United States Environmental Protection Agency

257th ACS National Meeting
Orlando, Florida
Mar 31- Apr 4 2019

Biogeochemistry of the treatment of mining-impacted water in mining legacy sites: integrating aqueous phase and solid phase analyses to elucidate efficiencies and mechanisms

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Mining-Impacted Water (MIW)

- There are above half million abandoned mines in the U.S. (46,000 of these identified in public lands)

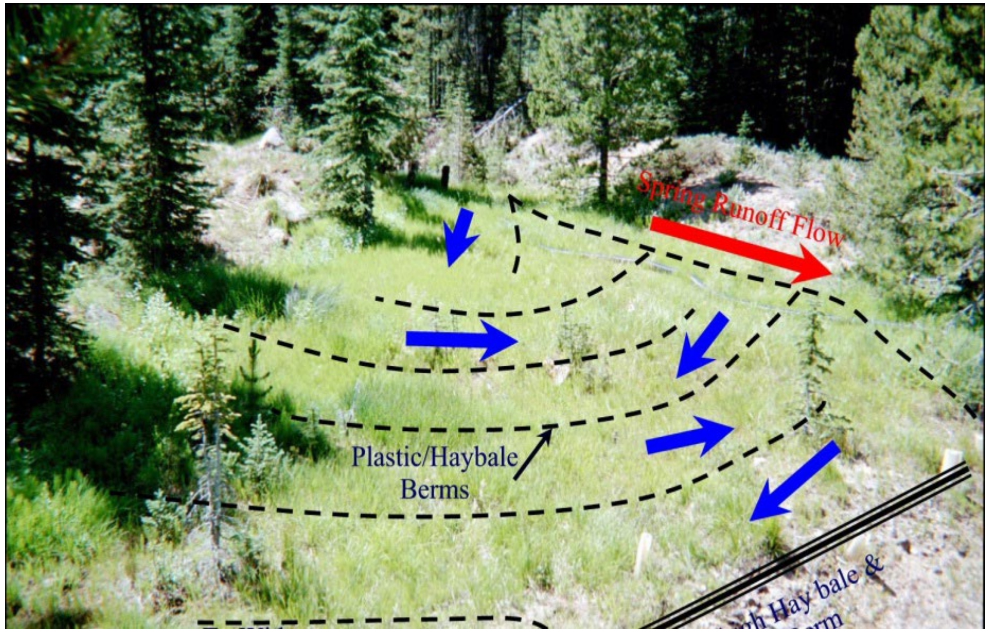
- Acidic MIW is formed when iron sulfides are oxidized through a series of chemical and biological processes to sulfates allowing metal dissolution from mine waste

$FeS_2\,(s) + 15/4\ O_2 + 7/2\ H_2O \longleftrightarrow 4H^+ + 2SO_4^- + Fe(OH)_3\,(s)$

- MIW remediation is challenging due to sites location, weather and variable flowrates

Active and Passive Systems

- Passive Systems: require minimal inputs of resources once in operation
- Active Systems: require continuous input or resources to sustain the process – site accessibility is a key factor



Underground SRBR at the Peerless Jenny King site, MT

Image taken from www.waterworld.com

MIW Remediation

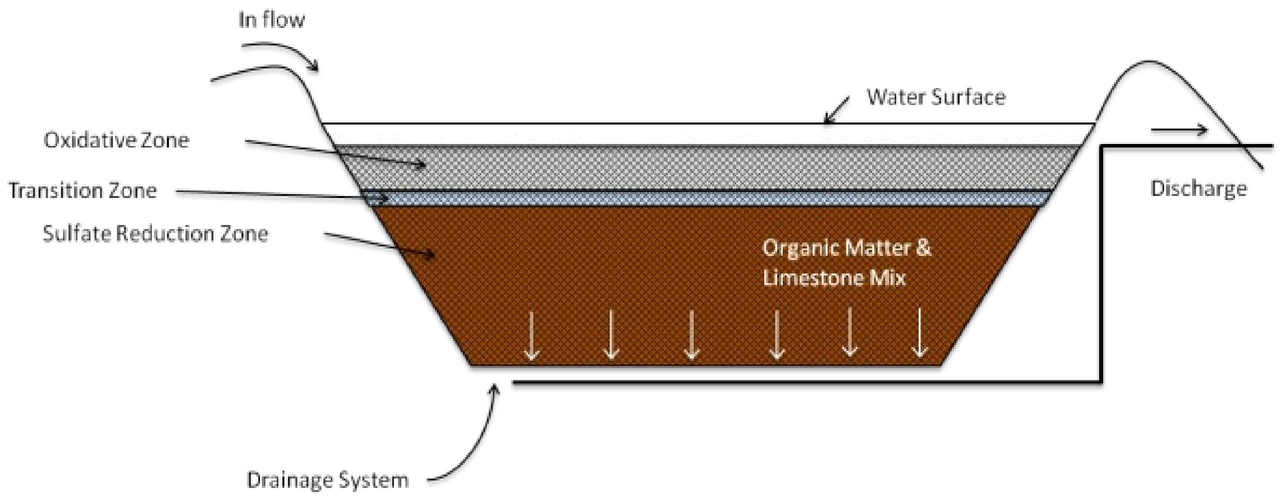
- Anaerobic sulfate reduction:

$$SO_4^{2-}{}_{(aq)} + 2CH_2O_{(aq)} \rightarrow H_2S_{(aq)} + 2HCO_3^-{}_{(aq)} \quad (1)$$

$$M^{2+}{}_{(aq)} + H_2S_{(aq)} \rightarrow MS(s)\downarrow + 2H^+{}_{(aq)} \quad (2)$$

Where $M^{2+} = Zn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}$ and CH_2O represents the substrate

- Other metallic cations precipitate as hydroxides (e.g., Fe^{3+}, Cr^{3+}, Al^{3+}), (bi-) carbonates (e.g. Fe^{2+}, Mn^{2+}), or co-precipitate with the generated sulfides



