Trace Metal Retention on Fe and Mn oxides in First Order Urban Streams

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I. Problem

Urban environments convey trace metals from local and atmospheric sources to stream channels.

Trace metals can be retained on Mn, Fe, Al oxides, or organic matter.

Mn oxidizes slower than Fe, and may be less available.

Previous Work

Manganese oxides have shown to be good sites for retention of Pb and other trace metals. They can take Pb into their crystal structure or retain them on their surfaces due to their flexible crystal structure and small particle size (Villalobos et al,2005, and included references).

In many previous studies it was found that oxides of Mn have highly preferential retention of Pb, when compared to Fe oxides.

Studies have shown that Pb emissions have peaked in the 1970's and has declined since (Weiss 2003).

II. Hypothesis:

1. Sediment particles in streams coated with Mn oxides will contain higher concentrations of trace metals (e.g. Pb) than particles with lower concentrations of Mn oxides.
2. Stream beds will have higher concentrations of trace metals than soils in adjacent forested areas.
3. The amount of manganese, iron and associated trace elements (Cd, Cu, Co, Pb, Zn) in the sediment will decrease with distance from the urban runoff source within these first-order streams.

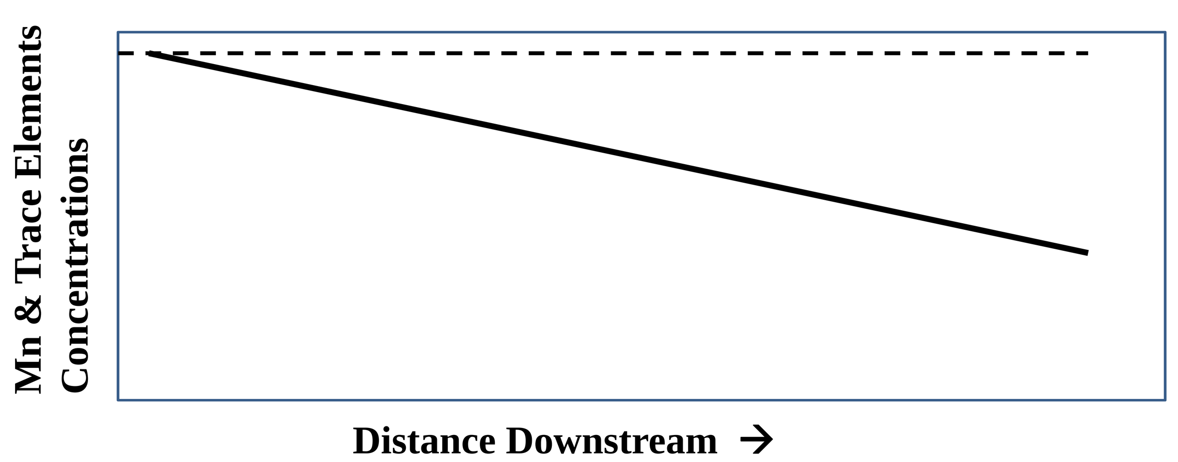


Figure 1: Predicted behavior of manganese and trace element concentrations in the sediment of a first order stream as a function of distance downstream. The dashed line indicates the null hypothesis.

III. Study Site and Methods

Fig. 2A: Yellow line shows the path of the 1st order channel in the location of the Adelphi subdivision (~ 1950's) near the NW Branch of the Anacostia River. The yellow pins show the collection sites of the reference hillslope samples.

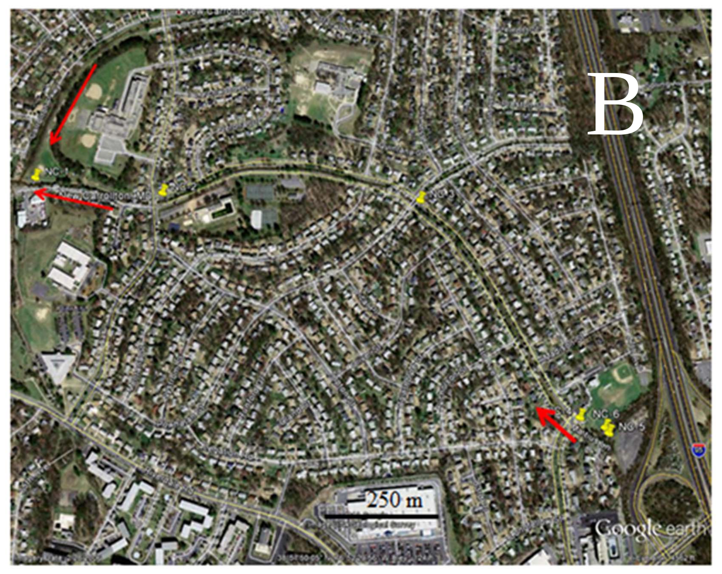


Fig. 2B: 1st order concrete lined channel the location is New Carrollton, MD. The yellow pins indicate the locations the samples were collected. The red arrow shows the direction downstream. This channel was made in the 1950's.

