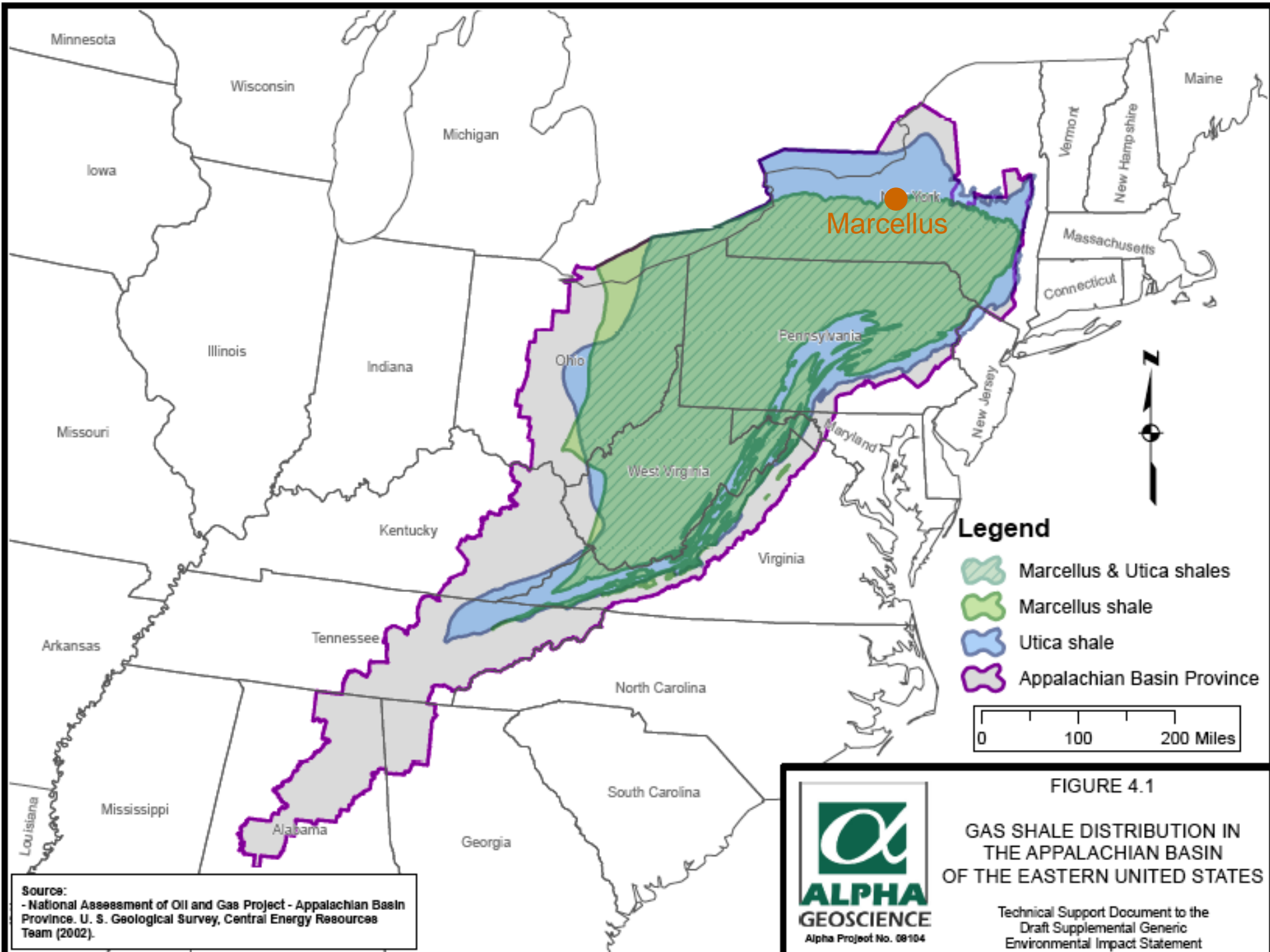






# A Protocol to Identify Flowback Water Contamination to Drinking Waters

Don Siegel (Syracuse University)

Melody Kight, Esq. (SUNY-ESF)



**Legend**

-  Marcellus & Utica shales
-  Marcellus shale
-  Utica shale
-  Appalachian Basin Province

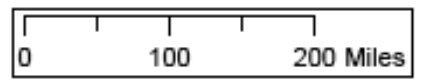


FIGURE 4.1

**GAS SHALE DISTRIBUTION IN THE APPALACHIAN BASIN OF THE EASTERN UNITED STATES**



Technical Support Document to the Draft Supplemental Generic Environmental Impact Statement

Source:  
 - National Assessment of Oil and Gas Project - Appalachian Basin Province. U. S. Geological Survey, Central Energy Resources Team (2002).

# The Fundamental Issue

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### Pennsylvania Families File Lawsuit Over Hydro Fracking Water Contamination

