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

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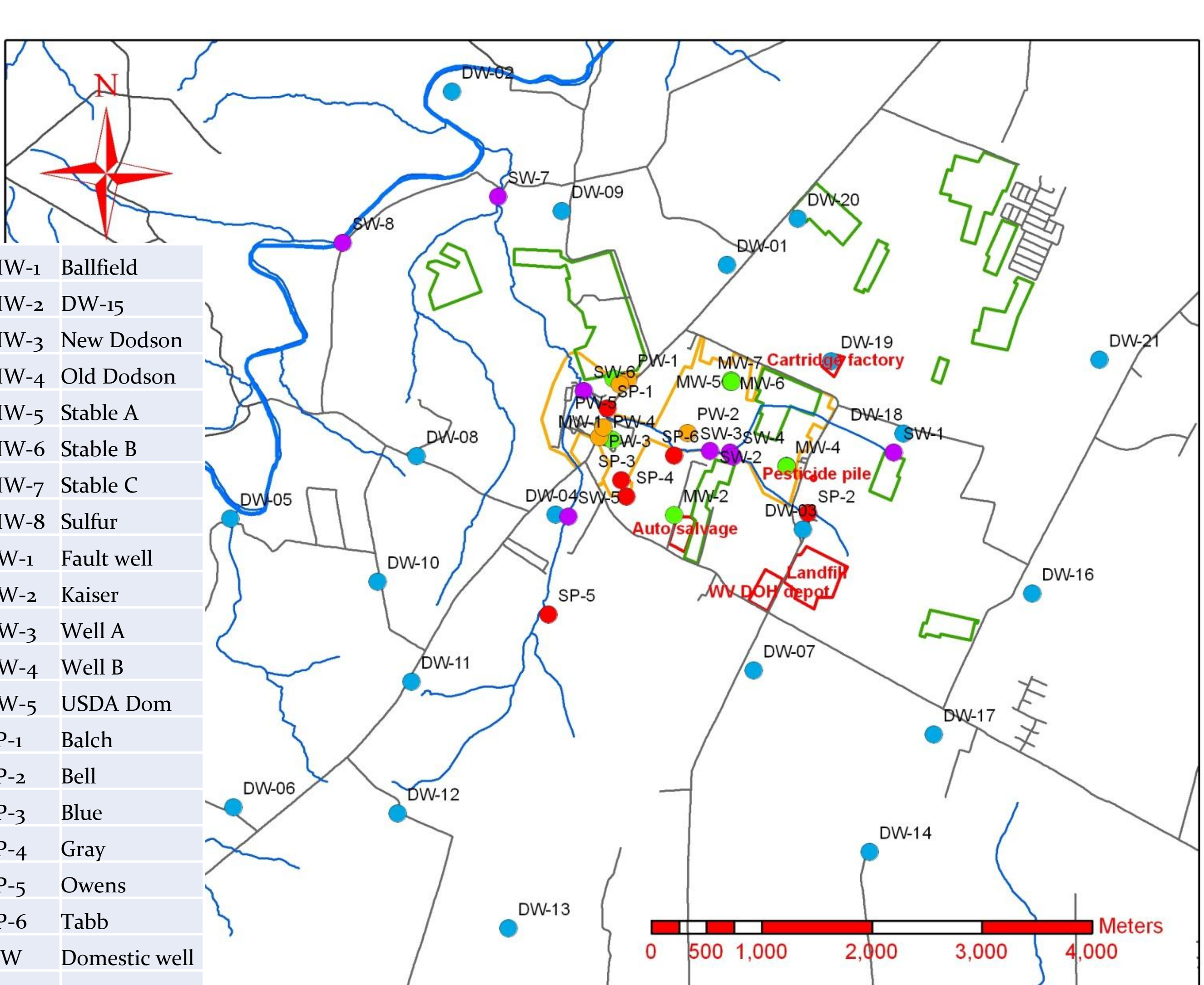
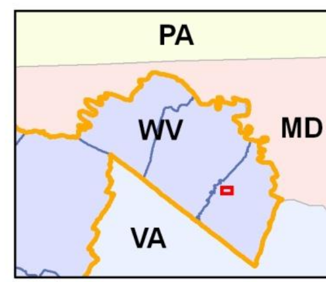
Leetown Sample Sites and Land Use

MW-1	Ballfield
MW-2	DW-15
MW-3	New Dodson
MW-4	Old Dodson
MW-5	Stable A
MW-6	Stable B
MW-7	Stable C
MW-8	Sulfur
PW-1	Fault well
PW-2	Kaiser
PW-3	Well A
PW-4	Well B
PW-5	USDA Dom
SP-1	Balch
SP-2	Bell
SP-3	Blue
SP-4	Gray
SP-5	Owens
SP-6	Tabb
DW	Domestic well
SW	Surface water



Study Area Location

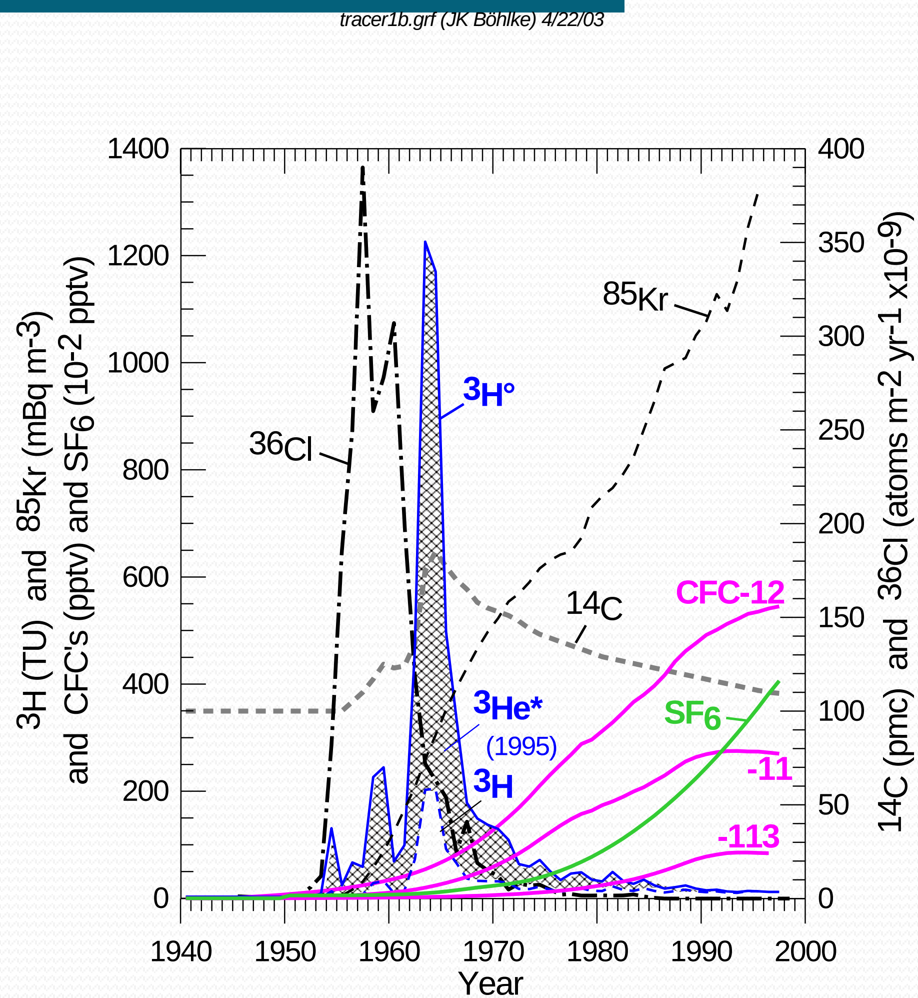


Objectives– What can measurements of a suite of environmental tracers in groundwater at the LSC tell us about?

- 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 (SF_6)
- Tritium (^3H)
- Noble Gases (^4He, Ne, Ar, Kr, Xe; ^3He); $^3H/^3He$ age
- Permanent Gases (N_2, Ar)
- Halogenated VOCs (PCE, Chloroform, TCE, etc.)
- Inorganic Water chemistry
- Stable Isotopes of Water
- Age: time elapsed since RC
- Age is an interpretation



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Samples Collected

- 2004, 2006. Initial sampling during Kozar study. (CFCs and $^3H/^3He$).
- 2008. Sampling of LSC springs and wells.
- 2008-2010. Monthly sampling at Gray spring.
- 2009. Sampling of LSC springs, wells (comparison tests: $^3H/^3He$), 21 domestic wells and 10 local surface water sites.

USGS

Dating Groundwater with Helium

1. Dating Young Groundwater: With tritium and helium-3. Timescale about 0-30 years. Measure tritium, Helium-4, Neon, helium-3/helium-4 isotope ratio.

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.

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Tritium/Helium-3 age is age of the young fraction in binary mixtures of old and young

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

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

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

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).

λ is the decay constant (0.05626 yr^{-1}) (λ=ln2/12.32, where 12.32 is the half-life of tritium).

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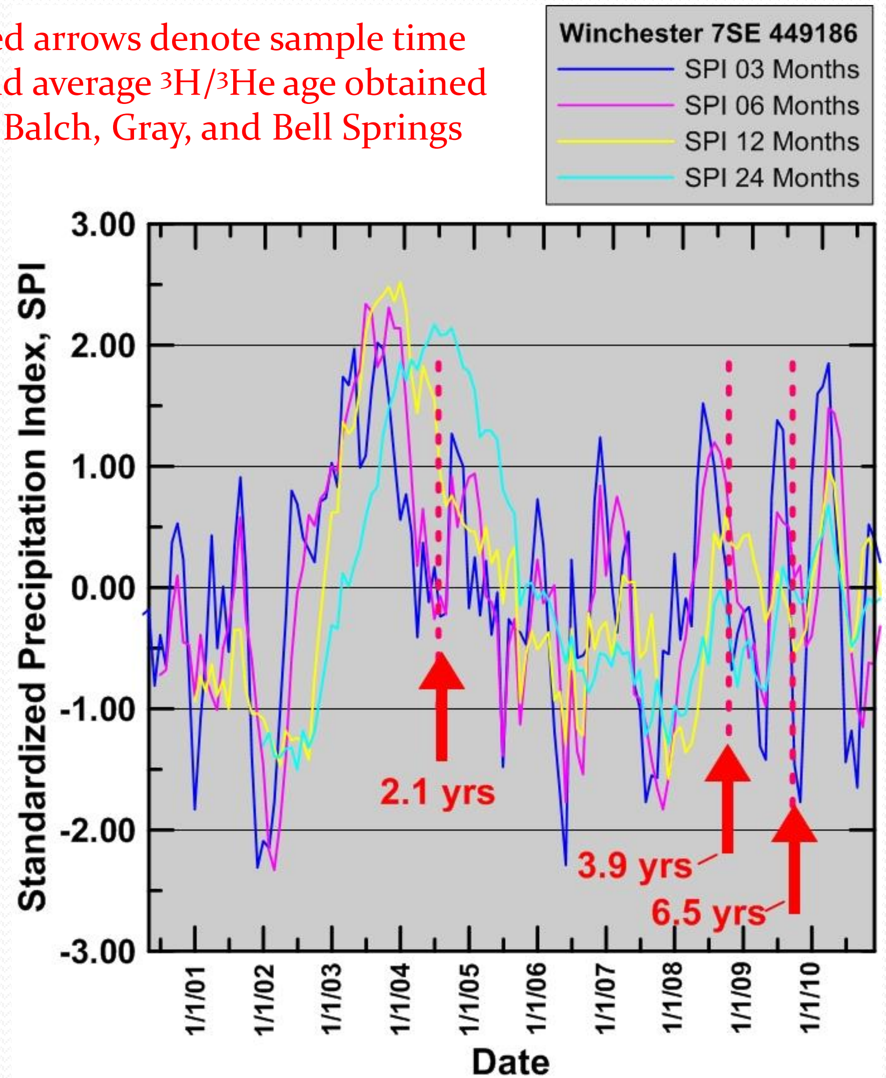
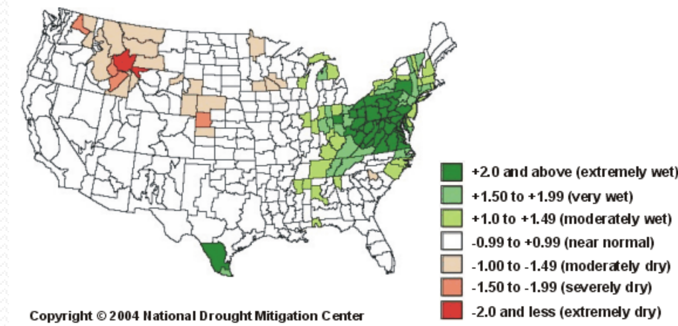
$^3H/^3He$ sampling relative to SPI at Winchester

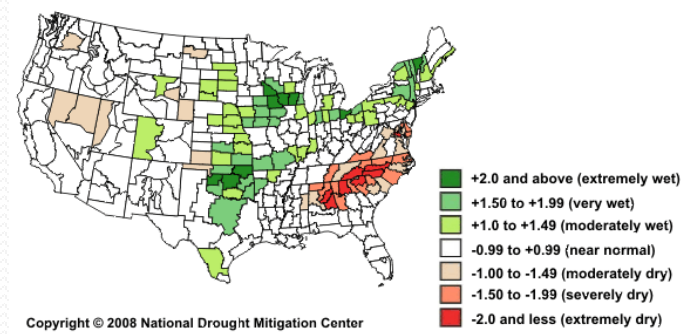
Red arrows denote sample time and average $^3H/^3He$ age obtained at Balch, Gray, and Bell Springs



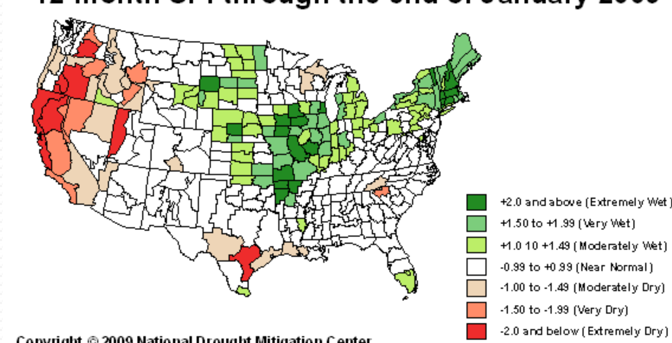
12-month SPI through the end of April 2004



