

Bromide Concentrations in Discharges from Coal Mines in Pennsylvania

Charles A. Cravotta III,
U.S. Geological Survey Pennsylvania Water Science Center

with contributions from Keith Brady,
Brent Means, Gary Greenfield, Scott Hoffman, Angela McFadden

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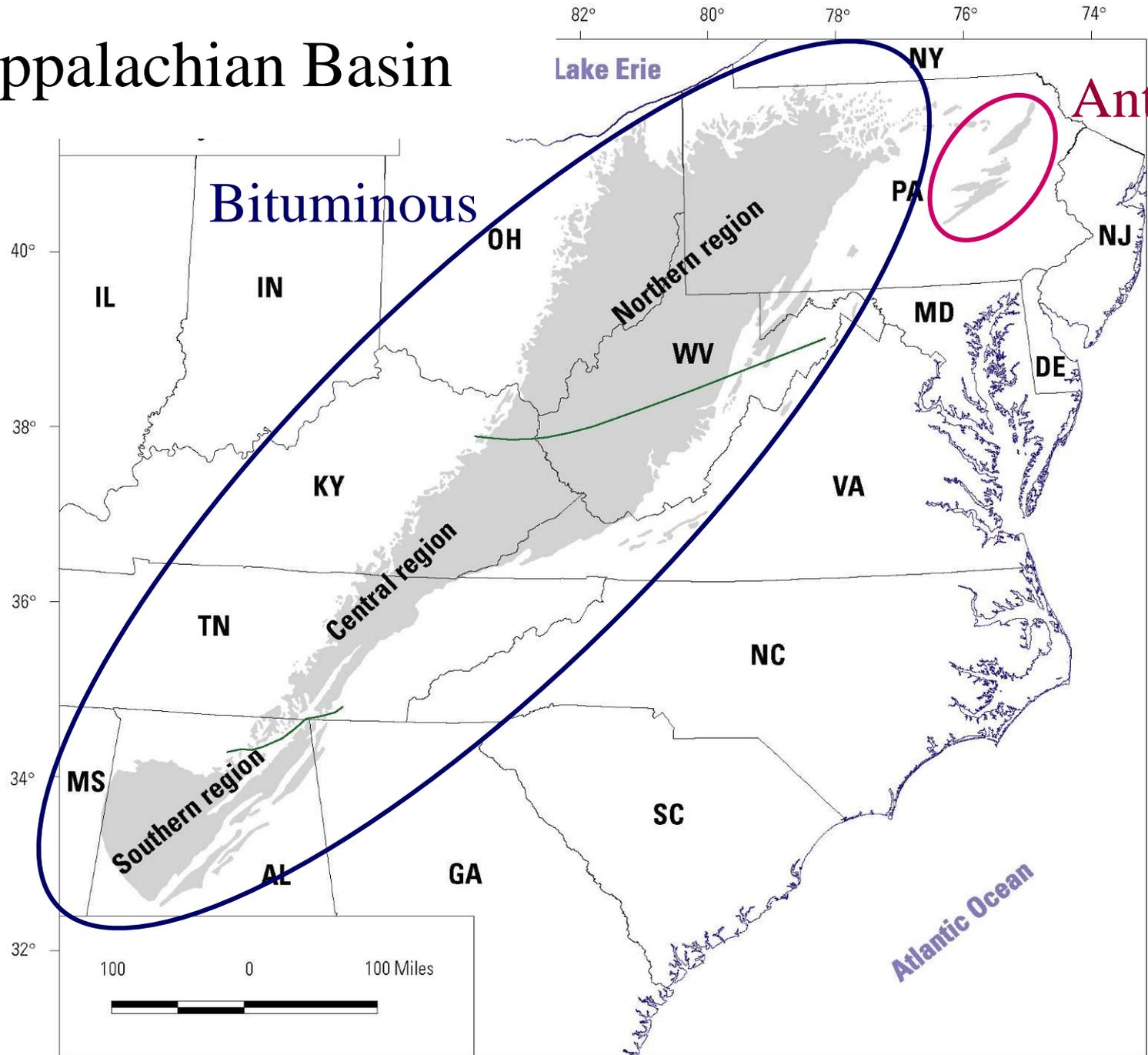
Alerts Due to Wastewater Discharges

- In 2008, PaDEP was alerted to elevated bromide (Br^-) in Monongahela, Allegheny, and Ohio Rivers, linked primarily to gas produced water discharges.
- Br^- is a concern because of its potential to oxidize to bromate (BrO_3^-) or to interact with organic carbon forming brominated trihalomethane (THM) disinfection byproducts (DBPs).
- The drinking-water MCL is 0.010 mg/L for bromate and 0.080 mg/L for total trihalomethanes (TTHM).

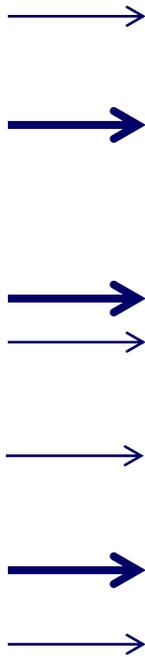
Brine Constituents in Coal-Mine Drainage

- Various halogen (Cl, Br, I), alkali earth (Na, K, Li), and alkaline earth (Sr, Ba) elements are present in oil and gas brines *and* CMD in western PA.
- Bromide (Br^-) concentrations in CMD in western PA sampled in 1999-2011 ranged from <0.003 to 12.8 mg/L, with median 0.036 mg/L.
- Management of Br^- from coal-mine sources requires an understanding of the origin of Br^- .

Appalachian Basin



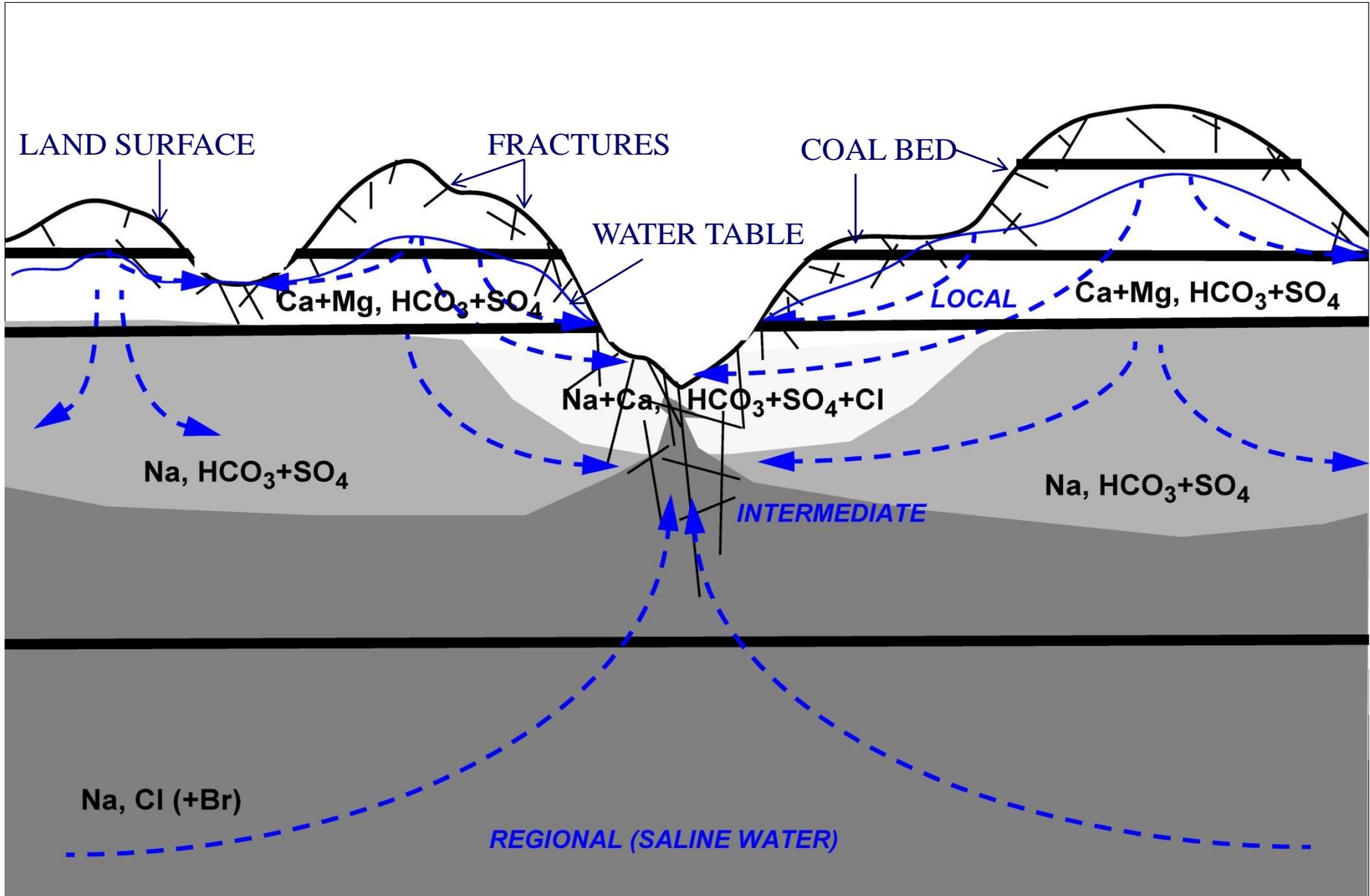
SERIES	NORTHERN APPALACHIAN BASIN Pennsylvania, Ohio, Maryland, and northern West Virginia		CENTRAL APPALACHIAN BASIN eastern Kentucky, Virginia and southern West Virginia	
	Unit	Group	Unit	Group
LOWER PERMIAN	Washington coal zone			
	Waynesburg coal bed	Dunkard		
UPPER PENNSYLVANIAN	Sewickley coal bed	Monongahela		
	Redstone coal bed			
	Pittsburgh coal bed			
	Duquesne coal bed	Conemaugh		
	Ames Limestone			
	Bakerstown coal bed			
MIDDLE PENNSYLVANIAN	Brush Creek Limestone	Allegheny		
	Mahoning coal bed			
	Upper Freeport coal bed			
	Lower Freeport coal bed			
	Upper Kittanning coal zone			
	Middle Kittanning coal zone			
	Lower Kittanning coal bed			
	Clarion coal bed			
	Brookville coal bed			
	Pottsville		Allegheny	
MISSING SECTION		Stockton 'A' coal bed		
LOWER PENNSYLVANIAN	Pottsville		Fire Clay coal zone	
			Pond Creek coal zone	
			New River and Lee Formations	
			Pottsville	
		Pocahontas No. 8 coal bed		
		Pocahontas No. 4 coal bed		
		Pocahontas No. 3 coal bed		
		Squire Jim coal bed		



LITHOLOGY	SEQUENCE	DEPOSITONAL ENVIRONMENT	PHASE
shale		swamp and marsh	DELTA PLAIN
coal		overbank and levee silts and muds	
underclay			
argillaceous limestone			PROXIMAL PROGRADING
sandy shale		alluvial plain sheet sands	
sandstone and siltstone		distributary and barrier sands	DELTA
		channel sands	
gray fossiliferous shale		delta slope and prodelta muds and silts	DISTAL MARINE
fossiliferous limestone		marine platform limestones and muds	
black fossiliferous shale		destructional phase muds and silts	
limestone			
gray shale pyritic concretions			
coal			
underclay			

(adapted from Pryor & Sable, 1974)

Conceptual Hydro-Geochemical Model



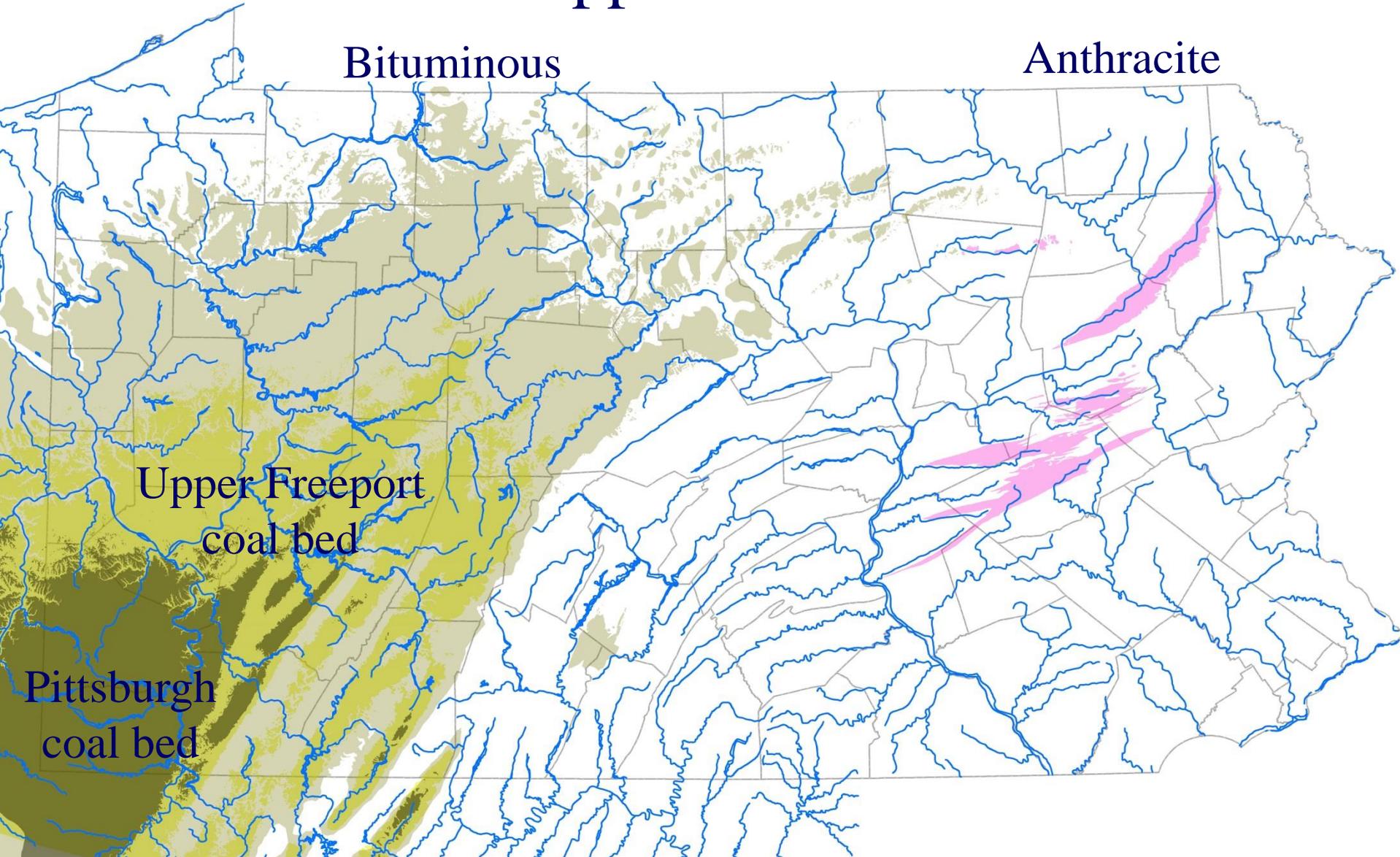
Spatial (and Temporal) Trends

- Water chemistry data: USGS-CMD 1999, 2003, 2006, 2011; OSM-CMD 2006; NURE 1977-78.
- Coal chemistry data: USGS “coalqual” 1970-1990 (depth not indicated).
- Rock chemistry data: NURE 1980 (very limited)

