How Metal Partitioning Affects the Remediation Approach of a Mining-Impacted Watershed

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Contamination Sources in Abandoned Mining Sites

- More than half million abandoned mines in the U.S.
- Mining operations generate large amounts of ores and waste material which generally accumulate on site.
- Weathering of the mine waste (e.g. tailings, chat, etc.) produces acidic, metal-laden runoff (with both particulate and dissolved metals), which causes erosion.
- Mine site remediation is challenging due to the sites' locations, weather, and variable flowrates throughout the watershed.
- Even when waste piles are removed, they leave a new layer of exposed soil that may lead to more acidic runoff and metal transport.

Factors affecting metal transport

- Mineralogy of the mine waste.
- Chemistry of the water contacting the waste.
- Amount of water available (rainfall).
- Anthropogenic intervention.

Metal Partitioning

Metal partitioning is the distribution of a particular metal in the aqueous phase (dissolved) and in the solid phase (particulate). The particulate form can be present as a suspended solid or as a sediment.

Dissolved metals

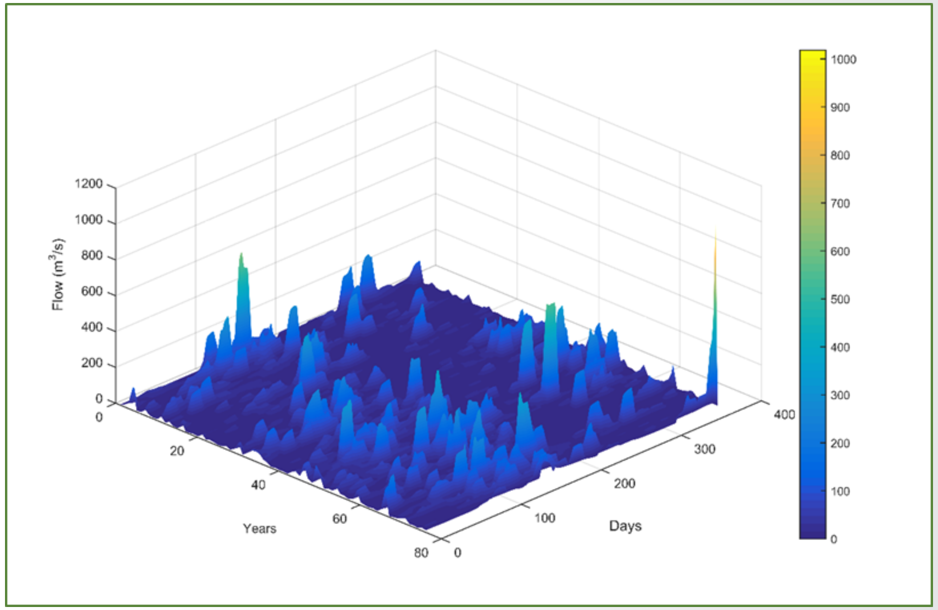
- Can be difficult to remove, typically require a water treatment plant.
- Require chemical/biological treatment to prompt their precipitation prior to being captured in a physical system.
- Adsorption in sorbent media could be effective for remediation.

Particulate metals

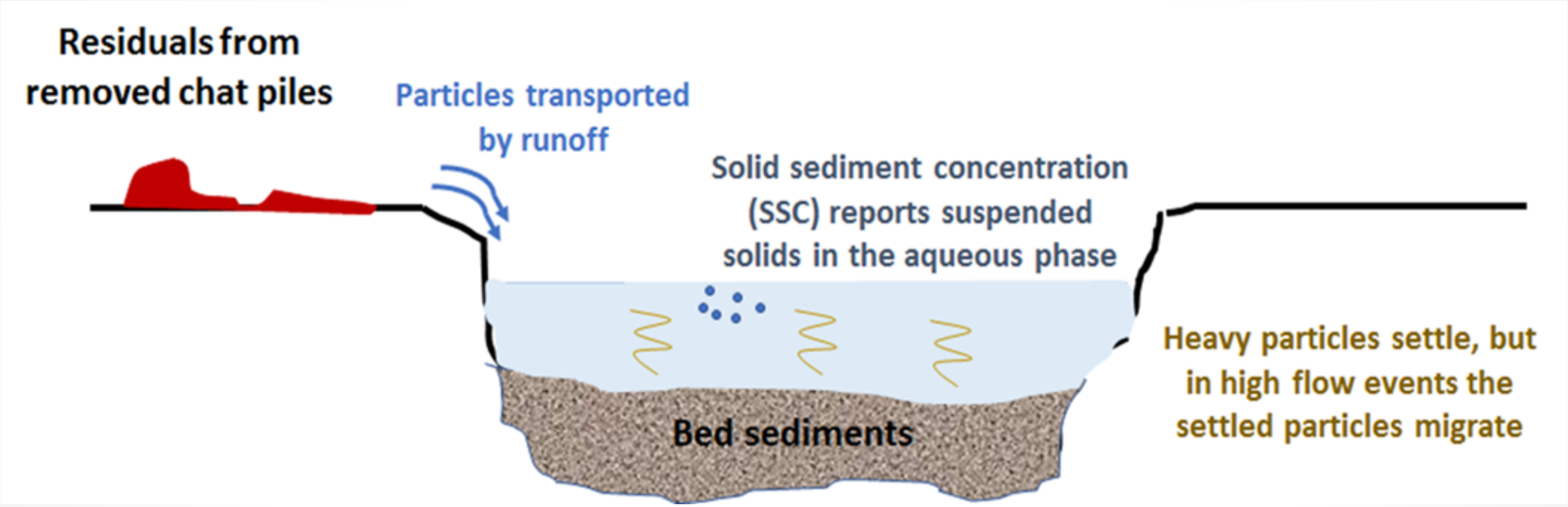
- Metal particles form aggregates and are adsorbed by bigger particles, often settling down.
- Tend to accumulate under low flow conditions forming streambed sediments.
- Physical barriers are usually the preferred best management practices (BMPs) for remediation.

Why do we need a large dataset?

- Measured parameters (metal content, flowrate, suspended sediment concentration, etc.) changes with time (due to weather, human impact, etc.) and collecting data during a long period in several points in a watershed in the only way to study the parameter's trends to make valid conclusions about remedial approaches.
- The more data we have, the smaller the error we manage, but also gives us more confidence in our assumptions.
- When we estimate the health of a watershed, we need to understand the main variables affecting the system and how these might change in the future.

