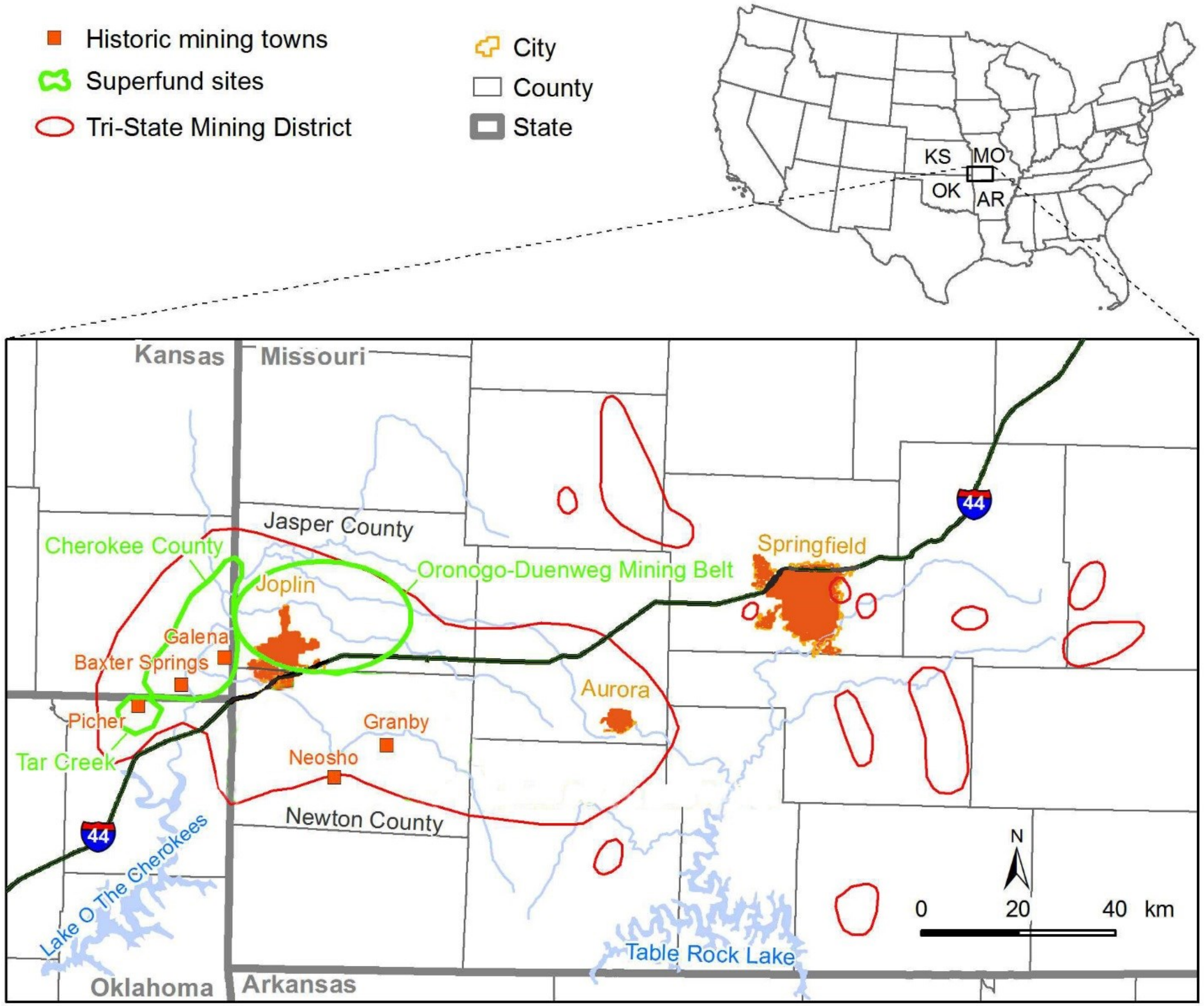
FRACTIONATION OF METALS IN SEDIMENTS AFFECTED BY MINING WASTES IN THE TRI-STATE MINING DISTRICT

Mélida Gutiérrez, Ph.D.
Geography, Geology and Planning, Missouri State University

Geological Society of America, North-Central Meeting

Ames IO, March 2018



Remaining Superfund Sites:

Missouri: Oronogo-Duenweg

Oklahoma: Tar Creek

Kansas: Cherokee County SF

History of Mining (and Remediation) in the Tri-State Mining District of Kansas, Missouri, and Oklahoma

Museums

Miners Museum, Granby, MO

Joplin History & Mineral Museum, Joplin, MO

Tri-State Mineral Museum, Joplin, MO

Galena Mining and Historical Museum, Galena, KS

Digital Library

Missouri Digital Heritage https://www.sos.mo.gov/mdh/

USFWS Natural Resources Damage Assessment: Missouri Portion of the Tri-State Mining District https://www.fws.gov/midwest/es/ec/nrda/motristate/index.html