Northern Appalachian Coalfield

Bituminous

Anthracite

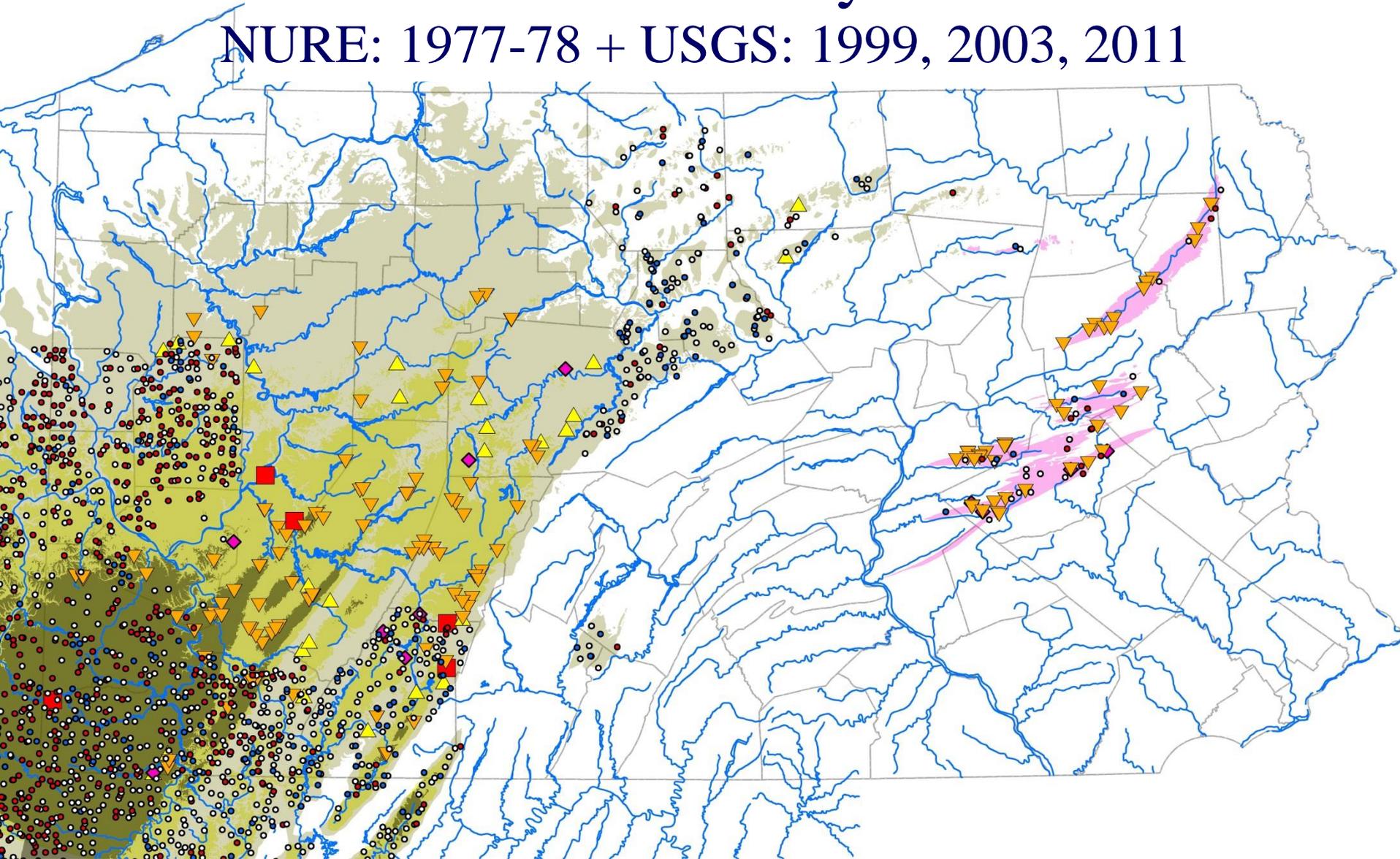


Upper Freeport
coal bed

Pittsburgh
coal bed

Water-Chemistry Data

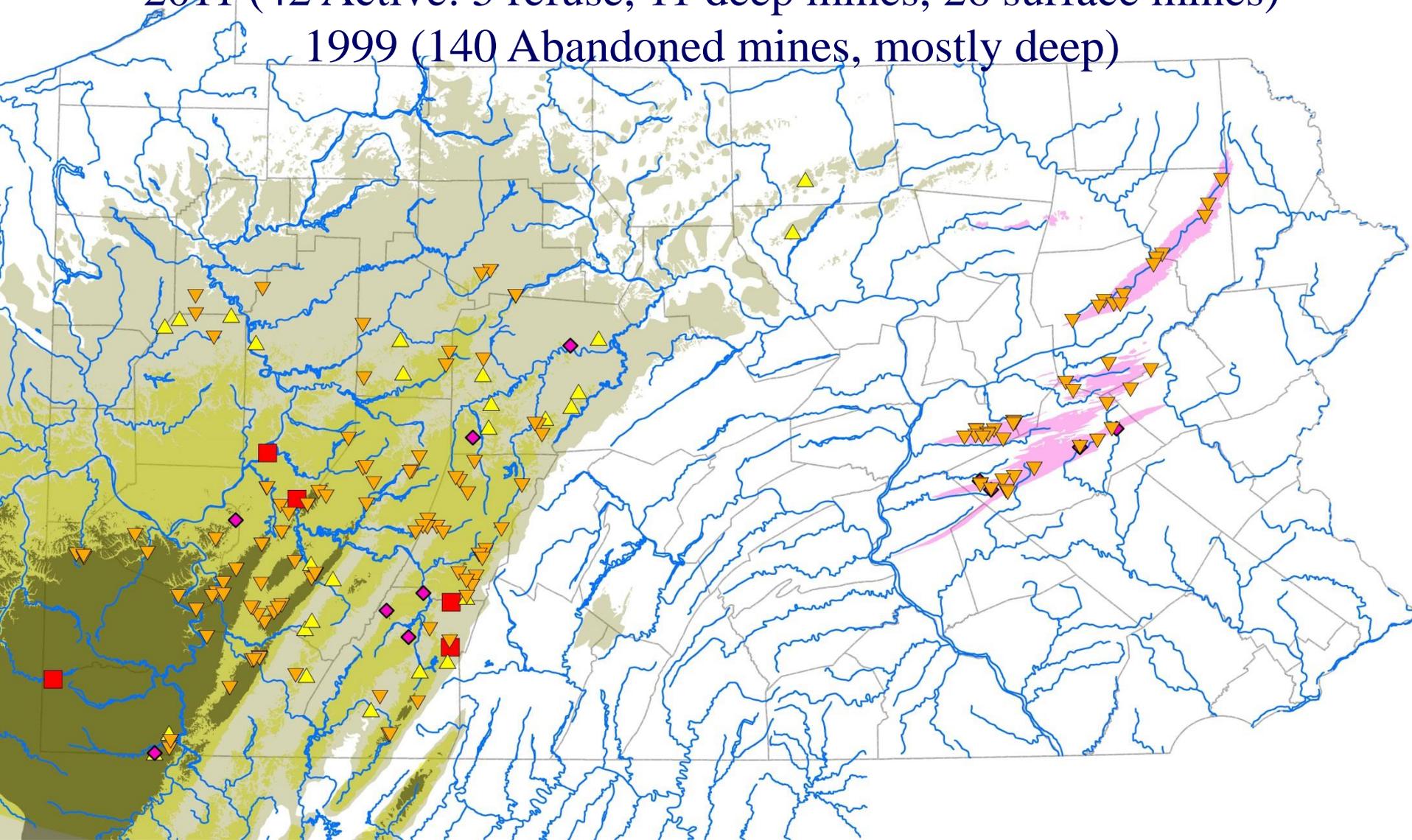
NURE: 1977-78 + USGS: 1999, 2003, 2011



Water-Chemistry Data – USGS CMD

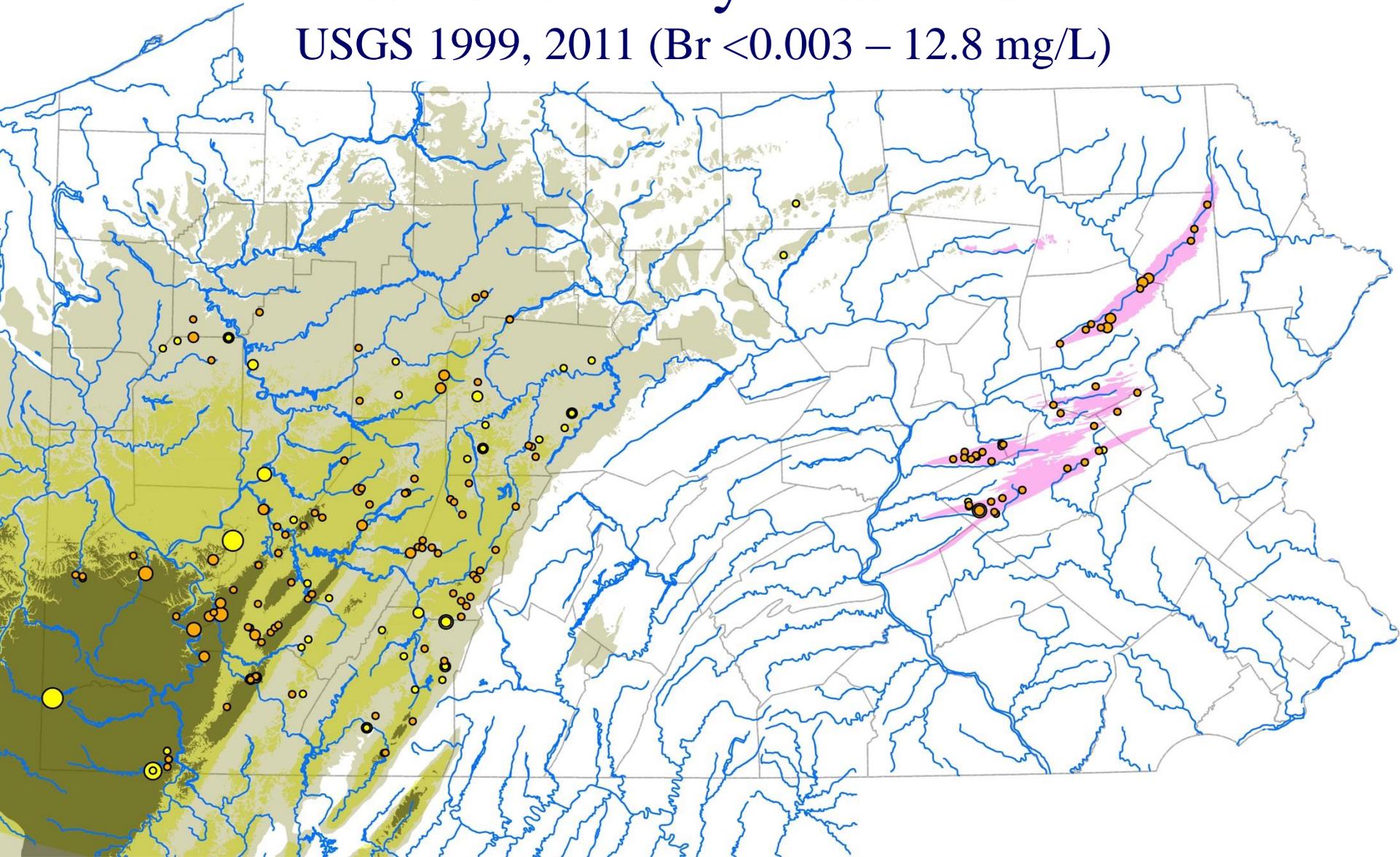
2011 (42 Active: 5 refuse, 11 deep mines, 26 surface mines)

1999 (140 Abandoned mines, mostly deep)



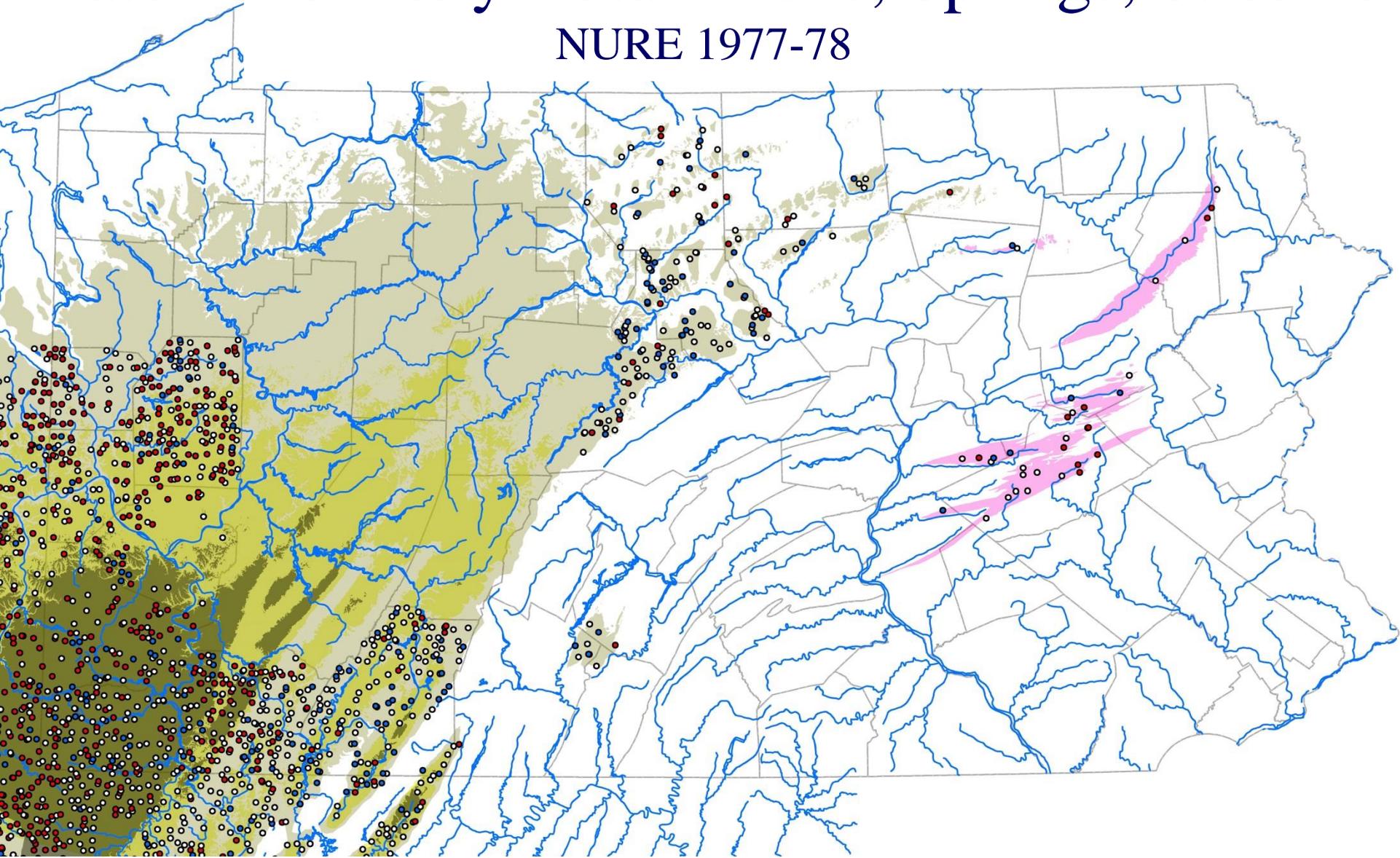
Water-Chemistry Data -- CMD

USGS 1999, 2011 (Br <0.003 – 12.8 mg/L)



