

SOURCE IDENTIFICATION OF PHOSPHORUS CONTAMINATION PATHWAYS IN SURFACE WATER AND GROUNDWATER OF WESTERN WISCONSIN; RECONGNIZING A PHOSPHORUS PROBLEM

Melissa Hackenmueller, Carly Mueller, Adam Wiest, J. Brian Mahoney, Sarah Vitale, and Laurel Mc Ellistrem
 Departments of Geology and Material Science and Engineering - University of Wisconsin - Eau Claire

The Power of
AND

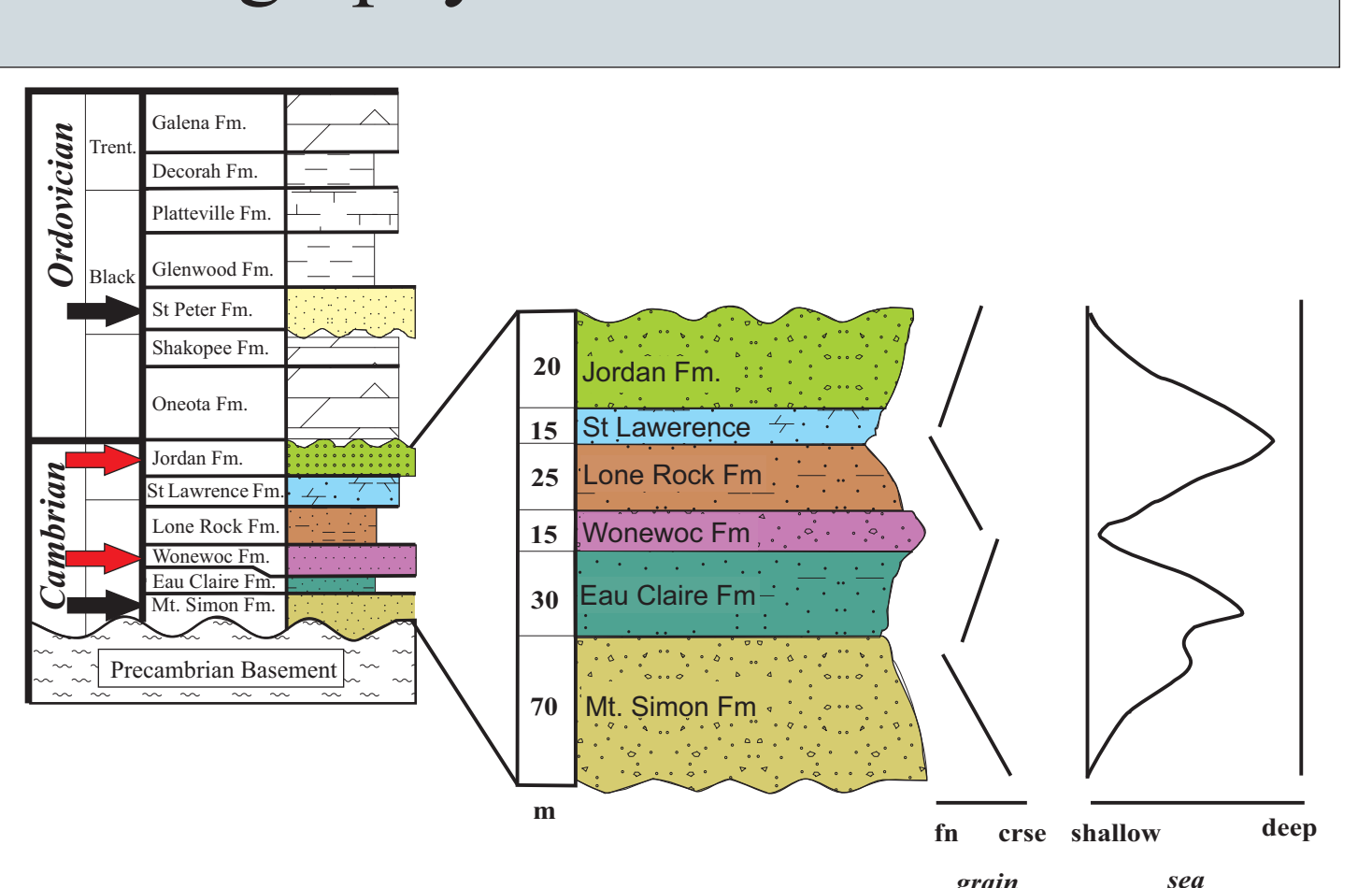
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Abstract

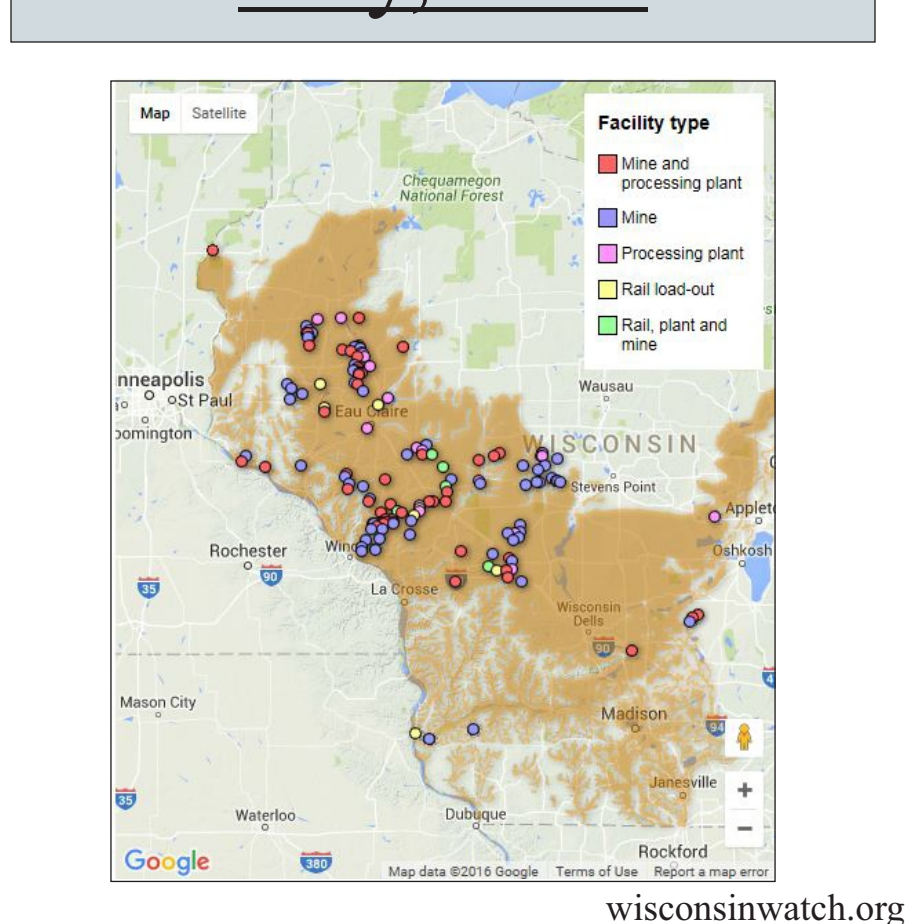
This investigation involves a comprehensive source to sink assessment of phosphorus (P) transport pathways in the hydrologic system of western Wisconsin. Excess P loading in surface water causes eutrophication events that result in degradation of water quality. Understanding the source and mobility of P is becoming urgent as 60% of the 225 bodies of water on the WDNR 2016 Impaired Water list exceed the total P criteria. Western Wisconsin has seen an increase in silica sand mining (300% since 2011) and CAFOs (600% since 2000) making it vital to determine the potential impact that these growing industries have on surface water and groundwater quality.