Documentaries

The Ozarks Uplift: The Story of Tri-State Mining, by Paul Wannenmacher, 2013

Tar Creek, 2009. The *Tar Creek* Superfund Site

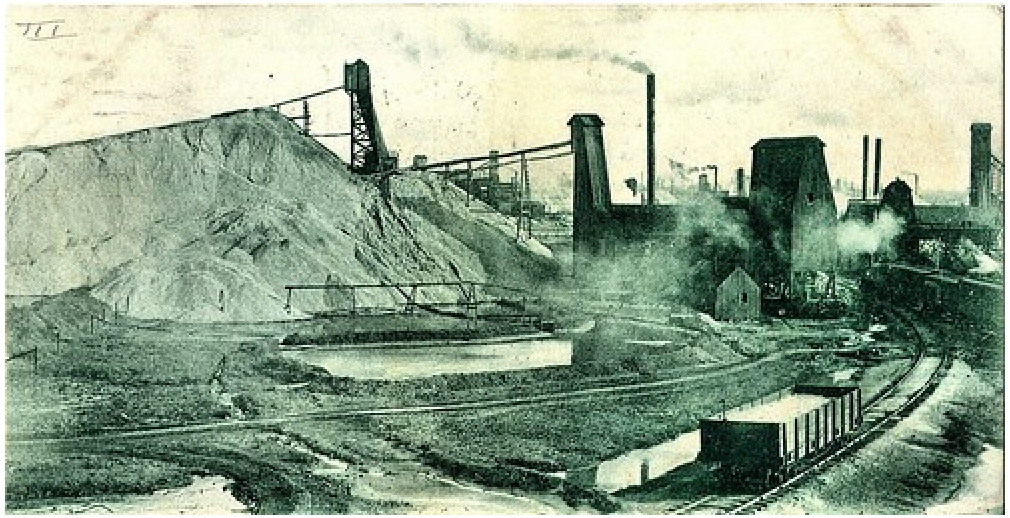
Web sites

Historic Joplin http://www.historicjoplin.org/

Missouri Lead Mining History https://dnr.mo.gov/env/hwp/sfund/le ad-mo-history-more.htm#tristate

Most mining in the Tri State Mining District (TSMD) of Kansas, Oklahoma and Missouri ended in the 1950s, with a few operations continuing to early 1970s.

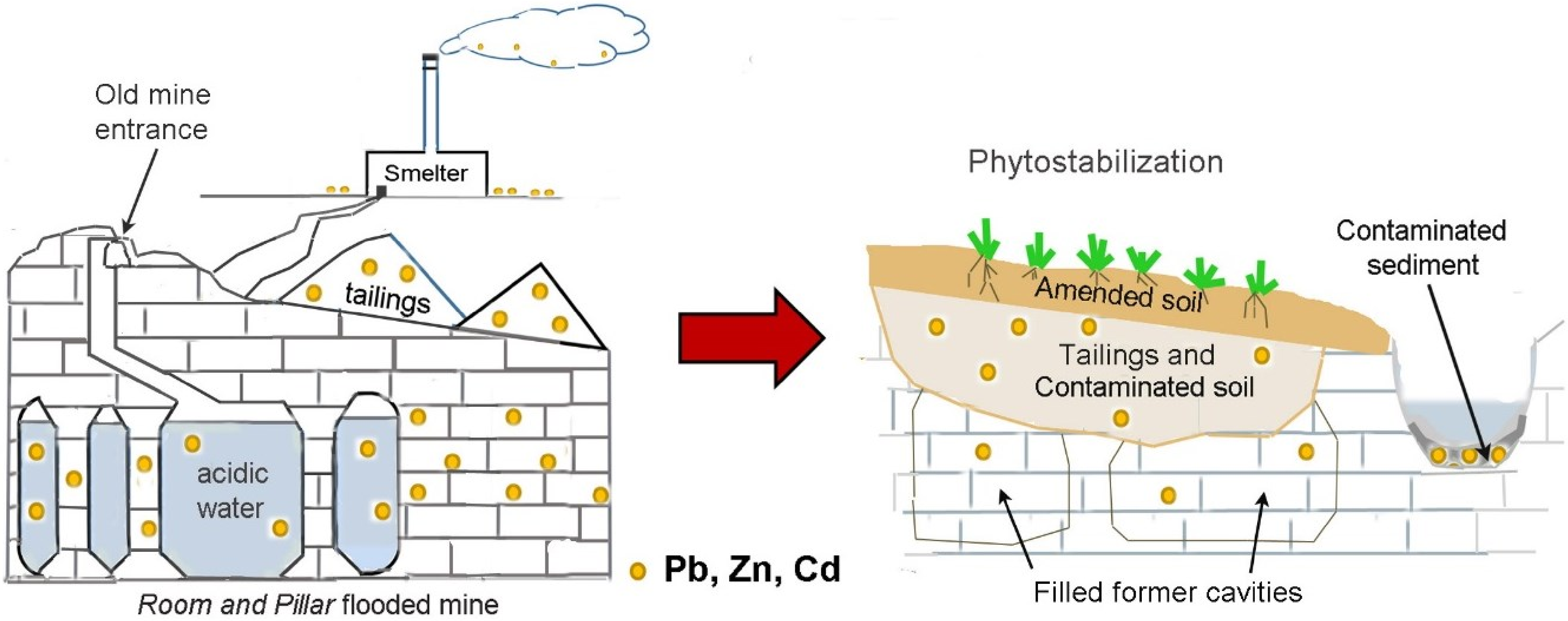
The abandoned wastes (chat piles and fallout from smelters) remained in place for decades, releasing contaminants to soils and streams.



