Quaternary Ammonium Compounds as Sewage-Source Specific Tracers of Processes Affecting the Distribution of Contaminants and Sediments in Hempstead Bay, a Long Island Coastal Lagoon.

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Introduction

There are generally multiple point and non-point sources of chemical contaminants to urban or highly developed estuarine and coastal environments. Sewage outfalls are often one of these sources. Recent research has suggested that a group of hydrophobic organic cations, quaternary ammonium compounds (QACs), can serve as stable, particle-reactive tracers to characterize the spatial extent of sewage contamination and be useful in separating the relative sources of other strongly sorbed sediment contaminants (Li 2009, Li and Brownawell 2010). Finding a wide range of household uses, QACs have been detected in sediments throughout the lower Hudson River Basin as a result of inputs from large sewage treatment plants (STP) in the area.

Hempstead Bay (Figure 1) is located on the southwest shore of Long Island, NY and receives 57 million gallons per day (MGD) of sewage from four municipal treatment plants located in the western portion of the Bay. The majority of the effluent comes from the Bay Park STP outfall (50 MGD) with additional effluent emanating from the nearby Long Beach STP. Unlike other sewage impacted NY estuaries and coastal waters that are influenced by inputs from multiple sewage sources, Hempstead Bay provides a unique environment to study the transport of sewage contaminants and affected sediments away from a concentrated area of inputs. In this case, these inputs are hypothesized to act as a "point source" to the rest of Hempstead Bay. The Bay Park outfall is situated in a high flow channel to facilitate the flushing of sewage effluent out of the Bay through Jones Beach and Rockaway Inlets. However, recent observations suggest this flushing may be limited. The Bay has been experiencing eutrophication, areas of hypoxia, and high incidences of macro algae, leading to concern that sewage might be circulating within the Bay.

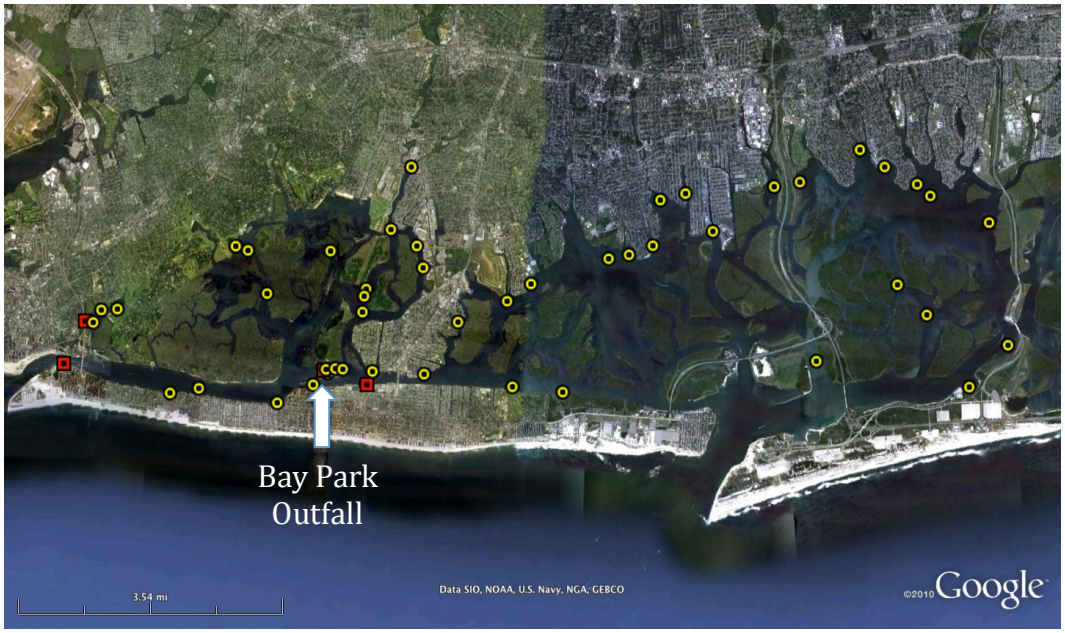

Figure 1. Hempstead Bay, NY. Sewage treatment plant outfalls are marked in red dots and sample locations in yellow. Bay Park outfall represents the largest source of sewage to the area (50 MGD).

QACs have been measured in very high concentrations in sewage-impacted environments (Li and Brownawell 2009; Li and Brownawell 2010), yet studies of the spatial distributions of QACs in environments with a single source of sewage have been lacking. These studies are important to better understand how QACs behave in a sewage-impacted environment. Hempstead Bay provides an ideal location for this, and a study was undertaken to better understand the distribution and extent of sewage affected particles within Hempstead Bay by measuring QACs. In addition, QAC measurements were used to understand sources and persistence of another particle reactive sewage contaminant, di-ethylhexyl phthalate.

Di-ethylhexyl phthalate (DEHP) is a high production volume chemical used as a plasticizer. It is a suspected endocrine disrupting compound and is listed as a priority pollutant by the U.S. Environmental Protection Agency (US EPA 2012). While sewage is known to be a source of DEHP to coastal estuaries, there have been no studies to separate sewage from other potential point and non-point sources, including atmospheric deposition. It's particle reactive nature means that a sewage tracer such as QACs can provide valuable information about the source of DEHP to coastal environments as well as what happens to DEHP once it is released from its source.