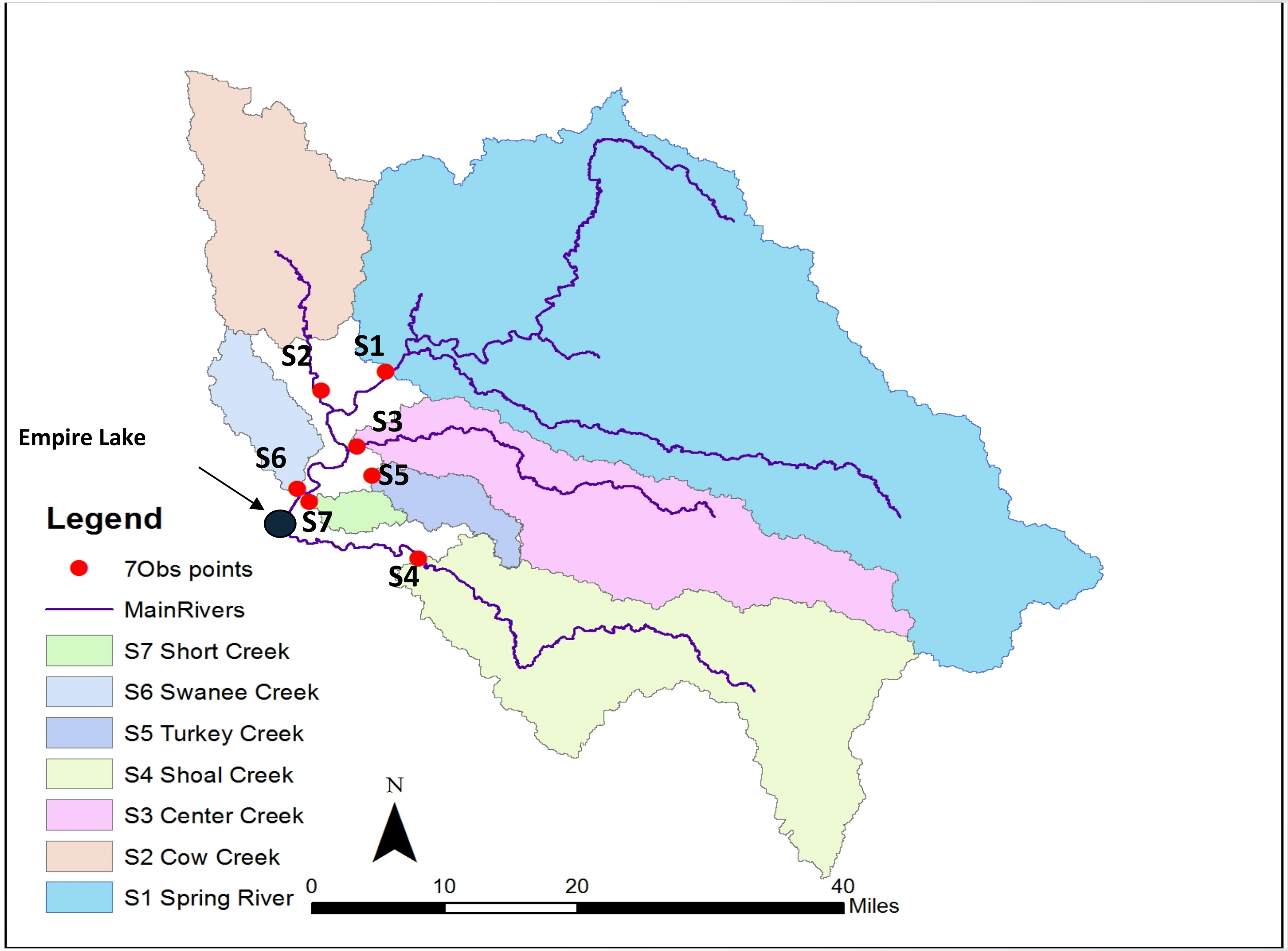


Metal transport in streams



- The metal concentration in streambed sediments are typically used to determine metal mobility and potential remedial actions, but it does not reveal the whole story about metal transport.
- Solid sediment concentration (SSC) is used to calculate sediment loading in streams, but it does not necessarily provides the metal transport trends in a watershed.
- The difference between total metal and dissolved metal concentrations in the aqueous phase are used to obtain the concentrations of metals in the suspended particles traveling in a stream.
- The use of these three parameters provide a more complete picture to make decisions about remedial actions.

Case Study: Zinc Transport in the Spring River Watershed (Missouri and Kansas)



Spring River Watershed Monitoring

Objectives

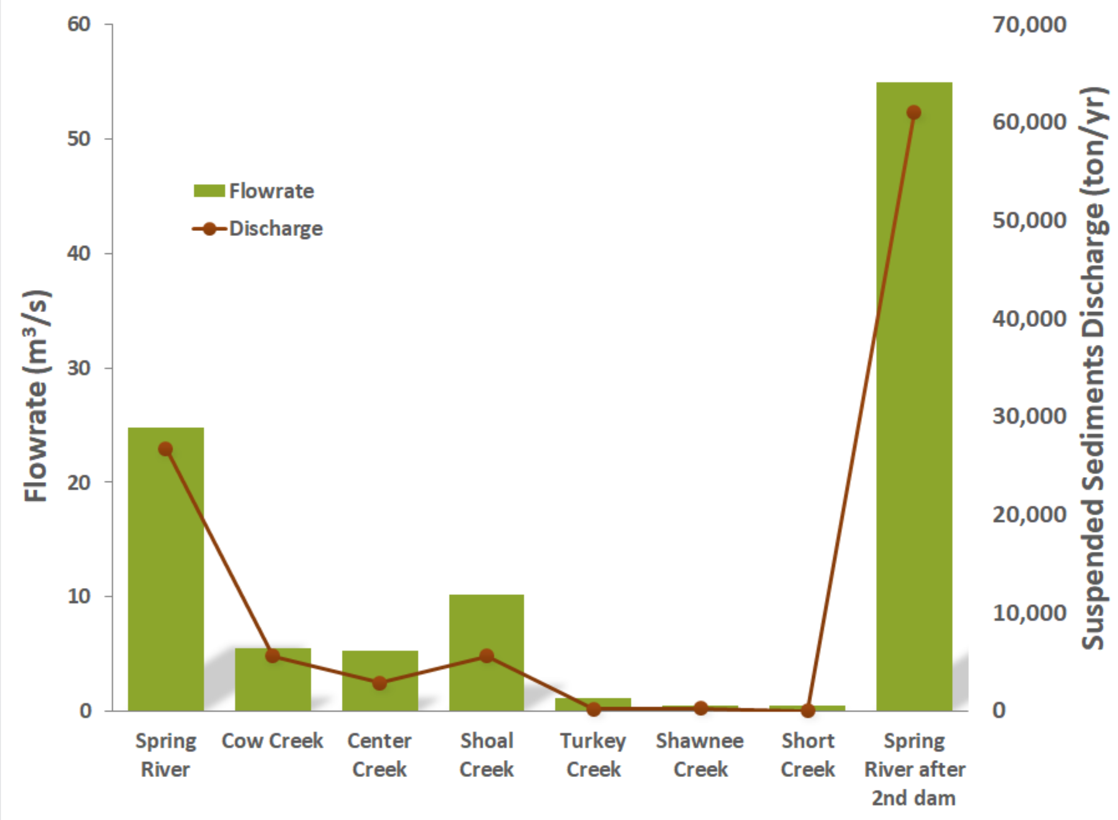
- To investigate the fate and transport of sediments and metals using 7 influent stations and 1 effluent station to Empire Lake
- To determine zinc transport in dissolved and particulate forms
- To recommend the effective BMPs for each stream