A multidisciplinary approach integrating stratigraphy, geochemistry, sequential extraction, surface water and groundwater chemistry, and hydrologic flow characterization will be used to assess the spatial and temporal distribution of P, and to constrain potential natural and anthropomorphic sources. Ongoing chemical analyses have documented differences in concentrations of P in geology, surface water, and groundwater. Whole rock geochemistry indicates that bedrock P₂O₅ values range from 0.25-2.5%. Surface water concentrations commonly exceed the Wisconsin surface water limit of 100 ppb, while groundwater concentrations are higher (10 to >1000 ppb); suggesting that P is mobile and concentrating in groundwater reservoirs.

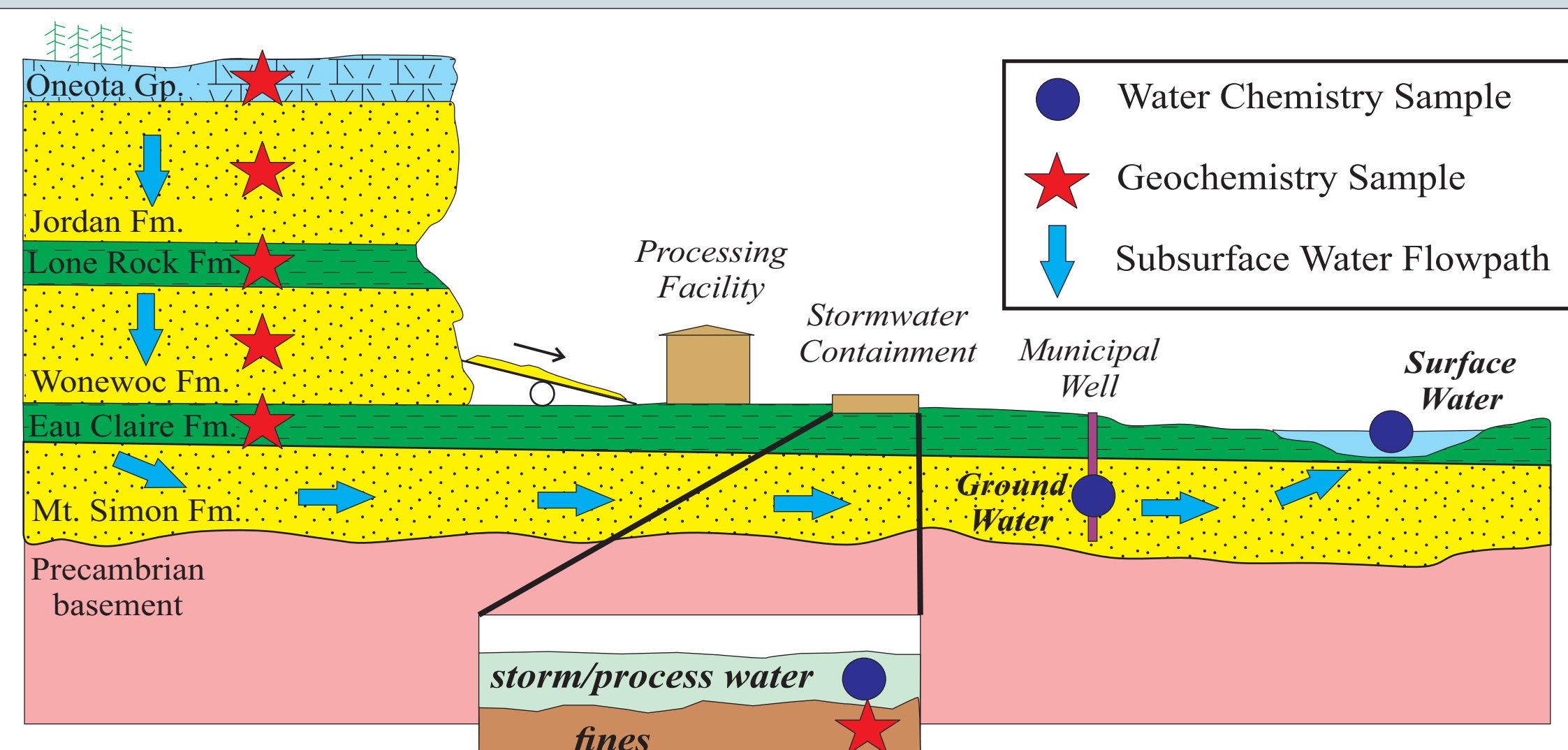
Stratigraphy of Western Wisconsin



Silica Sand Facilities May, 2014



Methodology of Water Project



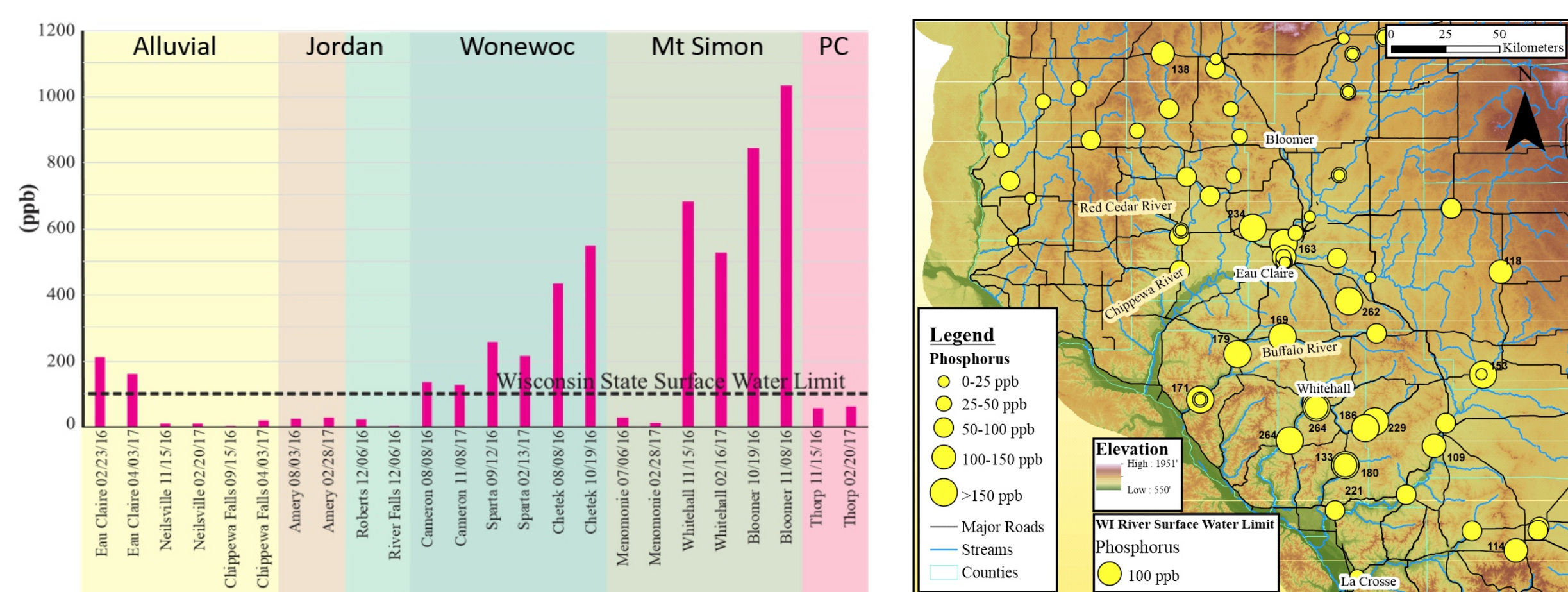
A comprehensive assessment of potential trace metal contamination associated with silica sand facilities requires an analysis of:

- Ambient Sources:**
1. Geochemical composition of target formations (Wonewoc and Jordan Fms.)
 2. Geochemical composition of overburden formations (Lone Rock/Tunnel City + Oneota Group)
 3. Groundwater chemistry
 4. Surface Water chemistry

- Potential Sources from Processing:**
1. Process/Stormwater chemistry
 2. Fine/Slime geochemistry