Methods

The top 5 cm of sediment was taken at sample sites throughout Hempstead Bay, as shown in Figure 1. Sampling sites were targeted to obtain muddy sediments as well as represent multiple potential contamination sources of DEHP, including marinas and landfills. QACs were measured using the method described in Li and Brownawell (2009). In short, 100 mg of sediment was extracted using acidic methanol in a heated sonication

bath. Extracts were cleaned up using a chloroform/water liquid liquid extraction as well as a final resin clean up step. Analysis was performed with an HPLC-ToF-MS.

Ditallowdimethyl ammonium compounds (DTDMACs) possess the best combination of properties for application as tracers (i.e. persistent, high concentrations) and as such have been focused on in this study.

DEHP was measured using a modified method from Ferguson et al. (2000). Sediment (.5 grams) was loaded into a stainless steel column with clean sand on either end. The column was placed in a heated sonication bath and methanol was pumped through at a rate of .5 mL/minute for 7 minutes for a total of 3.5 mL. Extracts were cleaned up using a Florosil column, adapted from Bartolome et. al (2005). DEHP was analyzed using a GC-MS.

Results

QACs were easily measured throughout Hempstead Bay, as seen in Figure 2. Concentrations decreased with distance from the Bay Park outfall as expected, and measurements indicate the presence of sewage-affected particles throughout the Bay. QAC concentrations within the Bay ranged from as high as 104 μg/g near the Bay Park outfall source to as low as .3 μg/g on the east side of the Bay. Elevated concentrations of QACs were found in most samples in the western portion of Hempstead Bay, with levels dropping off to an average of 2-3 μg/g east of Jones Beach Inlet. Additional characterization of sediment properties is underway to better understand local variability in concentrations and region-wide patterns observed.

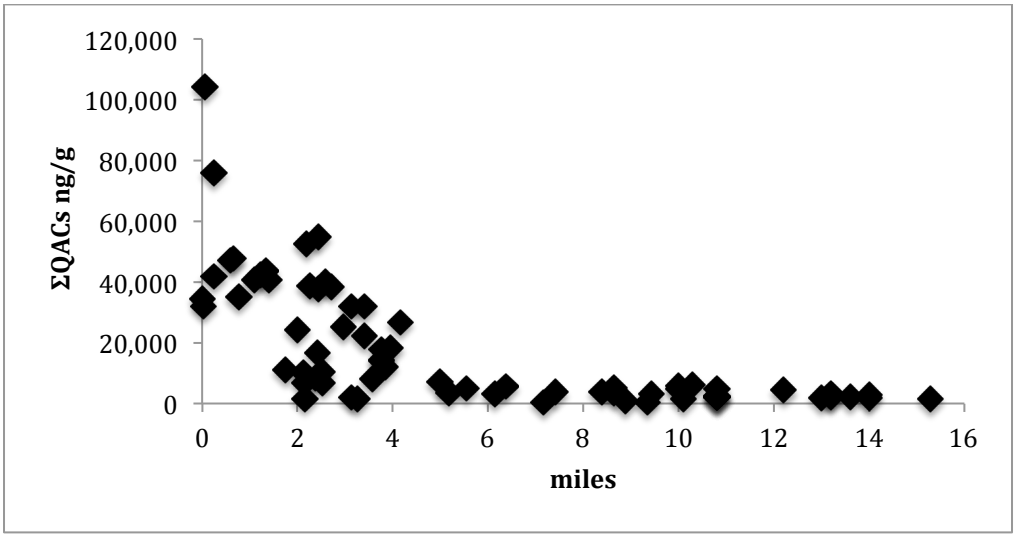

Figure 2. Total QACs with distance from the Bay Park outfall.

The mean concentration of QACs in the West Bay portion of Hempstead Bay was 32 μg/g. This value is very similar to the mean concentration of QACs in muddy sediments

from nearby water bodies such as Jamaica bay that are recognized as being impacted by sewage-derived nutrient inputs, as shown in Table 1.

Location	Year	Mean (μg/g)	Median (μg/g)
NY/NJ Harbor Complex	1998	34	27
Jamaica Bay	2008	29	35
Hempstead Bay (West Bay)	**2011**	**32**	**32**

Table 1. Mean and median total QAC concentrations in various water bodies in New York with known sewage contamination.

DEHP was also measured throughout Hempstead Bay. As seen in Figure 3, levels ranged from 4.3 μg/g at the Bay Park outfall to as low as 200 ng/g in the eastern side of the Bay.

