LANDUSE IMPACT ON METALS IN STORMWATER: MASS LOADS AND SIZE FRACTIONATION

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Introduction

Surface water impairment due to metals has been identified as a human health and ecosystem concern (e.g., Cd, Cr, Cu, Pb, and Zn; USEPA, 2011). Two novel fractionation approaches were employed to better understand metals distributions. Highway runoff was found to generally have the highest mass loads and greatest "dissolved" fraction. Cu, Zn, Cr, Ni, and Pb were commonly associated with colloidal organic matter. SEC-ICP-MS confirmed that Cu co-eluted with the organic matter (absorbance, $\lambda = 254$ nm); Ni and Pb were found to co-elute with organic matter as well as be found in smaller size fractions, and Cd and Zn were generally associated with lower molecular weight entities than the organic matter.

Methods

Sample collection. Eight collection events were conducted across four land uses: highway (H1, H2, H3), urban (U1), agricultural (A1, A2, and A3), and less impacted reference (N1; McKenzie and Young, 2013a)

Novel fractionation. A portable flow-through centrifuge was generally used in the field to continuously separate solids; grab samples were syringe filtered in the field both before and after centrifugation. Ultrafiltration was completed in the lab. Sample concentration were determined with an ICP-MS and fractionated concentrations, based on size and inferred density, were calculated; mass loading, partitioning distribution coefficients, and enrichment factors were also calculated (McKenzie and Young, 2013a).

SEC – ICP-MS. SEC with online ICP-MS was employed using Phenomenex s2000 column (300 x 4.6 mm) with an isocratic method (4 mM NaH_2PO_4, 86.5 mM NH_4NO_3, ionic strength 0.1, pH 7, 0.8 mL/min; method detailed in McKenzie and Young, 2013b).

Results

Highway and urban samples were generally found to be enriched in the metals of interest, suggesting that anthropogenic sources were present; Cd, Cu, and Zn were most enriched. Highway and urban land uses also had the greatest mass loading (mg/km^2); highway mass loadings were 10 to 500-fold greater than the

less impacted reference site, while urban loadings were often ~10-fold higher than the reference. The novel fractionation approach, exemplified in Figure 1, demonstrated that highway and urban samples contained the highest concentrations of dissolved metals (<10 kDa). Based on pseudo-partitioning distribution coefficient values, Cd and Pb were associated with large dense particles, and colloid organic matter sorbed Cu, Zn, Cr, Ni, and Pb.

SEC – ICP-MS analysis revealed that metal molecular weight distributions varied by land use, however many patterns existed across all samples (Figure 2). Many metals were partially or wholly associated with the organic matter peak suggesting that the metals were complexed by the organic matter; this was most prevalent for Cu, but also for Ni and Pb. Mg presented a well-defined peak (~700 Da), particularly in agricultural samples; this is thought to be chlorophyll. Mn, Ni, Pb, and to a lesser extend Zn, were found to present multiple peaks in most samples, suggesting that there were multiple complexing agents. Cd and Pb were also commonly observed ~100 Da apparent MW.

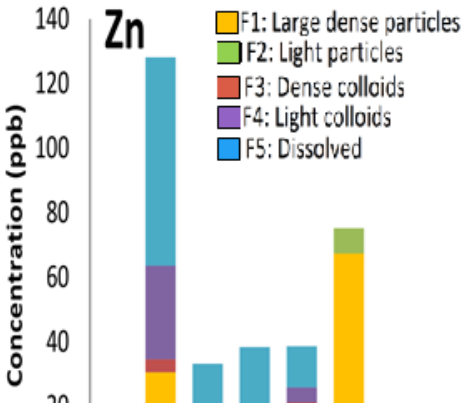

Figure 3. Zn results from novel fractionation approach (McKenzie and Young, 2013a).

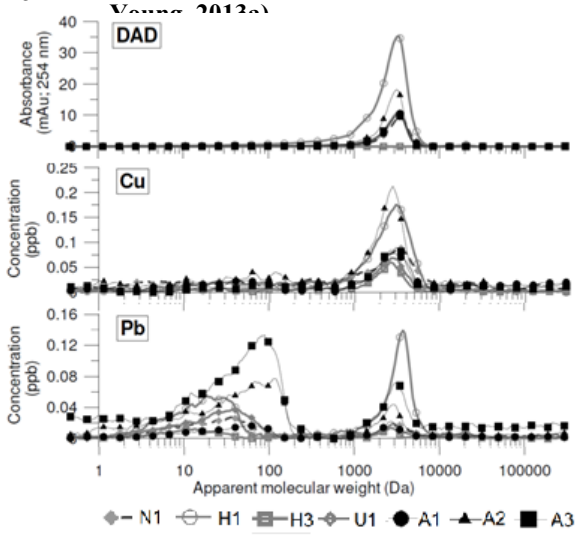

Figure 2. SEC – ICP-MS chromatograms (McKenzie et al., unpublished).

Conclusion

Fractionation is an important tool for understanding the fate and transport of contaminants. In this work, two new approaches were employed to fractionate metal concentrations in stormwater samples from four land uses. Highway and urban runoff likely pose the greatest concern as they contain the highest total and dissolved concentrations, which likely reflects anthropogenic sources.

References

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