Bromide in Underground Mine Water of the Pittsburgh Coal

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Photo: Tim Denicola

bromide as indicator for shale gas wastewater

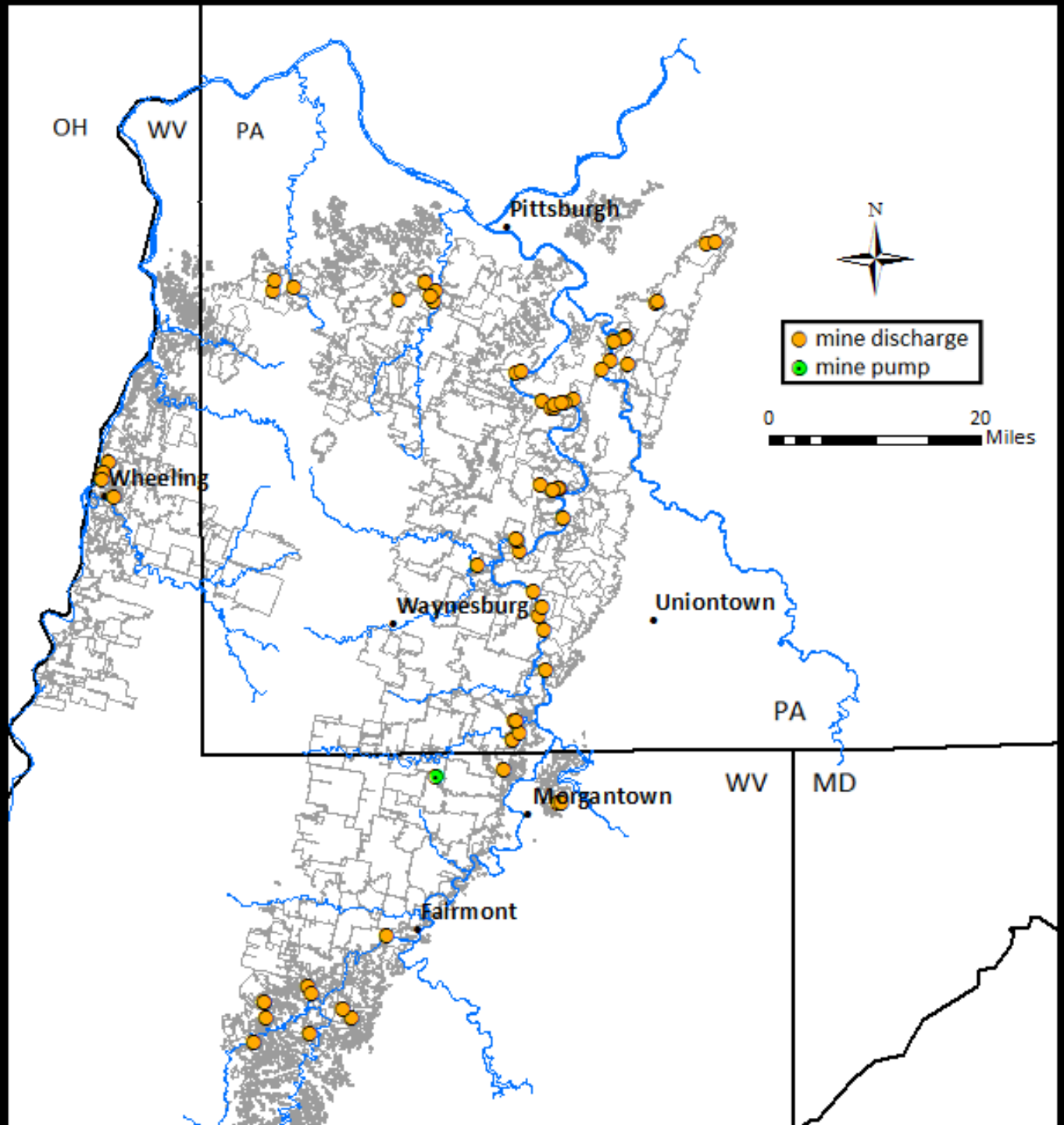
- Br present in mine drainage at low concentrations (generally < 0.1 mg/L) but reaches concentrations of 300-1600 mg/L in flowback (FB) and produced waters (PW)
- geochemically conservative
- different molar ratios of Cl/Br for mine water (170-250) compared to Marcellus FB/PW (100-130)
- estimated chronic toxicity limit of 1 mg/L in groundwater (Flury and Papritz, 1993)
- the main reservoir of Br is in seawater and marine brines

chemical signature of coal mine discharge

- elevated TDS is the main signature of mine drainage
- mainly calcium, sodium, sulfate w/ low or high pH
- TDS of discharge varies with age of discharge and degree of flooding
- very low Br
- about half the mine drainage entering the Monongahela River is from AMLs
- Active mines treat discharge to remove metals but show generally higher TDS than AMLs
- big flows mainly from underground mines

datasets for Br in mine water

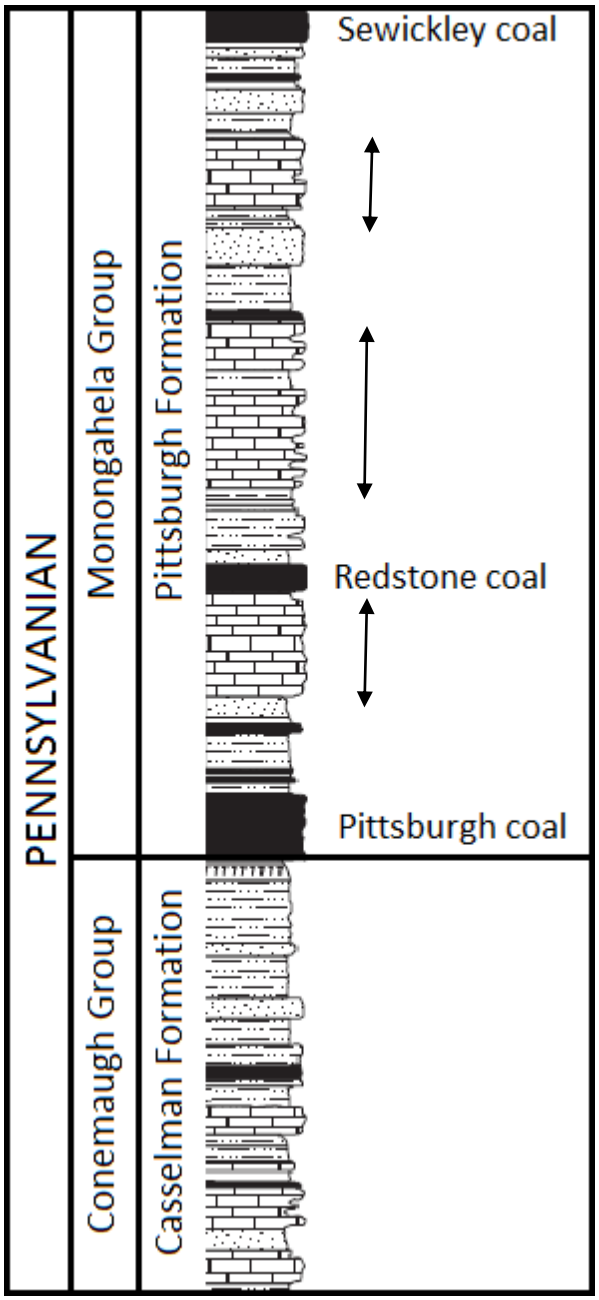
- 2012 synoptic sampling of “large” AMLs in Pittsburgh seam, WV and PA (Denicola MS thesis, 2013)
- flows and inorganic chemistry
- water level monitoring in some pools
- Br in surface water (Mon & tributaries) from 2011-15



sample sites, Pittsburgh coal basin (Denicola, 2013)