Published: September 17th, 2010



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The View from My Block

10/23/10

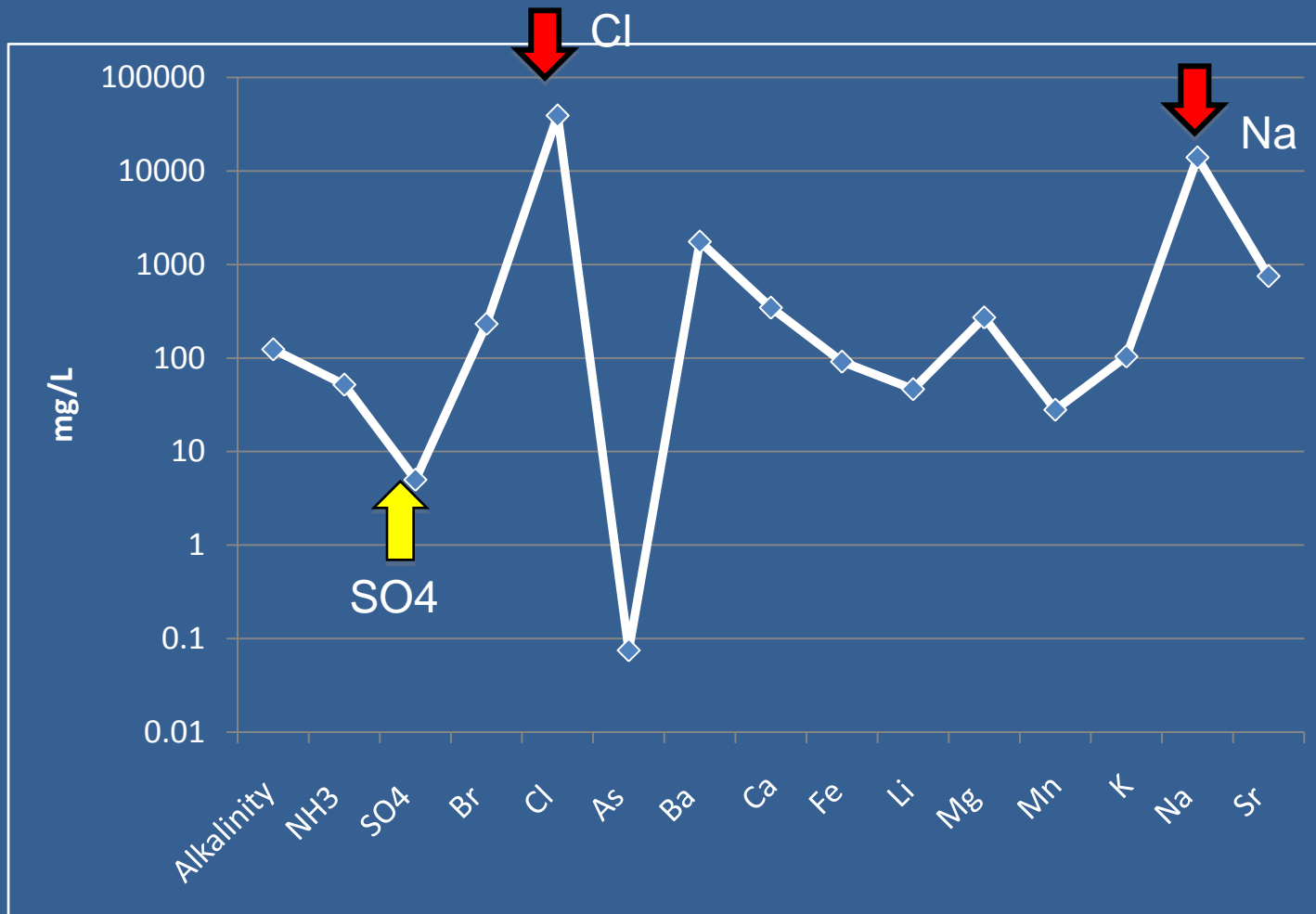
### The Fracking Lawsuits Begin

Thirteen families in Allentown, Pennsylvania, in the heart of the natural gas-rich Marcellus Shale, have filed one of the nation's first lawsuits linking hydraulic fracturing or "hydrofracking" for natural gas to tainted groundwater.

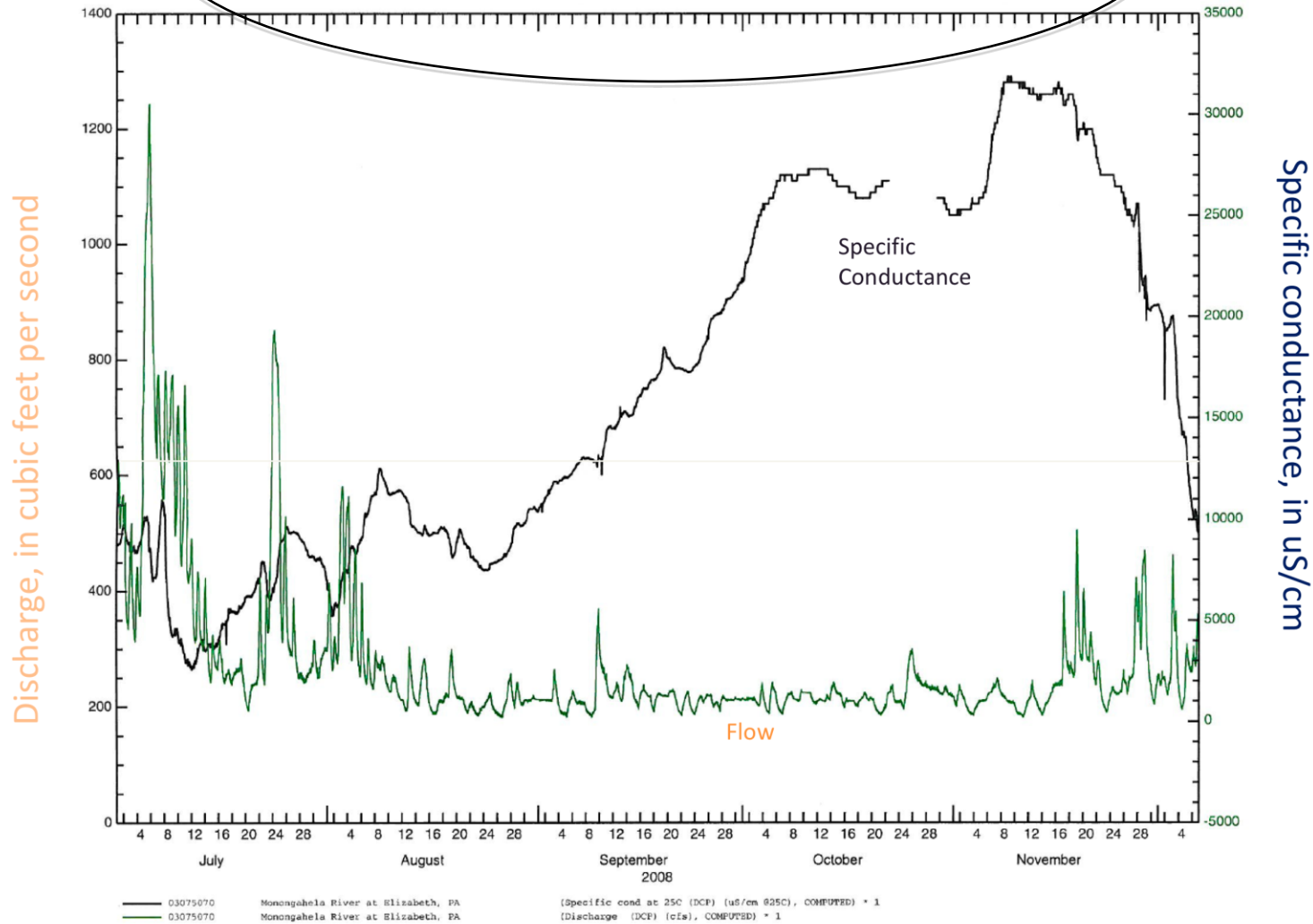
The lawsuit alleges that a faulty gas well drilled by Houston-based Southwestern Energy Co. contaminated local groundwater