Historic Joplin. A typical mine in SW Missouri. A mine with chat pile

After assessing the level of contamination, some TSMD sites made it to the National Priority List (EPA), known as Superfund in the 1980s. Remediation followed. Some places were more difficult to remediate than others.

In the TSMD, most of the chat piles have been since removed and former mining sites have been remediated by various forms of **phytostabilization**; some using amendments (wood chips, biosolids, manure, compost, etc.) mixed with the soil.

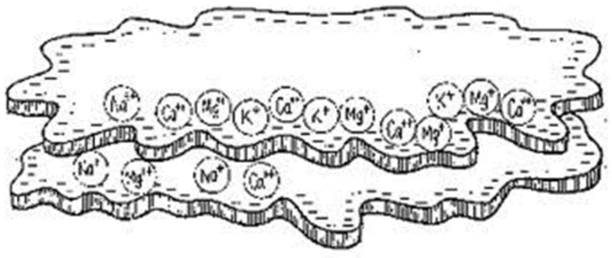


Remediation in the Oronogo-Duenweg site consisted on recontouring and application of amendments to reduce metal availability and to restore a self-sustaining plant cover on the amended tailings, 1998-2001

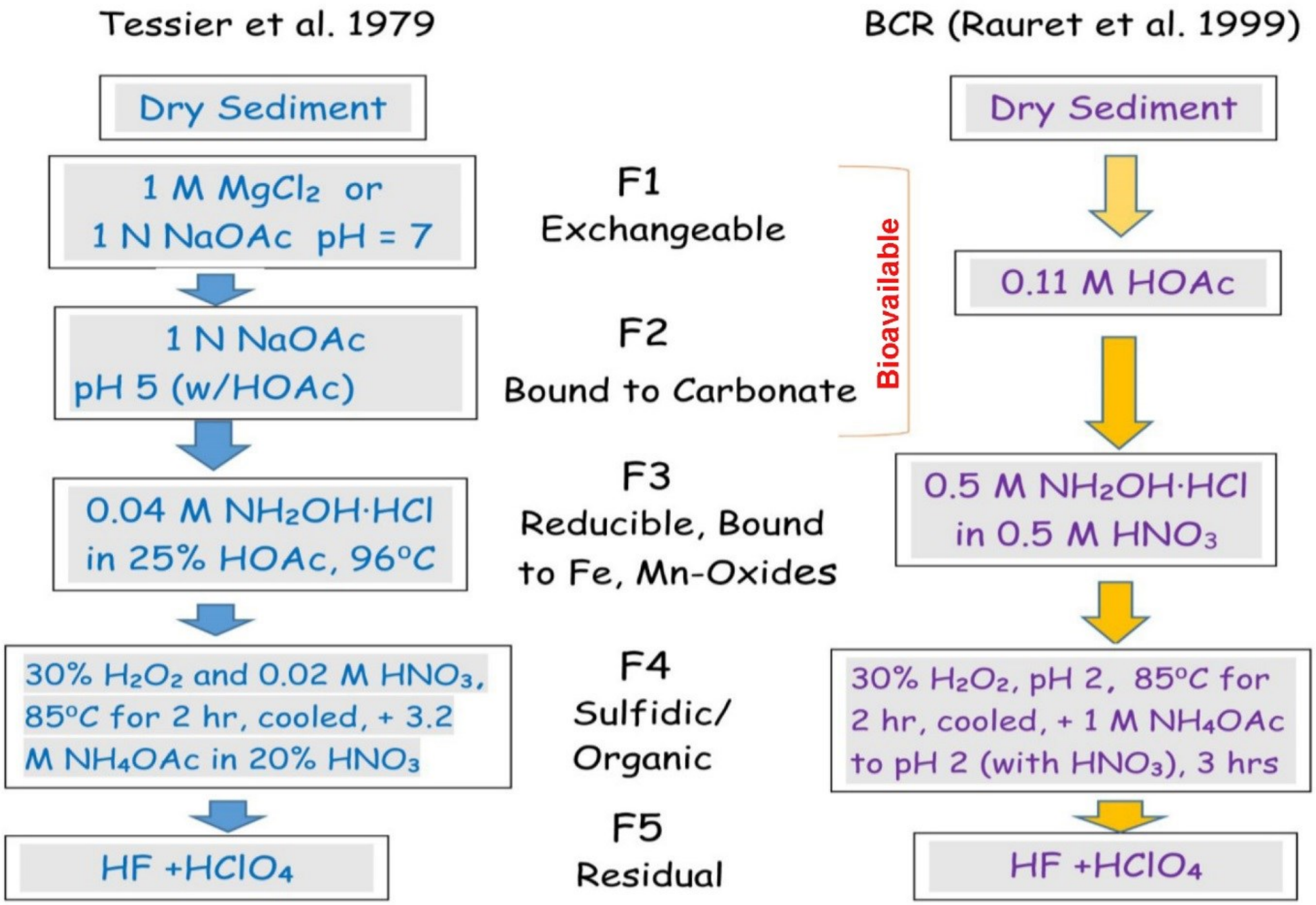
2000

2002

- High concentrations of Zn Pb and Cd continue to be present in the sediment of some stream segments.
- Metals preferably adsorb onto the solid phase (sediment) where they stay immobile for a long time, but under certain conditions they could remobilize.
- The **metal to be remobilized** is determined by fractionation, a method where sequential extraction is applied using extractants of increasing strength.
- By fractionation, we know how much of the total metal would be released under specific conditions of pH, oxidation state, and/or presence of other chemicals.



Most Common Fractionation Procedures



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

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

			% of Pb or Zn extracted			
extractant	target	extraction conditions	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
SBET	metals bioaccessible in gastric fluid	pH 1.5 (0.32 M HCl), 0.4 M glycine, 1 h, 37 °C	0	65	3	97
PSF	metals bioaccessible in lysosomes of alveolar macrophages	pH 4.5, salts, organic acids,[b] 5 d, 37 °C	1.7	2.8	0.4	14

100% (sequential extractions I–V)

Hemimorphite $Zn_4Si_2O_7(OH)_2 \cdot H_2O$

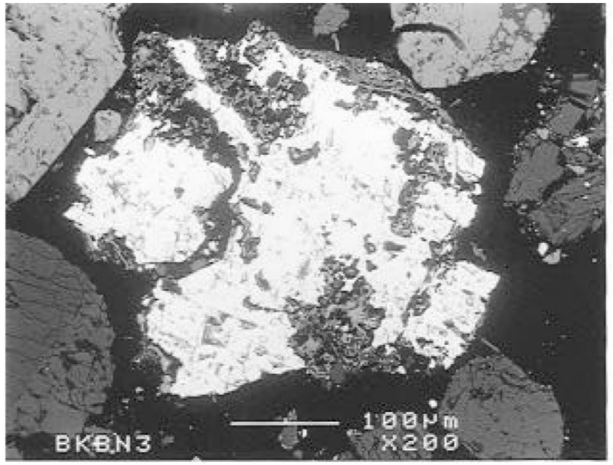
Schaider et al. (2007)

With time, chemical weathering transforms one mineral into another mineral and dissolved species. This reaction may change the chemical composition of the water (and pore water) and the size distribution of fragments.

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

Determination of mineralogical pathways and reaction rates is desirable. Some common products from weathering of sulfides include

