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Geochemical characteristics of an urban river: Influences of an anthropogenic landscape

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ABSTRACT

The Anacostia River in Washington, DC is among the ten most contaminated rivers in the USA, containing sewage, metals, PAHs, and PCBs. Seventy-five percent of its watershed is urban or impervious. The biogeochemical characteristics of urban rivers, including the Anacostia, remain largely unstudied. Here we examine the base-flow geochemistry of the tidal freshwater Anacostia over a two-year period (April 2010–April 2012), concentrating on water chemistry (pH, hardness, SAR, alkalinity, Ca, Mg, Na, K, Fe, Mn, Zn, Al, Ba, Ni, total P, S, Sr, NO_3^-, NH_4^+, PO_4^{3-}) at 3 locations in the stream. Anacostia pH is between 7.3 and 8.2, indicating rapid buffering of precipitation (pH 4.9). Mean NO_3^- was generally between 1.1 and 1.3 mg/L, although occasionally concentrations increased to 3–4 mg/L at all sites. Ammonium was very low generally 0.0–0.3 mg/L with occasional peaks of 1.5–3.9 mg/L downstream. A Principle Components Analysis (PCA) of stream chemistry showed two components that explained two-thirds of the data variance. One component was correlated with Ca, Mg, Na, and hardness, all associated with bedrock or concrete dissolution. A second component was correlated with NH_4^+, NO_3^-, K and associated with nutrients. Na and Ca had the highest concentrations. This trend has been observed in other urban streams, suggesting urban stream syndrome and dissolution of concrete. Plotting Na/(Na + Ca) versus total dissolved solids indicates contributions from groundwater, but also produces a signature that is dramatically different from major world rivers. The data presented here demonstrates the need for understanding the geochemistry of highly urbanized systems and the extent to which urban inputs drive stream chemistry.

1. Introduction

The Anacostia River is a major urban watershed in the Washington, DC area encompassing 440 km^2 throughout Maryland and the District of Columbia. It is one of the nation's 10 most contaminated rivers and has been cited by the U.S. EPA as a "major area of concern" for the Chesapeake region (Maa, 2008). Contained within the sediments and water column are sewage, metals, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs). The metals and organic contaminants originate from industrial and suburban effluents (Velinsky et al., 1994, 2011; Wade et al., 1994; Foster et al., 2000; Hwang and Foster, 2008; Shala and Foster, 2010). It is also listed as "impaired" by the State of Maryland with respect to biological integrity, nutrients, sediments, certain organic compounds and bacteria (Maryland DOE, 2012a). Seventy five percent of the river's watershed is urban or impervious, 20% is forested and 5% is agricultural (Maryland DOE, 2012b; U.S. EPA, 2008). Much of the urban and impervious infrastructure was built before modern storm water runoff controls were required. Sediment control regulations were authorized in the 1960s, however state management plans for storm water and land management plans were not implemented until the early 1980s (Maryland DOE, 2012b). The "flashy" nature of the urban watershed has led to channelization and scouring resulting in degraded conditions for fish and invertebrates. Forty percent of the stations sampled in the tidal portion of the river were considered degraded by the Benthic Index of Biological Integrity (McGee et al., 2009).

Increased exposure to PCBs and PAHs has negatively impacted the general and reproductive health of invertebrates and bivalves (Phelps, 1985, 1993, 2004), catfish (Pinkney et al., 2011) and other species of fish (Iwanowicz et al., 2009) as well as top predators such as osprey (Rattner et al., 2008). For PCB's, storm flow events significantly increase concentrations in the particle phase indicating storm water runoff as a major influence in the transport of the contaminants (Pinkney and McGowan, 2006). From the geochemical perspective, there is a strong knowledge base on the chemistry

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of contaminants but less is known about the general geochemical controls of the Anacostia River system (Kaye et al., 2006; MacAvoy et al., 2009).

Understanding the geochemistry of urban rivers is critical as it can inform how attributes of urban areas, e.g., the increased extent of impervious ground cover, may impact watersheds in developed or developing regions (Paul and Meyer, 2001; Walsh et al., 2005; Kaye et al., 2006; Conway, 2007; Kaushal and Belt, 2012). Given increasing development and strain on limited water resources, understanding how urban landscapes impact those resources is imperative (Kaushal and Belt, 2012; Gold et al., 2013). The literature bears multiple examples of the dramatic effects that impervious surfaces can have on watersheds (reviewed in Paul and Meyer (2001), Walsh et al. (2005), Kaye et al. (2006)). Urban systems are characterized by altered channel morphology, flashier hydrology, decreased biotic richness and elevated concentrations of nutrients and contaminants (Walsh et al., 2005). With respect to geochemistry, runoff from urban areas has contributed to increased pH, conductivity, and modified ionic compositions (Gaillardet et al., 1999; Gallo et al., 2013; Hasenmueller and Criss, 2013; Paul and Meyer, 2001; Wright et al., 2011; Kaushal and Belt, 2012). Interactions between water and rock can become limited to impervious surfaces in highly urbanized streams, which in turn limit interactions between water and deeper minerals. Changes in the chemical composition of runoff due to leaching of alkali from concrete and other urban infrastructure increases the availability and influence of Na, K, and Cl among others (Rose, 2007). The Chattahoochee River, which drains both rural and urban landscapes in Georgia, Alabama, and Florida, showed a 3–4-fold increase in Ca, Mg, Na and SO_4^{2-} in water column samples from urban, relative to rural, areas (Rose, 2007). Wright et al. (2011) found similar increases in alkalinity/buffering capacity, pH, Na, Cl, and Ca, in streams with concrete drainage systems in Sydney, Australia compared with reference streams. Additionally, they suggest that significant amounts of Ca, HCO_3^-, and K ions in urban streams could originate from contact with concrete drainage pipes (Wright et al., 2011). Collectively these studies describe what has been characterized as "urban stream syndrome", where alteration of the urban landscape is inextricably linked to the geochemistry of the river system. The syndrome is widespread in developed and developing countries, although the conditions associated with the "syndrome" are variable, and may or may not include elevated Na, Mg, K and fertilizer effects from lawns (Paul and Meyer, 2001; Walsh et al., 2005). Further examination of the geochemical controls of urban river systems is an important component needed to better understand the synergistic links between urbanization and overall stream structure and function.

