Mobility of Zn, Pb, and Cd from sediments contaminated with mining wastes

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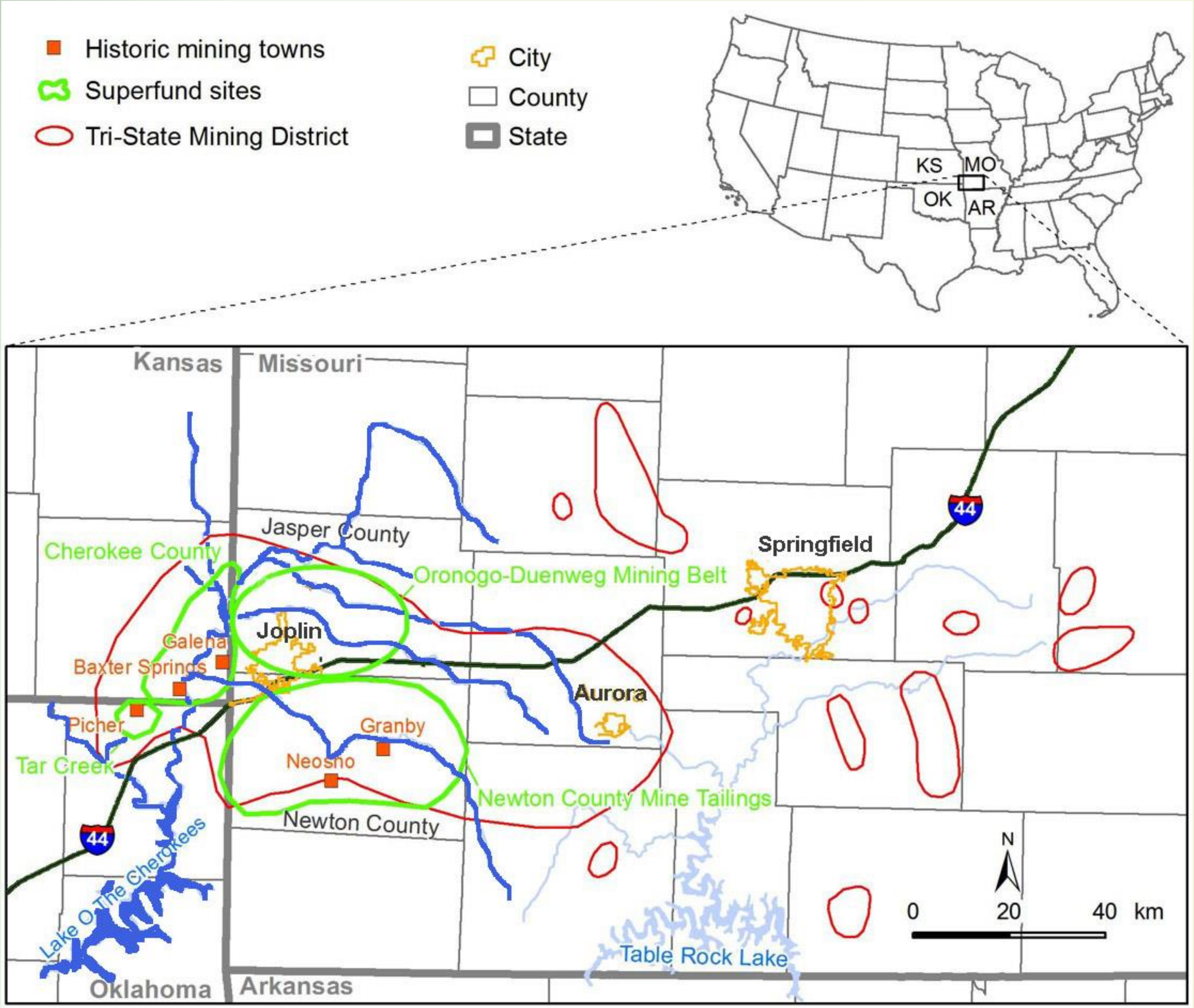


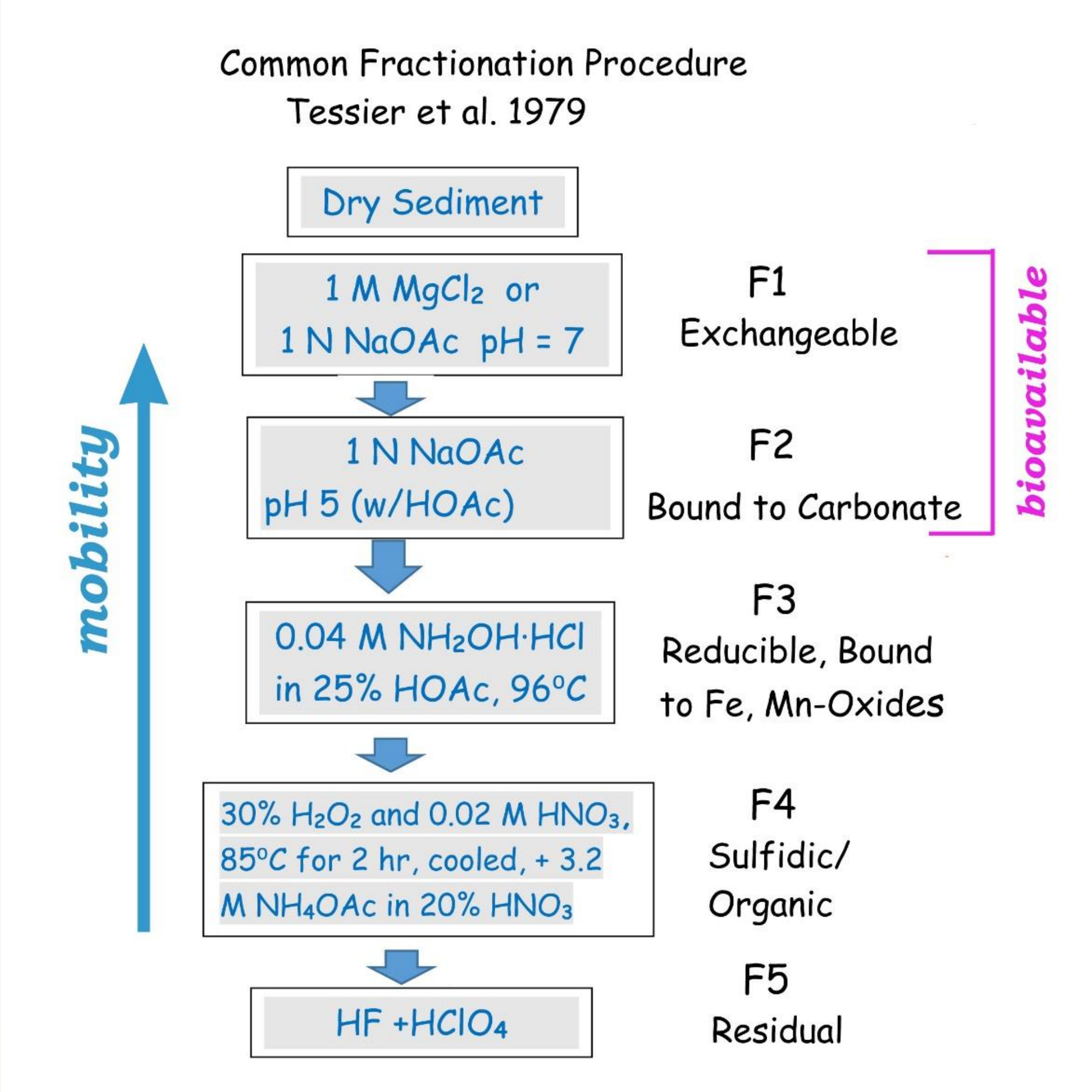
Main streams draining the Tri-State Mining District: Neosho, Spring, Center Creek, Shoal Creek.