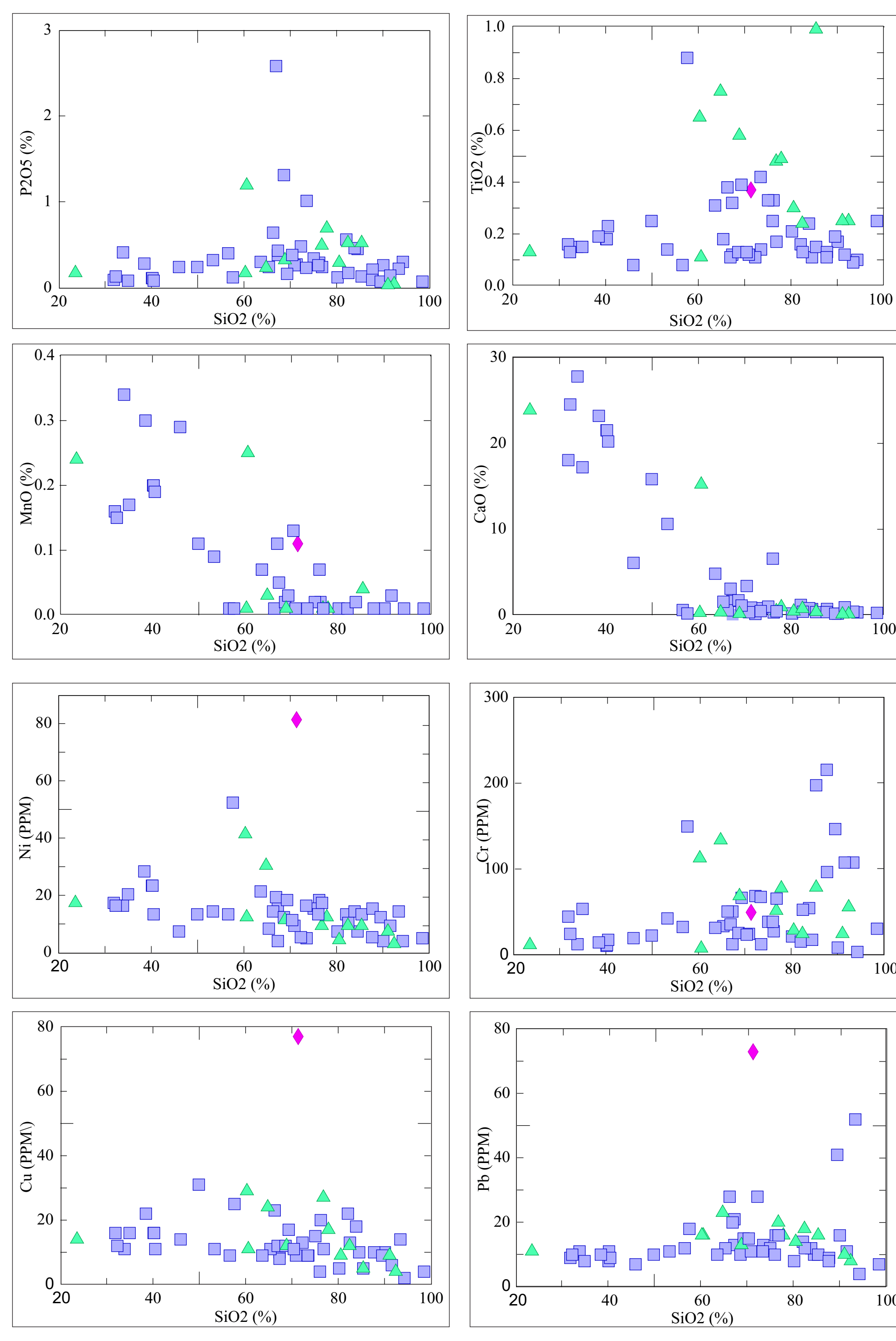
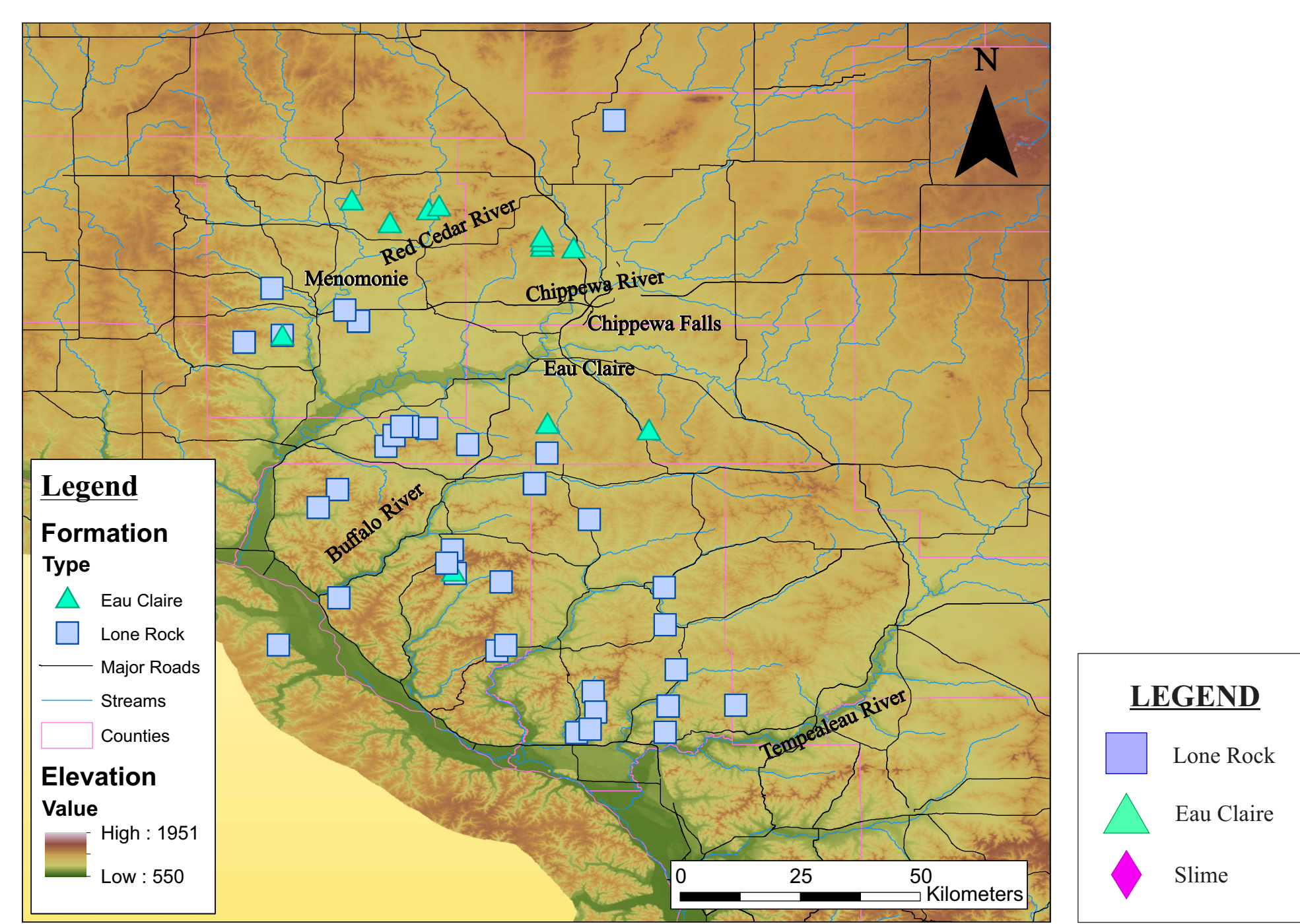
****A scientifically valid assessment of potential trace metal mobility requires the application of sequential extraction geochemistry on lithologic units containing elevated trace metal levels**

Water Chemistry Results



For comprehensive water chemistry data, see Wiest et al. (Poster #229)

