THE IMPORTANCE OF ZN FOR ASSESSING THE IMPACT OF HEAVY METALS IN URBAN STREAMS

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Abstract. Comparison of dissolved Zn, Ni, As, and Pb concentrations in highly and minimally impacted streams in Athens-Clarke County shows that only Zn is enriched in the impacted streams. This pattern is in part controlled by the large quantity of anthropogenic of Zn in our environment. However, this factor alone does not explain the uniformly low concentration of Pb. This metal is also an important anthropogenic metal. Pb, unlike Zn, is probably in low abundance in urban streams because it's inherent low solubility and strong adsorption properties.

INTRODUCTION

Comparison of selected dissolved heavy metal concentrations in highly and minimally impacted streams in Athens-Clarke County (ACC) reveals that most constituents in the impacted streams are not significantly elevated except for Zn. This paper addresses possible reasons for this and the implications of these observations.

DATA

Table 1 below presents a set of dissolved trace metal concentration data for selected streams in ACC collected through the Upper Oconee Watershed Network during the Winter of 2002. Similar concentrations for these same elements have been observed in samples collected other times. All samples were passed through a 0.45µ filter to remove particulate material and then chemically analyzed with an ICP-MS instrument at the Environmental Analysis Laboratory at the University of Georgia.

Among the streams, MIDO 301 and NORO 401 are minimally impacted by urban pollution. Both streams are located in forested areas or have wetlands upstream from the site of collection. Additionally, these streams have relatively low specific conductivities (~ 46µS) and high biological index scores, which likely indicates little or no pollution. In contrast, five stream sites (MIDO 803 and NORO 601, 502, 517, 615) are located within or immediately downstream from areas with identifiable pollution sources. All have relatively high specific conductivities (>120µS/cm) and low biological index scores indicative of possible pollution sources (see Wenner et al. 2003). NORO 601 is located downstream from a fertilizer factory. NORO 615 and MIDO 803 are located near major highways within older residential areas, NORO 517 lies in an abandoned, early 1900 era industrial site, and NORO 502 is near a cement plant.

DISCUSSION

It is noteworthy that of the trace metals examined, only Zn shows a consistent pattern of enrichment in the impacted streams compared to the minimally impacted streams. Concentrations of major cations (Na, Ca, K, Mg) and anions (Cl, SO_4) in these impacted streams are also generally elevated, reflecting their higher specific conductivities. The Zn concentrations in the impacted streams are at least an order of magnitude higher than the minimally impacted streams. The dissolved Zn concentration of Carr Creek is anomalously high, consistent with it's unusually high specific conductivity (480µS for the sample reported above).

A number of factors may explain the pattern of enrichment for Zn compared to the other metals. Among the more obvious is the likelihood that Zn is a more abundant anthropogenic pollutant. The geochemical properties of these trace metals also has to be evaluated. Each of these factors are discussed below.

Source Controls

Although it is not known what the specific source of the trace metals is for the impacted streams in ACC, a USGS study in the Atlanta metropolitan area (Frick et al., 1998) suggests that most trace metals probably originate from industrial air emissions. Their study, however, does not address such potentially important sources as smaller industrial producers and litter and debris within a stream. A toxic release inventory cited

Table 1. Specific Conductivity and selected dissolved trace metals in streams in the Upper Oconee Watershed in Athens-Clarke County collected during the Winter of 2002

Sample ID	Sample Location	Conductivity (µS/cm)	Zn (ppb)	Ni (ppb)	As (ppb)	Pb (ppb)
MIDO301	Tributary of Bear Creek	45	3	0.5	0.3	0.13
NORO401	Sandy Creek	46	2.4	0.7	0.4	0.14
MIDO803	Brooklyn Creek	120	20.1	0.6	0.4	0.12
NORO601	Carr Creek	480	205.9	28.2	0.3	bdl
NORO 502	Unnamed Ck. @Barber St So of ByPass	246	21.2	1.4	0.5	0.15
NORO 517	Unnamed Ck @College & Cleveland Ave	158	29.3	0.9	0.4	0.75
MIDO 615	Tanyard Ck @UGA Tate Ctr.	162	23.8	1	0.4	0.09
Detection Limit			*0.5*	*0.2*	*0.2*	*0.05*
EPA Guideline for Drinking Water			*5*		*0.01*	*0.015*