Receiving Water Body for Remobilized Metals

Lake O The Cherokees

Groundwater

Ozarks Aquifer



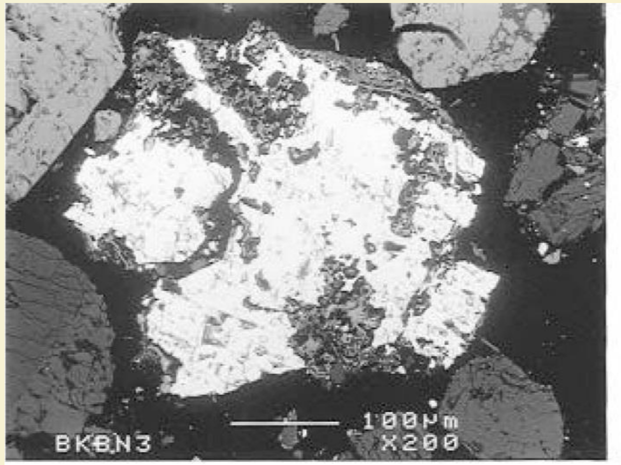
Common Fractionation Procedure
Tessier et al. 1979
Dry Sediment
1 M MgCl2 or
1 N NaOAc pH = 7
F1
Exchangeable
1 N NaOAc
pH 5 (w/HOAc)
F2
Bound to Carbonate
bioavailable
mobility
0.04 M NH2OH·HCl
in 25% HOAc, 96°C
F3
Reducible, Bound
to Fe, Mn-Oxides
30% H2O2 and 0.02 M HNO3,
85°C for 2 hr, cooled, + 3.2
M NH4OAc in 20% HNO3
F4
Sulfidic/
Organic
HF +HClO4
F5
Residual

With time, chemical weathering transforms one mineral into another mineral and dissolved species.

These transformations affect their fractionation and thus their availability to plants and animals (~their toxicity).

Some common products from weathering of sulfides include

1) Fe, Mn (oxy-)hydroxides, e.g., magnetoplumbite $Pb(Fe,Mn)_{12}O_{19}$
2) Carbonates e.g., cerrusite $PbCO_3$
3) Sulfates e.g. anglesite $PbSO_4$, and
4) Clays, e.g. epigenetic smectite



ZnS with rim of secondary mineral Fe-Zn-oxyhydroxides (e.g. woodruffite, hydrohetarolite)
(Hudson-Edwards et al. 1996)

Fractionation within the TSMD has been reported by Schaider et al. (2007, 2014), Pearson (2017), and ongoing studies by MSU students.

TABLE 1. Extraction Conditions for Sequential Extractions and Physiologically Based Extractions of Mine Waste Samples[a]

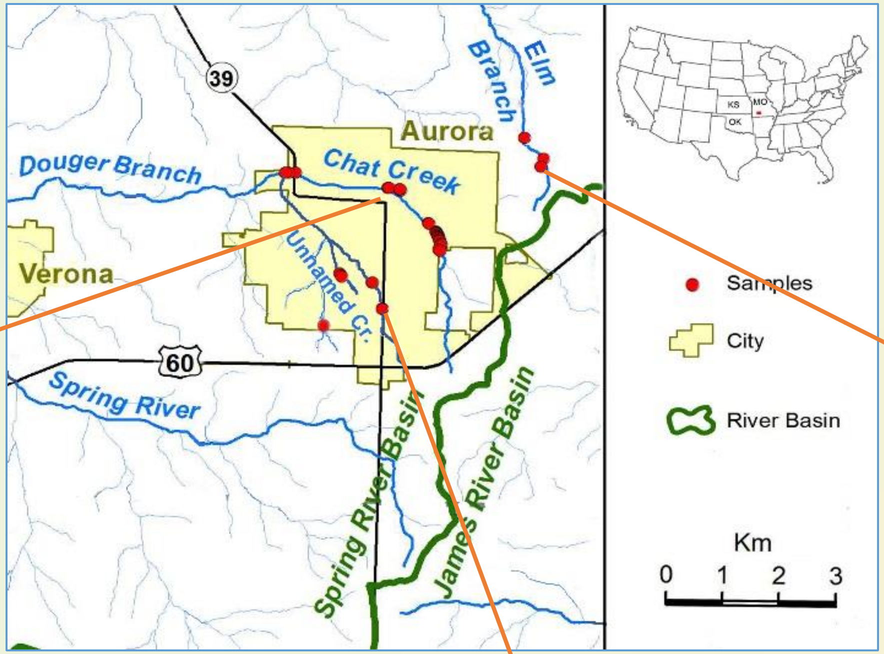
extractant	target	extraction conditions	% of Pb or Zn extracted: ZnS	hemi-morphite	PbS	$PbCO_3$
sequential extractions						
I MgCl2	ionically-bound (ion-exchangeable) displaced by cation exchange	1 M $MgCl_2$, pH 7, 1 h, 20 °C	0	0.04	0	3.3
II HAc	carbonate-bound and other phases mobilized by slightly acidic conditions	1 M NaAcetate, pH 5, 5 h, 20 °C	0	67	0.8	82
III HCl	amorphous sulfides or amorphous Fe (hydr)oxides and Mn oxides and sorbed or coprecipitated metals	1 M HCl, 12 h, 20 °C	1.9	11	22	4.5
IV HNO3	coprecipitated with pyrite or other crystalline sulfides	concentrated HNO_3, 2 h, 20 °C	63	0.01	34	0.03
V RES	residual, including silicates and other minerals not extracted by any of the previous solutions	XRF total − Σ extracted	35	22	44	10

