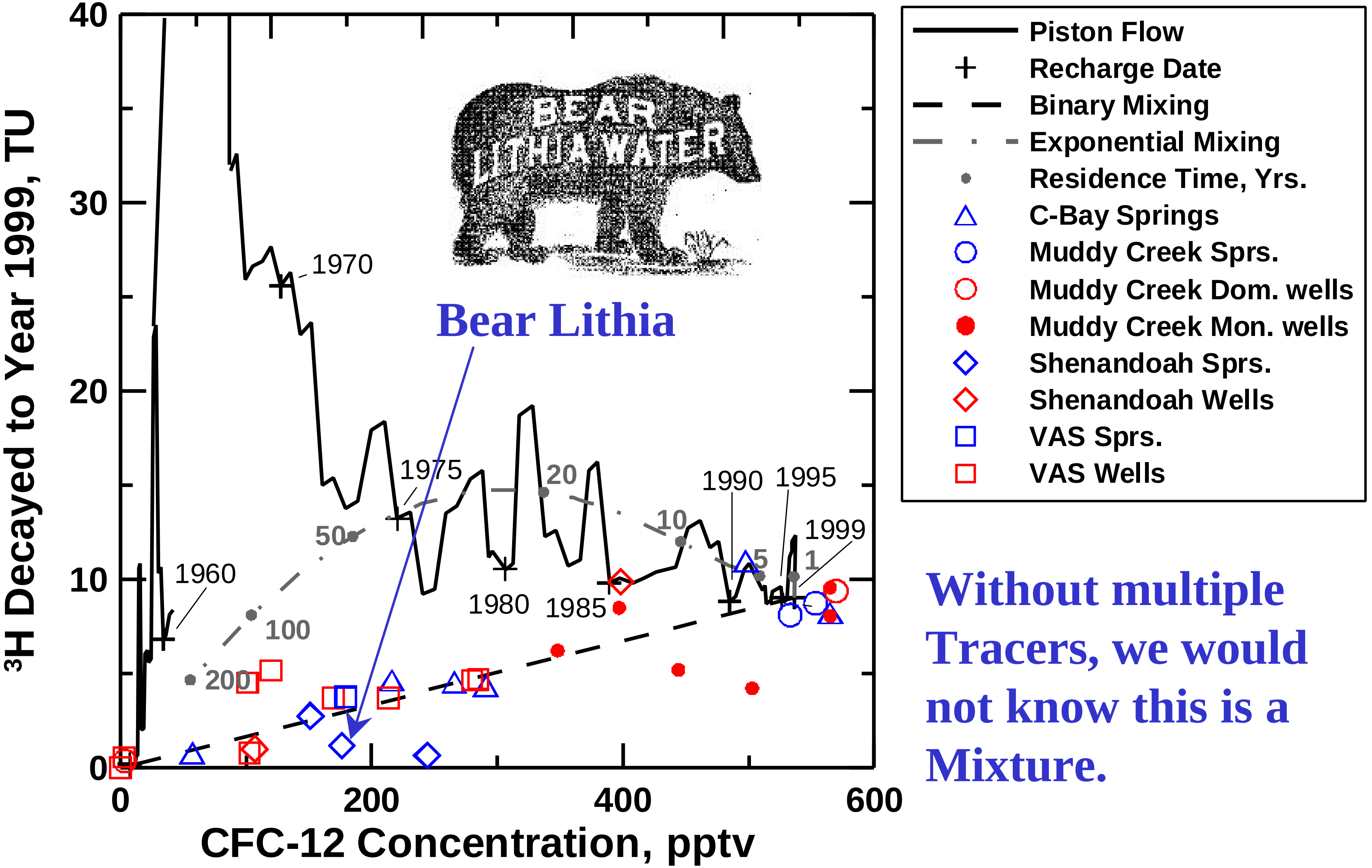
Bear Lithia Spring (9/2/99)