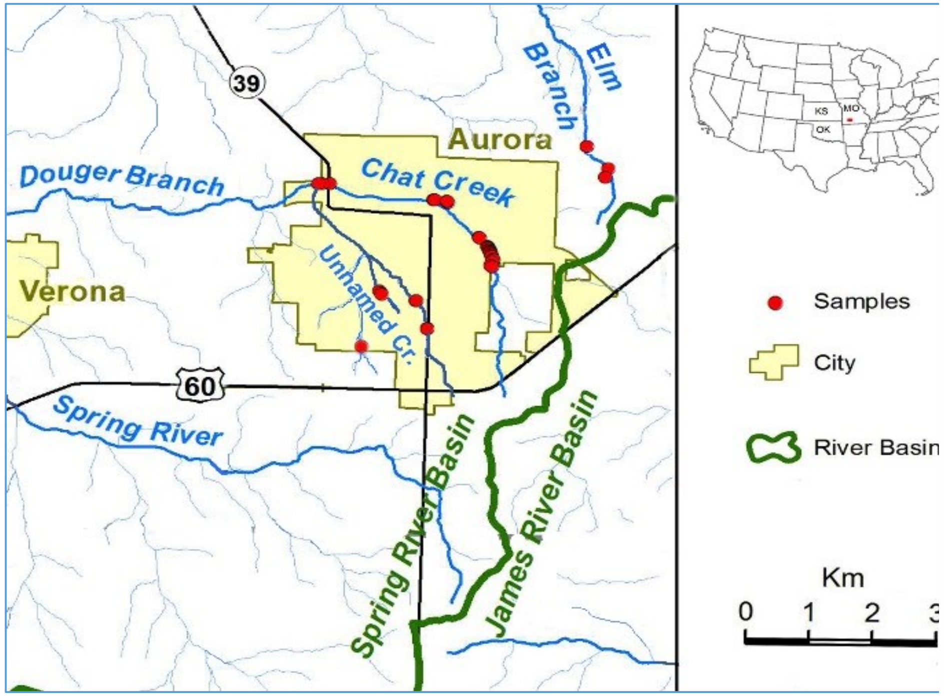
1) Fe, Mn (oxy-)hydroxides, e.g., magnetoplumbite $Pb(Fe,Mn)_{12}O_{19}$
2) Carbonates e.g., cerrusite $PbCO_3$
3) Sulfates e.g. anglesite $PbSO_4$, and
4) Clays, e.g. epigenetic smectite