Scope

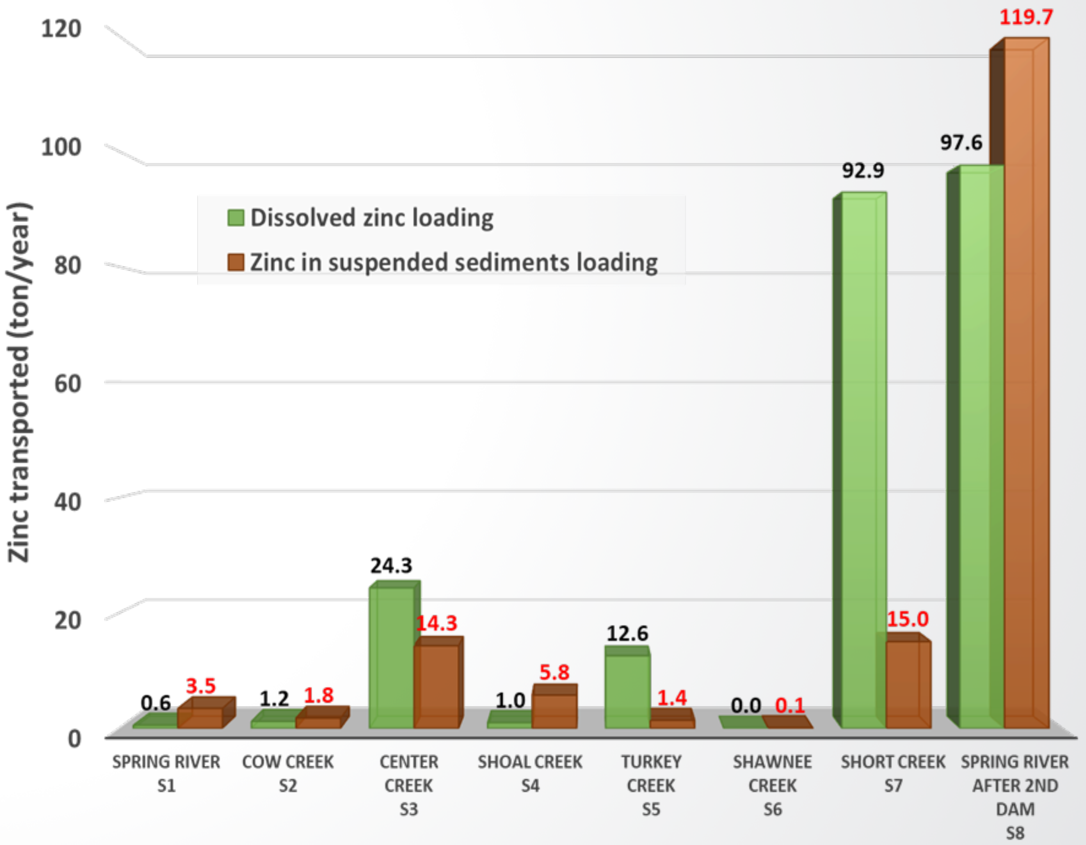
- Samples collected in all stations for total and dissolved metals in aqueous phase for a total of 5 years (2014 to 2018), after chat piles removal in the region
- Aqueous phase parameters: flowrate, suspended-sediment concentration (SSC), total metal and dissolved metal
- Solid phase parameters: metal content in streambed sediments