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

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

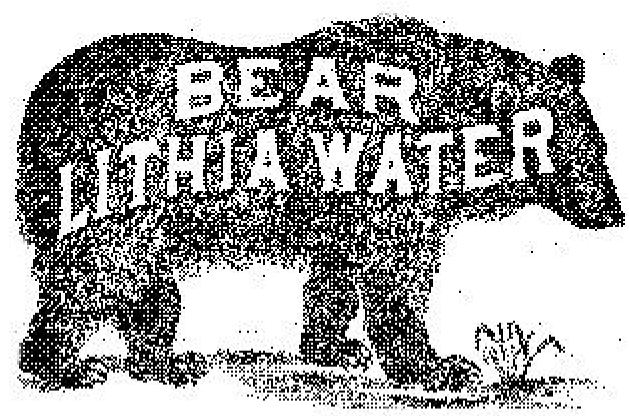
Major Contradiction:
Tritium = 1.2 ± 0.2 TU
1969.6 water would contained about 130 TU; decays to 25 TU





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

Bear Lithia Spring (9/2/99)

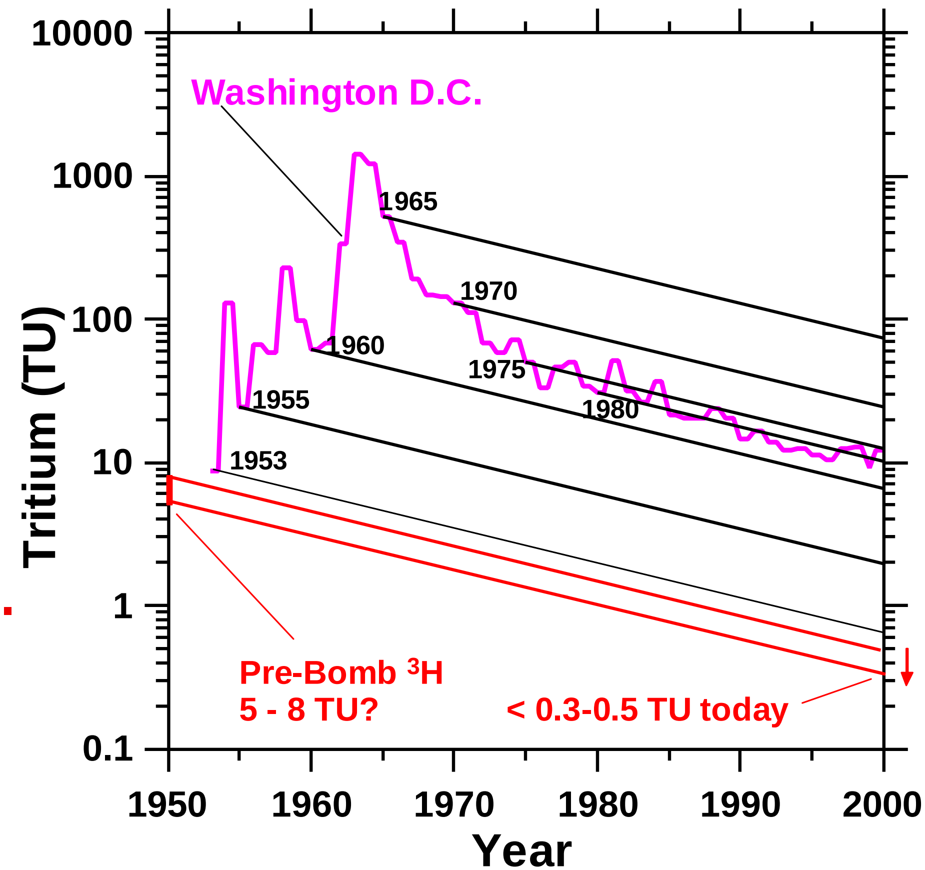


Correcting for assumed pre-bomb tritiogenic ^3He in the old fraction, young fraction varies from 5% at 30 yrs to 12% at 0 yrs age.

From CFC-11: 33.0 % 0 yrs water.
From CFC-12: 32.8 % 0 yrs water.

CFCs Imply ^3H should have been around 3 TU instead of 1.2 TU.

