TRACING COMBINED SEWAGE OVERFLOW DISCHARGE WITH QUATERNARY AMMONIUM COMPOUNDS

A Final Report of the Tibor T. Polgar Fellowship Program

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Fitzgerald, P.C. and B.J. Brownawell. 2012. Tracing Combined Sewage Overflow Plumes with Quaternary Ammonium Compounds. Section II: 1-31 pp. *In* D.J. Yozzo, S.H. Fernald, and H. Andreyko (eds.), Final Reports of the Tibor T. Polgar Fellowship Program, 2011. Hudson River Foundation.

ABSTRACT

Quaternary ammonium compounds are a novel class of chemical tracers for sewage-derived contaminants. In this study, it is hypothesized that these tracers make it possible to distinguish between treated and untreated sewage sources in estuarine surface waters. Sites around the Lower Hudson Basin were sampled from May 2011 through October 2011, with particular emphasis on the East River, Newtown Creek, and Gowanus Canal. Corresponding measurements of fecal indicator bacteria were made by another research group at these sites. Limited sampling was also conducted in the Hudson River along the Manhattan shoreline and at Piermont at the municipal sewage outfall. Samples were also collected during the raw sewage discharge that resulted from a failure in the North River Wastewater Treatment Plant in July. Samples were analyzed using high performance liquid chromatography with a time-of-flight mass spectrometer. Most samples were analyzed for particulate phase tracers only.

The first successful measurements of quaternary ammonium compounds (QACs) were made in estuarine surface waters of the U.S. The composition of these sewage-specific tracers was found to vary with the amount of rainfall on the previous day, more closely representing that of untreated sewage after large rainfalls. This finding lends credence to the idea that combined sewage overflow is one of the largest sources of contaminants to the water column in New York's industrial canals. The total concentration of QACs also exhibited a weak correlation with the abundance of fecal indicator bacteria. A pronounced compositional change was also observed during the North River Plant's failure. Although the ability to discriminate between treated and untreated sewage sources was not as great as expected, further specificity may be possible by measuring tracers in the dissolved phase.

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INTRODUCTION

Water quality in the Lower Hudson Basin has improved significantly over the last few decades, thanks in part to investments in improved waste water treatment, such as the 1986 construction of the North River treatment plant in Manhattan. This improvement has led to a renewed interest in recreational use of the river for activities such as swimming and fishing. However, the Hudson still receives a tremendous amount of sewage (not all of which is well-treated) and water quality issues persist. Combined sewage overflow (CSO) systems, which integrate stormwater and wastewater, may cause waste water treatment plants (WWTPs) to become overloaded during a precipitation event, and force them to discharge poorly-treated sewage into the Hudson. These systems are a significant source of pathogens, chemical contaminants, nutrients, and debris to the estuary. It is also possible that the spread of untreated sewage in the environment could promote the spread of antibiotic resistance (McLellan et al. 2007). Sewage-derived pathogens are among the most serious threats to swimmers and shellfish consumers (Donovan et al. 2008), and vary spatially and temporally in abundance (NYCDEP 2010). The inconsistent presence of harmful microorganisms presents a challenge to estuary managers seeking to issue safety advisories to the public. Although CSOs are an important source of pathogens, these organisms also enter the water column from other sources as well, and the relative contributions of these sources are poorly understood (Simpson et al. 2010). Currently employed water quality analyses in the Hudson do not impart a high degree of source-specificity, making it difficult to accurately assess the environmental impact of New York's aging CSO system. In this study, a novel class of sewage-derived chemical tracers is explored: quaternary ammonium compounds

(QACs). These information-rich tracers have the potential to assess contamination sources with high specificity.

The metric currently used to estimate the threat posed by pathogens in surface waters is the abundance of fecal indicator bacteria (FIB). These organisms are not necessarily pathogenic, but their abundance is thought to correlate with that of more harmful sewage-derived pathogens (Wheeler et al. 2002). In the Lower Hudson Basin and other estuaries, *Enterococcus* is the primary FIB, as it is ubiquitous in the guts of endothermic organisms and can survive some time in salt water (Freis et al. 2008). *Enterococcus* measurements are appealing because they can be done easily and cheaply (after an initial investment in equipment). However, this technique does not provide information regarding pathogen sources. More sophisticated molecular biological techniques have been tested and are still developing (Simpson et al. 2010; Stoeckel and Harwood 2007) to identify FIB by their original host organisms (humans, ducks, etc.). While potentially powerful, the accuracy of molecular source-tracking is hindered by the ever-fluctuating compositions of the gut flora found in animals, and because the population of enteric bacteria in an animal's digestive tract varies as a function of the host's health and diet (Simpson et al. 2010). Furthermore, identification of a host organism is only one part of source trackdown, because pathogens from a single species of host (notably humans) can still be introduced into the water column by a variety of mechanisms.

Reduction of pathogen loading into the estuary is dependent on understanding how pathogens enter the water column. CSO discharge is one of the most prominent loading mechanisms, but high FIB abundances can still be measured at times during dry spells or in areas of the Hudson Basin which are not proximate to a CSO outfall. Several FIB sources have been identified, including:

- Undertreated sewage: This can be introduced to receiving waters through CSO discharge, or as a result of mechanical failures in the wastewater treatment process. Significant discharges of untreated sewage entered the Hudson as a result of the fire at the North River WWTP in July 2011, and again in August 2011 when a waste pipe was damaged in Ossining, NY. Furthermore, illicit discharges of wastewater can feed into storm drains, entering receiving waters directly.
- Treated sewage: Although disinfection of wastewater removes most pathogenic organisms, it is not always 100% effective. Particles can shelter some microorganisms from disinfection, while organisms such as *Giardia* are resistant to chlorination (Jarrol et al. 1981).
- Resuspended Sediments: Certain sewage-derived pathogens can persist in the sediment for significant periods of time after settling out of the water column. Resuspension of sediments by storms or ship wakes can then mix pathogens back into the water column (Jeng et al. 2005) independent of CSO discharge.
- Surface runoff: Surfaces can be contaminated with bacteria from animal feces, including pets, livestock, rodents, birds, and others. During rain events, this contamination can be washed into storm drains, directly into estuaries (e.g., through streams), or into CSO systems—particularly on impervious surfaces in urban areas with no riparian buffer zone.

