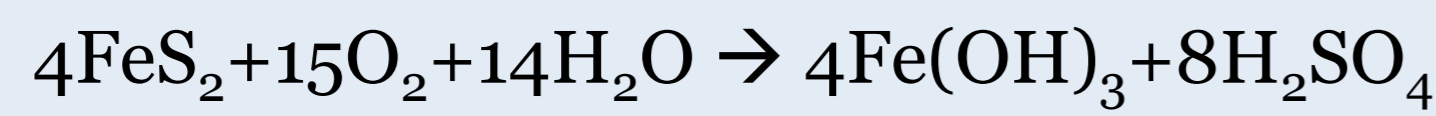


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Acid Mine Drainage

Acid mine drainage (AMD) is a prevalent issue throughout the world that contaminates ecosystems and negatively impacts surrounding communities. AMD results when pyrite contained in coal is exposed to weathering through mining activities and oxidized to release ferrihydrite, sulfate, and acidity according to the following chemical reaction (Nordstrom 1982):



Treatment systems are installed at AMD-impacted sites with the intent to treat water by increasing pH in limestone channels and removing ferrihydrite. However, due to the site complexity, the contamination may not be fully treated. We use concentration-discharge relationships at the stream outlet to evaluate contaminant behavior under different flow regimes and determine the effectiveness of a treatment system in Northeastern Ohio.