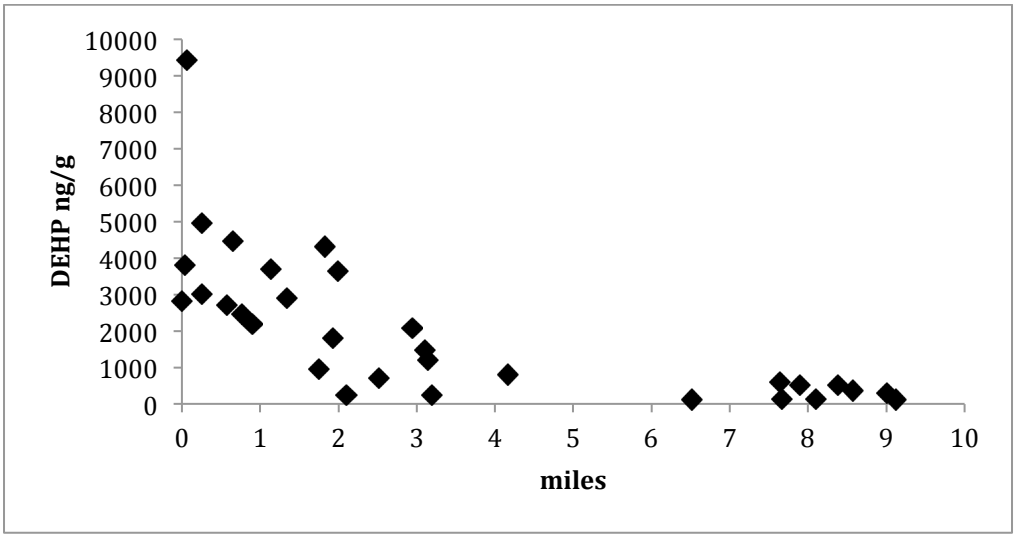

Figure 3. DEHP concentrations (ng/g) in sediment samples with distance from the Bay Park outfall.

A very strong correlation is observed when DEHP concentrations are plotted against total DTDMAC concentrations, as indicated in Figure 4, with an R^2 value of .93 and an intercept near zero.

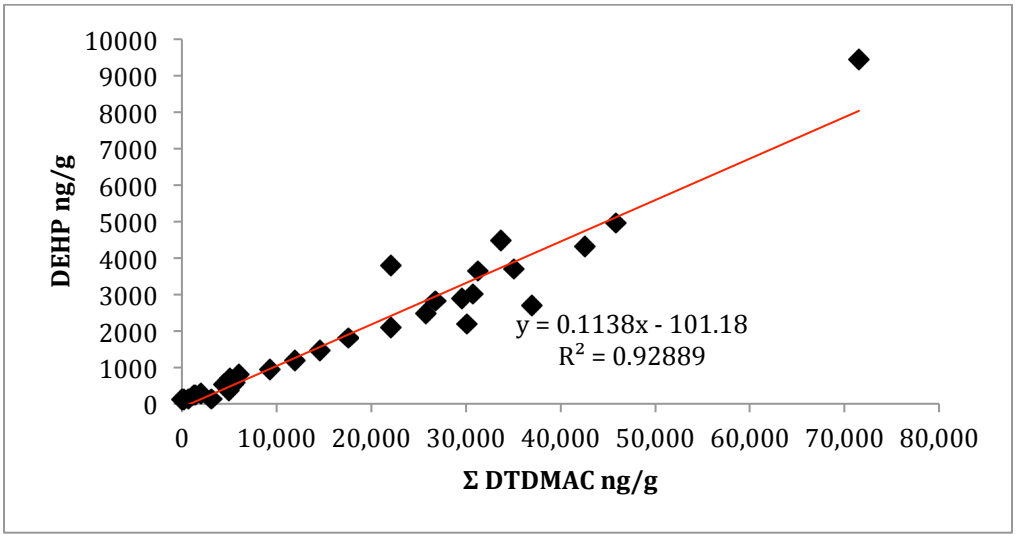

Figure 4. DEHP (ng/g) versus total DTDMAC (ng/g) in Hempstead Bay sediment samples.

Discussion

The presence of QACs throughout Hempstead Bay indicates that sewage affected particles are transported beyond the western side of the Bay. In addition, QAC concentrations near the outfall rival those of nearby Jamaica Bay and New York/New Jersey Harbor Complex, areas with water quality concerns linked to sewage contamination. These two factors support the hypothesis that sewage contaminants are appreciably retained and redistributed in the western portion of the Bay. Other related studies are aimed at determining whether associated nutrient loads may be contributing to eutrophication and hypoxia problems observed in the area. There is a pronounced drop in QAC concentrations east of Jones Beach Inlet that may be related to exchange with the Atlantic Ocean or other mechanisms that disperse waters as they transport eastward.

DEHP was measured throughout Hempstead Bay. These measurements, as well as the strong correlation with the very persistent DTDMACs, indicate that DEHP is most likely a very persistent contaminant. In addition, the extremely good correlation between DEHP and DTDMAC indicates that the two most likely share a similar source of sewage. An intercept close to zero further supports this hypothesis as DEHP in this environment is only measured in the presence of QACs. Even though Hempstead Bay has other potential sources such as landfills, marinas and atmospheric deposition, the sewage source appears to be dominant. Ongoing research is aimed at similarly comparing the distributions of QACs and a selection of trace metals, some of which are likely to have significant non-sewage sources to Hempstead Bay.

Acknowledgements

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