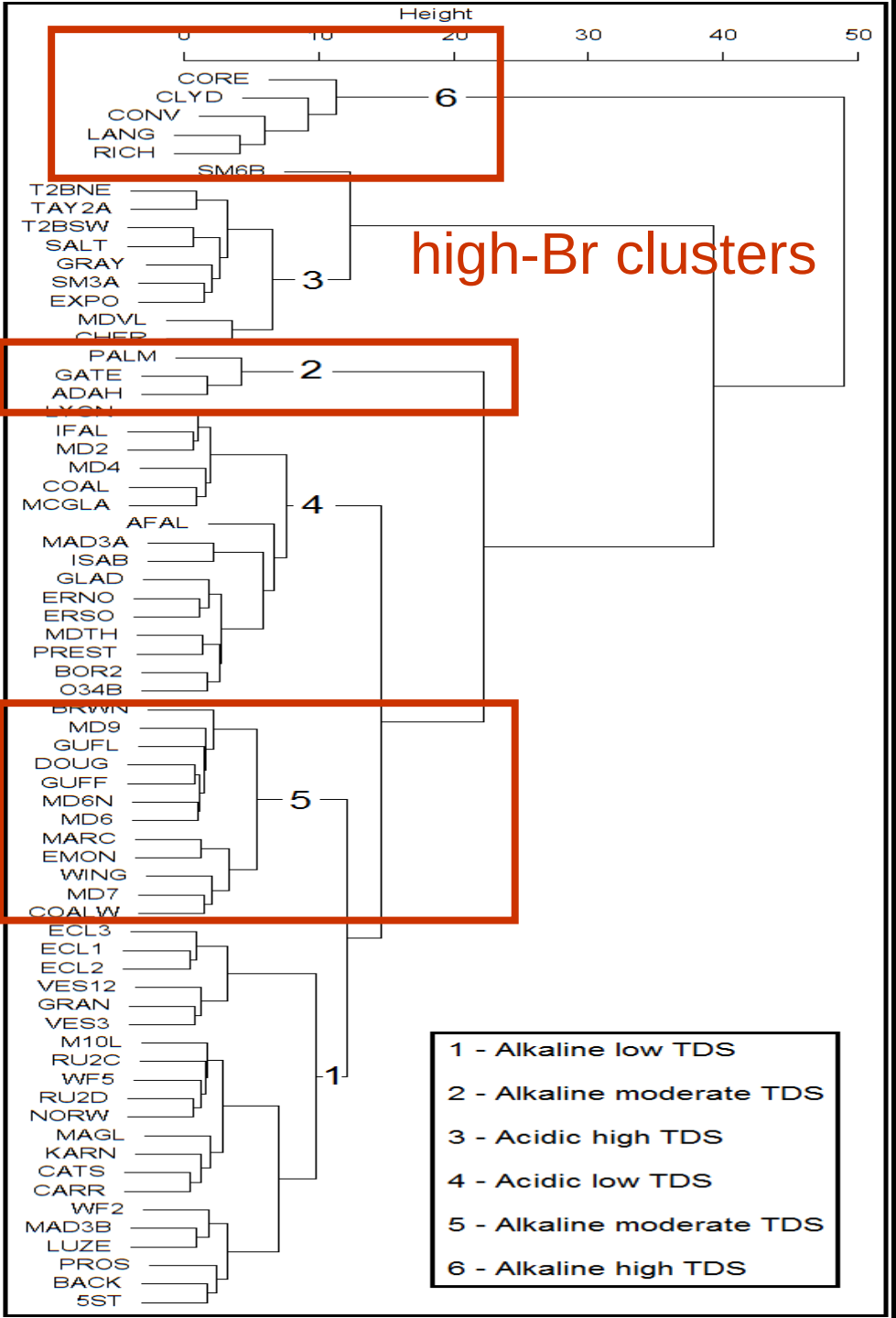
research questions

- detectable bromide (Br) appears in approximately 45% of large mine water discharges in this sample – about 22% are “elevated” (>0.5 mg/L)
- what’s the source?
  - connate or “first flush” mine-water ?
  - leaky gas wells in mines?
  - injected wastewater?
- let’s examine the context