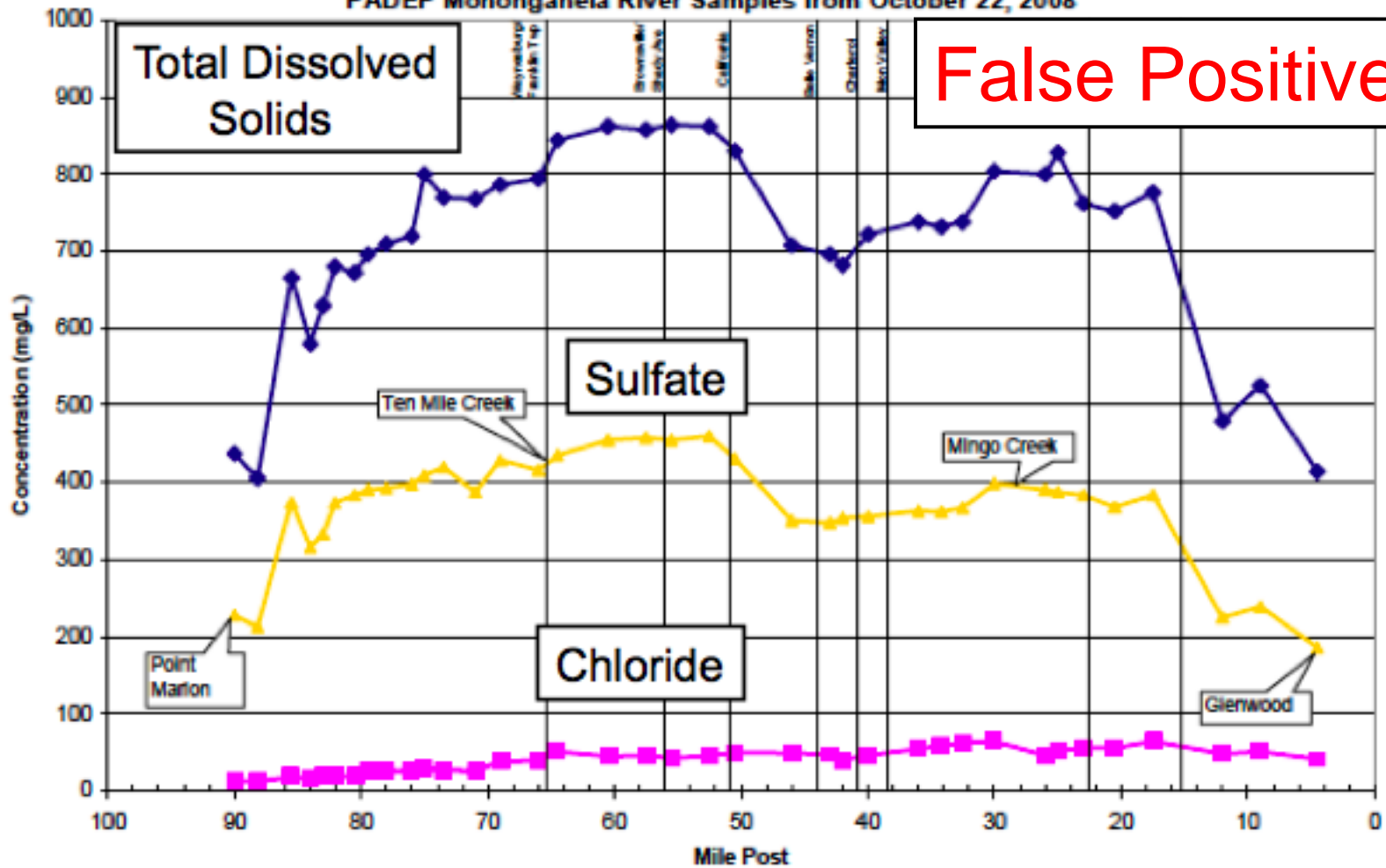
# Typical Marcellus Flowback

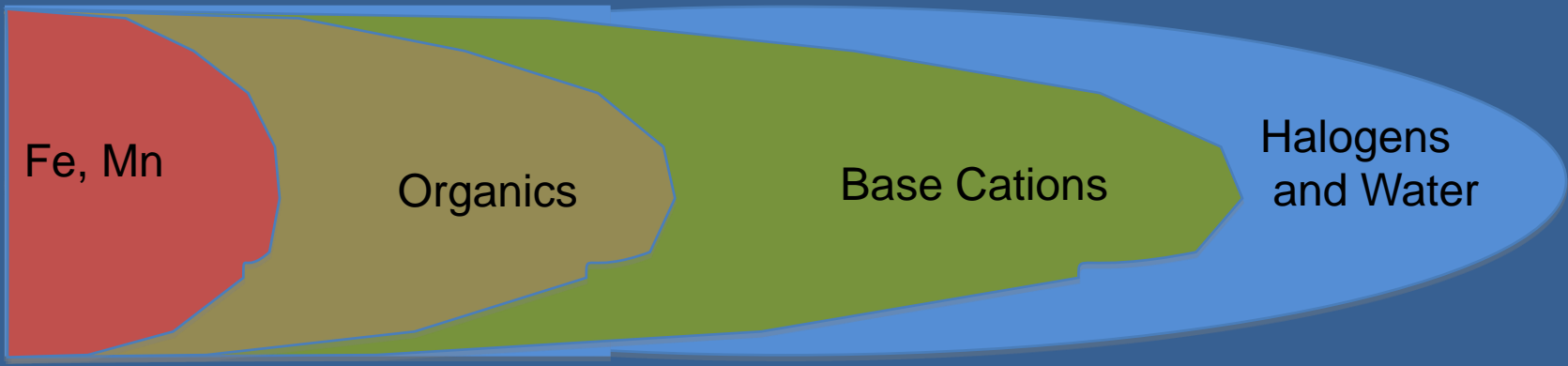
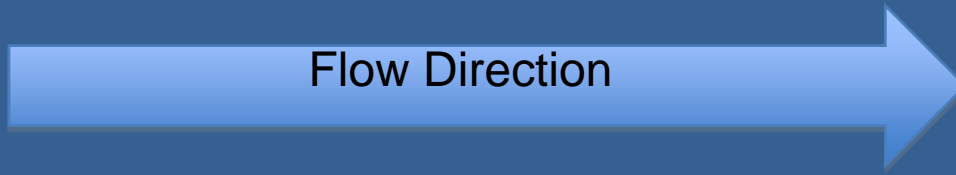