12-month SPI through the end of April 2008



12-month SPI through the end of January 2009



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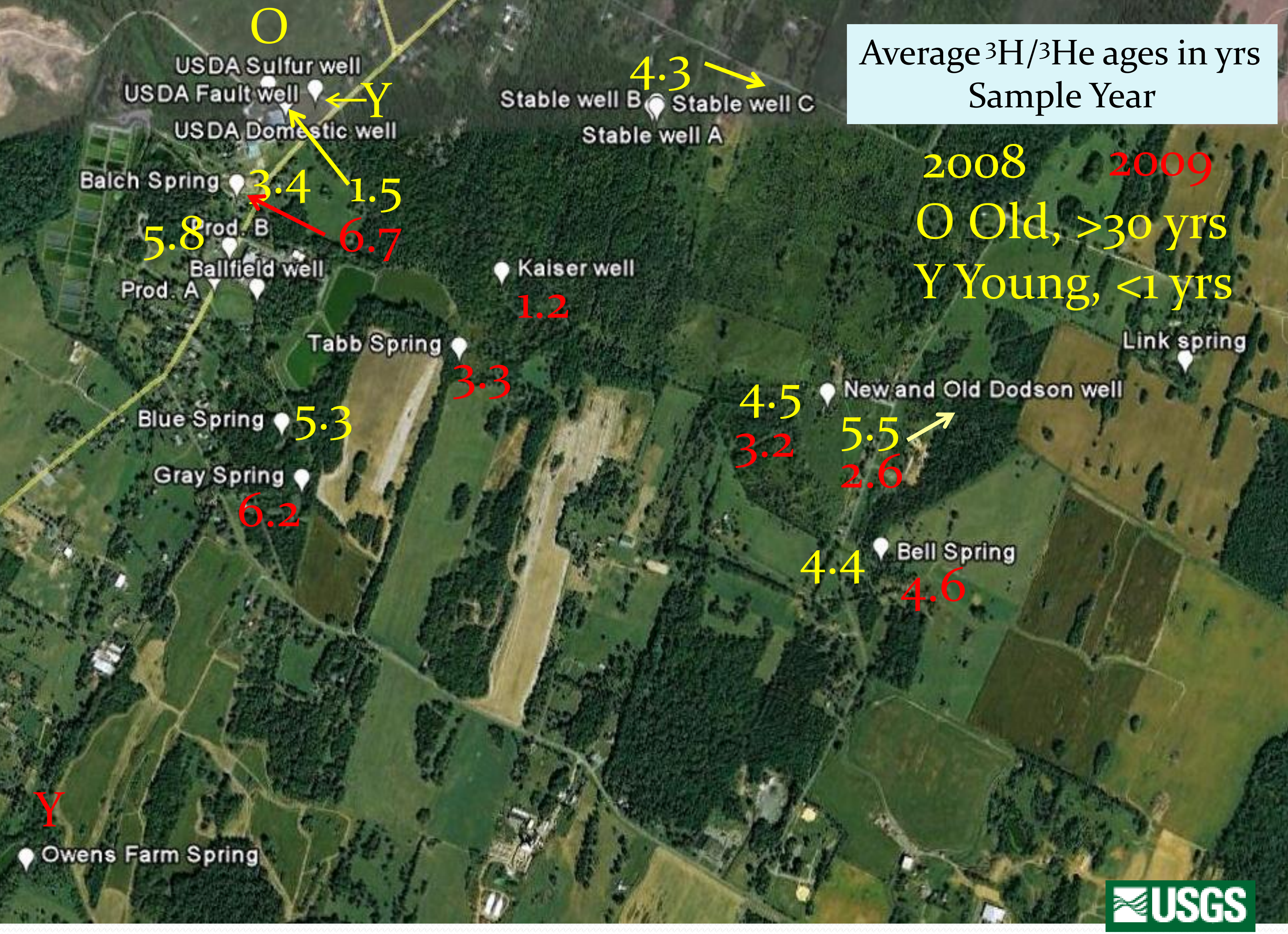
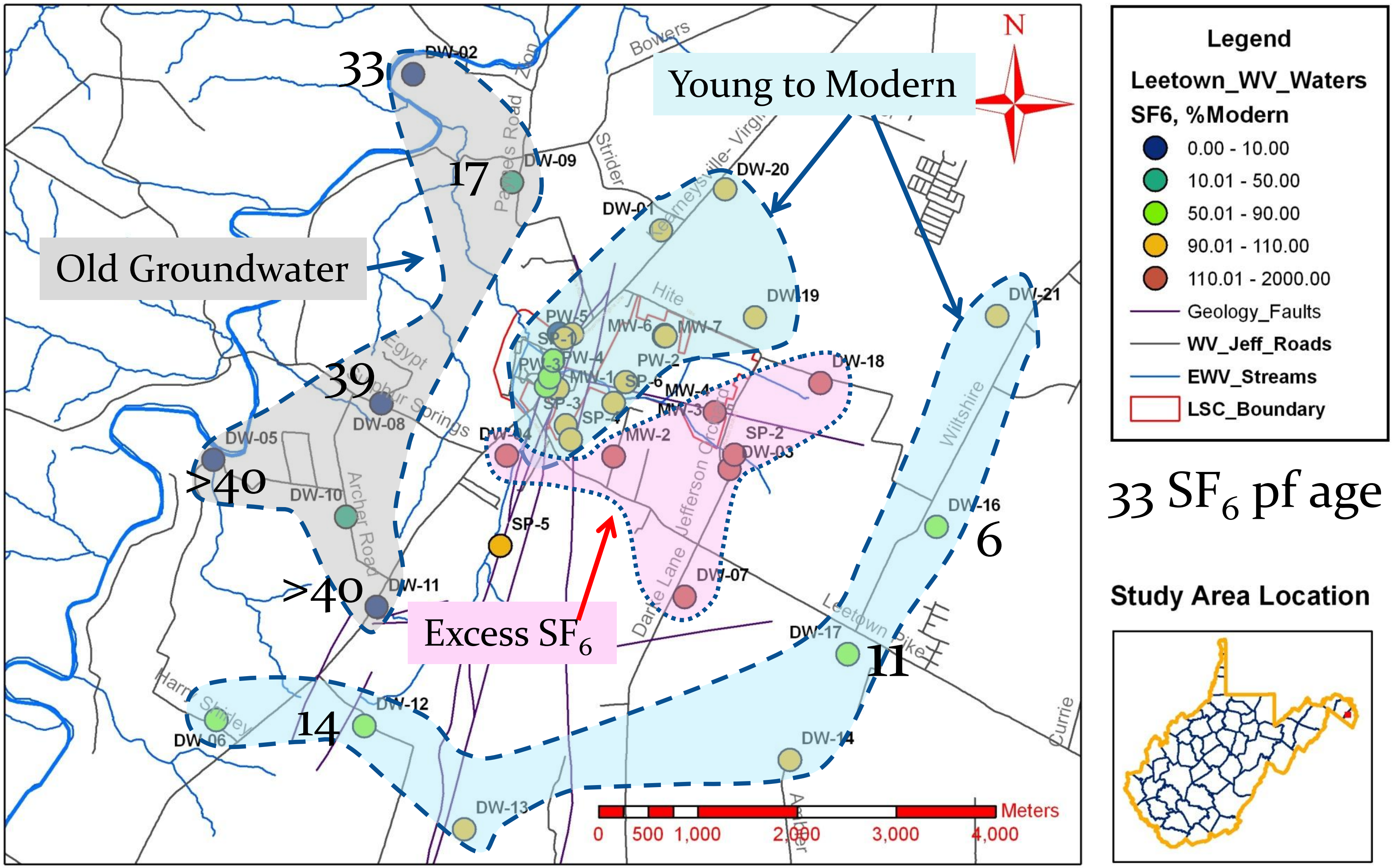
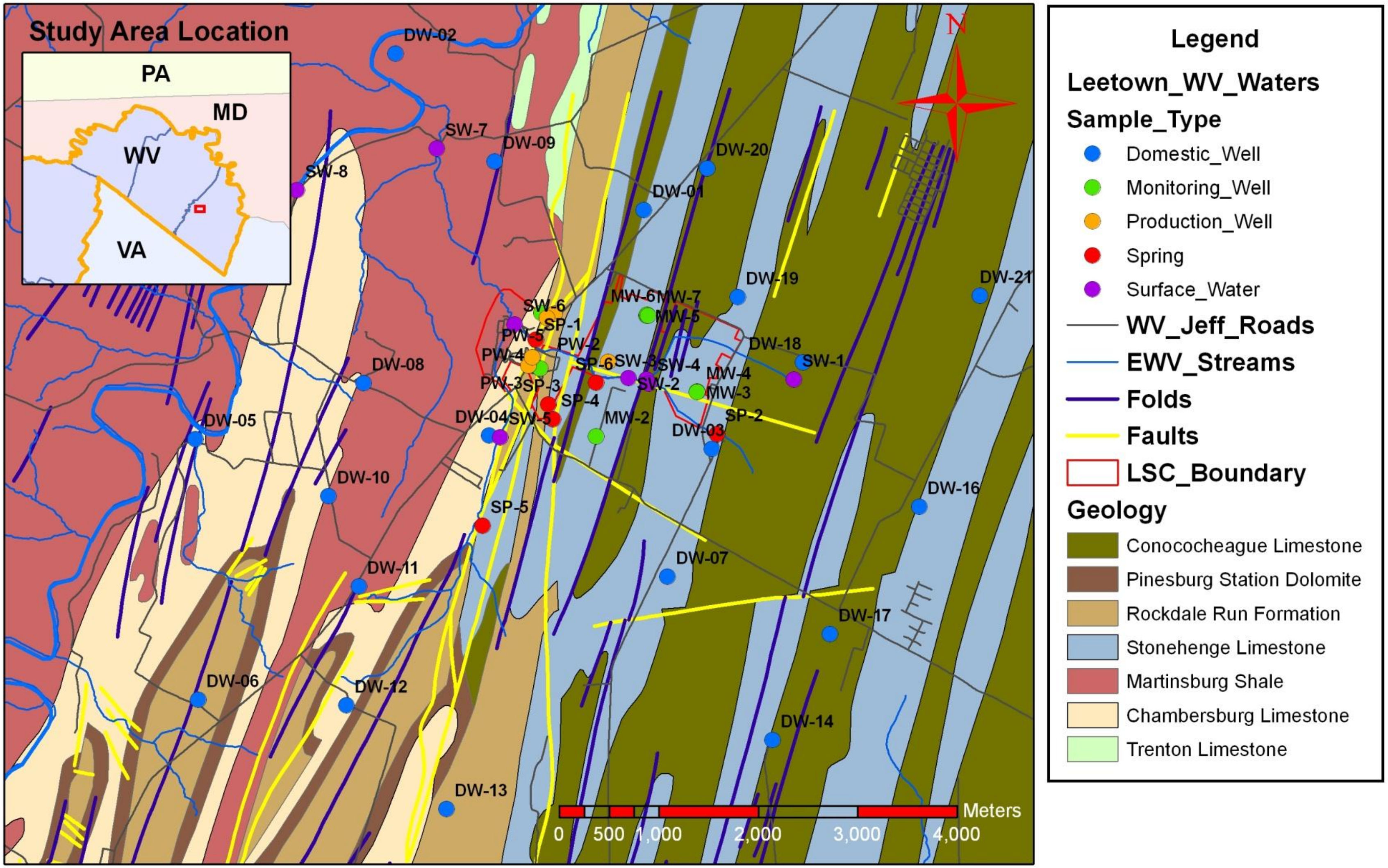

Average ³H/³He ages in yrs
Sample Year
2008
2009
O Old, >30 yrs
Y Young, <1 yrs
O
USDA Sulfur well
USDA Fault well
Y
USDA Domestic well
1.5
Balch Spring
3.4
6.7
5.8
Prod. B
Ballfield well
Prod. A
4.3
Stable well B
Stable well C
Stable well A
Kaiser well
1.2
Tabb Spring
3.3
Blue Spring
5.3
Gray Spring
6.2
4.5
3.2
New and Old Dodson well
5.5
2.6
Link spring
Bell Spring
4.4
4.6
Y
Owens Farm Spring
USGS

Leetown Sites - SF6



Leetown Sample Sites



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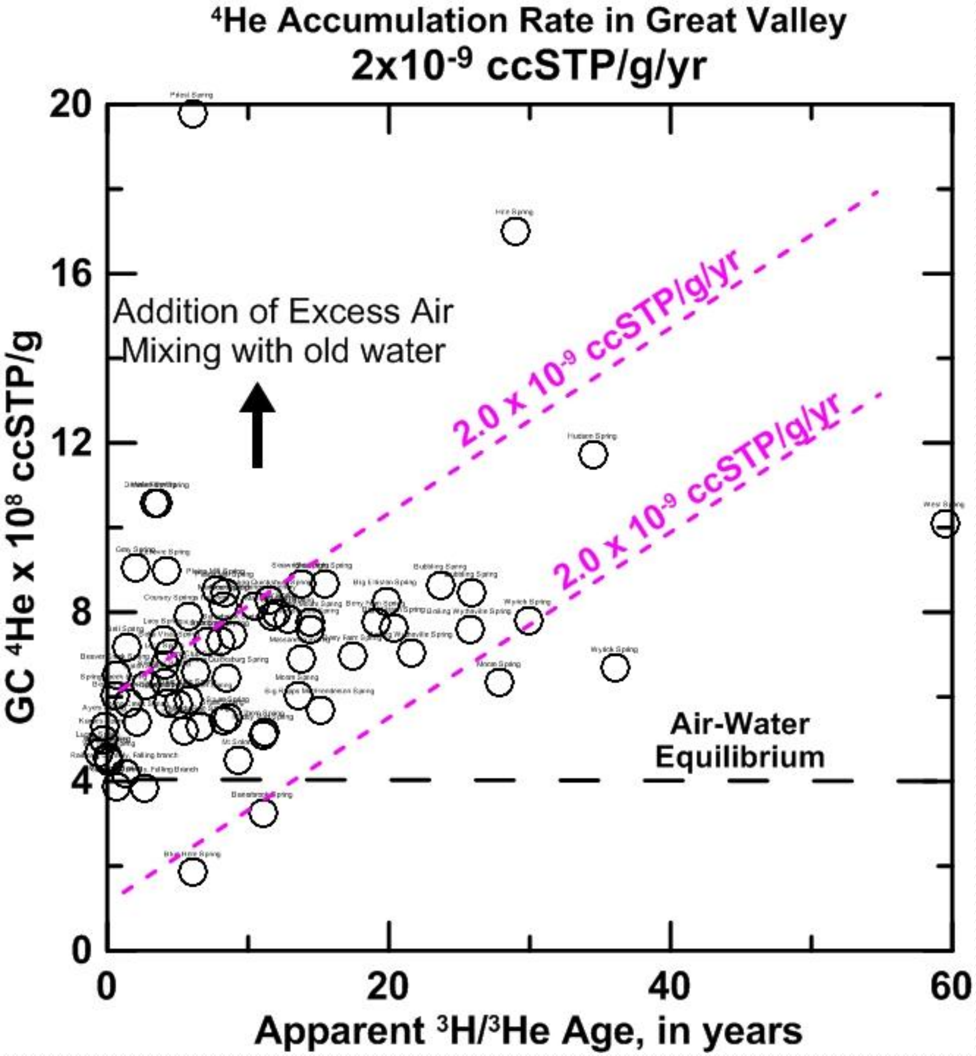
Finding the "age" of old water at LSC from radiogenic ^4He

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

$$Age = {}^4He_{rad(old)} / A^4{}_{He}$$

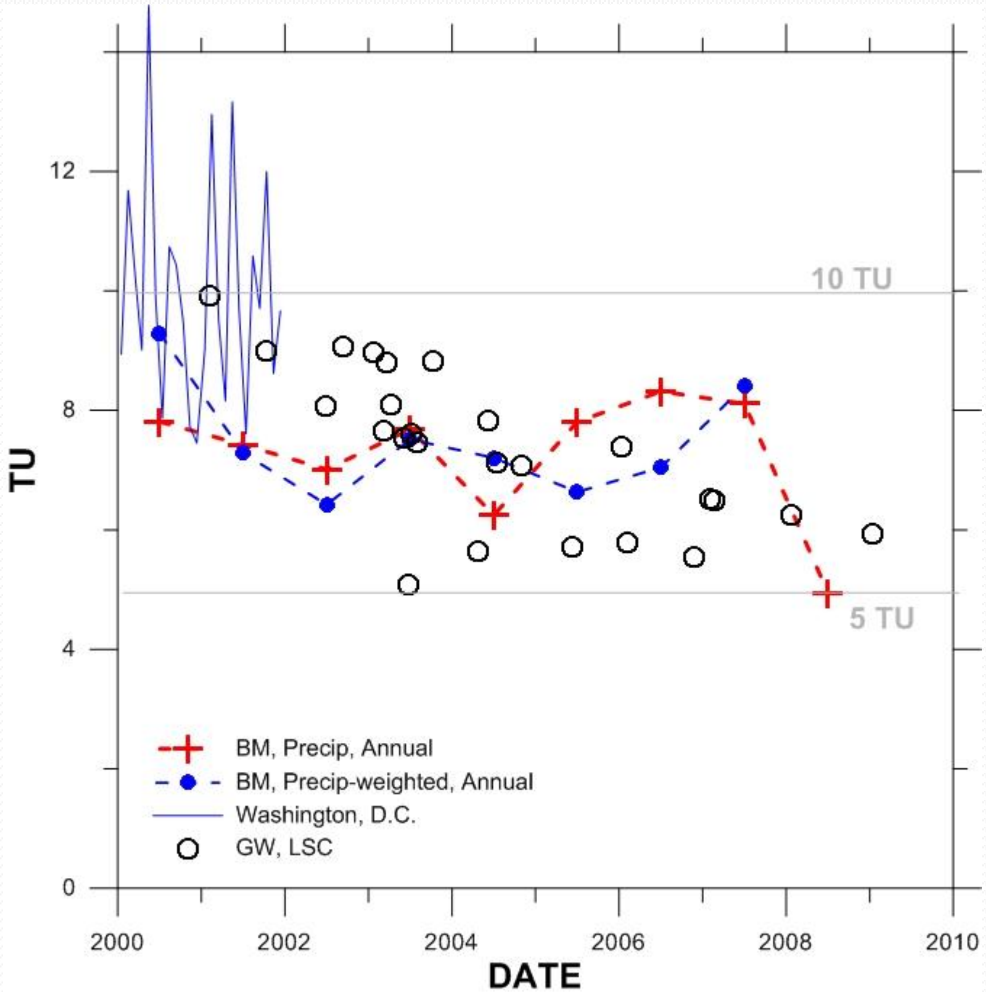
^4He accumulates in groundwater with age