III: Methods

1. Collection of sediment samples at Sample sites

A. **Hillslope Divide Sediment Samples**: 0 – 2.5 cm depth , 5 samples sieved into 3 size fractions.

B. **Natural Channel Sediment:** Surface and depths of 0 – 2.5 cm. The samples were collected in increments of 6.1 meters determined with a tape measure. Samples were sieved into 3 size fractions (< 63 um, 63-1 mm, > 1 mm) for a total of 27 samples analyzed.

C. **Concrete Channel:** Fe and Mn oxide coatings chipped from concrete lining was collected at landmarks. Distances were measured by using air photos from Google Earth. There were six samples distributed along the 1st order channel length.

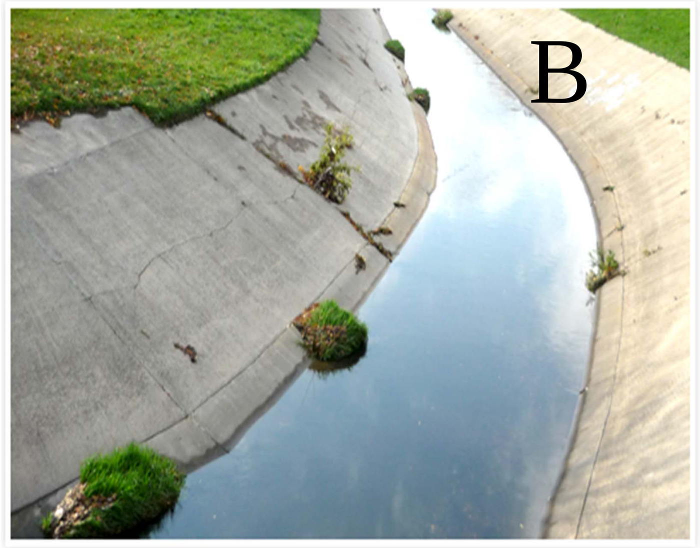


Figure 3: A. Natural urban stream study site at outlet showing coarse bed material
B Concrete lined stream (no bed sediment),

2. Grain size analysis and weighing of samples of ICP-MS analysis.
3. Sample preparation for ICP-MS by dissolving coatings with 10% Nitric Acid .
4. Preparation of standards for ICP-MS analysis and analysis of solutions

IV. Results

Grain Size Distributions

The hillslope has finer grained particles than the alluvial stream channel. The bed sediment size did not show downstream variations.

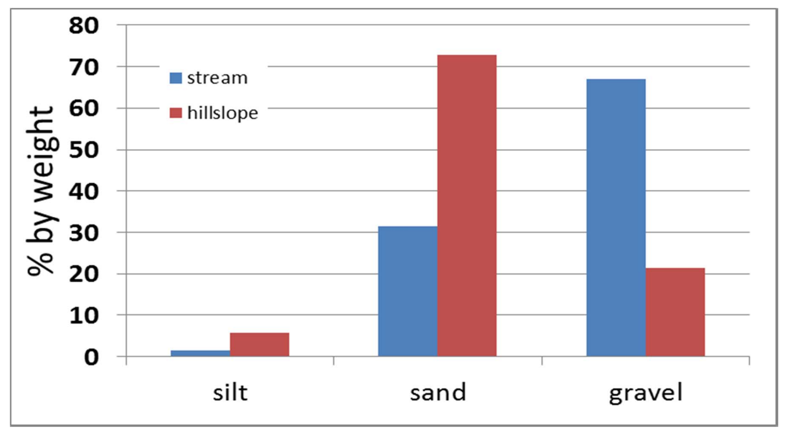


Figure 4: Grain size fractions

Mn coatings on surfaces: Comparison among sites

Fig. 5 compares the site-averaged amount of Mn that was acid leached from samples from each site. Mn amount is expressed as ug Mn leached per weight of sample. The alluvial channel has much less Mn on surface coatings of coarse bed grains (~ 4 mm).