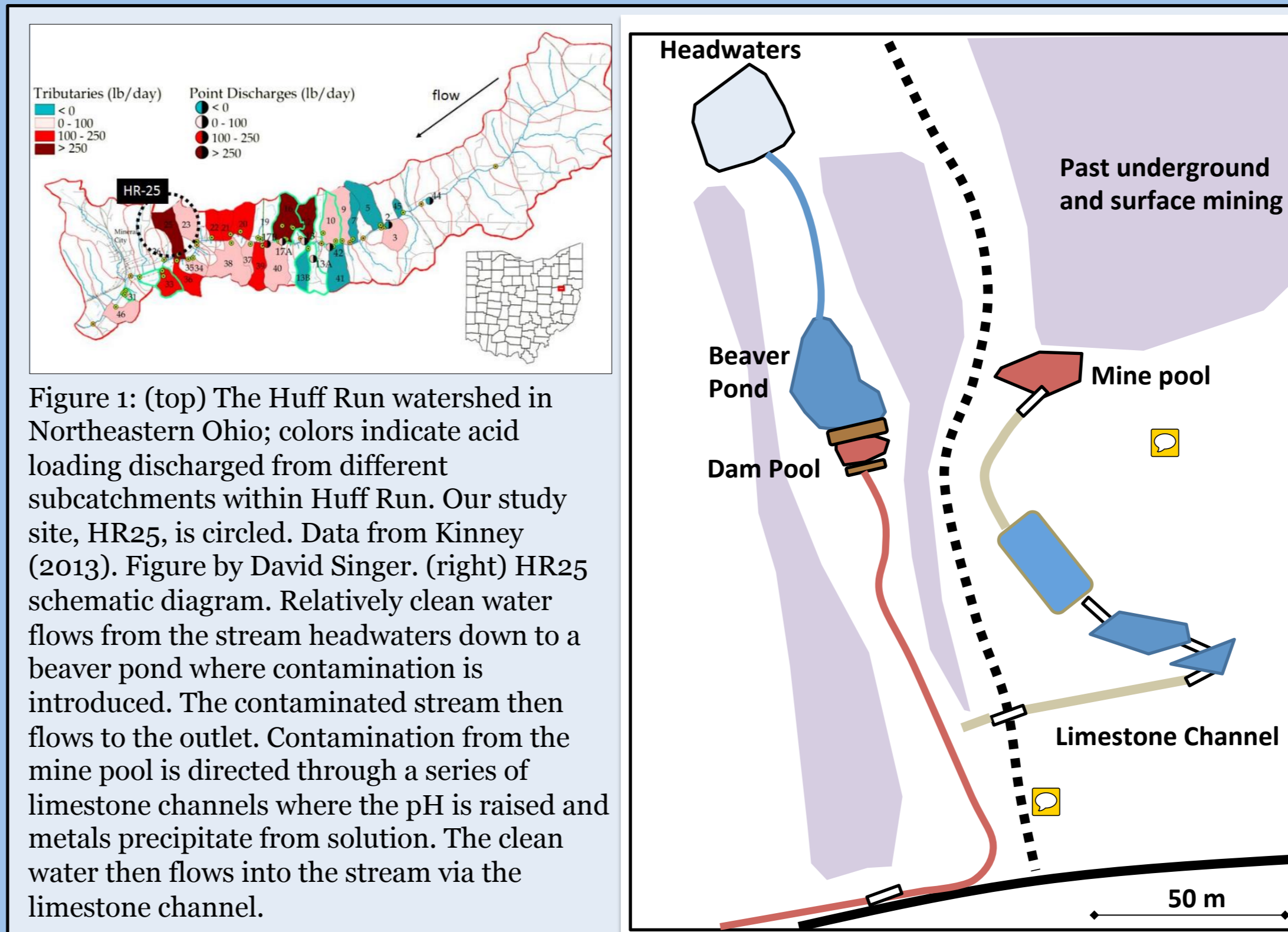


Figure 1: (top) The Huff Run watershed in Northeastern Ohio; colors indicate acid loading discharges from different subcatchments within Huff Run. Our study site, HR25, is circled. Data from Kinney (2013). Figure by David Singer. (right) HR25 schematic diagram. Relatively clean water flows from the stream headwaters down to a beaver pond where contamination is introduced. The contaminated stream then flows to the outlet. Contamination from the mine pool is directed through a series of limestone channels where the pH is raised and metals precipitate from solution. The clean water then flows into the stream via the limestone channel.

Methods

Sample collection and analysis
Water samples were collected from the stream outlet using a Teledyne 6712 ISCO autosampler. Stream velocity was measured using a Teledyne 2150 Area Velocity Flowmeter. Samples collected once per day periodically from April to November; storm samples collected hourly during select rain events. Stream flow recorded every 15 minutes.

Water collection: Two samples gravity-filtered through a 0.45 μm Supor filter (Kim et al 2012) each collection time: one for cation analysis (acidified with ultrapure nitric acid) and one for anion analysis (unacidified).

Sample analysis: Ion Chromatography (SO₄²⁻, Cl⁻, F⁻, Br⁻, NO₃⁻, PO₄³⁻); Inductively coupled plasma-optical emission spectrophotometry (Na⁺, Ca²⁺, K⁺, Mn²⁺, Al³⁺, Mg²⁺, Fe_{total}); Total Organic Carbon Analyzer (DOC)

Contaminant metals exhibit dilution behavior in the AMD-impacted stream

- Fe, Mn, and Al exhibit dilution behavior (log-log slopes = -0.51, -0.18, and -0.30, respectively) while SO₄²⁻ and base cations remain chemostatic (< ± 0.1).
- Acidity in the stream decreases (pH increases) with increasing discharge (log-log slope = -0.9).
- Stream contamination (pH, Fe, Mn, Al) at the outlet decreases when flow through the treatment system increases.