This Radiogenic ^4He 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

MW-1	Ballfield
MW-2	DW-15
MW-3	New Dodson
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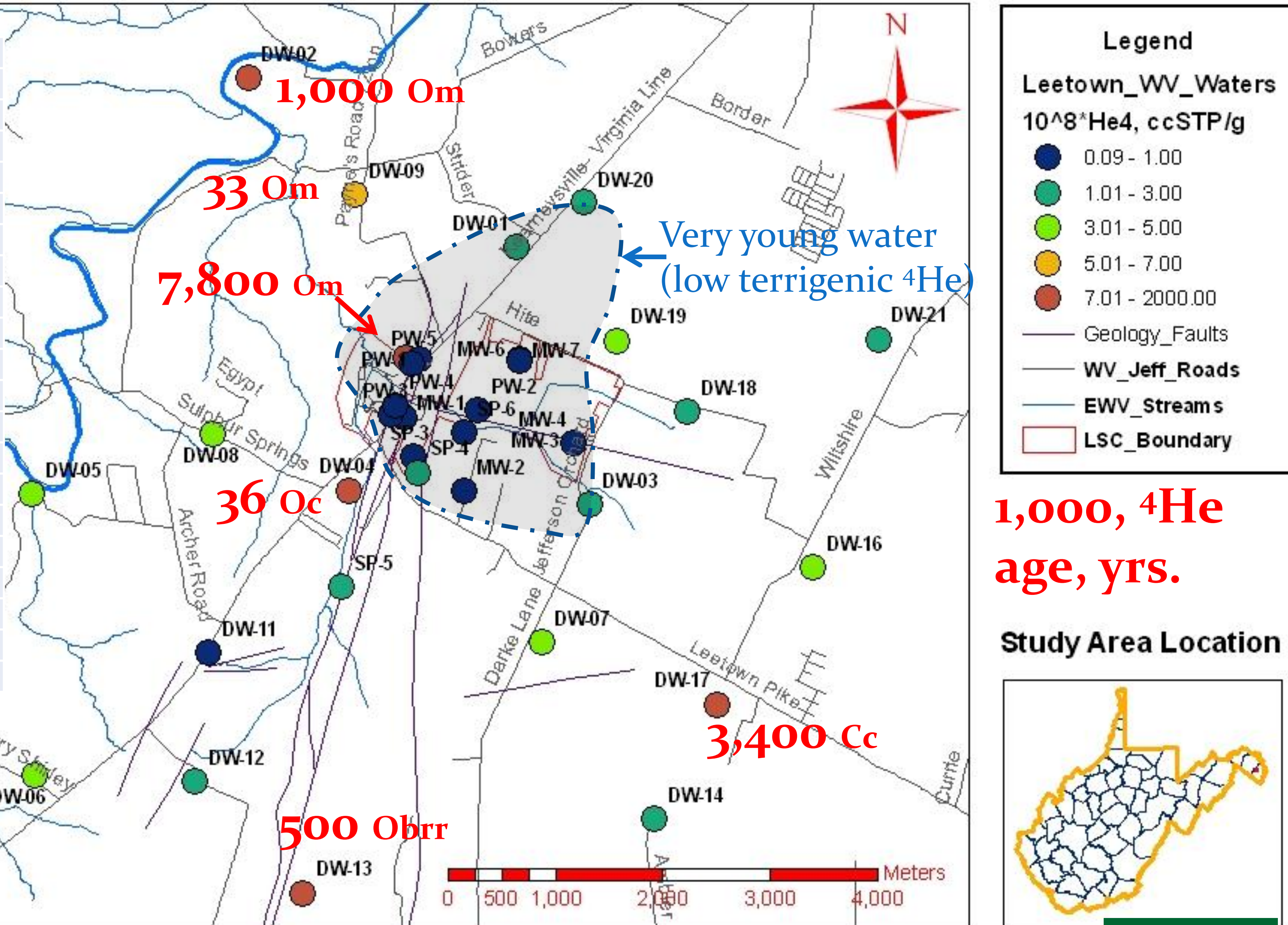

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Groundwater Volume

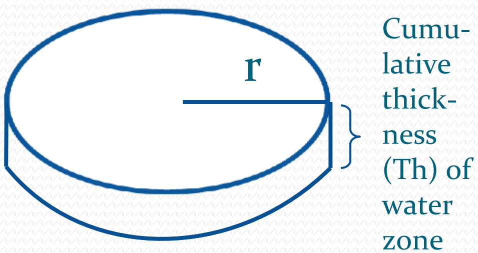
$$V = \textit{Discharge} \times \textit{Age} \quad [V=(V/t) \times t]$$

<u>Assumptions</u>

- 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.

				Assuming rule of thumb, 1 cfs=1 mi²		
Spring	Age range in years	Estimated discharge in cfs	Reservoir volume, millions of ft^3	Est. total thickness in ft of circular water zone	Diameter in miles of catchment zone	Area of catchment zone mi^2
Gray	2.1-6.5	1.1-2.7	90-500	2.5-7.5	1.2-1.8	1.1-2.6
Blue	4.8-5.3	0.13	20-22	5.5-6.0	0.4	0.1
Bell	1.4-6.4	1.8-2.0	90-400	2-7	1.5-1.6	1.8-2.1
Balch	2.2-8.5	0.45	30-120	3-10	0.7-0.8	0.4-0.5

If catchment were a circle



$$r=(V/(Th \times \pi))^{1/2}$$

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

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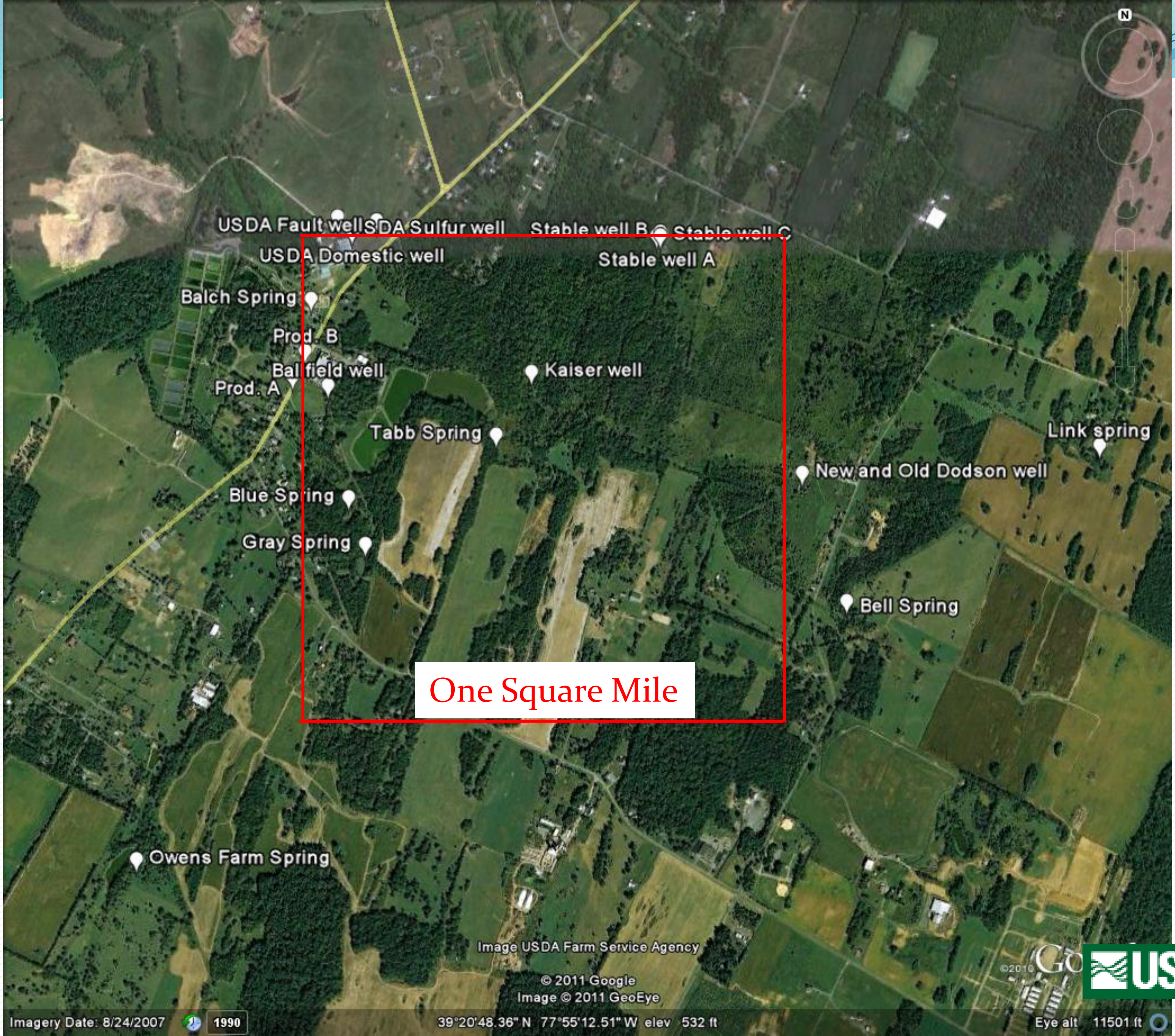
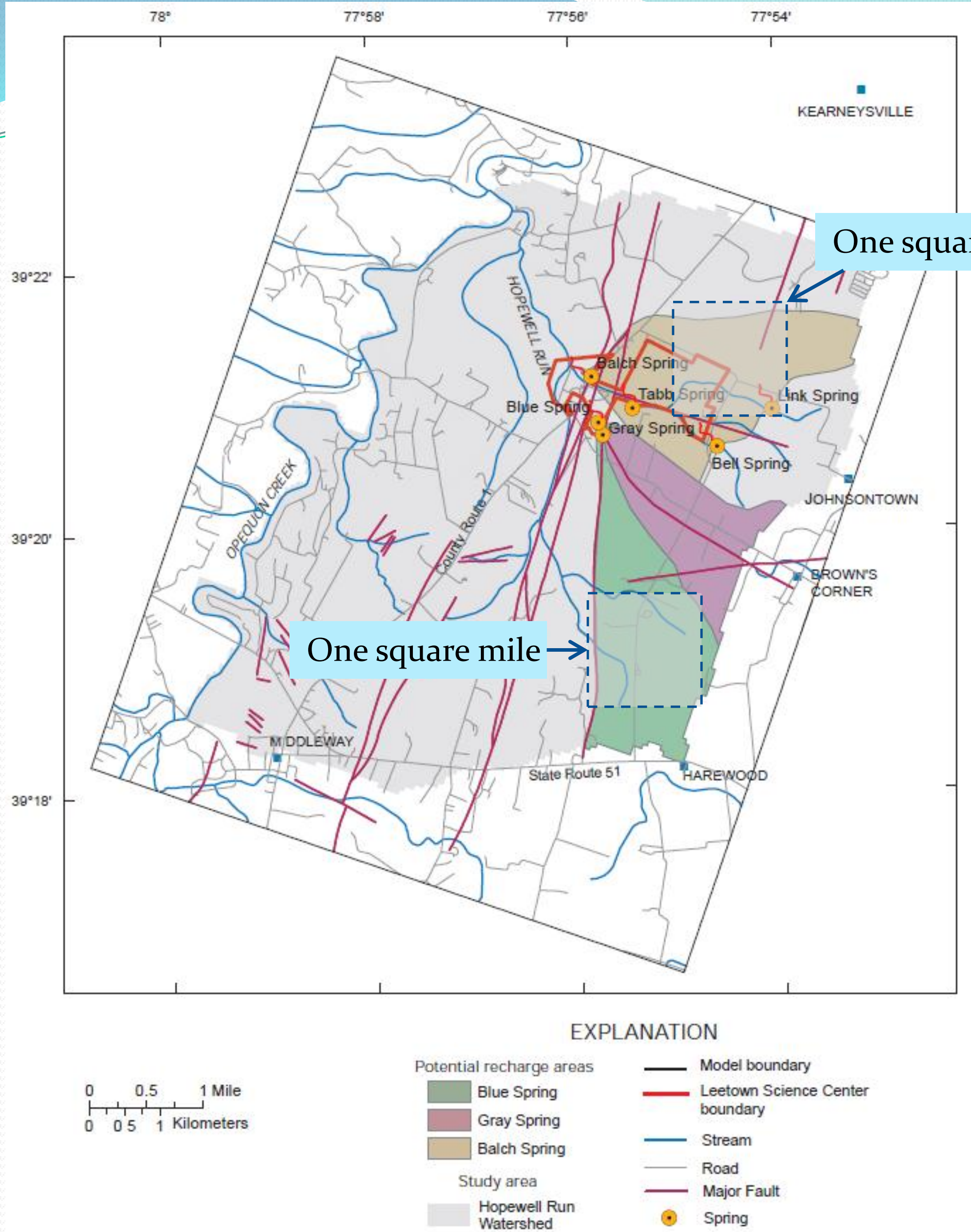

USDA Fault well
USDA Sulfur well
Stable well B
Stable well C
USDA Domestic well
Stable well A
Balch Spring
Prod. B
Ballfield well
Prod. A
Kaiser well
Tabb Spring
Link spring
New and Old Dodson well
Blue Spring
Gray Spring
Bell Spring
One Square Mile
Owens Farm Spring
Image USDA Farm Service Agency
© 2011 Google
Image © 2011 GeoEye
Imagery Date: 8/24/2007
1990
39°20'48.36" N 77°55'12.51" W elev 532 ft
Eye alt 11501 ft
USGS



Estimated recharge areas of Balch, Blue, and Gray Springs during average hydrologic conditions, Leetown, WV. From Kozar, McCoy, Weary, Field, Pierce, Scott, and Young (2007). USGS Open-File Report 2007-1358.

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 mi^2 (Jones and Deike, 1981)
Recharge = Discharge = 16.5 in./yr (Kozar, 2007) (normal climate)
Average discharge from watershed = 383 x 10^6 ft^3/yr = 12.1 cfs
Mean age of discharge 4-6 years (this study), use 5 yrs below.

V = *Discharge* x *Age* [V=(V/t) x t]

V = Volume of water in the reservoir = 383 x 10^6 ft^3/yr x 5 yrs
= 1.92x10^9 ft^3; = 54.2 x 10^6 m^3 water in storage

Median withdrawal at LSC = 1,473 gpm (Kozar et al., 2007)
= 2.93 x 10^6 m^3/yr. (= 3.3 cfs)

Annual withdrawal from storage = (2.93/54.2)x100 = 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 <u>transient flow model</u> could help evaluate sustainable utilization of the groundwater resource.

USGS

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.

Photo by Dr. Daniel Doctor, US Geological Survey, 7 March, 2010.