Suspended Solids and Zinc transport

Suspended sediments discharge and flowrate

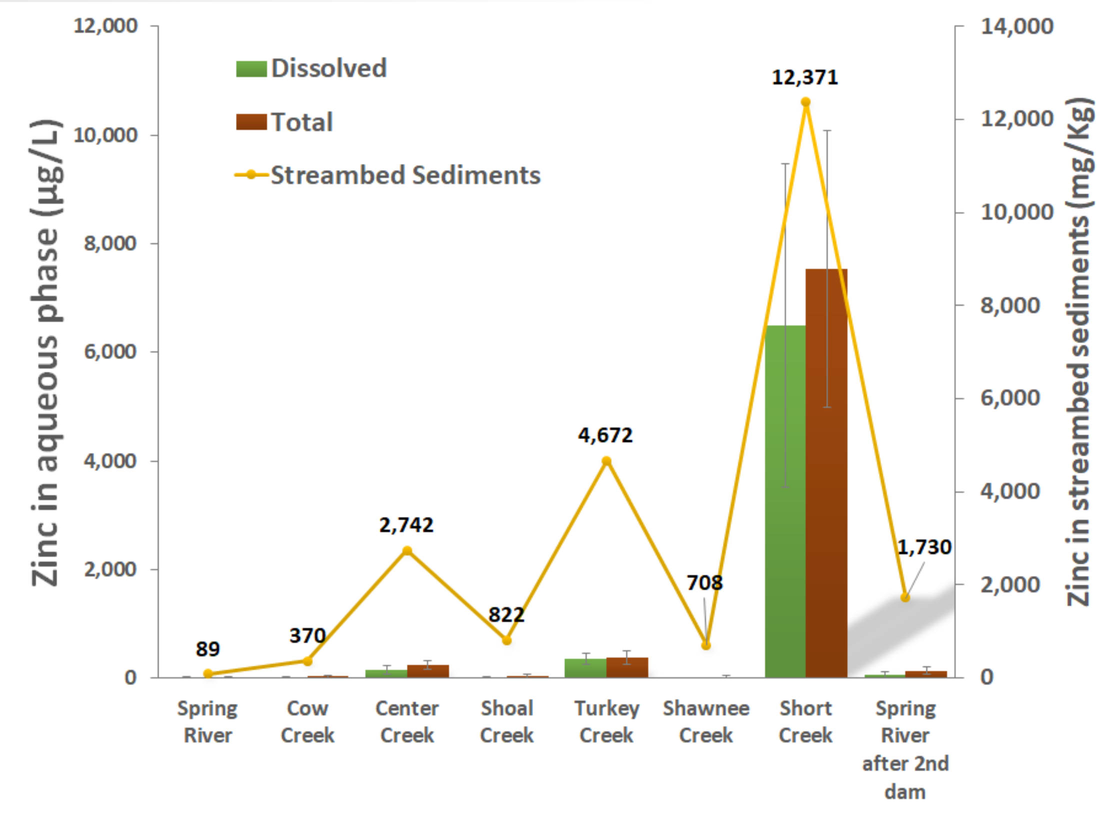


Zinc traveling dissolved and particulate

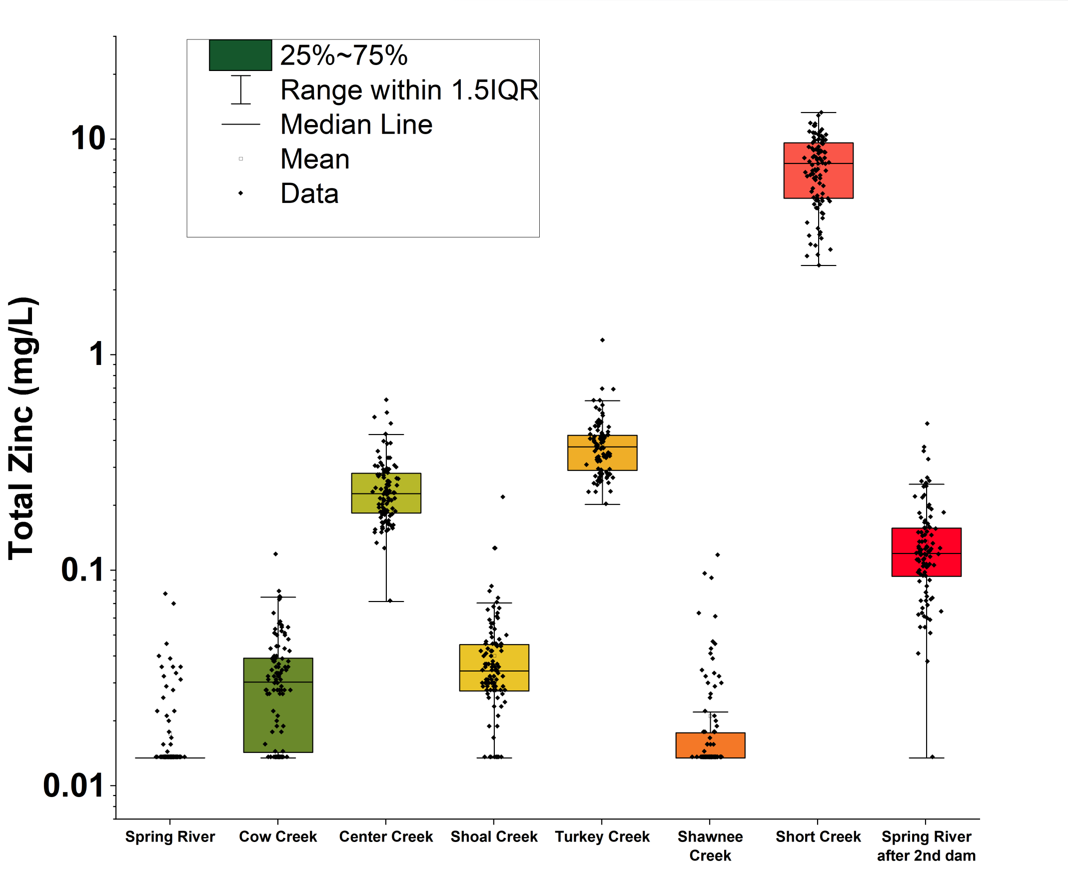


Suspended Sediments and Zinc in Water

Average total and dissolved zinc content

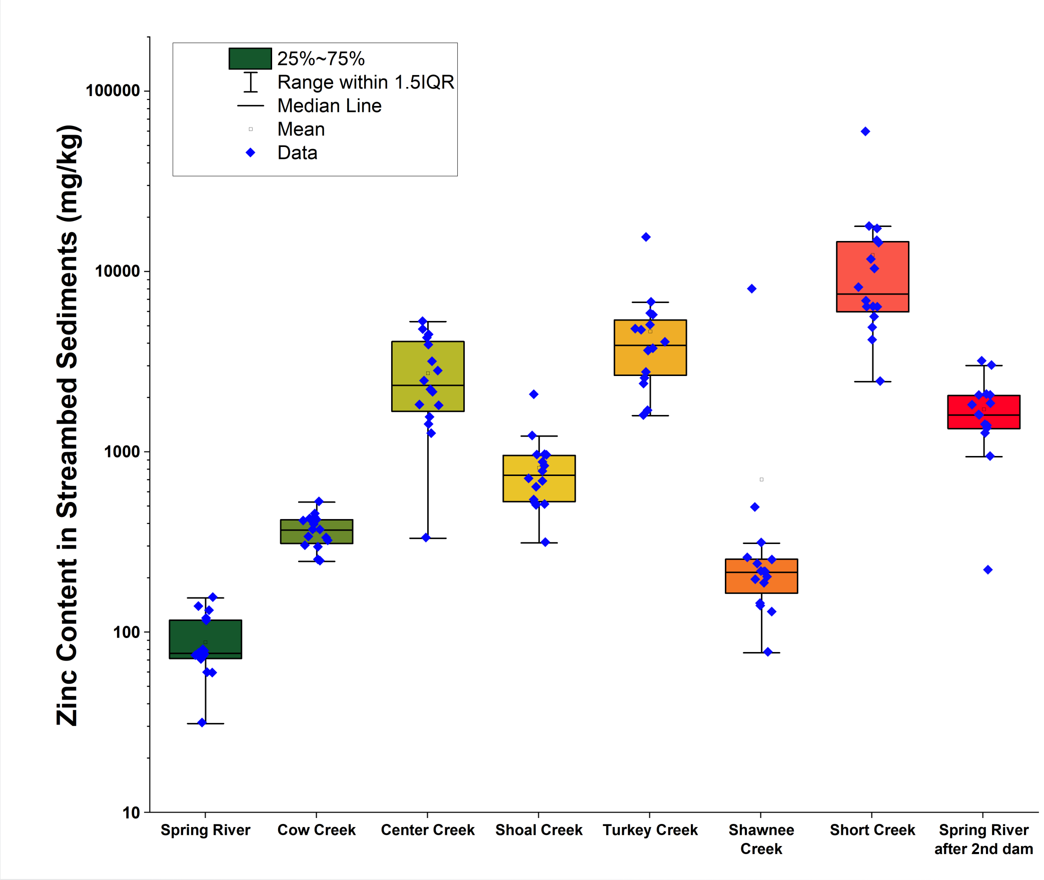


Total zinc variation in the streams

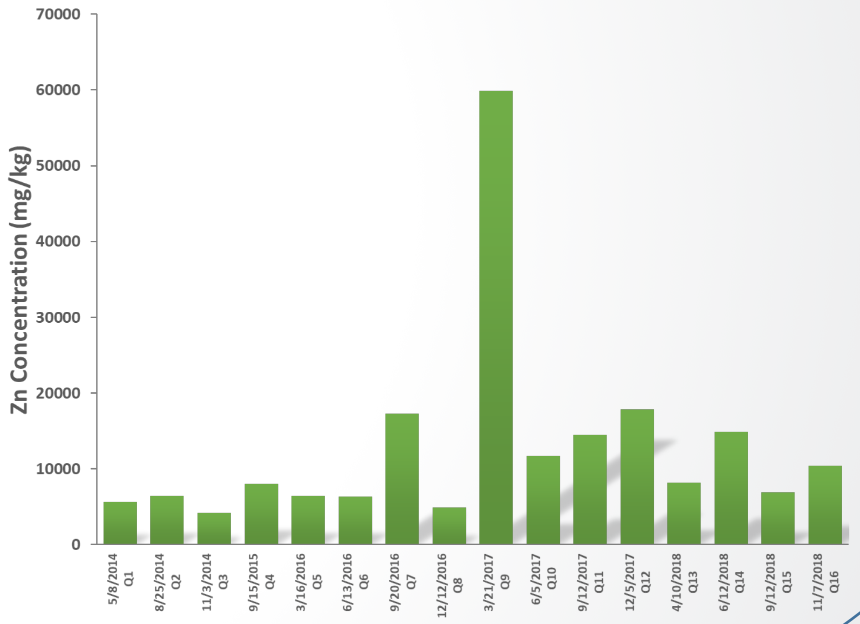


Zinc Content in Streambed Sediments

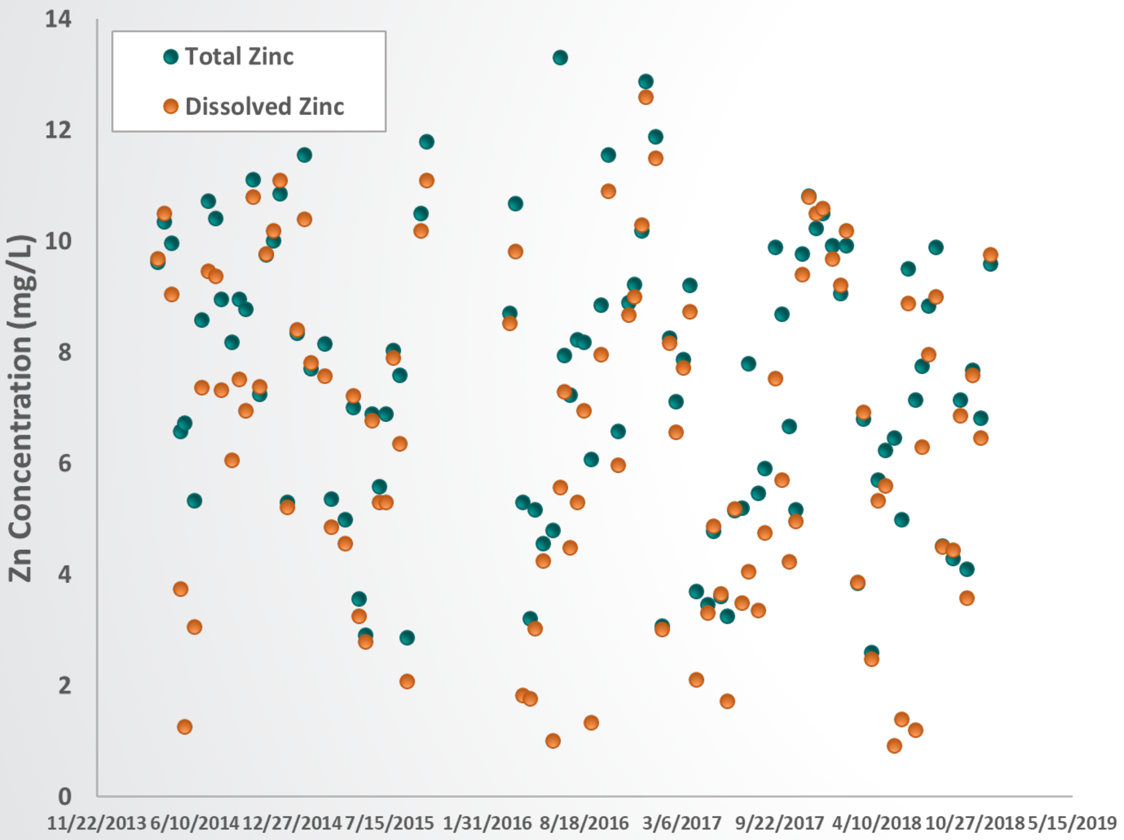
Zinc in all sampled stations

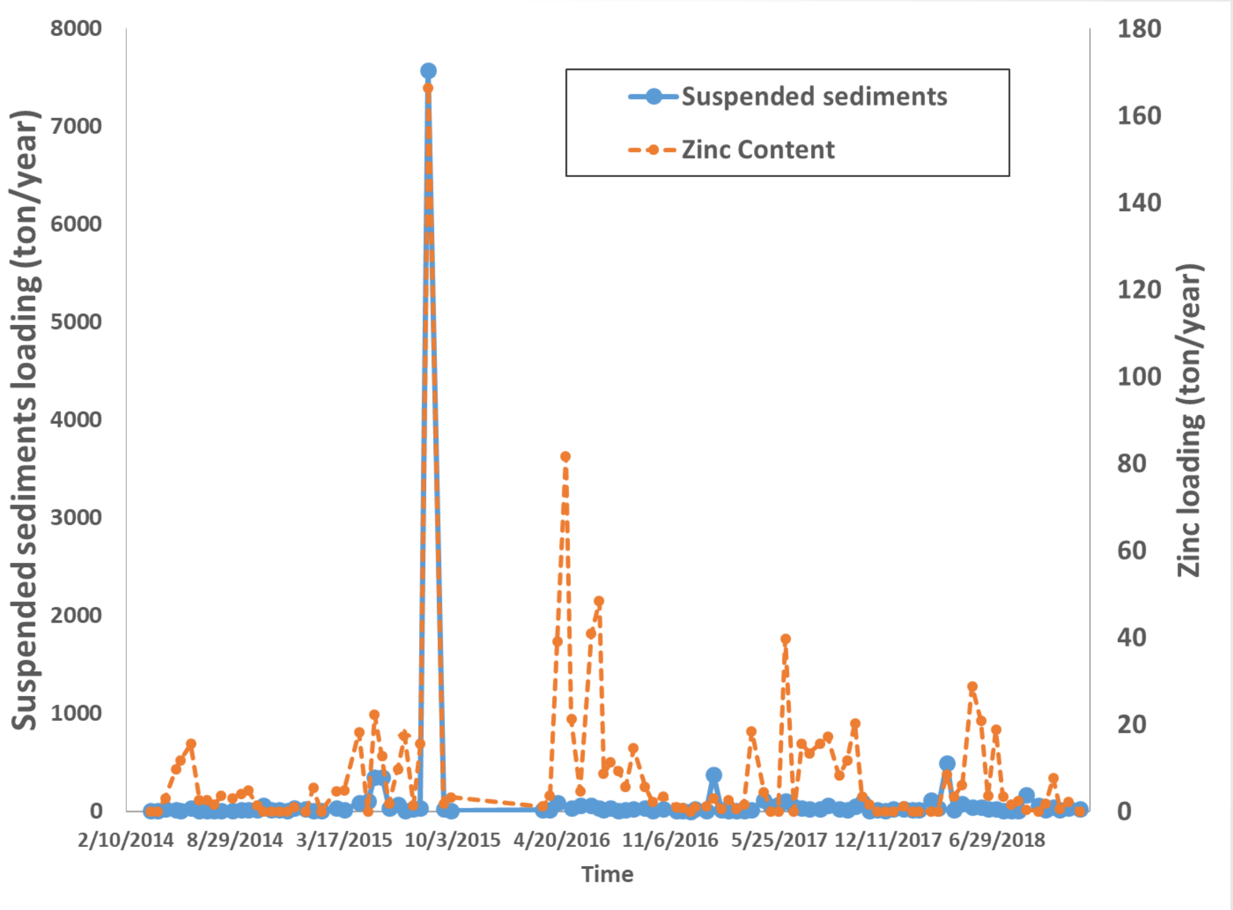


Example: Zinc content variation in Short Creek



