Chippewa River, Eau Claire, WI

Establishing an Environmental Baseline for Surface and Groundwater Chemistry in Western Wisconsin

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INTRODUCTION

The rapid expansion of silica sand mining in the upper Midwest has generated significant concerns about the environmental impact of industrial sand mining. Ongoing air quality (e.g. Richards and Brozell, 2015) and groundwater quality (Parsen and Gotkowitz, 2015) studies are addressing some of these concerns, but growing public interest about potential contamination of the surface water and groundwater system of western Wisconsin has not been addressed. One of the primary impediments to the assessment of potential surface water and groundwater contamination in western Wisconsin is the lack of data on the background composition of natural waters in the region.

The primary objective of this investigation is to conduct the first comprehensive analysis of surface water and groundwater chemistry throughout western Wisconsin. This analysis will establish a critically important environmental baseline that will document natural background variations in dissolved metal content in surface water and groundwater throughout the region. These data are essential for accurate assessment of the potential for public health risk, identifying the source of elevated metal content and for establishing a baseline that may be utilized in developing reasonable and responsible environmental regulations.

ANALYTICAL APPROACH

This investigation is designed to develop baseline data on surface water and groundwater composition, specifically concentrations and mobility of metals that are naturally occurring in geologic units in western Wisconsin. The analytical protocol has four distinct components:

1) ***Surface Water Chemistry***, which entails analysis of approximately 70 samples from second, third and fourth order streams throughout the region;

2) ***Groundwater Chemistry***, in which approximately 50 municipal water wells will be sampled;

3) ***Whole Rock Geochemistry***, with approximately 50 geochemical analyses of bedrock, mine tailings and wasterock storage piles composed primarily of fine-grained non-economic materials that may harbor heavy metals.

4) ***Sequential Extraction Geochemistry***, which involves progressive chemical leaching of potential sources of trace metal contamination (e.g. geologic units, mine tailings) to evaluate the true mobility of trace metals under realistic natural environmental conditions.

These analyses will be conducted by a multidisciplinary research team consisting of faculty, staff and students from the Department of Geology and Materials Science and Engineering at the University of Wisconsin-Eau Claire. The project requires close faculty/student interaction, and students will be involved in all aspects of the investigation, including sample collection, processing, analysis, data compilation, and dissemination of results.

ANALYTES OF INTEREST

Analytes of interest were selected primarily based on Environmental Protection Agency procedures for the determination of dissolved elements in ground waters, surface watersand drinking water (EPA Method 200.8). These analytes include elements of interest to the Wisconsin Department of Natural Resources (WDNR) for the establishment of environmental regulations.

Aluminium (Al)	**Cobalt (Co)**	**Phosphorus (P)**
Antimony (Sb)	**Iron (Fe)**	**Selenium (Se)**
Arsenic (As)	**Lead (Pb)**	**Strontium (Sr)**
Barium (Ba)	**Magnesium (Mg)**	**Thallium (Th)**
Cadmium (Cd)	**Manganese (Mn)**	**Uranium (U)**
Calcium (Ca)	**Nickel (Ni)**	**Vanadium (V)**
		Zinc (Zn)

PROCEDURES

Sample collection of surface water

Sample Collection
- Collect GPS location, temperature, and pH at collection site
- Sample is collected in 500 mL nalgene bottle
- Fill nalgene bottle and cap underwater
- Store for transportation

Sample Processing Procedure
- Take 50 mL aliquant and place into labeled filter apparatus
- Filter with vacuum filter
- Verify pH with field values
- Acidify with HNO_3 to pH of less than 2
- Samples are run on HR-ICPMS within 24 hours of collection

Sample filtering process

Sample preparation for HR-ICPMS

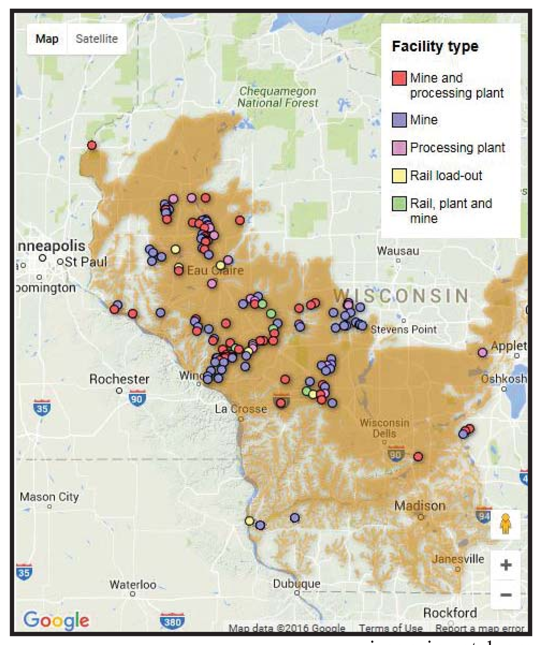
HR-ICPMS Preparation
- Sample protocol utilizes ~6 unknown samples, one total procedural blank, and one NIST standard run as unknown
- Add ~ 40 mL of HNO_3 to a clean, acid washed, 60 mL nalgene bottle
- Add ~10 mL sample aliquant to nalgene bottle
- Add ~1 mL Internal Standard (Y,Sc,In,Li) to nalgene bottle

UW MSEC Materials Science and Engineering Center

Samples are run within 24 hrs. of collection and follow EPA Method 200.8 Guidelines