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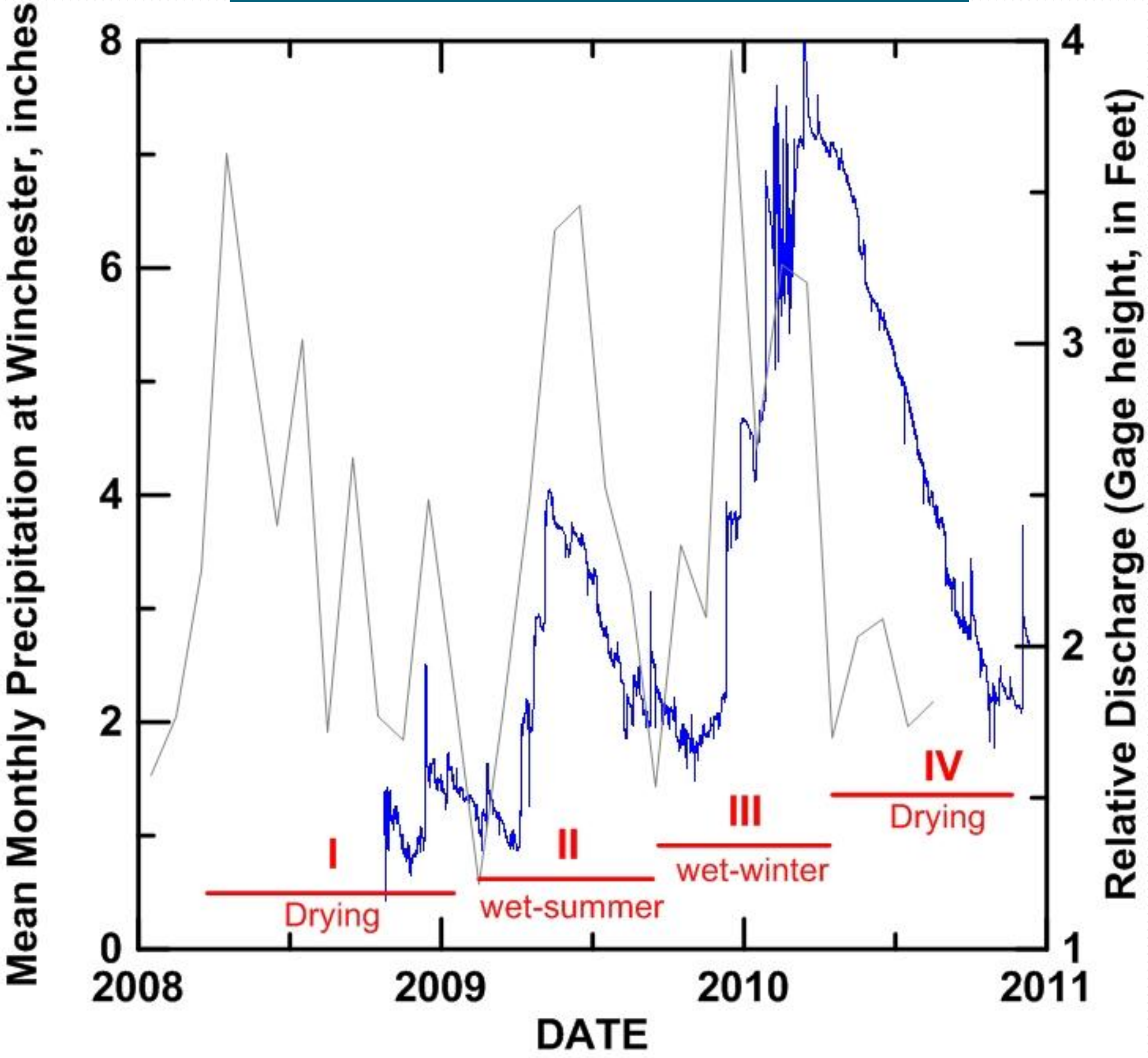
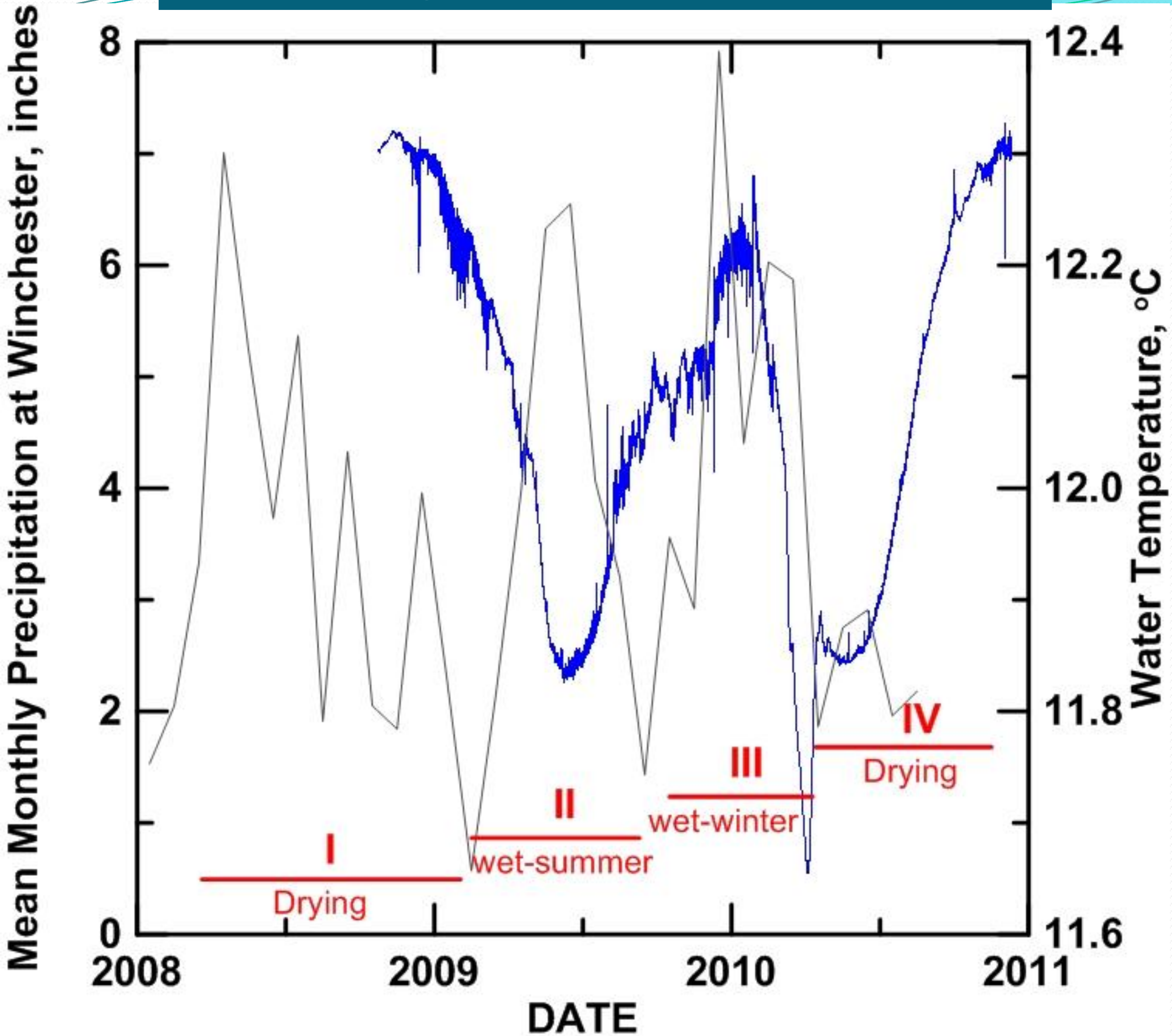
Gray Spring, LSC, Discharge

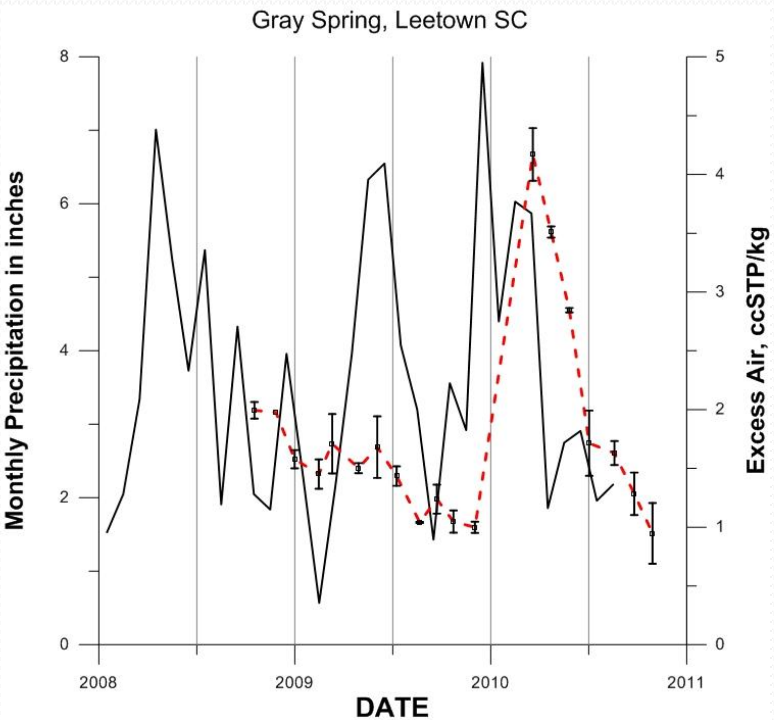


Gray Spring, LSC, Water Temperature



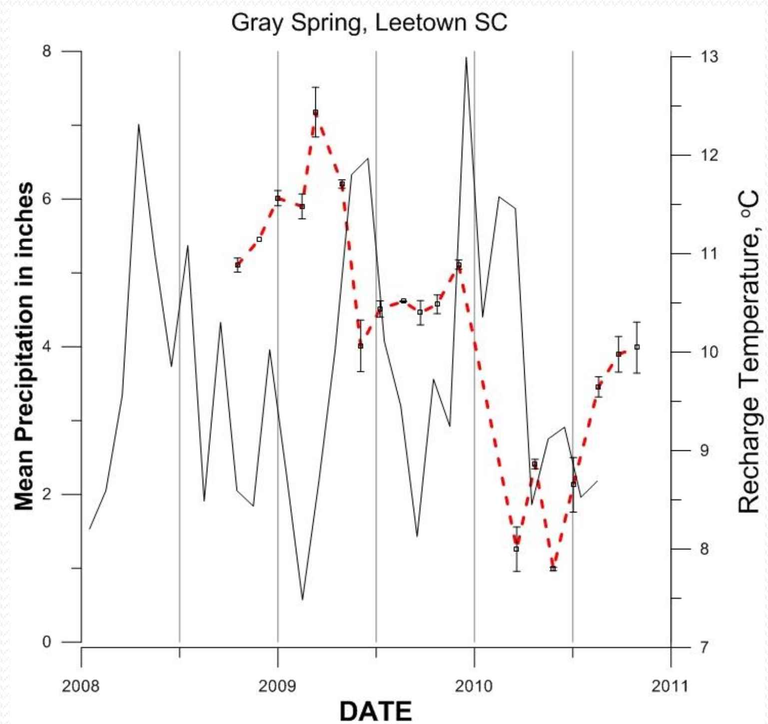
Excess air and recharge temperature of Gray Spring discharge, 2008-2010

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.

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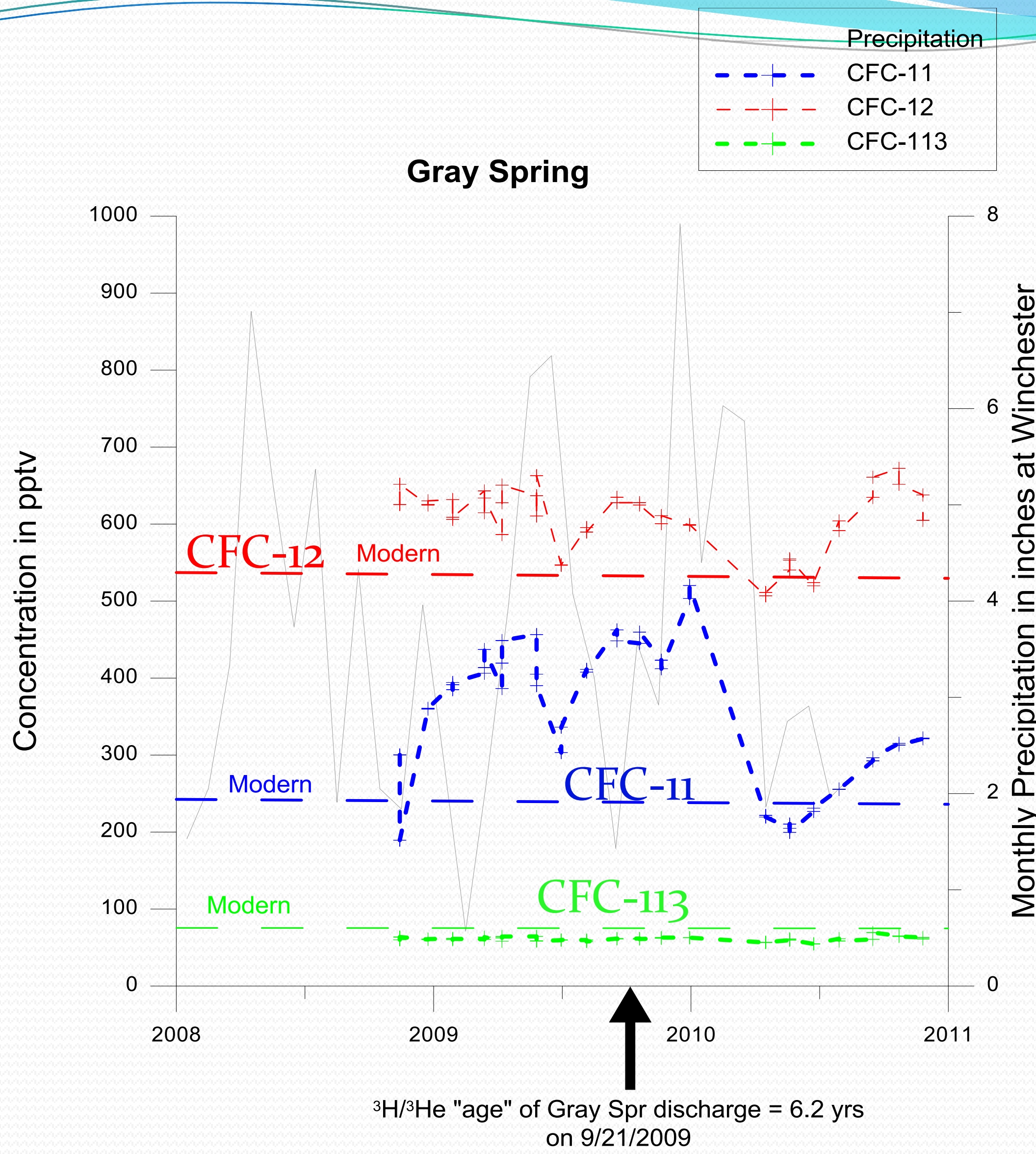
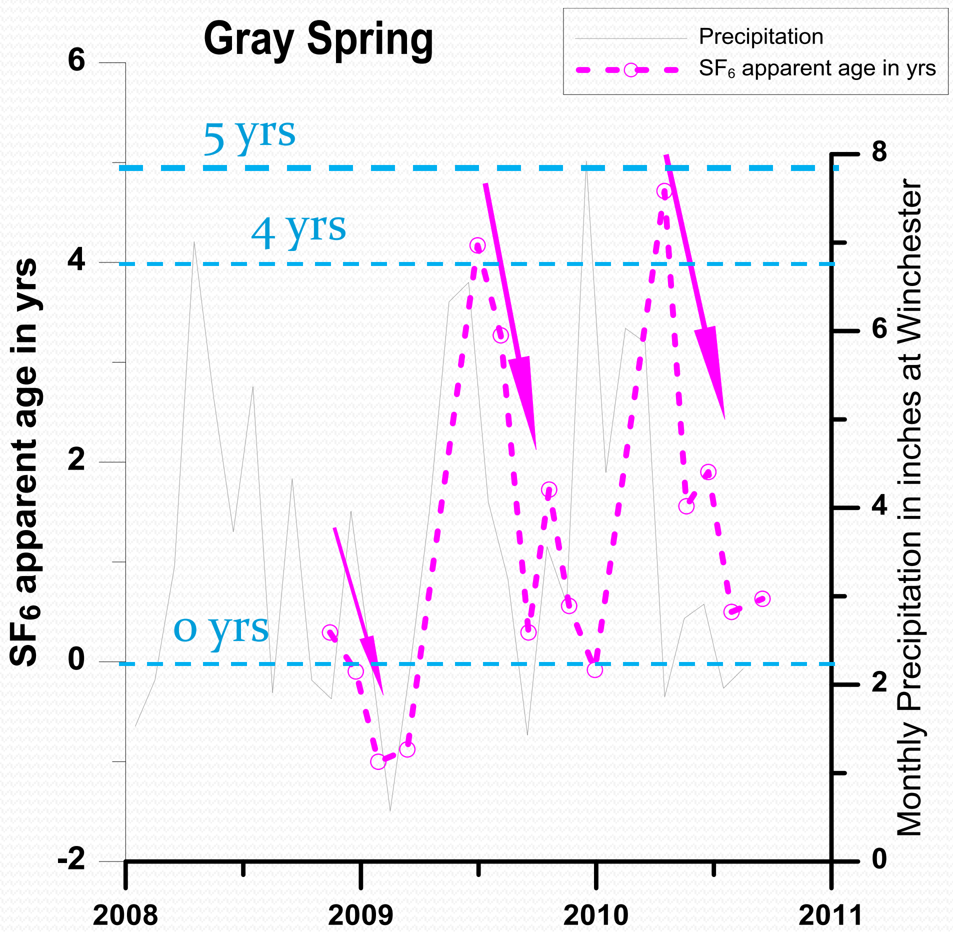
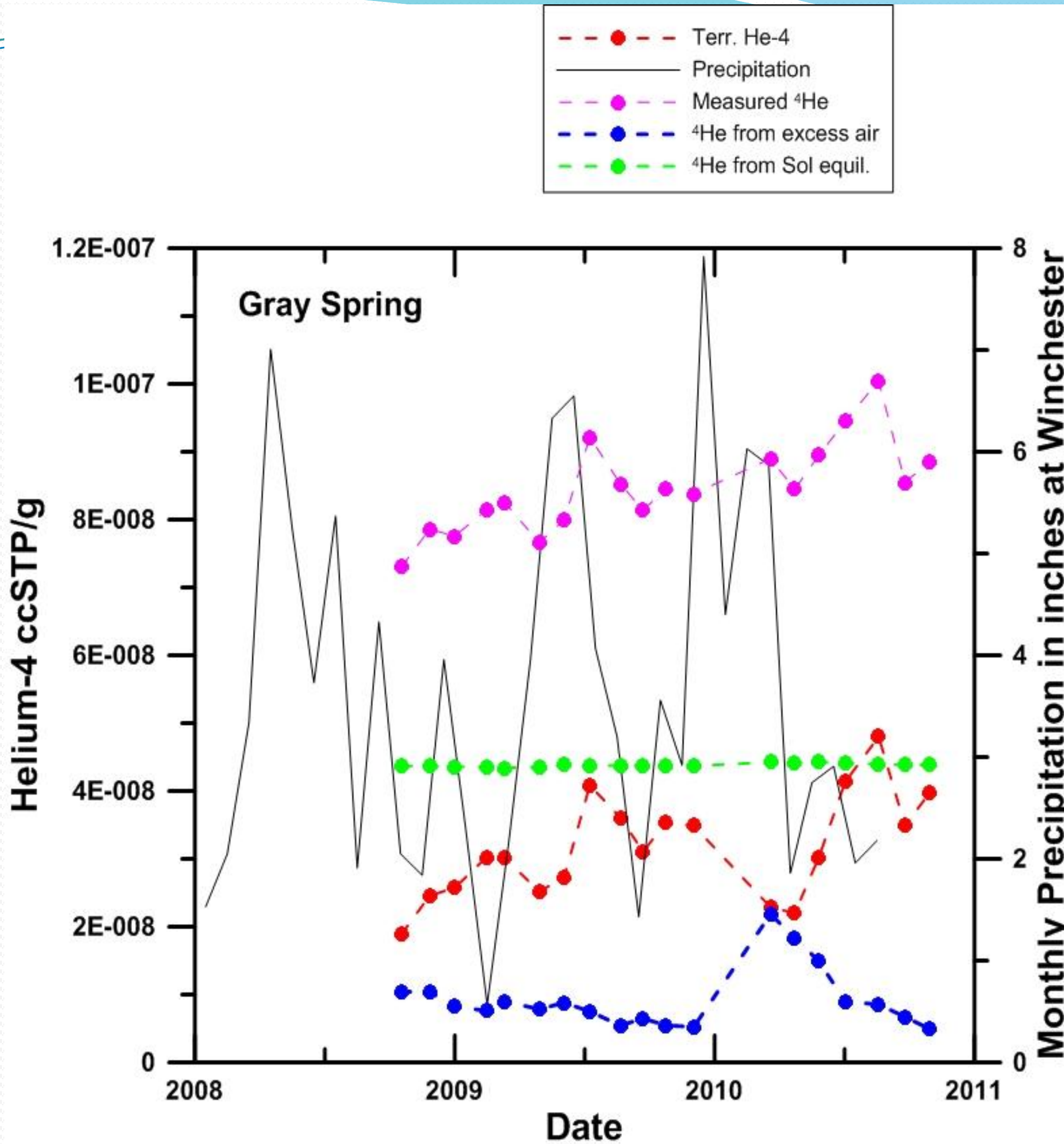