- Groundwater: Leaking septic tanks and aging sewer lines can contaminate groundwater with fecal organisms. Under the right conditions, pathogens can be carried into the estuary by the flow of groundwater (Hagerdorn and Weisberg 2009).

Given the multiplicity of sources, it can be difficult to attribute high FIB abundances in surface waters specifically to CSO. Chemical analyses which rely on the concentration or presence/absence of a single tracer can be further confounded by the large amount of dilution experienced by contaminants when sewage enters receiving waters. Tracers have included compounds such as caffeine, silver ions, nitrogen isotopes, fluorescent whitening agents (FWAs), pharmaceuticals, and others (Haack et al. 2009; Hagerdorn and Weisberg 2009; Simpson et al. 2010). Although these tracers can provide useful information about the extent of anthropogenic contamination in a waterway, they are often limited by factors including natural background concentrations, or dilution to concentrations below detection limits. Furthermore, as individual compounds, their presence alone cannot distinguish between treated and untreated sewage. A valuable analysis to complement existing tracers and generate more layers of information involves the use of quaternary ammonium compounds (QACs), which possess unique properties as tracers (Li and Brownawell 2009; Li and Brownawell 2010) but are to-date understudied in surface waters.

QACs are a class of permanently charged organic cations, commonly used as disinfectants, surfactants, and anti-static agents in a variety of personal care products, cleaning products, and industrial processes. They all consist of one nitrogen atom with a positive charge, bonded to four hydrocarbon groups. With large, hydrophobic carbon chains and a positive charge, QACs are highly particle-reactive in estuarine water, a property that increases in QACs with higher molecular weights. Due to widespread use, QACs are ubiquitous in sewage and abundant in sewage-impacted waters. Many of these compounds are not thoroughly degraded by microbial action in waste water treatment (particularly the largest, least bioavailable compounds). It has recently been shown that QACs are in many cases the most abundant organic contaminants measured in estuarine sediments around New York Harbor (Li and Brownawell 2009; Li and Brownawell 2010; Li 2009; Lara-Martin et al. 2010), and other sewage impacted estuaries including Long Island Sound and Hempstead Harbor (unpublished) because of high loading rates and significant persistence. Three homologous series of QACs have been identified as environmental contaminants, including alkyltrimethyl ammonium chlorides (ATMAC), benzalkonium chlorides (BAC), and dialkyldimethylammonium chlorides (DADMAC) (Figure 1).

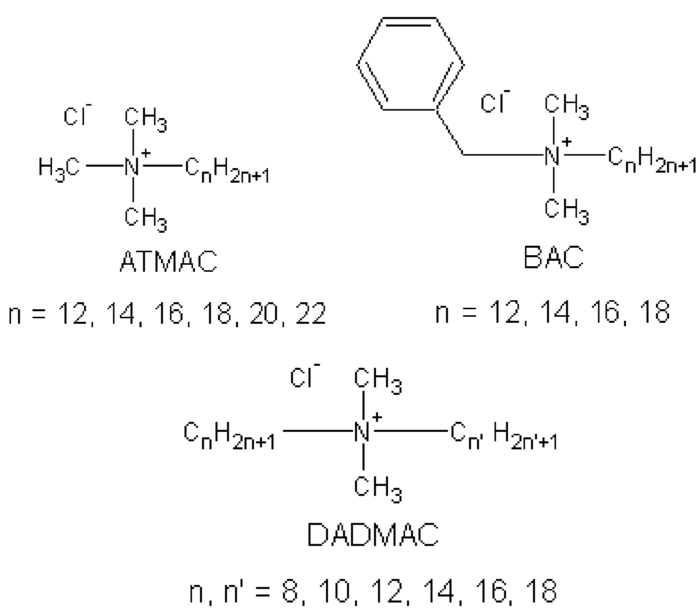

Figure 1. Three environmentally significant series of QACs: ATMAC, BAC, and DADMAC.

The large number of QACs which can be found in the Hudson River Estuary contributes to their potential as a set of highly source-specific tracers. Because they vary greatly in size, these compounds span a range of solubilities and bioavailabilities, and thus exhibit different behavior in waste water treatment and the environment. The more labile QACs (such as BACs, many of which can be used as algaecides at high concentration) are efficiently metabolized by heterotrophic bacteria, particularly in the sewage-acclimated microbial communities of WWTPs, and to some extent in waste-receiving waters. There is a continuum of degradation in wastewater treatment plants as a function of the alkyl chain length of QACs (Clara et al. 2007), with longer chain length DADMACs (Figure 1) found to be essentially inert, and recent findings suggest that many QACs are well-preserved once associated with estuarine sediments (Li and Brownawell 2010; Lara-Martin et al. 2010). Thus, in poorly treated sewage, the fraction of total QACs from the more labile group is higher, and in treated sewage, the labile fraction is markedly diminished. This has been observed in sediments proximate to CSO discharges (Li and Brownawell 2010), and it was proposed here that such distinctions can be used to discriminate between treated and untreated sewage sources to receiving waters by measuring the environmental concentrations of the compounds, and dividing the aggregate concentration of "labile" compounds by the total QAC concentration. The compounds are grouped as follows:

More labile QACs		Less labile QACs	
ATMAC 16	BAC 16	ATMAC 18	DADMAC 16:16
BAC 12	DADMAC 8:10	BAC 18	DADMAC 16:18
BAC 14	DADMAC 10:10	DADMAC 14:14	DADMAC 18:18
		DADMAC 14:16	

Table 1. Grouping of analytes into more labile and less labile fractions.

This list does not include all analytes measured in the present study, in order to allow direct comparison with harbor-wide sediment data reported by Li and Brownawell (2010). Several compounds were added to the list of analytes since sediment data were collected. Notably, ATMAC 22 (a common additive in personal care products, commonly known as behentrimonium chloride) has since been discovered as one of the most persistent QACs in New York Harbor (Lara-Martin et al. 2010). Another new analyte, ATMAC 12, is much more soluble, is detected at high levels in the influent of local WWTPs (unpublished data) and was anticipated to be present at much higher levels in untreated sewage compared to biologically treated effluents from WWTPs.

