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Heavy metal distribution in an urban wetland impacted by combined sewer overflow

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HIGHLIGHTS

- CSO discharge in dry weather introduced heavy metals to an urban wetland.
- Dissolved metals were detected both upstream and downstream of the CSO.
- Sediment in the vicinity of the CSO was moderately contaminated with Cu, Pb and Zn.
- Cu and Zn were complexed by organic ligands in the roots of *Phragmites australis*.
- Metals retained by *Phragmites* roots may be less mobile than sediment-bound metals.

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ABSTRACT

The heavy metal content and distribution in an urban wetland affected by combined sewer overflow (CSO) discharge during dry conditions was evaluated. Metals identified in the CSO discharge were also measured upstream and downstream of the CSO. Metals were detected in the acid-extractable fraction of the wetland sediments and the roots of *Phragmites australis* plants. Sediment from the banks of a pool created by the CSO, and from a clay bed upstream were found to be moderately contaminated with Cu, Pb and Zn. Micro X-ray fluorescence (μ-XRF) of *Phragmites* roots from the CSO banks showed a correlation in the spatial distribution of Fe and Mn, attributed to the formation of mineral plaques on the root surface. Micro X-ray absorption near edge spectroscopy (μ-XANES) revealed that Cu and Zn were complexed with the organic ligands phytate and cysteine. The findings indicated that continuous discharge from the CSO is a source of heavy metals to the wetland. Metals bound to sediments are susceptible to remobilization and subsequent transport, whereas those associated with *Phragmites* roots may be more effectively sequestered. These observations provide insight into the behavior of heavy metals in urban areas where CSOs discharge into wetlands.

1. Introduction

In urban areas, heavy metals are generated by several activities including commerce, industry and transport (Mahbub et al., 2010), and can be found in household or domestic wastes (Pantsar-Kallio et al., 1999). These pollutants may be introduced to surface waters and wetland areas adjacent to cities as runoff or sewage in combined sewer overflow (CSO) discharge (Reemtsma et al., 2000; El Samrani et al., 2004: Casadio et al., 2010). In cities, CSO networks shunt non-point source pollution and sewage to local water bodies when sewage and runoff exceed the capacity of treatment plants. This occurs primarily during storm events however, even when sewage is retained and treated, runoff can enter wetlands via these routes. This is of concern because for coastal wetlands and surface waters adjacent to cities, runoff from nearby urban areas is one of the main threats to water quality (Paul et al., 2002). Furthermore, continuous introduction of pollutants to urban wetlands by CSO discharge can result in sediment contamination and degradation of native vegetation and ecosystems (Iannuzzi et al., 1997). As surrounding urban areas tend to be densely populated, human exposure to accumulated and mobile contaminants, and the resulting impacts on human health, can also be cause for concern (U.S. EPA, 2004).

Metals entering wetland areas via CSOs can disperse throughout the drainage area and can be subsequently partitioned between water, sediment and plants. Dissolved metals in contact with sediments may adsorb to mineral surfaces, become incorporated into mineral phases, or complex to soil ligands such as organic matter (El Samrani et al., 2004; Galletti et al., 2012). Metals may be retained by sediments by these physicochemical processes. However, some metals may still exchange with, or remain in the

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dissolved phase and can therefore be bioavailable to plants and organisms. Certain wetland plants, such as the invasive species *Phragmites australis*, can effectively sequester metals in their roots precluding the uptake and transmission of metals to their above ground organs (Al-Taisan, 2009; Bonanno and Lo Giudice, 2010). This may take place by the formation of Fe or Mn (hydr)oxide plaques on root surfaces (Peverly et al., 1995; Hansel et al., 2002), which in turn can sorb additional metals; by the reduction of metal cations to metallic particles (Manceau et al., 2008); and by metal complexation with organic ligands (Terzano et al., 2008; Kopittke et al., 2011; Saraswat and Rai, 2011). The interaction of metals with both sediment and plants can reduce their mobility in wetlands, and may result in long term metal accumulation. This however does not preclude the potential for the remobilization and subsequent transport of metals if environmental conditions in the wetland change.