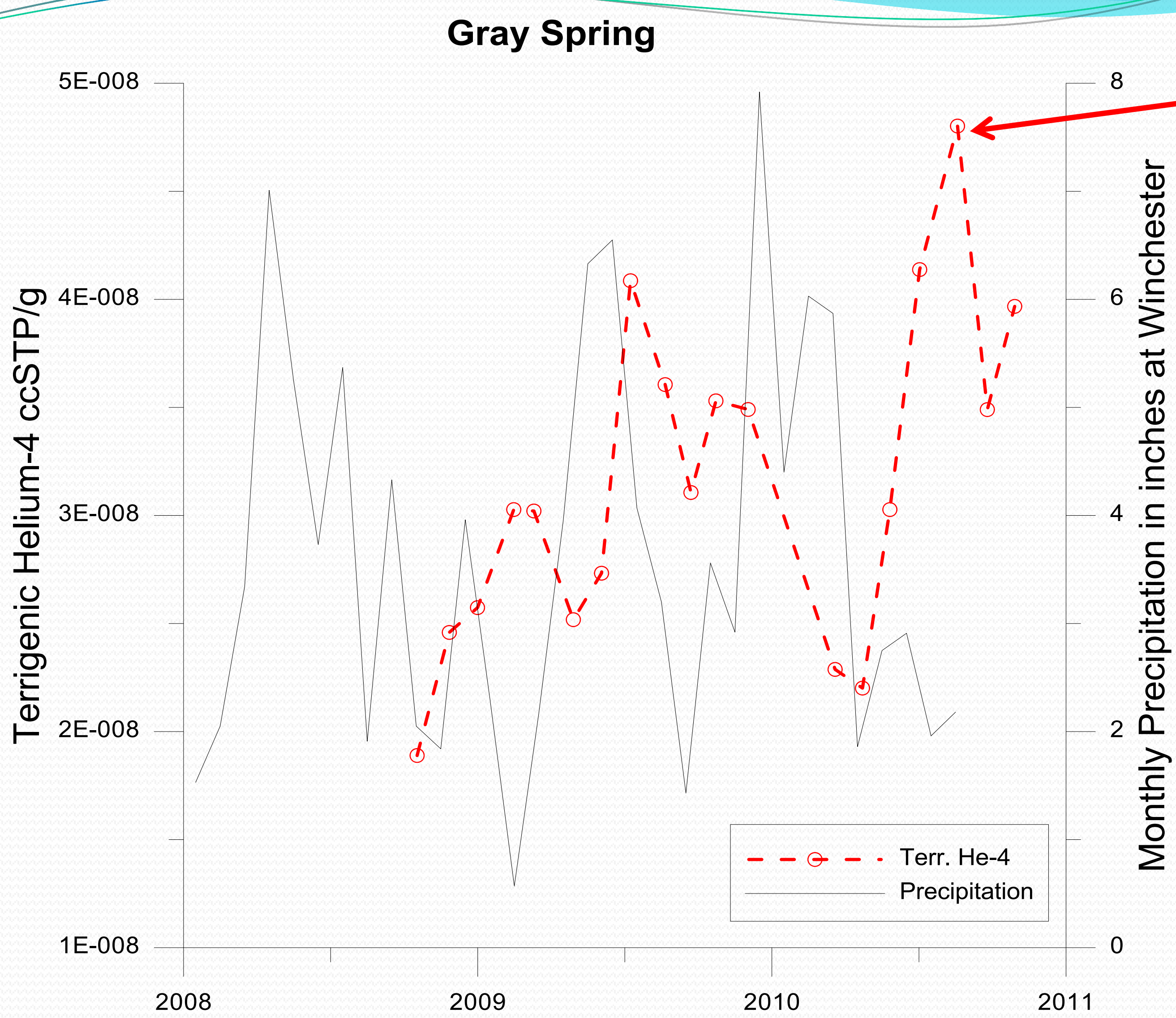
Precipitation
CFC-11
CFC-12
CFC-113
Gray Spring
1000
900
800
700
600
500
400
300
200
100
0
Concentration in pptv
8
6
4
2
0
Monthly Precipitation in inches at Winchester
2008
2009
2010
2011
CFC-12
Modern
CFC-11
Modern
CFC-113
Modern
$^3H/^3He$ "age" of Gray Spr discharge = 6.2 yrs
on 9/21/2009

SF_6 “age” in Gray Spring Discharge, 2008-2010





Terr. He-4
Precipitation
Measured ⁴He
⁴He from excess air
⁴He from Sol equil.
Gray Spring
Helium-4 ccSTP/g
1.2E-007
1E-007
8E-008
6E-008
4E-008
2E-008
0
Monthly Precipitation in inches at Winchester
8
6
4
2
0
2008
2009
2010
2011
Date



Old fraction in Gray Spring >25 yrs, based on ^{4}He accumulation rate of $2x10^{-9}$ ccSTP/g/yr

USGS

“Low-Level” VOCs

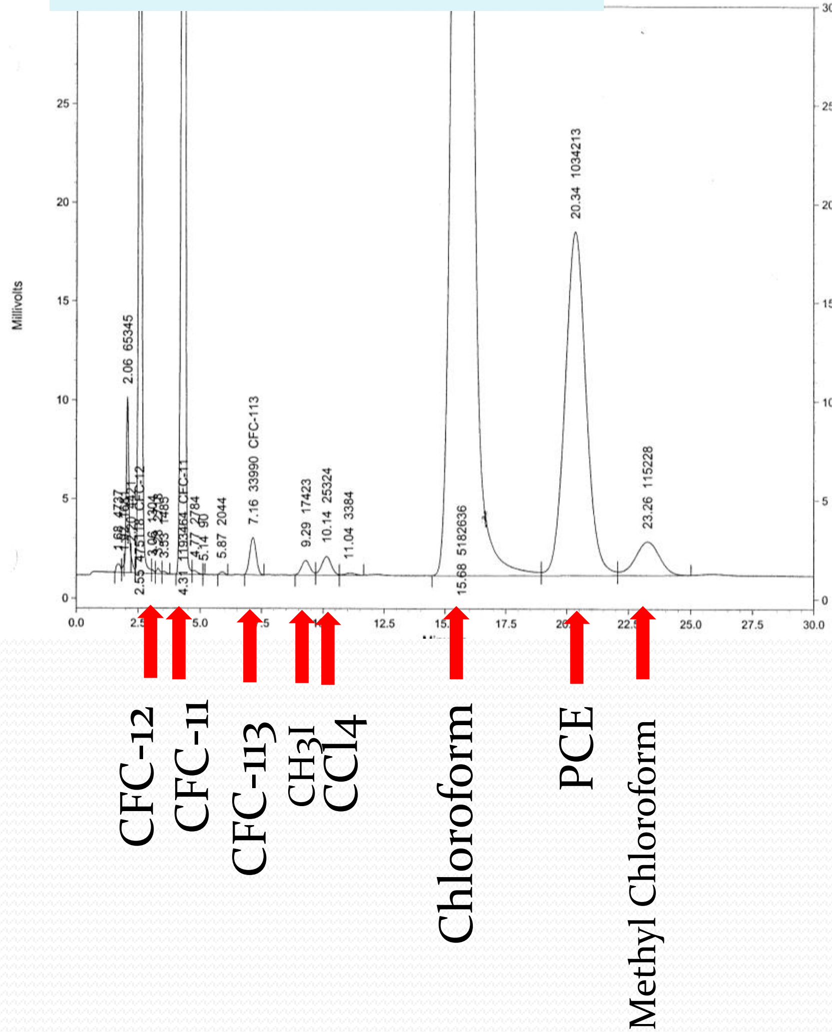
- Gas chromatography with an electron-capture detector is capable of detecting some halogenated VOCs at concentrations as much as 3 orders of magnitude below detections with GC-MS.
- Examples: chlorofluorocarbons, (CFC-11, CFC-12, CFC-113, CFC-114), trichloroethylene (TCE), tetrachloroethylene (PCE), carbon tetrachloride, and many others.

Measurement with Electron-Capture Detector

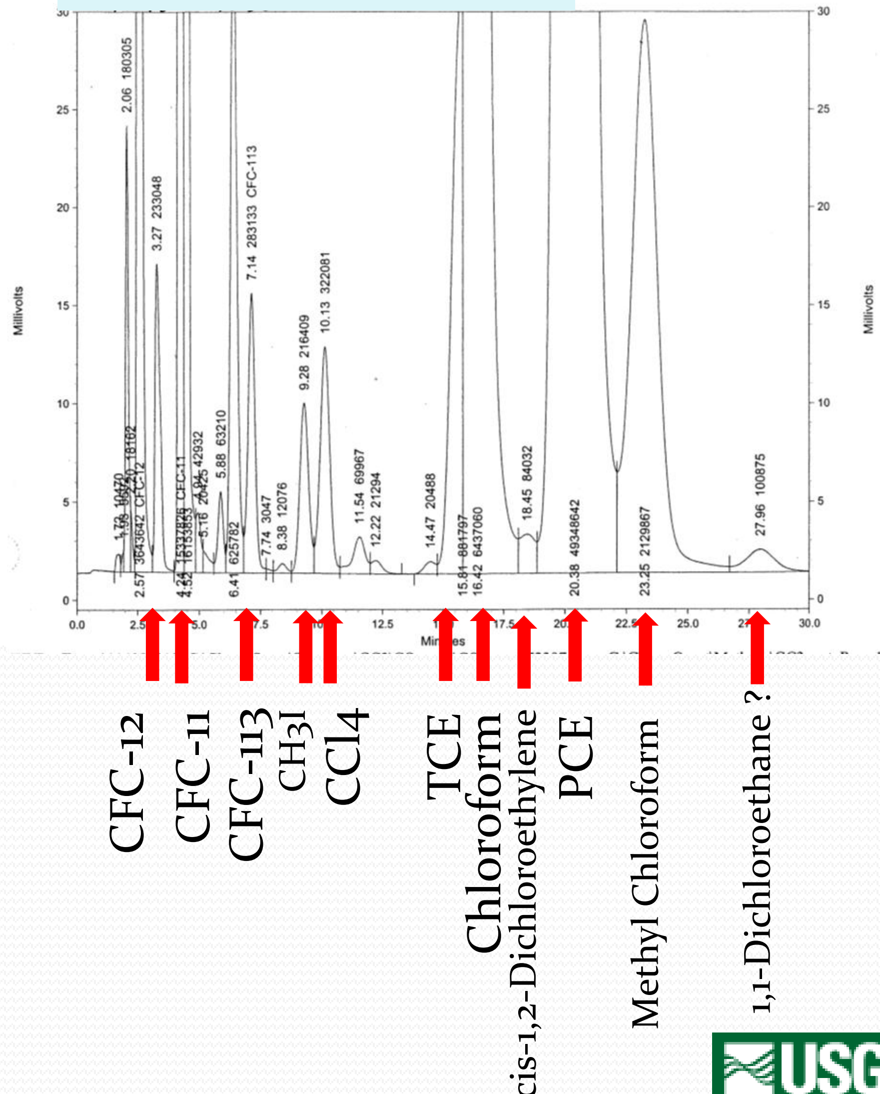
A small radioactive source containing ^{63}Ni ionizes the molecules of the nitrogen carrier gas, and a potential difference creates a small current. This current is reduced when an electronegative substance (such as a halocarbon) is introduced. The reduction in current is a measure of the concentration 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