Here we examine approximately two years of aqueous geochemical and nutrient data in order to identify urban influences on river chemistry along a gradient from suburban to urban in the Anacostia River, Washington, DC. The objectives are to (1) use relationships among geochemical components and concentrations of Ca, Mg, K and Na to assess urban influences, and (2) determine concentrations of nutrients (NO_3^-, NH_4^+, PO_4^{3-}) in this anthropogenically influenced river in the United States capital.

2. Methods

2.1. Study sites

The Anacostia River is a tidal freshwater system (mean amplitude approximately 1 m) that flows 13.4 km through Maryland and Washington, DC and has a watershed area of 440 km^2. Land use in the watershed is 75% urban, with 23% total impervious surface. In the tidal portion of the river (the lower 8 km containing the sampling sites) is 40% impervious (District of Columbia DDOE, 2010) Five percent of the watershed is agricultural and 20% is forested (Maryland DOE, 2012b). There are approximately 1,000,000 residents living in the watershed area, and 95% of the river was estimated to have fish or biological integrity indices in the "poor" or "very poor" range (Maryland DOE, 2012b). Sampling was conducted at three sites (UP, MID, DOWN) along a downstream gradient in the Anacostia River (Fig. 1). The sampling areas were downstream from the physiographic transition from the Piedmont to the Coastal Provinces, which marks the transition from tidal to non-tidal (Miller et al., 2013). The watershed draining in to the river is underlain by Precambrian phyllits (metamorphosed mica and quartz rich clays; aluminum, silicon, oxygen, potassium); sericite ($KAl_3Si_3O_{10}(OH)_2$ and muscovite mica ($KAl_3Si_3O_{10}(OHF)_2$), chlorite ($(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2{\cdot}(Mg,Fe)_3(OH)_6$), quartzite (metamorphosed sandstone quartz, SiO_2), and slate (metamorphose shale, 4–8% Fe_2O, 55–65% SiO_2, 15–20% Al_2O_3, 2–4% Na_2O and K_2O, 0.5–3.0% CaO, MgO) to the west; schist (metamorphosed clays, quartz), metagraywacke (quartz, biotite ($K(Mg,Fe)\ AlSi_3O_{10}(OHF)_2$); schist, albite ($NaAlSi_3O_8$) quartzite and marble ($CaCO_3$) to the immediate west; and Cretaceous sand with Quaternary alluvium in the immediate drainage area (Weaver, 1967). The upstream (UP) site is located in Bladensburg, MD, and drains the most suburban landscape (approximately 30% impervious area and 70% urbanized estimated from District of Columbia DDOE (2010)), while the middle stream site (MID) is near Kenilworth Marsh and the downstream site (DOWN) is located under the 11th street bridge near the Navy Yard, the most urban of the sites (80% + impervious estimated from District of Columbia DDOE (2010)) (see the Woods Hole Research Center (http://www.whrc.org/mapping/chesapeake/impervious.html) for a map showing impervious surface in the area, and District of Columbia DDOE (2010) for impervious area broken down by sub-watershed). The UP and DOWN sites are adjacent to combined sewage outflow pipes. The MID site is in an urban park not directly associated with sewage outflow. The main channel of the Anacostia River starts at the UP site where two tributaries connect (the north west branch and north east branch), forming the Anacostia. The UP site and tributaries are located wholly in Maryland and have soils of the Manor–Glenelg–Chester (well drained loam) or Sunnyside–Christiana–Muirkrik (weathered clay) soils.

Water collections were made during eight outings between April 2010 and April 2012. Due to logistical difficulties, the time between sampling was not evenly distributed during the two years of the study, so most samples were collected during the spring and summer months. Water column samples were collected in triplicate using 500 mL acid washed HDPE bottles. All samples were placed on ice for transport. Water column samples were immediately filtered onto glass fiber filters (45 μm GFF) once they reached the lab, while replicate samples were sent to Cornell's Nutrient Analysis Lab for analysis of water nutrients and inorganics (pH, hardness, SAR, alkalinity, Ca, Mg, Na, K, Fe, Mn, Zn, Al, Ba, Ni, total P, S, Sr, NO_3^-, NH_4^+, PO_4^{3-}). Methodology for nutrient and inorganic ion analysis was based on EPA requirements (Standard Methods for the Examination of Water and Wastewater, http://www.standardmethods.org/). Colorimetric Bran-Luebbe Automated Ion Analyzer was used for NH_4^+, PO_4^{3-}), and NO_3^-. Elements were analyzed by plasma-atomic emission spectrometry (ICP-AES), which determines trace elements, including metals, in solution. Nutrient ions are reported with charge, elements are not.

2.2. Quality assurance/quality control

For ammonia analysis, every 20 samples analyzed had one sample duplicate and one sample spiked at the low and high levels. The relative percent difference (RPD) of the duplicate was with in 20%.