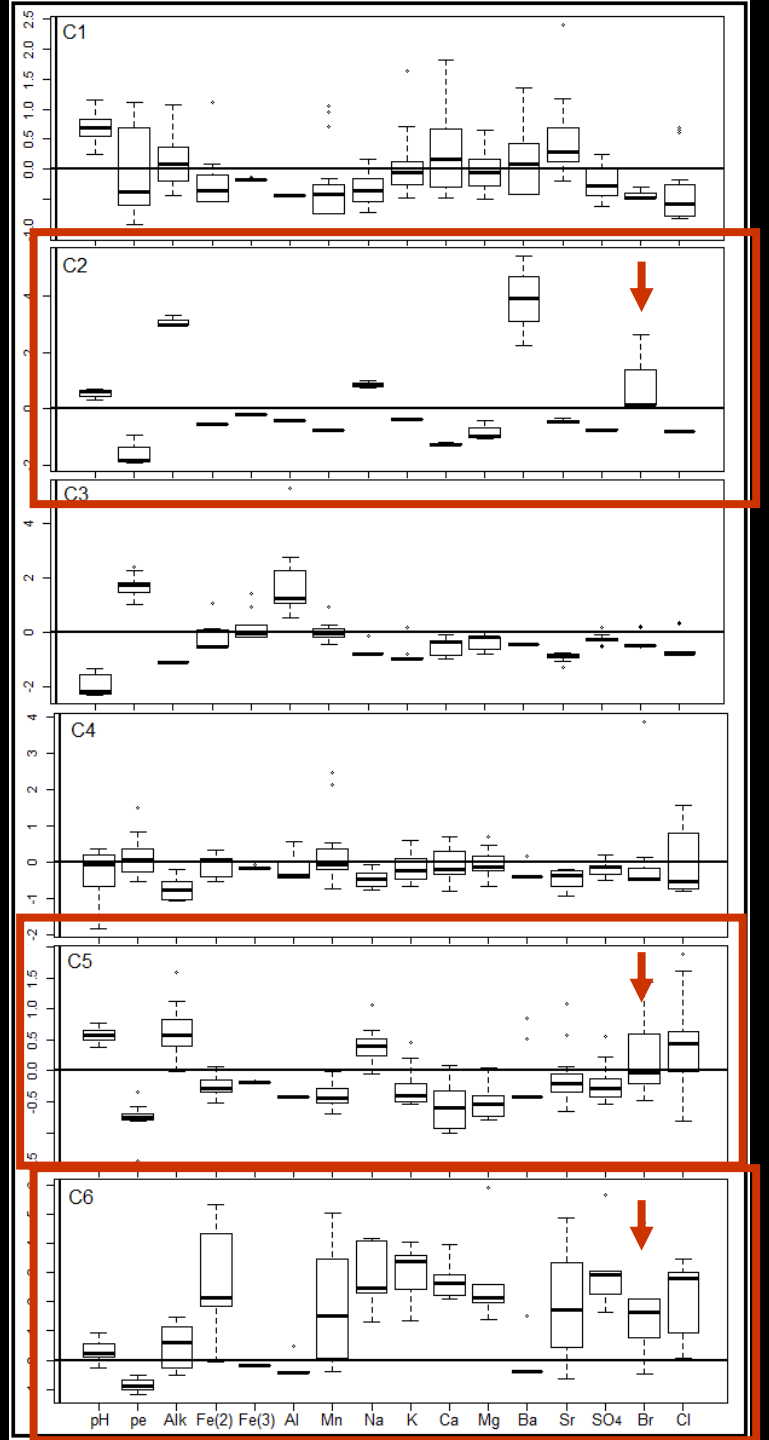


alkaline strata above the Pittsburgh coal

after Cecil 2012



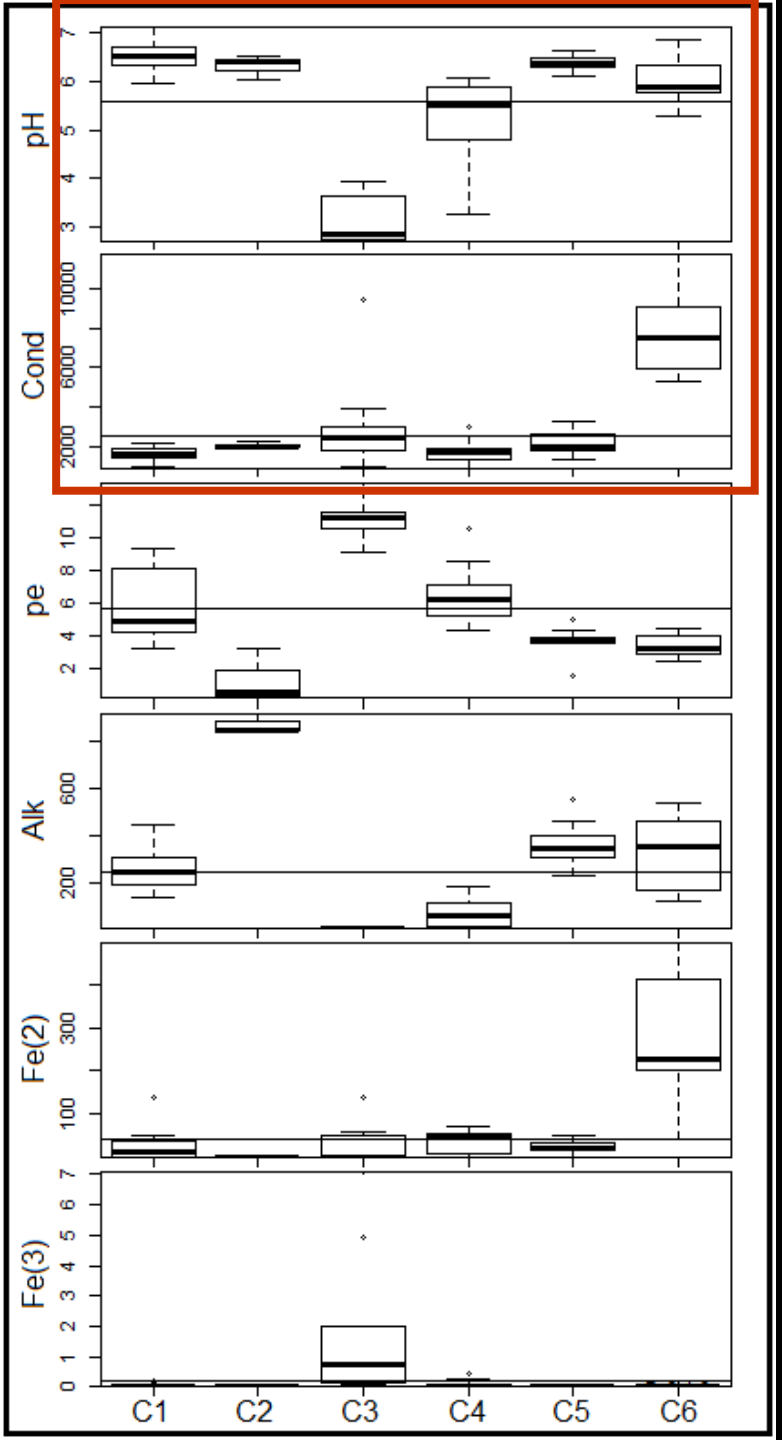
cluster analysis (CA) dendrogram (Denicola, 2013)



