Analysis of metal contaminated sediments in the Tri-State Mining District: procedures revisited

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A common occurrence

Metals in mine wastes and/or exposed ore progressively contaminate areas (streams, soil, groundwater), especially areas near abandoned mining and smelting centers

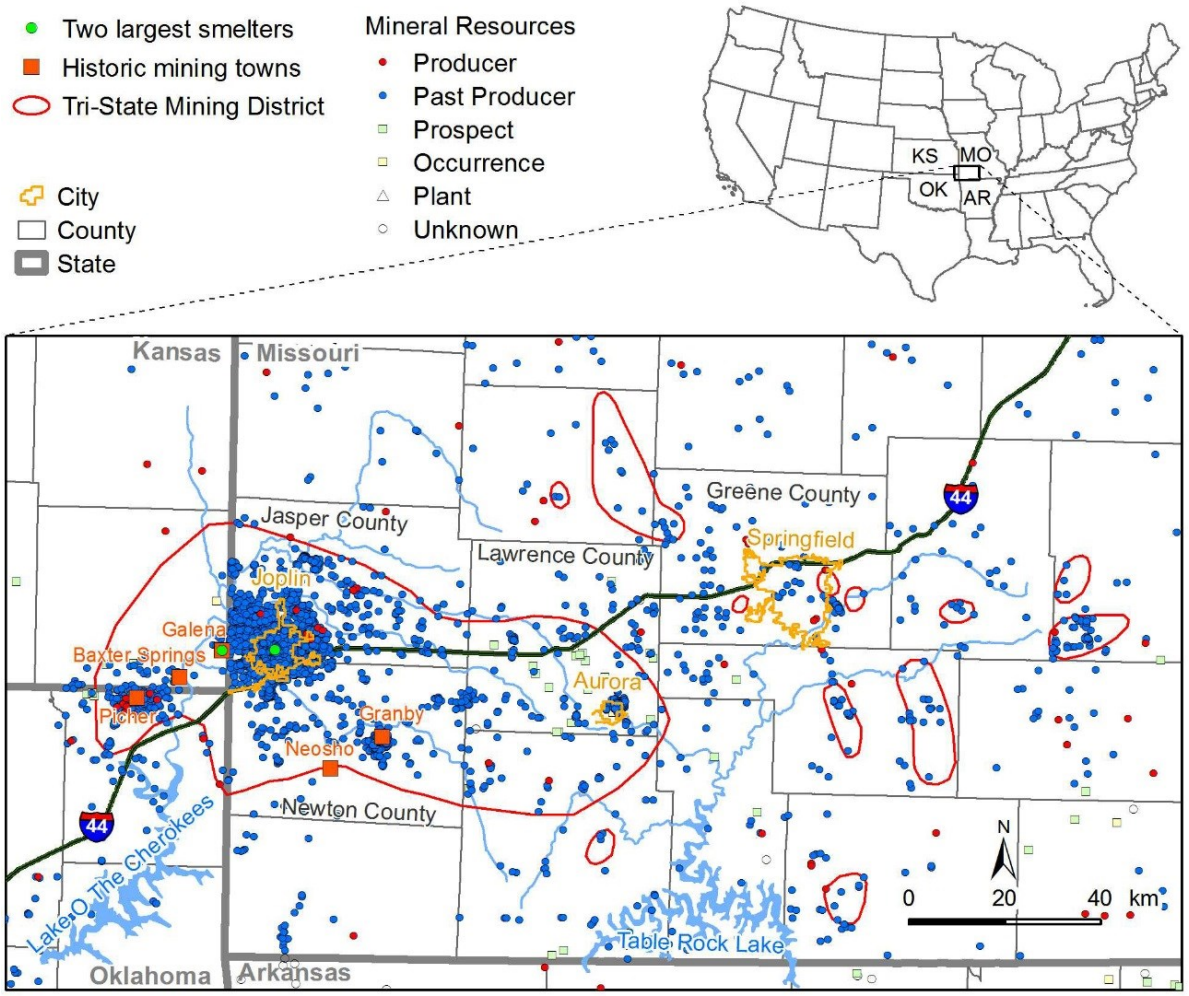
Photo: NASA

The Tri-State Mining District of Missouri, Kansas and Oklahoma (TSMD)

Operated from 1850 to 1970s; peaked 1916-1925

Metals mined: zinc and lead. The buffering capacity of limestone exposed at TSMD limits mobilization of the metal. Toxic levels of Pb in groundwater and of Cd in streams remain a concern.