CONCLUSION: Discharge 67-88 % pre-bomb water mixed with approx. 12-33% modern water. $^3H/^3He$ and CFC age of young fraction is very uncertain (0-30 yrs).



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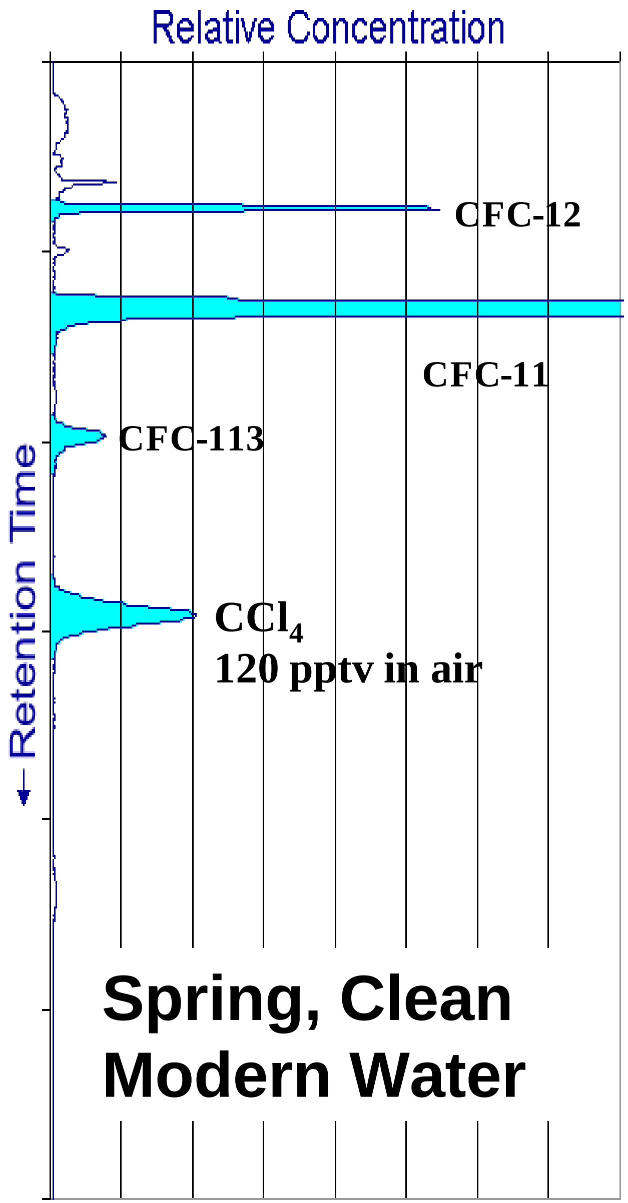
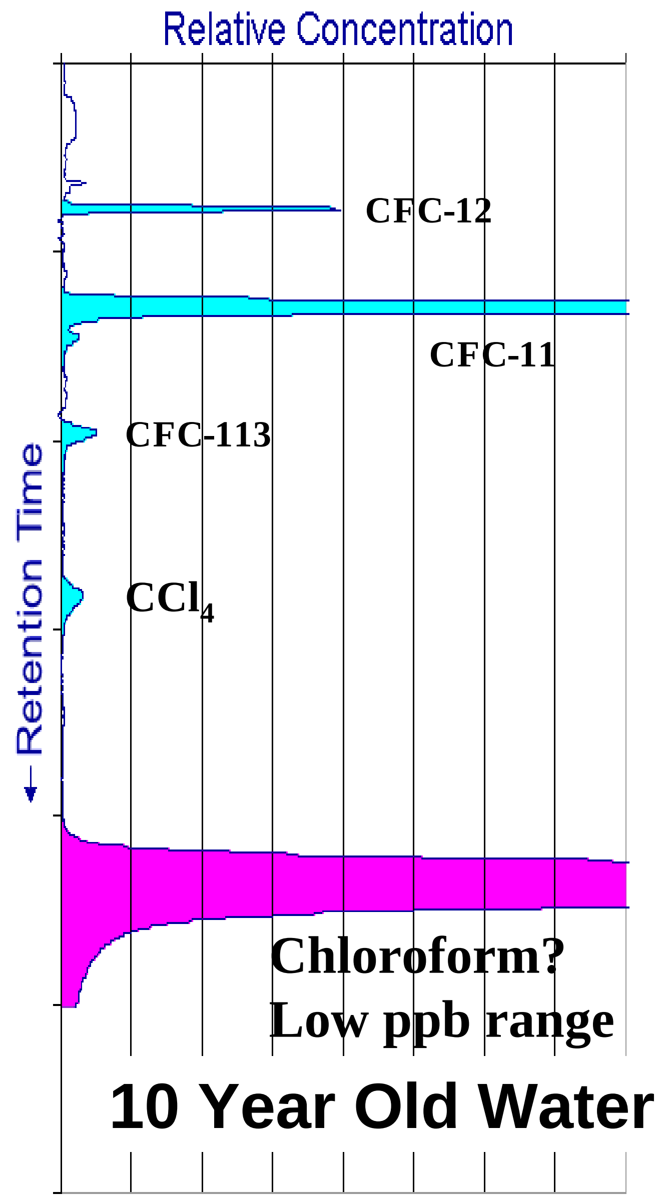
GC-ECD Chromatograms