CA centroids, clusters 1-6

3,4 = net acidic

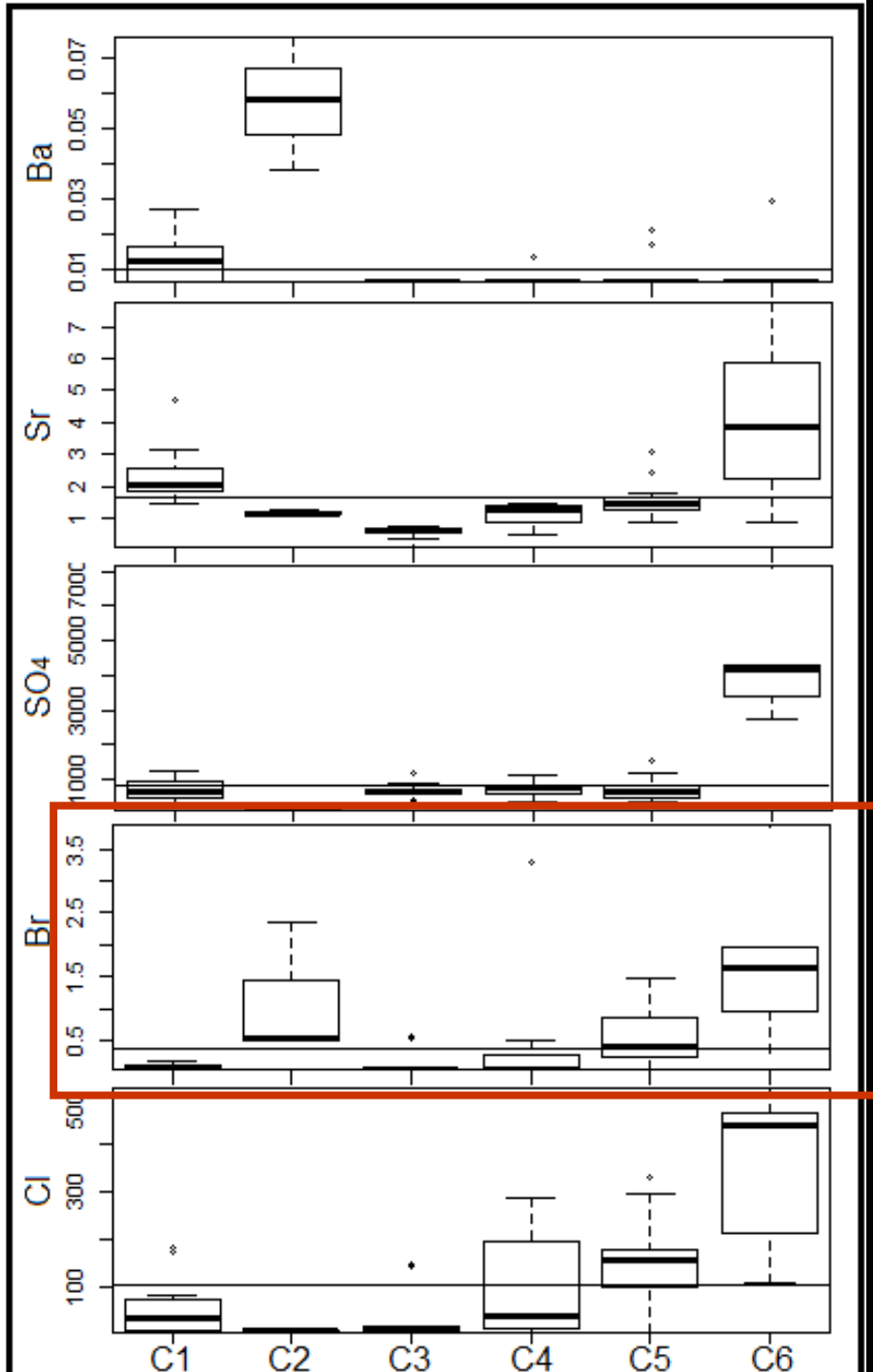
1,2,5,6 = net alkaline pools



CA solute boxplots – 1

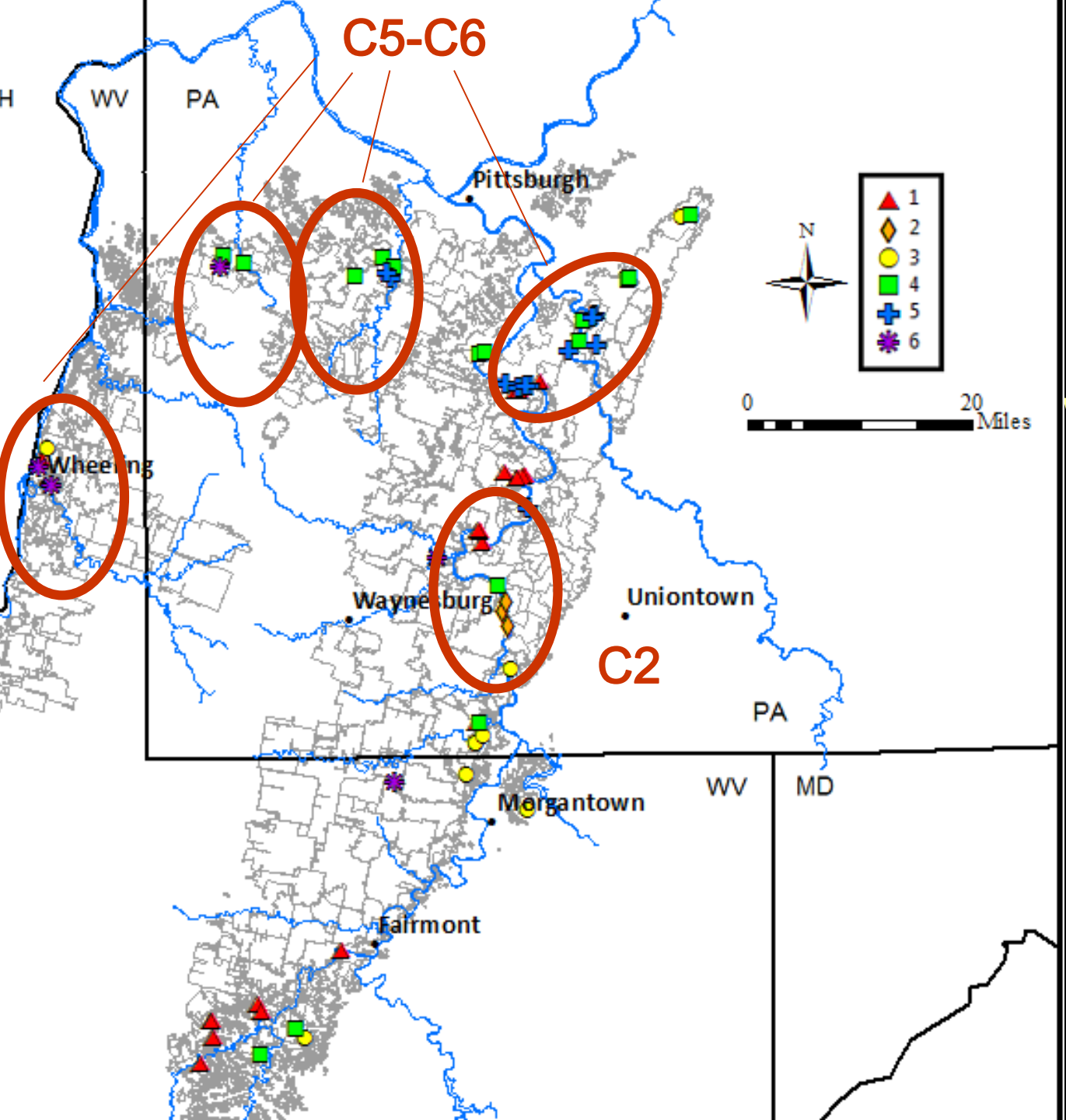
C2 = low TDS
C5=intermediate TDS
C6 = high TDS

all net alkaline
(pools)