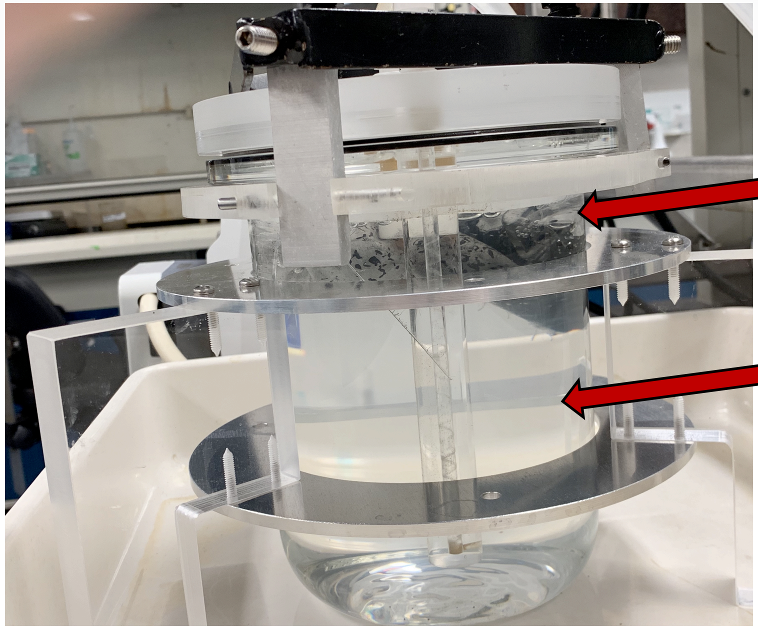
Zinc content in Short Creek water





Example: Short Creek BMPs

Treated Phase	Suggested BMPs	Justification
Aqueous phase	Adsorption onto phosphogypsum, mold, activated carbon, biochar, etc.	Total Zn~8 mg/L
Bed sediments	Sediments basin to capture fine particles	High Zn content in sediments ~13,000 mg/Kg, high zinc loading (17 ton/year)
Exposed surfaces in remediated areas	Revegetation, soil amendment with lime, biochar, compost, FGD, sediments from Empire Lake	To prevent erosion from contributing further contaminants into the creek