Location and extent of TSMD



Notice ore enrichment locations are highly irregular and dispersed

Contamination sources: chat piles, smelter dust/fallout, walls exposed in abandoned mine shafts

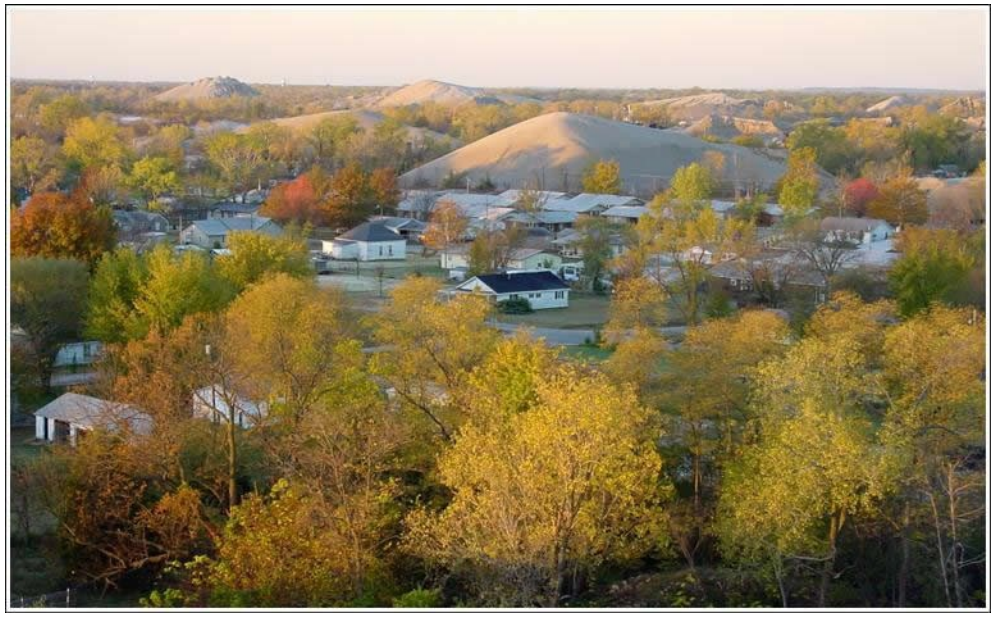


Photo: EPA

What to measure and how often?

Knowing which parameters better measure the intensity and extent of the contamination is needed for a meaningful, cost-effective study.

Chemical: ICP inductive plasma spectroscopy, AA, titration, etc. Destructive, costly, time consuming.

Physical: XRF, XRD, petrographic microscope. Non-destructive, instruments are costly but running samples is not (few to none required reagents).

Biological: e.g., Bioessay, requires organisms in observation/testing. Organisms can be fish, birds, nematodes, insects, crayfish, plants, etc.

.. How often?

- Water composition changes rapidly (hours), especially if the residence time is short (running water)
- Soils/sediments. Composition remains stable for longer periods of time (years) as metals will adsorb to clay particles of mud. Solid fragments will also settle and remain relatively immobile.
- Organisms. Each has a life cycle, may adapt to changing environment, also have ‘memory”. Excellent indicators of quality of water/habitat

Parameters to consider when designing a study

1. Metals to analyze (some trace metals are harder to analyze),
2. Depth at which the sediment sample will be collected
3. Location within the stream channel,
4. Size fraction of the sample,
5. Mobility and/or bioavailability of the metal, and
6. Toxicity to a particular organism

… revisiting…..

Parameters to consider when designing a study

1. Metals to analyze (some trace metals are harder to analyze)

   Hg needs additional fittings to an instrument and sample preparation, Cd, Co, Cr are trace elements and more difficult to measure; major elements may interfere with reading, XRF instruments are calibrated for either light or heavy metals.

2. Depth at which the sediment sample will be collected.

   Sediments generally collected at surface, soils can be collected at different depths of the soil profile.

3. Location within the stream channel.

   locations include bank, 1 foot inside channel, middle of channel.

Parameters to consider when designing a study

4. Size fraction of the sample, commonly < 2 mm

   fine sand only, only clay+silt

5. Mobility and/or bioavailability of the metal,

   Mobility is determined by how much it dissolves in water, weak acid, strong acid →sequential extraction

   Bioavailability by various methods, e.g. measuring metal in plant tissue or fish tissue, dissolution in acid with same composition of acids present in the gut.