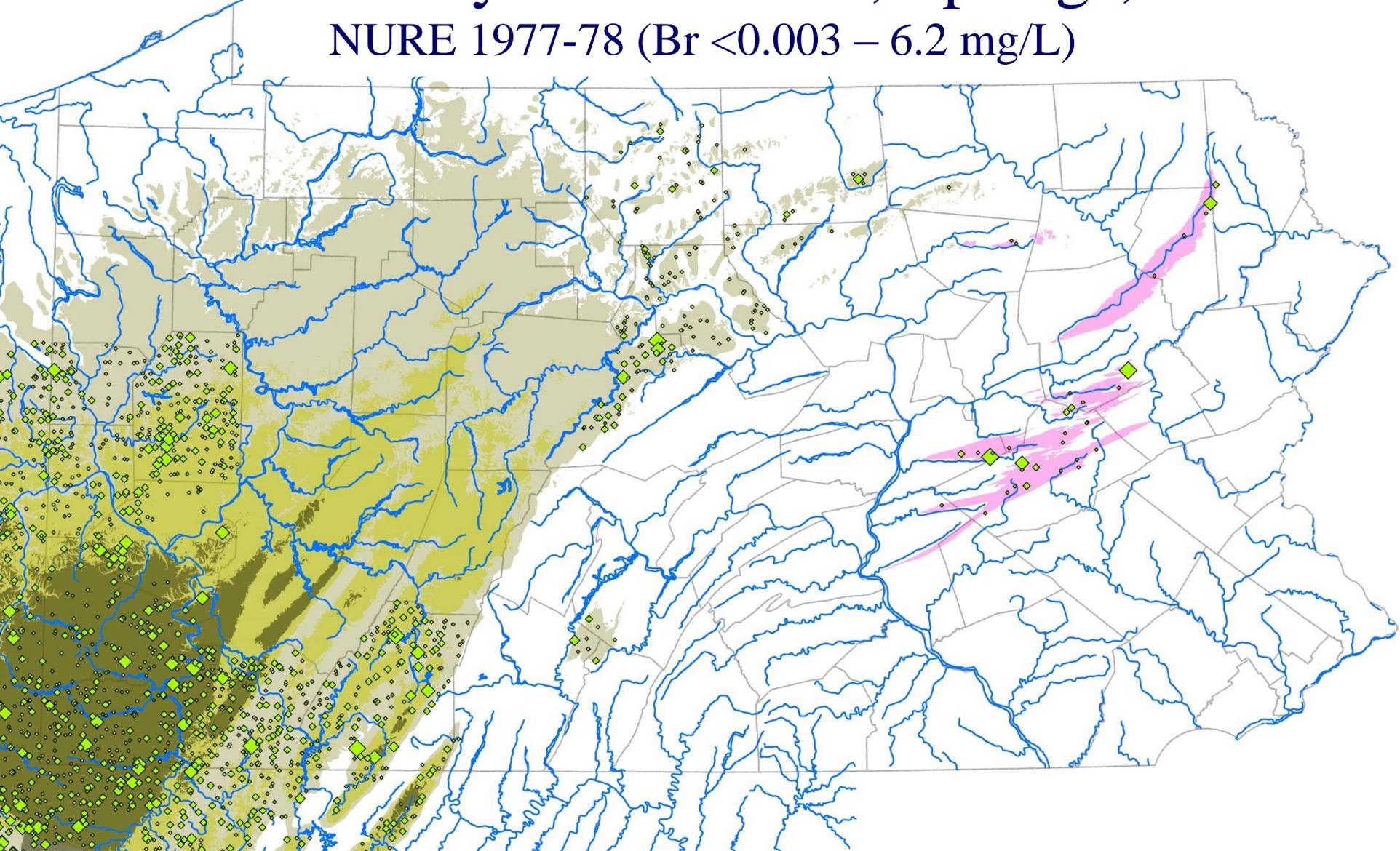
Water-Chemistry Data – Wells, Springs, Streams

NURE 1977-78



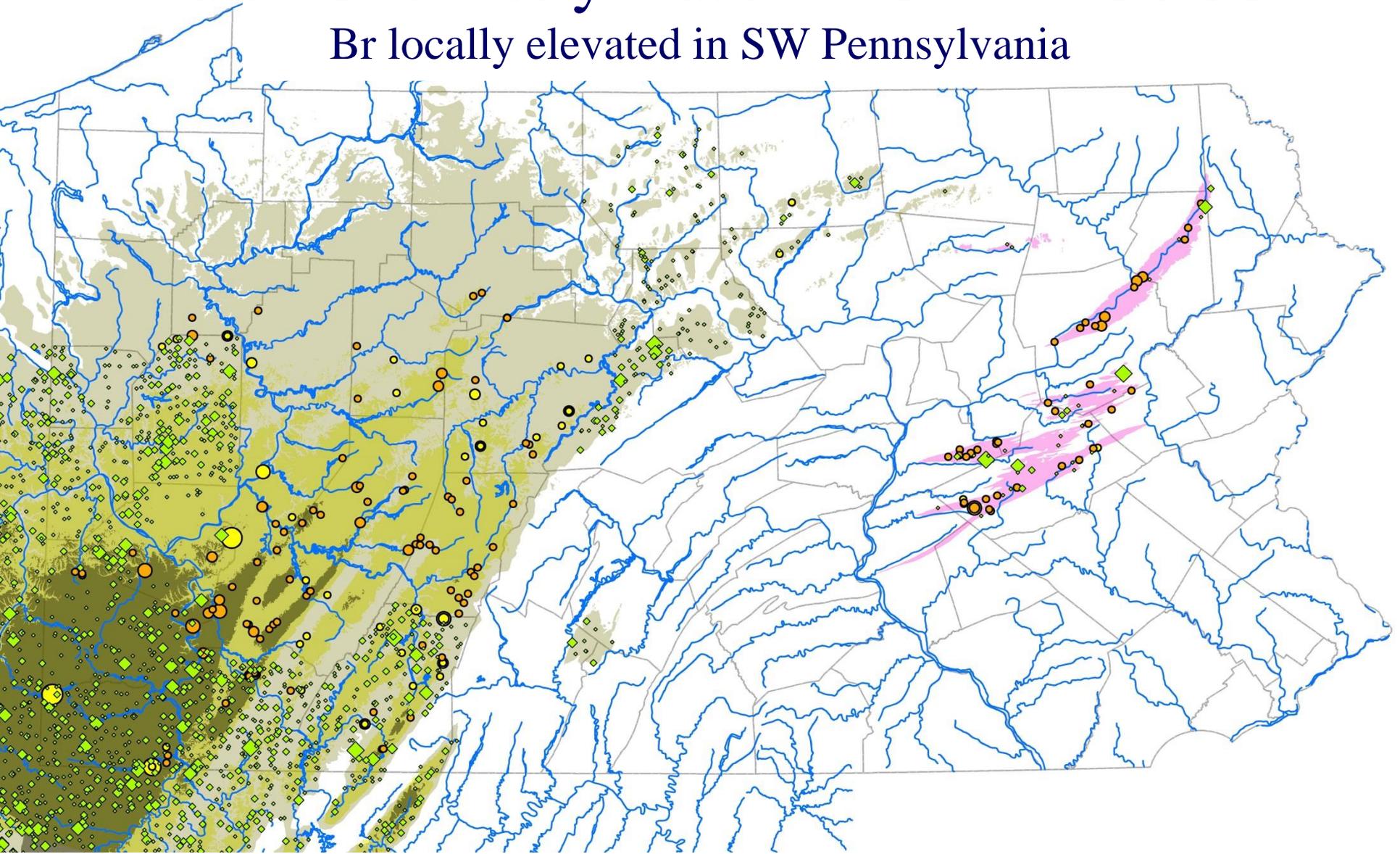
Water-Chemistry Data –Wells, Springs, Streams

NURE 1977-78 (Br <0.003 – 6.2 mg/L)

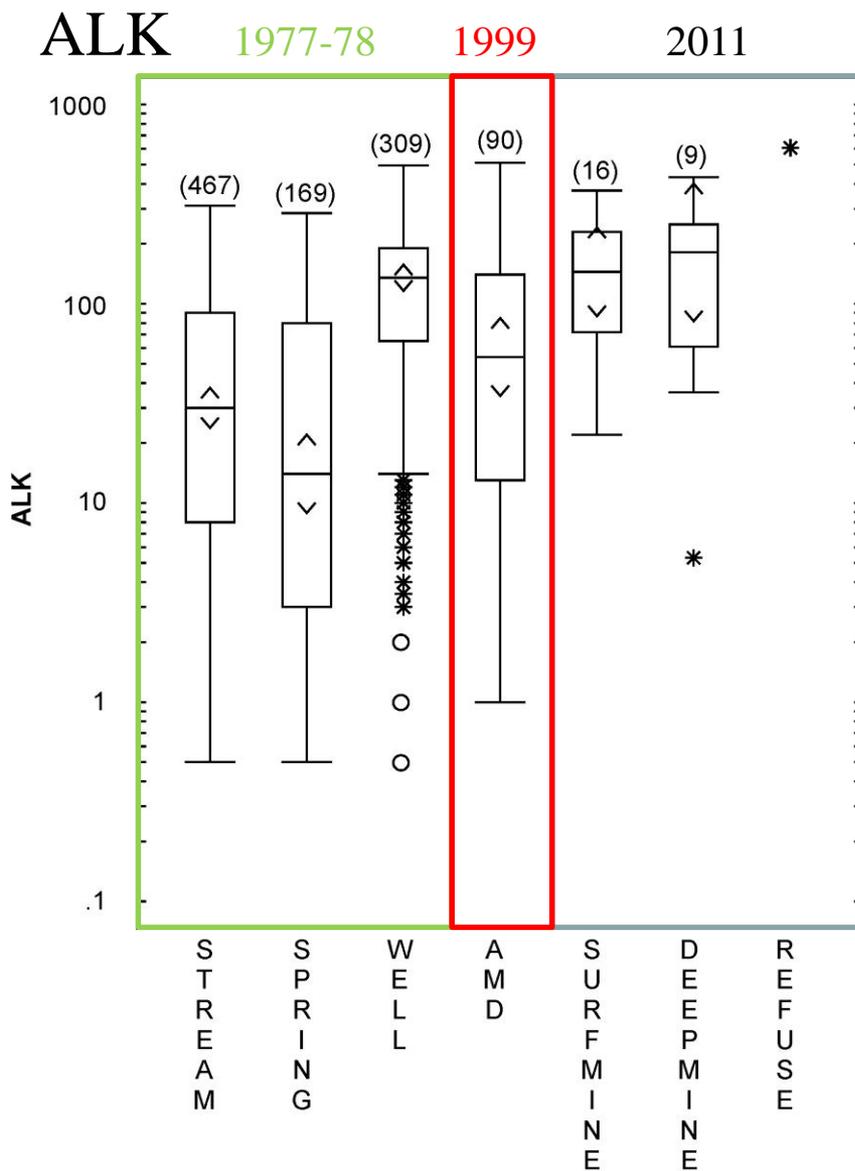
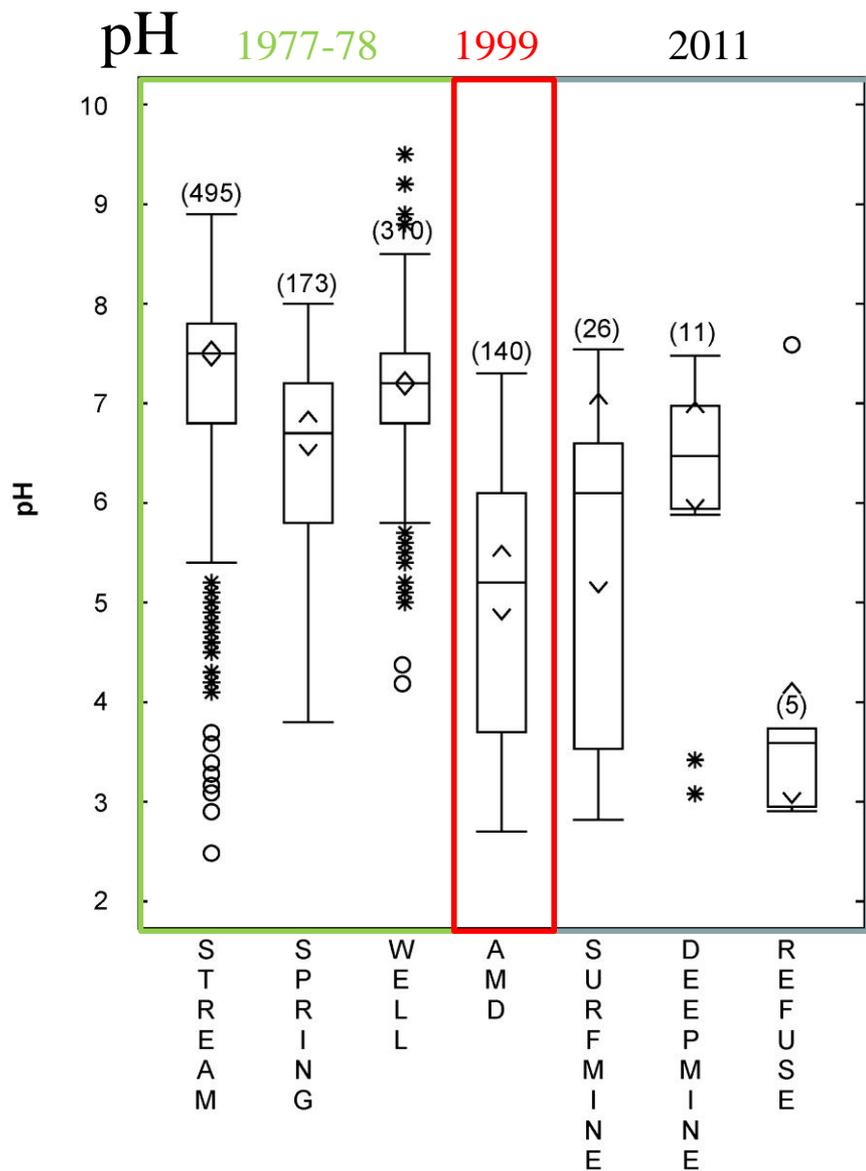