Bag filled with biochar

Short Creek Water

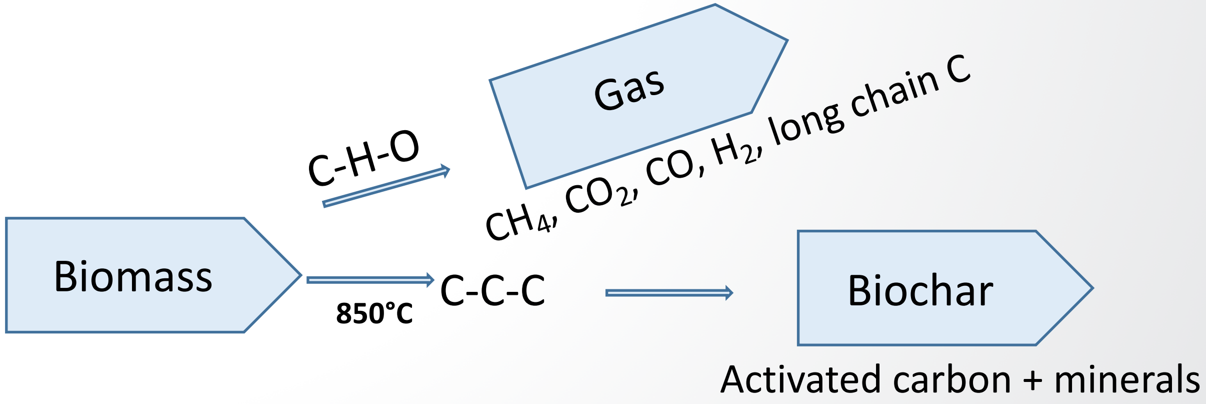
Using Sorbent Materials to Remove Zinc From a Water Stream (Tea-Bag Approach): The Test on Short Creek Water

Why Biochar?

Source: https://farmandlivestockdirectory.com/biochar-feds-states-could-help-it-live-up-to-its-soil-saving-potential/)

- Biochar is a granulated carbon product of the pyrolysis of cellulosic biomass (e.g. wood chips, corn stover, manure, rice hulls, etc.)
- It is commonly used as a soil amendment to increase fertility of acidic soils, but can also be used as a carbon sink and in water treatment

4 different types of biochar are being tested

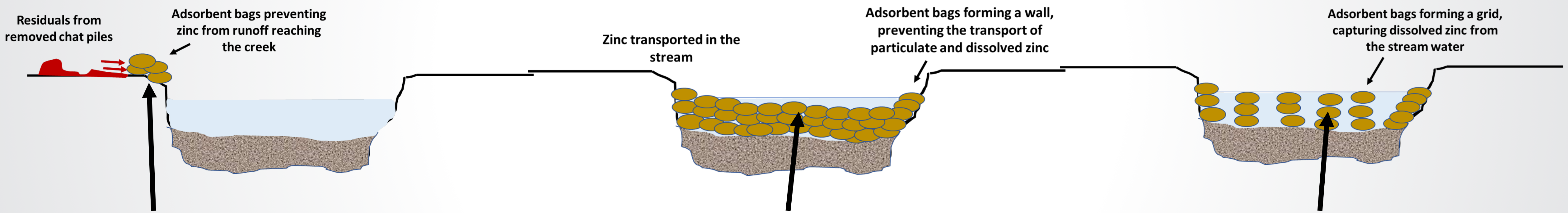


BMP Options: In-Situ Runoff and In-Stream Adsorption Bags (ISABs)

Runoff capture barriers

Adsorbent wall

Submerged cartridges grid



ISABs bags interrupting runoff contamination reaching the creek

ISABs forming a wall blocking further metal transport

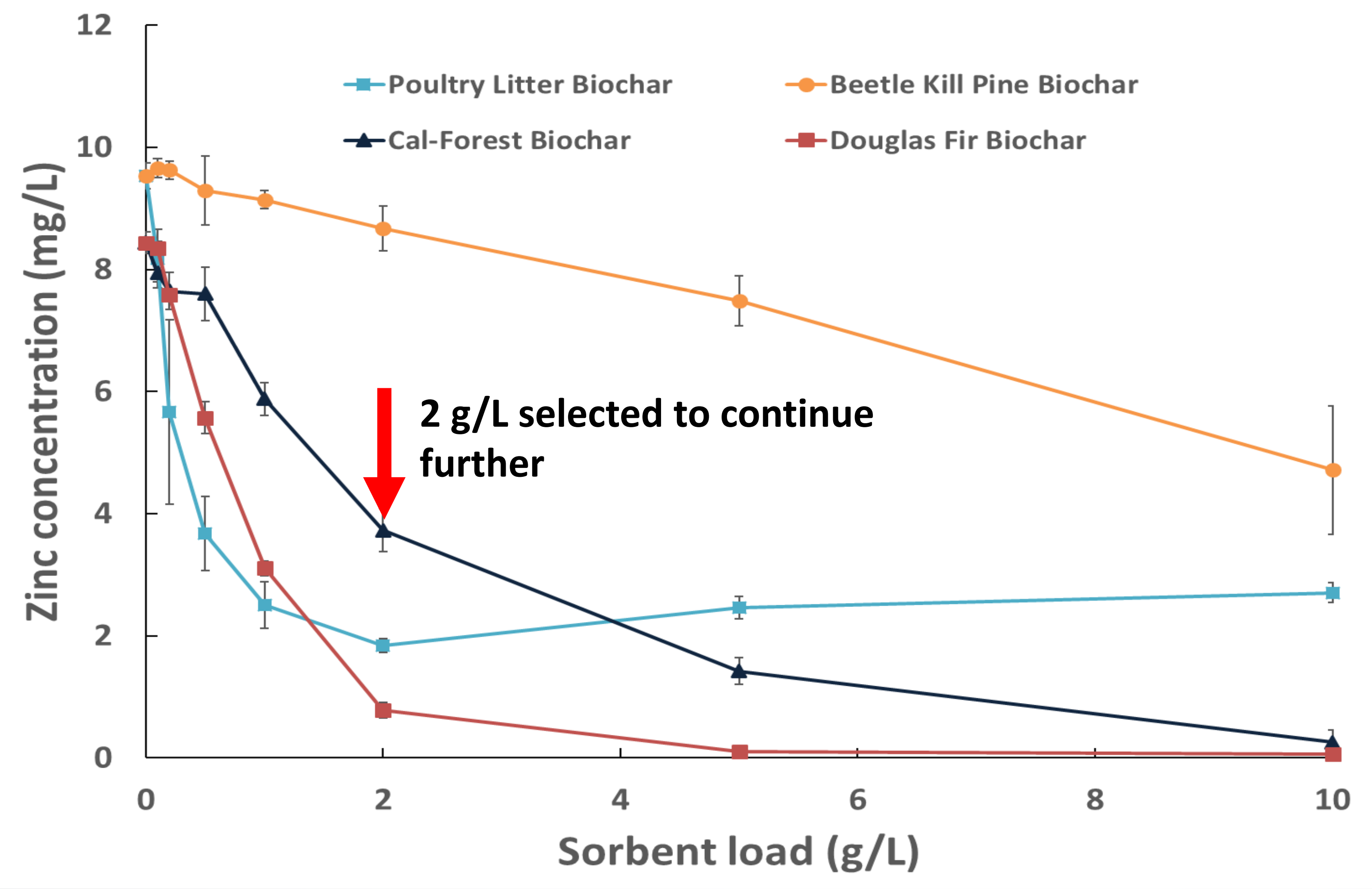
ISABs forming a grid capturing dissolved zinc