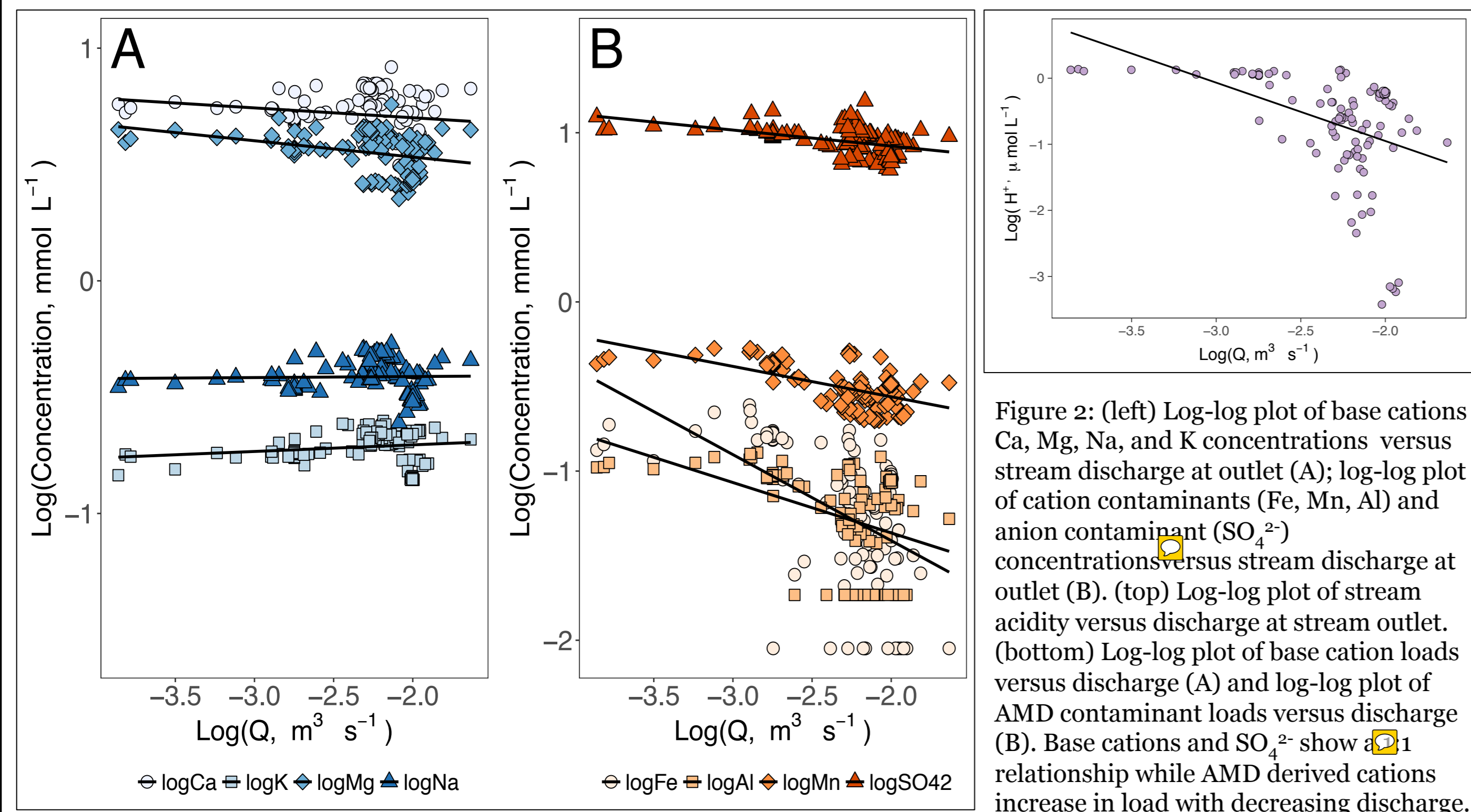


Figure 2: (left) Log-log plot of base cations Ca, Mg, Na, and K concentrations versus stream discharge at outlet (A); log-log plot of cation contaminants (Fe, Mn, Al) and anion contaminant (SO₄²⁻) concentrations versus stream discharge at outlet (B). (top) Log-log plot of stream acidity versus discharge at stream outlet. (bottom) Log-log plot of base cation loads versus discharge (A) and log-log plot of AMD contaminant loads versus discharge (B). Base cations and SO₄²⁻ show a chemostatic relationship while AMD derived cations increase in load with decreasing discharge.

Mixing and reactive transport control stream chemistry at the watershed outlet

- Treated water (limestone channel) and base flow contamination (below dam pool) have distinct ratios of metals and base cations. Outlet water plots between these two sources and is thus a product of mixing.
- Mixing behavior caused by the ephemeral limestone channel tributary (confluence shown at right) controls chemistry of outlet.
- Mn concentration at outlet controlled by dilution only while Fe concentration at outlet is controlled by dilution as well as reactive transport.