- 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)

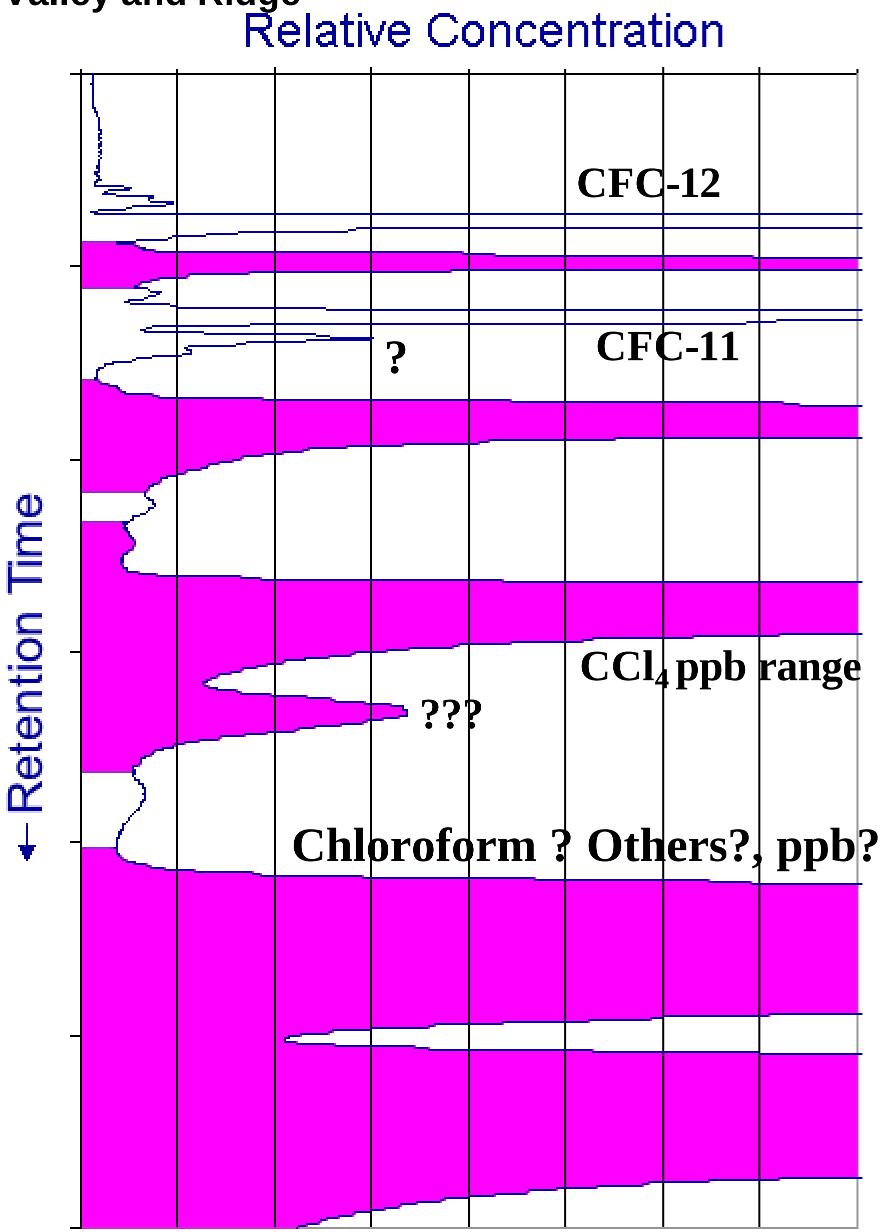
Shenandoah National Park
Spring
Drinking Water
Modern Clean Water