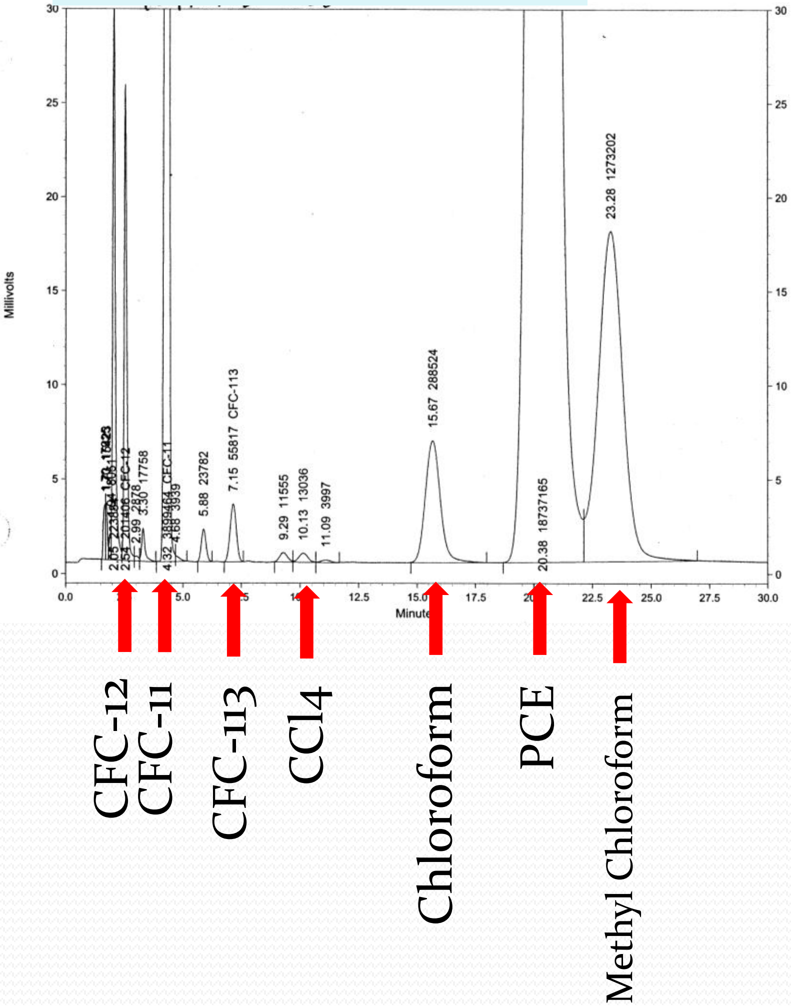


Bell Spring on 10/16/08

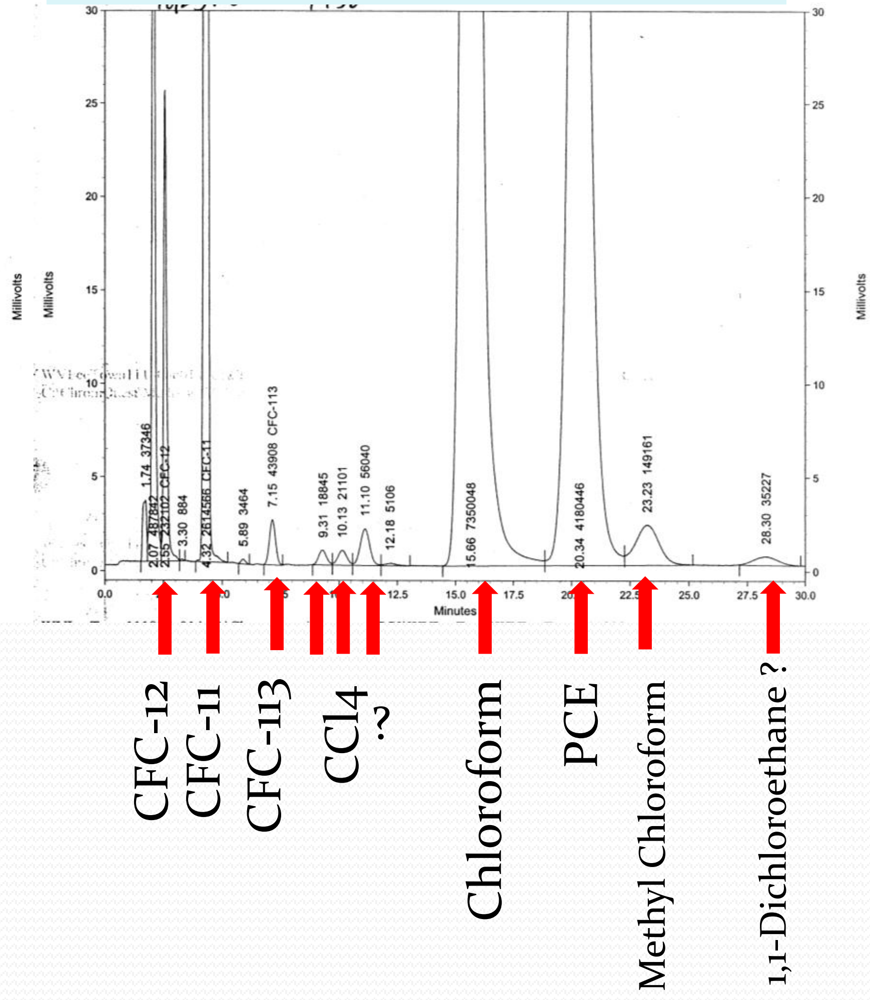


LSC Chromatograms: Detections of Halogenated VOCs

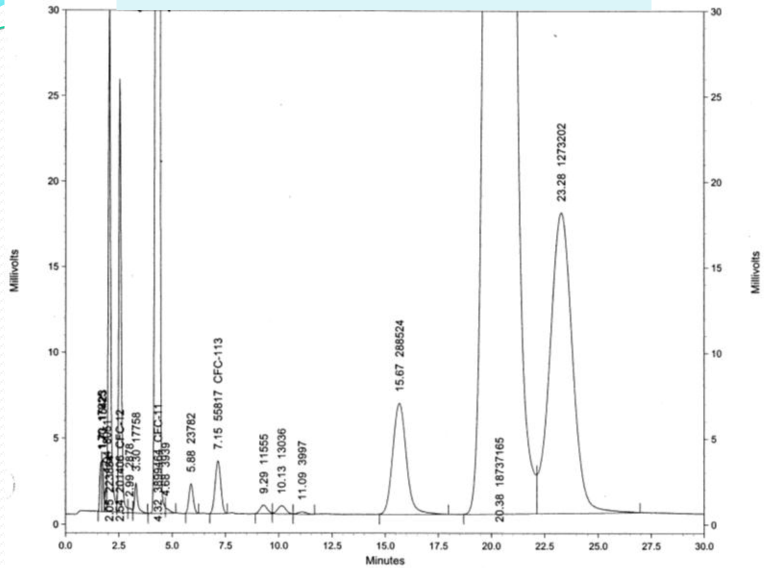
Gray Spring on 10/16/08



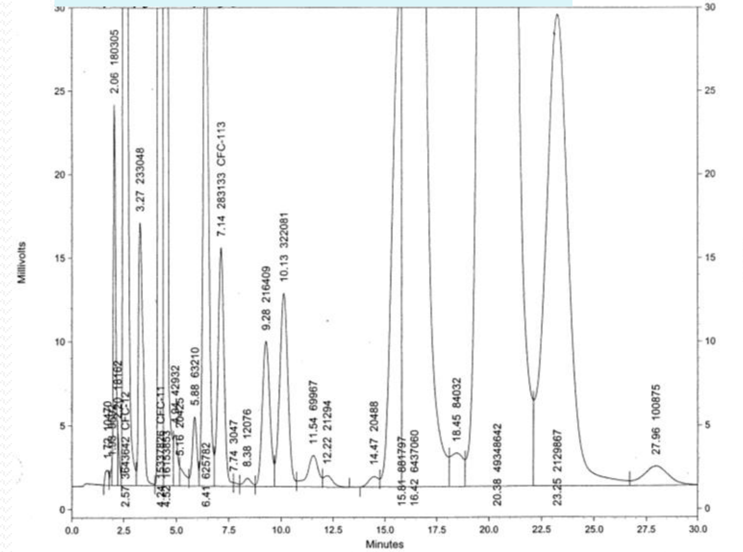
USDA Domestic well on 10/23/08



Gray Spring on 10/16/08

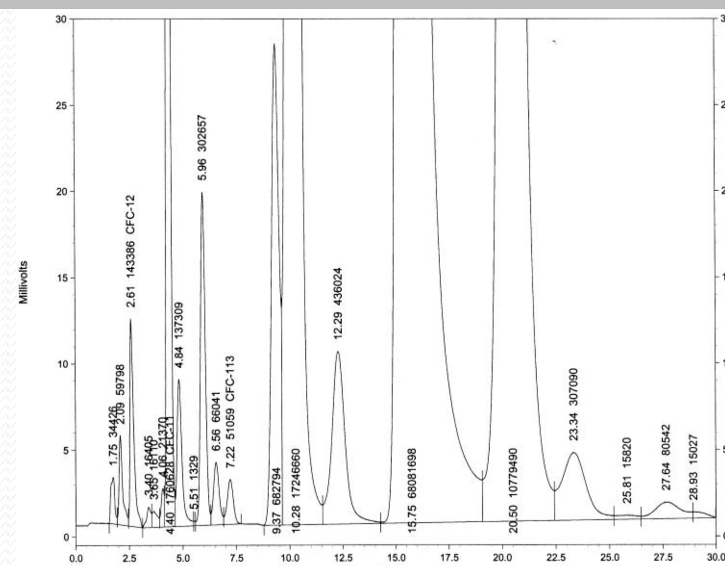


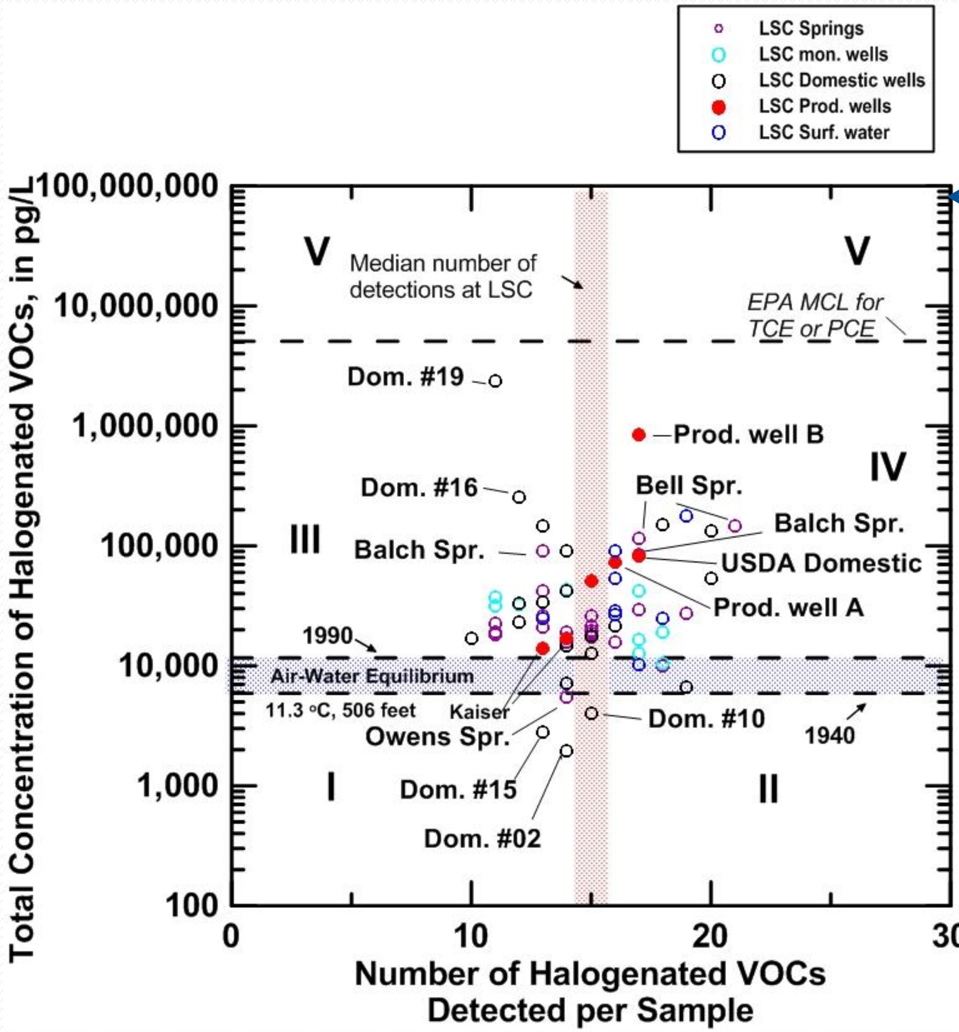
Bell Spring on 10/16/08



- 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.

