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Dissolved trace metals in low-order, urban stream water, Columbus, Ohio

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ABSTRACT

Urban areas are thought to possess different geochemical characteristics than more natural regions due to large human population densities and intensified human activities that produce large quantities of waste products. In this work we have analyzed a number of urban streams in Columbus, Ohio, the 15th largest city in the U.S., for their dissolved trace metal concentrations. The three streams have subtle but measurably different land use patterns. Although, in general, the dissolved metal values observed are higher than global average river concentrations, there were no statistically different values between the streams. This suggests that urbanization may help to homogenize trace metal sources and fluxes, even on the small watershed scale, or that dissolved trace metals are not a variable that can be discriminated by land use subtype.

1. Introduction

The majority of people on our planet live in urban areas and this population is estimated to increase over the next decades by 3.9–6.3 billion people (United Nations, 2012). In areas of high human population density, natural geochemical and hydrological processes are greatly compromised, which, in turn have great consequences for biogeochemical dynamics, and the transport and fate of chemical constituents (Chambers et al., 2016). For example, land use change through urban development can lead to increased "patchiness" and heterogeneity in the landscape (Grimm et al., 2008). Hydrologic cycles in urban areas are highly modified by the increase in impervious surfaces, which changes the flow characteristics of streams, decreases recharge, and washes particles from impervious surfaces into the local aquatic systems (Connor et al., 2014). In turn, urban aquatic systems can have both natural and human-made components which also lead to heterogeneity in the system (Gessner et al., 2014). Recent work on urban ecology and biogeochemistry has strongly suggested that the role of heterogeneity must be quantified if we are to develop a better understanding of the workings of urban landscapes (Kaye et al., 2006; Cadenasso et al., 2007; Grimm et al., 2008; Kaushal et al., 2014).

Although much detailed and excellent work has been done on the geochemistry of trace metals in urban soils (e.g. Wong et al., 2006), less has been undertaken on urban river systems, and even less on low order urban streams. In the U.S., The Clean Water Act greatly helped decrease metal input into urban waters by reducing many of the point source inputs, but nonpoint sources are still significant contributors (Sanudo-Wilhemy and Gill, 1999; Neumann et al., 2005). A major source of both particulate and dissolved metals into urban rivers is the transportation sector (e.g., tire and engine wear, fossil fuel consumption — Councell et al., 2004; Gardner and Carey, 2004). Although great progress has been made in our understanding of the behavior of trace elements in natural aquatic systems, due in large part to better collection and more sensitive analytical techniques, fewer advances have been made in the understanding of trace element behavior in human dominated landscapes.

Past work on trace metal dynamics in natural settings suggests strongly that land use subtype can play a significant role in determining elemental speciation and other behavior (Gaillardet et al., 2004). In addition, much of the work done on the trace metal concentrations in urban settings has been directed toward particulate and/or sediment-soil analyses. In this work, we use state of the art sample collection and analytical techniques to describe the concentration of dissolved (0.45 μm filtered) trace

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metals in first-order urban streams during base flow conditions. The streams under investigation have subtle but distinct differences in land use/land type that we initially postulated would have consequences on trace metal concentrations, and thus transport and potential accumulation in these stream ecosystems. The heterogeneity of land use and hence of nonpoint elemental sources in urban settings could potentially lead to variations in metal concentrations in urban aquatic systems. These sources include human produced green space such as lawns/gardens, impervious surfaces such as highways, roads, parking areas, and buildings, and other urban features such as industrial areas. This variation makes non-point source quantification of trace metal fluxes very difficult to characterize (Kaushal et al., 2014; Chambers et al., 2016). This work was done, in part, to test the importance and impact of land use on urban aquatic geochemistry on the small hydrologic scale of first order streams. The primary research question of the study was, "do urban environments contribute various trace metal signals to streams depending on the distribution of land use subtypes?"