HR-ICPMS Procedure
- Tune and calibrate instrument for elements of interest and internal standard elements over the typical concentration range using externally sourced, certified standards
- Analyze samples listed above with additional blank sample and certified NIST sample to monitor method performance
- Check the quality of the data:
  - Confirm the quality of the calibration curves (correlation coefficient >0.999) using 4 or more standards
  - Check relative standard deviation for all element measurements in each sample run so that they are <5%
  - Normalize sample element signals with respect to the controlled internal standard element's signals to account for instrument drift
  - Confirm the success of the run by confirming NIST samples measured concentrations are within tolerable ranges of reported NIST values according to the EPA method
- Using calibrated signal intensity, calibration curves, and known dilution, calculate the concentration of the elements

FRAC SAND FACILITIES AND FACILITY TYPES AS OF MAY, 2014



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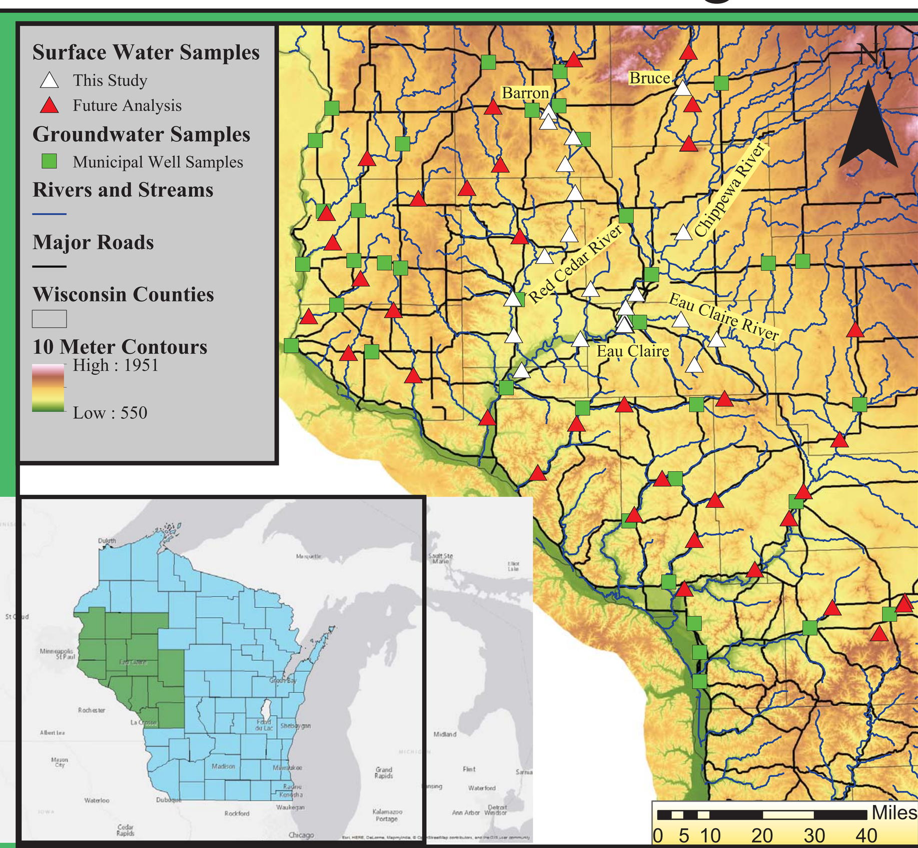
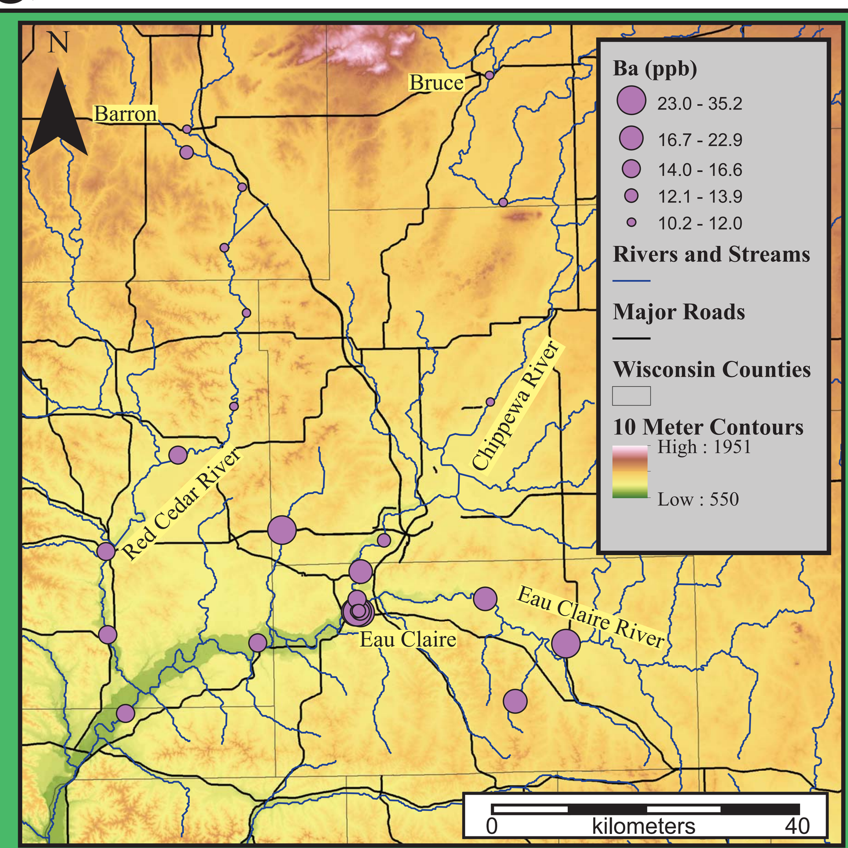
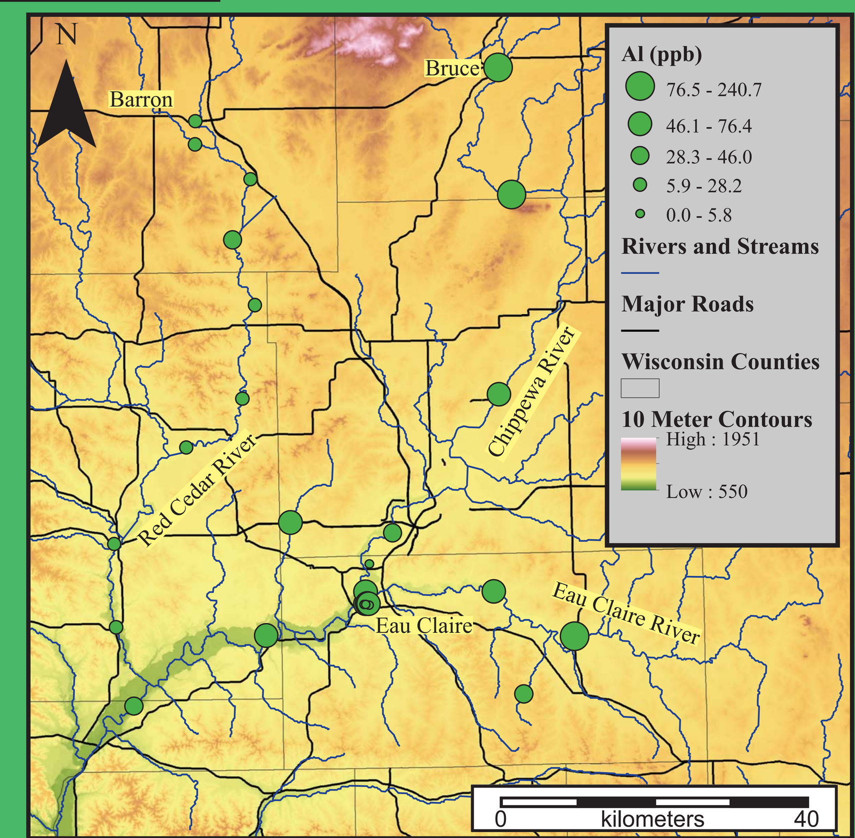
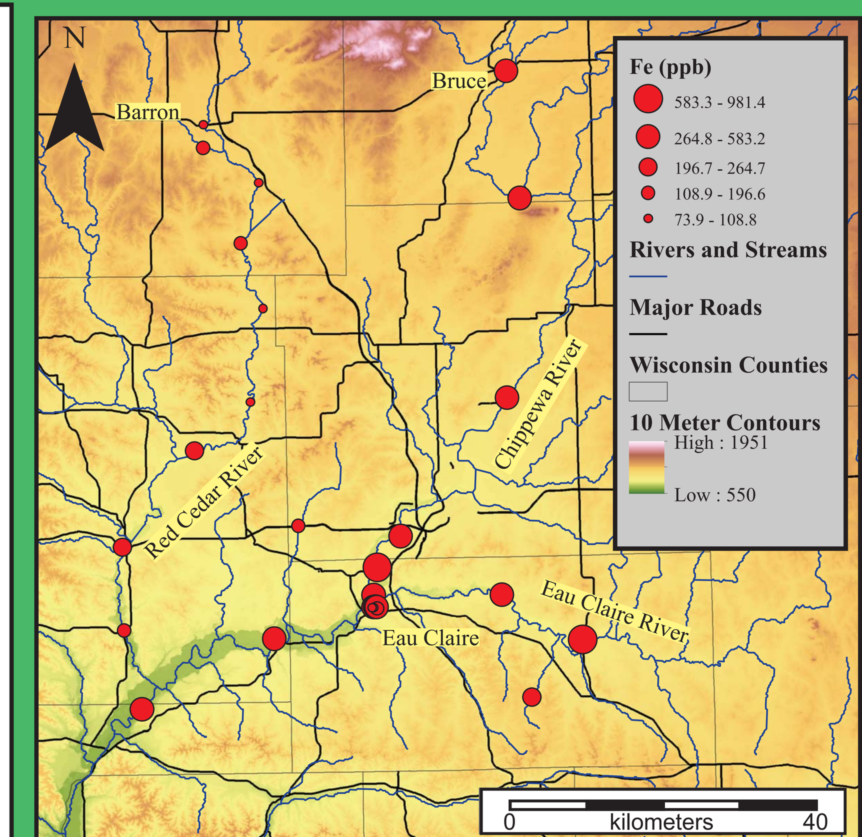
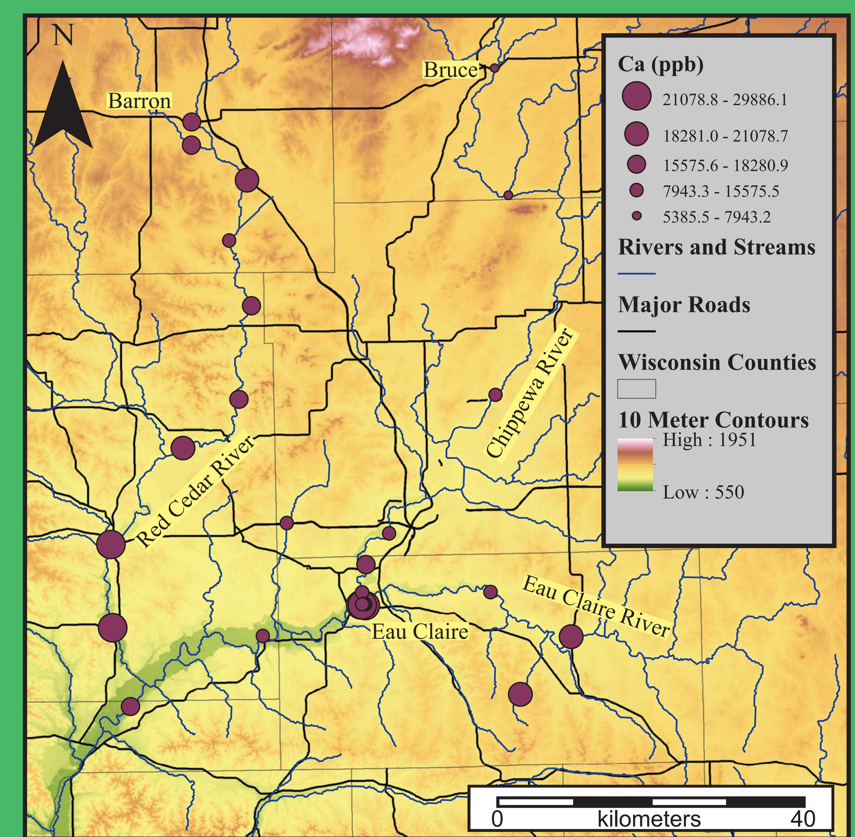
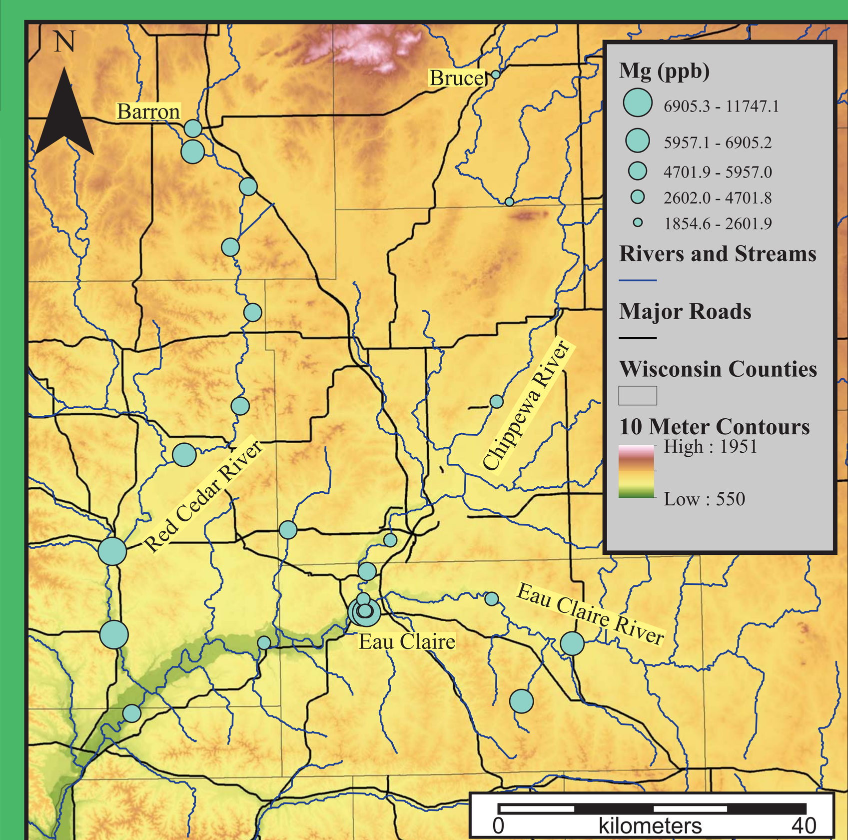