# DISPOSAL OF FRAC WATER BY MUNICIPAL WASTEWATER TREATMENT PLANTS AND DISCHARGE TO SURFACE WATER



PADEP Monongahela River Samples from October 22, 2008





Fe, Mn

Organics

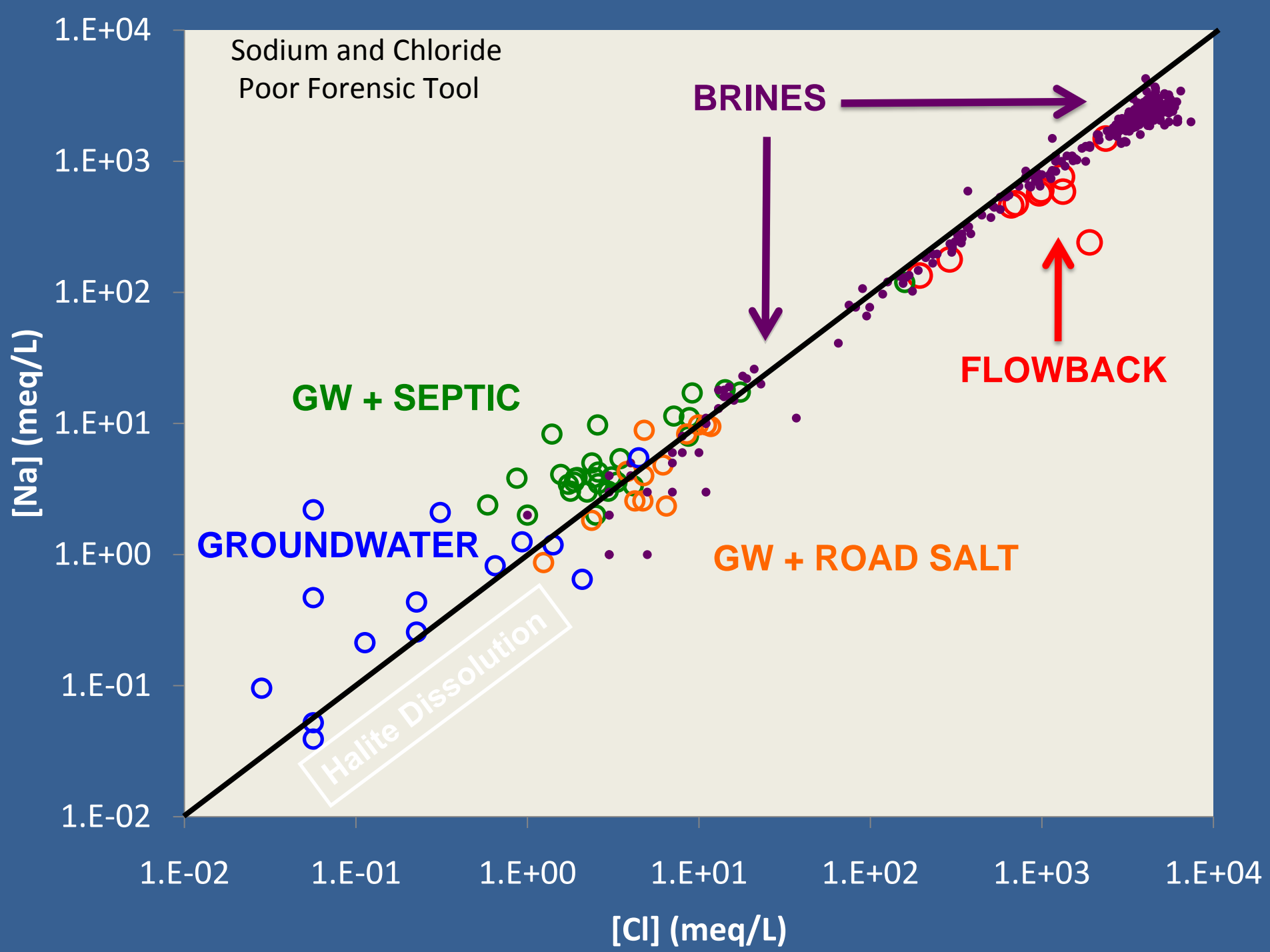
Base Cations