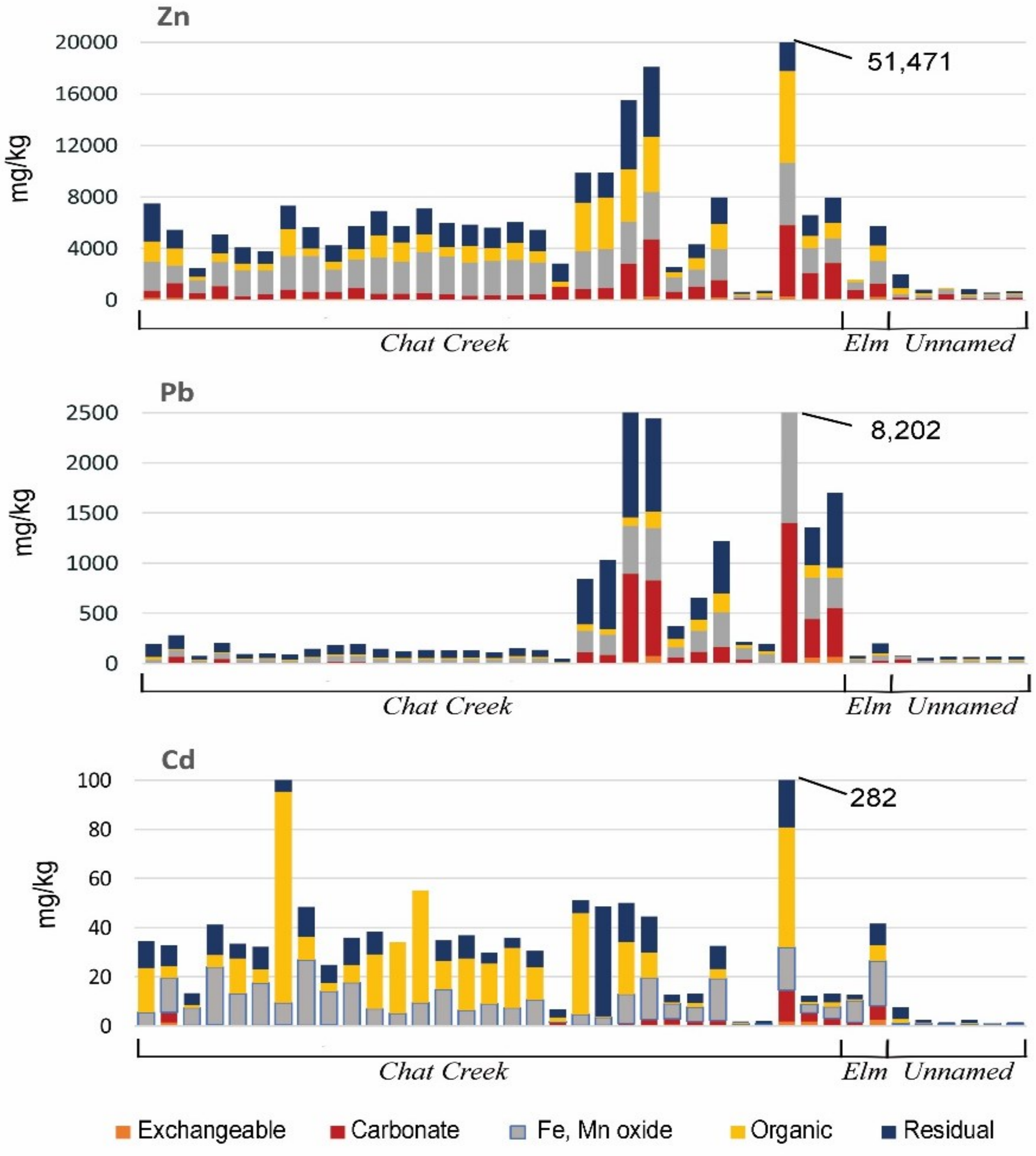


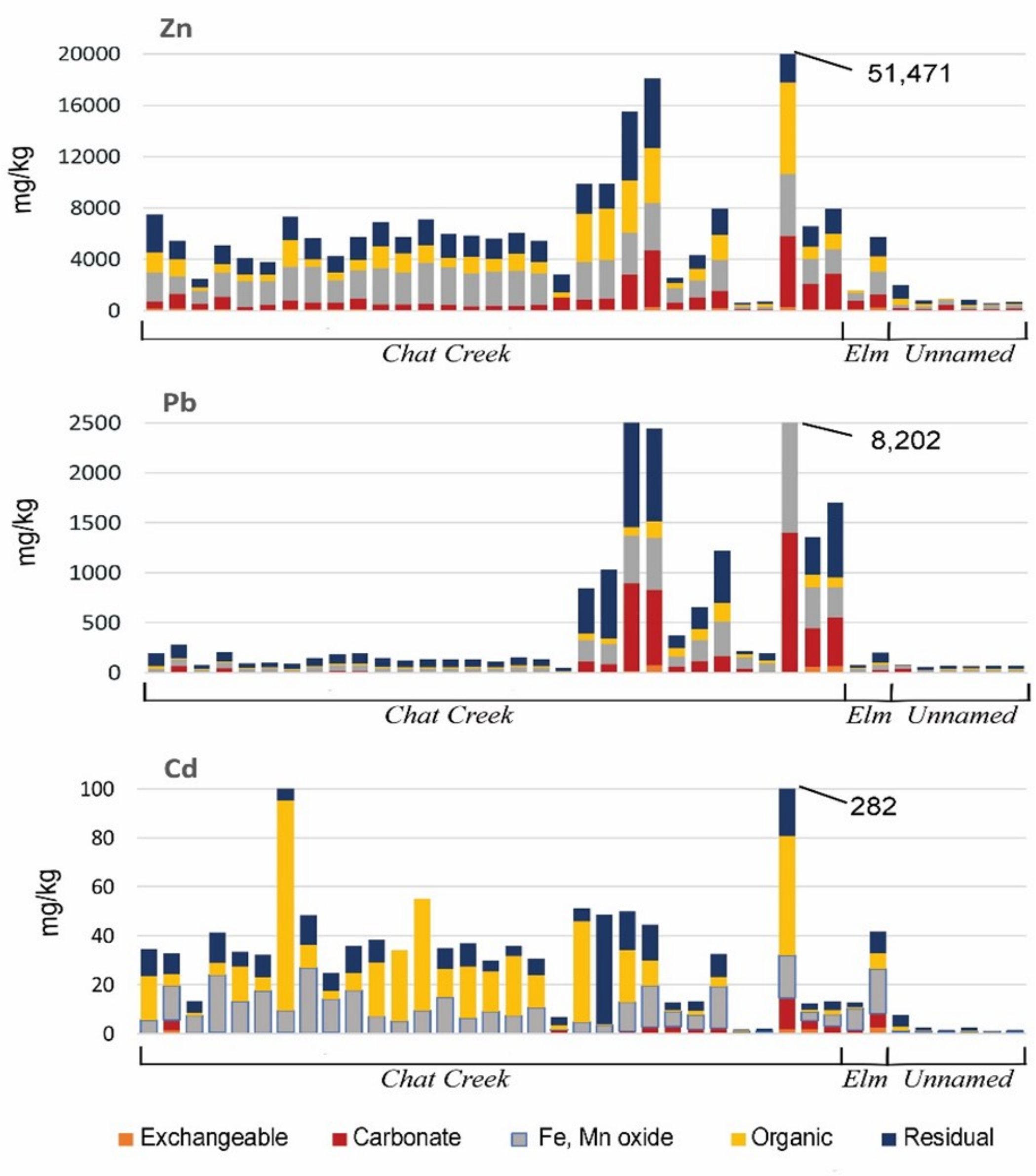
ZnS with rim of secondary mineral Fe-Zn-oxyhydroxides (e.g. woodruffite, hydrohetarolite)
(Hudson-Edwards et al. 1996)

Case Study

Aurora, MO (Thesis by M.A. Pearson, 2017). Sequential extraction following the method by Tessier et al. (1979)







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.