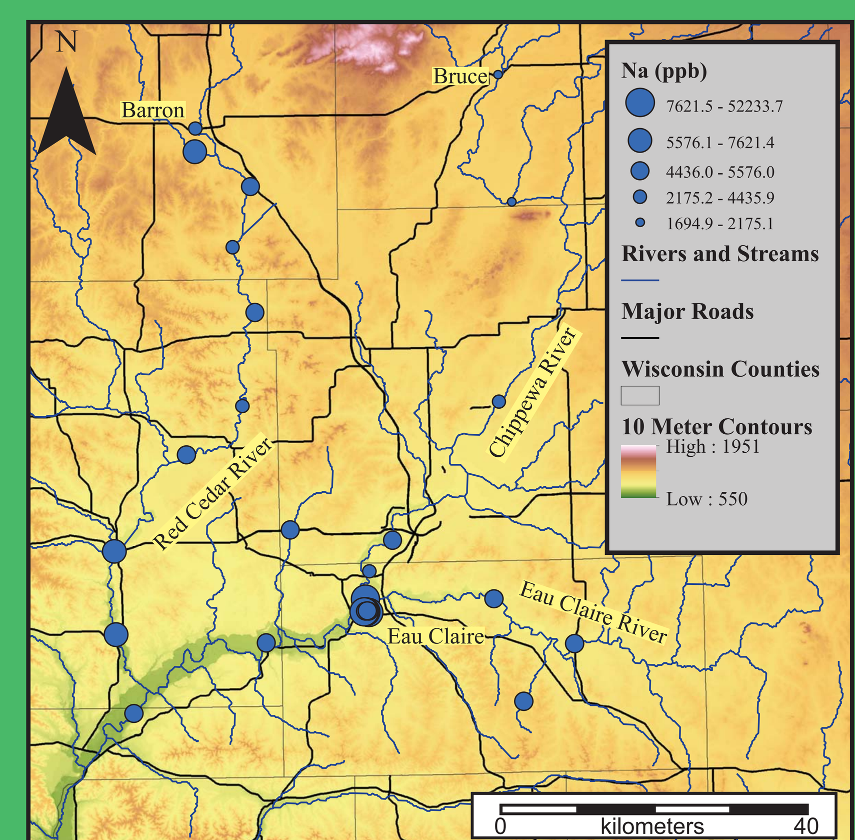


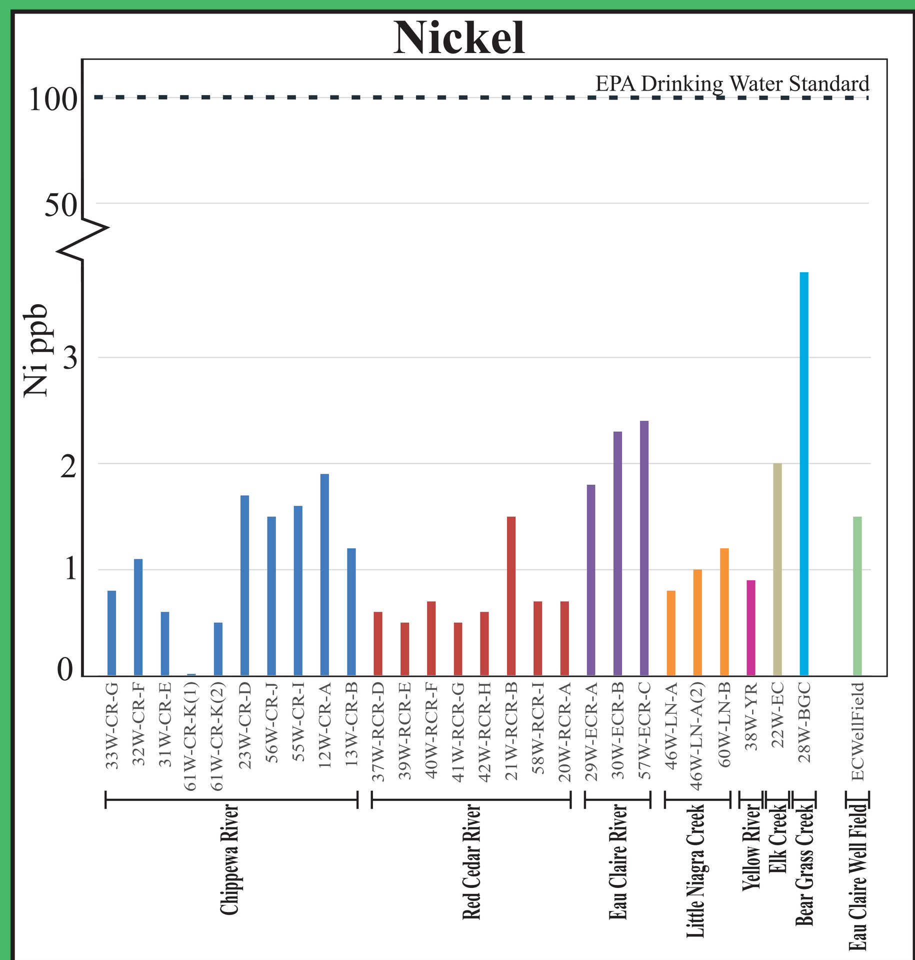


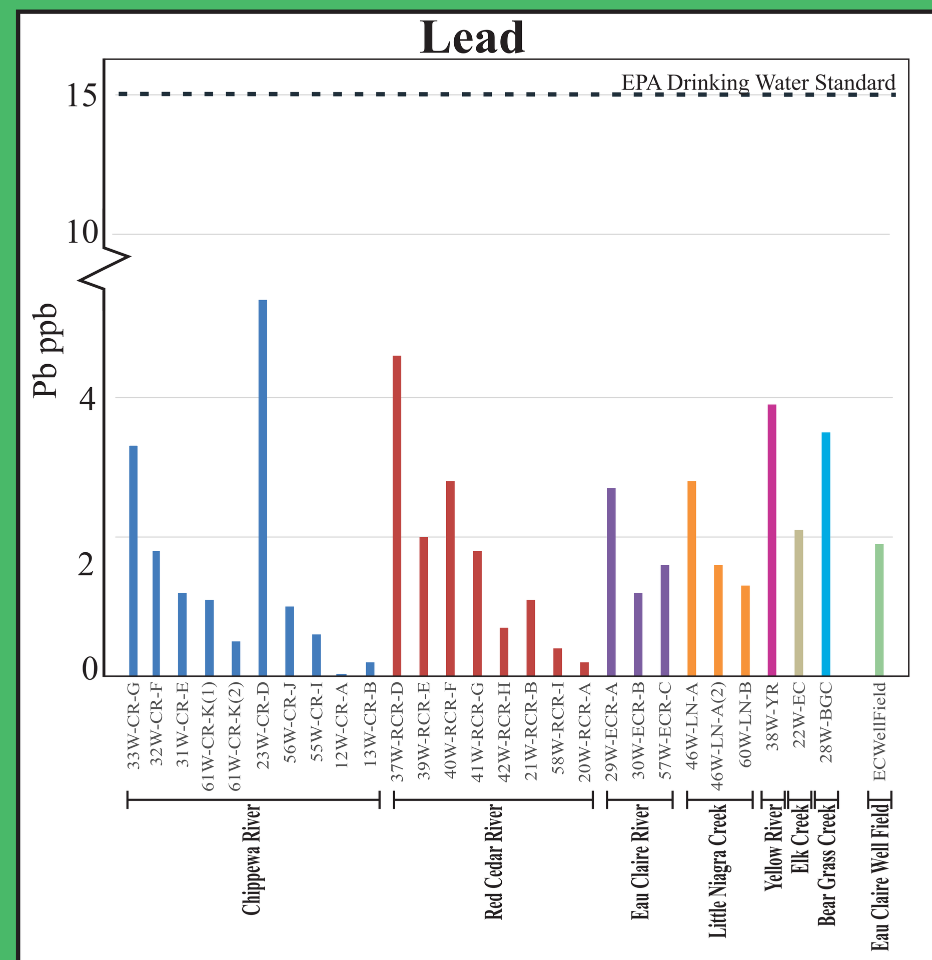


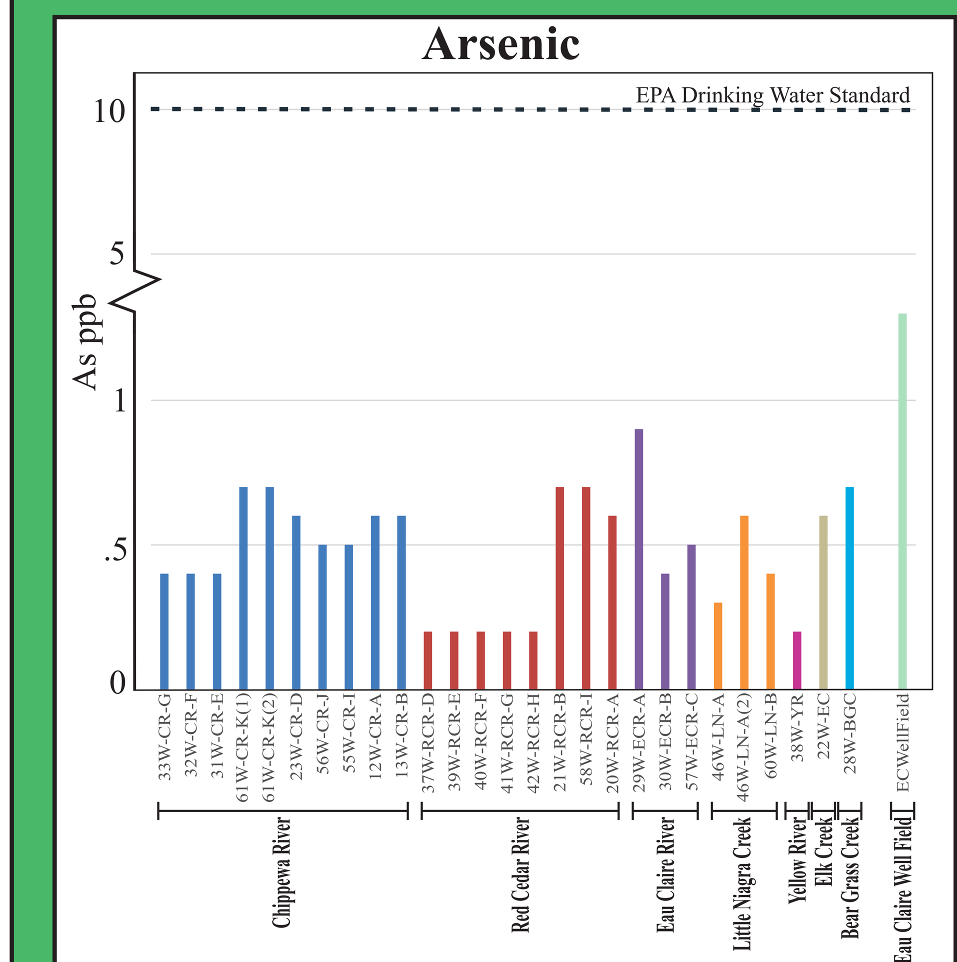


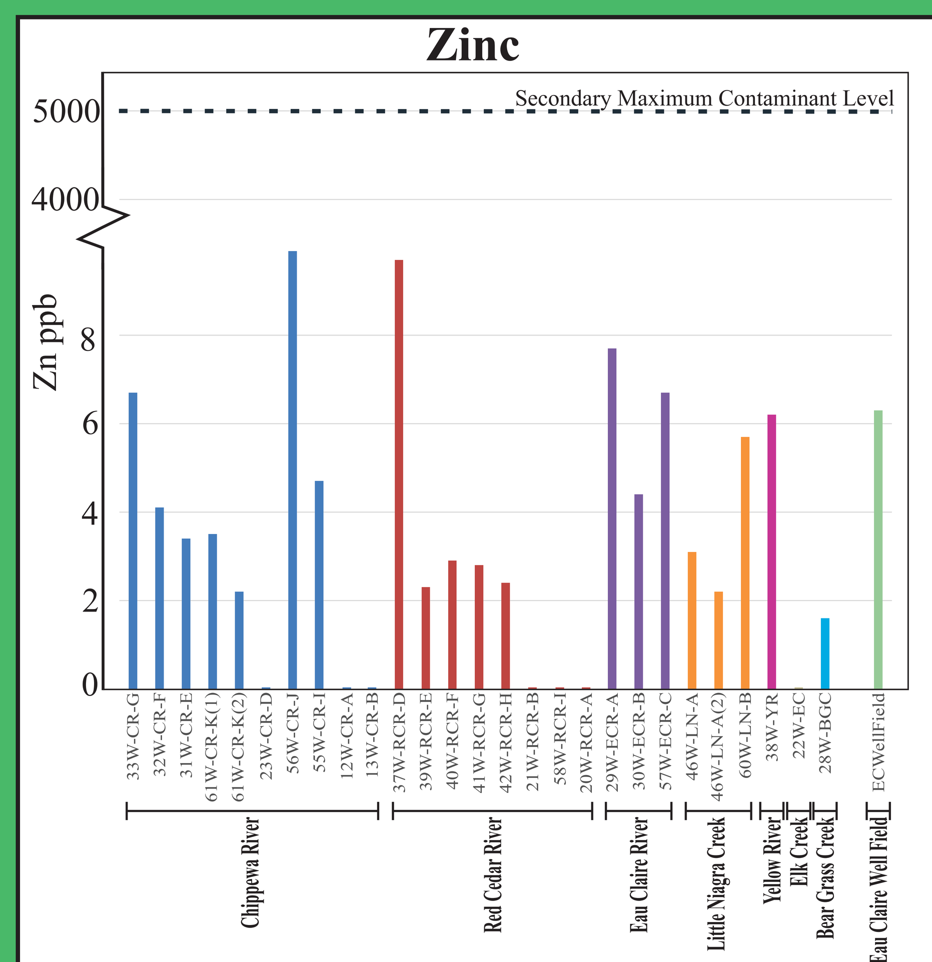


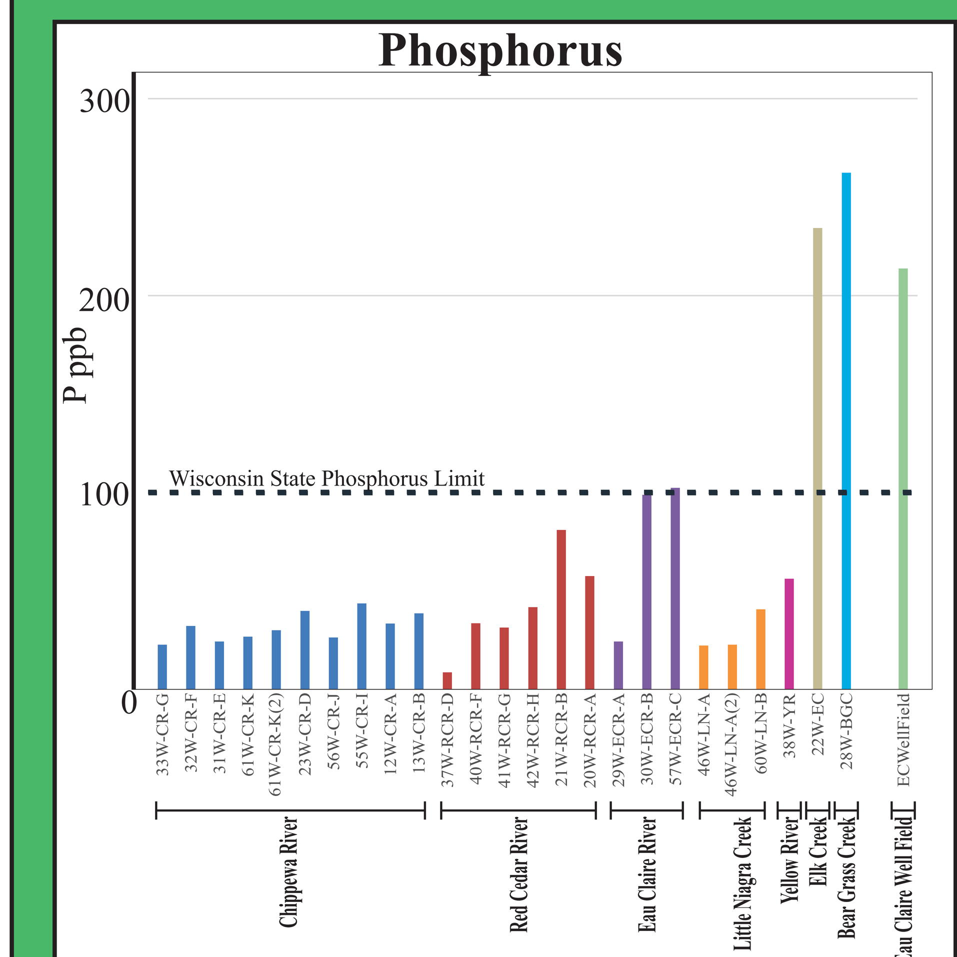


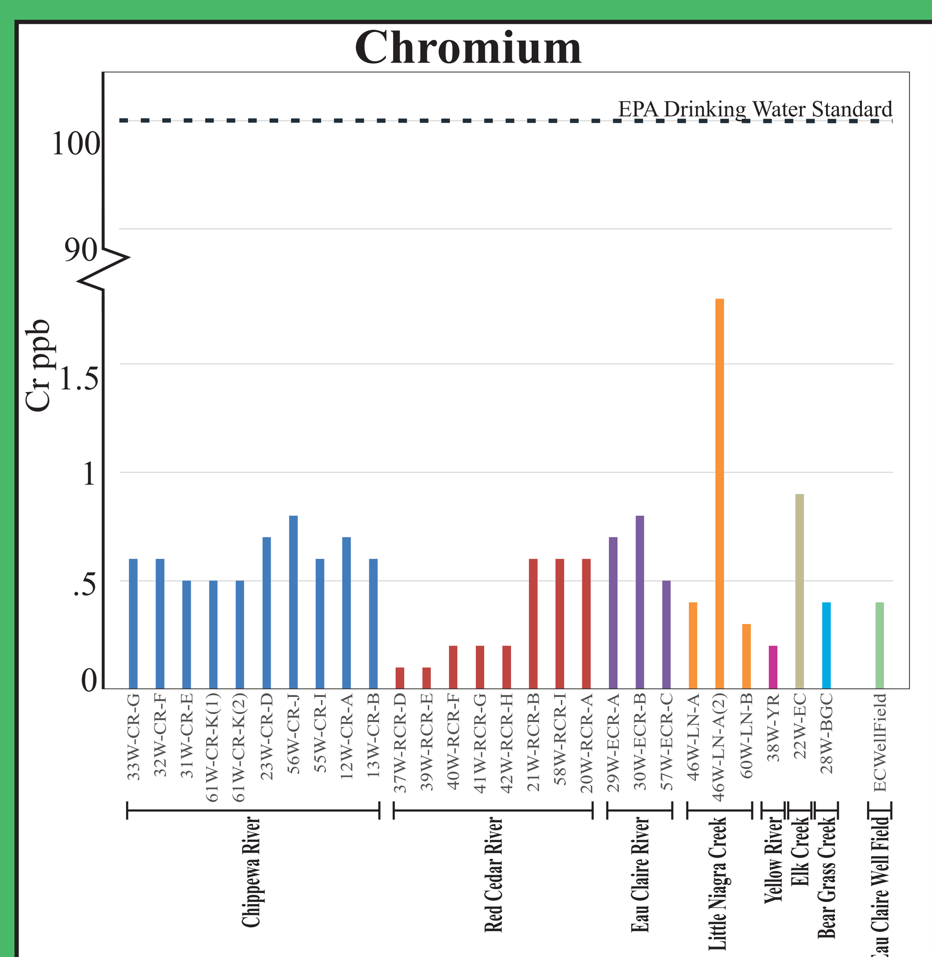