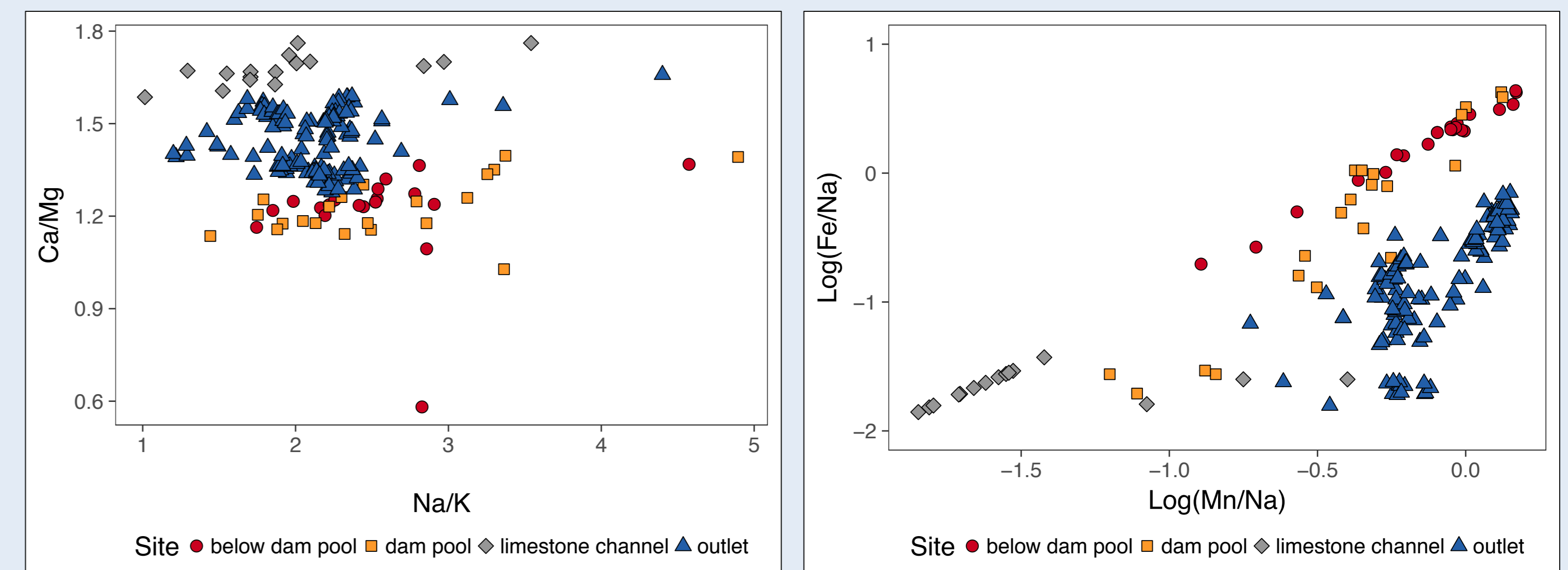


Figure 6: (top, left) Base cation mixing diagram shows outlet water plots between two distinct water sources: contaminated baseflow from the dam pool and below the dam pool and treated flow from the limestone channel. (top, right) Log-log plot of Fe/Na ratio versus Mn/Na ratio shows outlet chemistry has similar Mn/Na ratio as contaminated baseflow. However, Fe concentrations are lower at outlet than baseflow even for highest contamination levels. This indicates that Fe is also controlled by reactive transport along the stream channel, where the redox-active Fe precipitates from solution and leads to a decrease in Fe concentration at the outlet.

Fe and H⁺ contamination mitigated by flow from treatment system

- During the wet season, the outlet stream chemistry plots closer to that of the limestone channel (treatment system).
- Flow from treatment system ceases during dry season.
- During dry season, at low flow, the outlet chemistry more closely resembles that of contaminated water below the dam pool.