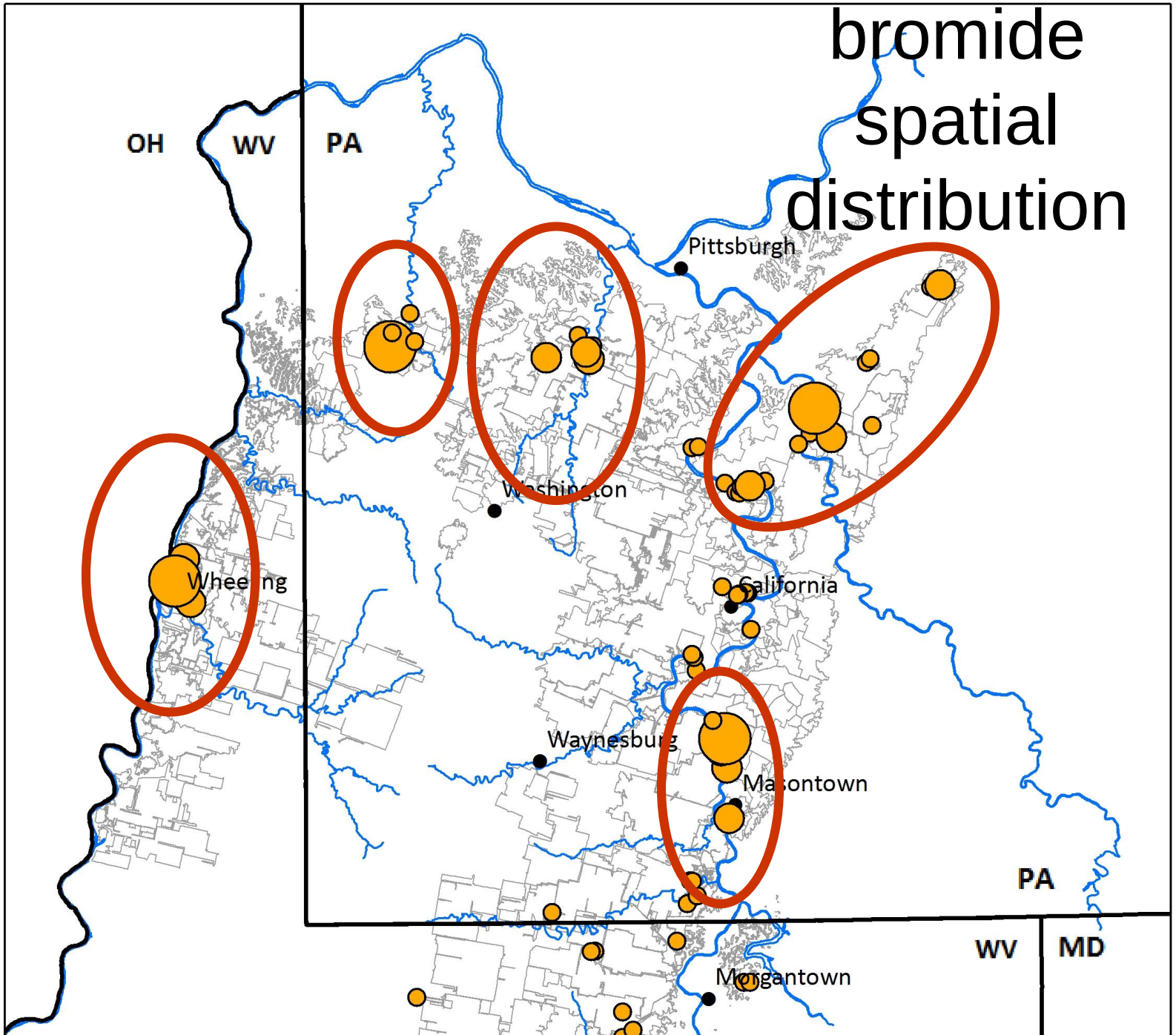


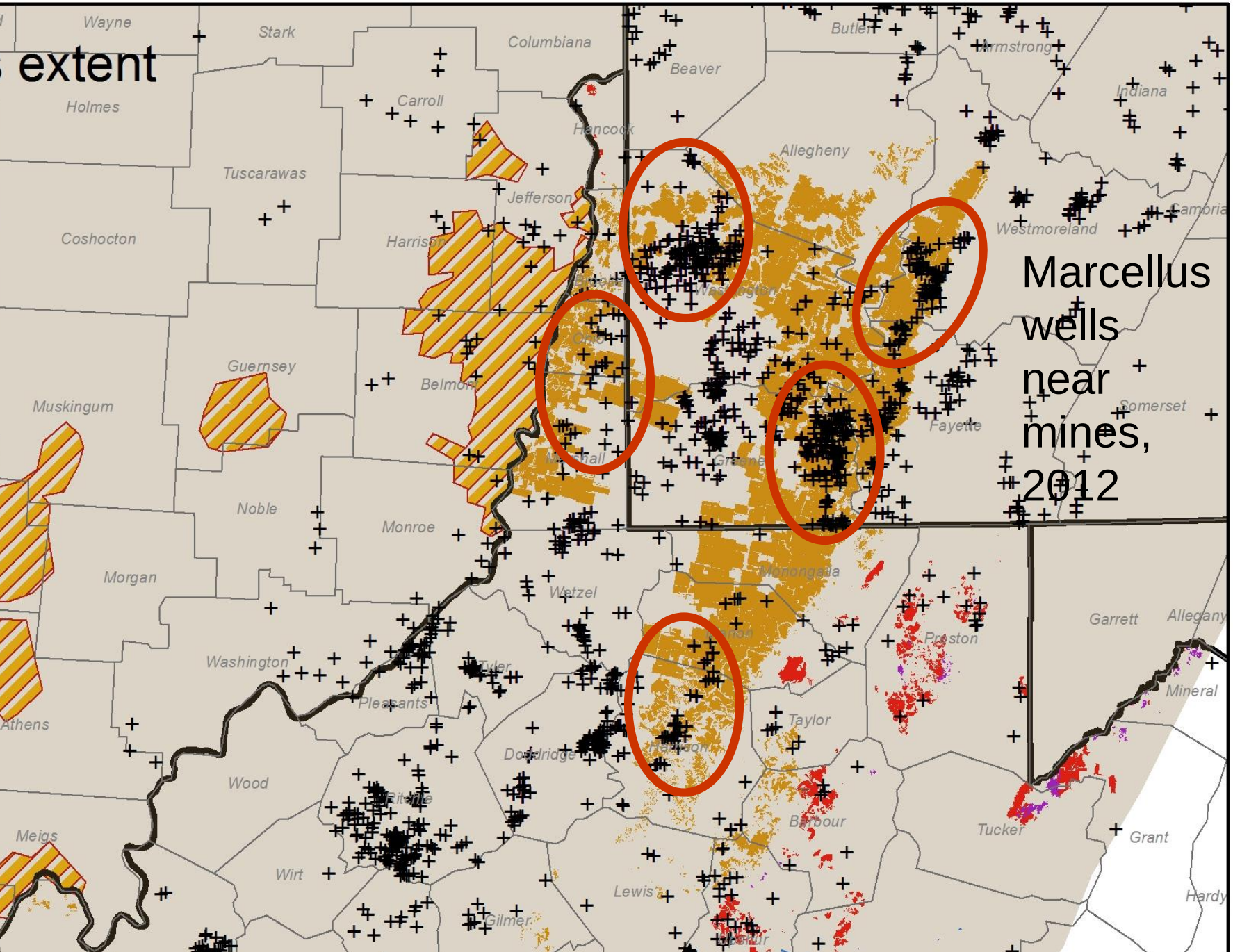
CA solute boxplots – 2

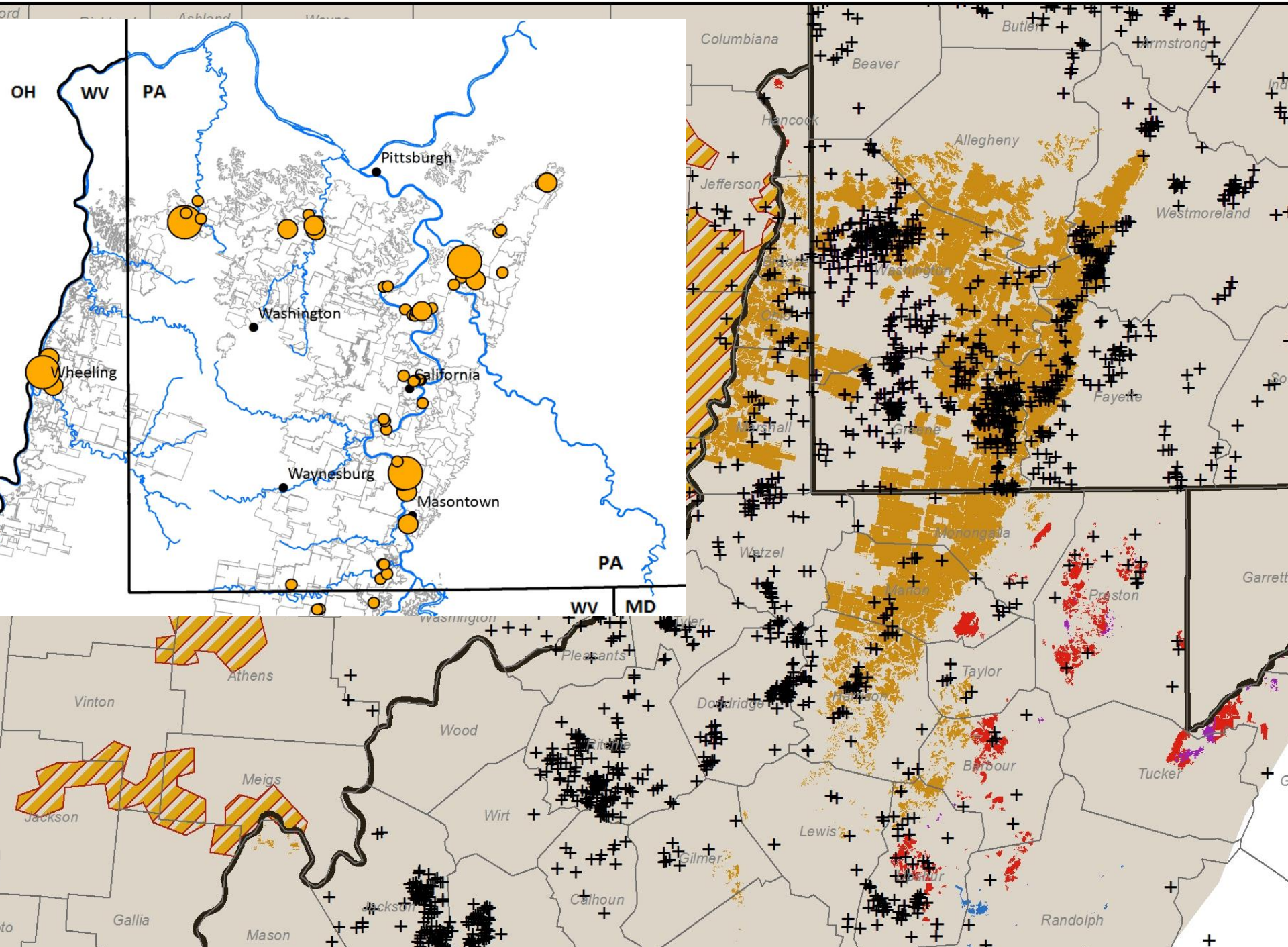
C2, C5, C6 have high Br

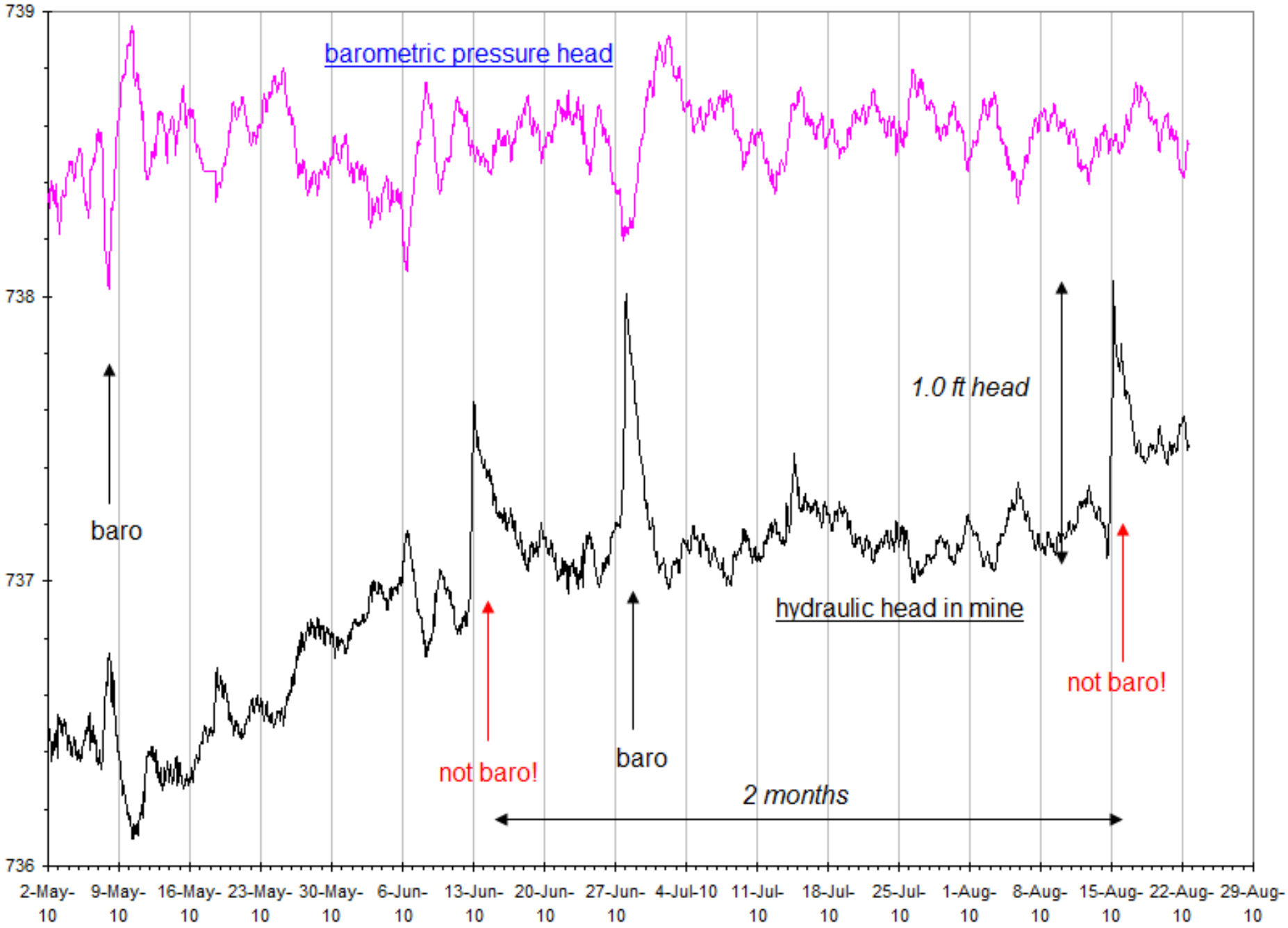


clusters with high Br: spatial distribution


bromide
spatial
distribution
OH
WV
PA
Pittsburgh
Washington
Wheeling
California
Waynesburg
Masontown
PA
WV
MD
Morgantown


extent
Marcellus wells near mines, 2012
Wayne
Stark
Columbiana
Butler
Armstrong
Beaver
Indiana
Holmes
Carroll
Hancock
Allegheny
Tuscarawas
Jefferson
Cambria
Coshocton
Harrison
Westmoreland
Guernsey
Belmont
Muskingum
Somerset
Fayette
Noble
Monroe
Morgan
Monongalia
Wetzel
Garrett
Allegany
Preston
Washington
Tyler
Mineral
Athens
Pleasants
Taylor
Doddridge
Wood
Barbour
Tucker
Grant
Meigs
Wirt
Lewis
Hardy
Gilmer


OH
WV
PA
Pittsburgh
Washington
Wheeling
California
Waynesburg
Masontown
PA
WV
MD
Columbiana
Beaver
Butler
Armstrong
Hancock
Allegheny
Jefferson
Westmoreland
Fayette
Marshall
Wetzel
Monongalia
Preston
Garrett
Taylor
Barbour
Tucker
Lewis
Randolph
Gilmer
Calhoun
Wirt
Wood
Pleasants
Athens
Vinton
Meigs
Jackson
Gallia
Mason

