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Size characterization of dissolved metals and organic matter in source waters to streams in developed landscapes

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ABSTRACT

Individual and mixed water samples from wastewater treatment plant effluents, stormwater runoff, streams from developed areas were characterized with respect to organic matter concentration and spectral properties and metal concentration and size distribution. In addition, asymmetric flow-field flow fractionation coupled to inductively coupled plasma mass spectrometry was used to measure concentration, size distribution and association of metals in the colloidal size range. Results reveal that Fe, Cu, Zn and Pb in the colloidal size range were mainly associated with the less than 5 nm, or less than 10 kDa size range. Cu was most strongly associated with organic matter, while Zn and Pb were mixed between Fe and organic matter. Effluent showed higher binding capacity for metals, while stormwater, even with higher organic matter concentrations showed more exchangeable metals. Upon mixing of source waters, colloidal metal concentrations and size distributions were conserved.

1. Introduction

Stream systems receive water from various sources that contain metals in different size, stability and lability classes which can affect their mobility, bioavailability, and toxicity (van Leeuwen et al., 2005; Bradac et al., 2010; Brooks et al., 2006). Two major sources that typically contribute elevated metals compared to the background waters include treated wastewater effluent and stormwater runoff. From these sources, typical sampling only distinguishes between particulate and dissolved fractions by filtration through a 0.45 μm filter, but the dissolved fraction contains a continuum of sizes of both organic and inorganic colloids that can bind metals to varying degrees, (Reuter and Perdue, 1977; Wu et al., 2004) as well as free metals. The environmental fate of metals in the dissolved fraction may vary depending on dissociation, aggregation, sedimentation, sorption, or biouptake processes.

Several studies have measured size distribution of dissolved phase metals in streams and large rivers and found that iron oxide and organic matter colloids are important for binding and transporting metals (Stolpe et al., 2013; Vega and Weng, 2013; Dahlqvist et al., 2007). Measured metal concentrations as a function of filtration and ultrafiltration of waters have shown that in river and lake systems that are not highly polluted, the greatest percentage of metals are in the colloidal phase (Town and Filella, 2002). The fraction in the higher end of the colloid size range typically coincide with increased Fe concentrations, while the lower size range typically associates with the low molecular mass organic matter fraction. Organic matter (OM) and iron-rich colloids have exhibited notably different affinities for trace elements (Neubauer et al., 2013; Stolpe et al., 2005). While many studies have found that Cu is typically associated with dissolved organic carbon (DOC) of less than 5 nm (Neubauer et al., 2013; Vega and Weng, 2013), Pb and Zn are more typically associated with larger inorganic particles.

While previous measurements of stream waters and natural inputs suggest typical OM and inorganic colloid size distributions and metal associations, fewer observations have been made from anthropogenic inputs to these streams, such as wastewater effluent or stormwater runoff, specifically in urban streams. Effluent discharges from municipal wastewater treatment plants contribute a significant source of organic matter to streams, around 5 mg C L^{-1} (Quaranta et al., 2012). This organic matter is mostly in the small size range, less than 10 kDa, with some components in higher size ranges >50 kDa (Quaranta et al., 2012; Worms et al., 2010). The organic matter characteristics are more similar to microbial sources typical of the bacterial-based treatment processes. Advanced size fractionation techniques such as flow field-flow fractionation (F4)

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coupled to highly sensitive metal detectors like inductively coupled plasma-mass spectrometry (ICP-MS) have shown variations in the molar mass and size distribution of metal complexes in effluent. Metals such as Cu, Zn, and Cd are typically associated with the low molecular mass fraction, while Al, Fe, and Pb were distributed between both size fractions (Worms et al., 2010). Less is known about stormwater runoff inputs. A higher molecular mass distribution was observed in streams impacted by large rain events in a mostly pristine river (Li et al., 2003), but a closer look at the dissolved fractions entering with stormwater runoff has not been conducted for streams in developed areas.

Organic matter and trace metals in impacted streams are expected to exhibit different size distributions dependent on source waters and when subjected to changing hydrochemical conditions, i.e. varying ionic strength or hardness cation concentrations (Bolea et al., 2006; Ledin et al., 1993). While the source waters may enter with one set of characteristics, upon mixing of effluent or stormwater runoff with stream water, redistribution of metals to different binding phases or size fractions may occur. The importance of size in stream systems relates to feeding habits of macroinvertebrates and higher organisms. The high molecular mass (HMM) organic fraction can play a major role in increasing the uptake of metals by some filter feeders (Roditi et al., 2000) or be subject to aggregation and sedimentation with mineral colloids when the ionic strength is elevated (Stolpe and Hassellov, 2007). In contrast, smaller size colloidal fractions of organic matter in effluent may concentrate metals which can disproportionately influence bioavailability in primary producers, such as the benthic periphyton, and increase trophic transfer to macroinvertebrates. Also, small organic matter is expected to be more mobile in aquatic ecosystems (Stolpe and Hassellov, 2007) and will likely promote longer distance transport of metals.