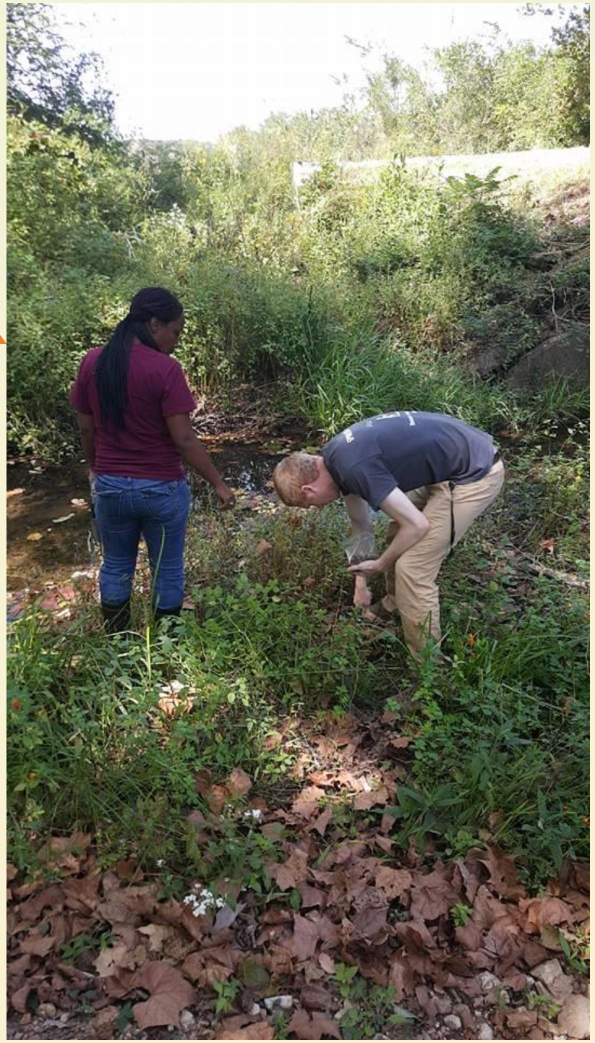
100%

Hemimorphite $Zn_4Si_2O_7(OH)_2 \cdot H_2O$

Schaider et al. (2007)

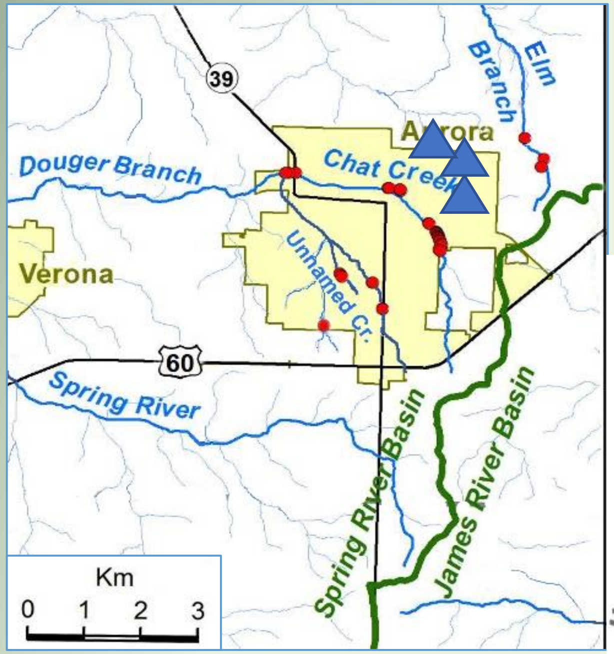
Case Study - Aurora, MO (Students' undergraduate project and Thesis by M.A. Pearson, 2017).