Biochar is effective at entrapping particulate metals while adsorbing dissolved metals

Characteristics of Used Biochars

Product	Douglass fir biochar	Beetle kill biochar	Cal Forest Biochar	Poultry Litter Biochar
Matrix Source	Douglas fir wood	Beetle kill pine wood	Coniferous tree wood	Poultry litter
Bulk density (kg/L)	0.077	0.166	0.134	0.584
Porosity (%)	29.8	38.3	43.8	43.1
Surface Area (m^2/g)	475	250	722	4.2

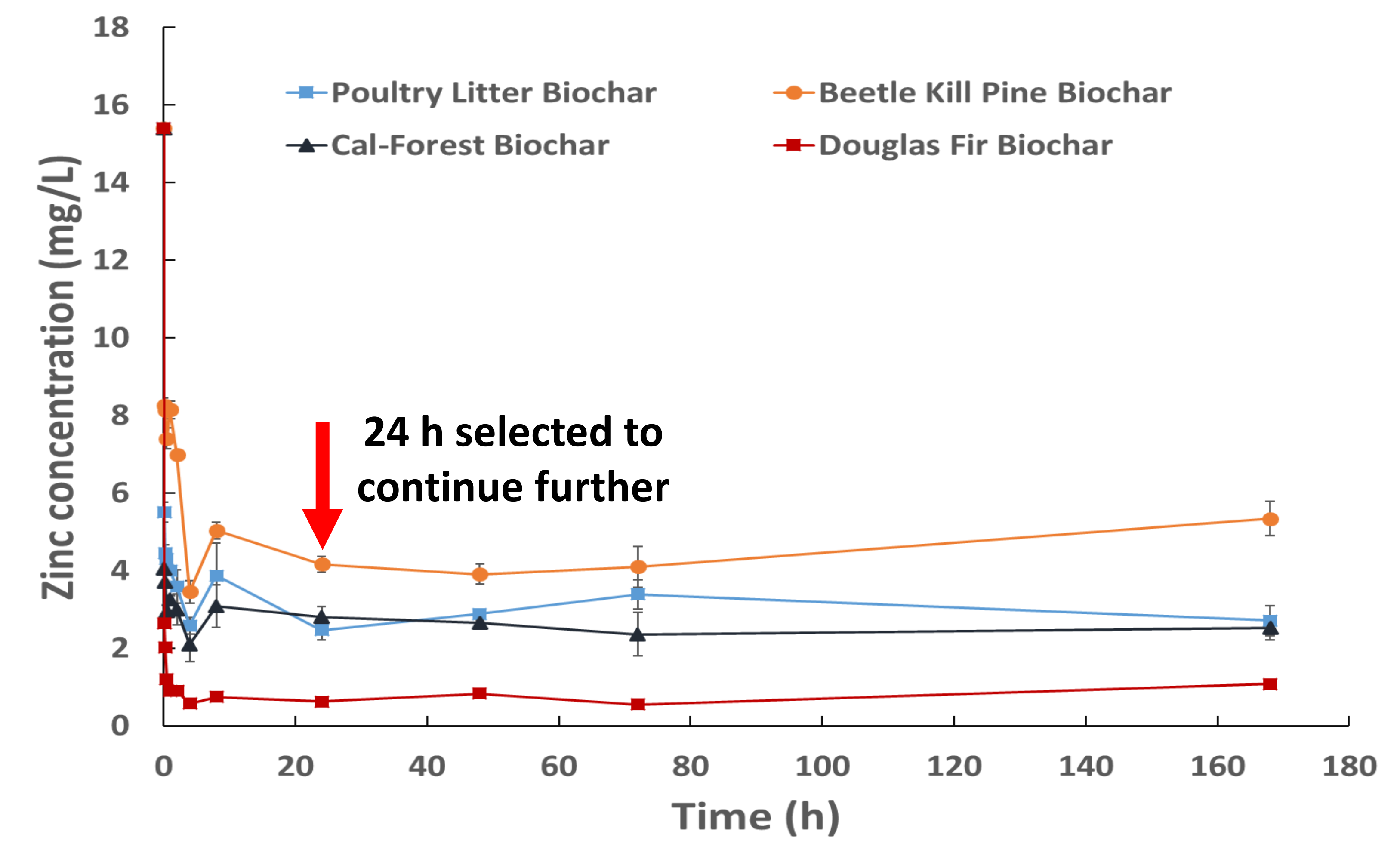
Adsorption Test: Sorbent Load



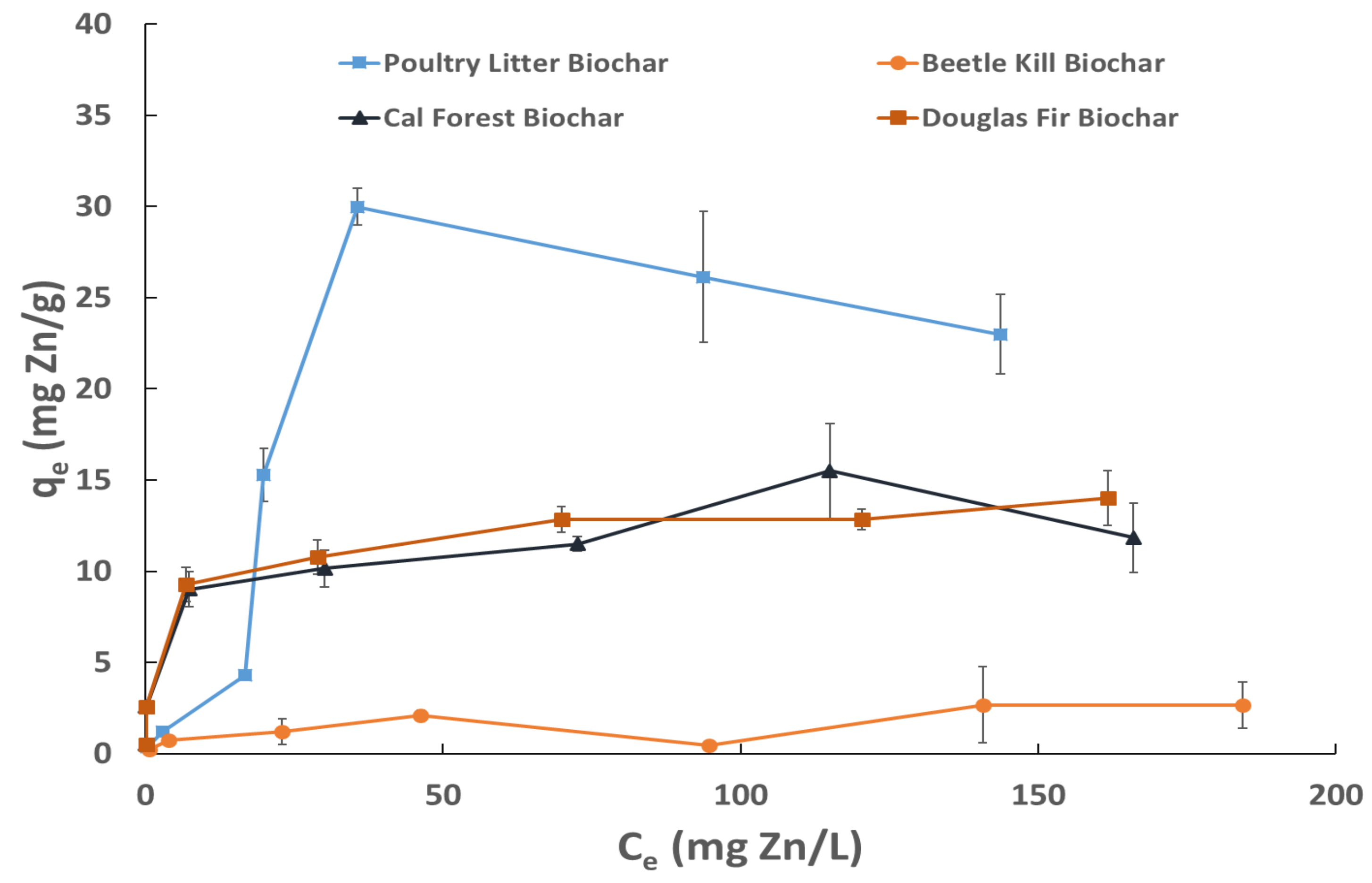
At 2 g/L loading	Final pH
Poultry Litter Biochar	8.40
Beetle Kill Pince Biochar	8.40
Cal-Forest Biochar	7.87
Douglas Fir Biochar	8.40