Whole Rock Geochemistry



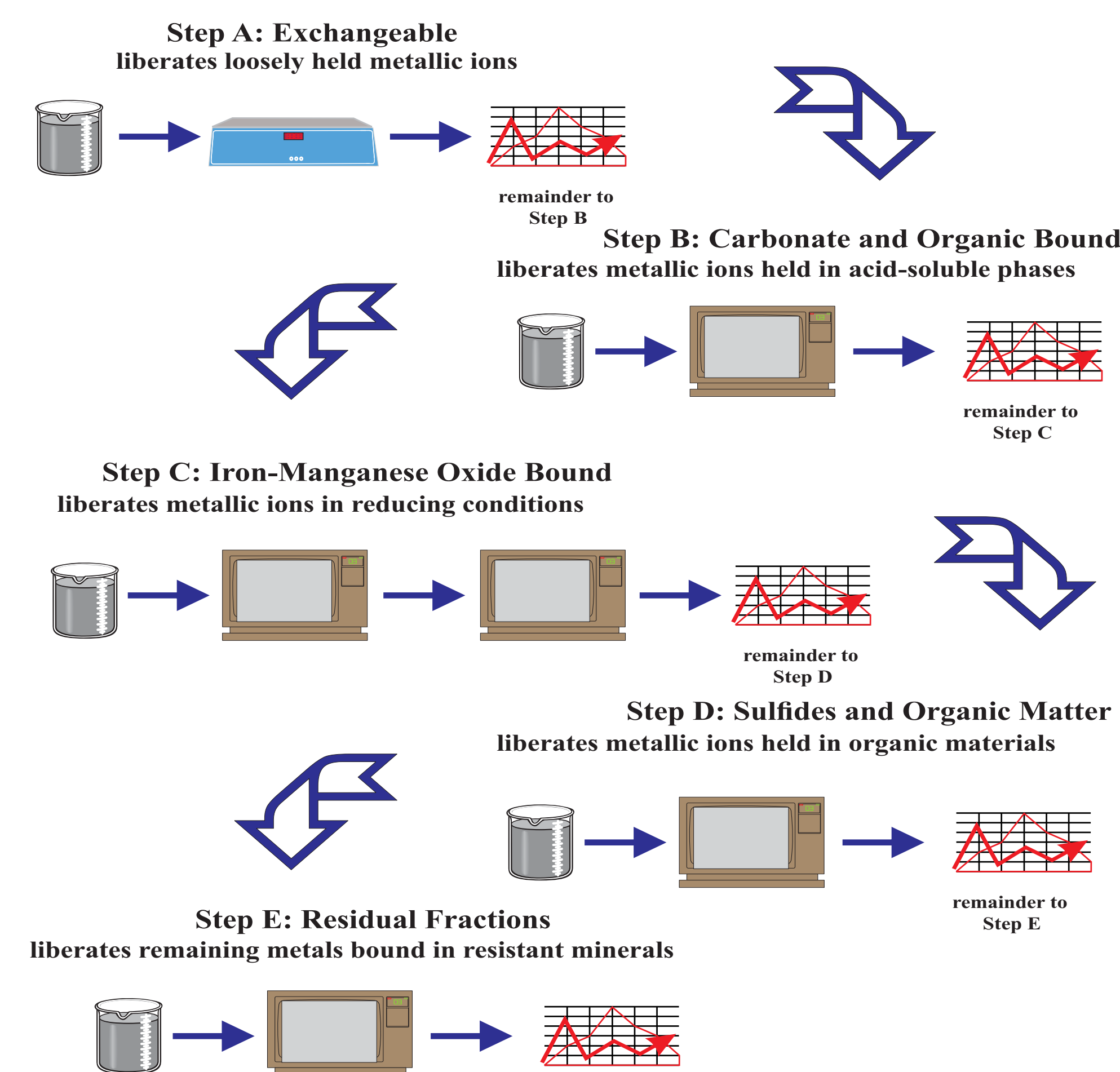
Preliminary Geochemistry Results

A comprehensive analysis of potential trace metal contamination requires an understanding of the natural flux of these metals between bedrock and adjacent surface water and groundwater. Documenting the natural concentration of trace metals in fine-grained units (Eau Claire and Lone Rock formations) that are stripped and stockpiled during mining operations is particularly important.

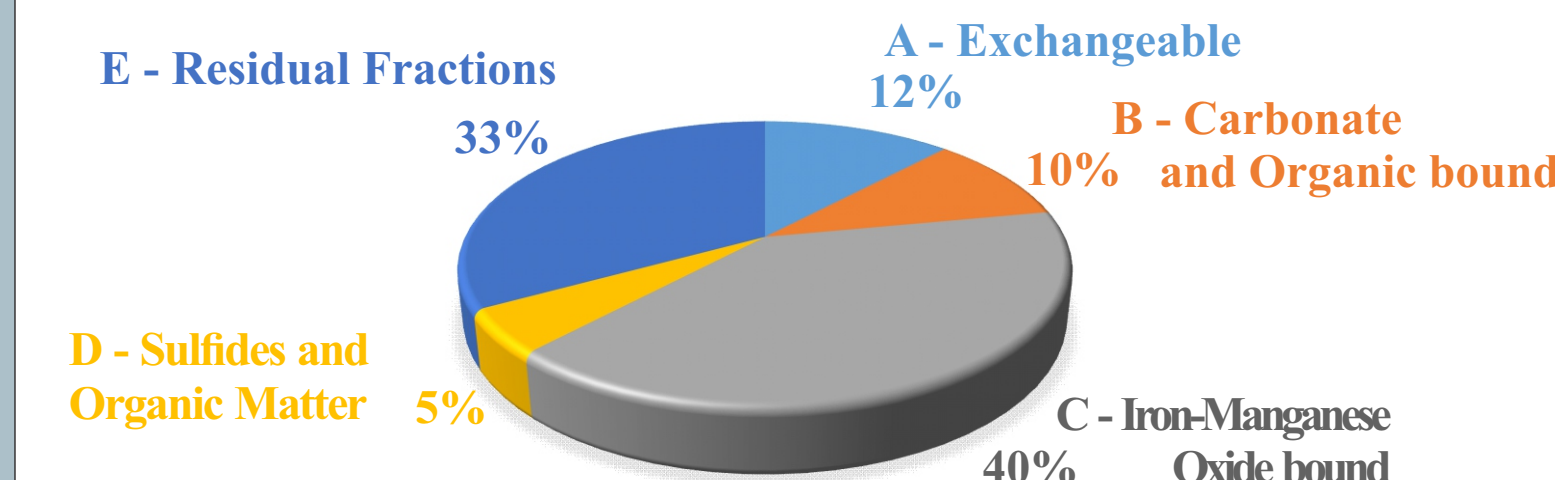
Our initial results suggest:

- There is a three order of magnitude difference (ppm to ppb) between trace metal concentration in Paleozoic strata and the composition of surface water and groundwater, suggesting Paleozoic strata yield minimal trace metals to the regional hydrogeologic system.
- Compositional difference between the Eau Claire and Lone Rock formations may influence trace metal concentration. The Eau Claire formation has a higher percentage of clay as shown in increased K and Al.
- The Lone Rock formation has a higher carbonate content as shown in increased Ca, Mg, and LOI, probably due to the proximity to the Prairie du Chien Group.
- Fine-grained material collected during silica sand processing ("slimes") indicates concentration of Ni, Pb and Cu, but minimal impact on Zn, Ti, and Cr values