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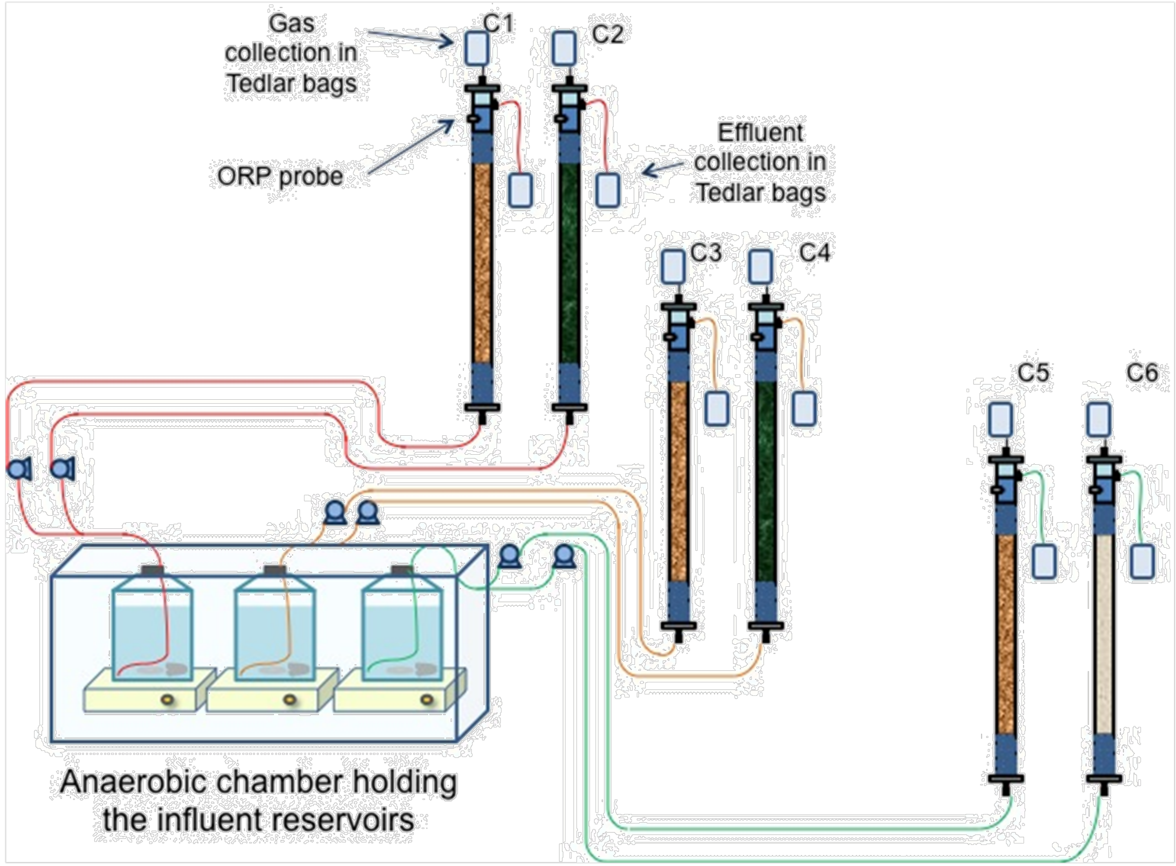
Case Study I: Formosa Mine Water Treated and Untreated

Parameter	Untreated Influent	Pretreated Influent
pH	2.5	6.62
Al (mg/L)	16.7	<0.095
As (mg/L)	<0.036	<0.036
Cd (mg/L)	0.29	0.25
Cu (mg/L)	16.6	0.10
Fe (mg/L)	28.4	<0.105
Pb (mg/L)	0.08	<0.017
Zn (mg/L)	74.3	49.6

- **Al, Cu, and Fe were effectively removed from the Formosa water by the pretreatment**
- **Zn concentration also decreased with pretreatment**
- **Since the water was aerated, it was necessary to purge the influent bottle with nitrogen to reduce dissolved oxygen prior to feeding it to the bioreactor**

Anaerobic Bioreactors using SRB



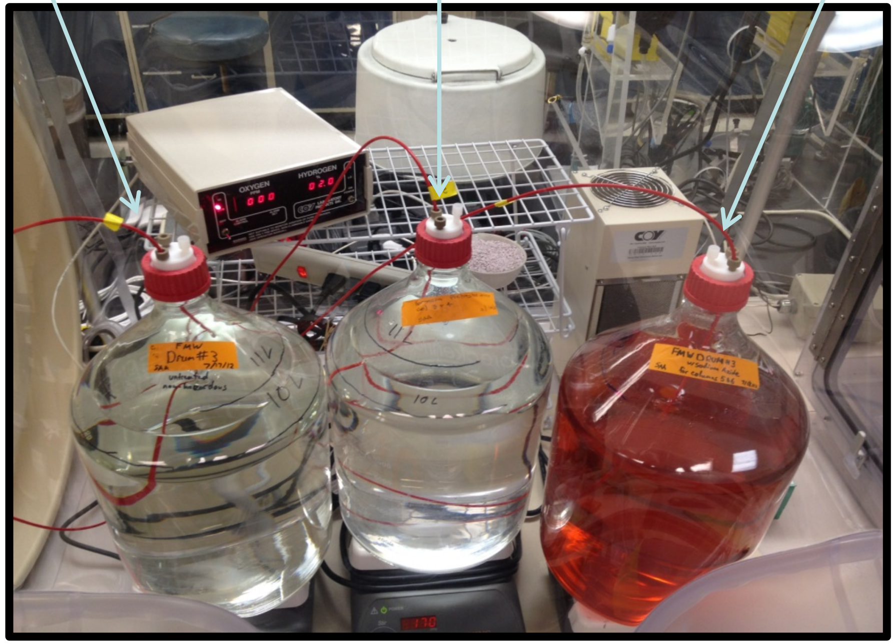
Two different substrates, same carbon loads

- 140 g Chitin (SC-20) = 31.9 g Carbon in columns 1, 3, and 5
- Wood chips (253 g) + hay (17 g) + manure (4 g) = 31.9 g Carbon in columns 2 and 4
- Column 6 was a sand-filled control

Period	Days 1-119	Days 120-458
HRT (h)	90	45
Flowrate (mL/h)	3.7	7.4

Anaerobic Bioreactors: Influent Reservoirs

Untreated FMW	Pretreated FMW	Untreated FMW with Sodium Azide
• Column 1 • Column 2	• Column 3 • Column 4	• Column 5 • Column 6