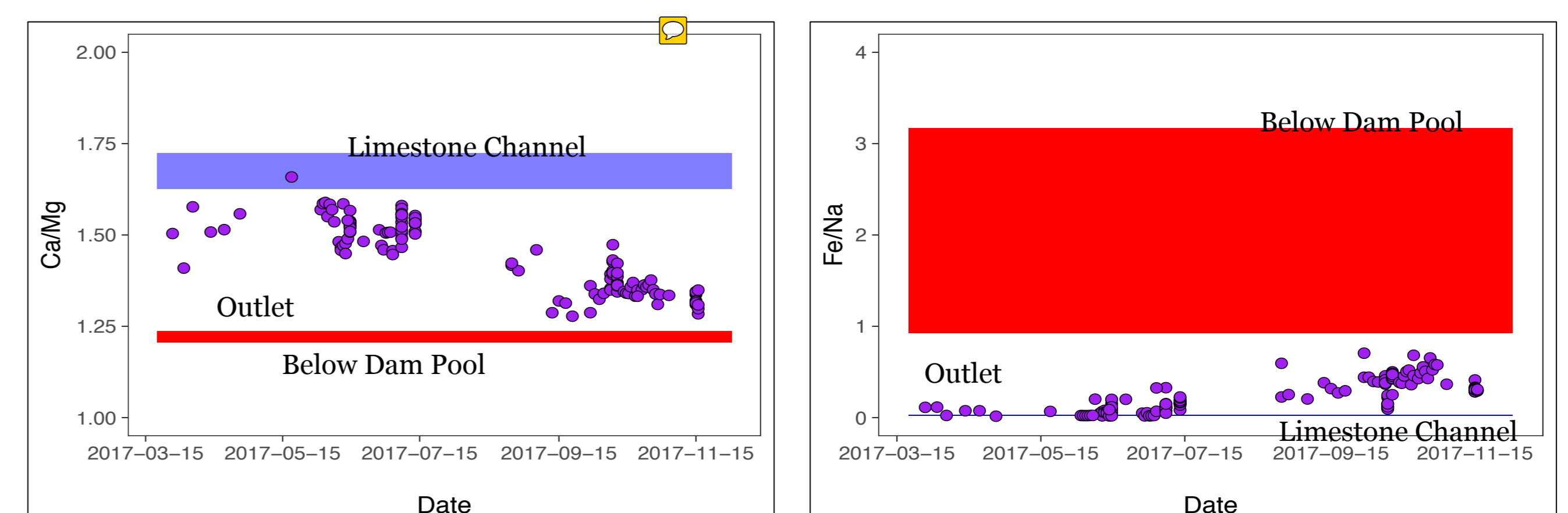


Figure 5: (top, left) Ratio of Ca to Mg versus date for the limestone channel (blue bar), stream below the dam pool (red bar), and outlet (purple circles). (top, right) Ratio of Fe to Na versus date for the limestone channel (blue line), stream below the dam pool (red bar), and outlet (purple circles). In both plots, the outlet chemistry mirror the limestone channel at the beginning of the year and then tends toward the contaminated baseflow at the end of the year.

Stream baseflow is contaminated by upwelling groundwater

- Concentration of contaminants decreases towards the surface indicating contaminated groundwater.
- Hydraulic head measurements indicate upwelling in the stream below the dam pool and, thus, the introduction of contamination to the surface streamwater.