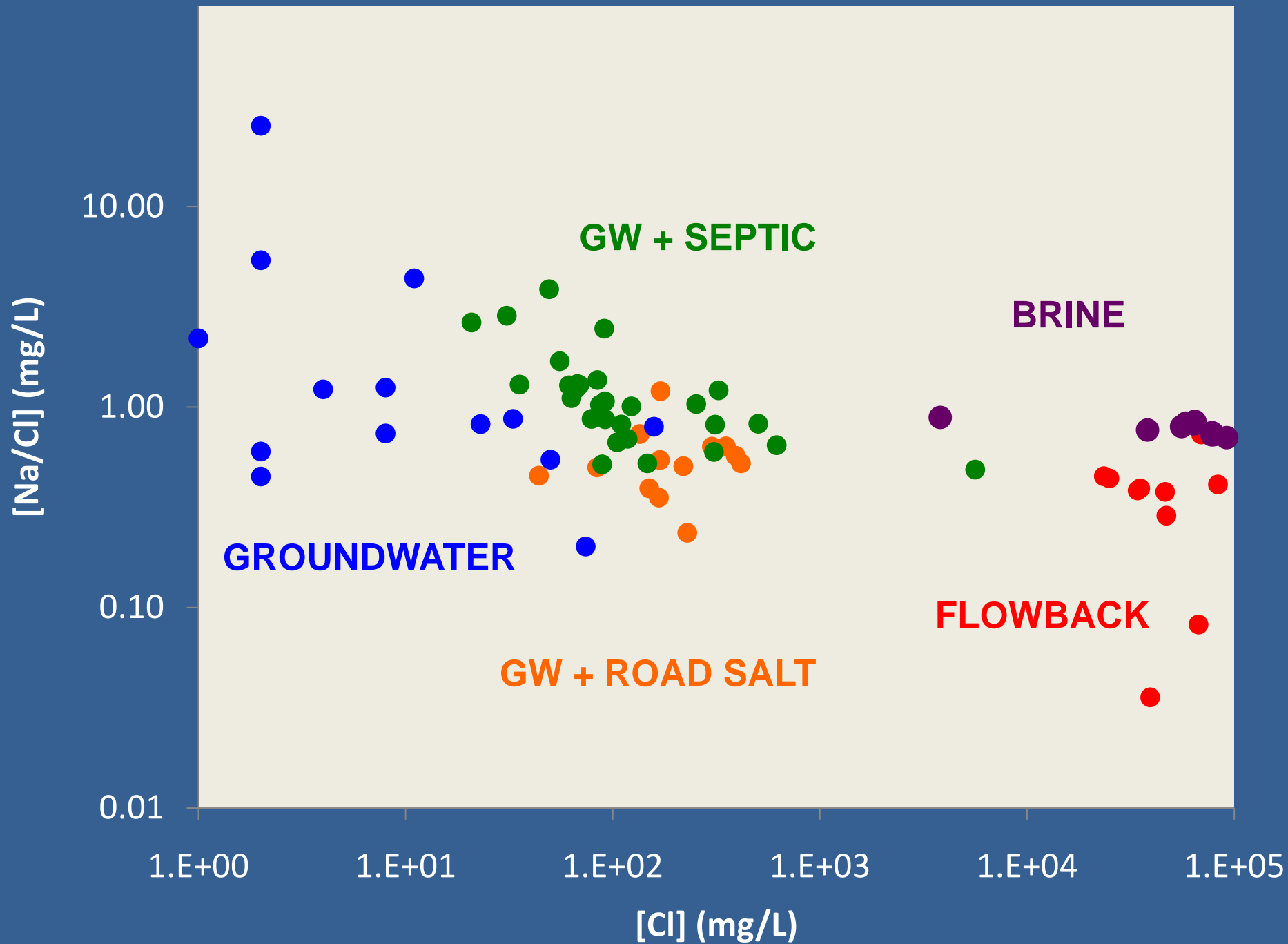
Halogens  
and Water

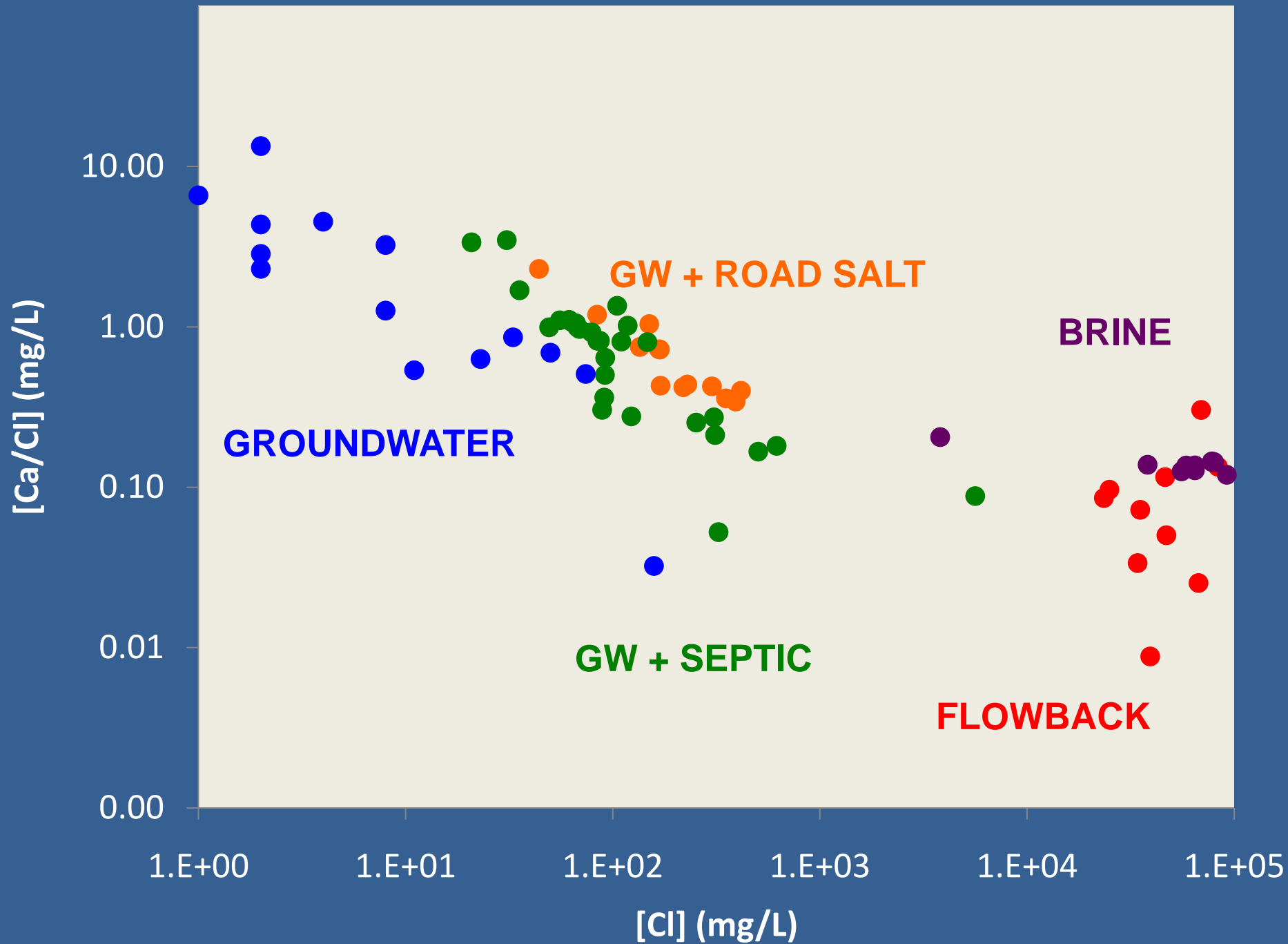
# Salinity: other sources

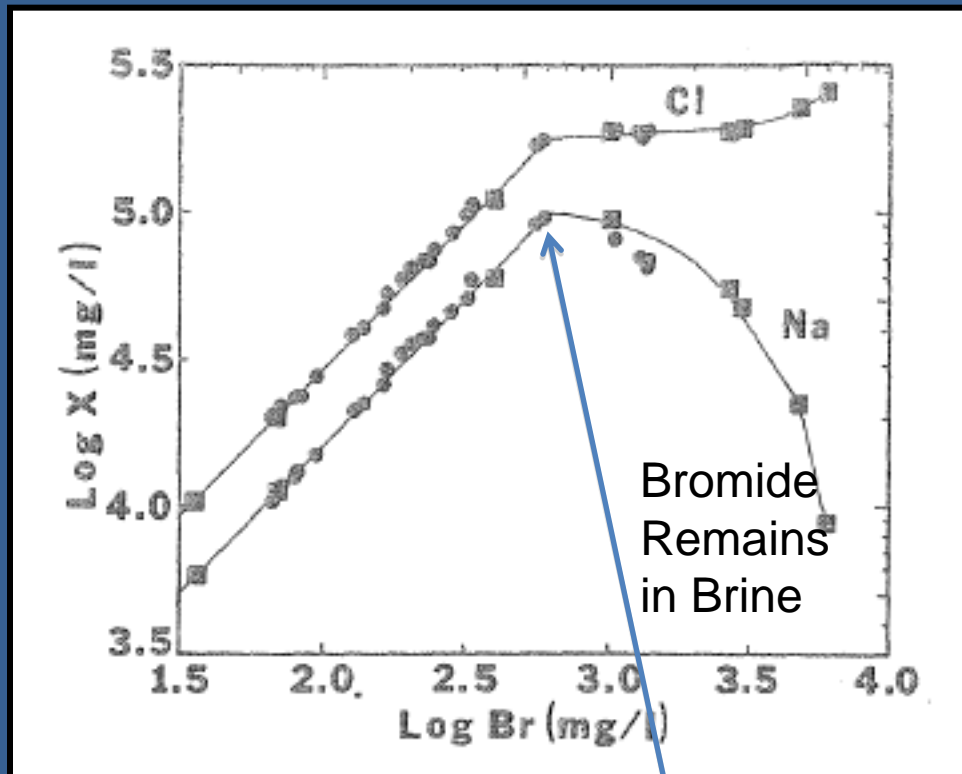
- Road salt
- Septic discharge
- Formation brine
- Water softeners