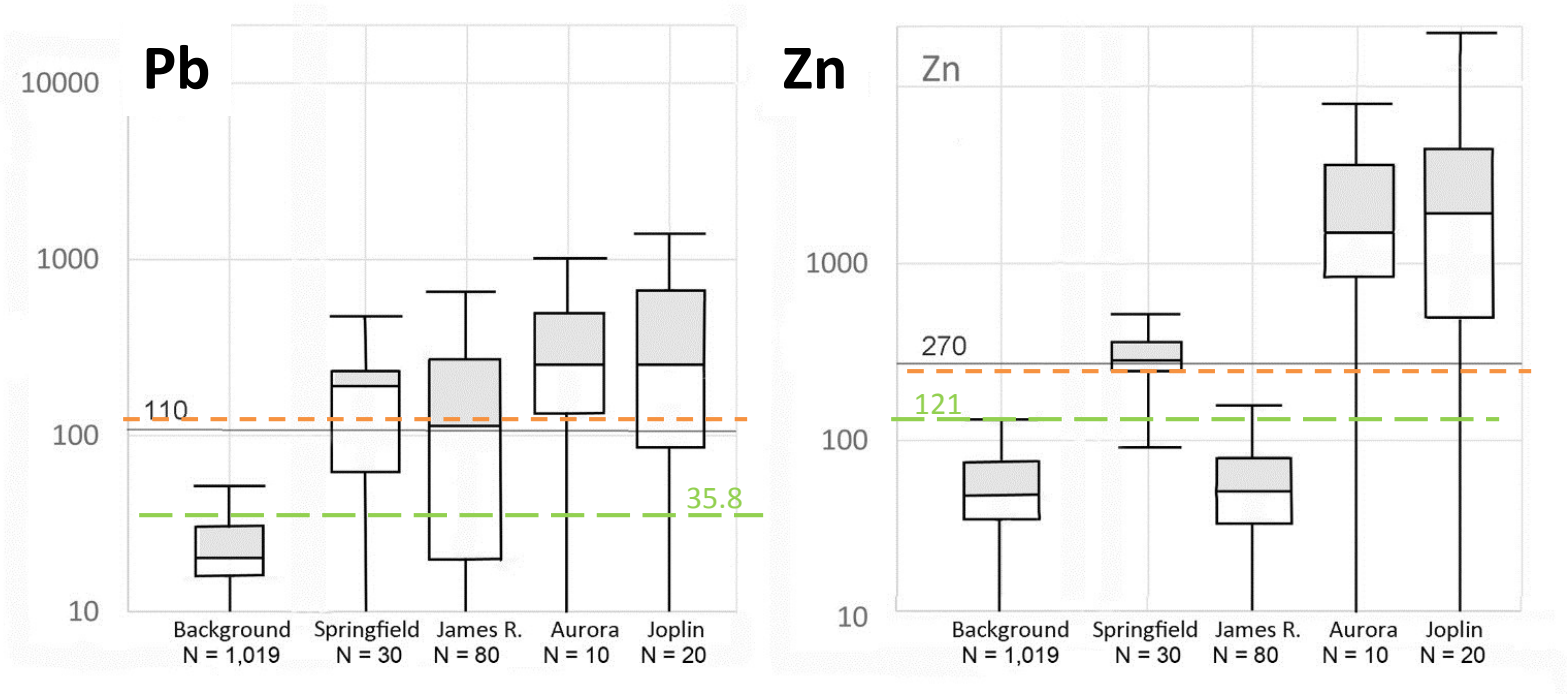
6. Toxicity to a particular organism, e.g., LD_{50} which is the dose at which 50% organisms die. Besides mortality, studies may determine changes in behavior.