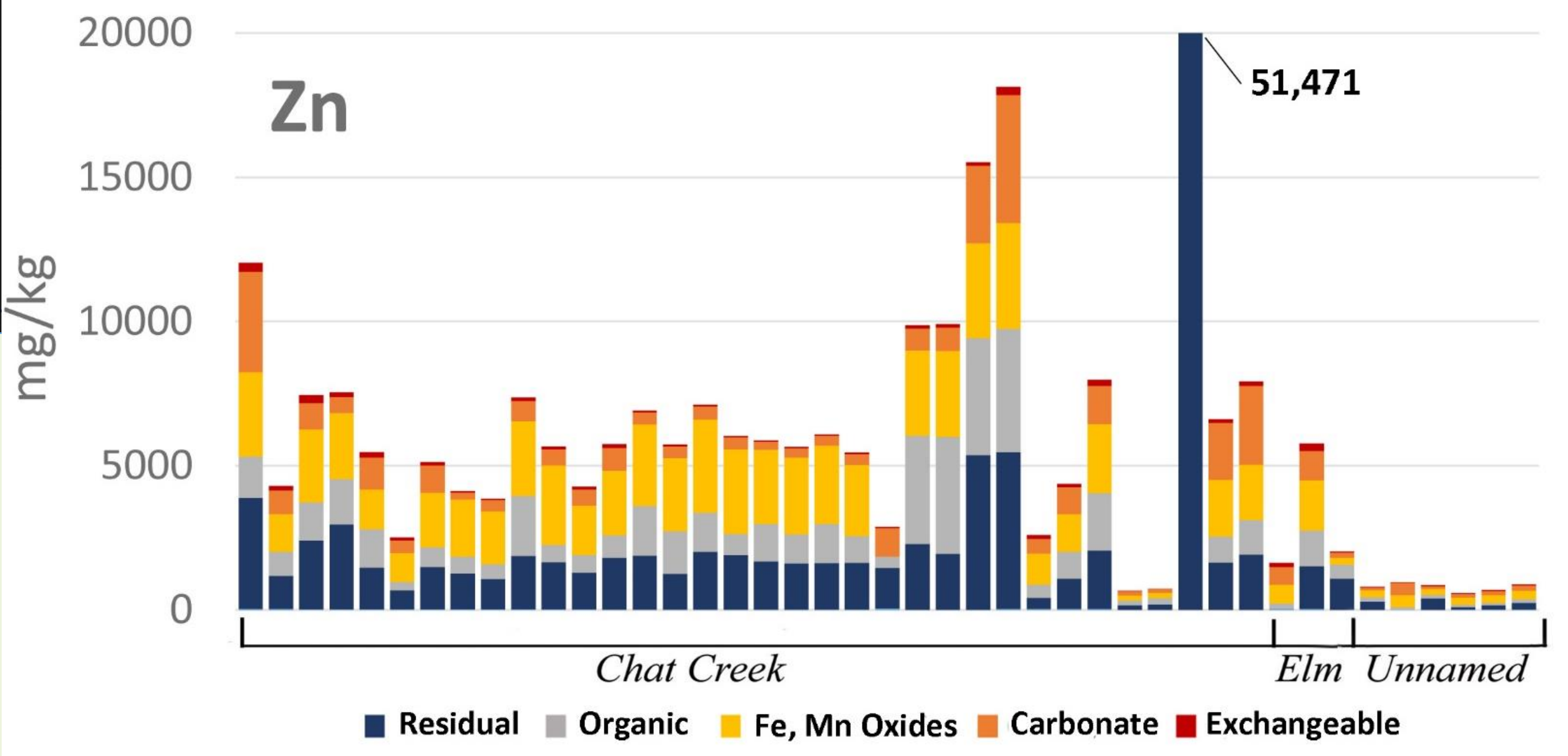




Methods

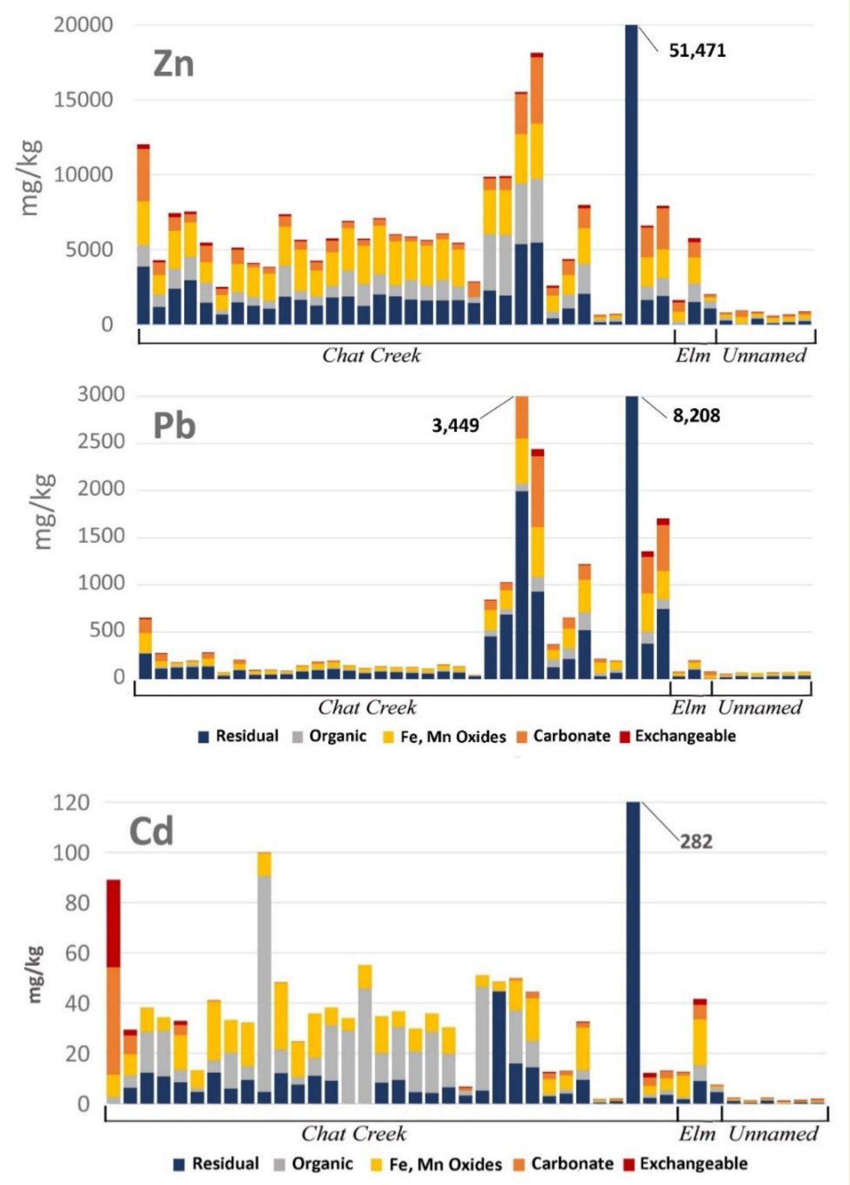
- Sediments were air dried and sieved to < 1 mm
- Total metal content
- pH, organic matter (LOI), color
- Sequential extraction following the method by Tessier et al. (1979)