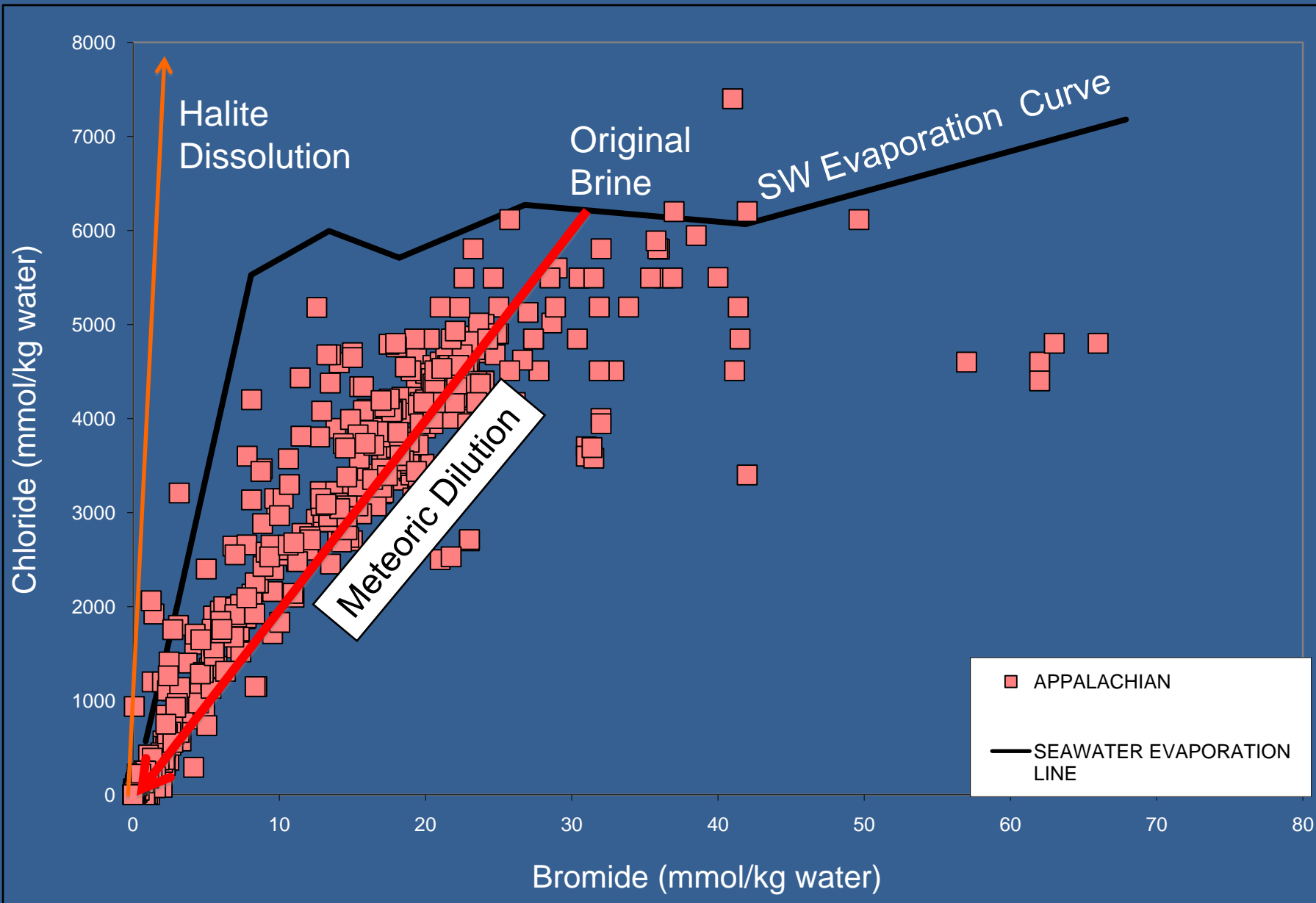


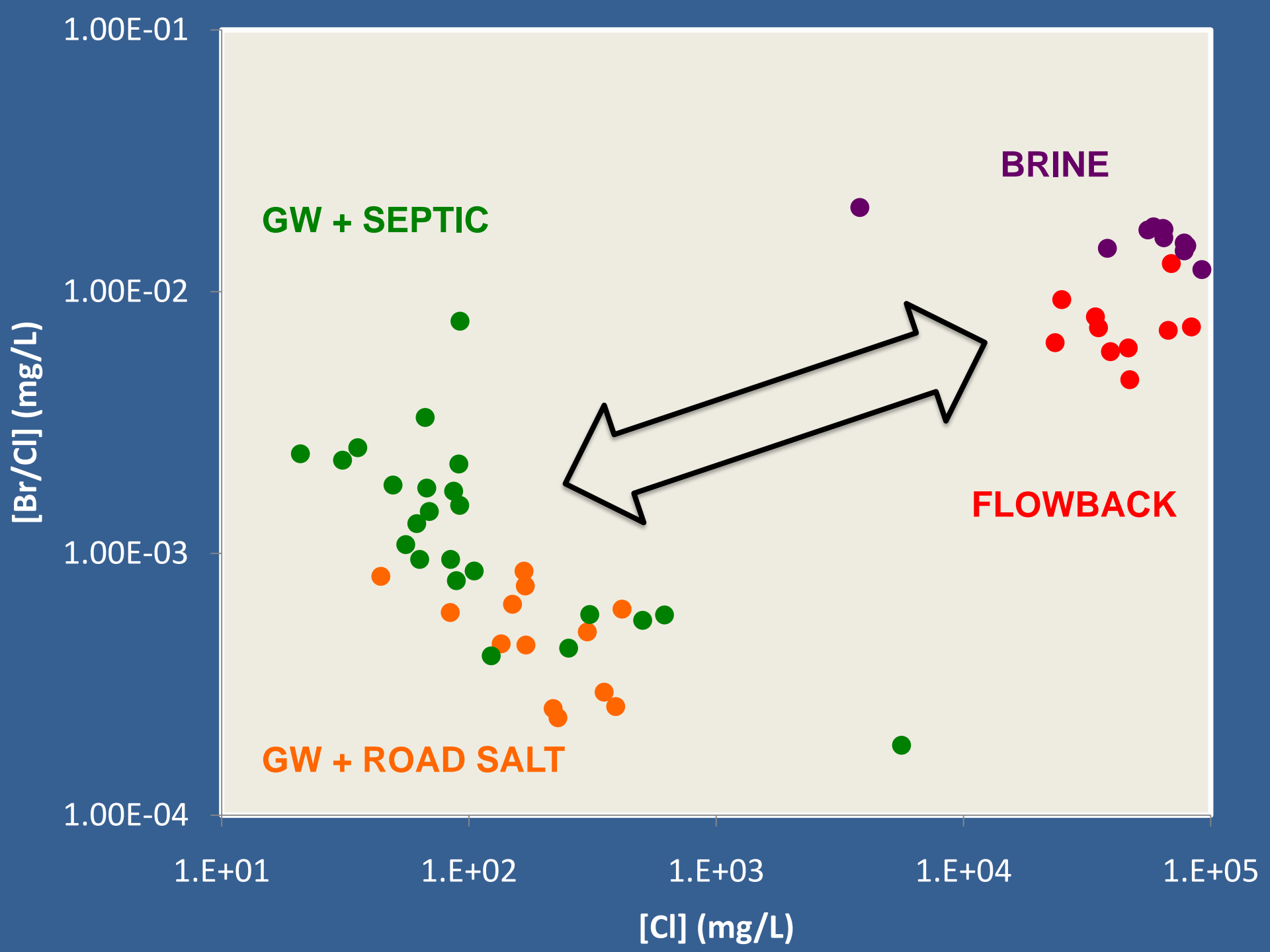


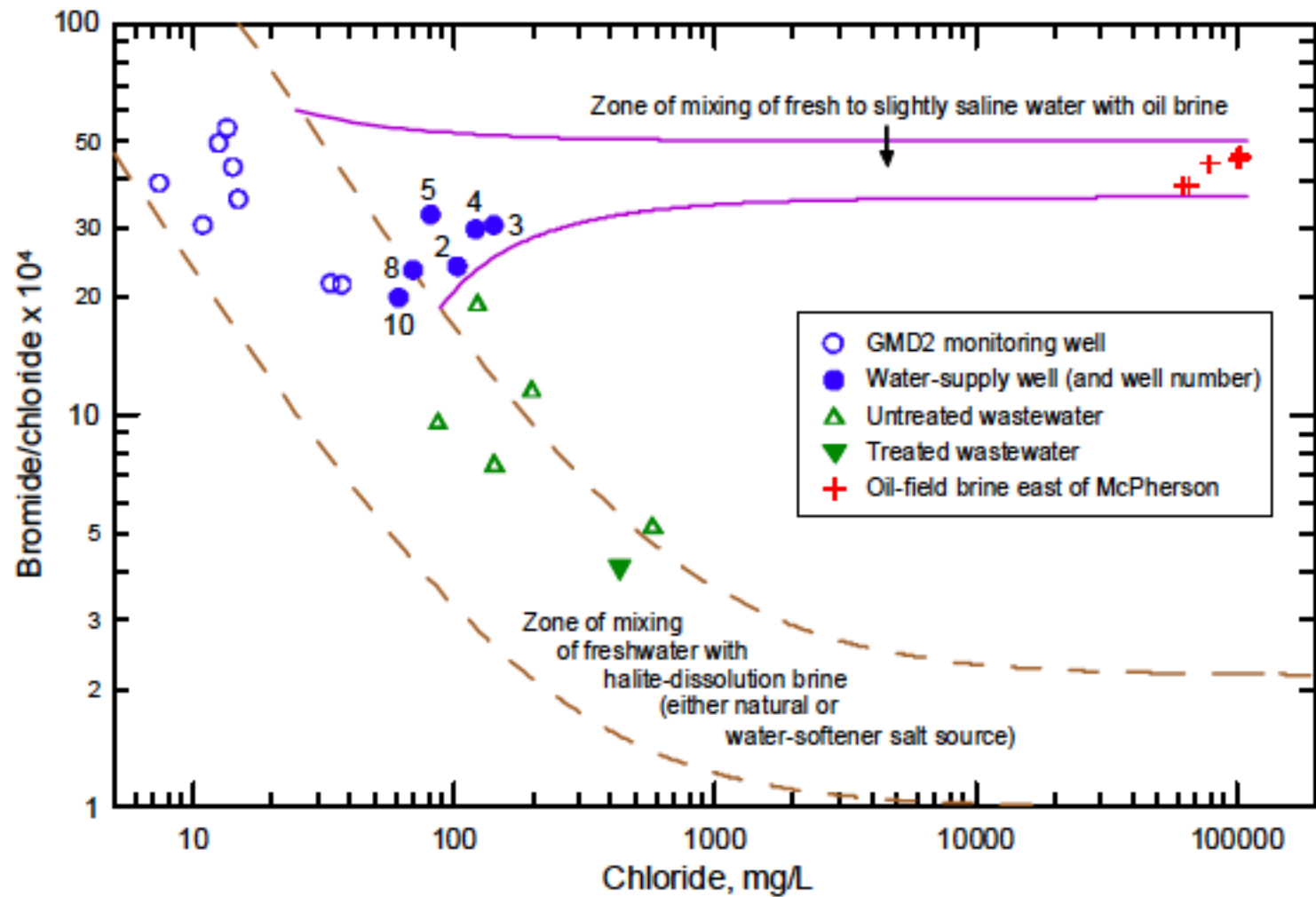


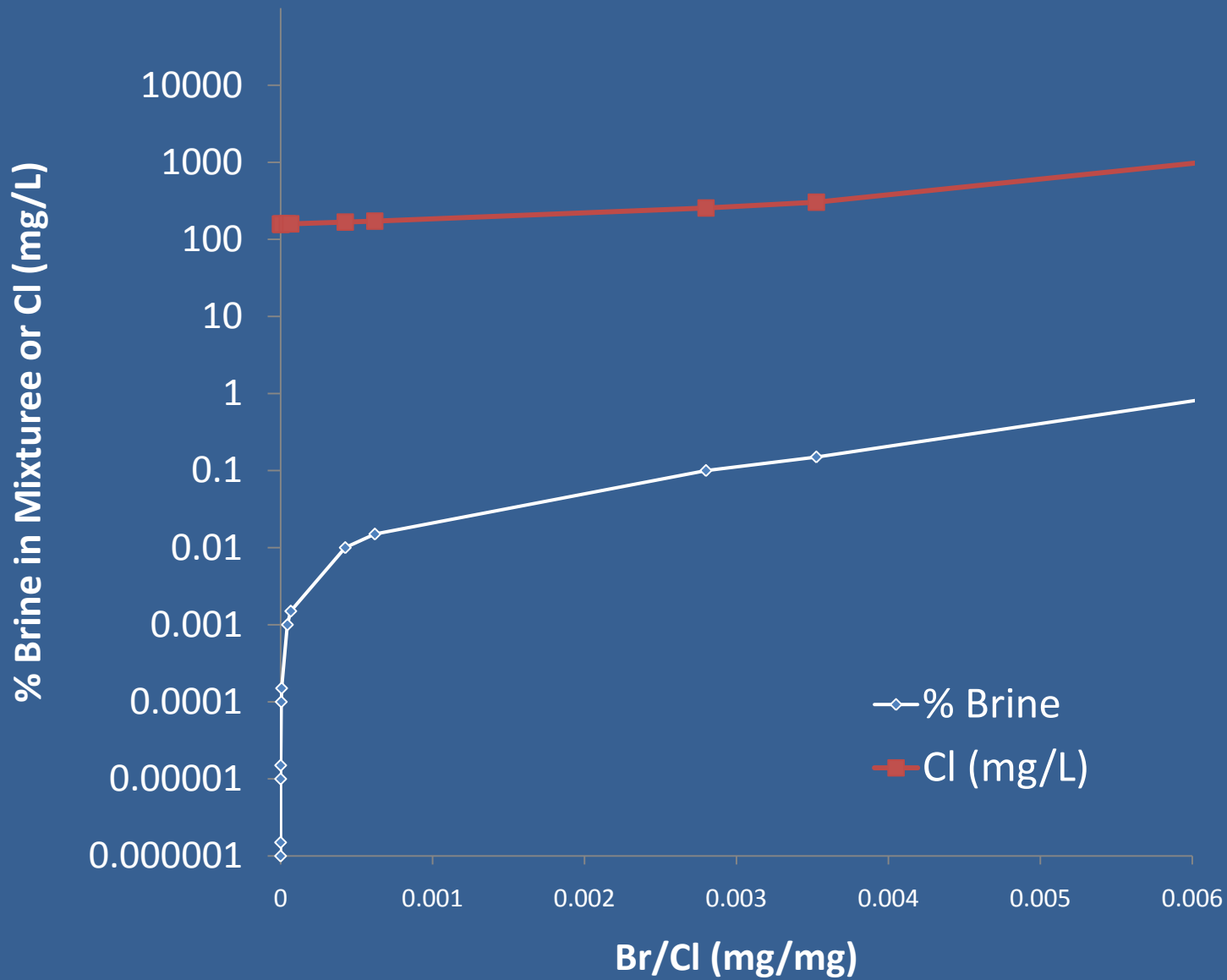
Halite Precipitation

Halite---very low Br/CL  
 Brines—higher Br/Cl