A second piece of information lies in the partitioning of QACs between the particulate and aqueous phases. In receiving waters, sewage becomes highly diluted, and this dilution causes a portion of the QACs sorbed to particles to dissociate and enter the aqueous phase. In the aqueous phase, they are more vulnerable to biodegradation and so are less persistent. Accordingly, surface water which has received recent sewage discharge (treated or otherwise) should contain a higher dissolved fraction of the more soluble ("labile") QACs, relative to water which has not experienced sewage discharge for a period of several days. This difference should be observable in the environment by filtering water samples and analyzing the particles and filtrate separately. Furthermore, resuspended sediment should have a QAC pattern similar to that of "old" sewage discharge, because the sediment in heavily sewage-impacted areas acquires most of its QAC content from past discharge as it settles to the bottom.

Other sources of estuarine pathogens are not significant sources of QACs. As very particle-reactive cations, QACs do not travel though the water table, as in some cases pathogens and some nutrients can. For tracking groundwater contamination, soluble tracers such as stable pharmaceuticals (e.g., carbamezapine and sulfamethoxazole), FWAs and potentially caffeine may be useful tools if dilution is not too great, as they can travel through groundwater (Swartz et al. 2006; Hagerdorn and Weisberg 2009). However, the absence of QACs is itself a form of information. In rural estuaries where groundwater is a suspected source of pathogens, it would be strong evidence to find the presence of caffeine coupled with low levels of QACs, indicating that pathogens assigned a human source are coming from the water table and not from treatment plants. In the event that pathogens from animal feces are washed into the river by runoff, again no QACs are expected to come from this pathway. Terrestrial surfaces should not contain significant amounts of these compounds. Thus, while this study in the highly sewage-impacted urban portion of the lower Hudson is most useful for distinguishing between treated and poorly-treated sewage sources, QACs have potential applications for additional source-specificity distinction between many possible pathogen sources.

METHODS

Sampling sites

The majority of sampling was conducted by ship in collaboration with John Lipscomb of Riverkeeper. These samples were taken in parallel with the FIB monitoring project operated by Dr. Gregory O'Mullan of Queens College and Dr. Andrew Juhl of Lamont-Doherty Earth Observatory. Shipside monitoring stations included:

- <u>The East River</u> (ER): This station was mid-channel near the mouth of Newtown Creek. A tremendous amount of treated sewage is discharged into the East River on a regular basis. Although it is very fast-flowing, the tidal reversal acts to increase the residence time of contaminants in this section of the river.
- <u>Newtown Creek—Dutchkills</u> (DK): Once a natural creek, Newtown has long served as an industrial canal. It receives CSO discharge and is also contaminated with oil and other industrial contaminants, and is now a federal superfund site. This station is at the intersection of Newtown and one of its tributaries, the Dutchkills, not far from the mouth of the creek.
- <u>Newtown Creek—Metropolitan Avenue Bridge</u> (MB): This station is far in the back of the canal, and thus is somewhat isolated from the East River, with exchange of water between the two bodies occurring primarily as the result of tidal mixing.
- <u>Gowanus Canal</u> (GC): This superfund site in Brooklyn is one of the most polluted waterways in the country. In addition to CSO discharge, the canal is contaminated by creosote and other industrially-derived pollutants. The sampling station here is a short distance inland from the mouth of the canal.

- North River Plant (NR): This plant treats much of the sewage of upper Manhattan and discharges it into the Hudson near 125th St. Sampling was conducted both at the sewage outfall and at the nearby recreational pier.
- Dyckman St. Beach (DB): A small recreational pier is located on the Hudson at the far north of Harlem. There is a CSO outfall pipe nearby.
- Piermont (PM): This site is north of New York City at a recreational pier in the town of Piermont. A local WWTP discharges close to the pier; a limited number of samples were collected at the outfall and just off the pier.

In addition to shipboard sampling, samples were taken from land in response to the fire which disabled the North River Plant for three days in July 2011. Hundreds of millions of gallons of undertreated sewage were redirected to a series of CSO outfalls around Manhattan. Samples were taken near two of those outfalls on July 22nd, near the end of the event. At 125th St., an outfall just south of the recreational pier was cordoned off with a boom. Samples were taken from inside the boom as well as from the pier at two distances away from the CSO. While sampling at these sites, the ebb tide was observed to slacken to where the flow from the CSO towards the pier was very weak. At Dyckman St. Beach, samples were taken from the pier proximate to the outfall, which was also boomed off (Table 2).

(a) (b) (c)

Figure 2. Maps of sampling locations: (a) Brooklyn sites including East River, Newtown-Dutchkills, Newtown-Metropolitan Ave. Bridge, and Gowanus Canal; (b) Stations along the Hudson River including North River Plant, Dyckman St. Beach, and Piermont; (c) Sites around North River Plant including WWTP outfall, CSO outfall, and two piers, 44m and 111m away from the CSO outfall, respectively.

Date	Sites	Prior Rainfall (inches)		
		24 hours	48 hours	72 hours
May 16th	ER, DK, MB, GC	1.1	1.1	1.1
June 27th	ER, DK, MB, GC, NR, PM	0	0	0
July 19th	ER, DK, MB, GC	0.1	0.1	0.1
July 22nd	NR, DB	0	0	0
August 16th	ER, DK, MB, GC, NR, DB, PM	0.6	6.4	6.4
October 21st	ER, DK, MB, GC	0	1.1	1.1

Table 2. Sampling sites and dates. Rainfall is given as a cumulative total over three different intervals.

Procedure

The analysis for surface water samples is based on the sediment analysis designed by Li and Brownawell (2009), and further modified to include behentrimonium by Lara-Martin et al. (2010). Surface water samples were collected in methanol-rinsed 1-L glass bottles and fixed on-site as 1% formalin solutions to prevent further biodegradation of analytes. In the laboratory, samples were filtered through pre-combusted Whatman GF/C glass fiber filters under vacuum pressure to separate the particulate and dissolved phases. Filters were then placed in vials and immersed in 10 ml of 10% HCl in methanol. To extract analytes from the particulate phase, the filters were next sonicated at 60°C for one hour in a water bath. After sonication, filters were centrifuged for 15 min at 2500 RPM, and the solvent was decanted into a larger collection vial. This extraction process was repeated two more times, and all three extracts were combined in the collection vial. Extracts were evaporated to dryness with nitrogen gas and a 60°C water bath. For purification, dry extracts were then resuspended in 2.5 ml of methanol and loaded onto a weak anion-exchange resin (AG-1-X2 from BioRad). The analytes were then eluted using 12.5 ml of methanol.

