Fly Ash and Coal Ash in the Mohawk River

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Introduction

Fly ash and coal ash are silicate byproducts of coal-burning furnaces. Both have elemental chemistry dominated by (Si+Al+O±Fe), with or without additional elements (e.g., Zn, Ti). Fly ash is distinguished by a relatively smooth, glassy surface and typical droplet or sub-spherical shape, whereas coal ash has a rough and porous, typically dark, surface (Guedes et al., 2008). Both are essentially glass bubbles (cenospheres) and thus are buoyant in water. Our research indicates that fly ash and coal ash make up part of the particle load in the Mohawk River.

Methodology

We are working on a project aimed at quantifying the microplastic load in the Mohawk River (see Smith et al., this volume). In total, 63 trawl samples were collected between Rome (west) and the Crescent Dam in Cohoes (east) during summer and fall of 2016 (Figure 1). Sampling was conducted from a 4-m (13’5”) Zodiac Futura Mark II rigid inflatable boat, and samples of surface and near-surface particulates were captured by a manta trawl with a 333-µm net (Eriksen et al., 2013) that was towed approximately 12 m behind the boat. Trawls were conducted upstream for an average trawl length of 1.71 km (1.06 mi), with actual trawl lengths ranging from 1.17 km to 2.34 km. Samples were processed using a modified version of NOAA laboratory protocol (Masura et al., 2015), which removed much of the organic material.

Visual examination of non-organic particles remaining after processing allowed us to distinguish most of the anthropogenic particles on the basis of shape, plasticity, presence of dye, and/or overall appearance. Definitive identification of particles as plastic polymers was accomplished primarily by Raman spectroscopy, with additional analyses by scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS). For further analysis, ten fly ash and two coal ash or coal residue (inertite) particles from MT1 (Amsterdam) were prepared as a thin-section.

Raman measurements were made with a Bruker Optics Senterra® Spectrometer coupled to an Olympus BX51 reflected light microscope. Raman spectroscopy was performed at 500x using a 633 nm external He-Ne laser at 20 mW, and an aperture of 25 x 1000 um. An integration time of 5 to 60 s was used during acquisition of the Raman shift, and automated collection was done for background and monochromatic wavelength. Raman spectra from trawl particles were compared to spectra from in-house plastic standards acquired using the same instrument. Raman spectra for unbroken fly ash and coal ash particles are distinctive, but not definitive.

We used the Zeiss® EVO-MA15 SEM with a back-scattered electron (BSE) detector and a Bruker EDX system with a Peltier-cooled XFlash 6/30 silicon drift detector to acquire images and elemental analyses of particles. The SEM was operated at high vacuum and an accelerating voltage (EHT) of 15 keV; for EDX, a target square measuring approximately 100 µm on each side was outlined on the side of the particle most directly illuminated by the beam. We concentrated our efforts on particles suspected of being fly ash and coal ash, but also included some plastic particles for comparison.

Findings

Fly ash particles, and to a lesser extent coal ash particles, were found in 89% (56/63) of the trawl samples (Figure 2). The greatest abundance of fly/coal ash particles overall was found in samples collected between Amsterdam (MT1) and Glenville (MT24), with the highest total particle count (123 fly ash, 19 coal ash) in MT25, which was collected downstream of Lock 9 in Rotterdam Junction. In a few of the samples, such as MT1 (Amsterdam), fly ash and coal ash particles (total = 33) were more numerous than plastic particles (total = 25).

SEM back-scatter electron imaging and EDX elemental analysis readily distinguish fly ash from plastic particles (Figure 3). Fly ash contains aluminum and silicon whereas plastic consists primarily of carbon and oxygen.
Raman spectroscopy shows that glassy material (fly ash) is distinct, but complex, and that carbon fragments (inertinite) are clear and distinctive the structure (Figure 4). The carbon fragments have diagnostic Raman active modes and these are distinguished by the presence of several primary modes, the position of primary modes, and the intensity ratio of those modes. In our preliminary work, the two samples from Amsterdam (MT1) have the distinctive D1 and G bands, but the S1, S2 and D3 bands are not present. Bands used to characterize ordering of unburned carbon are the D1 (disordered structure), the G (ordered structure of graphite), and the integrated density ratio, which is a function of the intensity of D1 and G (given by ID1/IG - see Guedes et al., 2008). The relative intensity of the D1 and G peaks is a function of structural order related to degree of combustion, and for sample A1 and B1 the ID1/IG ratio is 1.2. Thus these preliminary results are similar to samples from coal-burning low-sulfur power plants (see Guedes et al., 2008; Rodella et al., 2016).