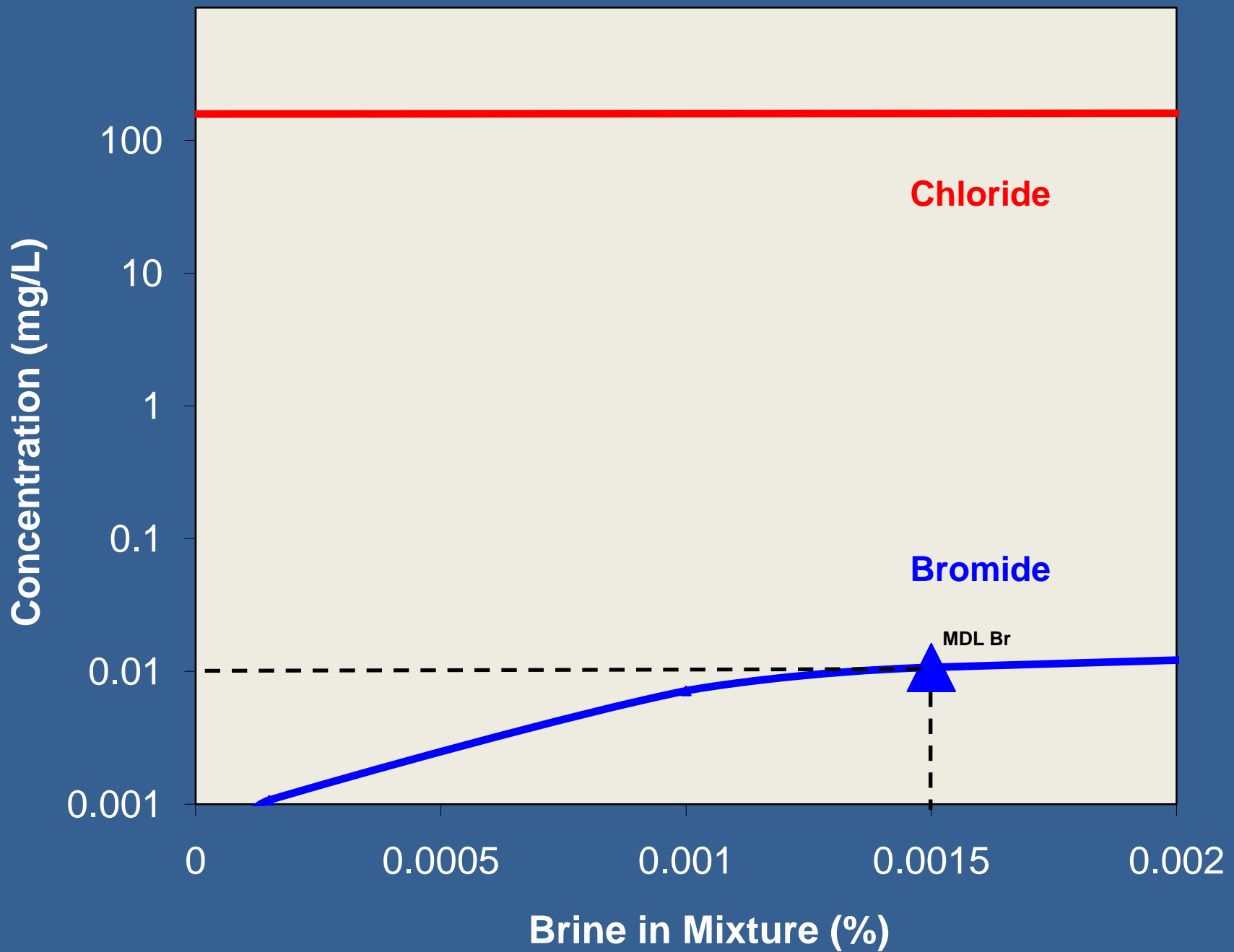












# Site Specific

- Flowback variability
- Background
- Simple and clean forensics
- Working on other halogens and isotopic and chemical characterization of fugitive gas