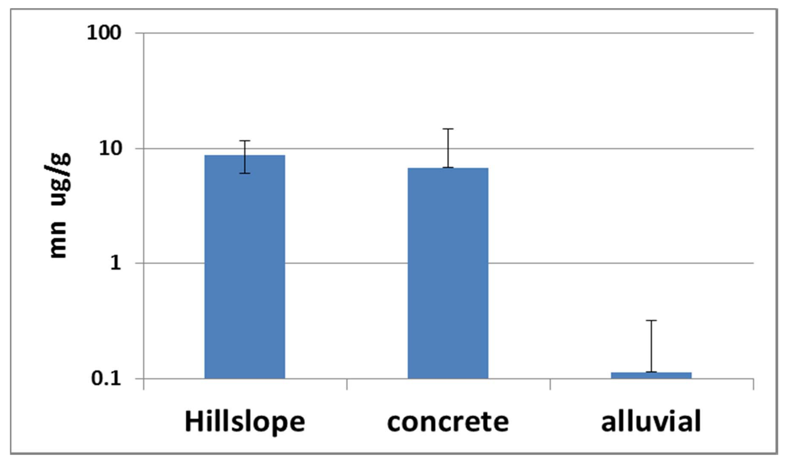


Figure. 5: Mn coatings on surfaces

Comparison of Mn/Fe ratios and Pb/Mn ratios among sites

Molar ratios (fig. 6) were calculated for Mn/Fe, Pb/Mn, and Pb/Fe.
Mn/Fe ratios were similar for all 3 sites.

Pb/Mn ratios are highest in the hillslopes and the lowest in the alluvial channel. This difference might reflect residence times. Pb/Mn ratio is less than 0.1 ,which is consistent with the amount of Pb that can be on or in Mn oxide minerals (Villalobos, 2005).