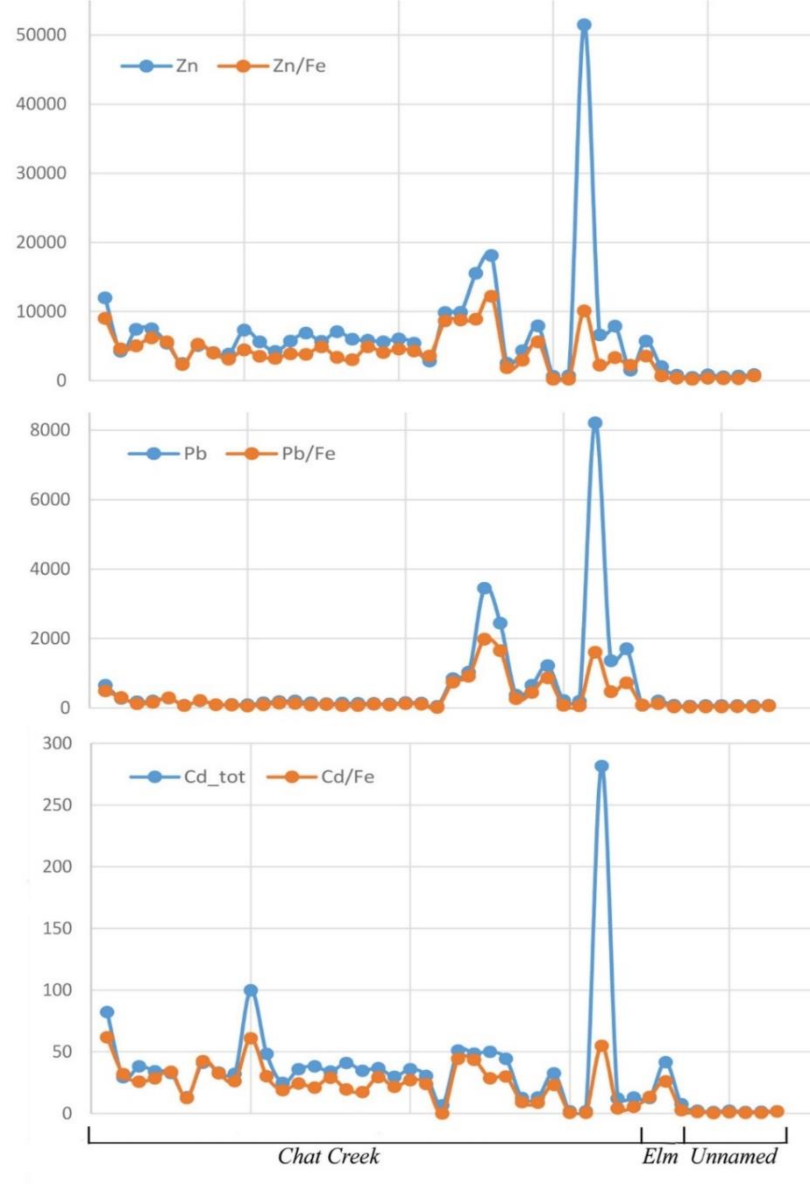


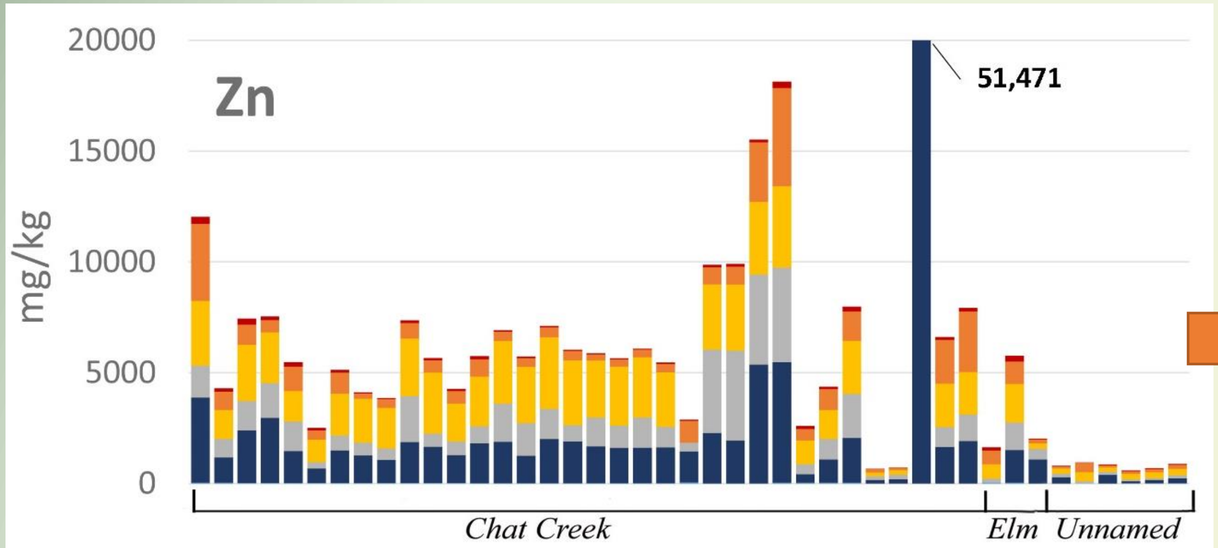


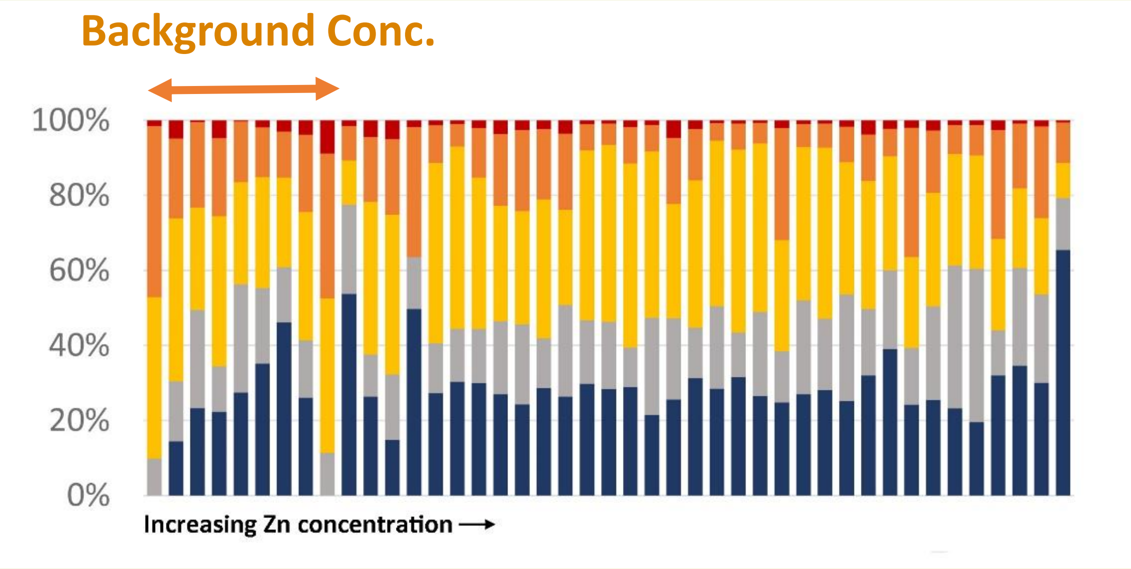
Unnamed Creek has the lowest concentrations ➲ background concentration