Tap water, USGS, Reston, VA 05/27/09





80 ppb TTHM MCL

5 ppb

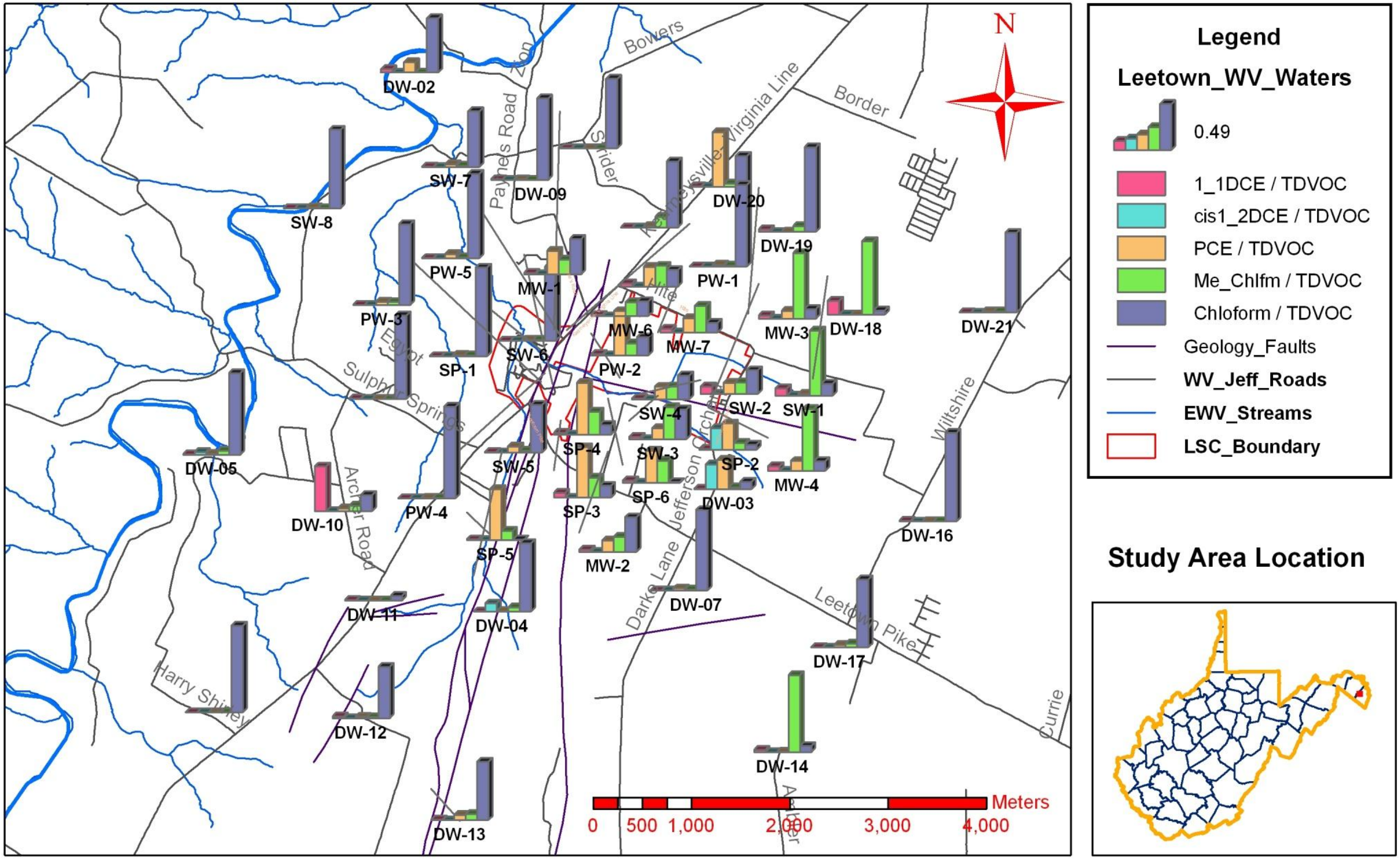
1 ppb

0.1 ppb

0.01 ppb

Max. PCE from urban air peaked at about 1,000 pg/L in 1970

Leetown, WV - Normalized VOC



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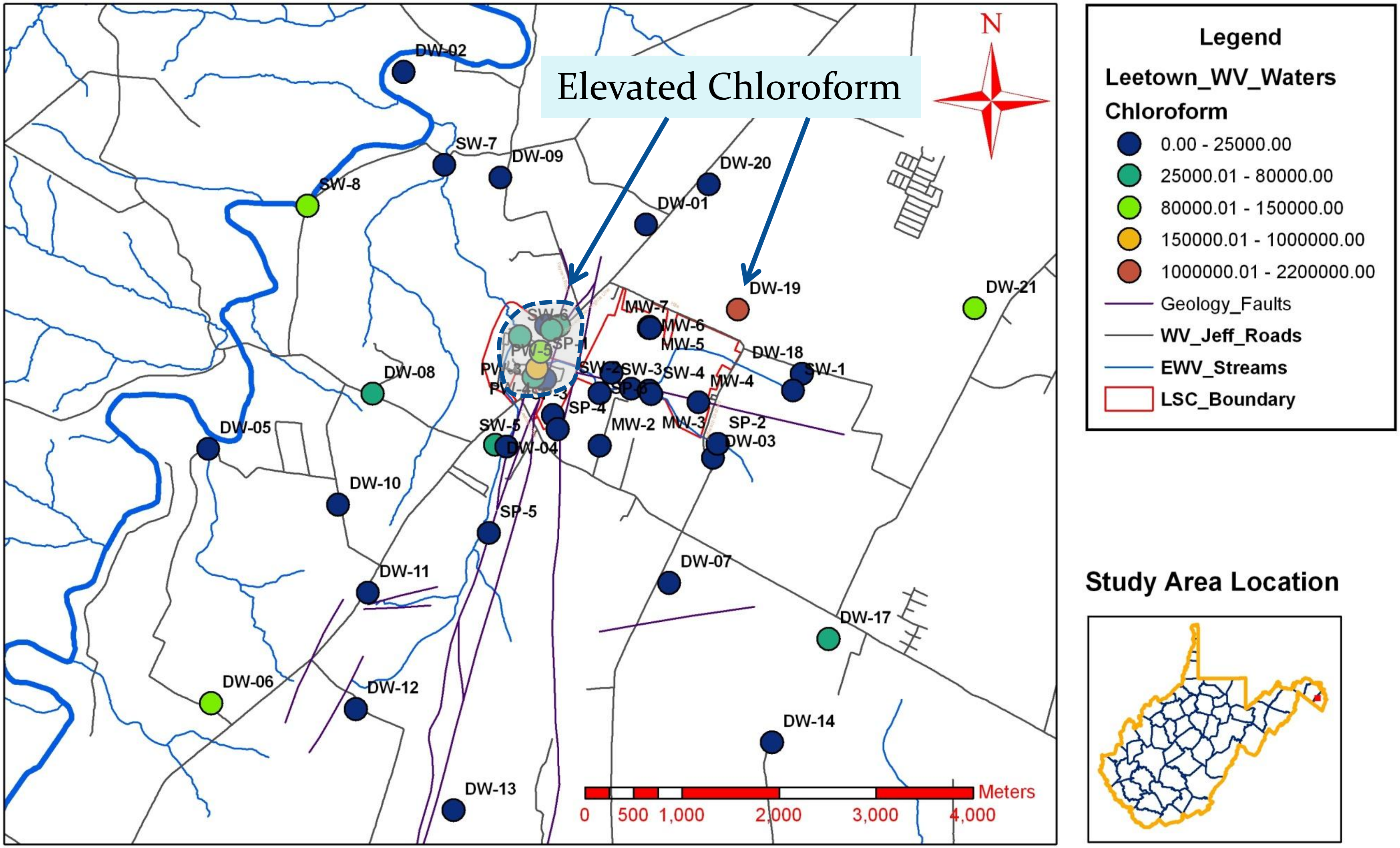
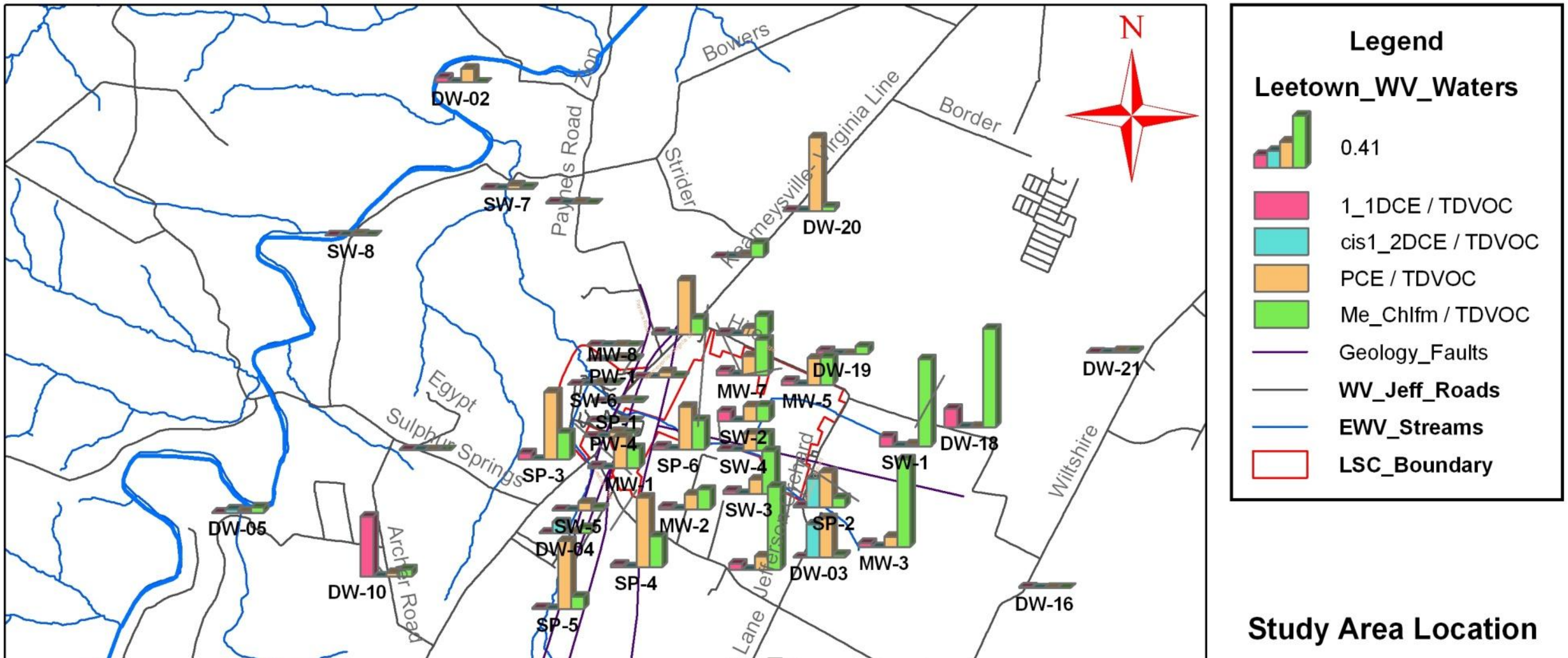
Leetown, WV - Chloroform

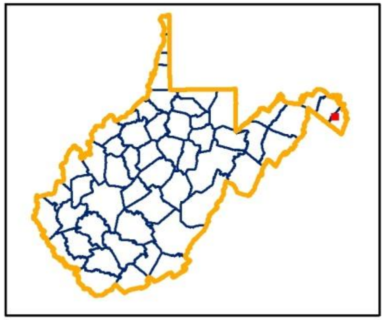


USGS

Leetown, WV - VOC, No Chloroform



Study Area Location



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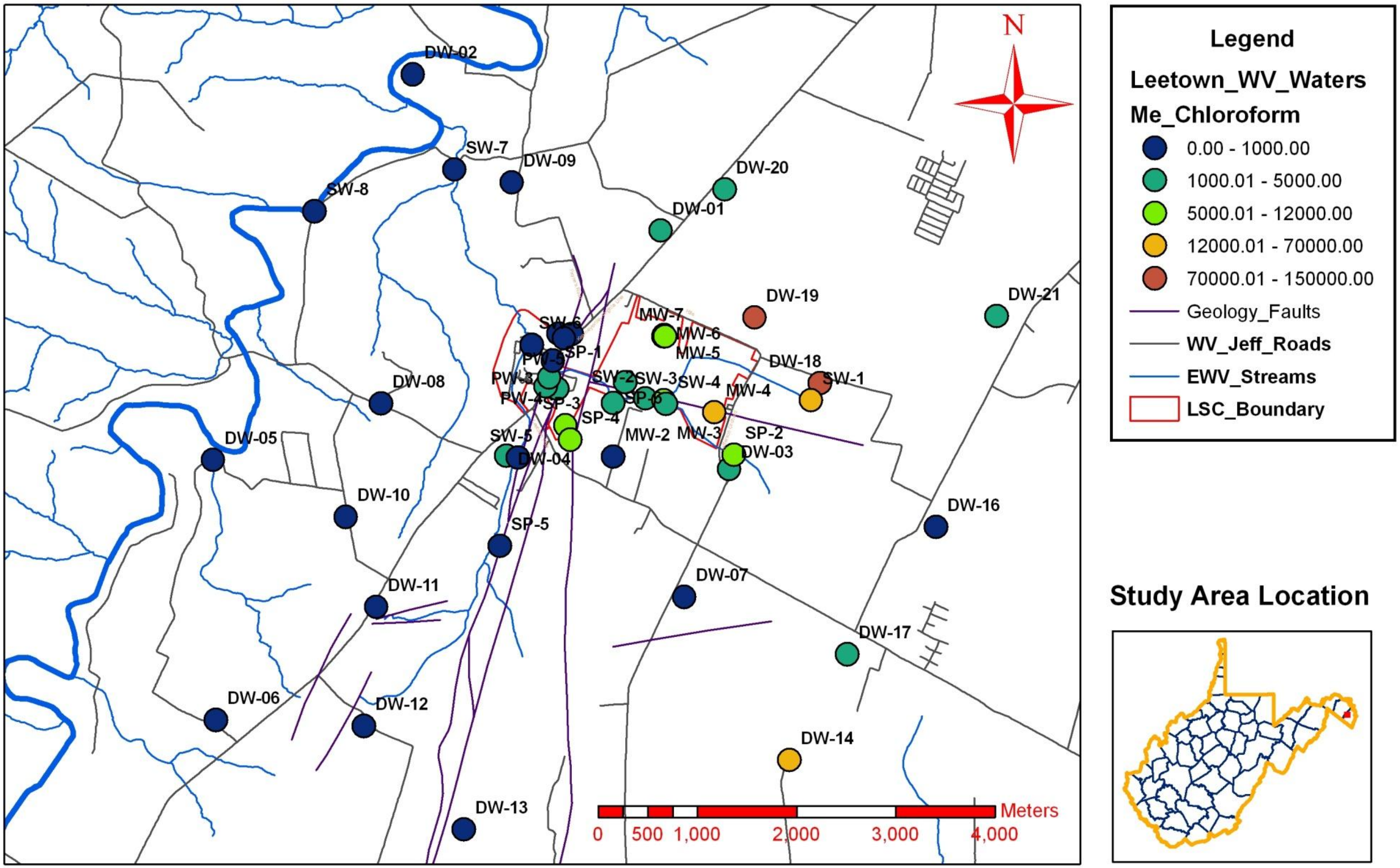
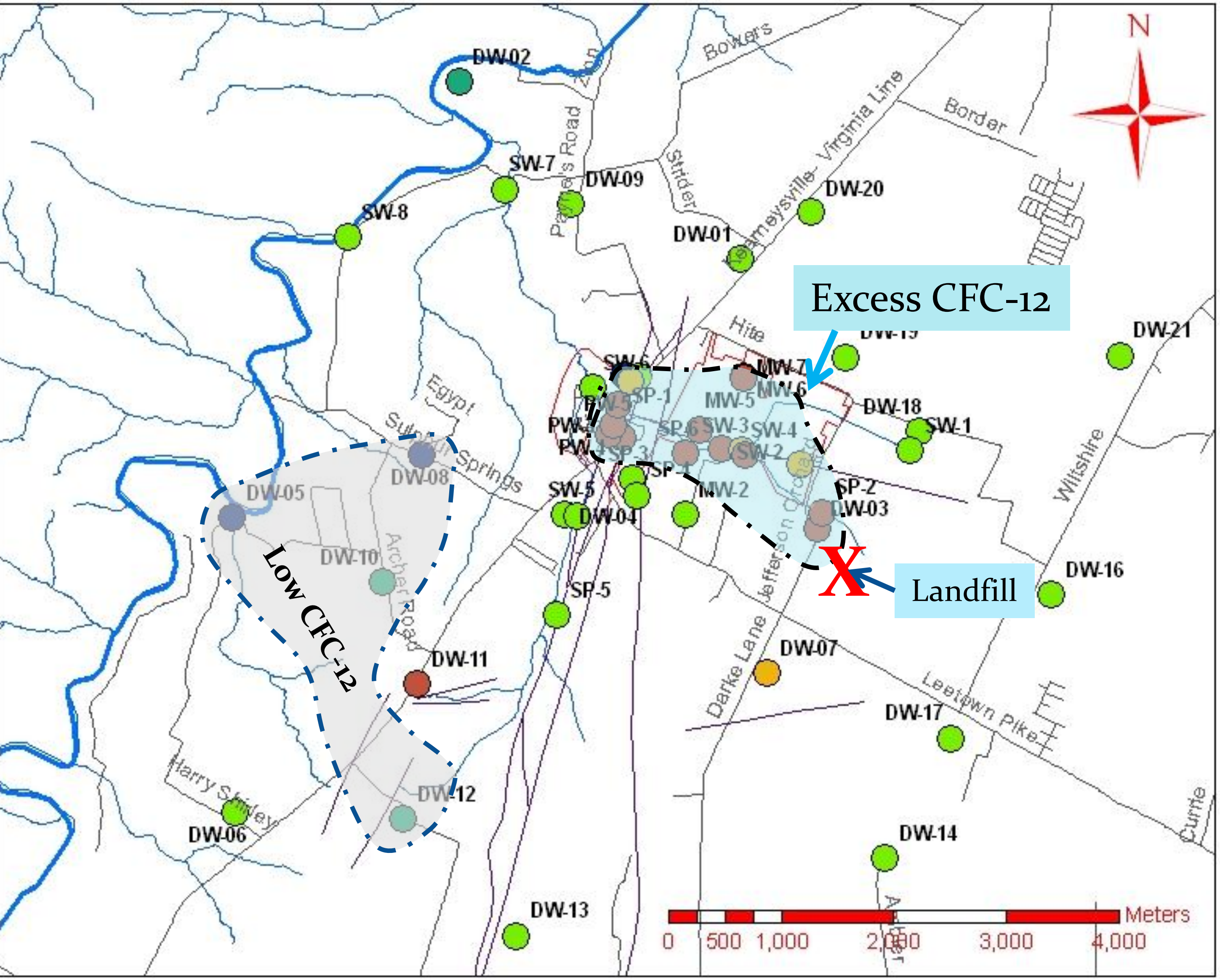
Leetown, WV - Methyl Chloroform

