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ASSESSING CONTINUOUS CONTAMINATION DISCHARGE FROM A COMBINED SEWER OUTFALL (CSO) INTO A TIDAL WETLAND CREEK: BACTERIOLOGICAL AND HEAVY METALS INDICATORS

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ABSTRACT

Continuous discharge from a combined sewer overflow (CSO) into a tidal wetland creek in the New York City urban area was analyzed to assess the extent of water quality degradation during both dry and wet weather. A combination of fecal indicator bacteria (FIB), total suspended solids, and dissolved metals were used to infer the presence of sewage and fecal pollution from the CSO discharge and to constrain the spatial and temporal impact on water quality and dry season creek flows. Upstream of the CSO, creek flow was dominated by groundwater input, and FIB levels were very low or undetected, indicating the absence of contamination. Low-volume loading was detected in dry weather, in contrast to the expected impact when a CSO is operating as designed (flowing only following wet weather). In wet weather, a “first flush” peak was detected for some contaminants, followed by diluted contaminant concentrations due to increased flow volume but resulting in greater total loading that affected a larger area. The correlation of bacteriological and metal indicators in paired spatial and temporal samples revealed a positive relationship between the concentration of some metals (e.g. Na, Fe) and FIB. Variable patterns of peak metal concentration in the creek, with respect to precipitation and FIB level, also suggest changes in contaminant source and the influence of tidal backwater.

Keywords: CSO, metals, Enterococci, sewage, storm-water, urban

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1. INTRODUCTION

In major metropolitan areas in the United States [1] and worldwide [2,3], millions of people are served by wastewater treatment systems with combined sewer overflows (CSO). These combined sewer systems normally collect only sanitary sewage in dry weather, but storm events add to the volume of this wastewater, such that either the delivery system or wastewater treatment plants (WWTPs) can often no longer accommodate the total combined stormwater and sewage. In this case, excess sewage and stormwater overflowing from designated outfalls impair adjacent water bodies [1,4]. Nearby coastal communities are then faced with CSO-derived human health and environmental threats depending on how the contamination spreads and degrades. CSO discharges have often been described, however, few have reported data on resultant pollution dynamics in tidally-affected receiving waters [5,6], specifically wetlands, or from malfunctioning CSOs that include both dry and wet weather discharge. For this reason, dry season CSO impacts are of particular interest.

Receiving water quality varies daily and seasonally depending on the amount and frequency of precipitation and flow through CSO systems functioning as designed [7]. Changing ratios of stormwater and sewage, and accumulation of sediment within the CSO system often cause a "first flush" spike in contaminant contribution after the onset of rain [8]. Under dry weather conditions, properly functioning CSOs do not discharge sewage pollution, and unanticipated discharge is rarely observable, because CSO sites are not often instrumented for routine monitoring. If CSOs are malfunctioning in dry weather and also discharging in wet weather, patterns of contamination could be quite complex [4,9-10], and further confounded by hydrodynamics of the tides [11]. Therefore, in estuaries with high population density, humans may be exposed to variable concentrations of chemical and microbiological contaminants threatening to their health [1,12-14].

In this study, we examine a site where a malfunctioning CSO discharges, during both dry and wet weather, into a tidal wetland at the head of an embayment of Long Island Sound in the New York City area. The objectives of this work are: 1) to determine if dry, as well as wet weather, discharge from this CSO contained evidence of sewage pollution; 2) to determine the spatial distribution of contamination from the CSO discharge and how it changed following storm events; and 3) to evaluate the correlation between bacteriological and metal indicators of pollution. We hypothesized that: sewage pollution would be confirmed in the CSO discharge under both dry and wet weather conditions; an increase in spatial distribution of surface water contamination would follow precipitation and, following the first flush, contaminant concentration would be diluted by stormwater in wet weather compared to dry weather; and finally, that bacteriological and metal indicators of contamination would be positively correlated.

2. MATERIALS AND METHODS

2.1. Hydrologic Setting

The study area is located near the southeastern end of a groundwater-fed, vegetated tidal wetland in Alley Pond Park, at the head of Little Neck Bay, an estuary discharging into Long Island Sound, in the New York City metropolitan area (Figure 1).