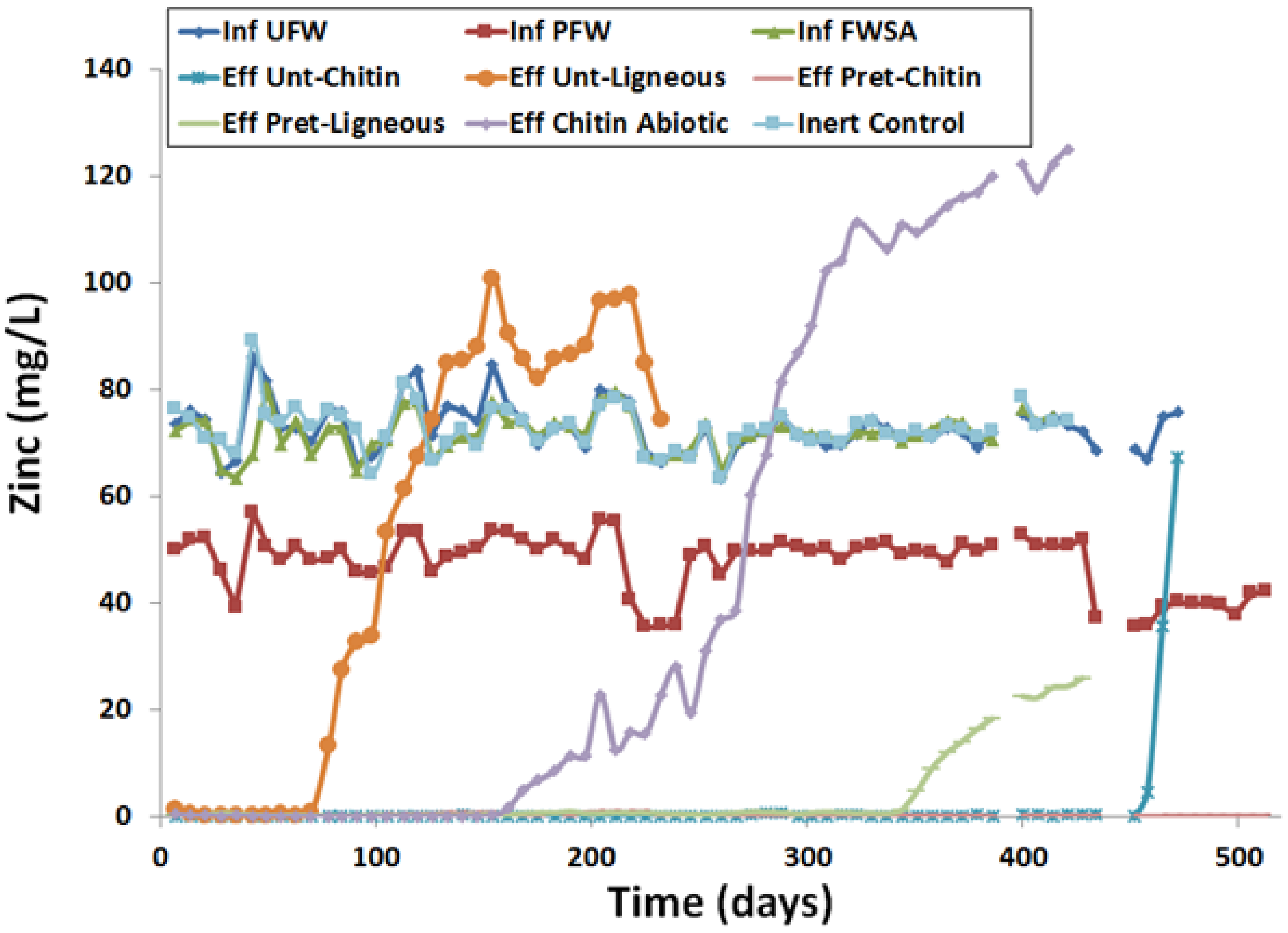


- All influent reservoirs were kept in an anaerobic chamber to maintain low dissolved oxygen
- Sodium azide was added to Columns 5 and 6 to prevent microbial growth, those served as 'abiotic controls'

Anaerobic Bioreactors: Zinc Removal

- The chitin substrate columns performed better for Zn removal

- The biomass helped to obtain a better performance in Zn removal (column Pretreated chitin had the longer operational period)



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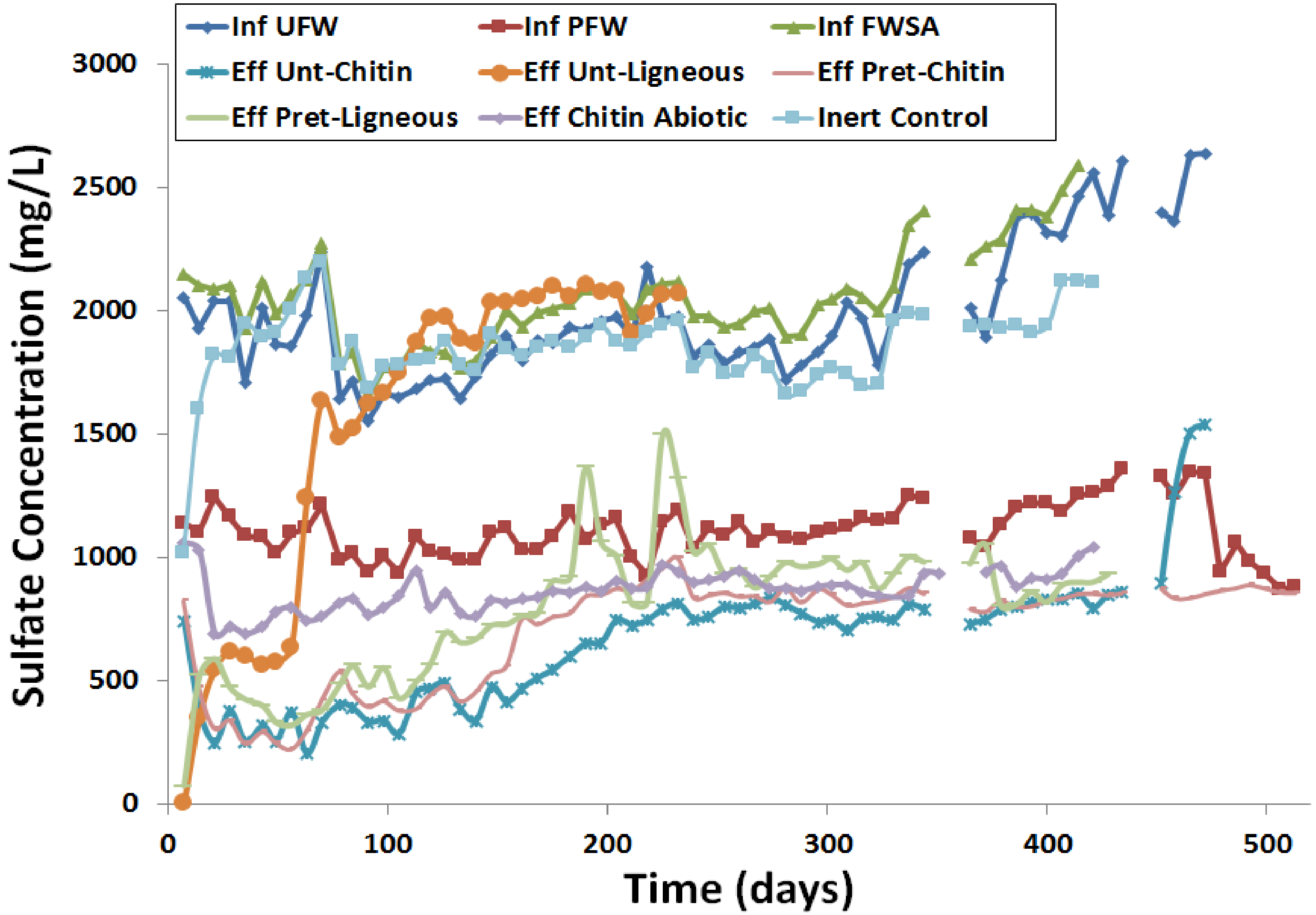
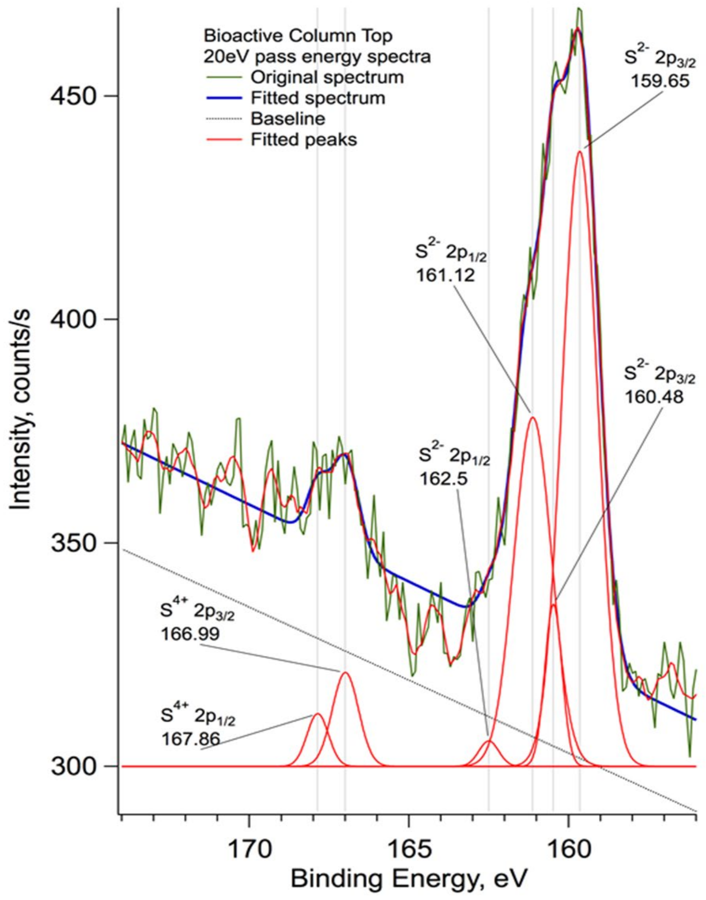