Water-Chemistry Data – NURE + USGS

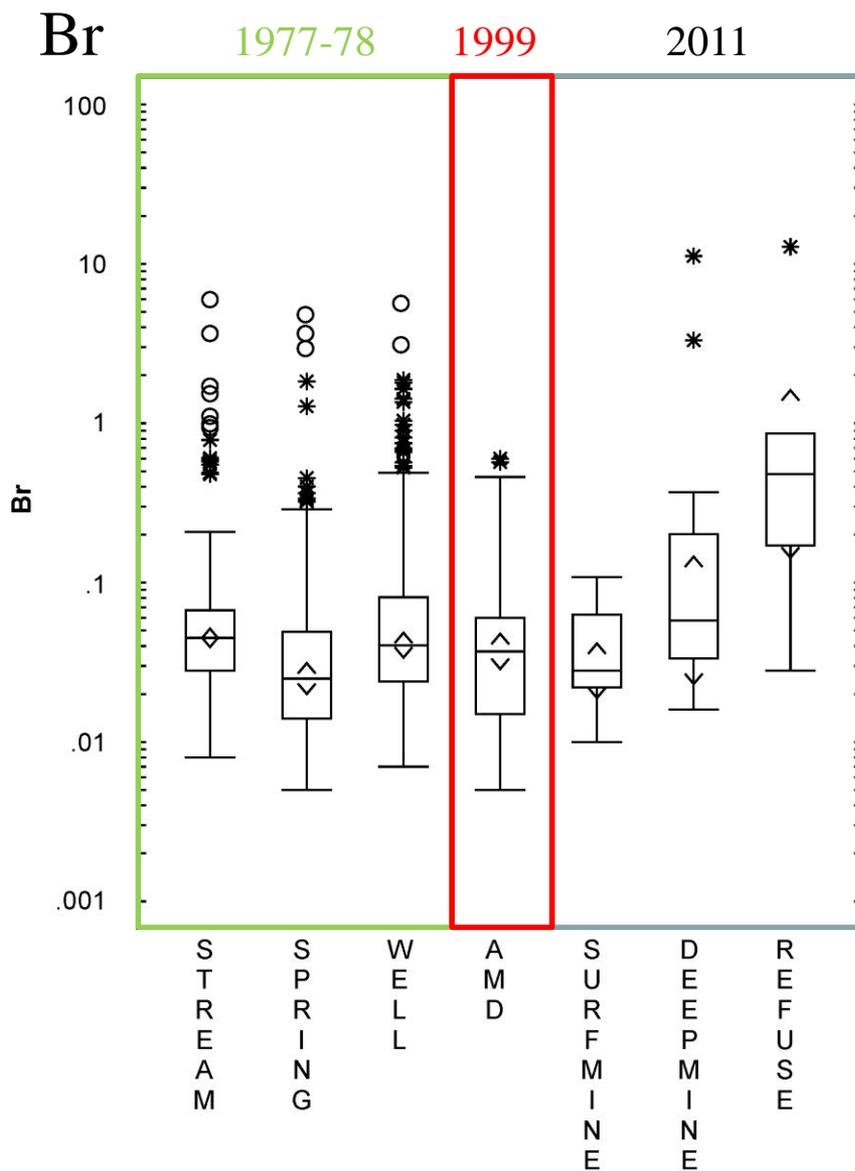
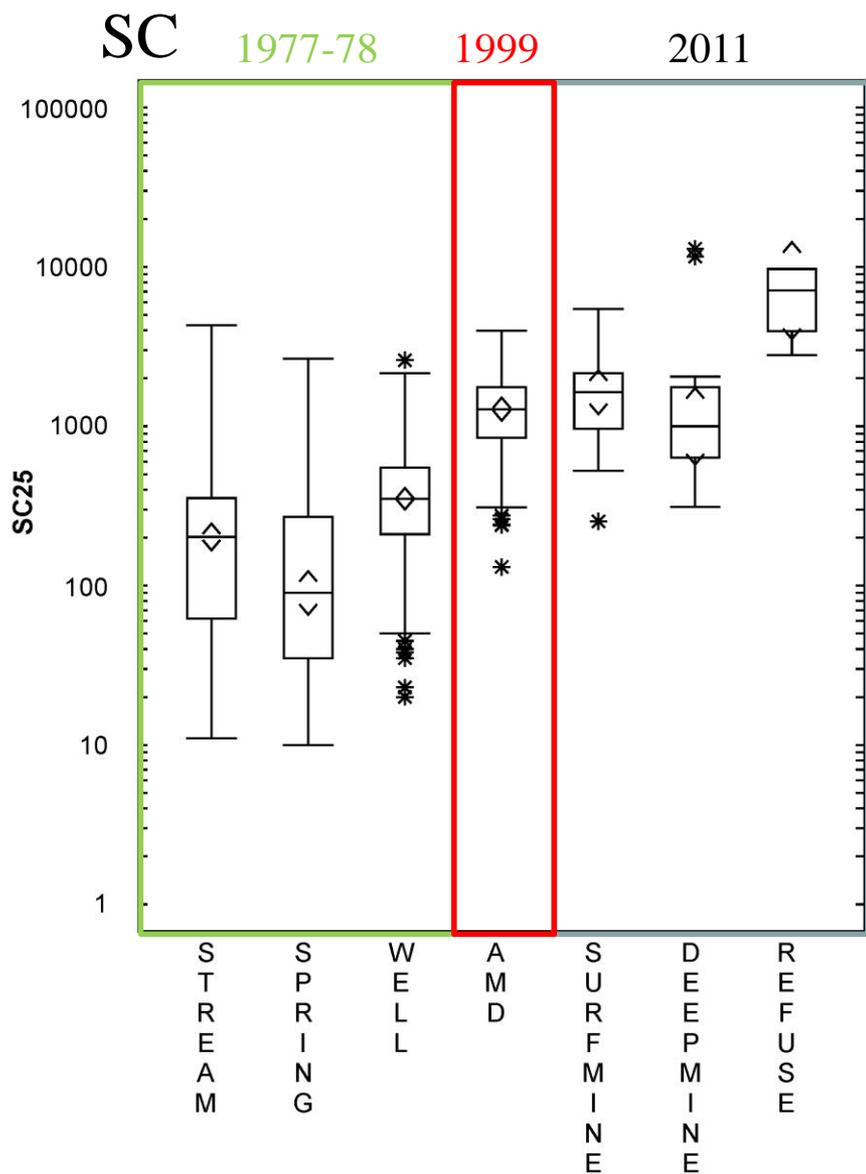
Br locally elevated in SW Pennsylvania



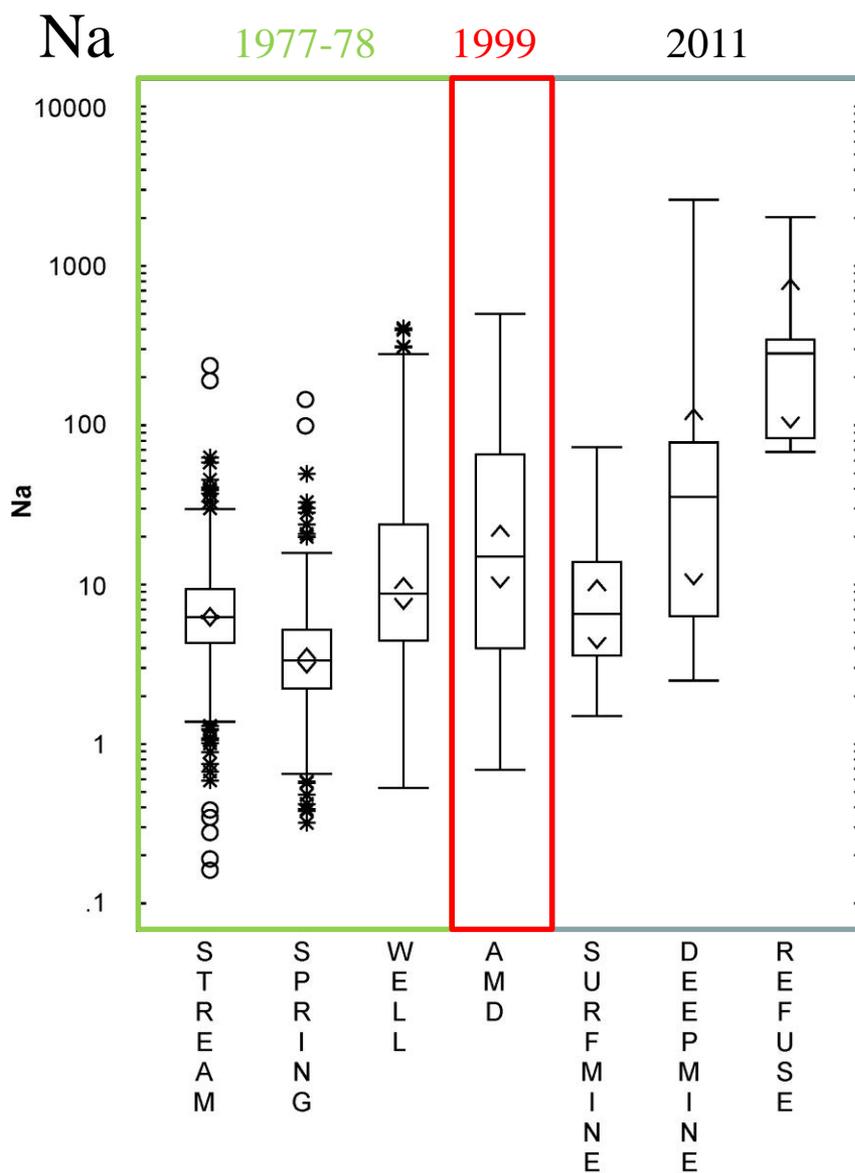
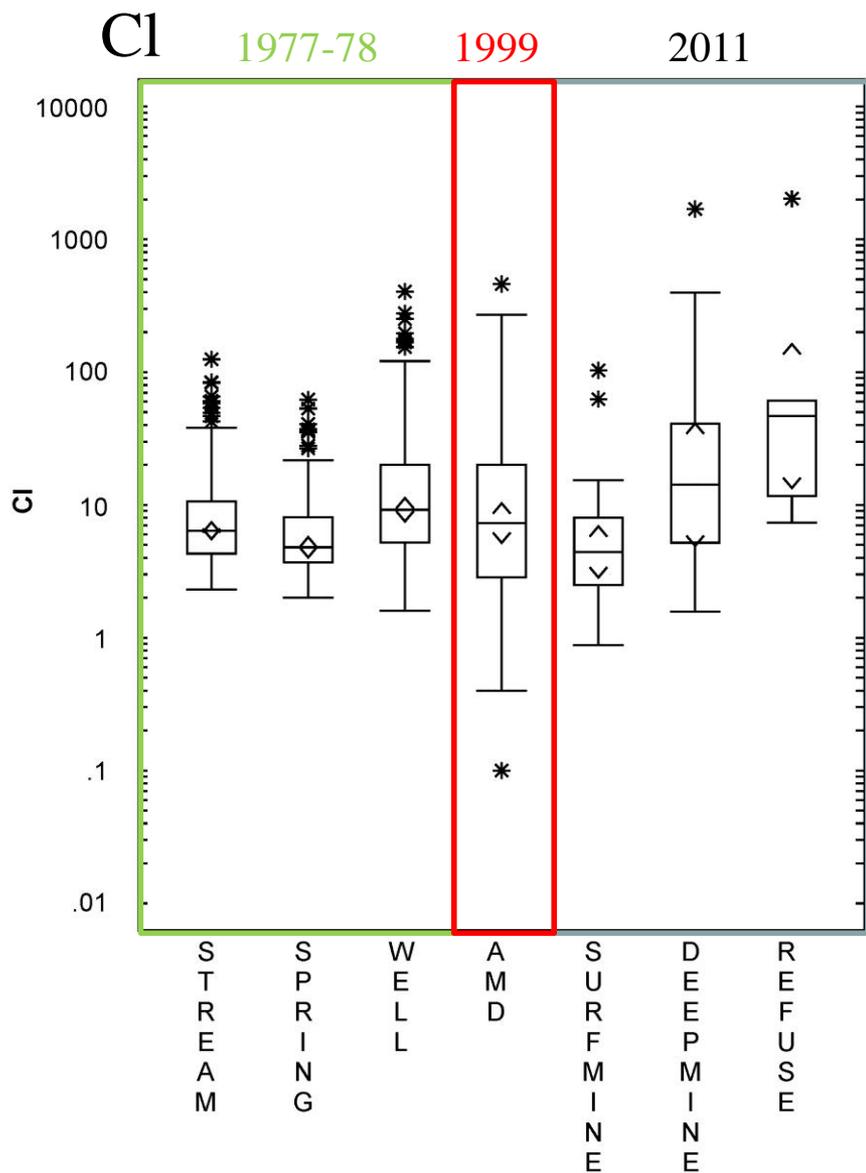
Comparison Water Chemistry Sources