Dissolved phase analytes were isolated from filtrate in select samples by solid phase extraction, utilizing a method that is still under development, modified from the procedure by Ferrer and Furlong (2001). Filtrate samples were converted to 25% acetonitrile solutions and run through a Waters brand Oasis HLB cartridge under vacuum pressure. Analytes were then eluted off the cartridge using 15 ml of 100% acetonitrile. Both dissolved-phase and particulate extracts were analyzed with high performance liquid chromatography using a time-of-flight mass spectrometer (HPLC-ToF-MS) according to the procedure outlined by Li and Brownawell (2009; Li and Brownawell 2010).

RESULTS

QACs were successfully measured in surface water samples at all stations in the Lower Hudson Basin (Table 3), although not all of the 19 targeted QACs were detected in all samples. Samples exhibited a range of concentrations with a high of 31,200 ng/L, and a low of 112 ng/L, both seen at Gowanus Canal (Figure 3), with a median of 652 ng/L. The composition of QACs ranged from 0% labile compounds to 52%, with a median of 19% labile QACs by mass (Figure 4). Across all Brooklyn stations (ER, DK, MB, GC), the labile fraction of QACs was found to have a positive relationship with the amount of rainfall on the prior day, as measured at Central Park (Figure 5). Rainfall two days prior to sampling was not found to have a significant relationship with the QAC composition. Behentrimonium was among the most abundant QACs in all samples. Behentrimonium concentration was found to have a weak positive relationship with the abundance of *Enterococcus* (Figure 6). The relationship between behentrimonium and *Enterococcus* had a higher correlation than the relationship between prior day rainfall and

Enterococcus (Figure 7). At the East River station, the total concentration of QACs was less variable than in the industrial canals (Figure 3), as was the composition (Figure 4).

Site	Date	Ln(entero)	Ln(behentrimonium)	% disinfectants	24 hour rainfall (in)	48 hour rainfall (in)	72 hour rainfall (in)	Total QACs (ng/L)	Turbidity	log[total QACs] (ng/L)	Total QACs (µg/g)	TSS (mg/L)
Piermont	8/16		8.65	40%	0.6	6.4	6.4	19412		4.3		
	6/27		4.40	26%	0	0	0	477		2.7		
Gowanus Canal	10/21	4.56	6.80	8%	0	1.1	1.1	2501	9	3.4	1.1	2.3
	8/16	7.86	5.04	10%	0.6	6.4	6.4	1525	22	3.2	0.3	5.7
	7/19	6.95	4.14	12%	0.1	0.1	0.1	1398	18	3.1	0.3	4.7
	6/27	1.61	2.51	15%	0	0	0	112	28	2.1	0.0	7.3
	5/16	10.09	8.95	48%	1.1	1.1	1.1	31196	121	4.5	1.0	31.6
Newtown Metro Bridge	10/21	7.74	3.75	0%	0	1.1	1.1	121	3	2.1	0.2	0.8
	8/16	6.42	6.24	40%	0.6	6.4	6.4	1335	9	3.1	0.6	2.3
	6/27	1.61	2.59	6%	0	0	0	120	43	2.1	0.0	11.2
	5/16	6.97	4.87	43%	1.1	1.1	1.1	554	97	2.7	0.0	25.3
Newtown Dutchkills	10/21	7.89	5.35	10%	0	1.1	1.1	669	9	2.8	0.3	2.3
	8/16	7.73	5.82	19%	0.6	6.4	6.4	906	8	2.96	0.43	2.1
	7/19	2.30	3.22	7%	0.1	0.1	0.1	503	8	2.70	0.24	2.1
	6/27	1.61	3.06	9%	0	0	0	185	11	2.27	0.06	2.9
	5/16	5.78	7.54	41%	1.1	1.1	1.1	1886	197	3.28	0.04	51.4
East River	10/21	3.71	4.43	0%	0	1.1	1.1	1051	14	3.02	0.29	3.7
	8/16	4.58	4.22	14%	0.6	6.4	6.4	373	18	2.57	0.08	4.7
	7/19	1.61	3.30	9%	0.1	0.1	0.1	230	5	2.36	0.18	1.3
	6/27	1.61	3.80	7%	0	0	0	315	24	2.50	0.05	6.3
	5/16	5.08	4.64	20%	1.1	1.1	1.1	669	160	2.83	0.02	41.7

Table 3. **Summary of project data collection. *Enterococcus* measurements below the detection limit of 10 cells/100 ml are reported as half the detection limit.**