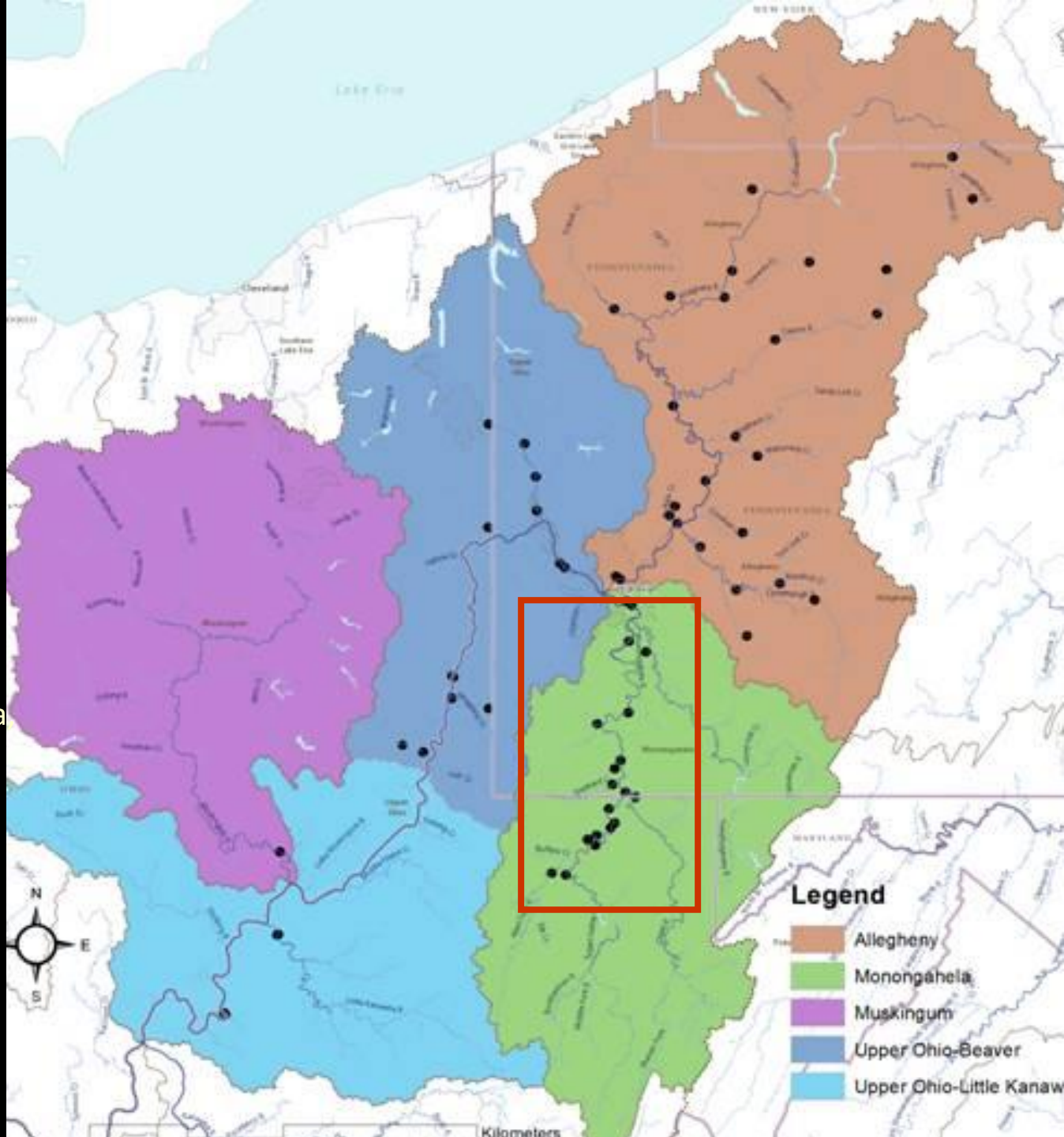

739
738
737
736
barometric pressure head
hydraulic head in mine
1.0 ft head
baro
baro
not baro!
not baro!
2 months
2-May-10
9-May-10
16-May-10
23-May-10
30-May-10
6-Jun-10
13-Jun-10
20-Jun-10
27-Jun-10
4-Jul-10
11-Jul-10
18-Jul-10
25-Jul-10
1-Aug-10
8-Aug-10
15-Aug-10
22-Aug-10
29-Aug-10

3RQ sampling sites

Bi weekly monitoring for Flow and:

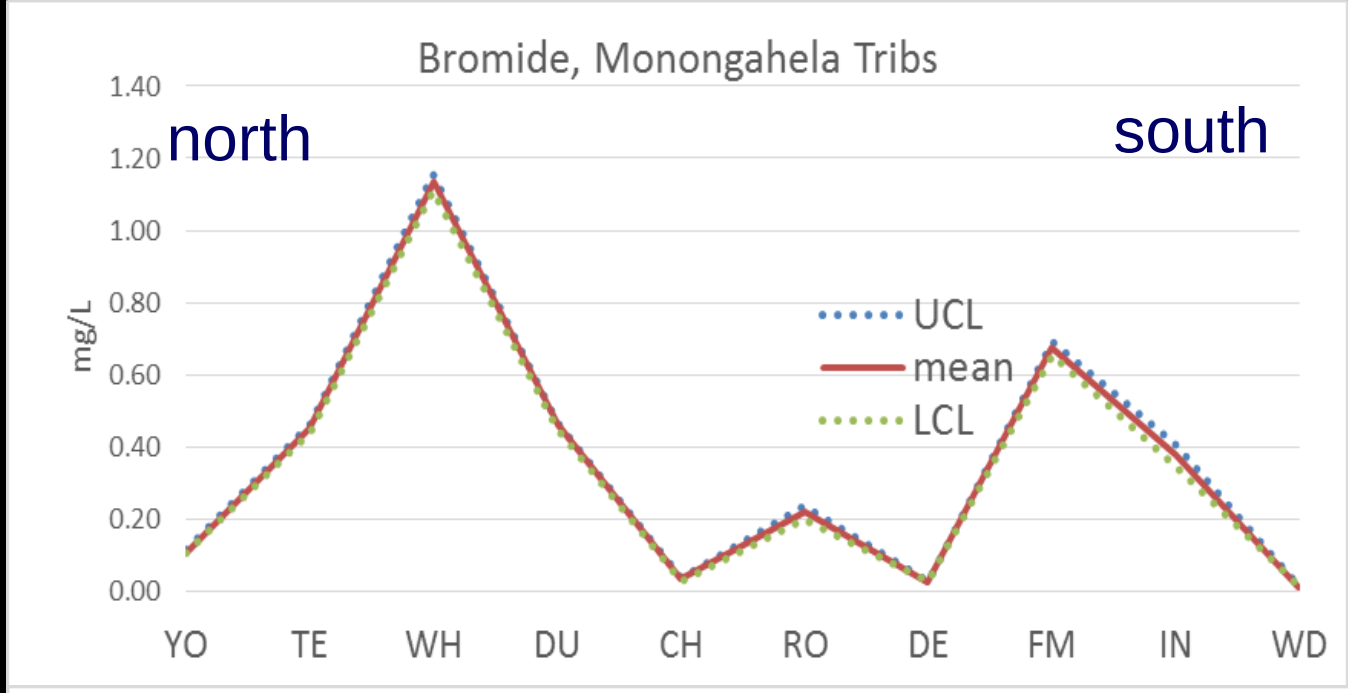
pH, Acidity, Alkalinity, EC, ORP, Temperature, TDS, TSS, Al, Br, Ca Cl, Fe, Mg, Mn, Na, SO_4