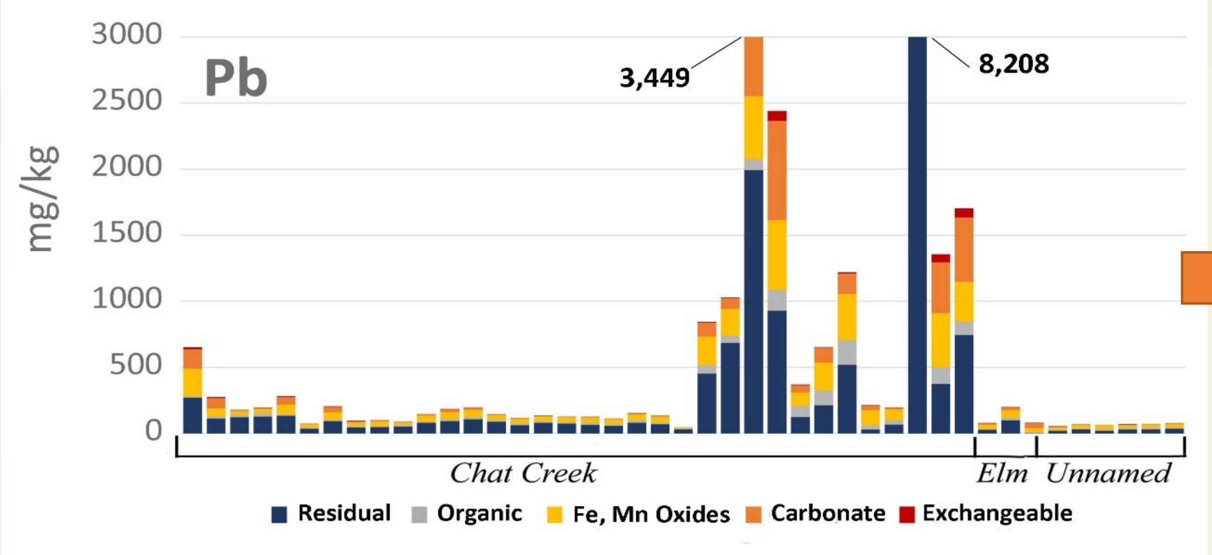
Normalized Concentrations

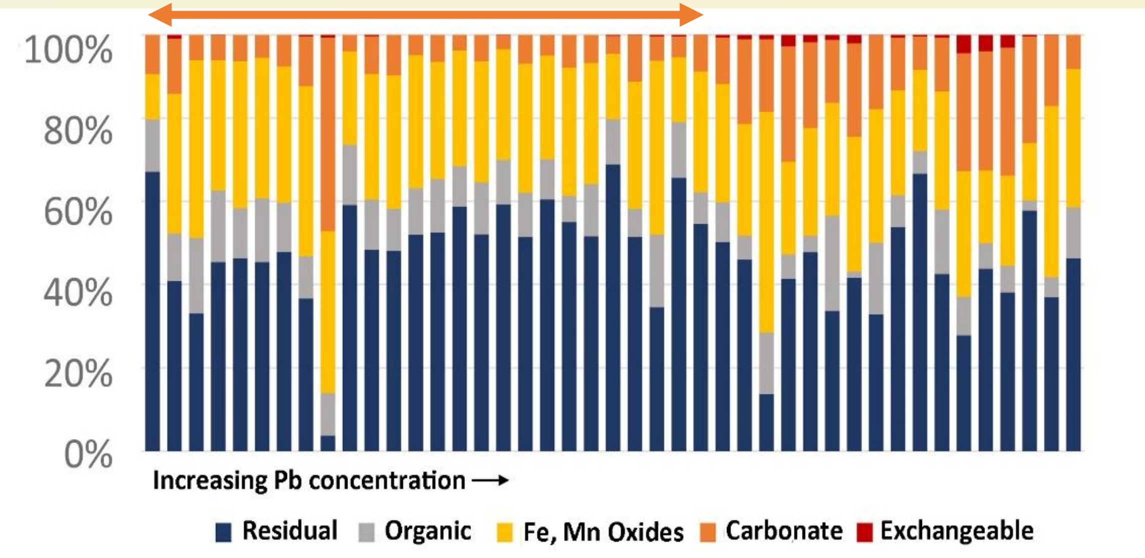


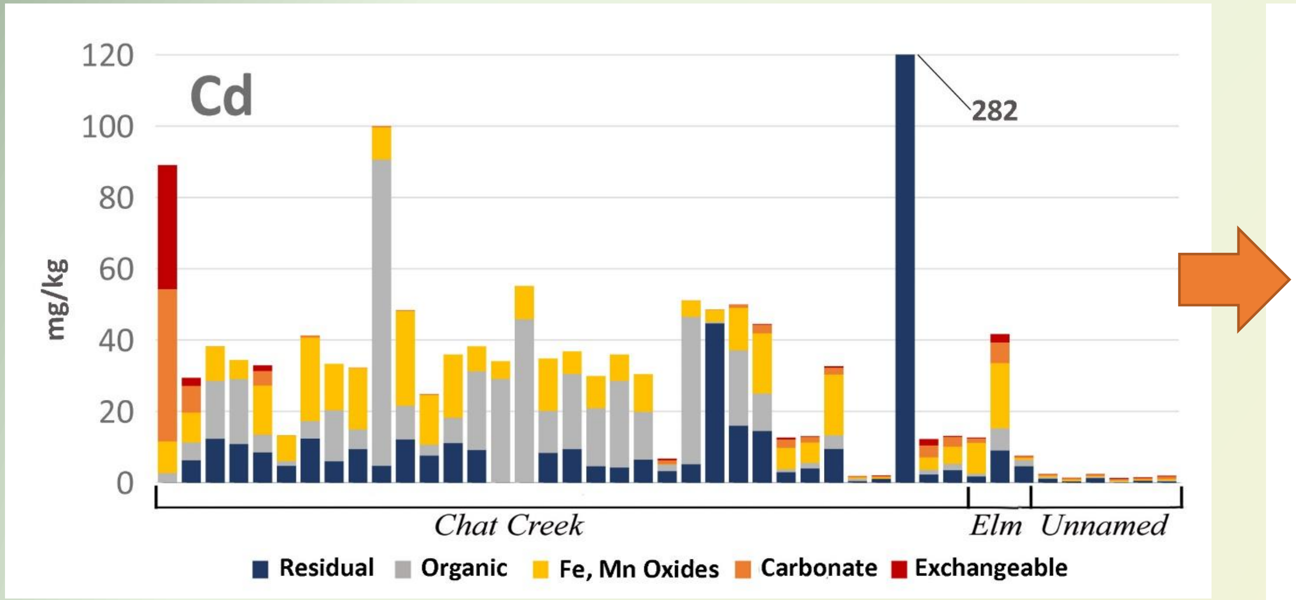


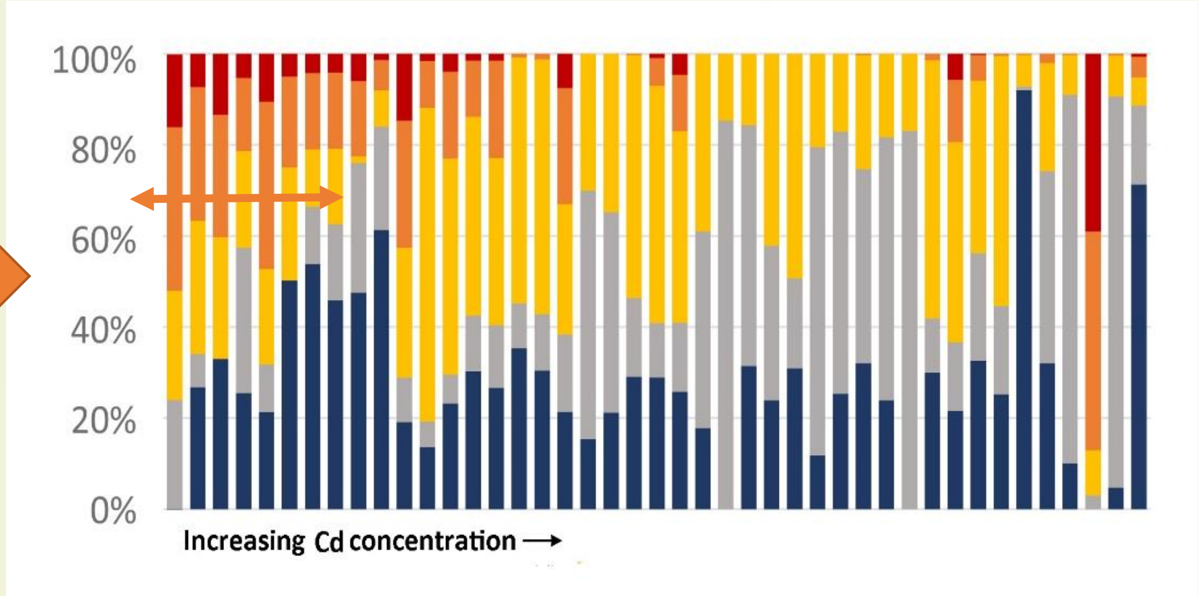

Zn
mg/kg
20000
15000
10000
5000
0
51,471
Chat Creek
Elm
Unnamed


Background Conc.
100%
80%
60%
40%
20%
0%
Increasing Zn concentration →


Pb
mg/kg
3000
2500
2000
1500
1000
500
0
3,449
8,208
Chat Creek
Elm
Unnamed
Residual
Organic
Fe, Mn Oxides
Carbonate
Exchangeable