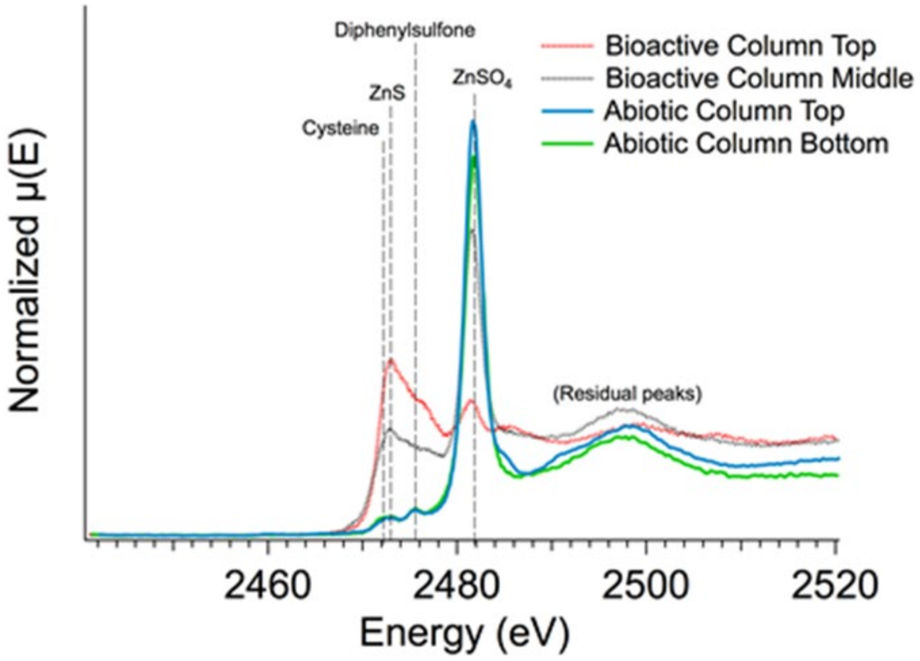
Anaerobic Bioreactors: Sulfate Removal

- The chitin substrate columns removed higher amounts of sulfate
- The SRB generated higher removal rates in the bioactive columns, but the chitin abiotic had better removal than the ligneous columns in the long term