Comparison Water Chemistry Sources

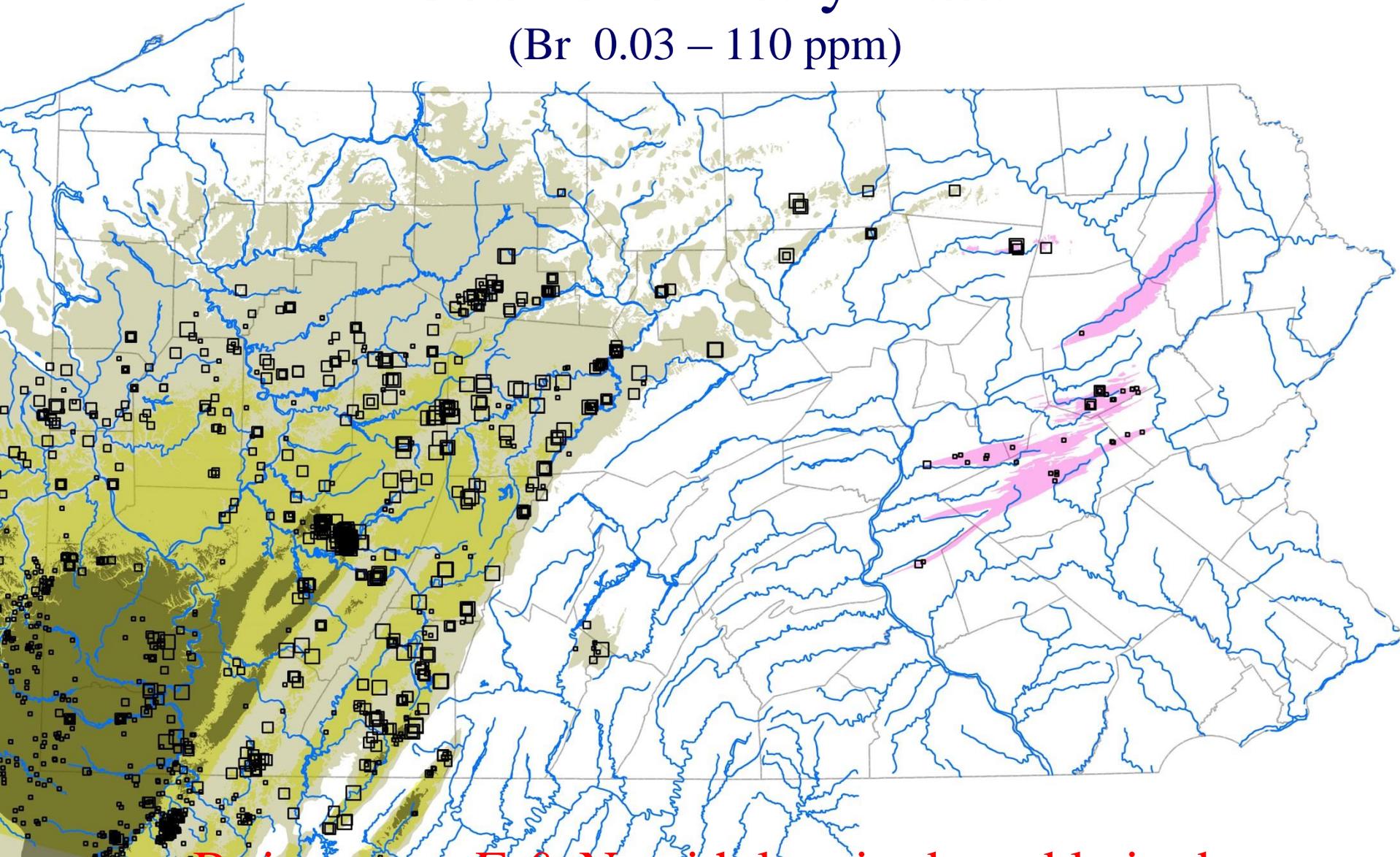


Comparison Water Chemistry Sources



Coal-Chemistry Data

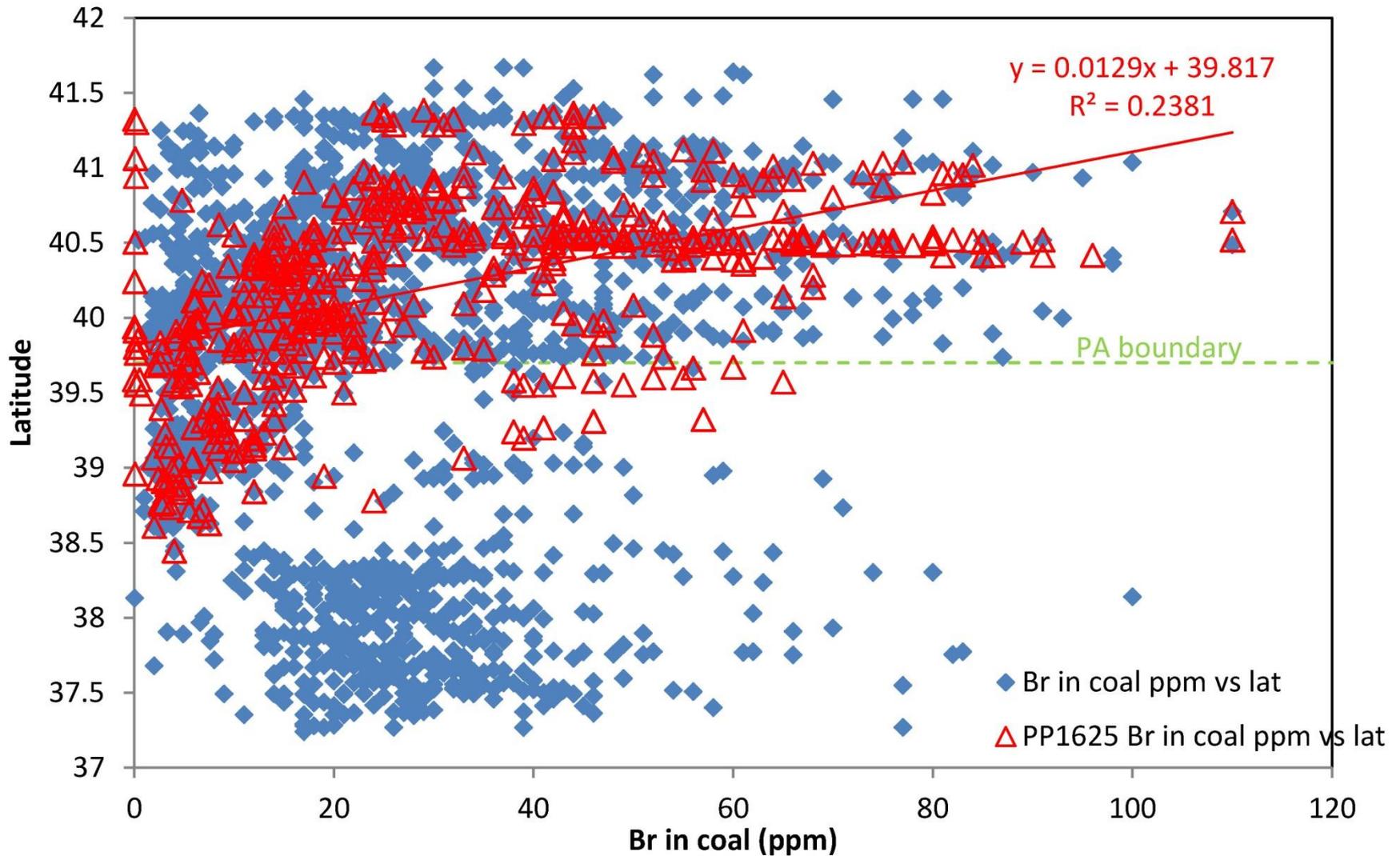
(Br 0.03 – 110 ppm)



Br increases E & N, with longitude and latitude

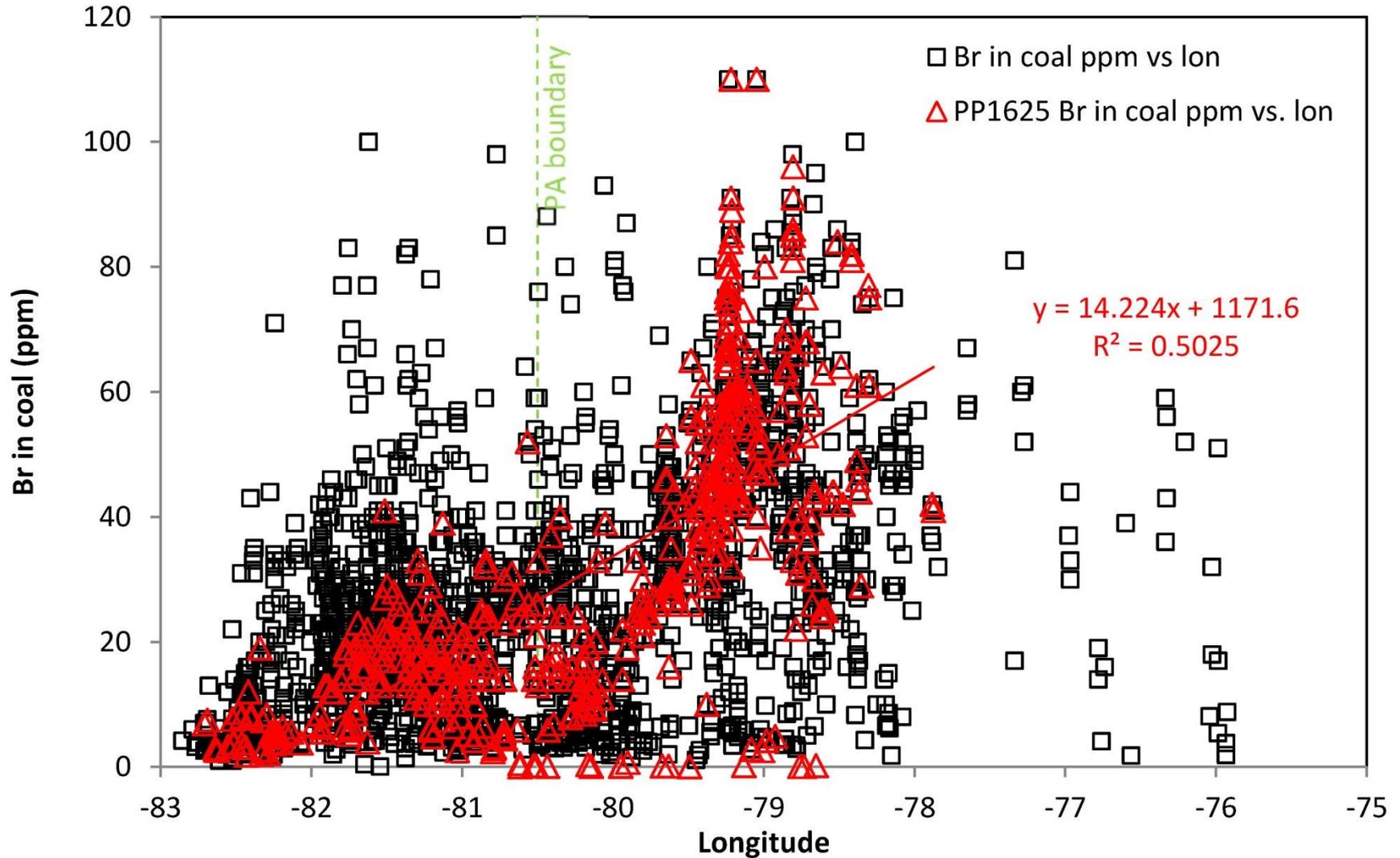
Coal-Chemistry Data

Bimodal with latitude (increases northward in PA)



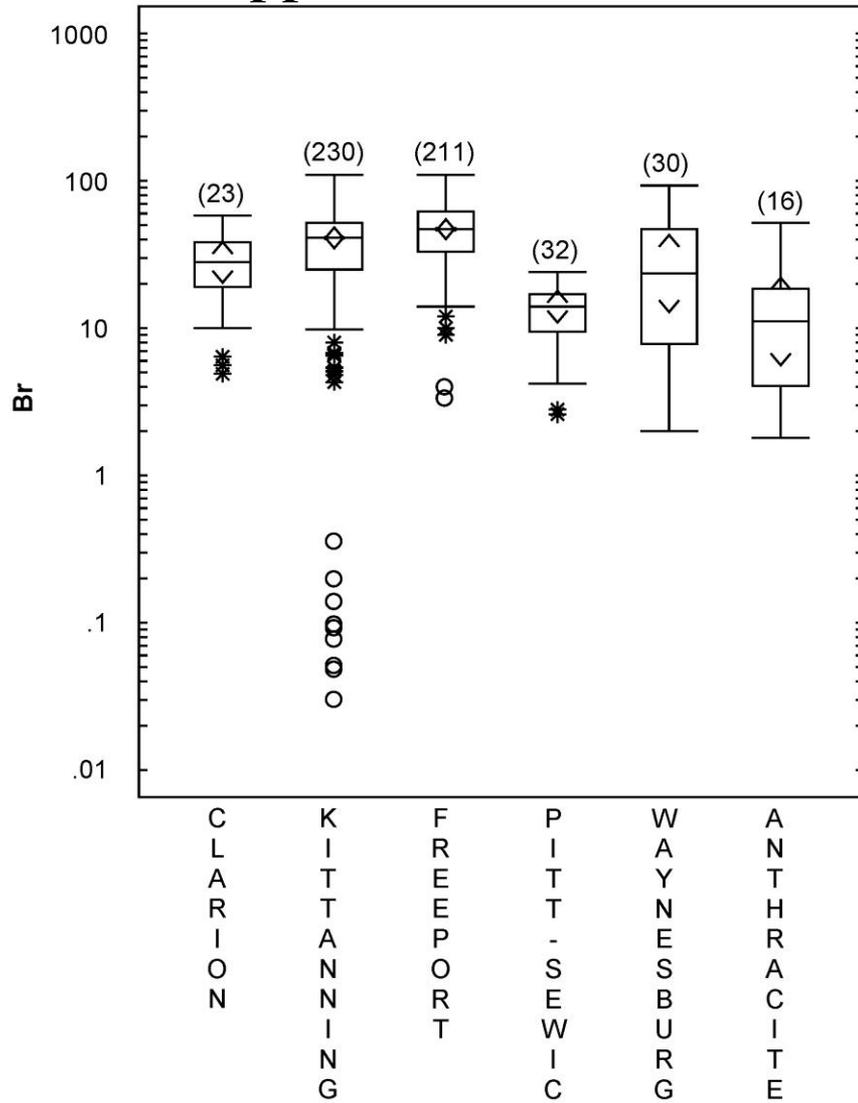
Coal-Chemistry Data

Unimodal with longitude (increases eastward in PA)