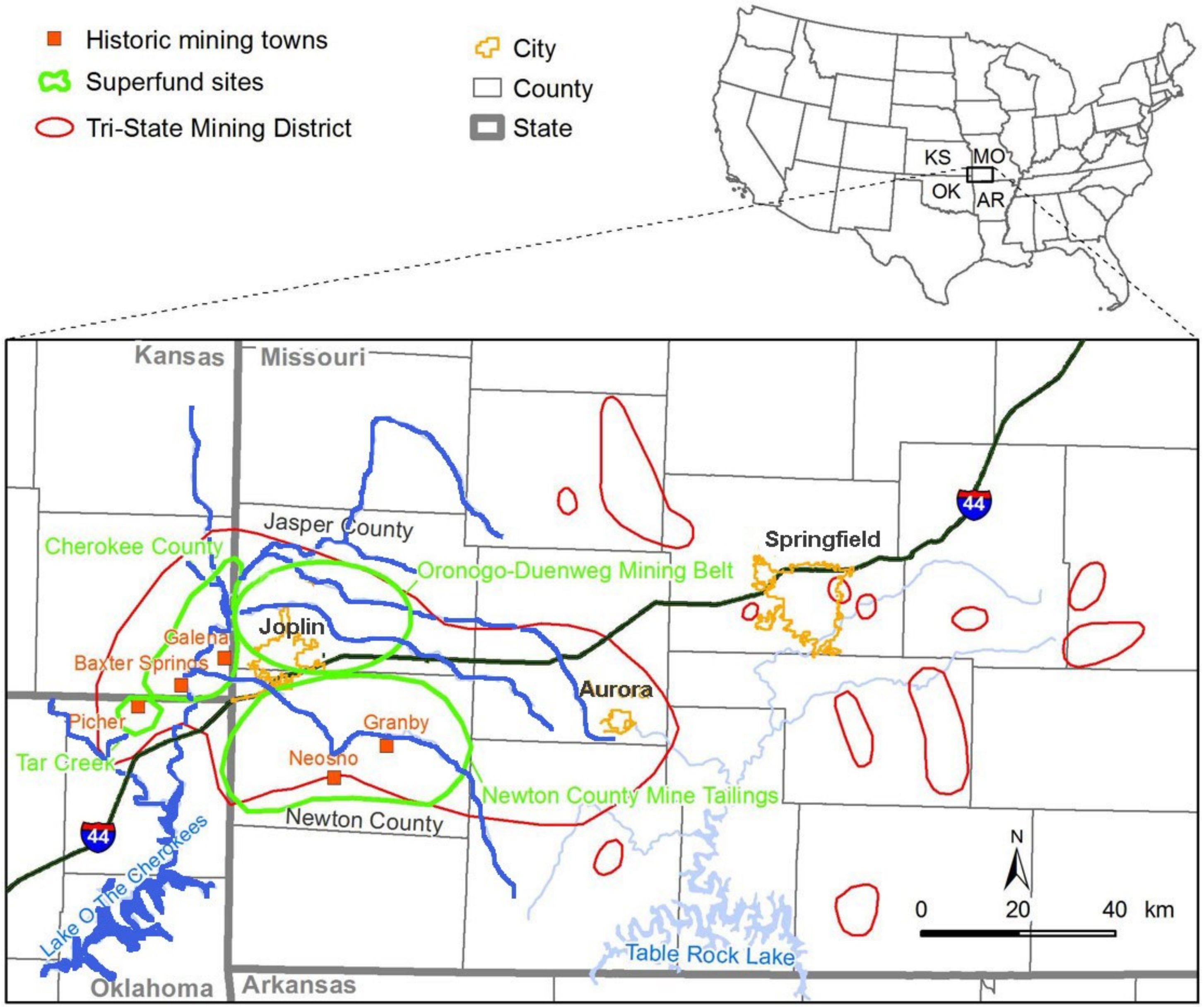
Differences in which geochemical phase is the metal attached to, indicates significant differences in the chemical weathering and mobility between Pb, Zn, and Cd.

- Although small, the bioavailable (exchangeable and carbonate fractions) becomes more significant in sediments with high metal content.
- Within the bioavailable fraction, the carbonate-bound 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 mobilize Pb.
- Cd seems to blend more uniformly within the sediment (higher mobility) and to store in the organic fraction. Its higher mobility allows Cd to incorporate to plants (mostly at/in their roots).
- Zn will be released if system shifts to reducing conditions (and associated low pH). Cd competes with Zn for adsorption sites in Fe-oxides and clays.