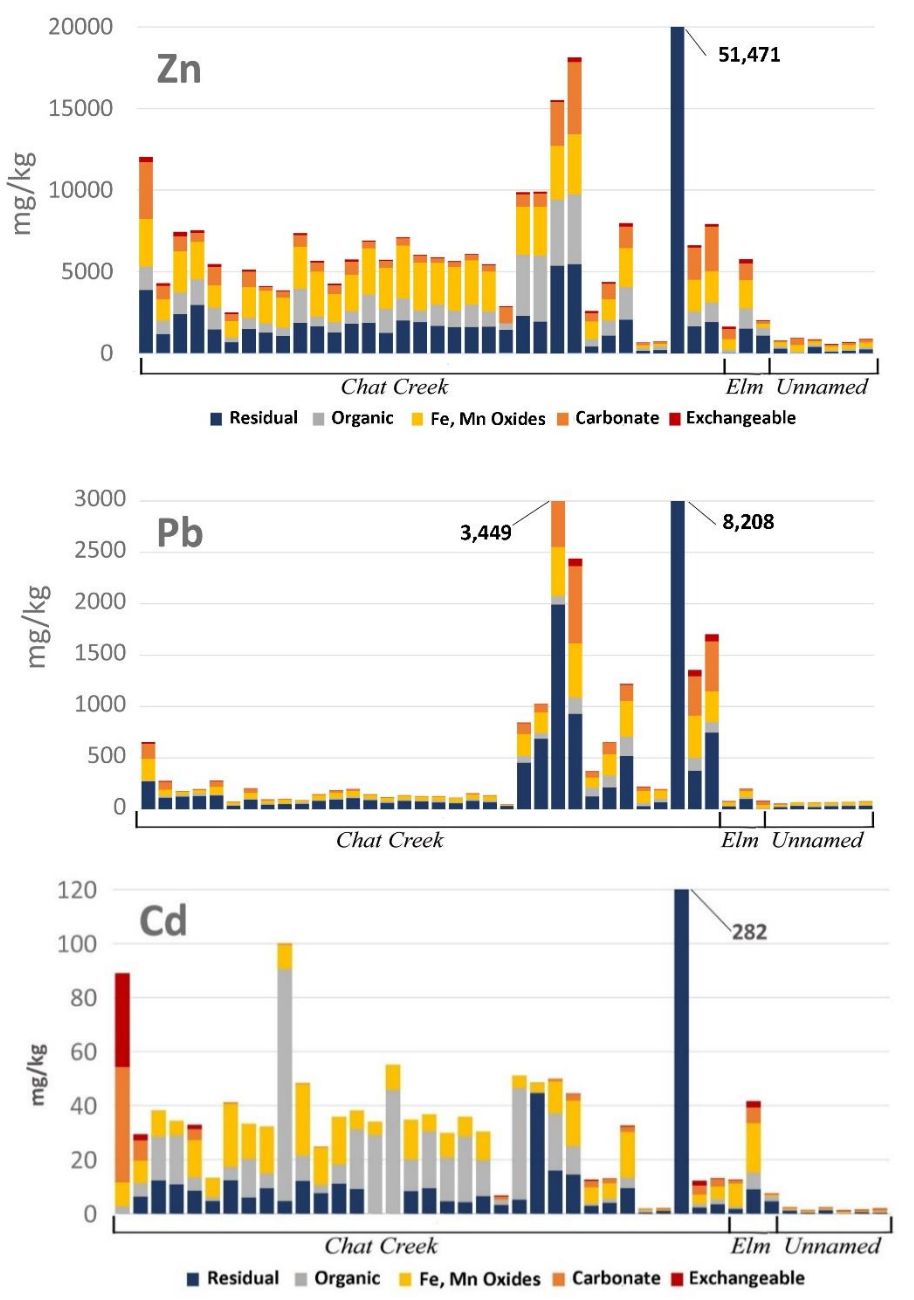

100%
80%
60%
40%
20%
0%
Increasing Pb concentration →
Residual
Organic
Fe, Mn Oxides
Carbonate
Exchangeable





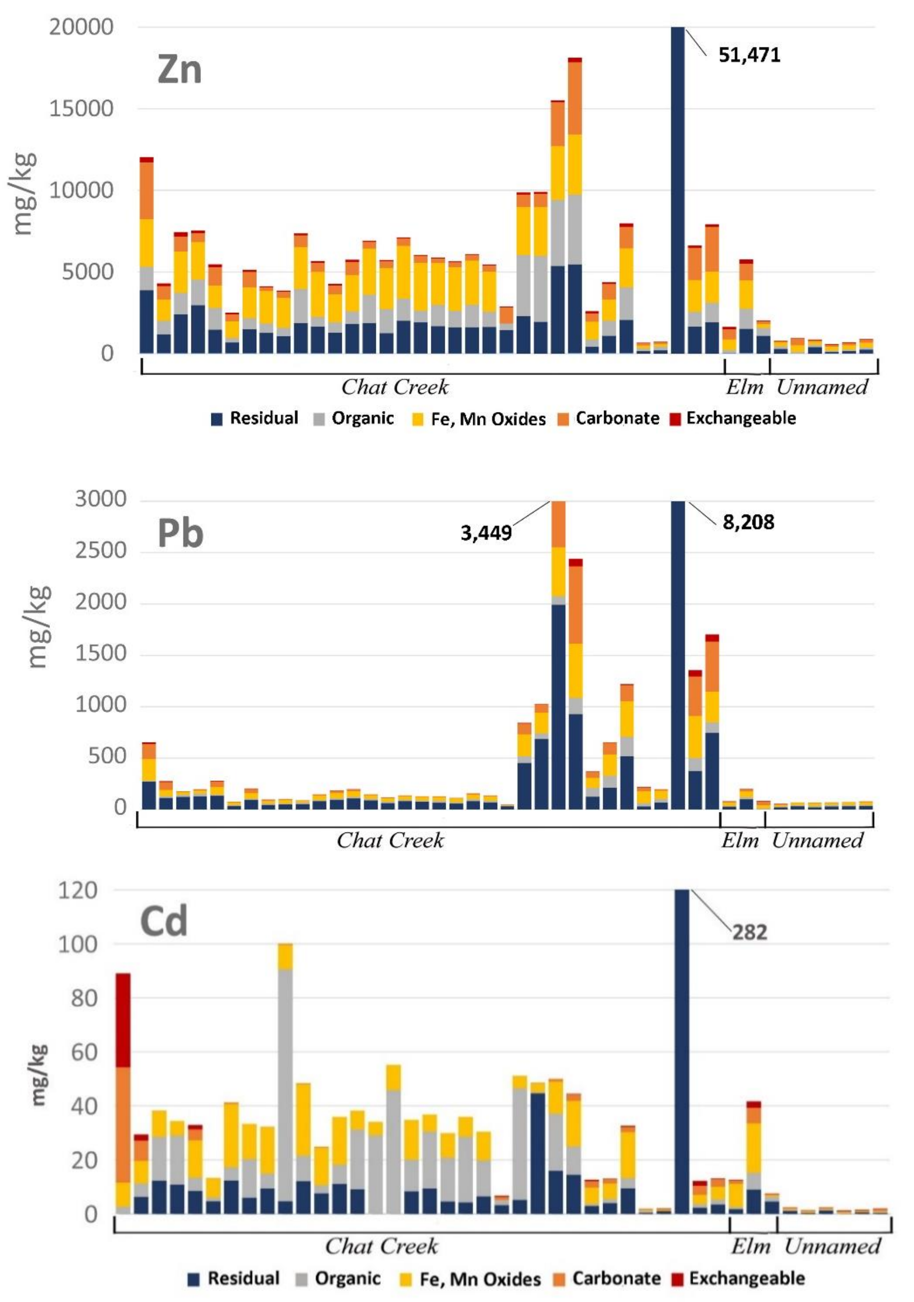
The increase in metal at the end of Chat Creek that was identifiable in Zn and Pb plots, is missing here.

The Cd concentration pattern is irregular, although a definitively background concentrations is present in the Unnamed creek.