Zn, Pb and Cd in selected sites within the TSMD

mean, median*, range of values for TSMD

Site	Cd, mg/kg	Pb, mg/kg	Zn, mg/kg	Method	Reference
KS , stream sediments, N=87	42 **13*** 0.6 - 460	650 **180*** 22 - 7,400	5,600 **1,800*** 100 - 45,000	AA, ICP digestion with HCl-HF-HNO_3-$HClO_4$	Pope et al. 2004
OK, Tar Creek, stream sediments N= 9	n/a **9.0*** 1 - 40	n/a **200*** 30 - 400	n/a **2,000*** 500 – 5,000	ICP-MS digestion with *Aqua Regia*	Andrews et al. 2009
MO, Turkey Creek, stream + floodplain sediments N= 65	14.0 **9.1*** 0.5 – 65	368 **145*** 14- 3,880	2,494 **1,755*** 35 – 9,230	ICP-MS digestion with *Aqua Regia*	Peebles 2013
MO, Center Creek, stream sediments, N=11	56.2 **10*** 5 - 370	333 **300*** 10 – 1,020	1,557 **<459*** 30 – 11,500	ICP-MS digestion with *Aqua Regia*	MDNR, 2011b Median values read from graph
MO, Granby, soils, N= 18	19.9 **BDL** BDL – 146.2	3,836 **499*** 22 – 55,215	17,648 **11,146*** 92 – 67,367	XRF	Carbone et al. 2007
TSMD, stream sediments, N= 79	19.4 **9.0*** 0.62- 376	244 **91.2*** 6.4- 3,020	2,701 **1,190*** 35.2- 19,900	ICP-MS digestion with *Aqua Regia*	Ingersoll et al. 2008
PEC (Probable effect) Quality Guidelines	5	128	459		Mc Donald et al. 2000

Box-Plot notation



Ecological guidelines for sediment quality

- - - Effect Range-Median (Long and Morgan, 1990) 110 µg/kg Pb; 270 µg/kg Zn

— — Threshold effect concentration TEC (MacDonald et al., 2000), 35.8 µg/kg Pb; 121 µg/kg Zn

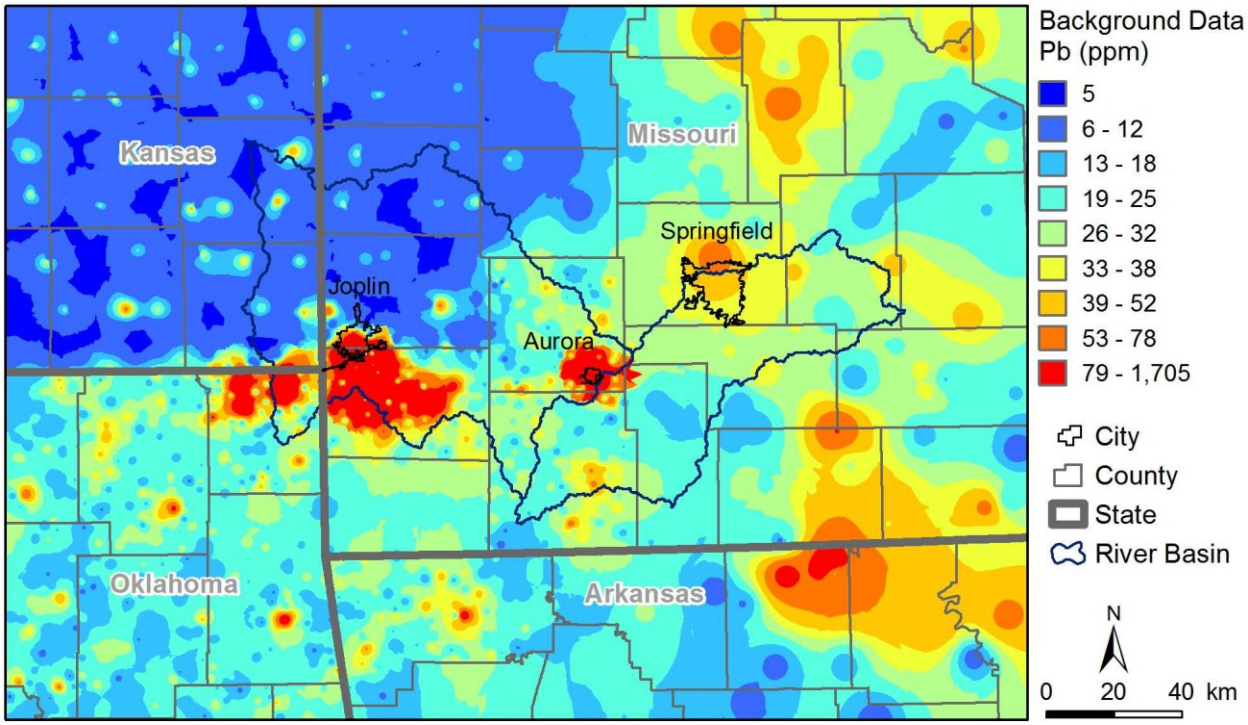
Sediment toxicity

- EC_{20} = effect concentration 20%
- PEC = probable effect concentration
- PEQ = probable effect quotients
- ESBs = equilibrium partitioning sediment benchmarks