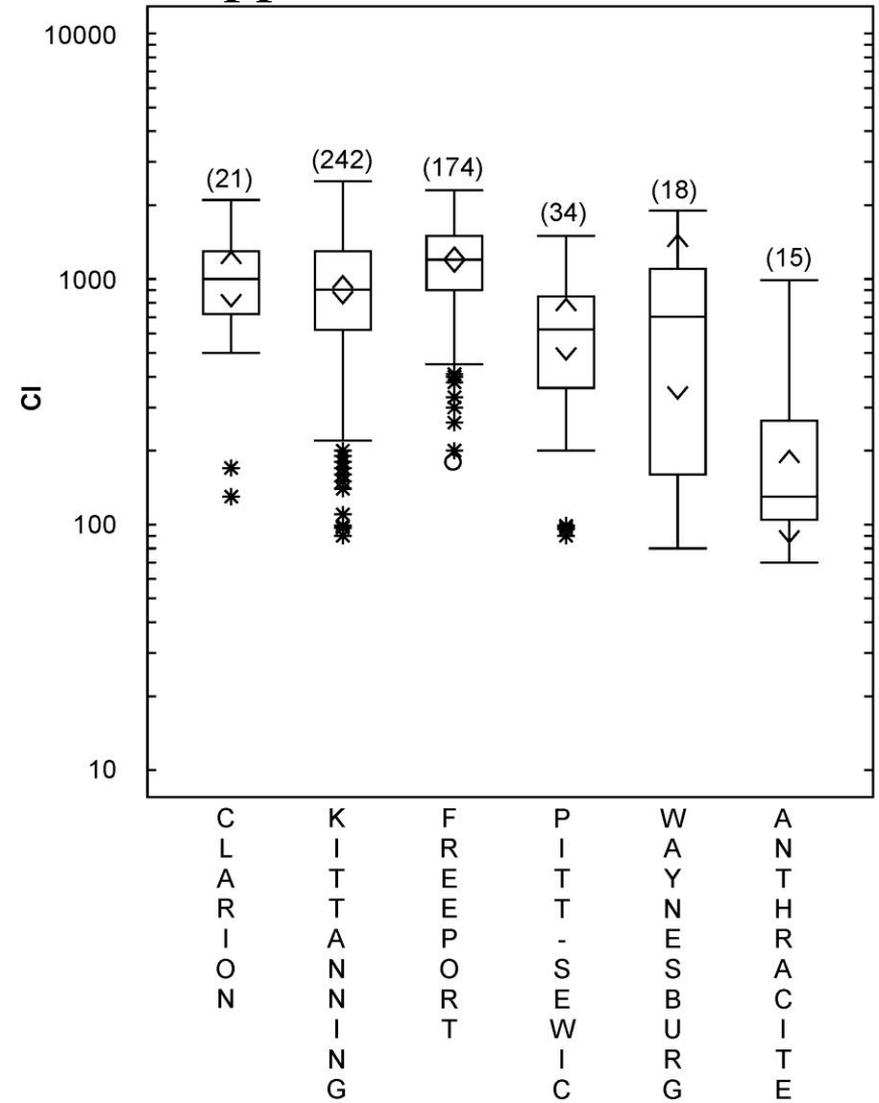


Coal Chemistry

Br, ppm

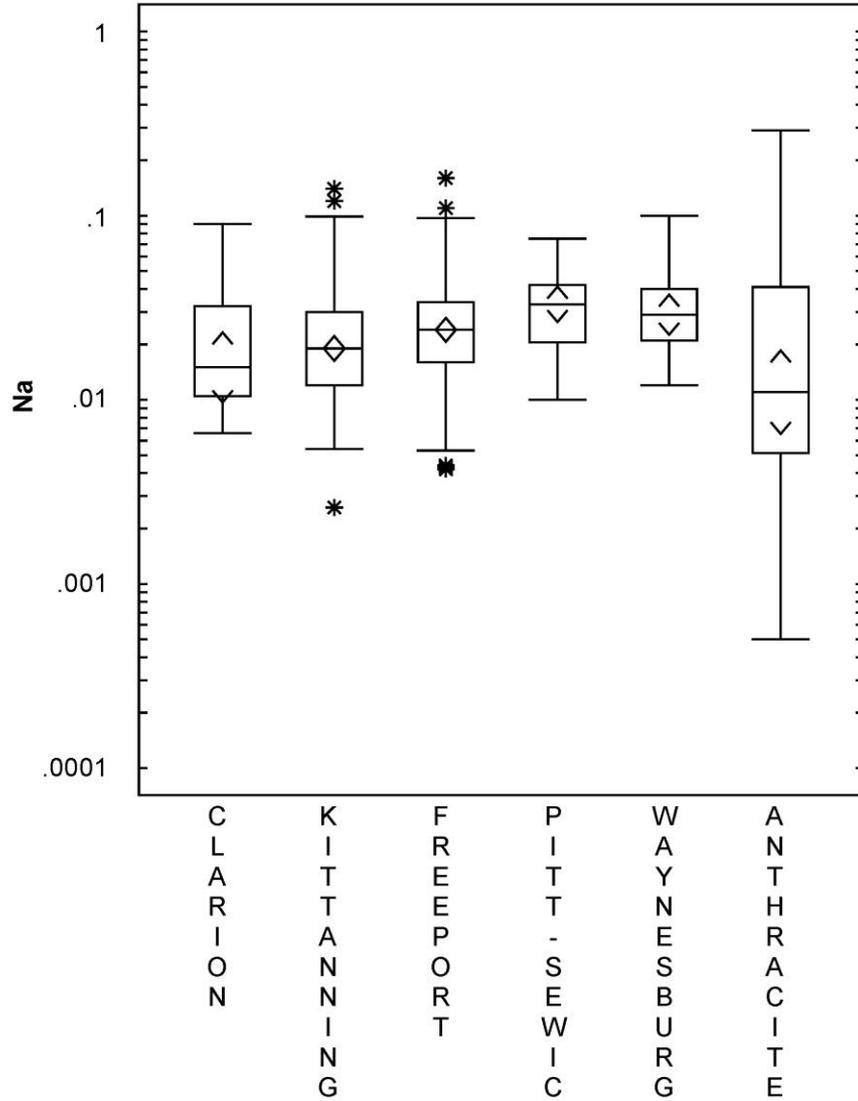


Cl, ppm

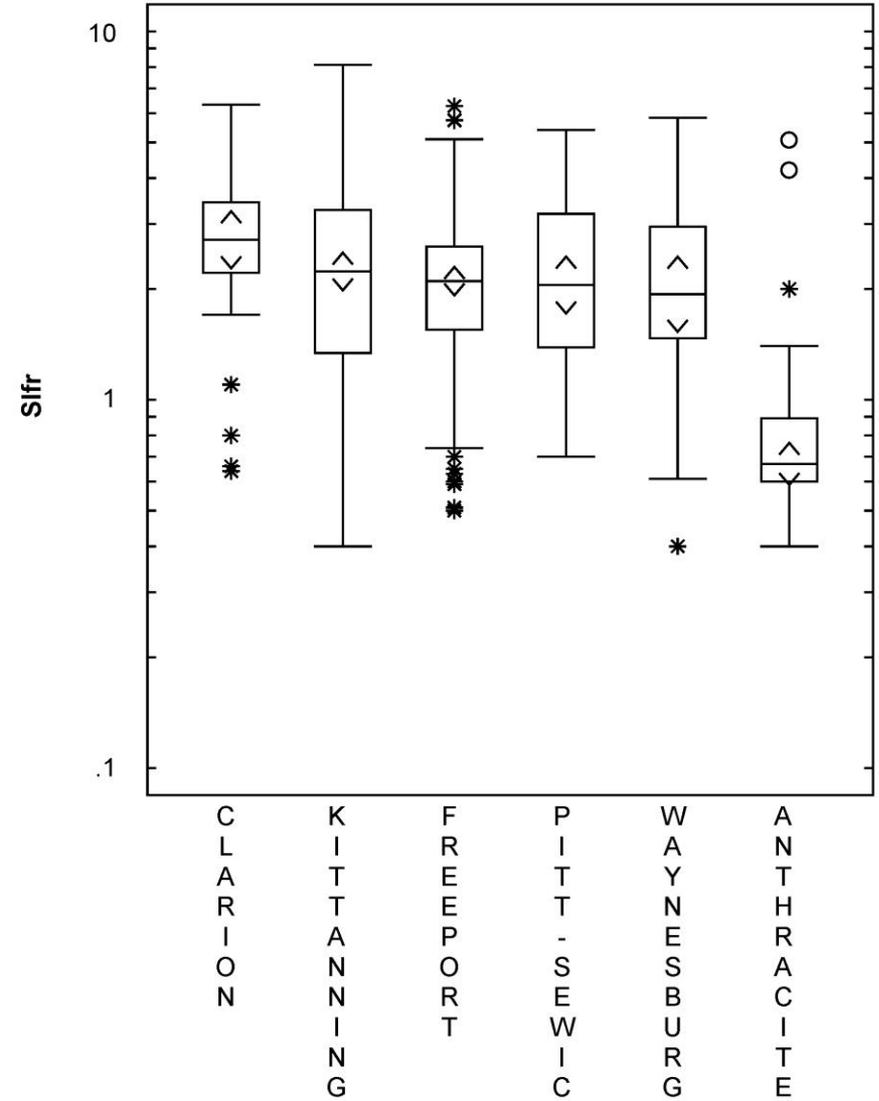


Coal Chemistry

Na, ppm

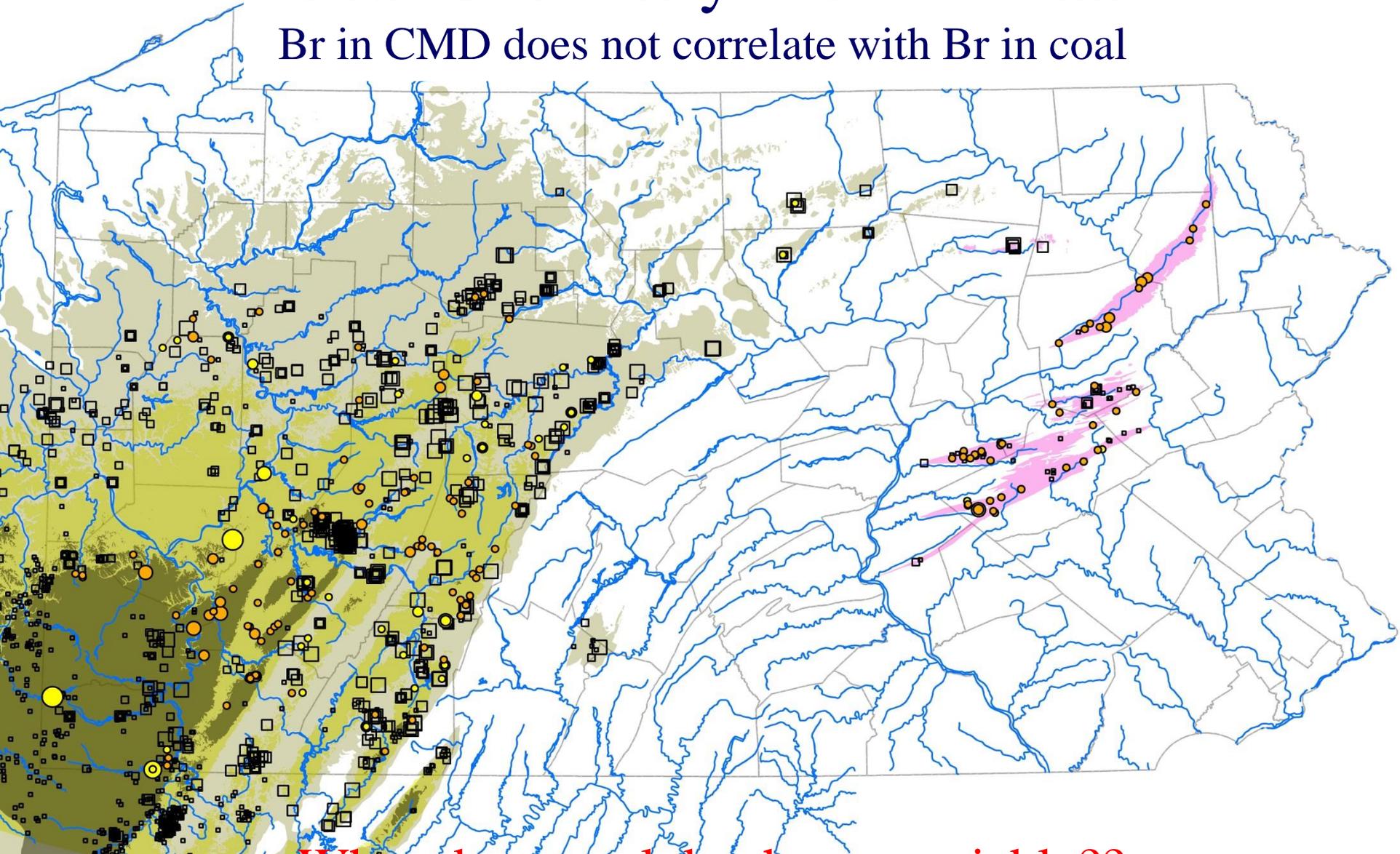


S, percent



Coal-Chemistry + CMD Data

Br in CMD does not correlate with Br in coal

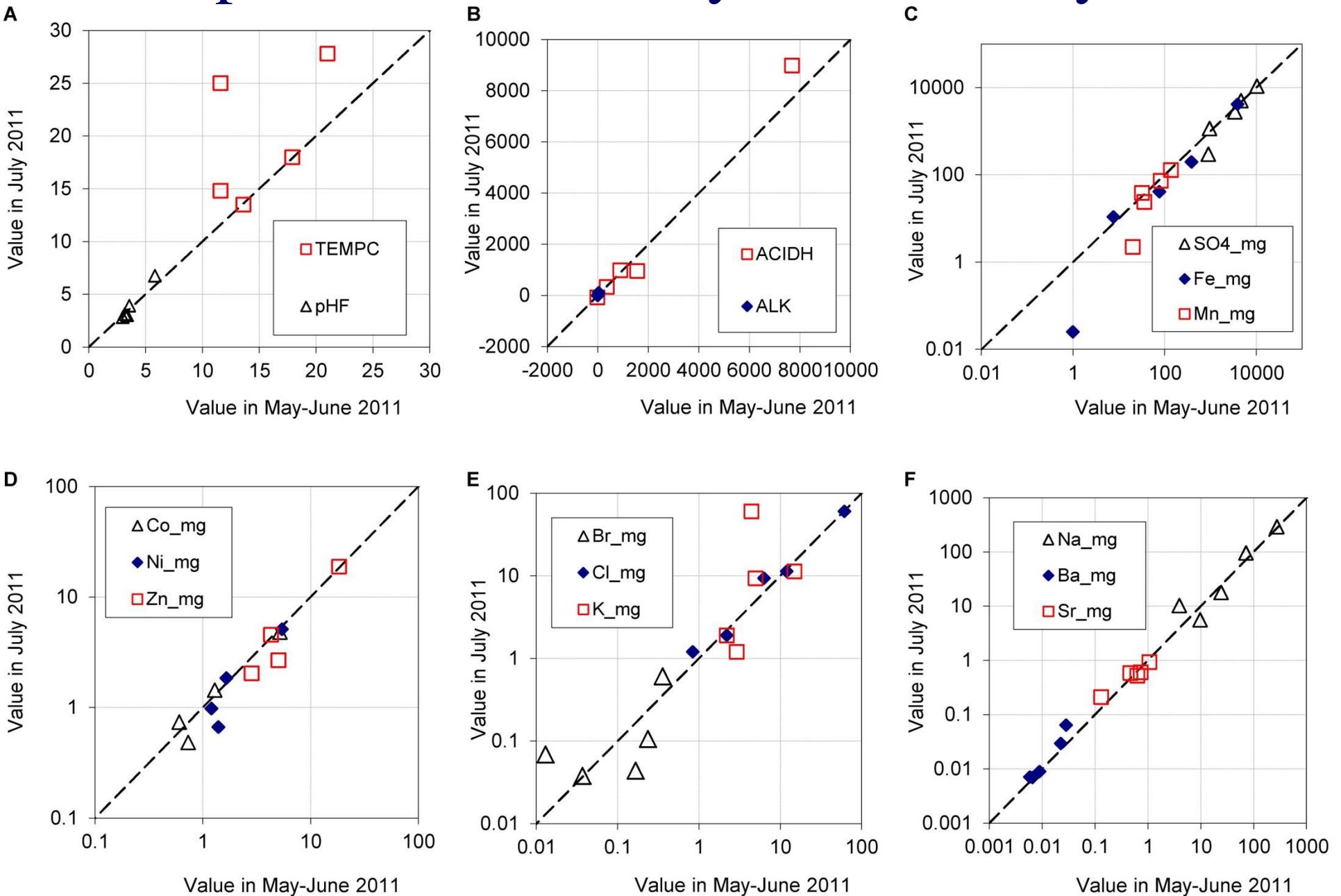


What about coal depth as a variable??