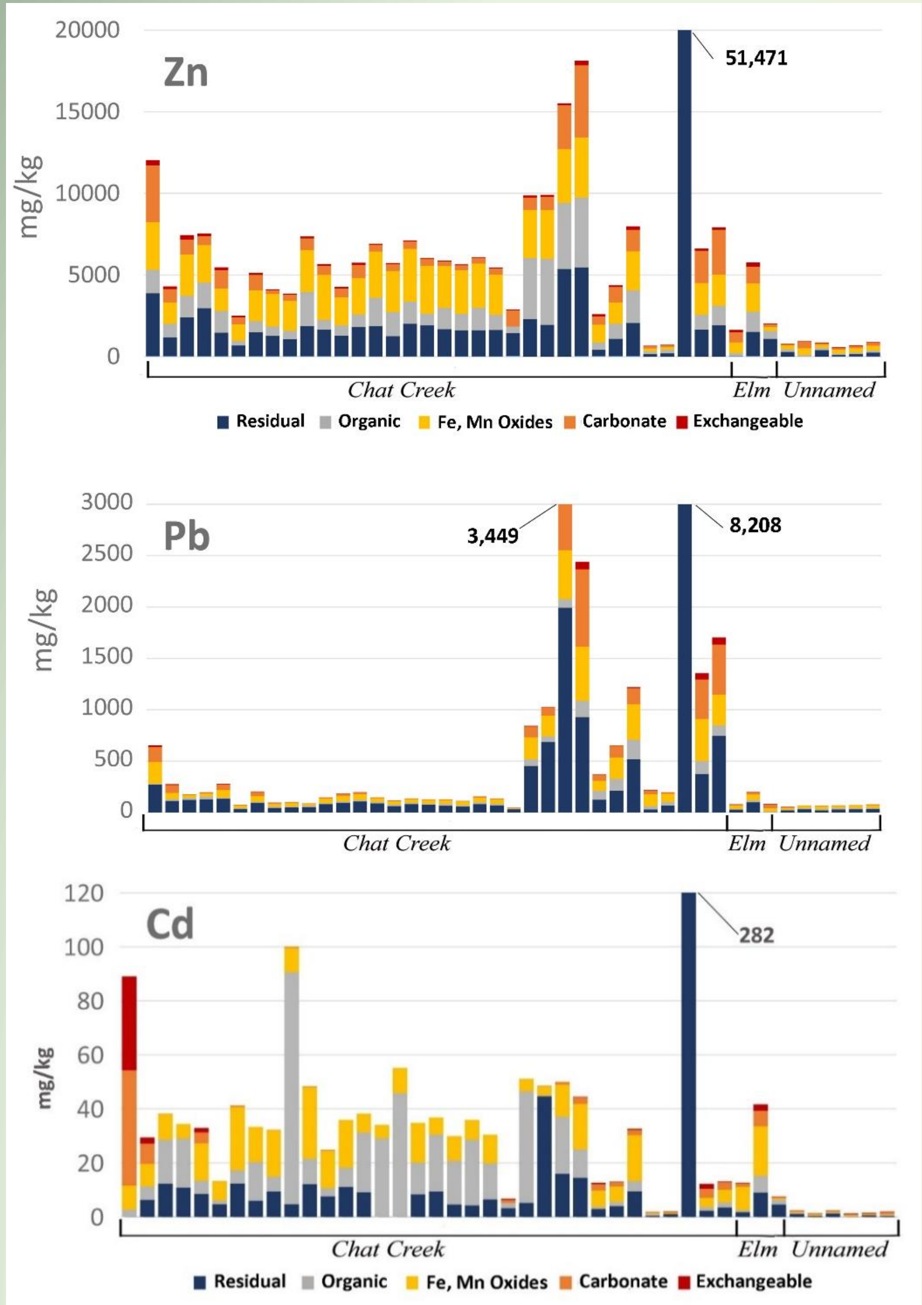
Results

- Sediments contain metals Zn>Pb>Cd
- Roughly speaking, Pb binds preferentially to residual and carbonate fractions, Zn to Fe-Mn oxyhydroxides, and Cd to organic.
- The **impacted segment of Chat Creek** is clearly delineated by a contrast between low and high concentrations of Pb, a pattern that is still noticeable for Zn but more subdued in the case of Cd.
- Although quite small, the bioavailable Pb (exchangeable and carbonate fractions) becomes more significant in sediments with high Pb content.



- Within the bioavailable fraction, the **carbonate-bound** metal was about 10 times larger than the exchangeable fraction for Zn and Cd, and 50 times larger for Pb, which means that a drop in pH would preferentially (5X) mobilize Pb.

- Differences in concentration pattern and the geochemical phase the metal attaches to, indicate that there are significant differences in the chemical weathering and **mobility** between Pb, Zn, and Cd.



- **Cd** seems to blend more uniformly within the sediment (**higher mobility**) and to store in the organic fraction/sulfides. The higher mobility allows Cd to incorporate to plants (mostly at/in their roots).

- Zn will be released from the sediment and into the water column if the system shifts to reducing conditions. Reportedly, Cd competes with Zn for adsorption sites in Fe-oxides and clays.

How is metal fractionation important?

1. Toxicity to aquatic organisms based on the bioavailable fraction

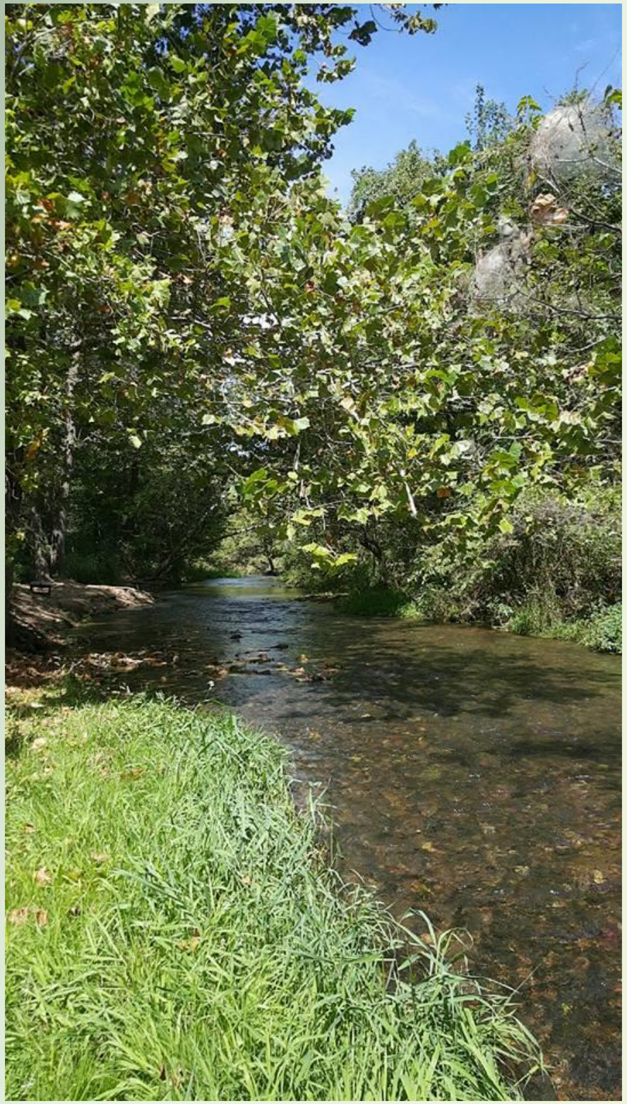
2. Plant absorption and bioaccumulation is favored by mobilized metal,

3. Remediation effectiveness can be determined as a function of pH, Eh, and weathering reactions

Proposed Remediation Methods in the TSMD

Phytostabilization and Wetland

Both will work better by adding amendments, and if near-neutral pH and oxidizing conditions persist


Spring River near Aurora, MO

Besides obtaining results of sediment characterization of mining impacted areas, this project provided research opportunities for more than 10 students of the geology and chemistry departments, each student (or group of students) looking at a particular aspect of it.

The fractionation work of Miles Pearson (MSU Thesis) is included here.

Thank you!