Zinc Speciation in the Solid Residues



XPS spectral fitting in the Bioactive Column

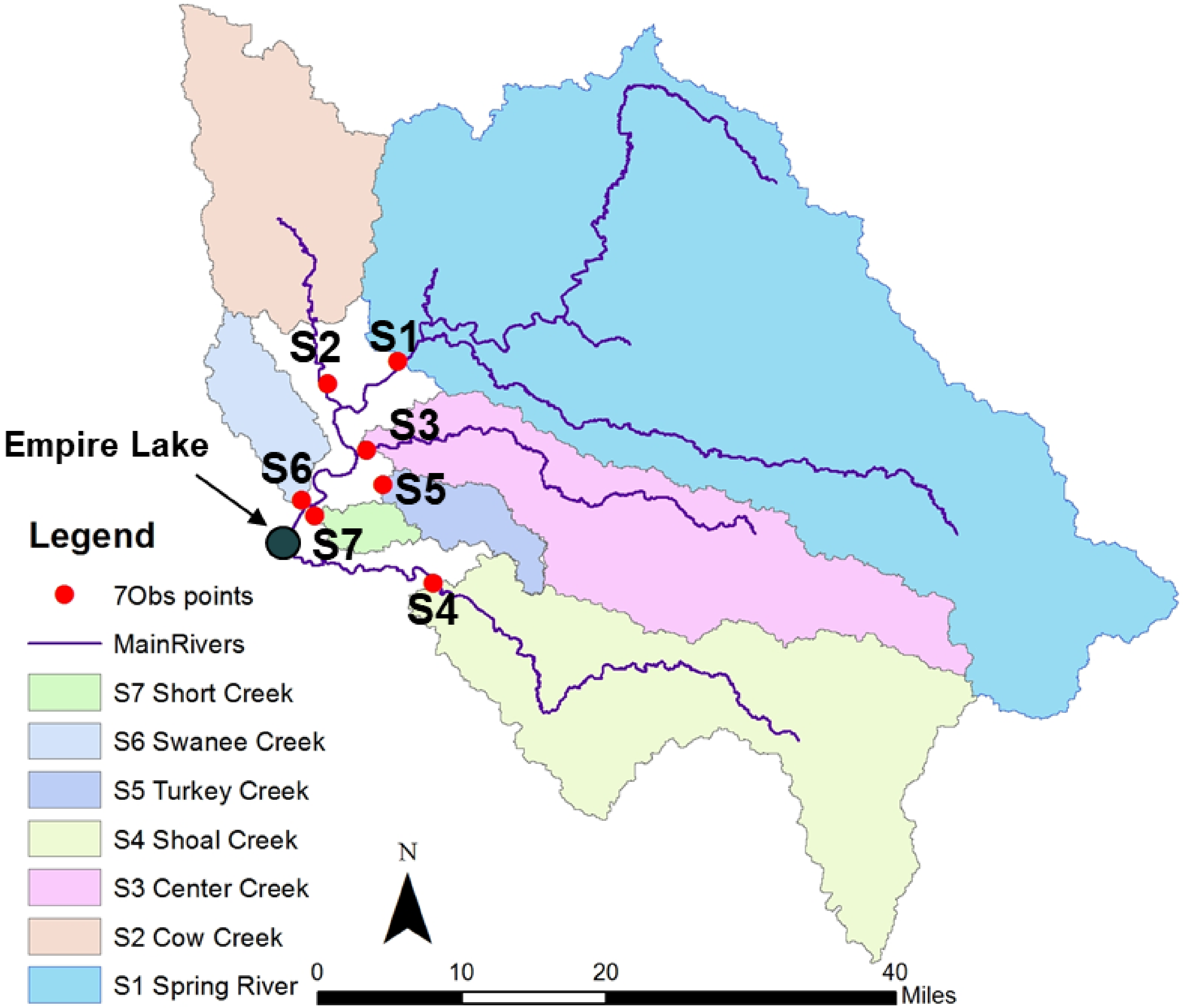


XANES spectra of the experimental solid residues

- **Sulfur found as sulfide (S^{2-}) by the XPS in the bioactive column**
- **Zinc associated with sulfur as ZnS in the bioactive column at higher level than the abiotic column**

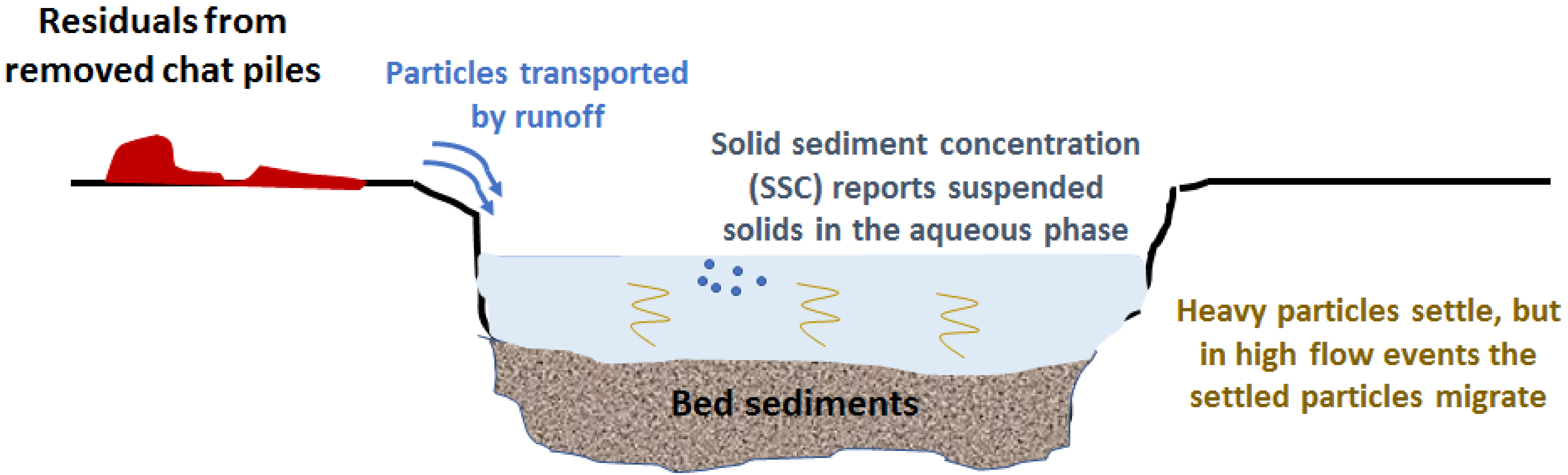
Aqueous Phase and Solid Phase Integration Conclusions

- Aqueous phase contained ~2,000 mg/L of sulfate, none of sulfide.
- Sulfide was predominant in the solid phase samples of the bioactive column analyzed by XPS. Hence, the metal removal mechanism was proven to be sulfate reduction to sulfide.
- The XANES spectra revealed ZnS and $ZnSO_4$ as the main peaks in the bioactive solid residues, but only $ZnSO_4$ in the abiotic column. Since $ZnSO_4$ is soluble, adsorption played an important role in zinc removal, but the SRB were able to reduce and precipitate zinc, increasing the substrate's capacity.
- The integration of aqueous phase and solid phase analyses provided data to make a better decision about the substrate composition, allowed to quantify the actual sulfide reduction, and validated the proposed zinc removal mechanisms.



Case Study II: Metal Speciation in Contaminated Sediments at Short Creek

Contaminants Migration in the Watershed



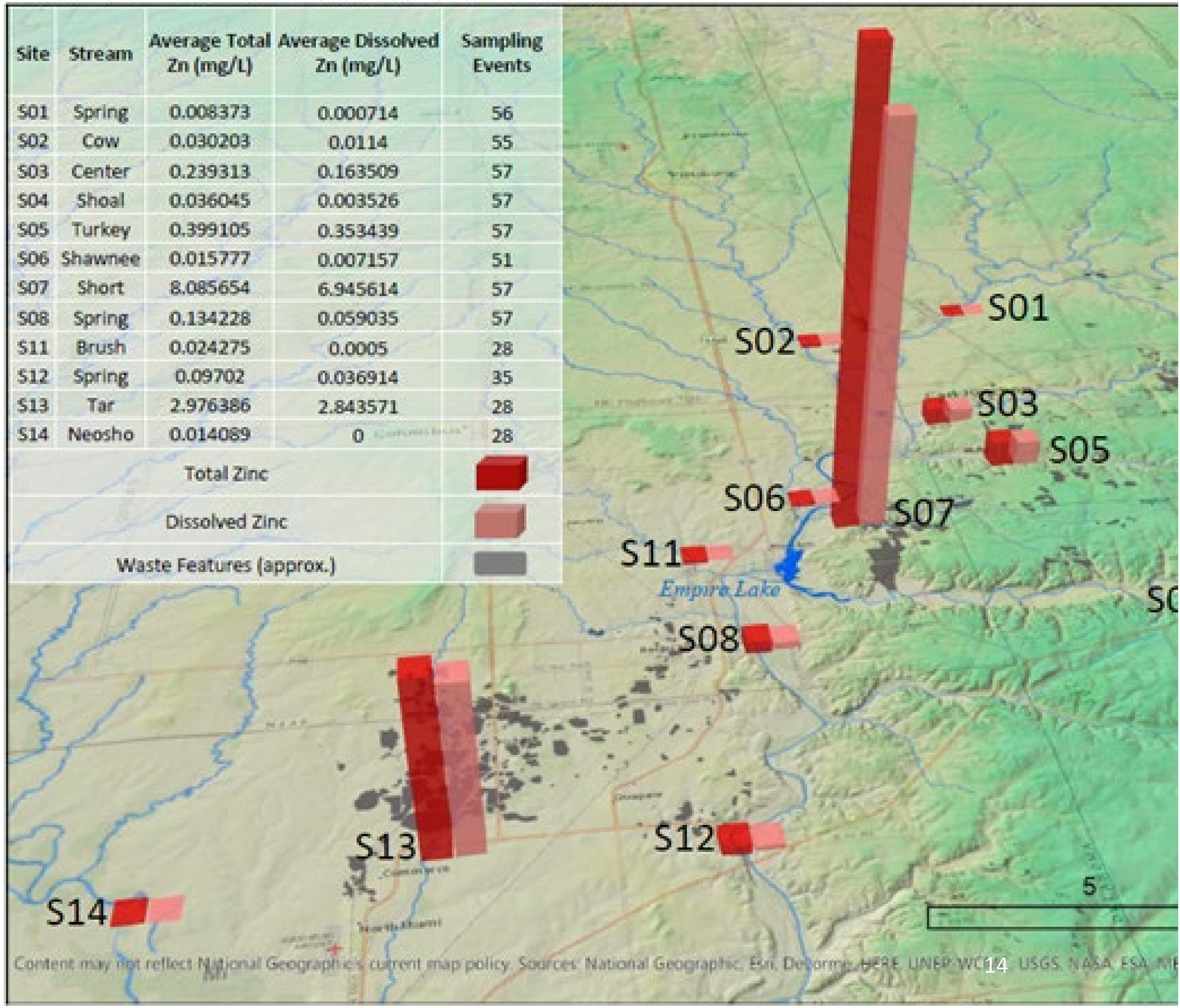
***Zinc was the main contaminant found in the chat, in the aqueous phase, in the suspended matter and in the bed sediments**