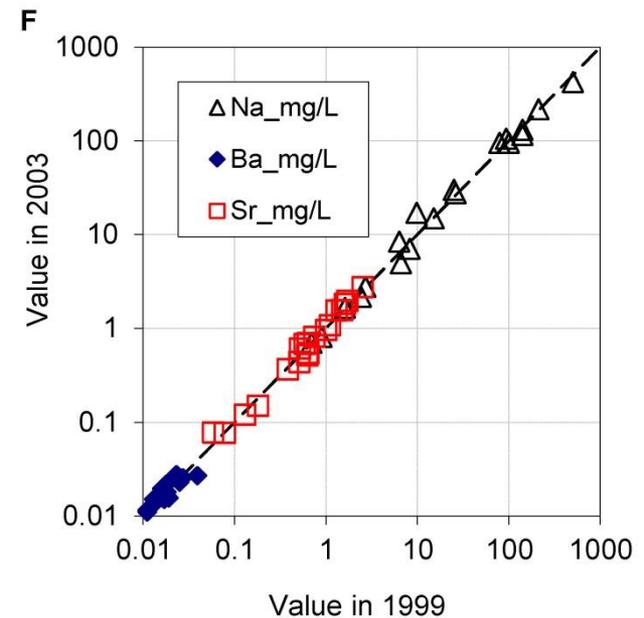
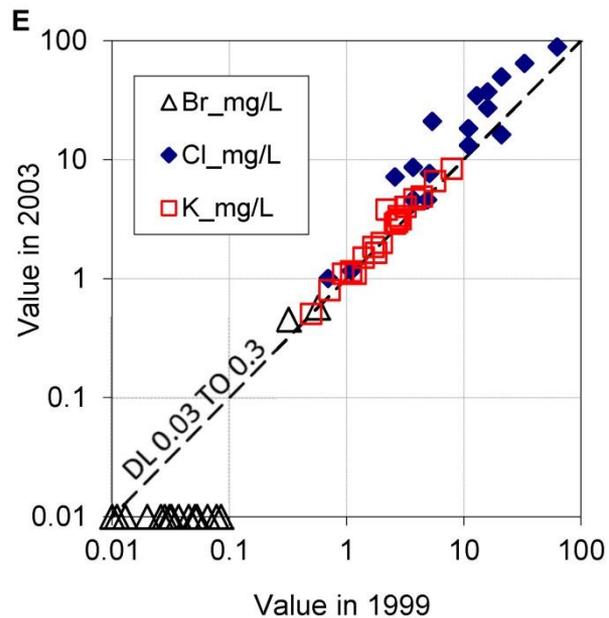
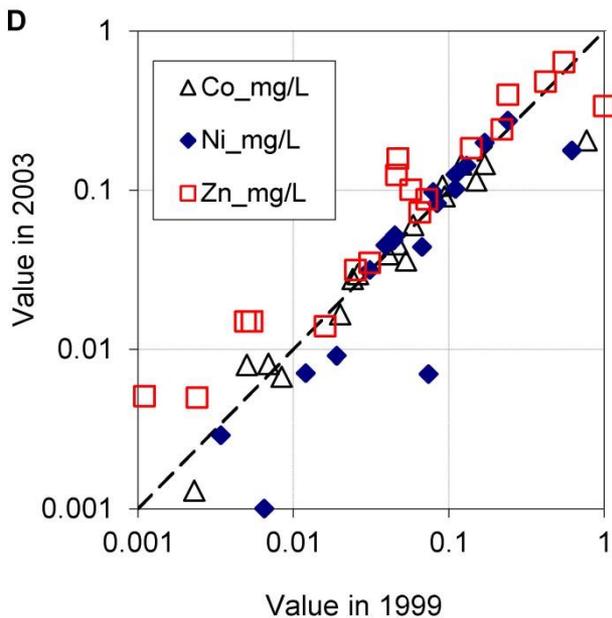
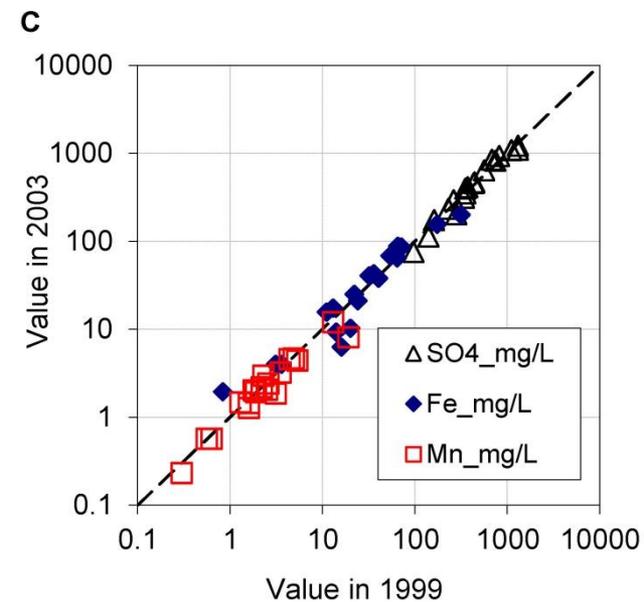
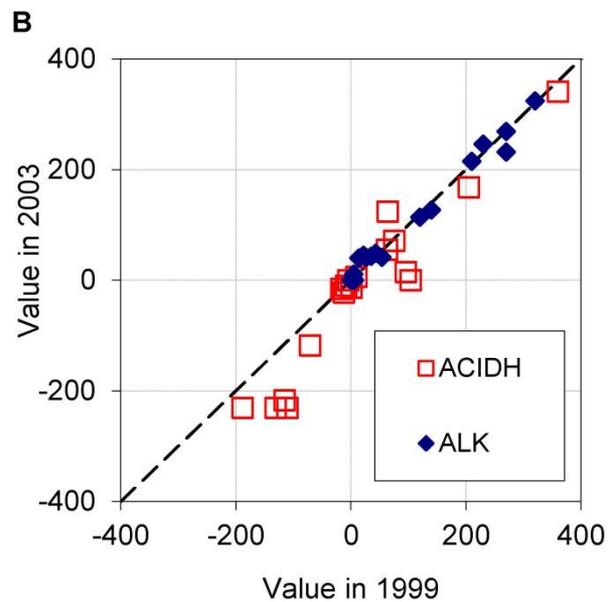
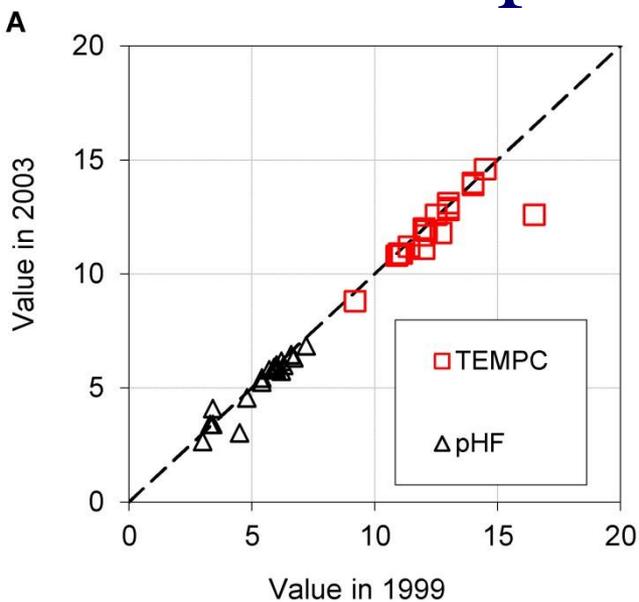
Temporal (?) Trends

- USGS-CMD: 1999, 2003, 2006, 2011.
- OSM-CMD: 2006.
- NURE Streams, springs, wells: 1977-78