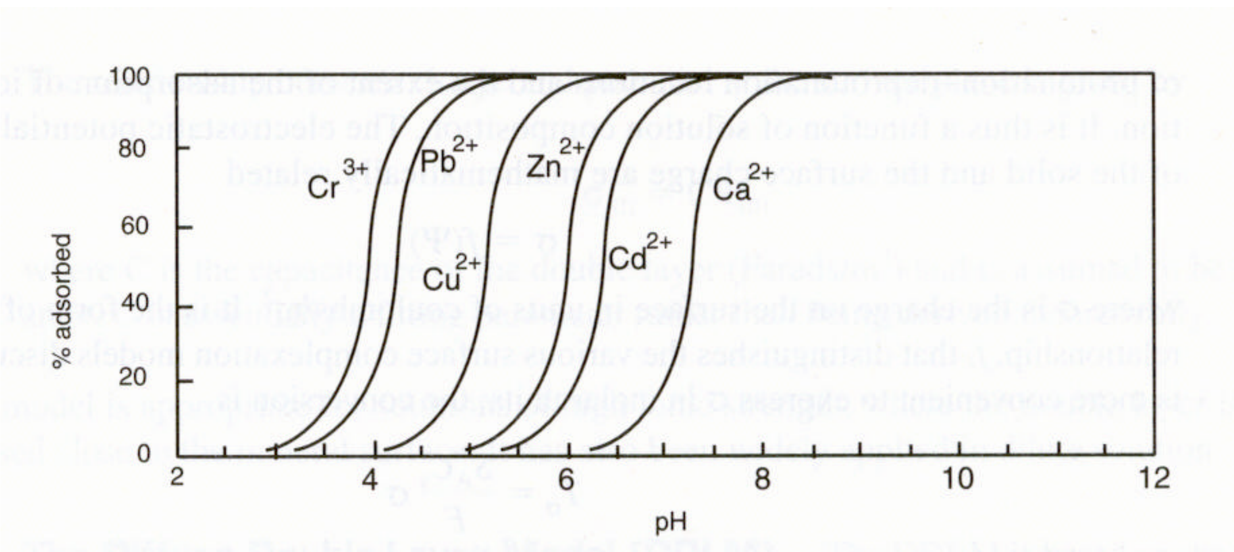

Figure 1. Adsorption of various dissolved constituents on hydrous ferric oxides as a function of pH (reproduced from Drever, 1998).

in this study reveals that three metals, Zn, Cu, and Pb, account for 99 percent of all trace metals released by industrial facilities. There is no reason to believe that the ACC area didn't receive a similar loading of trace metals. Their study, which focused on trace metal concentrations in stream bed sediments, also showed that when comparing urbanized and suburbanized streams with those in forested sites, some trace metals (Zn, Pb, Cd) were significantly enriched whereas others (As and Cu) were not. Frick et al. (1998) speculated that the trace metal enrichments in urbanized and suburbanized streams occurred when air borne contaminates migrated to streams during storm water runoff from impervious surfaces.

Although the enrichment of Zn within the impacted streams in ACC may in part reflect the abundance of anthropogenic Zn, this factor alone cannot explain all trace metal patterns. Although the toxic release inventory in the USGS study reveals that Zn is the metal in greatest abundance, Pb is also an important anthropogenic metal. The Frick et al. (1998) study found that the proportion of Pb to Zn was about 1 to 5. Since our data reveals that Pb concentrations in impacted and minimally streams are similar, another explanation is required to explain the Pb data.