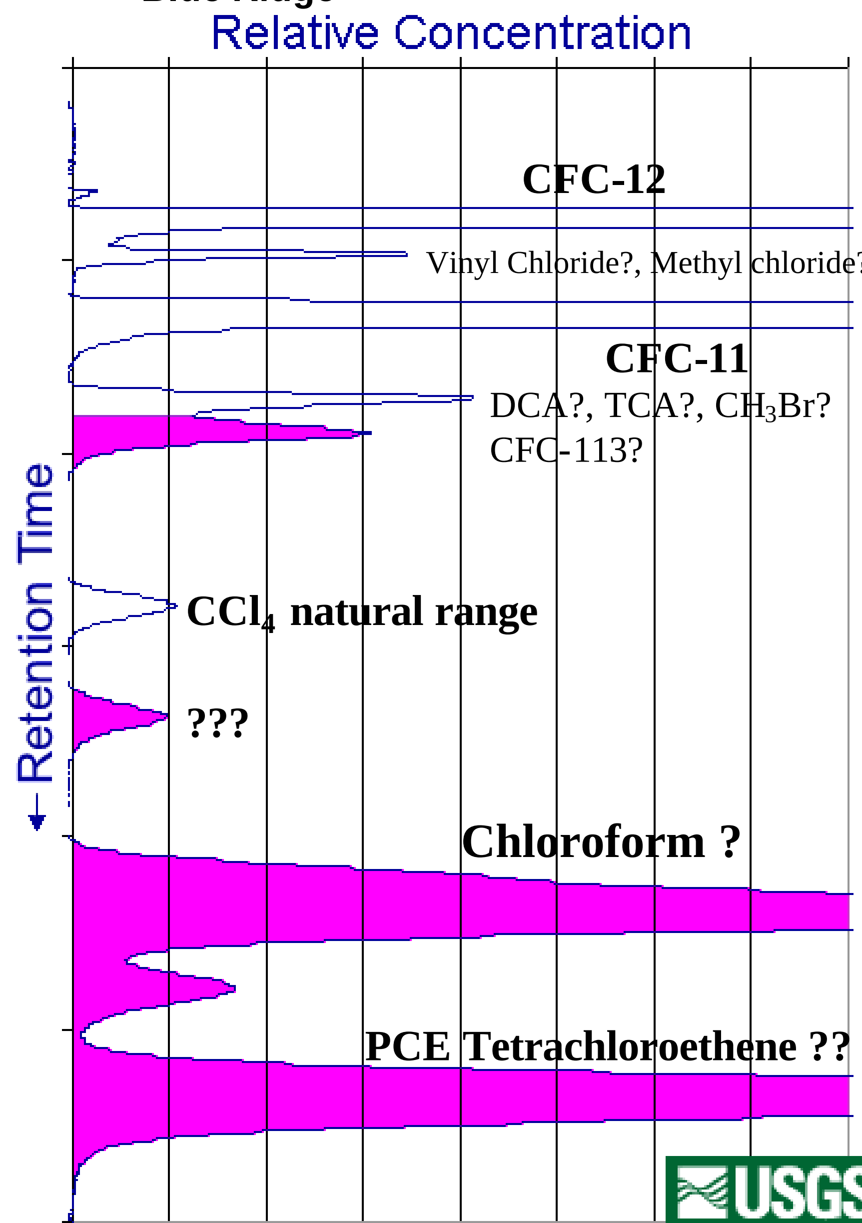
Spring
Yorktown, VA
Drinking Water



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

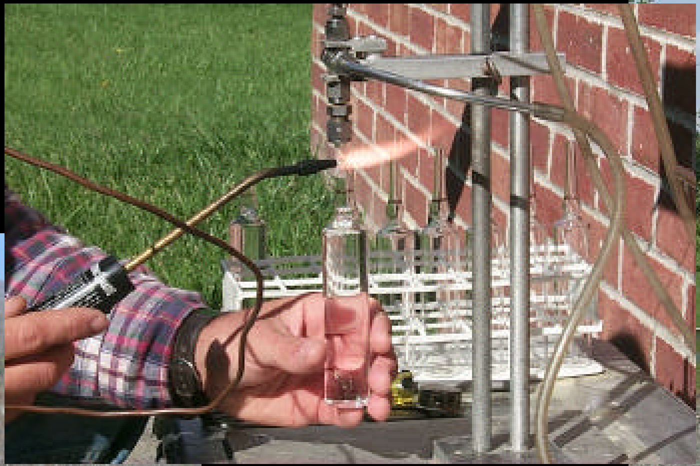


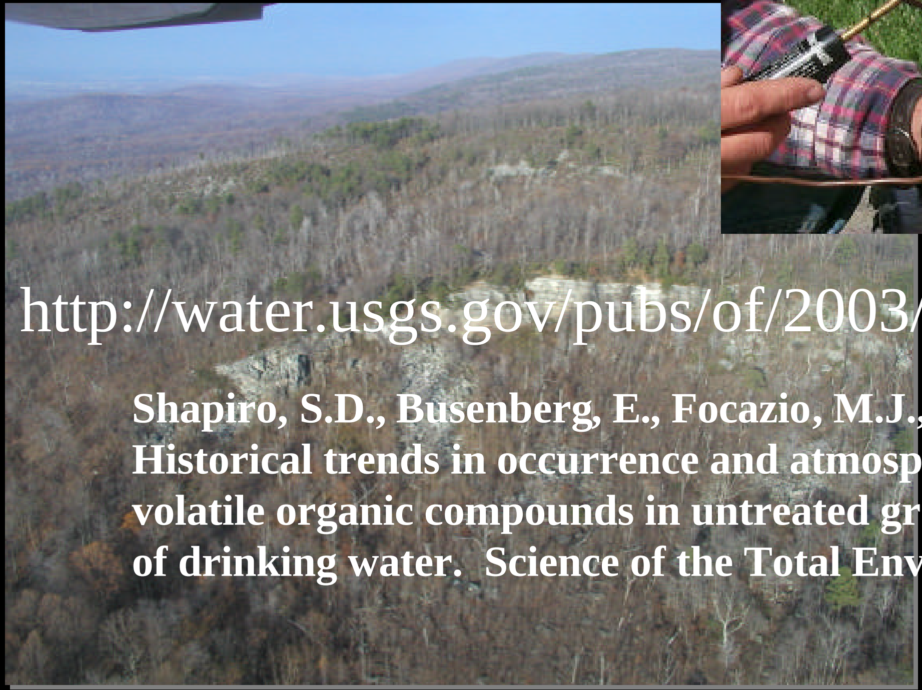
A Town well in VA
Drinking Water Well
Depth: 115 meters
Blue Ridge



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

Shapiro, S.D., Busenberg, E., Focazio, M.J., and Plummer, L.N., 2004, Historical trends in occurrence and atmospheric inputs of halogenated volatile organic compounds in untreated ground water used as a source of drinking water. Science of the Total Environment, v. 321, 201-217.