Zinc Contamination Found in the Aqueous Phase Samples

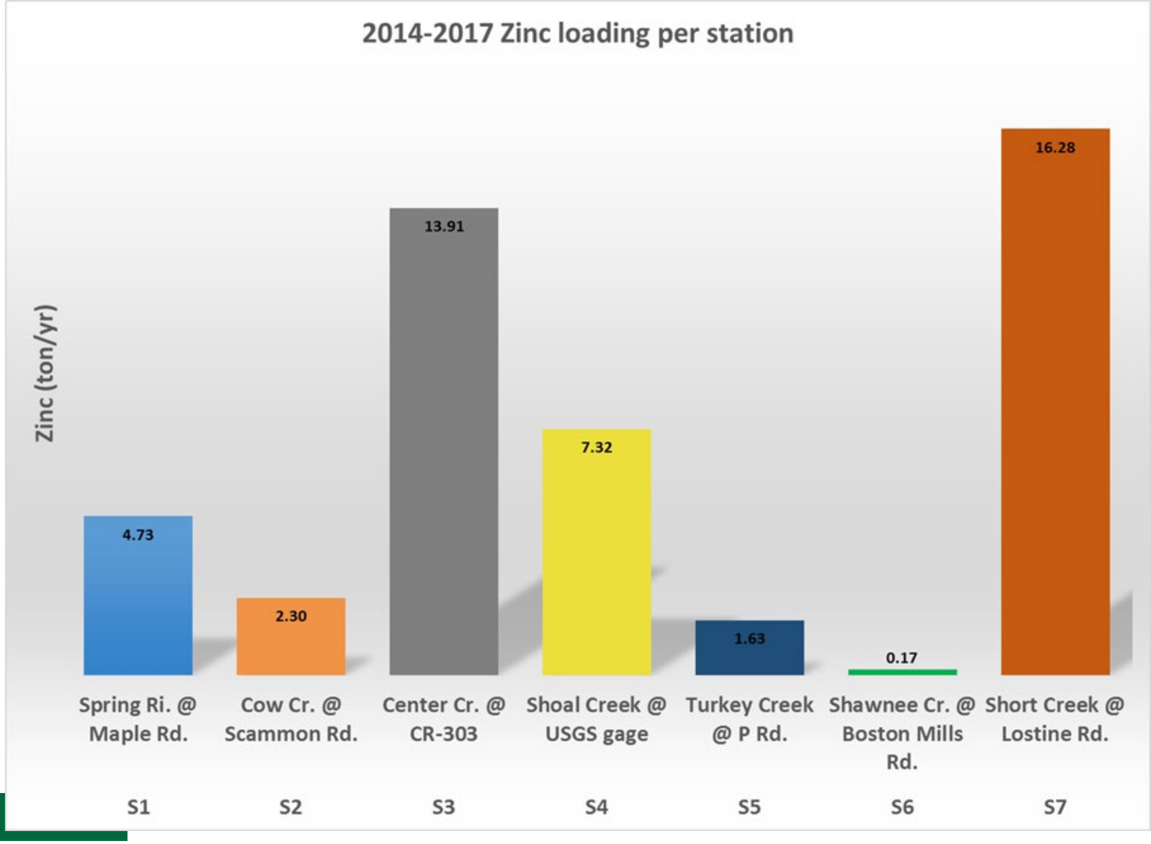
- Short Creek (S7) is part of the Spring River Watershed, which leads into Empire Lake
- Mine waste (chat) around the creek is the source of contamination as dissolved and particulate zinc
- Among all seven tributaries, Short Creek had the highest dissolved and total zinc concentrations