Geochemical Controls

In general, most dissolved metals are in very low abundance in most streams and rivers. A notable exception is streams associated with mine sites. It is well known that low pH waters originating from many mines have high concentrations of heavy metals such as Pb, Cu, Cd, Zn, As, etc. (USGS, 1995).

The high solubility of these metals in low pH waters can readily be understood by inspection of appropriate Eh-pH diagrams, which are readily available in the literature (e.g., Drever, 1998). For example, these diagrams show that Pb has very limited solubility at most Eh-pH conditions and only becomes appreciably soluble at low pH (<5) conditions. Many other trace metals behave similarly. A notable exception is Zn. Under oxidizing conditions, Zn is appreciably soluble at pH values up to 8 (see Drever, 1998). These diagrams further show that as pH decrease, solubility of many metals increases. Because the pH of most streams in ACC range from 6.0 to 7.0, it seems possible that Zn concentrations could be significant in streams whereas Pb should be very low.

Another factor that limits the concentration of dissolved metals in streams is that many metals adsorb onto the finely suspended material that is ever present in streams. If a metal strongly adsorbs onto particulate material, then it's solubility becomes very low. Inspection of the adsorption behavior of different trace metals onto hydrous ferric oxides shown in Figure 1 below provides useful information in this regard.

This figure shows that Zn^{+2} has a relatively low degree of adsorption at pH values below 6, but increases to nearly 100% at pH values above 7. Thus it seems possible that Zn may exist in it's dissolved ionic form at appreciable concentrations in many streams in the ACC area since the pH of most streams is less than 7. This behavior contrasts with Pb, which as Figure 1 shows is strongly adsorbed at pH values above 5. This readily explains why we do not observe a significant concentration of dissolved Pb in most streams of the ACC area, despite the fact that this element in probably an important anthropogenic metal. Arsenic, another toxic trace metal, is also observed at very low concentrations in streams and shows no enrichment in the impacted streams. This element, which occurs as an arsenate species at near neutral pH values, is also strongly adsorbed onto iron oxyhydroxides as well as (Drever, 1998).

CONCLUSIONS

The analysis of selected dissolved trace metals in streams in the ACC area reveals that the concentration of Zn in impacted steams is elevated at least an order of magnitude above minimally impacted streams. Other trace metals such as Pb, As, and Ni show no such similar pattern. The likely explanation for this behavior may in part be due to the abundance of Zn introduced into the environment. Zn is one of the most abundant anthropogenic metals in our environment, whereas metals like As and Ni comprise only a very small amount of the total atmospheric addition. However, this explanation does not account for the low abundance of dissolved Pb in highly impacted streams. Pb is also an important anthropogenic metal in urbanized areas.

For Pb, consideration of it's geochemical properties best explains it's low concentration streams. Dissolved Pb and many trace metals have very low abundances in most streams because of their inherent low solubility at the pH conditions prevalent in most streams. Additionally, finely suspended particulate material in streams adsorbs many trace metals, which also limits their solubility. The notable exception is Zn. At the pH conditions of most streams, this element is somewhat soluble and does not strongly adsorb on onto ferric oxides.

IMPLICATIONS

Although the USGS study shows that other toxic trace metals such as As, Cd, Hg are introduced into the environment in only very minor amounts (<1%), Cd is of particular concern because it has similar geochemical properties to Zn. Dissolved Cd is a heavy metal that is toxic at extremely low concentrations. EPA lists Cd as a primary pollutant in drinking water with an MCL of 0.005 mg/L, one of the lowest concentrations listed for heavy metals. Inspection of the Eh-pH diagram for Cd (Drever, 1998) and Figure 1 suggests that, if introduced into a stream, Cd might be appreciably soluble. Zn is a listed by EPA as a secondary pollutant for drinking water, although this element can be toxic at low concentrations to some macroinvertebrate species (Ahsanullah, 1976).

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