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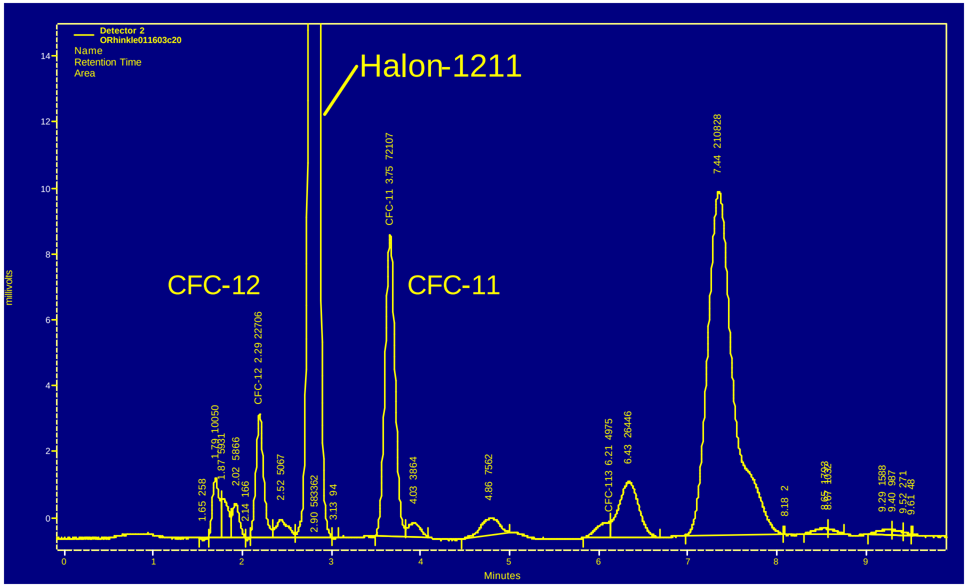
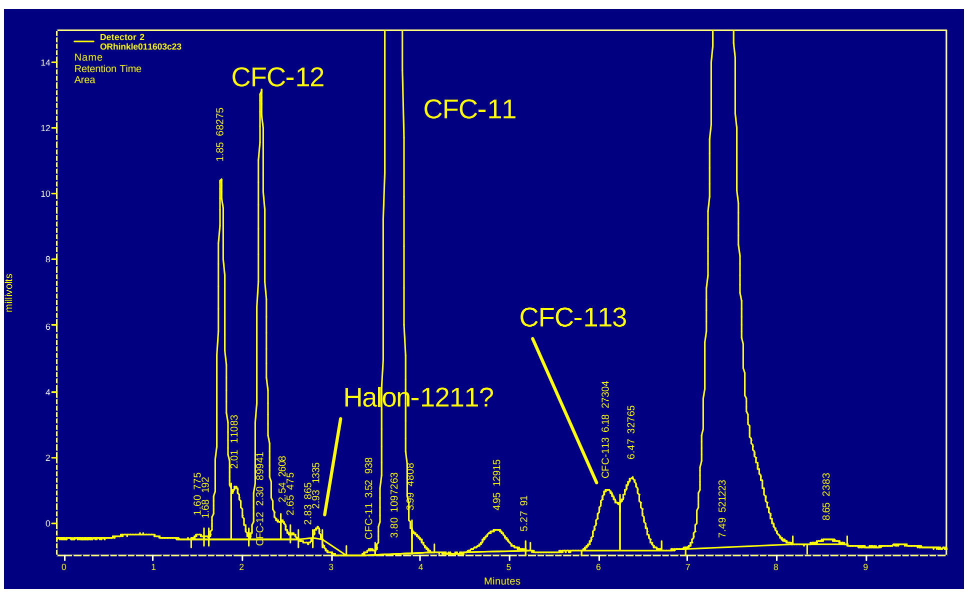
Halon 1211
Drilling Tracer



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

- 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. Is this the result of the sampling process?
- 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.

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CONCLUSIONS (cont.)

- CFC-113/CFC-12 data demonstrate cases of piston flow and binary mixing too, but can be affected by contamination.
- Most ground water from fractured rock or karstic aquifers is vulnerable to contamination.
- Should include tracers in well drilling.

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 the interpretation of age, refine hydrologic concepts, and identify vulnerability to contamination.

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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.**