Besser J.M., Brumbaugh W.G., Ingersoll C.G. 2014. Characterizing toxicity of metal-contaminated sediments from mining, Appl Geochem,

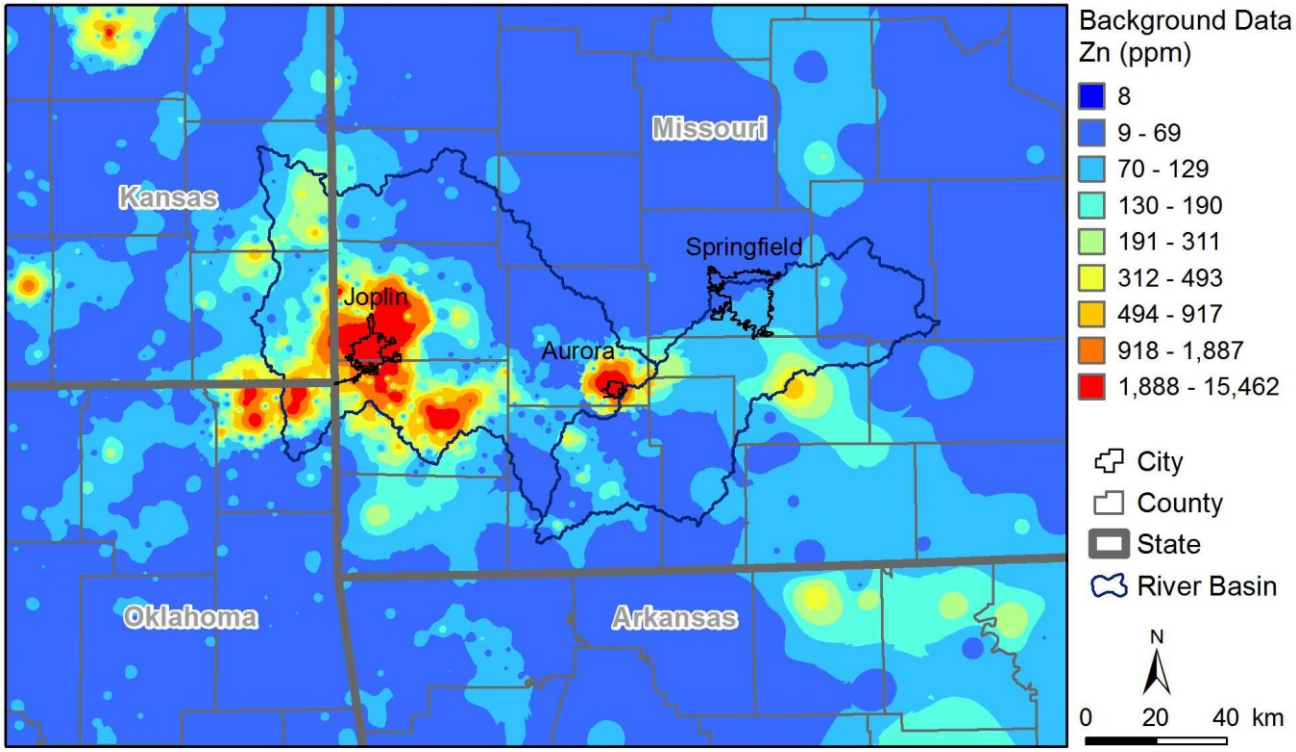
MacDonald D.D., Ingersoll C.G., Berger T.A. 2014. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch Environ Contam Toxicol, 39, 20-31.

Sediment background data (N= 1,019) from the National Geochemical Database -available online-



Long and Morgan, 1990; 110 µg/kg Pb

Sediment background data (N= 1,019) from the National Geochemical Database -available online-



Long and Morgan, 1990; 270 µg/kg Zn

Conclusions

- Sediment studies follow different approaches, from which the more common are:

  -sampling: surface sediments collected in the middle of the stream,

  -analyses: determination of metal content of <2mm sediments using ICP after extraction with *aqua regia*.
- Cd, Pb and Zn are present in a wide range of values; median concentrations are similar among studies,
- Highest Cd, Pb and Zn concentrations are still found at or near former mining operation sites, but are expected to disperse with time

Thank you!