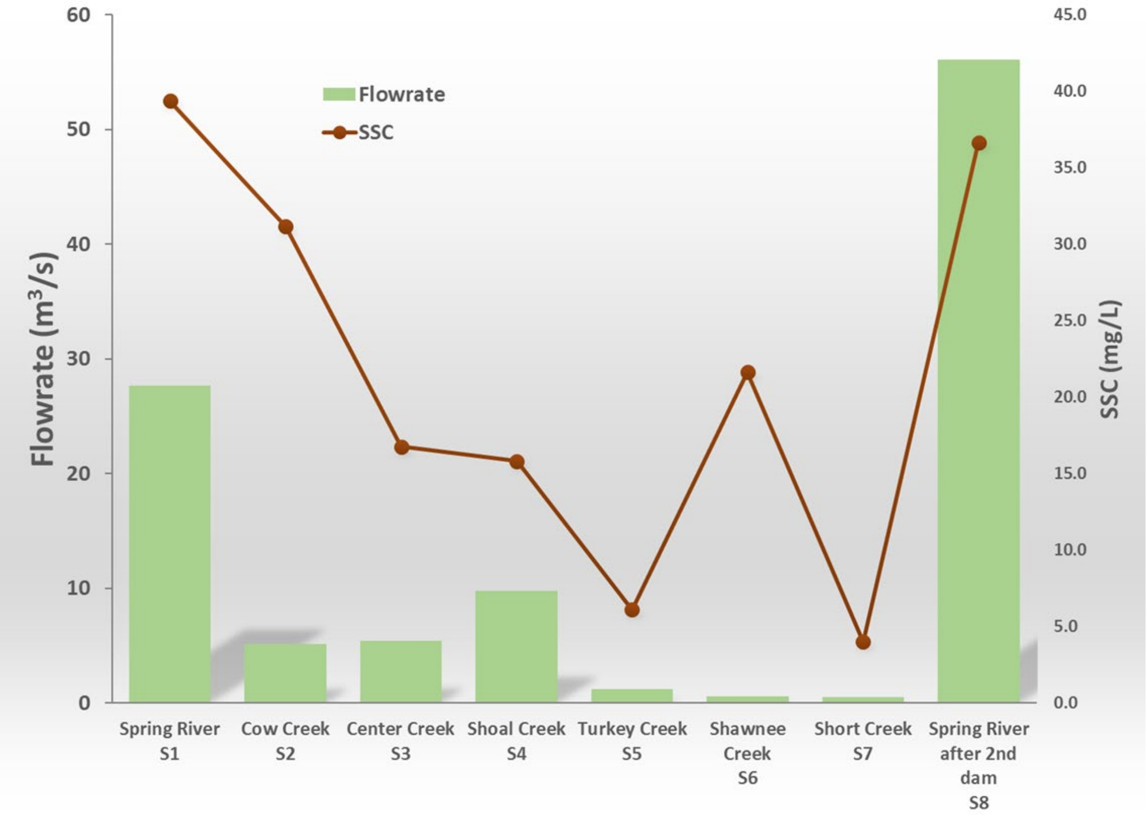
Total & Dissolved Zinc

Site	Stream	Average Total Zn (mg/L)	Average Dissolved Zn (mg/L)	Sampling Events
S01	Spring	0.008373	0.000714	56
S02	Cow	0.030203	0.0114	55
S03	Center	0.239313	0.163509	57
S04	Shoal	0.036045	0.003526	57
S05	Turkey	0.399105	0.353439	57
S06	Shawnee	0.015777	0.007157	51
S07	Short	8.085654	6.945614	57
S08	Spring	0.134228	0.059035	57
S11	Brush	0.024275	0.0005	28
S12	Spring	0.09702	0.036914	35
S13	Tar	2.976386	2.843571	28
S14	Neosho	0.014089	0	28