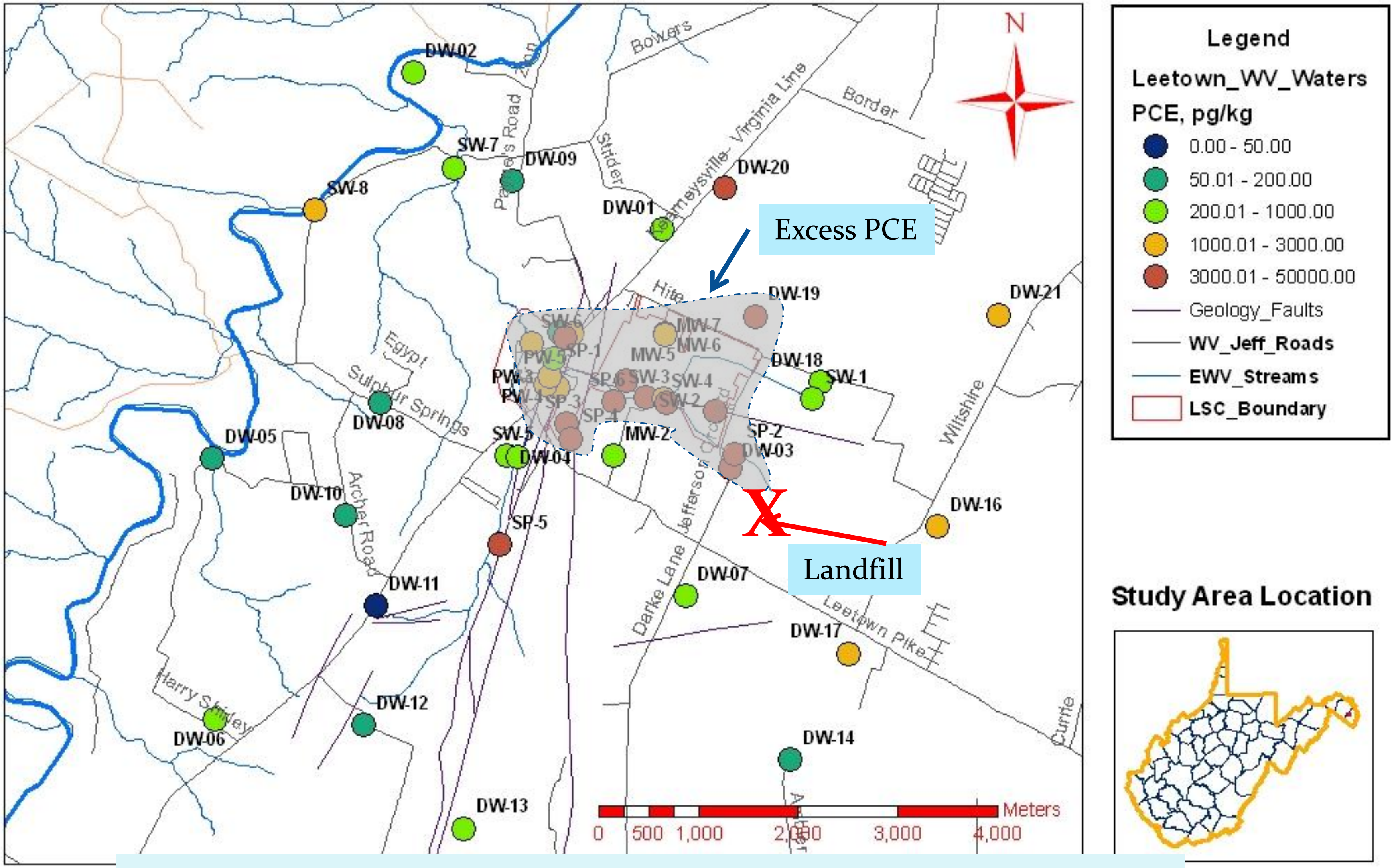


Leetown Sites - CFC-12



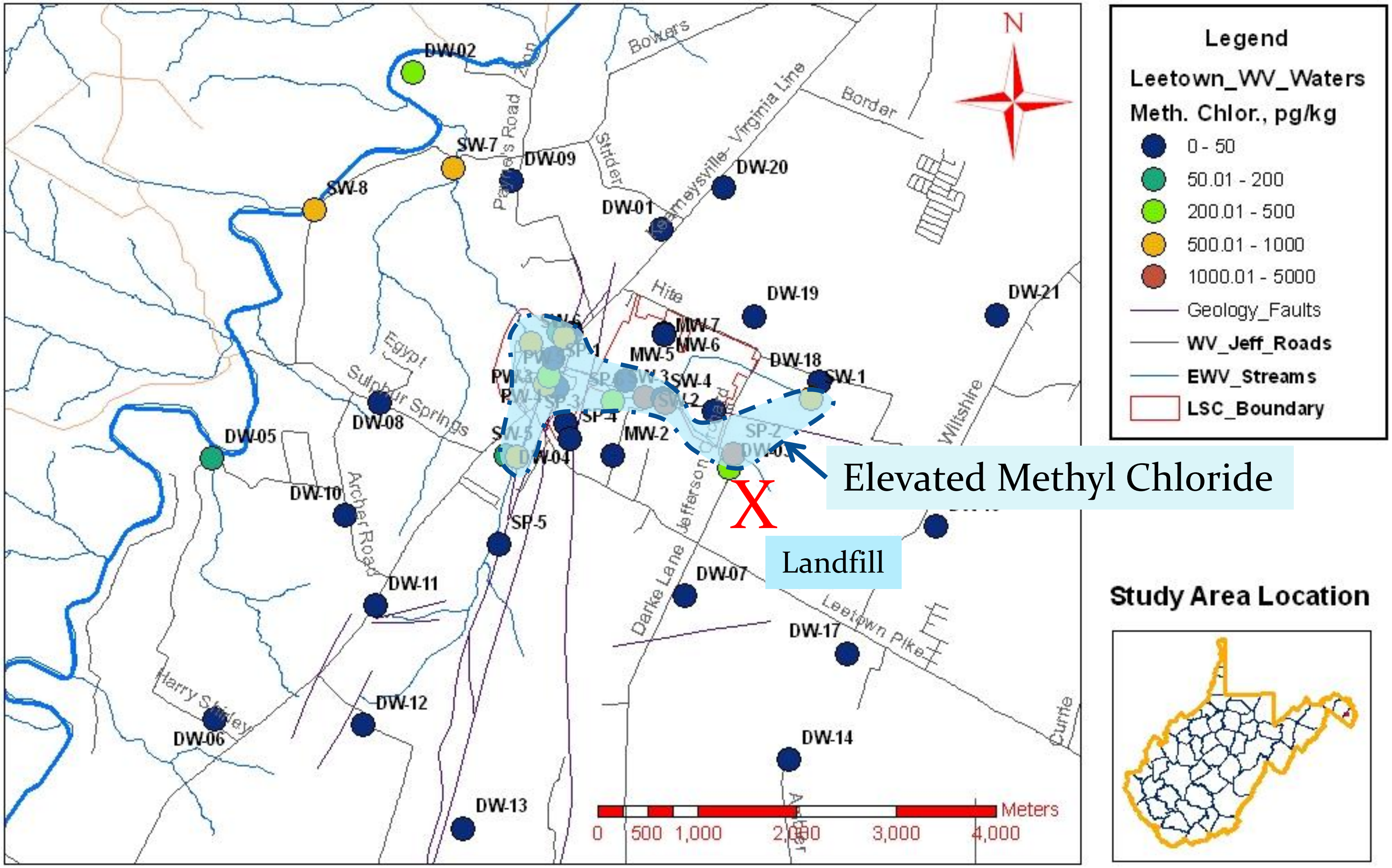
USGS

Leetown Sites - PCE



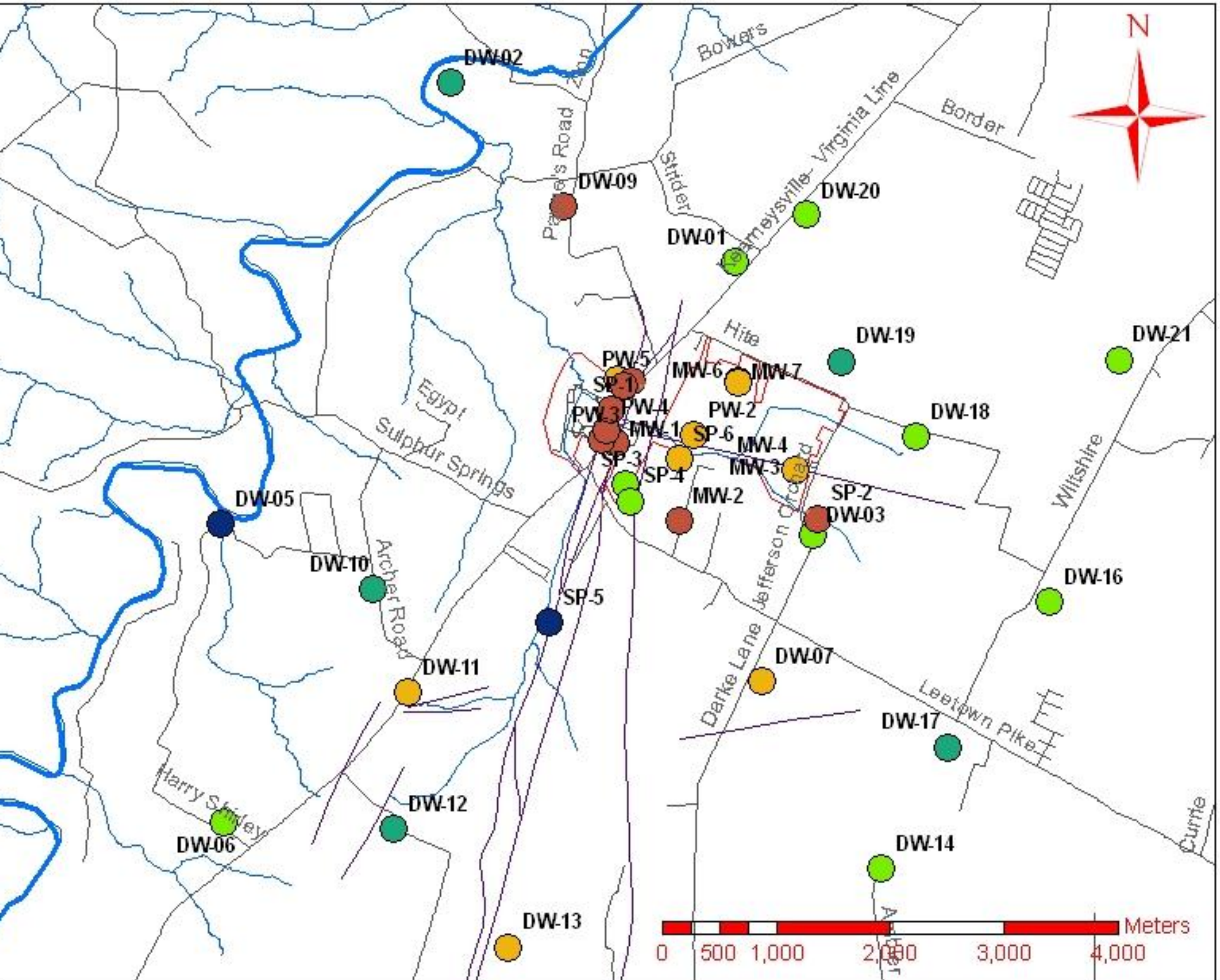
Modern Air-Water Equilibrium contains 800-1,000 pg/L PCE
Orange and Brown samples exceed; have anthropogenic source

Leetown Sites - Methyl Chloride



USGS

Leetown Sites - Recharge Temperature



Legend

Leetown_WV_Waters

Recharge Temp, C

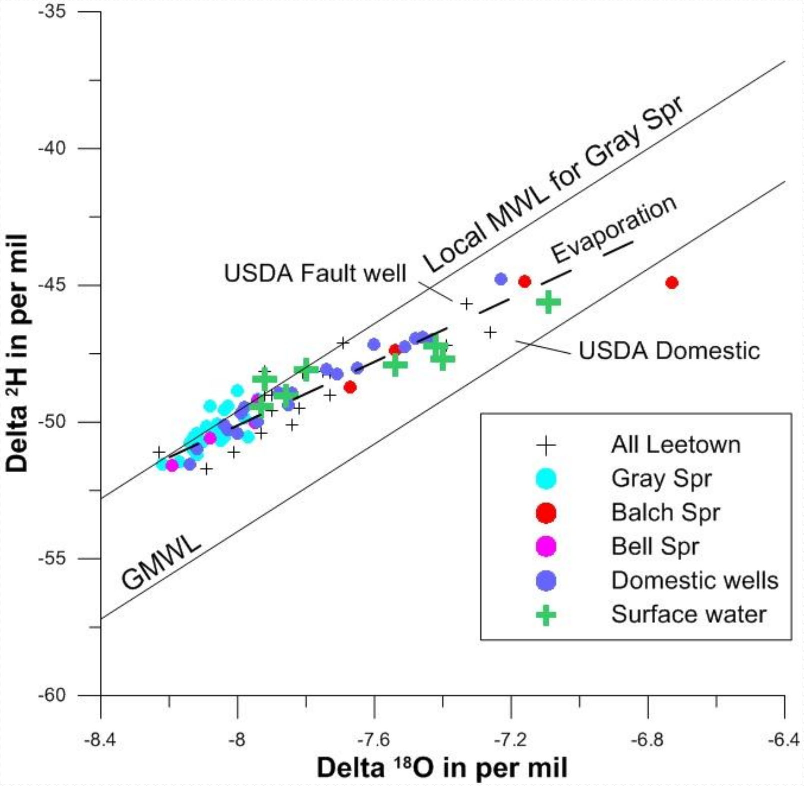
- 6.26 - 8.00
- 8.01 - 10.00
- 10.01 - 11.00
- 11.01 - 12.00
- 12.01 - 20.00
- Geology_Faults
- WV_Jeff_Roads
- EWV_Streams
- LSC_Boundary

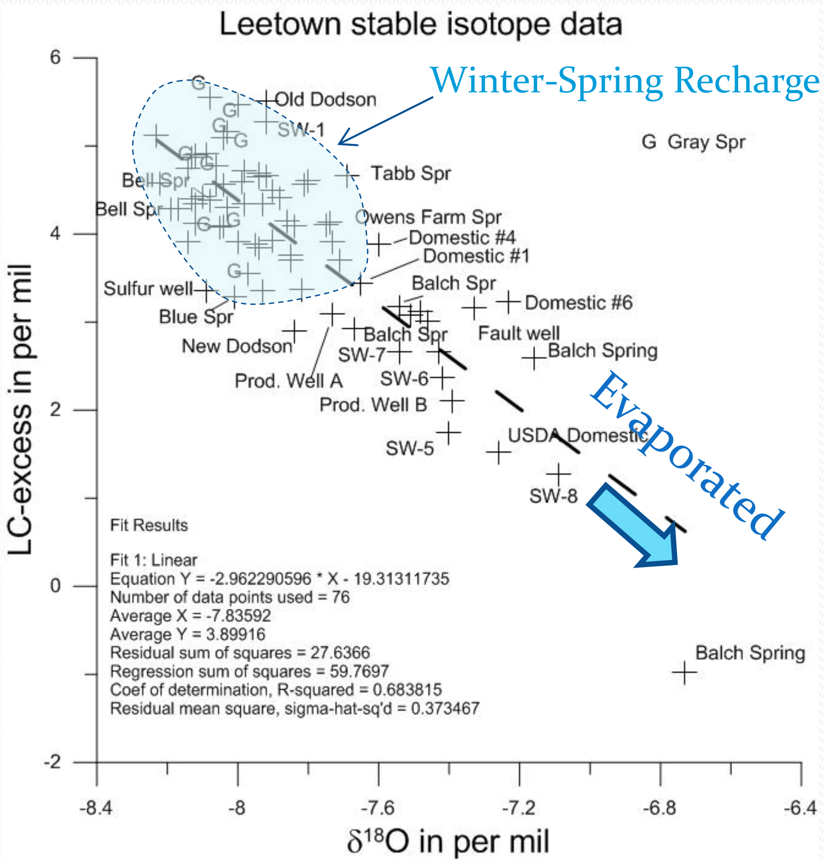
MAT = 11.9ºC

Study Area Location

USGS

Stable Isotope Data



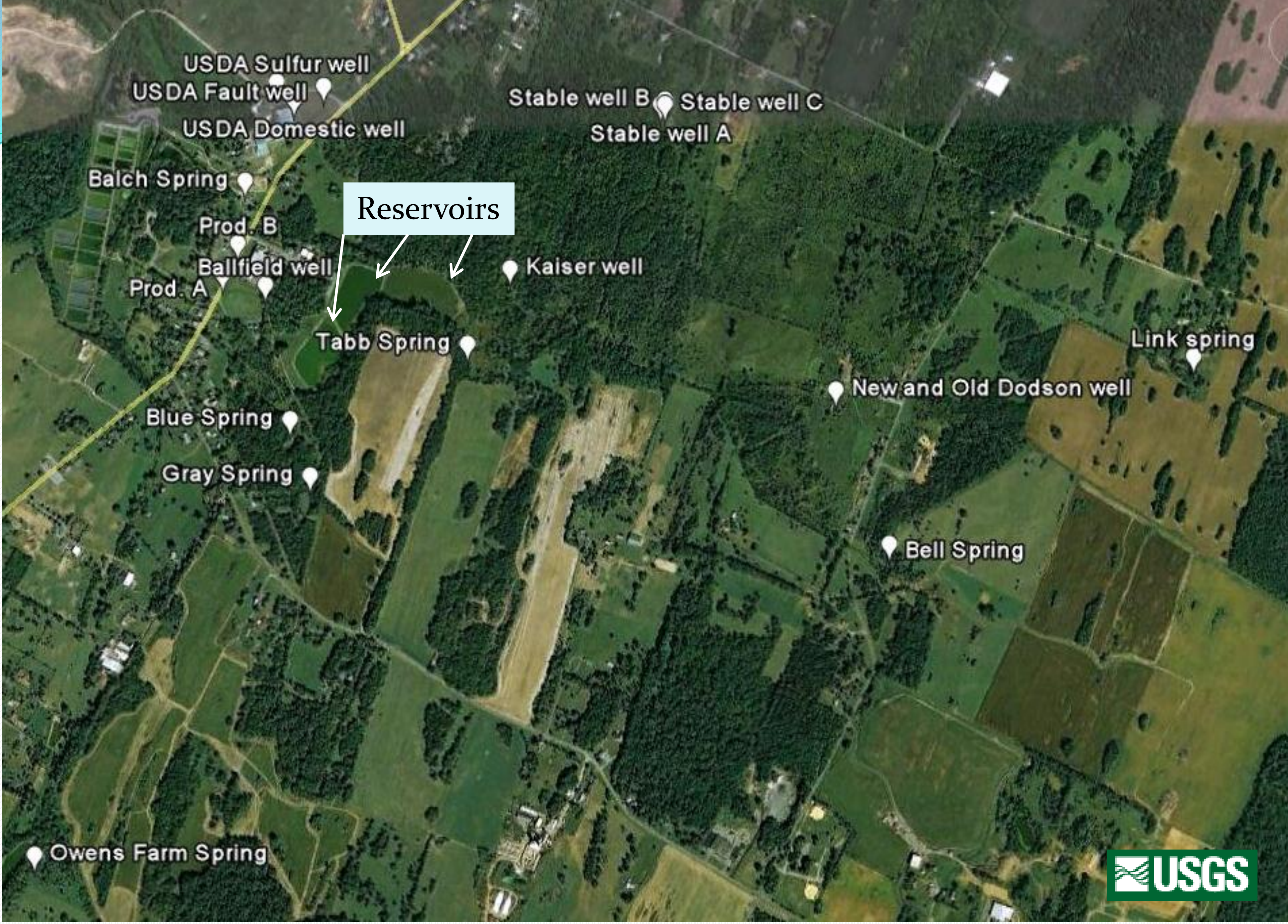


$$\delta^2 H = 8\delta^{18}O + 10$$

$$\delta^2 H = 8\delta^{18}O + 14.38$$

$$\delta^2 H = 8.2\delta^{18}O + 11.27$$

$$LC_{excess} = \delta^2 H - 8.2\delta^{18}O - 11.27$$


USDA Sulfur well
USDA Fault well
USDA Domestic well
Stable well B
Stable well C
Stable well A
Balch Spring
Reservoirs
Prod. B
Ballfield well
Prod. A
Kaiser well
Tabb Spring
Link spring
New and Old Dodson well
Blue Spring
Gray Spring
Bell Spring
Owens Farm Spring
USGS

Summary and Conclusions

- At LSC, SF_6, $^3H/^3He$ ages and ^4He 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.
- $^3H/^3He$ 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 ^4He in the Great Valley carbonates is on the order of $2x10^{-9}$ ccSTP/g/yr. Combined with ^4He 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 ^4He accumulation ages of more than 1,000 yrs (but ^4He 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.

USGS

Springs at or near the Leetown Science Center

USGS