Sequential Extraction Flow Chart



Sequential Extraction Procedure

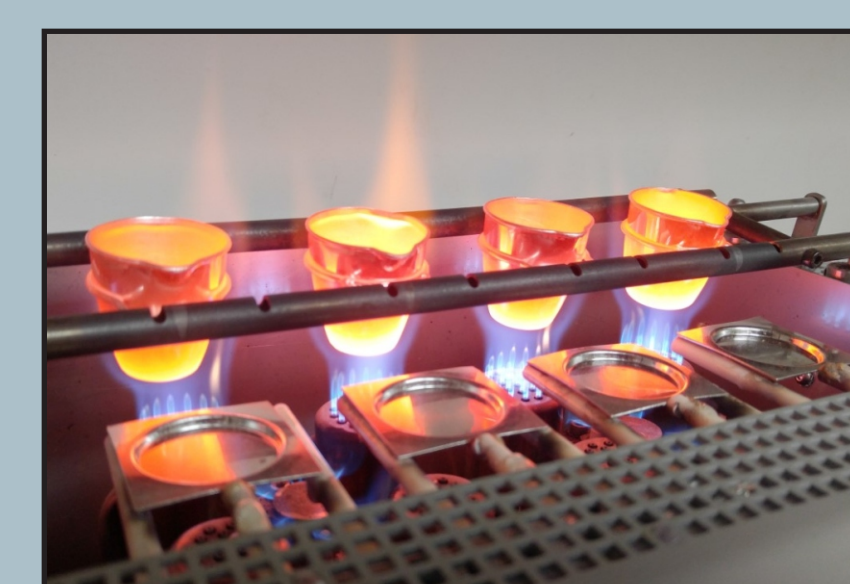


Trace metals accumulate in sediments, surface water and groundwater from both natural and anthropogenic sources. It is critical to evaluate the natural trace metal concentration and mobility in regional stratigraphic units in order to assess potential elemental flux between rock units and the hydrologic system. The total concentration of metals within stratigraphic units does not accurately represent their distribution and mobility. Trace element mobility and bioavailability depend strongly on the chemical and mineralogical forms in which these trace metals are held. Sequential extraction is a progressive, multi-step procedure in which trace metals are extracted from different physicochemical fractions using specific solvents that mimic different environmental conditions, including:

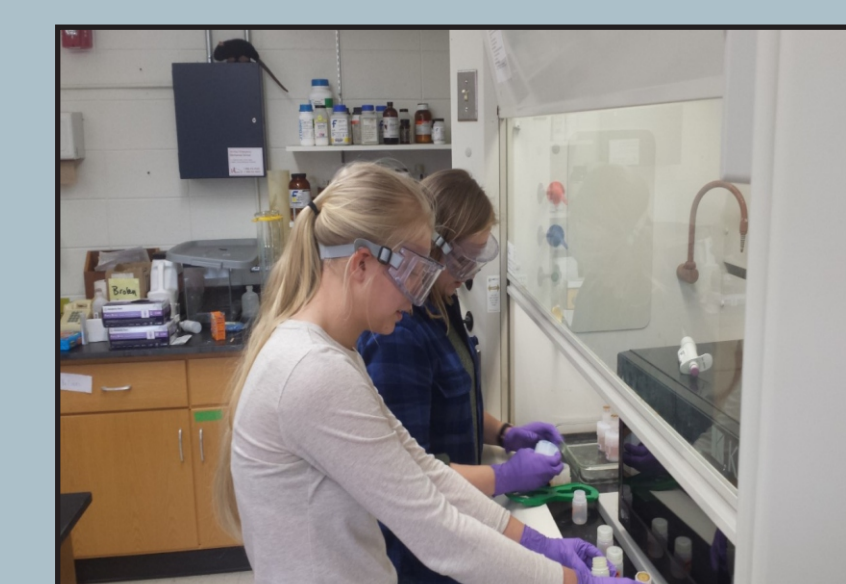
- Exchangeable:** Identifies metals that are loosely adsorbed onto clay surfaces and are mobilized by simple ion exchange
- Carbonate and Organic bound:** Carbonate tends to be a major adsorbent for many metals, particularly following reduction of oxide phases. Trace metals bound to carbonate are liberated under slightly acidic pH conditions.
- Iron-Manganese Oxide bound:** Iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles; these oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions.
- Sulfides and Organic bound:** Trace metal complexation or bioaccumulation processes concentrate metallic ions in organic and sulfide phases. These phases are unstable under oxidizing conditions.
- Residual fraction:** The residual fraction is dominated by primary and secondary minerals that contain trace metals bound in their crystal structure. These metals are only released by complete mineral dissolution, which are conditions not normally found in nature.



Sample preparation for geochemistry.



Geochemistry major element preparation.