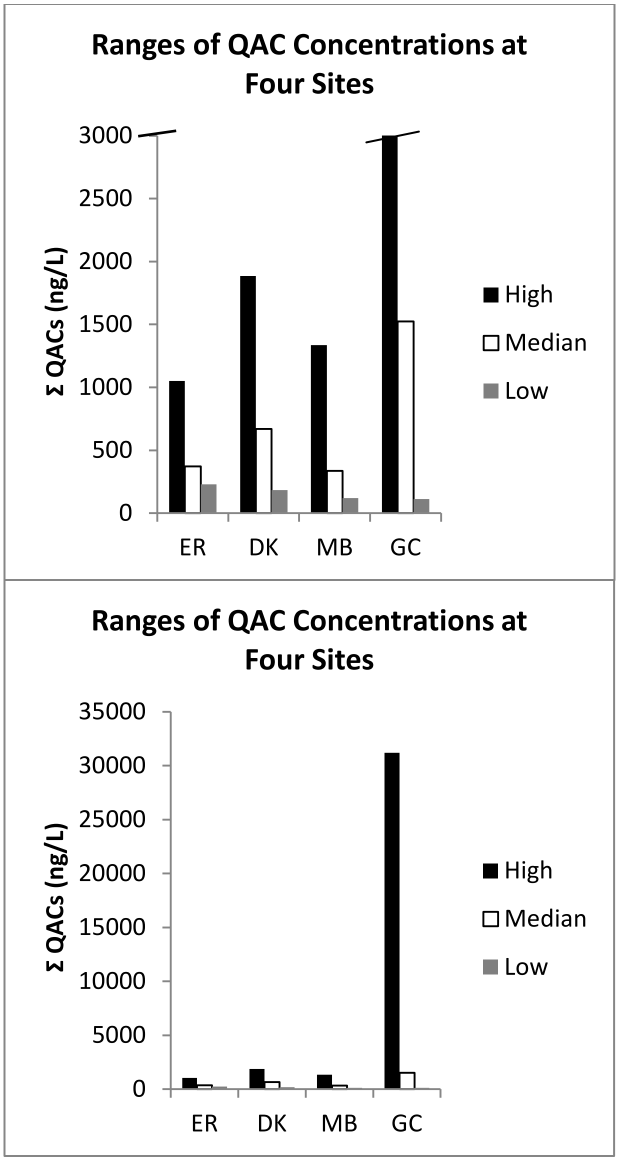

Figure 3. **Total QAC concentrations at East River, both Newtown Creek sites and Gowanus Canal, displaying the high, median, and low of five Sampling dates. The Y-axis has been truncated (left) to show variations in the lower samples, because the high concentration at Gowanus Canal is an order of magnitude higher than any other (right).**

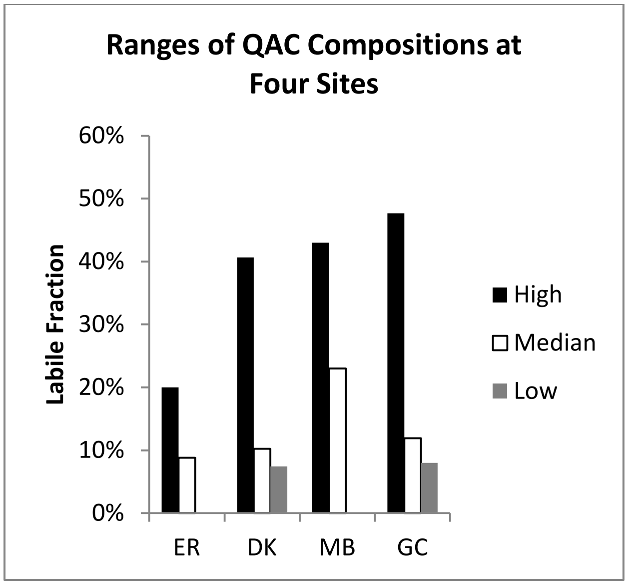

Figure 4. **Labile fraction of QACs as a function of recent rainfall at East River, both Newtown Creek sites and Gowanus Canal, displaying the high, median, and low of five sampling dates.**

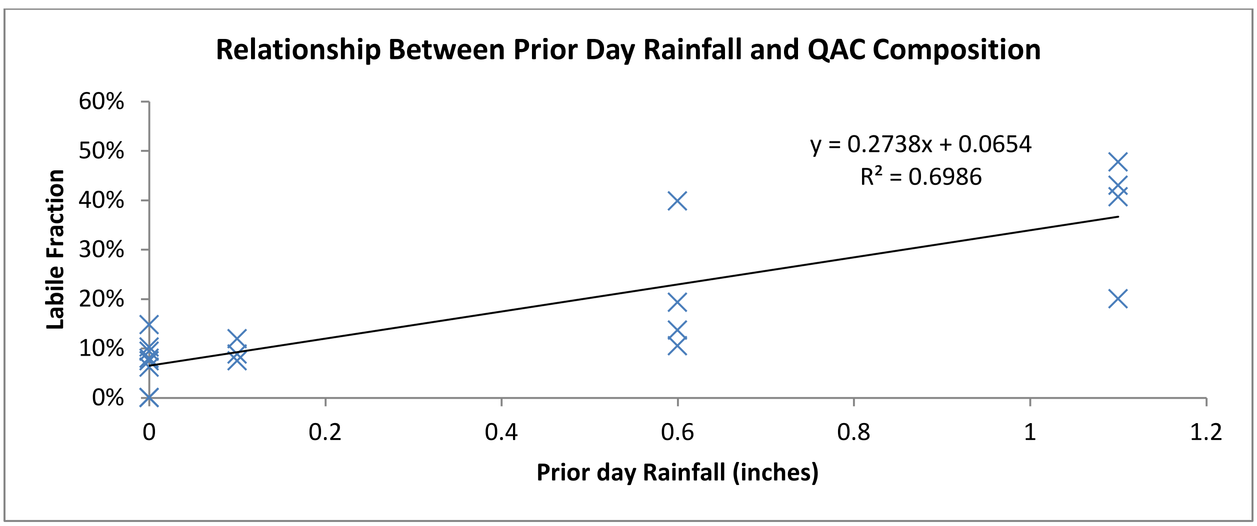

Figure 5. **Relationship between labile fraction of QACs and prior-day rainfall in the East River, both Newtown Creek Stations, and Gowanus Canal. Comparisons of mean values were determined for four of the dates where n=4 using a standard t-test conducted in Excel; the mean of the labile fraction percentage from the high-rain data set from May differs significantly from the low rain sets in June (P=0.0067) and October (P=0.0038); a higher mean for the labile fraction in May than that observed in August (0.6 inches of rain) was close to being significant (P = 0.058).**