This study investigates the role of CSO discharge on heavy metal input and mobility in an urban wetland. The selected site is a coastal wetland area in Queens, New York into which several CSOs discharge. Notably, the invasive species *P. australis* has proliferated in the study area. To assess the introduction of heavy metals to the wetland under normal conditions, samples were collected directly from, and in the vicinity of a CSO in dry weather. Though CSO discharge is limited in dry weather, the flow observed here at <0.008 $m^3\ s^{-1}$ is thought to be a combination of urban runoff, groundwater infiltration into the pipe, and some fraction of raw sewage. This continuous flow may have a greater impact on metal input to the wetland when compared to wet weather events in which the incoming metals may be diluted. In addition to water samples, sediment and *Phragmites* roots were also collected to assess the metal content. Synchrotron microprobe techniques were used to determine the metal distribution and speciation in the *Phragmites* roots, and to confirm the mechanism(s) of metal sequestration. The goal of the study is to provide an initial assessment of the input of dissolved metal contaminants introduced by continuous CSO discharge, and the potential for metal interaction with sediment, and sequestration by plants in the impacted area.

2. Materials and methods

2.1. Sample collection

Alley Pond Park is a tidal wetland located at the head of Little Neck Bay on the Long Island Sound, in the New York City metropolitan area (Fig. 1). Water, sediment and plant samples were collected within a 15 m radius of a CSO located in the southern end of the park. Additional samples were collected close to an artesian well 175 m upstream of the CSO, unlikely to be affected by CSO discharge, and thus representative of background conditions. A creek originates at the well and, as it approaches the CSO, flows over a weir and into a pool created by the CSO discharge. Downstream of the CSO the creek flows over and past a clay-like deposit. Ultimately the creek turns into a tidal channel and flows into the Long Island Sound via Little Neck Bay. The area surrounding the CSO and creek is dominated by dense stands of the common reed, *P. australis*.

Sampling was conducted in the summer under dry conditions, at least 24 h after the last rainfall event, so that the water samples would be representative of static conditions in the wetland. The weir upstream of the CSO, the CSO pool and environs, and the clay-like deposit downstream were selected as sample locations in addition to the upstream well. Water samples were collected directly from the CSO discharge before it entered the pool, from the CSO pool, upstream at the weir, and downstream of the CSO near the clay bed. Sample locations at the weir and the clay bed were both within 15 m of the CSO. Samples were also collected directly from the well outflow further upstream. The pH of all samples was measured in situ prior to sample collection using a YSI 600QS water quality sonde. Samples were collected in high density polyethylene bottles which were acid-washed, triple-rinsed with deionized water and air dried in the laboratory prior to use. In the field, the bottles were triple-rinsed with the sample prior to collection. Samples were filtered using 0.45 μm filters. This excluded suspended particles and sediment, with which associated metals are less mobile and bioavailable. The samples were acidified to pH < 2 with concentrated nitric acid at <0.1% of the sample volume. The samples were kept on ice in coolers in the field and then stored in the laboratory at 4 °C for subsequent analysis.

Surface sediment was sampled at locations close to where water samples were collected. Sediment was obtained directly from the bottom of the pool created by the CSO, and from the banks of this pool, in the vicinity of the *Phragmites* plants. Upstream of the CSO, sediment was collected near the weir, and downstream directly from the clay deposit. Sediments were primarily silt-sized, but included finer fractions from the clay deposits and coarser sand-sized fractions from the CSO pool and banks. Near-surface *Phragmites* roots were collected from the plants on the banks of the pool created by the CSO discharge, as these plants would likely be directly affected by repeated CSO input. Both sediment and plant roots were collected from the well location for use

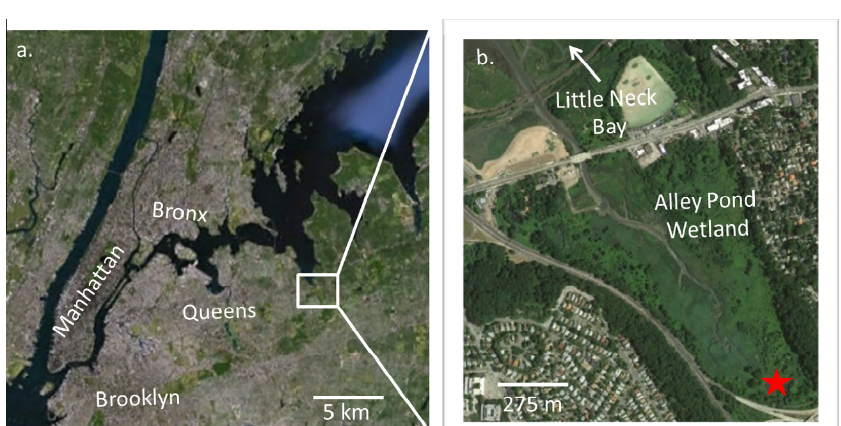

Fig. 1. (a) Location of Alley Pond in Queens, New York City, NY, USA. (b) Zoom in of the estuary showing the direction of flow towards Little Neck Bay, Long Island Sound, USA and the sampling location (red star). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)