The purpose of this study was to characterize the organic matter and size distribution of trace metals in different stream waters and source waters in developed landscapes. We sampled from three development impacted streams and treatment plants, as well as stormwater runoff over the course of a storm event and compared the particulate, dissolved and colloidal size fractions of metals using both standard and advanced tools such as asymmetric flow-field-flow fractionation (AF4) coupled to ICP-MS. Our objectives were to characterize differences in metal association as a function of colloid type and whether significant changes would occur upon mixing of the source waters. The influence of size distributions and OM properties with respect to transport and bioavailability are discussed.

2. Methods

2.1. Site description and sampling

Three wadeable streams in developed areas of Connecticut including the Hockanum River (HR), Quinebaug River (QR) and Willimantic River (WR) were selected for this research. The ten year average annual discharge of these three rivers was 4, 40 and 6.8 $m^3\ s^{-1}$, respectively, at the downstream United States Geological Survey (USGS) gauging stations. The wastewater treatment plants (WWTP) on each of these rivers are at minimum secondary treatment, with the QR and WR WWTPs also implementing advanced nitrogen removal. None of the WWTP received combined sewer and stormwater loads. The HR WWTP contributes about 10–40% of the flow of the HR at the point of input, while the others contribute less than 10%.

2.2. Sample collection and preparation

Upstream water (H_up, W_up, Q_up) and WWTP effluent (H_eff, W_eff, Q_eff) were collected from each of these watersheds during May and June. Upstream samples were obtained prior to the discharge point of the WWTP effluent. Stormwater runoff samples (H_st) were collected from a stormdrain outfall downstream of the WWTP. Samples were collected in 20 L HDPE carboys that had previously been acid washed with 0.1 M HNO_3 and rinsed with deionized water (>18.2 MΩ) to limit background metal contamination, and preserved in the dark at 4 °C before analysis. The pH and conductivity of the samples were measured in the field. The samples were divided into total and dissolved fractions by filtering through a 0.45 μm pore size nitrocellulose membrane. To assess any changes that may occur in the dissolved phase following mixing, the effluent and first time point stormwater runoff samples from the Hockanum River were mixed with upstream samples from the same catchment at a ratio of 3:7 or 1:1, respectively, common mixing ratios for receiving streams. In addition, samples were spiked with a 10-fold increase in Cu, Zn and Pb, and in some cases 2- or 10-fold increase in Ca concentrations to assess metal binding capacity of the different size fractions or the influence of an exchangeable cation on metal distribution. The mixed samples were shaken for 24 h prior to analysis.

2.3. Metal analysis of bulk samples

The total and dissolved metal samples were acidified to 2% HNO_3 (trace metal grade). Total metal sample were analyzed according to EPA Method 200.8 (1994). Inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700x with He collision cell, Agilent, Delaware, USA) was used for determination of the elements in this work. For batch sample analysis, Bi, Ho, In, and Sc were used as internal standards. Standards and QC checks were prepared from independent high purity standards (Spex-Certiprep, Metuchen, NJ, USA and VHG Labs, Inc., Manchester, NH, USA). Quality control samples, internal standards, and spike recoveries were within 10% or better of expected values. Particulate metal concentrations were calculated from the difference between total and dissolved metals.

2.4. Characterization of dissolved organic carbon

The DOC concentration was determined using a total organic carbon analyzer (Apollo 9000, Tekmar-Dohrmann, Mason, OH, USA). Potassium hydrogen phthalate was used for standards (Ricca Chemical, Arlington, TX, USA), and laboratory prepared standards from the same chemical were used for quality control samples, all of which were within 20% or better of expected values.

The absorbance spectra of samples was scanned between 200 and 550 nm by a Cary 50 spectrophotometer (Australia). Specific UV absorbance (SUVA in $L\ mg^{-1}\ m^{-1}$) was calculated by normalizing the UV-absorbance at 254 nm (in cm^{-1}) by the DOC-concentration ($mg\ L^{-1}$) and then multiplying by 100 (Weishaar et al., 2003). The pH of samples for fluorescence analysis was adjusted to 2 by the addition of HCl. All fluorescence data was collected on a Cary Eclipse fluorescence spectrometer (Australia) with a xenon flash lamp, 5 nm slit widths, and a scan rate of 1200 scans per second. Excitation wavelengths from 200 to 450 nm in 10 nm increments, as well as emission wavelengths from 250 to 550 nm in 2 nm increments were scanned. Excitation-emission matrices (EEMS) were corrected and plotted following established protocols (Quaranta et al., 2012). The fluorescence index (FI) was calculated as the ratio of the emission intensity at a wavelength of 450 nm to that at 500 nm for an excitation wavelength of 370 nm (McKnight et al.,