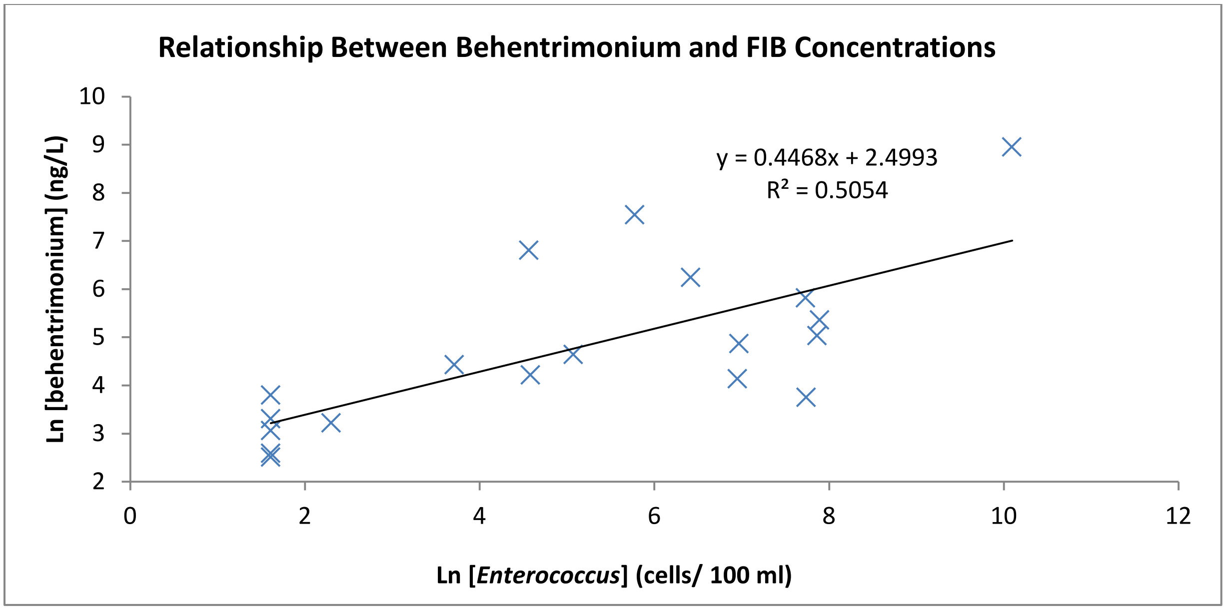

Figure 6. **Natural logarithm relationship between concentrations of behentrimonium and *Enterococcus*. Includes East River, both Newtown Creek sites, and Gowanus Canal.**

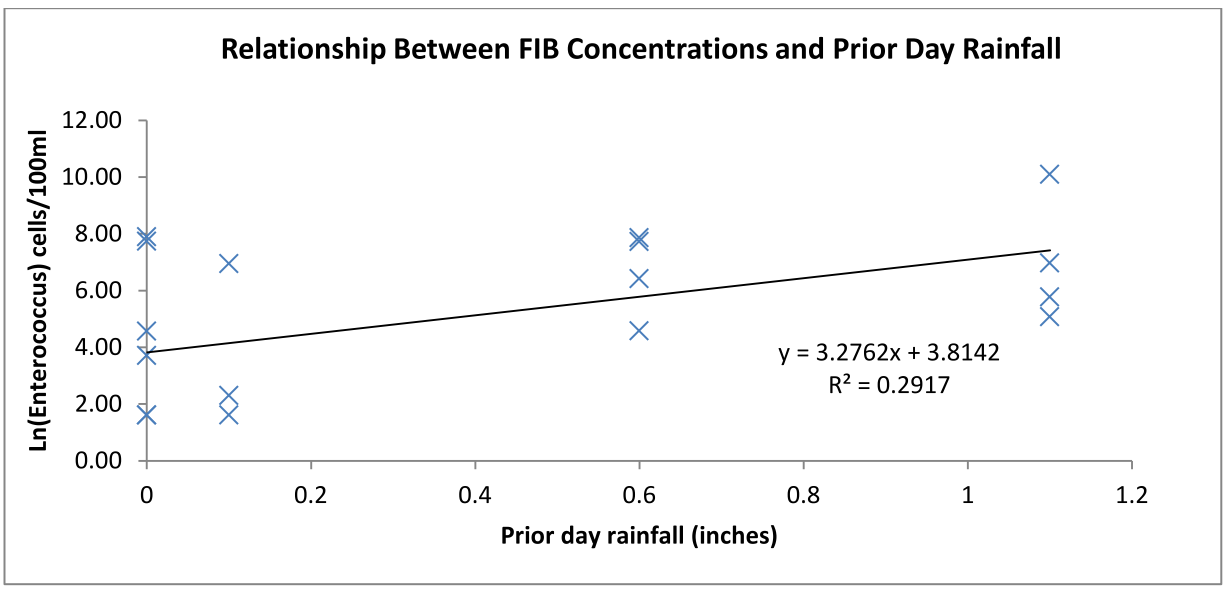

Figure 7. **Logarithmic relationship between the abundance of *Enterococcus* and prior day rainfall, at the East River, both Newtown sites, and Gowanus Canal.**

Dissolved phase QACs were successfully detected in some samples, including the August Piermont (Figures 8, 9), August Gowanus Canal, and the sample taken at the

125th St. CSO outfall during the North River accident. Preliminary data indicates that the dissolved phase detections were poor in all samples taken during October. At Piermont, the smallest QAC, ATMAC 12, is entirely found in the dissolved phase, while the larger DADMACs are associated primarily with the particulate phase (<12% dissolved). Such results could explain why the labile fractions determined in CSO affected waters were lower than expected.

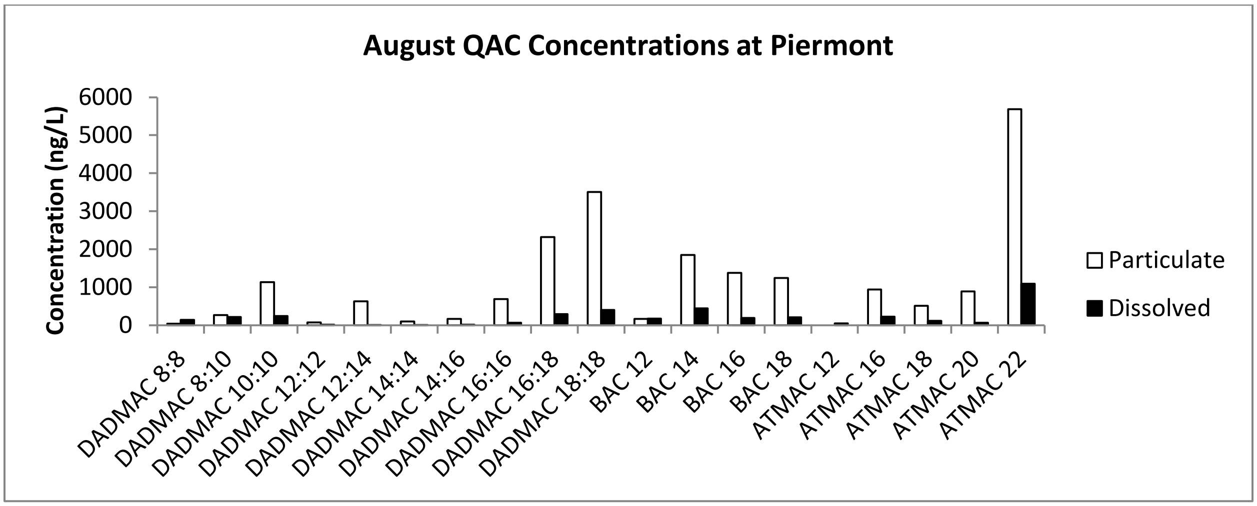

Figure 8. Concentrations of nineteen different QACs in a sample taken at Piermont. Measurements in the particulate and dissolved phases for each analyte are shown adjacent to each other.