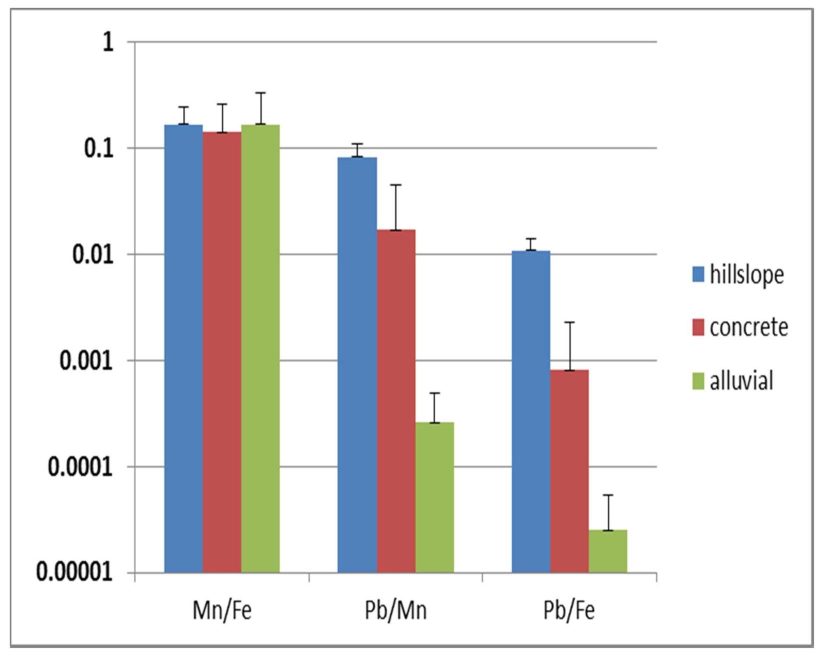


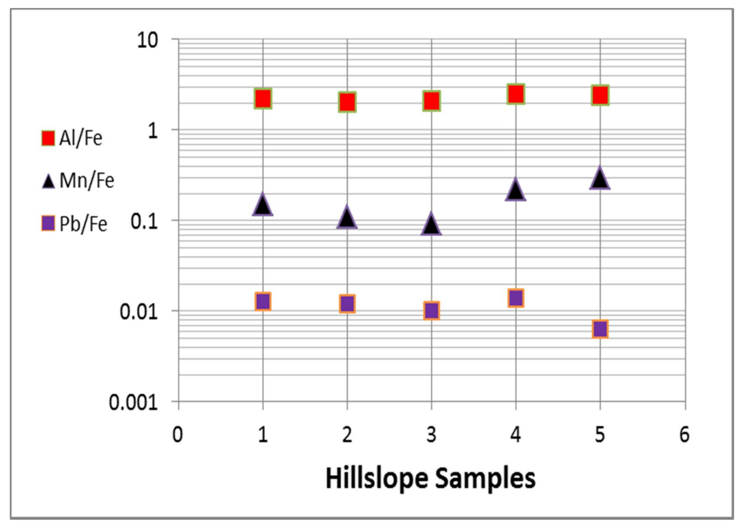
Figure 6: Averaged elemental ratio data from all three sites

IV. Results Continued

Variations within the Sites

Hillslope Samples

Figure 7: Mn/Fe ratios and trace element ratios are similar among the hillslope sites.



Concrete-lined Channels:

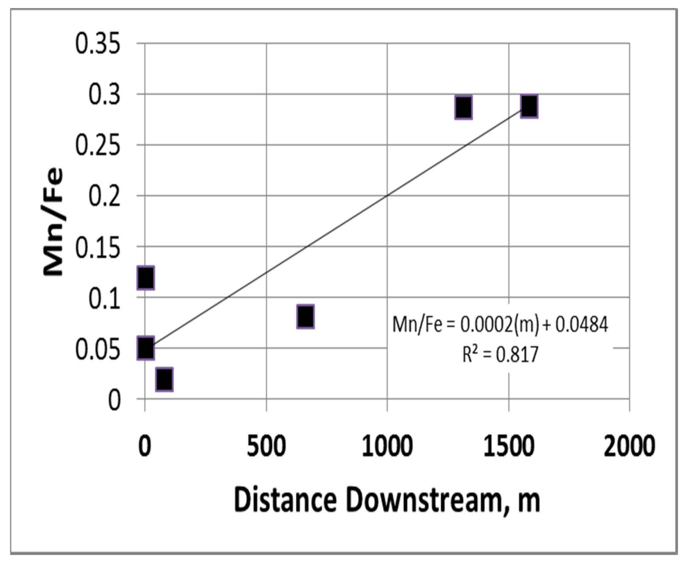


Figure 8: Mn/Fe ratios increase with distance downstream in the concrete lined channel.

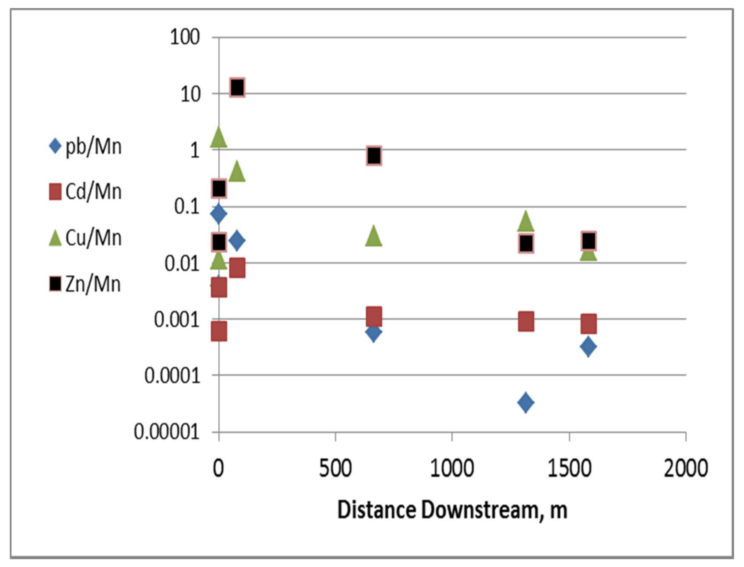


Figure 9: Trace element ratios decreased downstream (reflects trace element sorption to both Fe and Mn in the concrete lined channel)

Alluvial Channel:

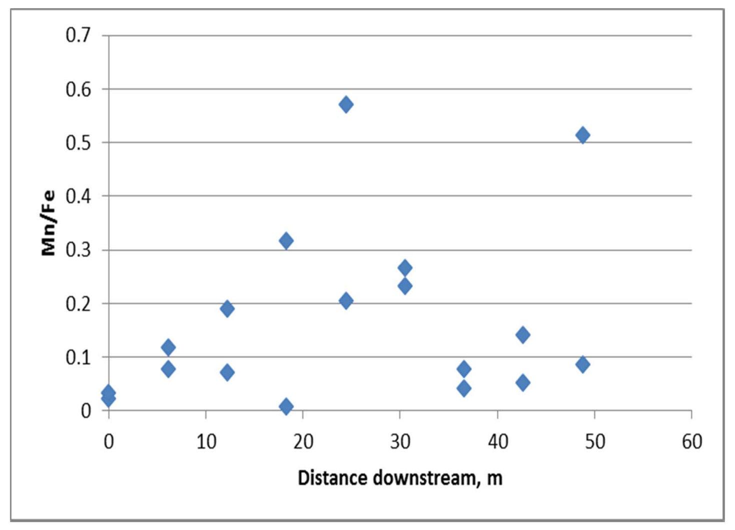


Figure 10: Mn/Fe ratios increase downstream.

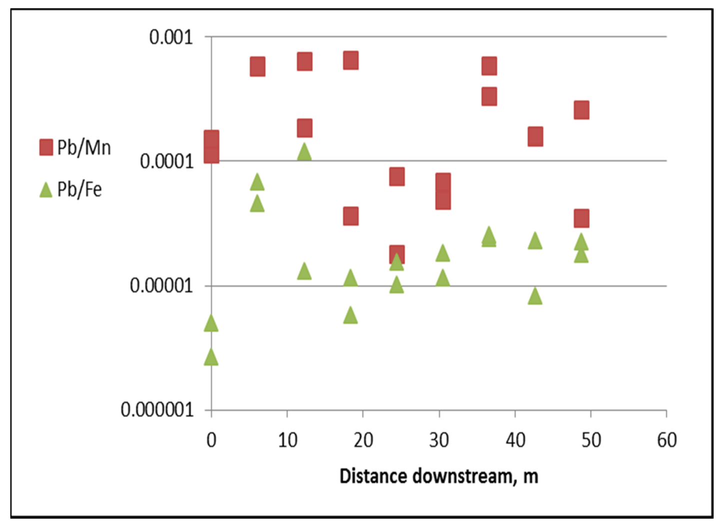


Figure 11: Pb/Mn ratios are much higher then the Pb/Fe ratios.

V. Conclusions

1. Acid-leached Mn coatings on hillslope and concrete channels were similar. The 4 mm particles in the alluvial channel had less Mn per gram of sediment than found in the < 63υ fraction of hillslope soils. The smaller amount in the alluvial channel may represent shorter residence time of these particles.
2. Mn/Fe ratios were similar among all the sites. This may reflect similar groundwater and soil water chemistry for the 3 sites. Pb/Mn ratios were significantly less for the alluvial channel site than the other 2 sites. If these alluvial particles have lower residence times, these particle might reflect the lower Pb levels in the atmosphere. This is opposite of the hypothesis (2).
3. In the concrete channel, Mn/Fe ratios increased downstream. Trace metal ratios to Mn or Fe decreased downstream.

VI. References

Nelson YM, Lion LW, Shuler ML, Ghiorse WC (2002) Effect of oxide formation mechanisms on lead adsorption by biogenetic manganese (hydr)oxides, iron (hydr)oxides, and their mixtures. Environmental Science & Technology 36: 421-425

O'Reilly SE, Hochella MF (2003) Lead sorption efficiencies of natural and synthetic Mn and Fe-oxides. Geochimica et Cosochimica Acta 67: 4471-4487

Post JE (1999) Manganese oxide minerals: Crystal structures and economic and environmental significance. Procceedings of the Natural Academy of Sciences USA 96: 3447-3454

Tebo BM, Bargar JR, Clement BG, Dick GJ, Murray KJ, Parker D, Verity R, Webb SM (2004) Biogenic manganese oxides: Properties and mechanisms of formation. Annual Review of Earth and Planetary Sciences 32: 287-328

Villalobos M, *Elements*; September 2005; v. 1; no. 4; p. 223-226; DOI: 10.2113/gselements.1.4.223

Weiss, Dominik. "Spatial and Temporal Evolution of Lead Isotope Ratios in the North Atlantic Ocean between 1981 and 1989." *Journal of Geophysical Research* 108.C10 (2003) Print.