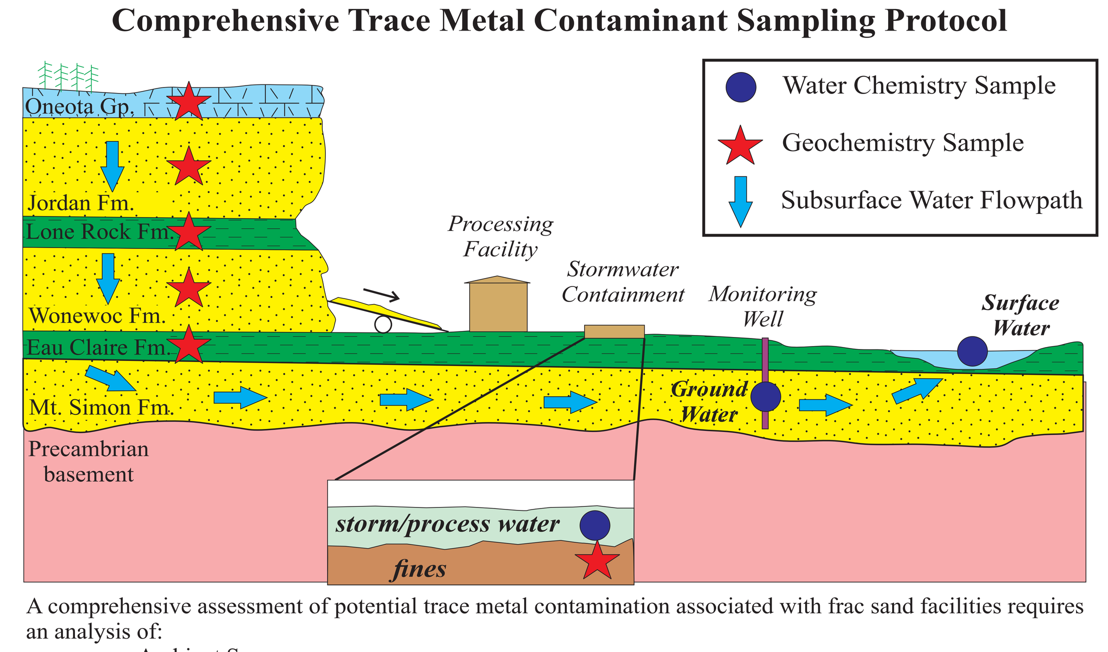


PRELIMINARY RESULTS

- Initial results indicate that trace metal values in the Red Cedar and Chippewa River drainages are low relative to established state and federal drinking water standards (As, Cr, Pb) and public welfare secondary standards (Zn)
- Major element chemistry varies regionally, and appears to be controlled by bedrock geology
- Establishment of regional environmental chemistry baseline in surface and underground water chemistry in Western Wisconsin is crucial prior to the development of a reasonable and realistic regulatory framework

FUTURE WORK

Comprehensive Trace Metal Contaminant Sampling Protocol



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

<u>Ambient Sources:</u>
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

<u>Potential Sources from Processing:</u>
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