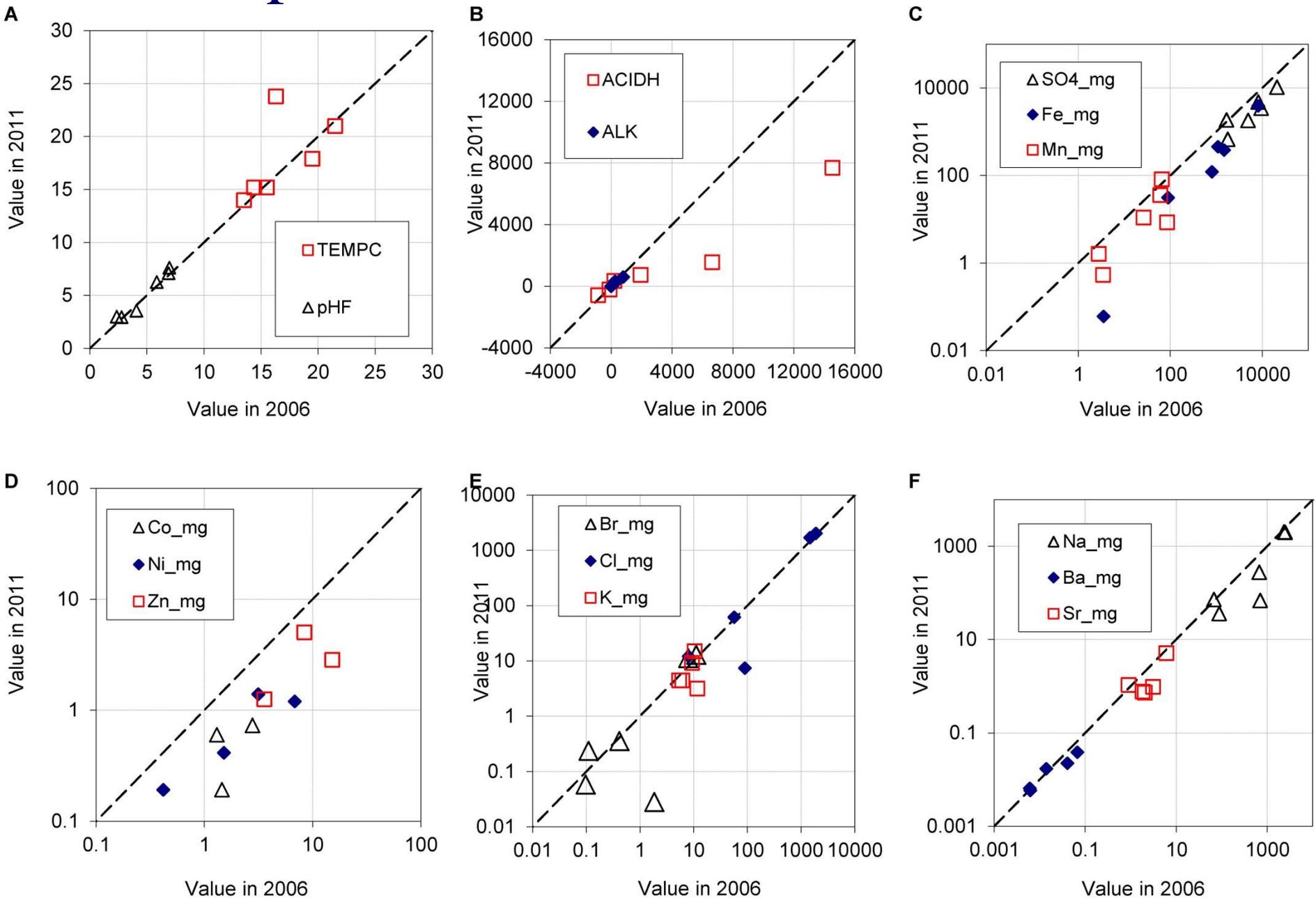
Comparison USGS May-June vs. July 2011



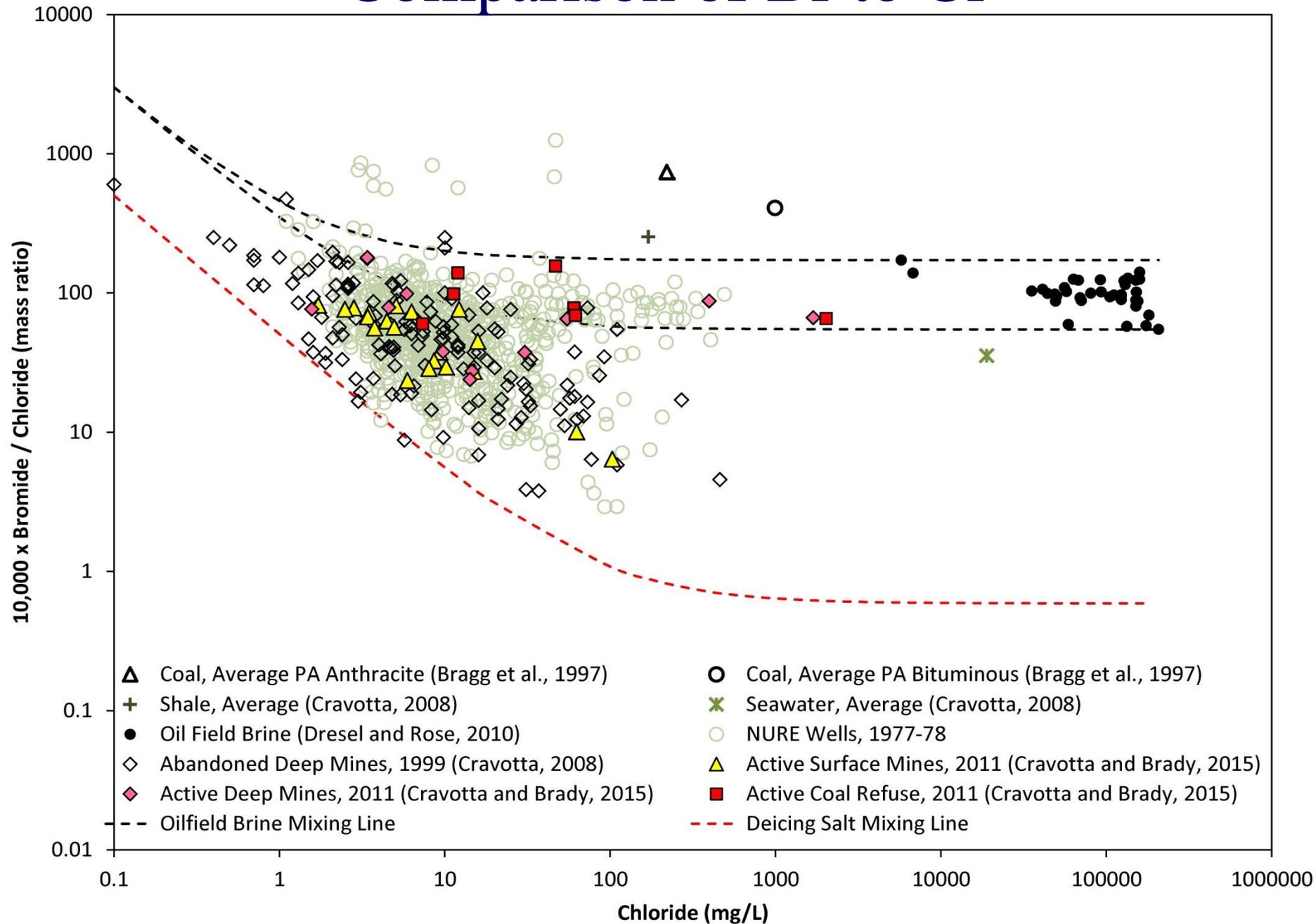
Comparison USGS 1999 vs. 2003



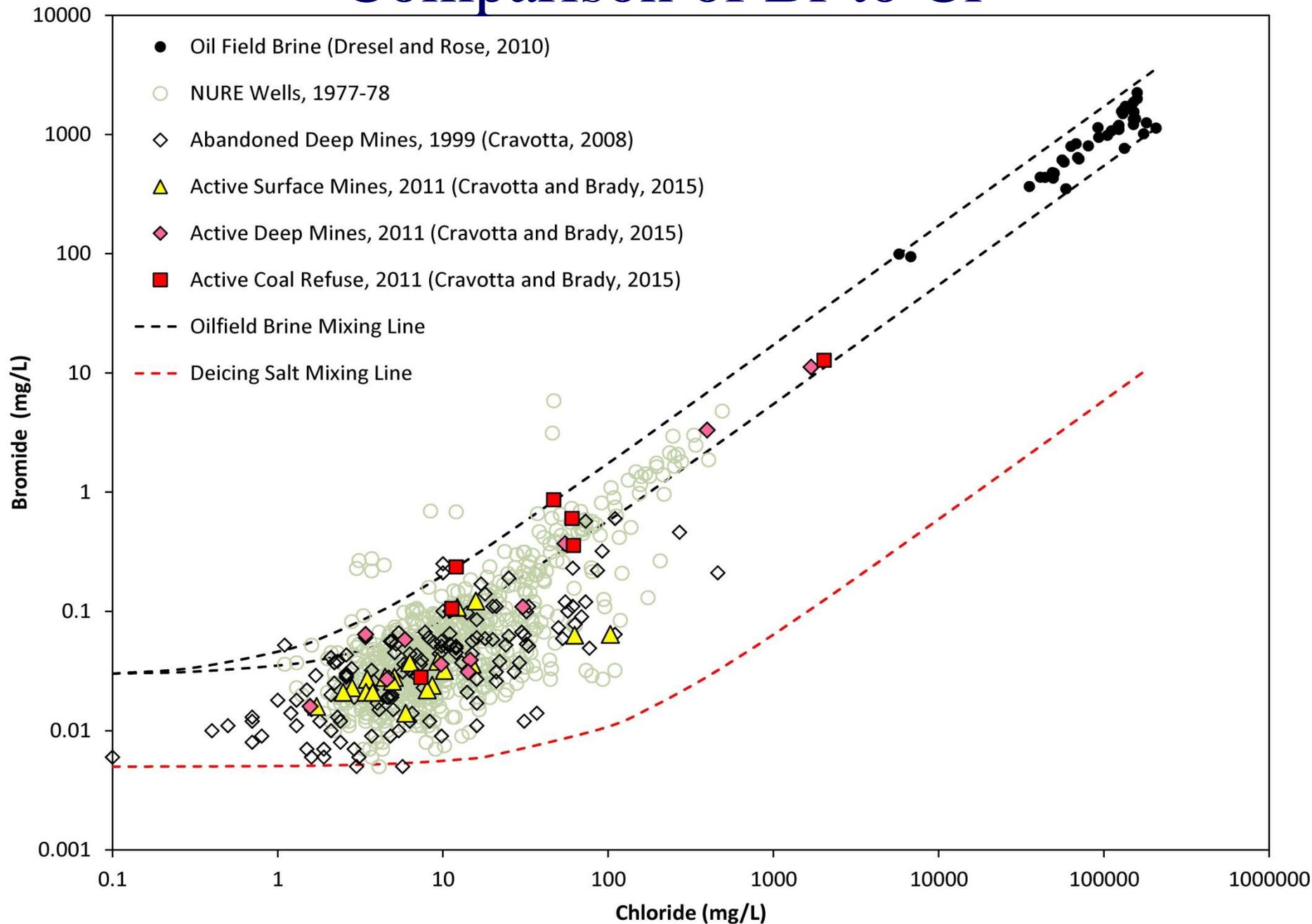
Comparison OSM 2006 vs. USGS 2011



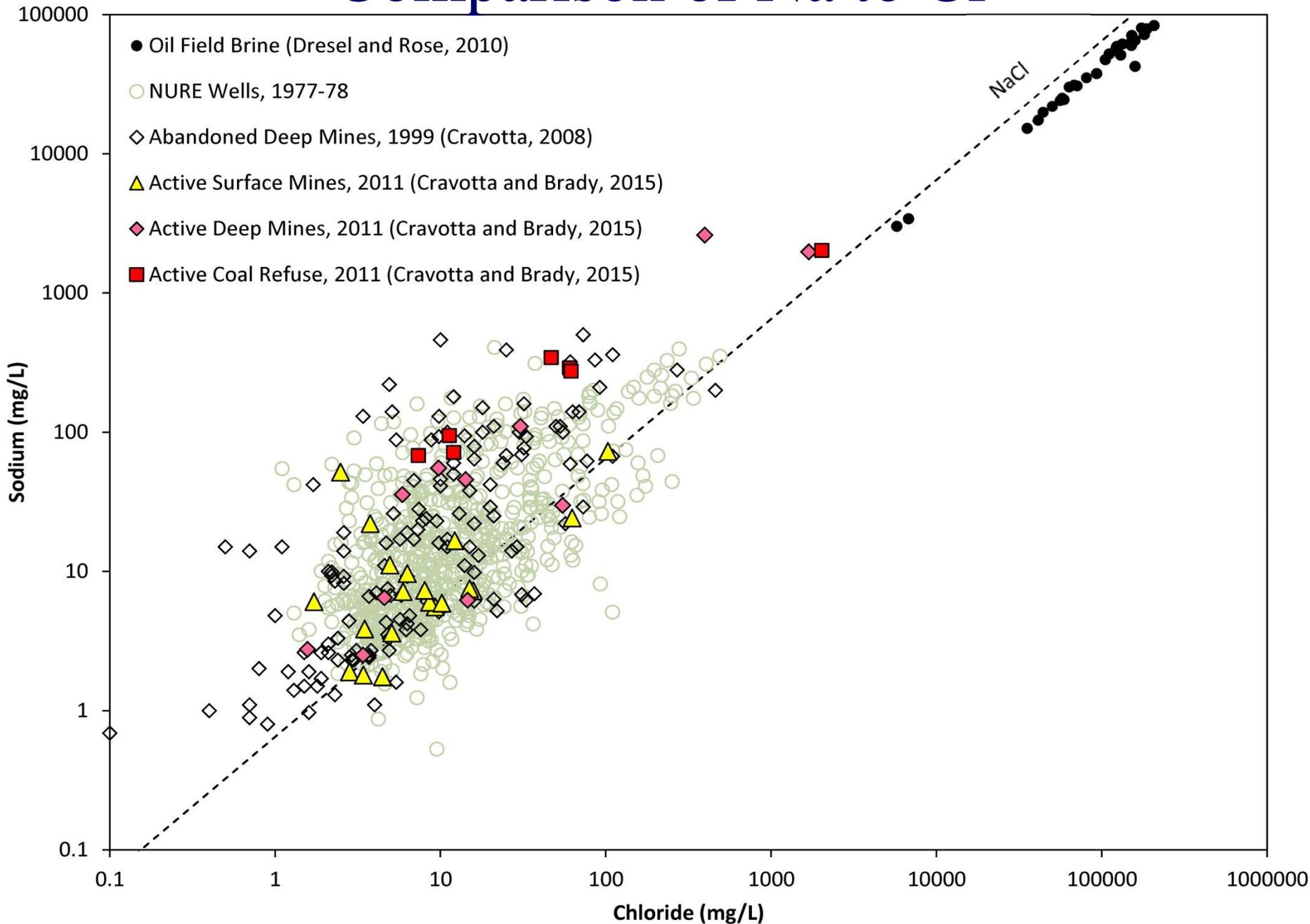
Comparison of Br to Cl



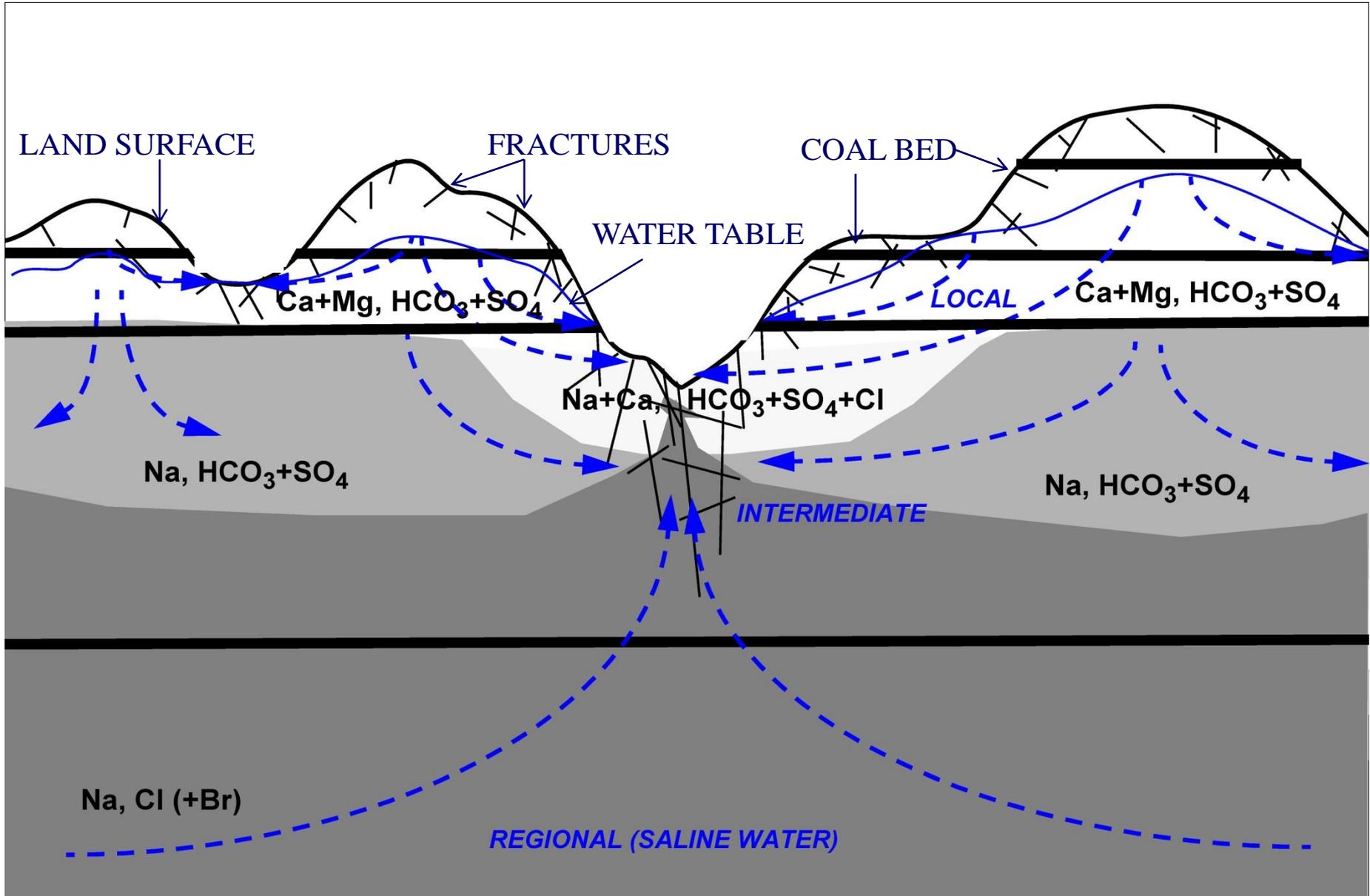
Comparison of Br to Cl



Comparison of Na to Cl



Conceptual Hydro-Geochemical Model



Brine Constituents in Coal-Mine Drainage

- Various halogen (Cl, Br, I), alkali earth (Na, K, Li), and alkaline earth (Sr, Ba) elements are present in CMD, wells, springs, and streams in western PA.
- Bromide (Br^-) concentrations in CMD ranged from <0.003 to 12.8 mg/L, with median 0.036 mg/L.
- Br/Cl ratios indicate deep mine waters with enriched Br^- compositions are consistent with residual brine (from deep bedrock) diluted with meteoric water.

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