Zinc Loading into Empire Lake by Tributary



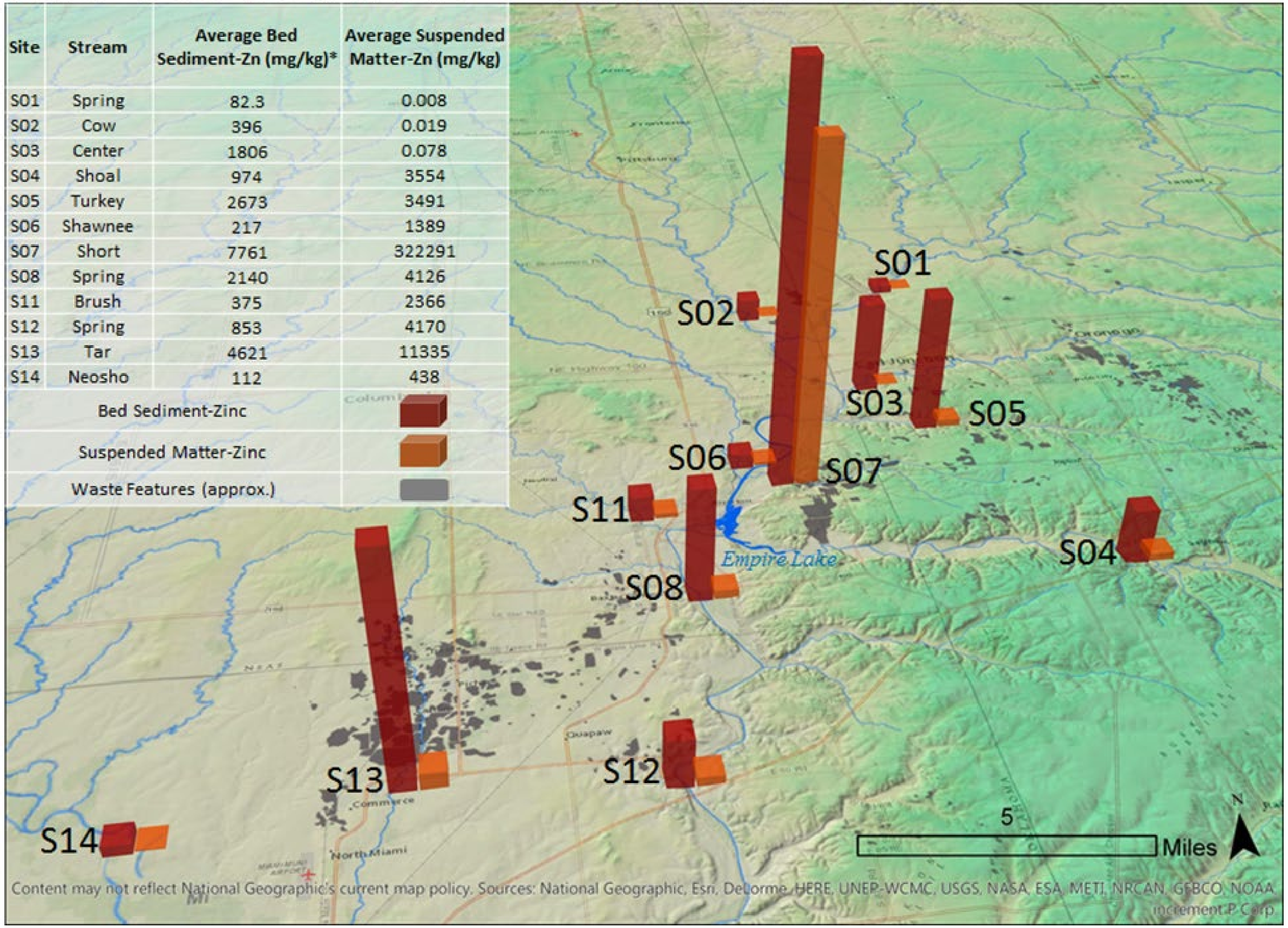


Zinc Concentrations in Bed Sediment

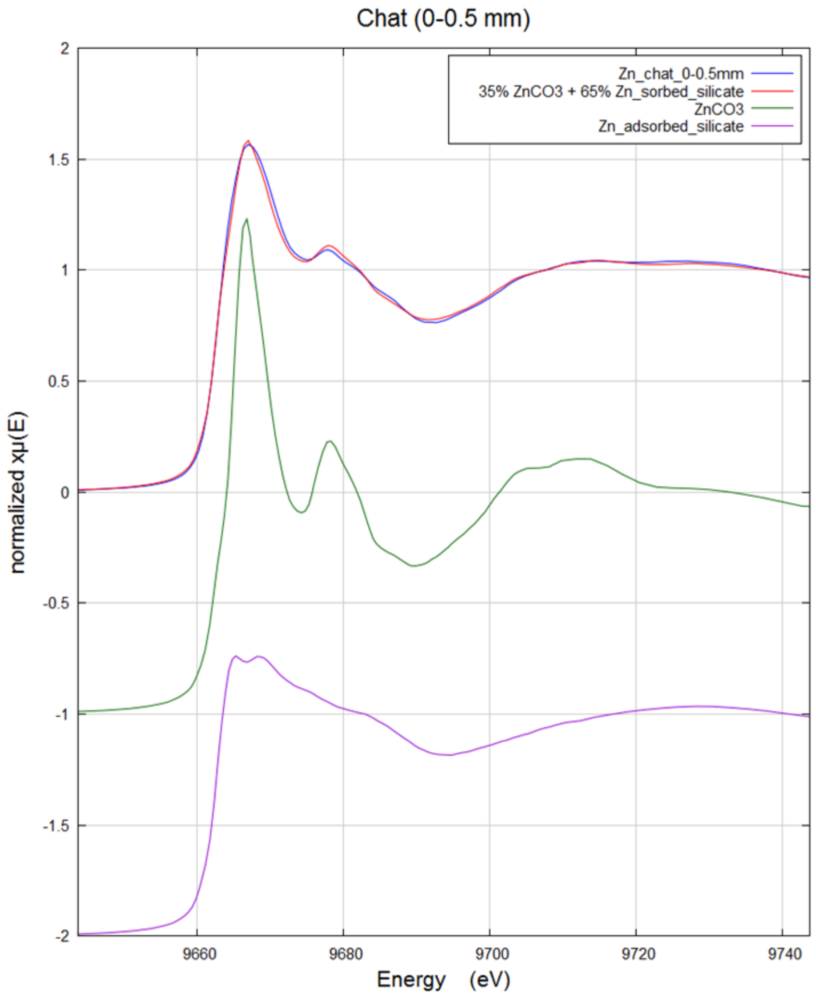
- Zinc had the highest concentrations in the bed sediments collected at Short Creek
- S7 also had high content of suspended solids in the aqueous phase samples

Zinc Bed Sediment & Suspended Solids

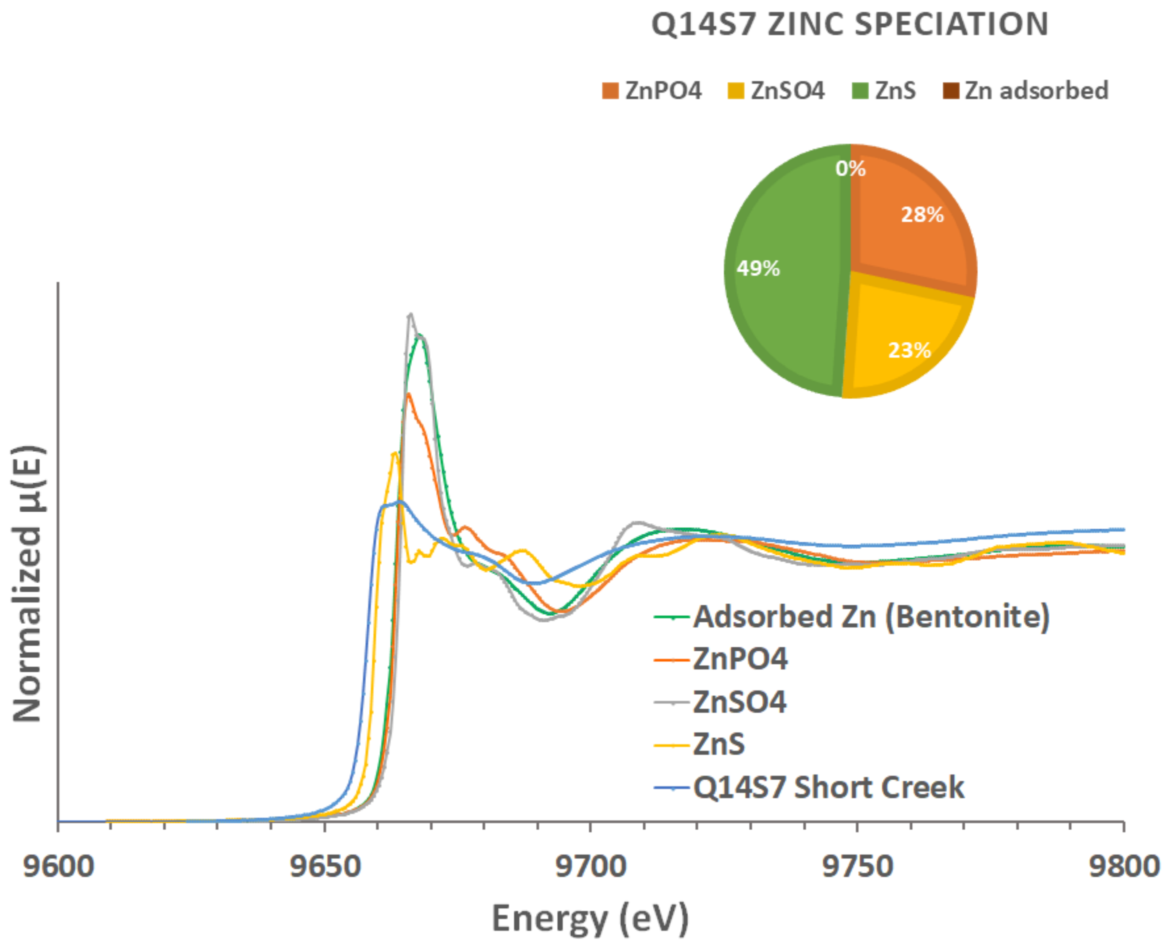
Site	Stream	Average Bed Sediment-Zn (mg/kg)*	Average Suspended Matter-Zn (mg/kg)
S01	Spring	82.3	0.008
S02	Cow	396	0.019
S03	Center	1806	0.078
S04	Shoal	974	3554
S05	Turkey	2673	3491
S06	Shawnee	217	1389
S07	Short	7761	322291
S08	Spring	2140	4126
S11	Brush	375	2366
S12	Spring	853	4170
S13	Tar	4621	11335
S14	Neosho	112	438



XANES: Zinc Speciation on Chat and Short Creek Sediments



Chat: 35% as $ZnCO_3$ and 65% sorbed



Bed sediments contained ZnS, $ZnPO_4$ and $ZnSO_4$

Aqueous Phase and Solid Phase Integration in Short Creek

- Aqueous phase contained ~8 mg/L of zinc and 120 mg/L of sulfate.
- The bed sediments have been accumulating zinc since the 1920's and have currently a concentration of 13,000 mg/kg. Zinc loading onto the lake from Short Creek represents 16 tons Zn/year.
- The XANES spectra revealed ZnS, $ZnPO_4$ and $ZnSO_4$ in the bed sediments. Not matching the geochemistry of the chat. Zinc is probably dissolved in the runoff, but precipitates and is deposited in the creek.
- The integration of these analyses help to decide the remediation steps: adsorption to remove the dissolved zinc from water and sediments basins to capture particulate zinc.

Questions?

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Work partially performed under U.S. EPA Contract No. EP-C-15-010 with Pegasus technical Services assigned as part of WA 3-18