Conclusions
Our investigation indicates that fly ash and coal ash are nearly ubiquitous in the surface waters of the Mohawk River and Erie Canal. The presence of fly ash and coal ash in many of the samples indicates that the legacy of coal-burning in the Mohawk River Watershed remains with us, likely both as spoils piles exploited as a resource and as particulates incorporated into soil over time and released to the river through bank erosion and surface runoff.

The relatively high concentration of fly ash and coal ash in samples bracketing the former power station located upstream of Lock 10 (now owned by Cranesville Block, which has a beneficial use determination to use fly/coal ash as filler in concrete; NYSDEC, 2016) suggests that byproducts of coal-burning were initially deposited close to the source, but are being remobilized in the course of both typical river flow and flood events. It is possible that erosion associated with Hurricane Irene and Tropical Storm Lee in 2011 exposed sources of fly ash and coal ash particles that are being progressively introduced into the river, especially between Amsterdam and Rotterdam Junction where Lock 10 and Lock 9, respectively, experienced significant structural damage and catastrophic channel-widening.

The potential environmental impacts related to leaching of heavy metals from fly ash and coal ash have been studied elsewhere (e.g., Pandey and Bhattacharya, 2016). Further investigation of the chemical stability of fly ash and coal ash in the Mohawk River may be warranted.
Figure 2. Total fly ash and coal ash particle counts in 63 trawl samples, broken down by type of particle. Sample IDs for each manta trawl sample (MT1-MT63) are ordered from west to east; numbers 1-63 in below the sample IDs correspond to track numbers on Figure 1. Approximate centers of urban areas and Lock 9 in Rotterdam Junction are indicated by dashed vertical lines. Sampling indicates that fly ash and/or coal ash particles are nearly pervasive in the lower Mohawk River, although the abundance varies between Rome (west) and the Crescent Dam in Cohoes (east). The highest fly/coal ash particle count was found in the sample collected immediately downstream of Lock 9 in Rotterdam Junction (MT25, total = 142), with generally higher abundance in the other samples collected between Amsterdam and Schenectady, a stretch of the Mohawk River that includes the former power plant located between Lock 10 and Amsterdam. Sample MT29, which had the second-highest fly/coal ash particle count (96), was collected adjacent to the former power plant. Sampling results suggest that fly ash and coal ash particles are present in soils and river banks, where they can be eroded by normal flow conditions and by extreme events such as the channel migration and sediment remobilization that occurred during Hurricane Irene and Tropical Storm Lee in 2011.

Figure 3. Scanning electron microscope (SEM) backscatter electron (BSE) image (upper right), energy-dispersive x-ray (EDX) elemental spectrum (bottom), and reflected-light photograph (inset) of a fly ash particle (left) and plastic microbead (right) from the trawl sample collected immediately downstream from Lock 9 in Rotterdam Junction (MT25). This sample had the highest abundance of fly ash/coal ash particles among the 63 trawl samples. The fly ash particle has the characteristic glassy sheen and droplet shape of fly ash cenospheres (vitreous bubbles); the elemental composition is dominated by O-Al-Si-C, which is typical of fly ash. The elemental chemistry of the plastic particle is dominated by C-O, which is typical of polymers.
Figure 4. Raman spectra (C) of targets marked by X’s in fly ash particles MT1-A1 (A) and MT1-B1 (B) from trawl sample MT1 (Amsterdam). Bands used to characterize ordering of unburned carbon are the D1, the G, and the integrated density ratio, which is a function of the intensity of D1 and G (given by ID1/IG - see Guedes et al., 2008). The two samples have the distinctive D1 and G bands, but the S1, S2 and D3 bands are not present. These preliminary results are similar to samples from coal-burning low-sulfur power plants (see Guedes et al., 2008).

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References


Poster Presentation