- Initial pH 7.1 for all
- The higher the sorbent load, the higher the metal removal, as expected

Adsorption Tests: Kinetic Test



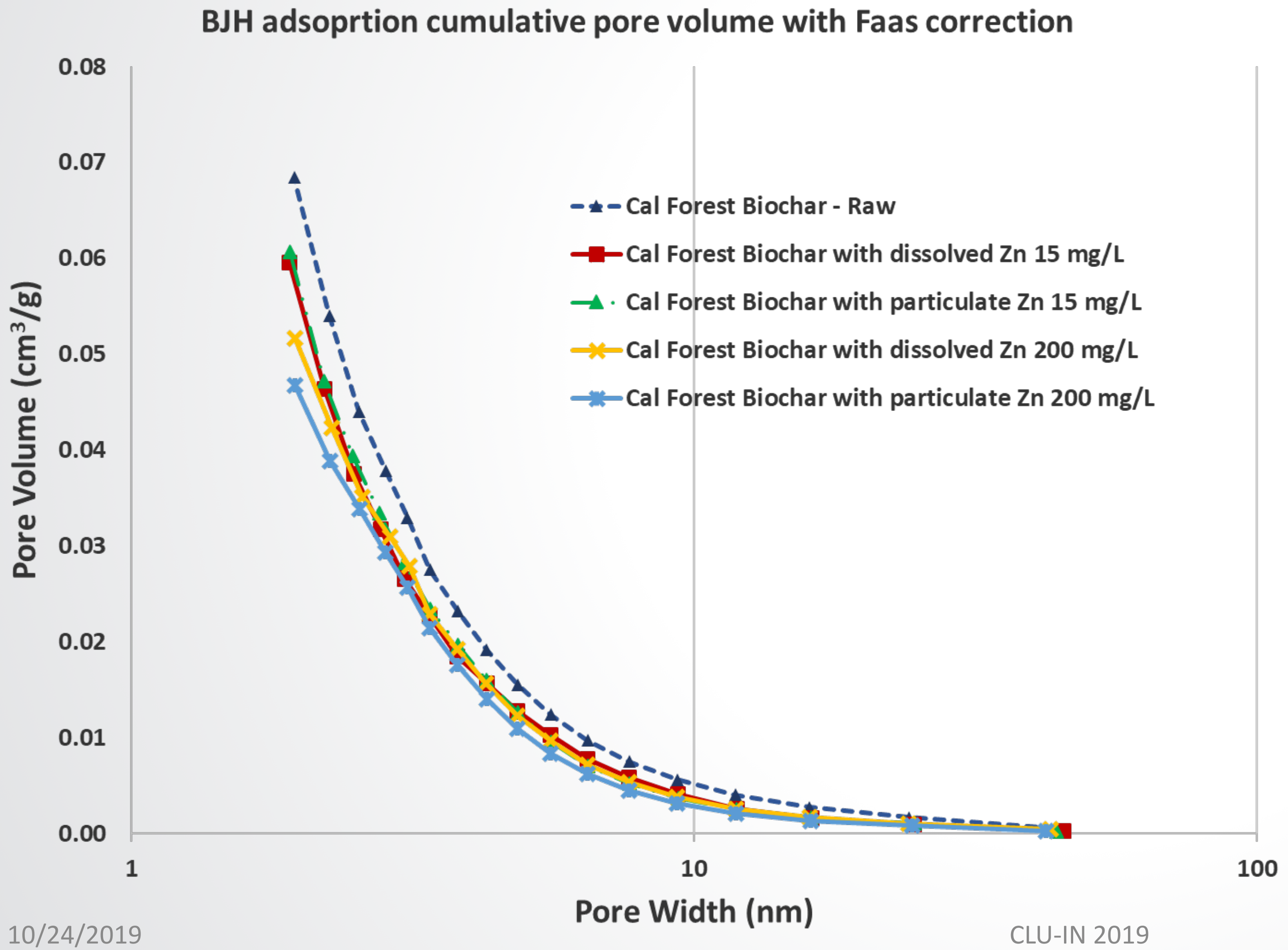
Adsorption Capacity Test (Isotherms)



C_e is the concentration at equilibrium (24 h)
C_o is the initial zinc concentration (0 h)
q_e is the amount of zinc adsorbed at equilibrium
V is the volume of solution (50 mL)
m is the mass of the adsorbent utilized

$$q_e = (C_o - Ce)V/m$$

Pore volume reduction due to zinc adsorption



Cal Forest Biochar:
Surface area = 732 m^2/g
Micropore area = 387 m^2/g

Zinc form	pH	Concentration	Δ Pore Volume
None	NA	0 mg/L	0
Dissolved	4	15 mg/L	-24.6%
Particulate	10	15 mg/L	-24.1%
Dissolved	5	200 mg/L	-35.7%
Particulate	9	200 mg/L	-33.3%

Conclusions

Zinc transport in a watershed

- The use of the three complementary datasets (streambed sediment, sediments loadings, and metal content in the streams) allows a wider picture for BMPs selection.
- Dissolved metals are suspected to be associated with active sources (unremoved chat piles or metal-laden exposed soil), but confirmation is needed by soil analyses.

Zinc adsorption on biochar

- Douglas Fir Biochar (second highest surface area) was the product with the highest rates of zinc removal, followed by Cal Forest Biochar (highest surface area) and Poultry Litter Biochar.
- Cal Forest Biochar reduction in pore volume showed that adsorption plays an important role in zinc removal.
- Metal removal by adsorption onto biochar can be useful in mining-impacted water remediation of particulate and dissolved metals.

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