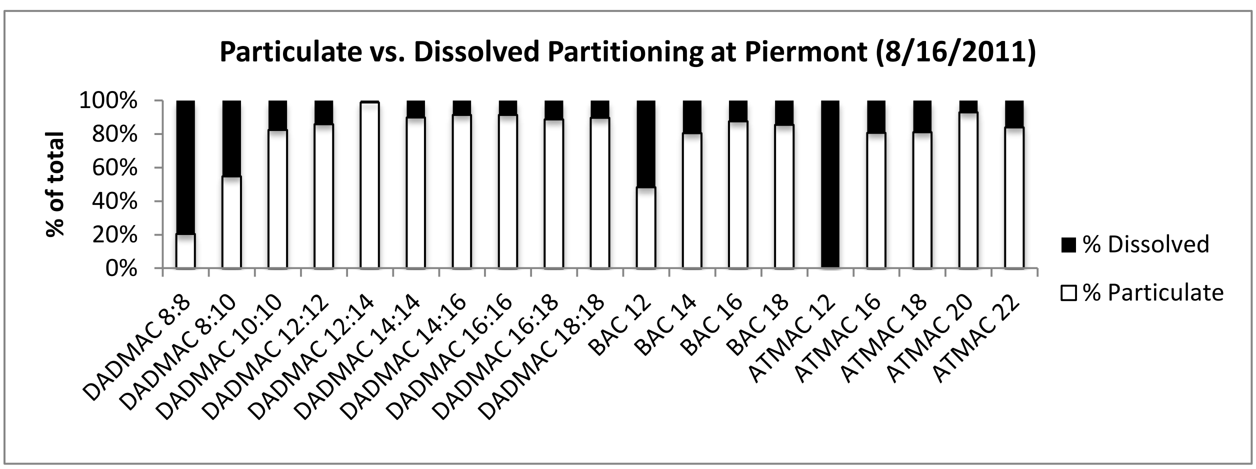

Figure 9. Partitioning of nineteen different QACs between the dissolved and particulate phases in a water sample taken at Piermont.

Results from sampling conducted at approximately 125th St. during the North River accident are illustrated in Figure 10. The concentrations are seen to have fallen sharply with distance from the CSO, and the change of composition is consistent with a loss of more labile components upon dilution. It should be noted that the concentrations of total QACs in the main stem of the river was not dramatically elevated over average levels measured in the lower estuary and the water in the river had experienced a couple days of input of untreated sewage.

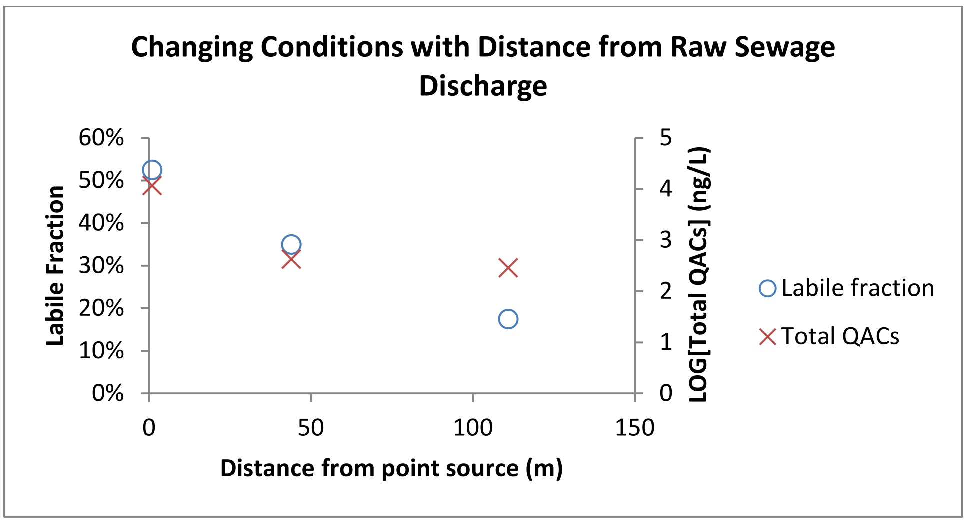

Figure 10. **Changes in QAC composition and concentration with distance from a point source discharge near the North River WWTP during its July 2011 failure. These samples were taken near the end of the three-day discharge.**

DISCUSSION

A significant result of this project is that the first successful detections of QACs were made in estuarine surface waters in the U.S. or anywhere in the world. Furthermore, the relationship between QAC composition and prior day rainfall at the Brooklyn sites suggests that CSO discharge causes surface waters to become measurably enriched in the more labile QACs which would otherwise be more depleted in waters impacted by treated sewage (Figure 5). This enrichment of the labile fraction appears muted at the East River site (Figure 4), because it receives a mixture of treated and untreated sewage during large CSO events. A second piece of evidence to support this idea is the fact that the East River experiences less variation in the total concentration of QACs, compared to the Newtown and Gowanus sites (Figure 3). The constant input of treated sewage into the East River has a dominant effect on the QAC concentration/composition of that water body, even when untreated sewage is added.