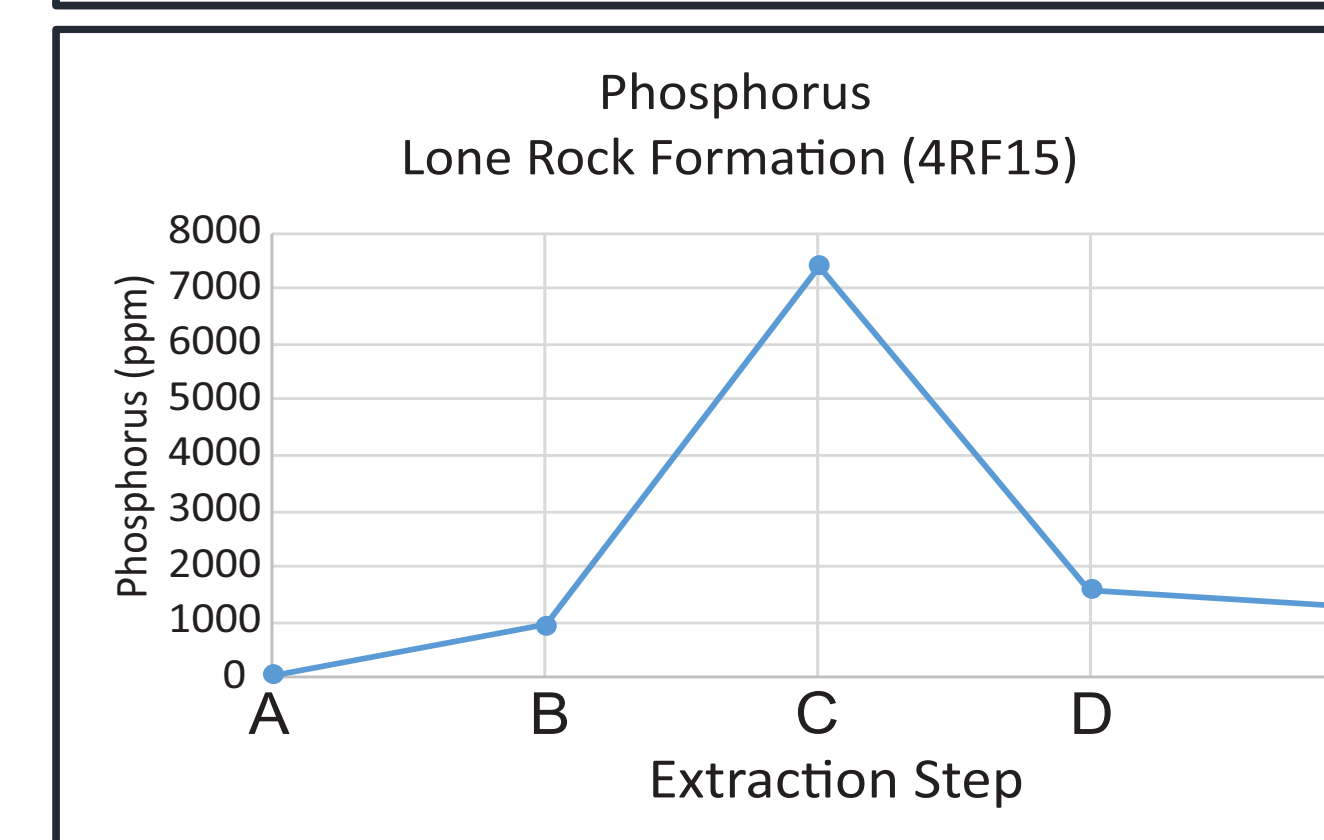
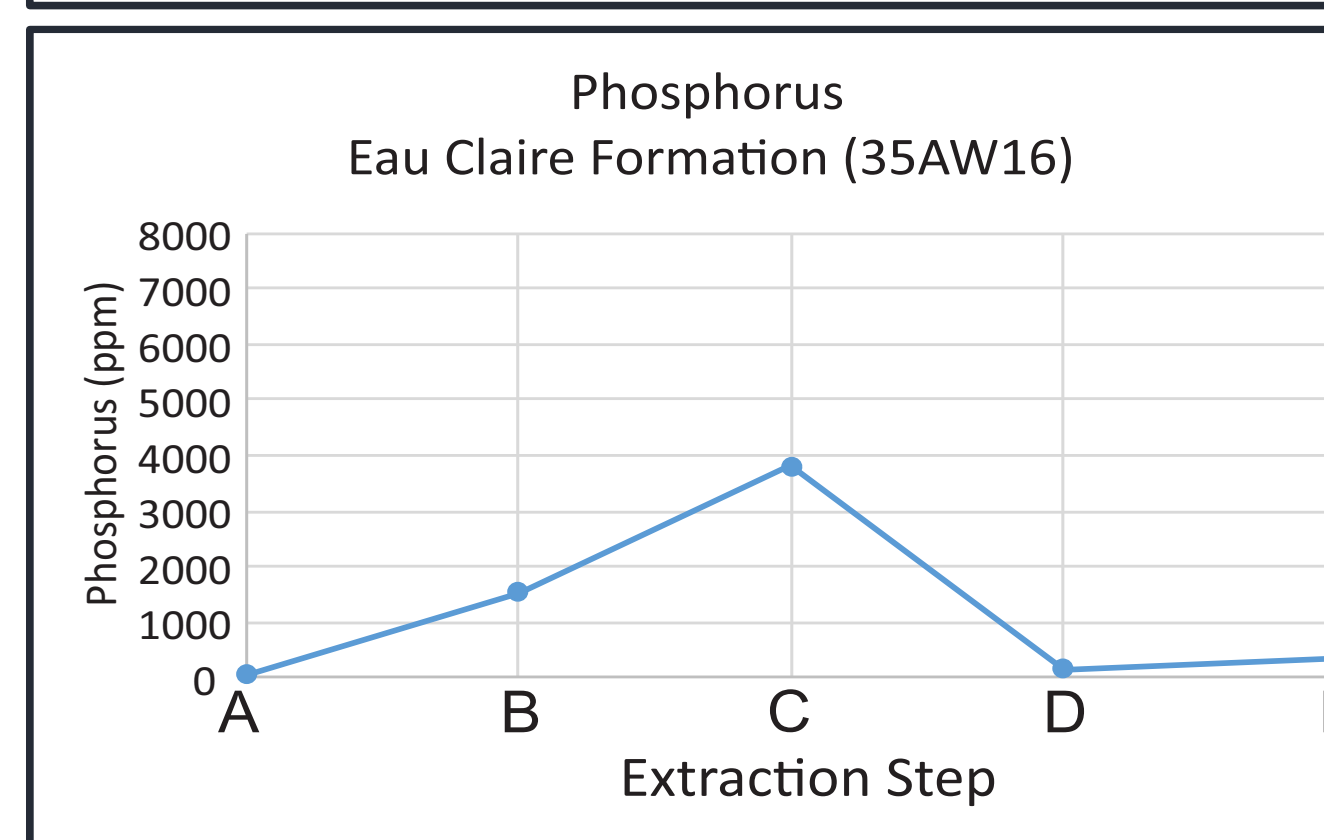
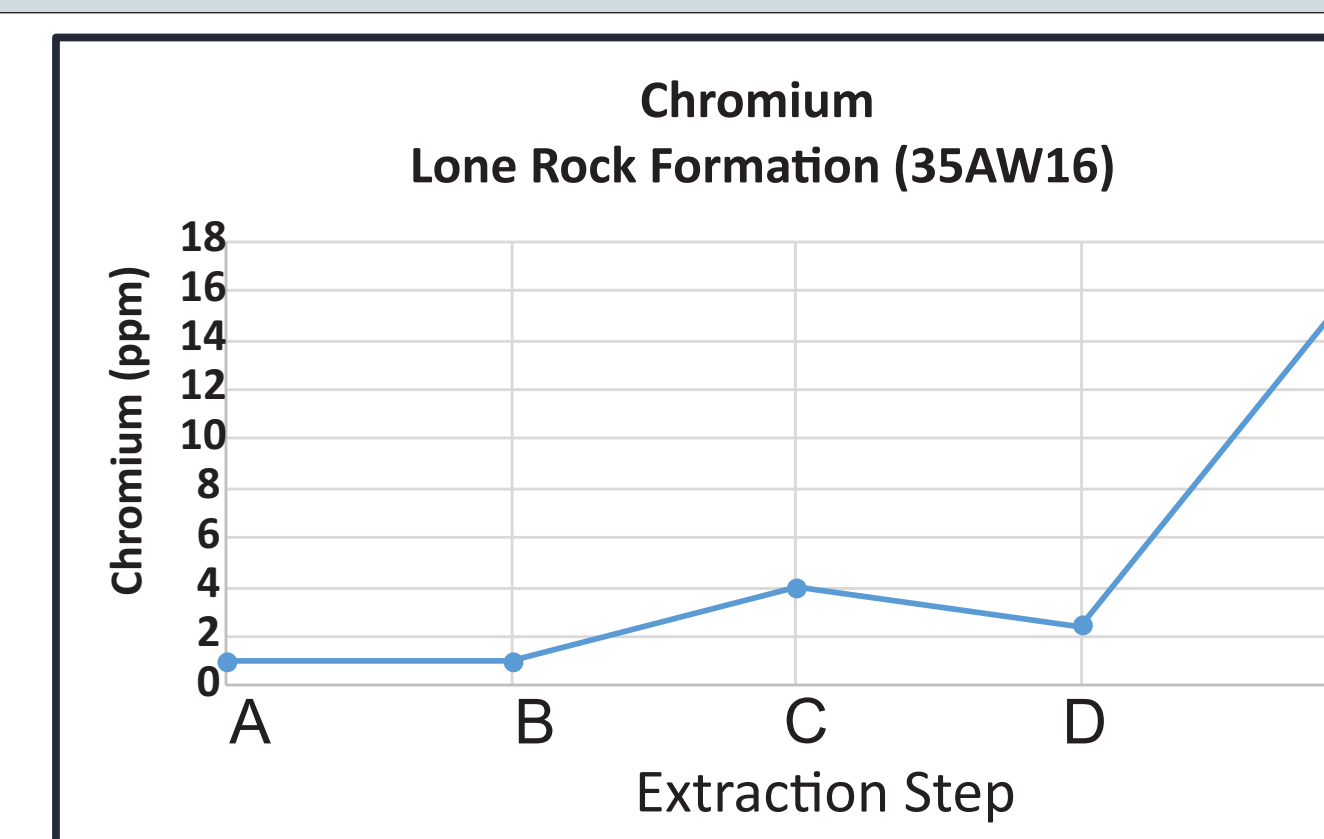
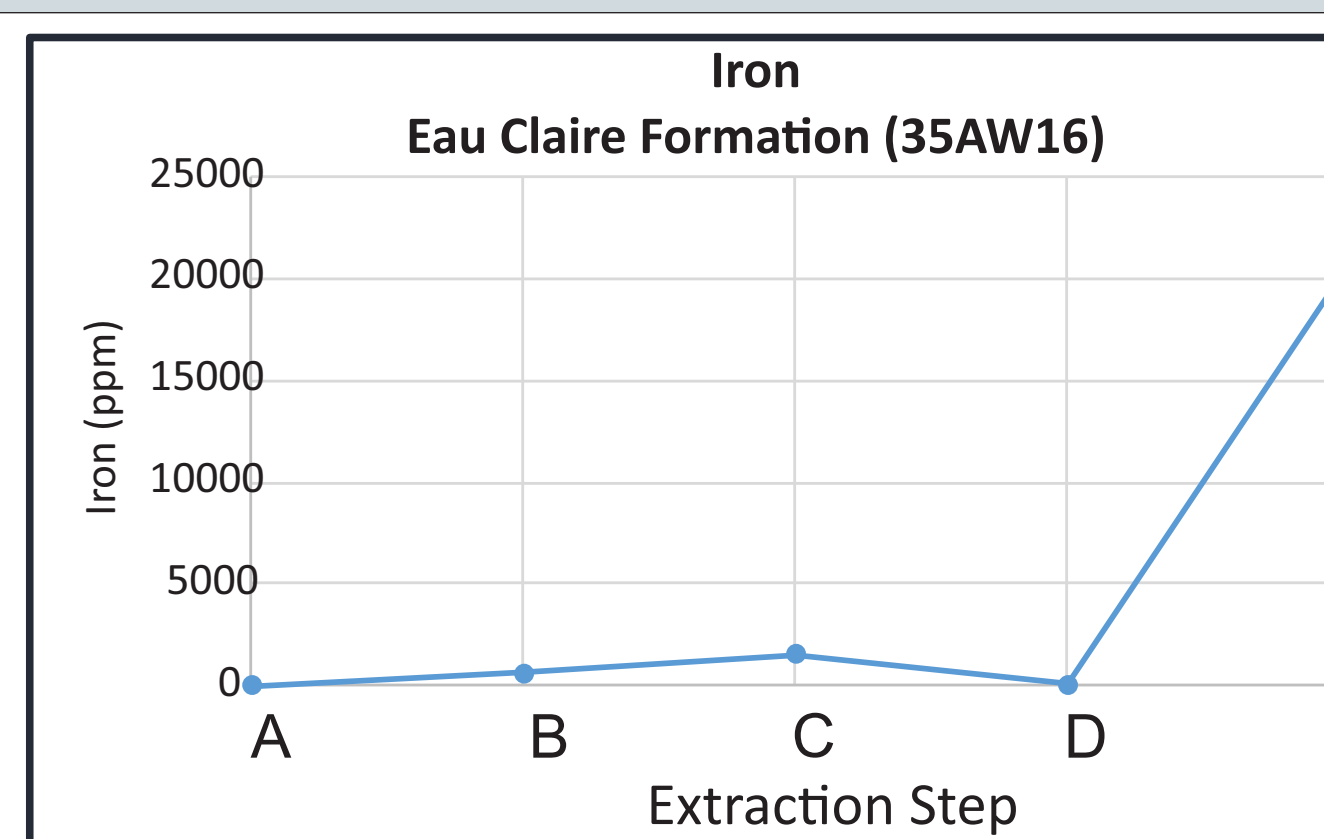


Sample preparation for the sequential extraction process.



Sequential extraction samples ready for HR-ICPMS analysis.

Preliminary Sequential Extraction Data



Preliminary Sequential Extraction Results

Sequential extraction results presented here are preliminary, and further technique development is needed to verify complete recovery of trace metals.

Preliminary results suggest:

- Water chemistry study found higher phosphorus levels in groundwater than in surface water.
- Sequential extraction shows that phosphorus is liberated during the iron-manganese oxide bound stage (C), which represents reducing conditions.
- This suggests that the bedrock is contributing to the elevated phosphorus in the groundwater.

Future Work

- Technique development will continue to verify the accuracy of results, focusing on quantitative trace metal recovery.
- Future objectives focus on a reproducible statistically valid sequential extraction data set representative of both Eau Claire and Lone Rock formations across western Wisconsin.
- Collect and run slime samples from the silica sand mining industry to assess the mobility of trace metals.