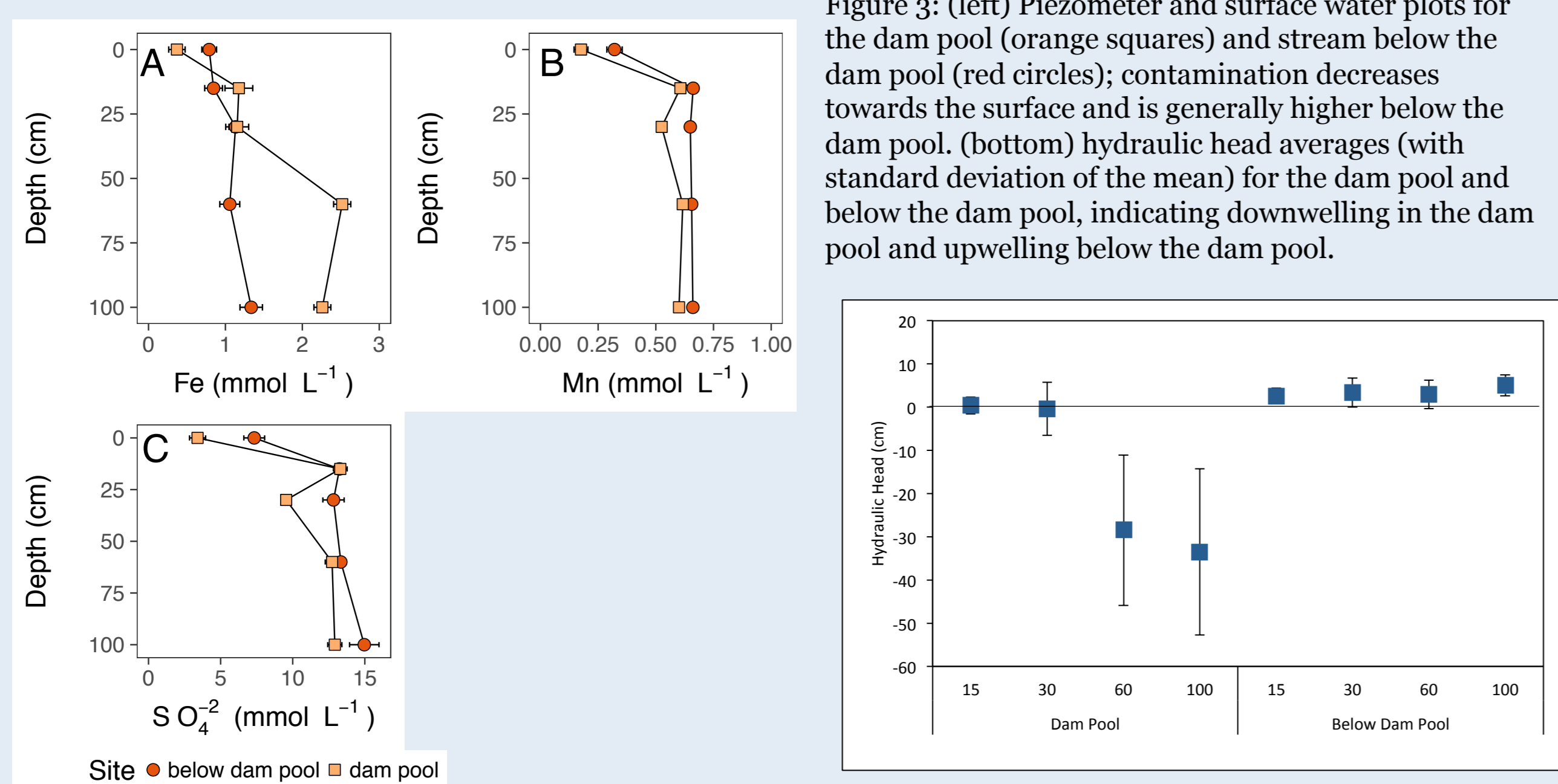


Figure 3: (left) Piezometer and surface water plots for the dam pool (orange squares) and stream below the dam pool (red circles); contamination decreases towards the surface and is generally higher below the dam pool. (bottom) hydraulic head averages (with standard deviation of the mean) for the dam pool and below the dam pool, indicating downwelling in the dam pool and upwelling below the dam pool.

Conclusions

- Stream baseflow is likely contaminated by upwelling groundwater near a beaver dam
- Baseflow contamination is mitigated by inputs from a treatment system, but the stream remains contaminated when flow from the treatment system decreases in dry periods
- Base cations and sulfate behave chemostatically while AMD-derived cations show dilution at the outlet due to mixing with treated water under high flow conditions
- Mixing and reactive transport control concentration-discharge behavior at the outlet

Acknowledgements and References

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