Dissolved phase measurements, although limited in number of samples, provided some useful information. At Piermont, a high level of dissolved QACs was discovered in August (Figure 8). The dissolved-particulate partitioning, the high labile fraction seen especially in the dissolved phase, and the large total concentration of QACs suggest that poorly-treated sewage was being discharged into the river at this time. The prior day saw 0.6 inches of rain, and two days prior there was a record-setting rainfall of 6.4 inches, so it is possible that a CSO discharge was responsible for this untreated sewage signal, or that the local WWTP became overloaded and there was some bypass of untreated sewage. In contrast, samples taken there in June had a much lower total concentration and a lower labile fraction, resembling a treated sewage source (although no dissolved-phase measurements were made that day). This further suggests that rainfall can have an adverse effect on water quality at Piermont, but more information about the sewage treatment operations and a larger number of samples are needed to test this. Dissolved phase measurements made during a drier period in October did not detect any of the analytes except the most abundant ones; however, the data for dissolved phase measurement are very preliminary, and it is unclear if analytical sensitivity was sufficient for this sample set. Further work must be done to perfect the dissolved phase analysis.

At the North River site, a dramatic change in the QAC population of the water column was observed during the July raw sewage discharge. At the discharge point source, the composition was enriched in the more labile QACs, relative to samples taken at the point source there in June or August. However, this enrichment dissipated rapidly with distance from the outfall, having attenuated to background levels (below the harbor-wide median of 19%) within 111m (Figure 10). Dilution is a likely cause of this attenuation. At the time of sample collection, discharge had already been happening for two days. Freshly discharged particles were mixed with sewage-derived QACs which had entered the estuary on previous days, and those older QACs were likely depleted in labile compounds due to time spent in the river. At the Dyckman St. Beach, there was a similar compositional change during the July failure event (30% labile QACs vs. 19% during August), but the total concentration of QACs was unchanged; it is possible that the discharge was beginning to diminish at the time of sampling as the WWTP came back into operation.

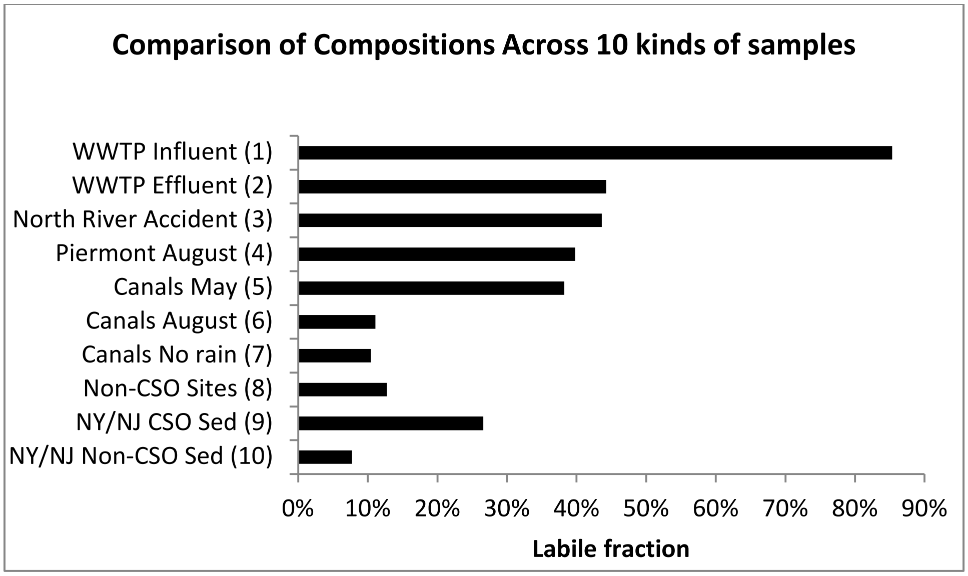

Figure 11. Average QAC composition across several kinds of water samples, with particulate-phase measurements. (1) Influent taken from a WWTP on Long Island; (2) Effluent taken from that same WWTP after undergoing tertiary treatment; (3) Samples taken from the North River sites on July 22nd during the raw sewage discharge; (4) Highly contaminated sample found at the Piermont outfall during August; (5) Samples taken at Newtown Creek and Gowanus Canal after a pronounced CSO event in May, (6) Samples taken from the canals in August, after a lesser rainfall than May; (7) Samples taken from the canals during drier periods; (8) Samples taken during any weather in the East River and Hudson River (9) Sediment samples from CSO-impacted sites around NY/NJ harbor; (10) Sediment samples taken from non-CSO sites around NY/NJ harbor.

Comparisons across sites (Figure 11) are a useful way of considering the data. Included for illustrative purposes, the WWTP influent and effluent cannot be directly compared to sites from New York City, since the plant in question receives low flows and different sewer shed inputs, and uses a different kind of treatment, but nonetheless it indicates that compositional differences between treated and untreated sewage are substantial. The highly contaminated samples from Piermont and the North River accident have a labile fraction that is quite high, especially considering the amount of dilution that occurs in some of those samples upon discharge. In the canals, May compositions were labile QAC-enriched compared to dry weather compositions, which yielded compositions very similar to those found at non-CSO sites. Unexpectedly, the August canal samples also resembled dry-weather compositions. Either the 0.6-inch rainfall the day before was not sufficient to trigger a large CSO event, degradation of the labile QACs occurred rapidly between the rain and the time of sampling, or after approximately a tidal cycle, the CSO signal in the canals was sufficiently diluted with surrounding water that the signal was masked. Since the microbial populations of the canals are highly acclimated to sewage contaminants, it is possible that labile QACs have a shorter residence time in the canals than in less-impaired waterways. Sediment measurements from non-CSO sites resemble the compositions found in the water column during dry periods or away from CSO sites. Finally, prior sediment measurements made near CSO outfalls had an intermediate composition, being more labile-enriched than dry-weather water, but less enriched than CSO water. This intermediate composition may reflect further loss of labile QACs prior to or after deposition, or that what is deposited near the CSOs represents mixed input of QACs to the sediment in such sites, as the water column above sees a range of concentrations and compositions depending on rainfall.

Compositional changes were generally not as pronounced as expected, based on comparisons between raw sewage and treated sewage samples taken inside of WWTPs. One possible explanation is that the difference would be greater if dissolved phase measurements had been included. Since the most degradable QACs are also the most soluble, they may have a more telling presence than anticipated in the dissolved phase, particularly for fresh sewage discharge.

ACKNOWLEDGMENTS

This research would not have been possible without the help of Riverkeeper's John Lipscomb, who took me sampling. I also need to thank Dr. Gregory O'Mullan, Dr. Andrew Juhl, and their FIB monitoring team, for providing data, and my fellow students Anne Cooper Doherty and Shawn Fisher, for their support and advice.

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