2. Study area

Columbus, Ohio is the capital and largest city in the state. It is the 15th largest city in the USA with an estimated (2015) population of ~850,000, and a population density of ~1400 km^{-2}. Samples were collected from three first-order streams and a stormwater outflow pipe draining parking lots in the Clintonville region and the suburb of Upper Arlington, in the north-central portion of the city. Clintonville has ~30,000 residents and is bordered on the east by Interstate 71. Upper Arlington was one of the first suburbs of Columbus, established by 1917. In 2010, it had a population of ~34,000 people, and a population density of 1325 km^{-2}. Upper Arlington sits at ~480 masl, and surface water flows into the Olentangy River to the east, as well as the Scioto River to the west. All the streams sampled flow into the Olentangy River, which in turn flows into the Scioto River, a tributary of the Ohio River, in downtown Columbus. The Olentangy River was also sampled downstream from the three tributaries and stormwater outflow pipe.

The three streams sampled were Rush Run, Adena Brook and Turkey Run, and their attributes are described in Table 1. In each of these low-order tributaries, samples were collected high up in the watersheds, as well as close to the discharge point at the Olentangy River. The stormwater outfall pipe is on the Ohio State University campus just north of the Drake Union, and its pertinent information is also shown in Table 1. The Olentangy River sample was collected south of the outflow pipe. Samples were taken at two locations (i.e. upstream, downstream) at the three streams under base flow conditions (Fig. 1).

3. Methods

3.1. Land use determination

Digital orthophoto quarter-quadrangles (DOQQ) from the Ohio Geographically Referenced Information Program in 2008 (OGRIP, 2010) were used in conjunction with land use zoning information (ODNR, 2010) and field observations to form generalized urban land use subtypes for all of the watersheds in this study. The land use zones assigned by the Ohio Department of Natural Resources (ODNR) were reclassified and grouped into the five subtypes: wooded areas, residential, industrial/commercial, impermeable, and green space. GIS was used to approximate polygon areas encompassing each distinguished urban land use subtype, and the areas of all polygons were then summed for each watershed and compared to the total watershed area to yield estimated percentages of each urban land use type within each watershed (Table 2). It is possible that the small scale and detailed differentiation of ODNR land use types into more general urban land use subtypes led to classification errors, but those errors are probably small and reclassification of questionably assigned urban subtypes would not significantly change the land use distributions summarized in Table 2. The accuracy of ODNR land use data conforms to United States Geological Survey (USGS) National Geospatial Program Standards and specifications of approximately ± 1 m for this scale (USGS NGP Standards and Specifications).

3.2. Sample preparation and analysis

Ultra clean trace metal techniques were utilized throughout the study. New low-density polyethylene (LDPE) bottles used for sample collection and storage were rigorously acid-cleaned prior to use (Gardner and Carey, 2004). After the acid cleaning, they were filled with 18.2 MΩ de-ionized water (DI) and placed in clean bags. Whatman 0.45 μm polypropylene syringe filters were cleaned with Optima™ grade HNO_3, thoroughly rinsed, and dried prior to use (Shiller, 2003). The "clean hands, dirty hands" technique was utilized to collect the water samples (Fitzgerald, 1999). DI water field blanks were opened and closed at the collection sites, and analyzed as samples. Samples were rapidly returned to the lab, filtered in a class 100 laminar flow hood through the pre-cleaned syringes, acidified to 2% v/v Optima™ HNO_3, and stored in the dark at 4 °C until analysis.

Trace metal analyses were performed using a Perkin-Elmer Sciex ELAN 6000 Inductively Couple Plasma Mass Spectrometer (ICP-MS). National Institute of Standards and Technology SRM 1643e was used to establish the accuracy of the method, and the precision was determined using duplicate analysis of random samples, as well as known standards. Precision data are shown in Table 3a and accuracy results relative to NIST 1643a are shown in

Table 1
Attributes of the sampled tributaries and the stormwater outflow pipe.

Name	Length km	Damage area km^2	Particular features
Rush Run	~6.1	7.4	Upstream 3.5 km ephemeral; 0.5 km through cemetery with channel modifications
Adena Brook	~4.1	7.1	Multiple parks, playgrounds; Intermittent flow
Turkey Run	~5.9	6.2	Multiple schools; 1.2 km^2 golf course with retention ponds – samples were taken before and after the golf course
Overflow Pipe	–	~2.3	100% impervious surface

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