# **A Protocol to Characterize Flowback Fluid Contamination of Drinking Water**

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*The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.*

The Appalachian Basin of New York, Pennsylvania and West Virginia contains one of the largest gas plays in the world in the organic-rich Paleozoic-age Marcellus and Utica Shales. The hydrocarbon-extraction industry has begun drilling and hydrofracturing (fracking) to produce methane sorbed in the shale lamina. One concern relates to the potential for flowback fluids and methane from the producing formation to contaminated drinking waters because of improper grouting of vertical well casings and/or surface disposal.

Much of the concern over flowback fluids stems from elevated concentrations of trace elements, radium-226, and trace organic substances. But, these constituents geochemically react and naturally attenuate. For example, reactive iron and manganese in the anoxic flowback fluid precipitate upon contact with oxygen. Also, barium in solution precipitates upon contact with dissolved sulfate. Small concentrations of dissolved organic carbon in flowback fluid, including possible aromatic hydrocarbons and glycols, biodegrade once discharged to fresh waters -- analogous to natural attenuation associated with UST spills with orders of magnitude greater concentrations of dissolved organic substances. Finally, rock formations can provide many trace substances common to that found in flowback fluid. For example, the Marcellus Shale in Appalachia contains barium and strontium mineralization that seals fractures (Siegel et al., 1987; Chamberlain et al., 1986). In short, elevated concentrations of trace metals and many dissolved organic compounds do not provide the means to unequivocally identify the extent of flowback fluid contamination of drinking waters.

Formation waters mixing with shale bed methane flowback fluids have high salinities associated with formation brines. But, in the Northeastern United States, road salt and septic discharge of salts associated with water softeners also contribute salinity to surface waters (Mullaney et al., 2009). Seawater intrusion can occur near coastal areas. Also, the surface disposal of acid mine drainage from coal mines can elevate the salinity of drinking water by the addition of calcium and sulfate, among other solutes (Tetra Tech, 2009).

Fortunately, the dissolved halogen elements associated with salinity: chloride, bromide, and fluoride, and iodide, can provide the means to unequivocally identify where flowback fluids or oilfield brines have contaminated drinking waters. Mineral-water reactions minimally affect these solutes, the ratios of which can distinguish among salinity sources (e.g. Panno et al., 2006;

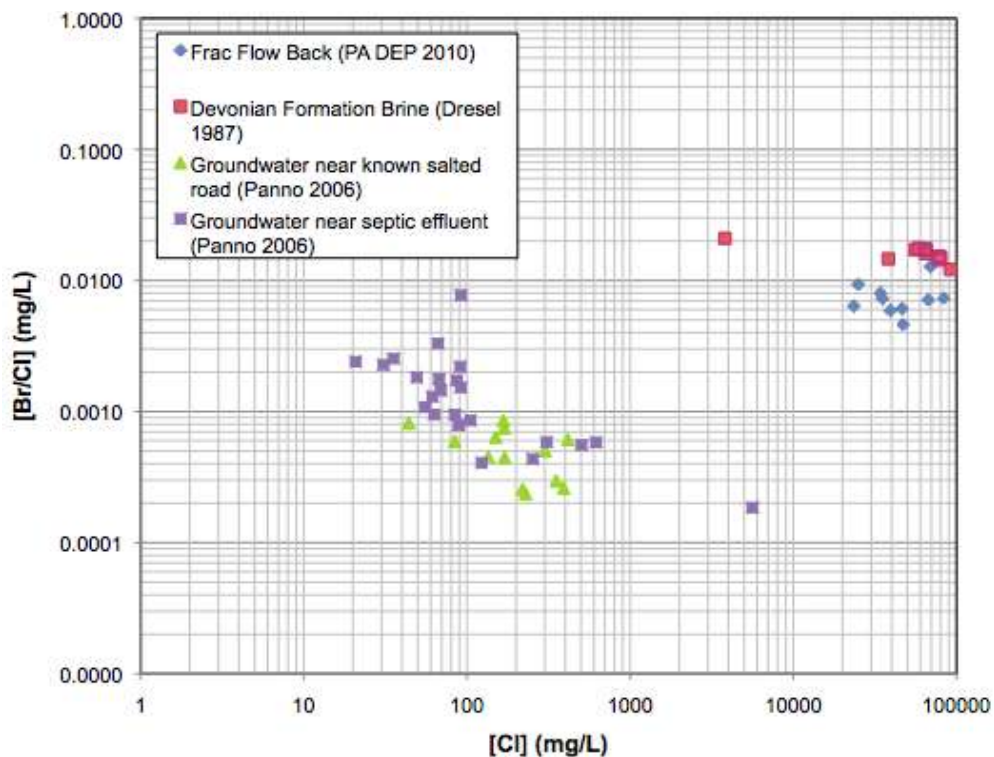


Figure 2. Bivariate plot of Br/Cl versus Cl concentrations for Marcellus frac fluids, Pennsylvanian Devonian sedimentary basin brines, and representative road salt contamination and septic effluent. Note the clear separation between the flowback fluid, brines and other sources of contamination (Kight and Siegel, 2011)

Townsend, and Whittemore, 2005). Therefore, any contaminants associated with flowback water that do not naturally attenuate must move with flowback fluid halogen salinity. We have heuristically investigated using halogen and major solute ratios and chemical mixing models to develop a protocol to characterize potential flowback water contamination of drinking waters in the Appalachian Basin. Our preliminary results (Kight and Siegel, 2011) show that plotting Br/Cl ratio versus Cl concentrations distinguishes the presence of flowback fluid contamination from other salinity sources (Figure 2).

The Br/Cl ratio of Marcellus flowback fluids also show that Appalachian Basin brine probably provides the source for flowback salinity, not dissolving rock salt as previously proposed (Blanch et al., 2009). The Br/Cl ratio of flowback fluid would have to be at least an order of magnitude smaller to reflect halite dissolution because bromide is excluded from halite when it precipitates. Either hydrofracking-induced vertical fractures beyond the contacts of the formation with more permeable and brine-filled formations, or the Marcellus contains disseminated brine, yet unrecognized.

Our geochemical mixing models enable us to identify extraordinarily small amounts of flowback water in mixtures, even when other salinity sources previously contaminated drinking waters.

Our protocol using halogen concentrations coupled to mixing models needs to be applied on a site-by-site basis. That is, the background chemical composition of potential drinking-water receptors must be obtained as well as representative analyses of flowback waters produced near them. Every shale gas methane basin has its own geochemical halogen fingerprint. However, once we have identified flowback from halogen ratios, the presence of solutes and substances that could potentially compromise drinking waters can be addressed without the fear of false positives.

We are continuing our work by addressing additional combinations of halogens and major solutes and characterizing the most plausible source for methane in drinking waters by using a combination of mixing models, coupled to methane isotopes and trace gases.

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