Proposed Remediation Methods in the TSMD

- **Phytostabilization**
- **Wetland**

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



In case metals may remobilize:

Receiving Water Body for Surface Water

Lake O The Cherokees

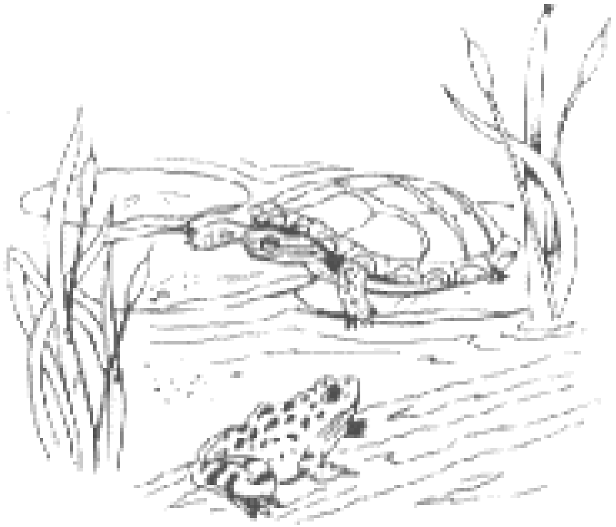
Groundwater

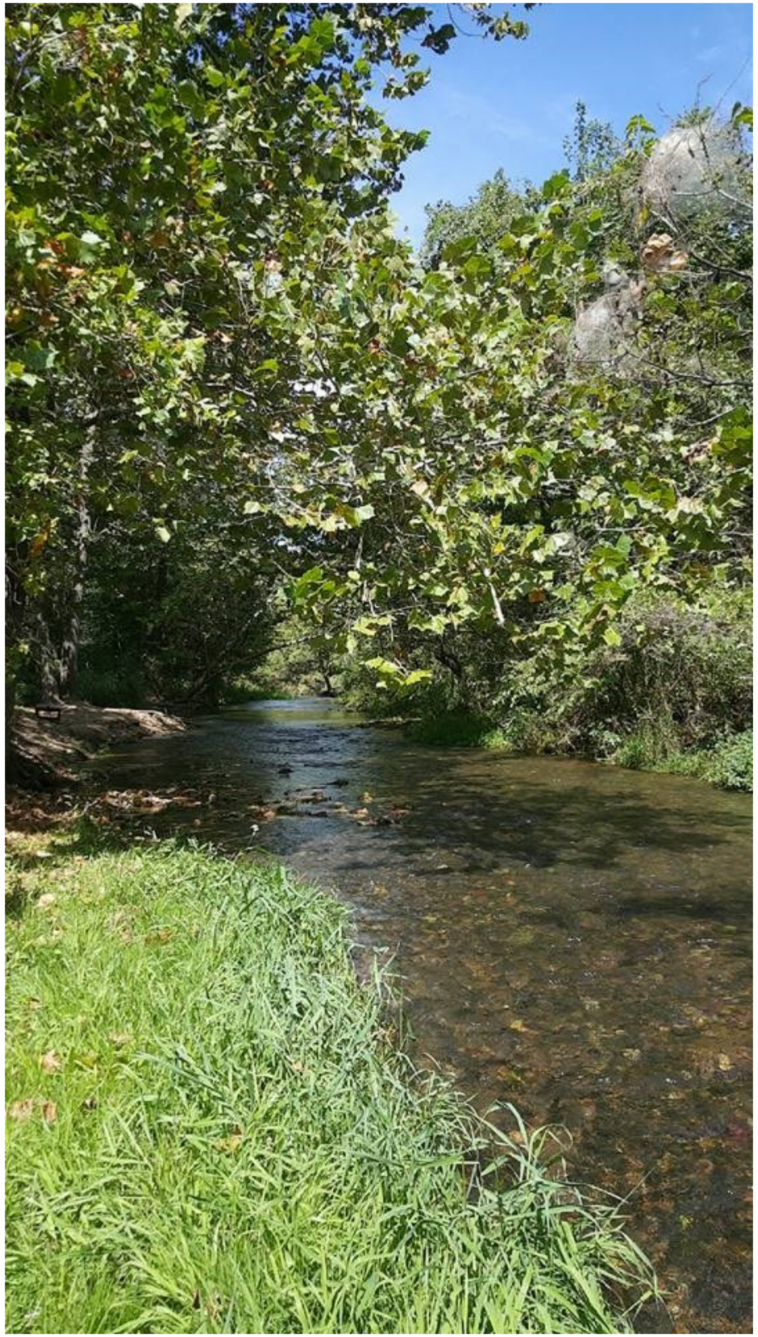
Ozarks Aquifer

Remediation is Effective (according to various studies, among them Brown et al. 2014; Gutierrez et al. 2016)

Future work

- Mapping metal content in sediments to verify the effectiveness of applied remediation actions,
- Conduct sequential extraction of more samples. In spite this technique being time consuming and interpretation of results being difficult, it provides a better understanding of the specific conditions at which metals stored in the sediments may become available, and which can be used to devise better strategies to contain any toxic metals.
- Zach Collette is conducting sequential extraction in samples of Turkey Cereek (Joplin, MO). See his poster at this meeting.





Spring River near Aurora

Thank you!

Questions??