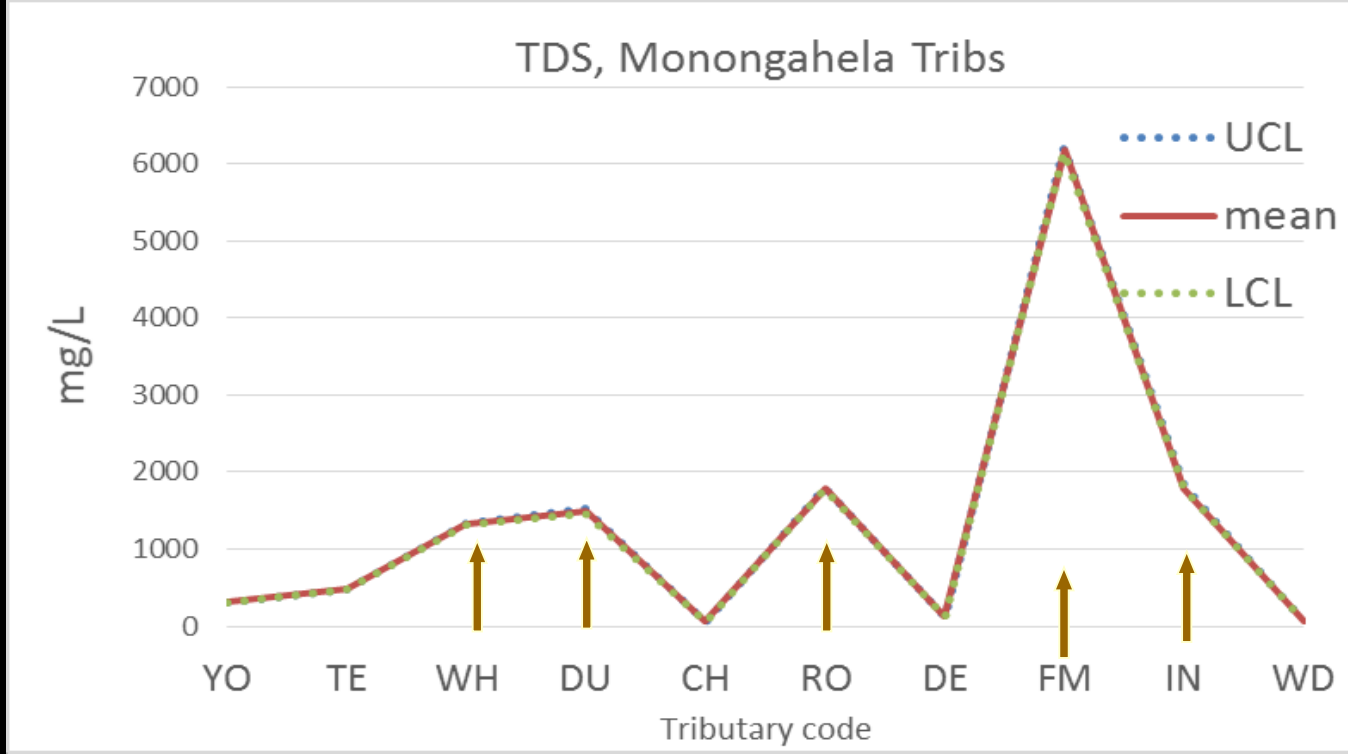
Results on 3RiversQuest.org



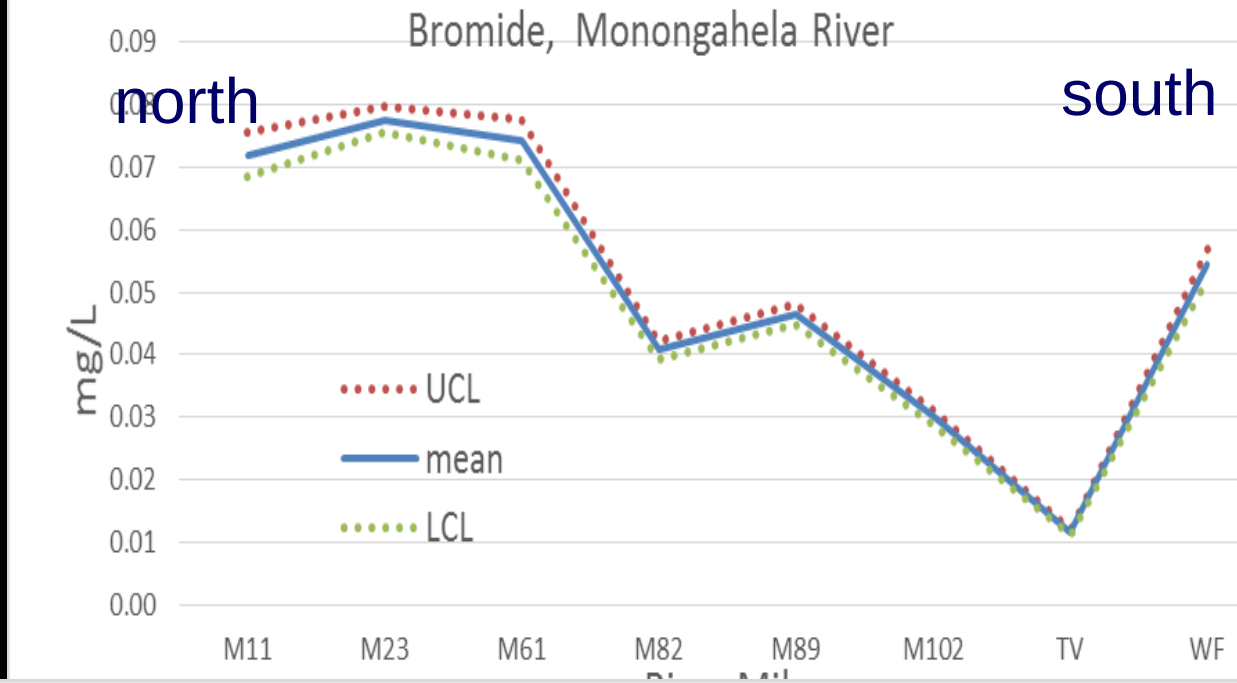
TDS/BROMIDE TRENDS SINCE 2009 in MON RIVER TRIBS

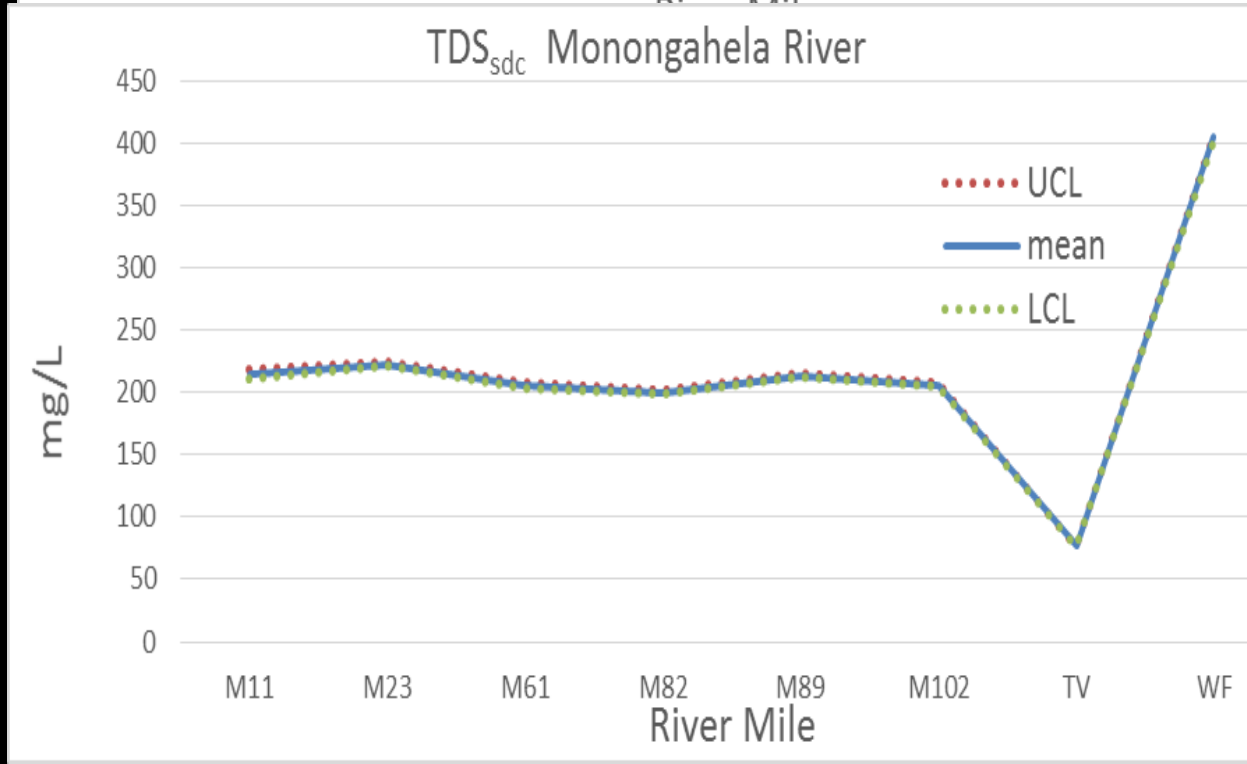
Whiteday Creek
Indian Creek
Flaggy Meadows Run
Deckers Creek
Robinson Run
Cheat River
Dunkard Creek
Whitely Creek
Tenmile Creek
Youghihenny R.





TDS/BROMIDE TRENDS SINCE 2009 in MON RIVER





Key observations

- Elevated mine-water Br concentrations 0.5-2.7 mg/L observed in about 16 AML discharges in 2012
- most are in flooded mine pools in Pennsylvania and Wheeling area
- Spatial pattern for high Br does not strictly correlate with “mining water” signatures (high TDS)
- But high Br occurs where Marcellus well density is high
- surface water chemistry of Monongahela and its tribs also shows divergence between “Br signal” and “TDS signal”
- hydraulic injection “events” have been observed in Pittsburgh seam mines

implications

- Br can serve as an indicator for contamination of mine water by formation water
- formation water leakage into mines? flowback waters? not clear which
- spatial distribution suggests Marcellus development areas are where high Br tends to be found, but this could be for a number of reasons
- underground mine pools targets may be targets for contamination by non-UIC disposal of wastewaters