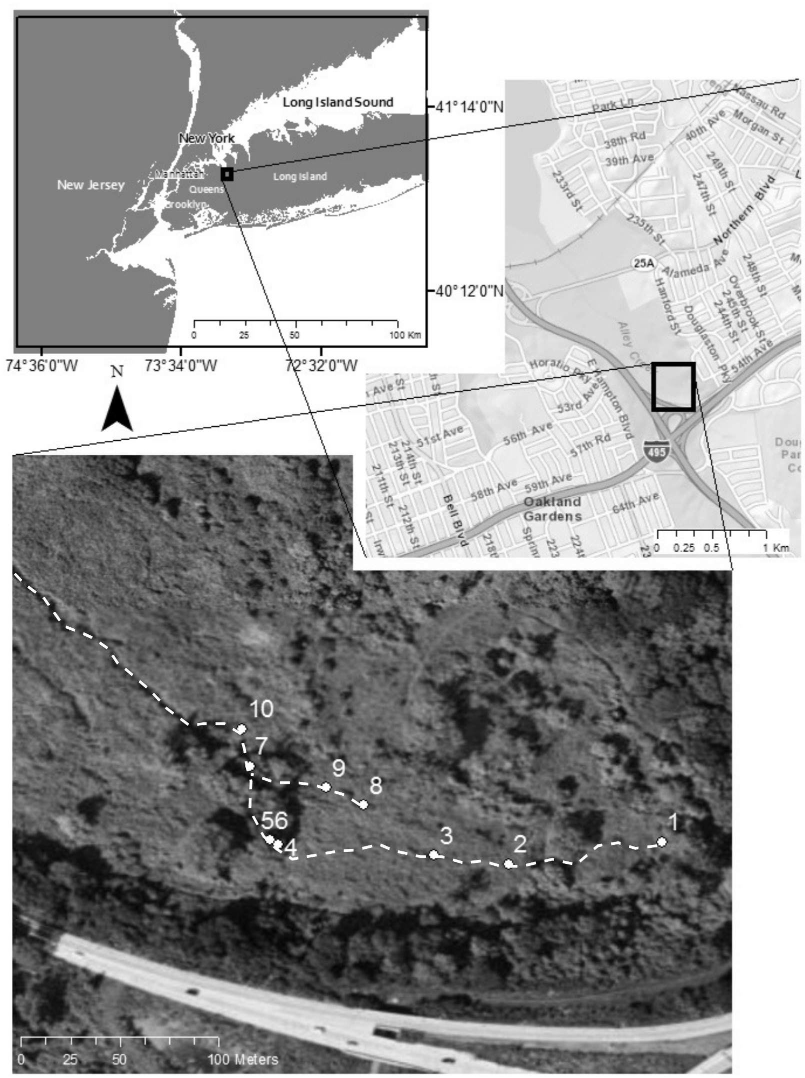

Figure 1 Site map showing study location, sampling sites and creek (dashed). Note that sites 5-6 are at the same location symbol at this scale. The USGS streamgaging station (not shown) is located on a downstream tributary to the tidal creek 200m west of the area of the sampling sites. Note that Sites 8 and 9 are deliberately located on a creek branch instead of downstream from the CSO discharge (see text).

A muddy-bottomed creek originates from a flowing (artesian) well at Site 1, flows past Sites 2 and 3, and discharges over a V-notch weir (Site 4) into a pool (Site 6) surrounding the CSO outfall (Site 5). The concrete outfall structure, from which flow emerges vertically, is in the center of the creekbed. Just downstream at Site 7, the stream channel is joined by a minor branch from the east, on which Sites 8 and 9 are located. These sites were specifically chosen because they are not directly downstream of the CSO and were expected to provide a strong contrast in water quality to the in-stream sites. Site 8 is a bubbling spring whose discharge flows past Site 9. Downstream at Site 10, the stream develops into a tidal channel as it flows northwest past a U.S. Geological Survey (USGS)-gaged tributary (not shown) to Little Neck Bay (Figure 1).

2.2. Hydrologic Methods

Elevation benchmarks are not available in the wetland, however leveling measurements were conducted relative to the top of the concrete CSO structure in the vicinity of Sites 4-10. Near continuous (15 min) water level data was obtained using pressure transducers installed in 2.54 cm diameter PVC standpipes perforated above and below the streambed at Site 7. These data were corrected using barometric data from the nearby weather station at Queens College (7 km to the west), jointly operated with the USGS. Instantaneous discharge was determined at Site 10 using areally-weighted velocity measured with a Global Water AT-210 flowmeter (globalw.com). Data were obtained from the real-time National Oceanographic and Atmospheric Administration (NOAA) Kings Point tidal gage, Queens College weather station, and USGS Alley Creek websites for use with Alley Creek water quality and hydrologic monitoring data.

Spatial Water Quality Sampling. Samples were collected synoptically at Sites 1-10 on April 15, 2011 in dry weather baseflow conditions, and on April 20 following a minor rain event (1.0 mm) the previous day. Prior to use, high density polyethylene (HDPE) sample bottles were acid-washed, triple-rinsed with deionized water (DI) and air dried, then triple-rinsed with the sample prior to collection. Samples for metals analysis were filtered using syringes equipped with 0.45 µm PTFE filters. The samples were then acidified (pH<2) with concentrated nitric acid (HNO_3) < 0.1 % of the total volume. Unfiltered, unacidified samples were collected for microbial analysis and Total Suspended Solids (TSS).

Storm Water Quality Sampling. An autosampler (Teledyne Isco Model 3700 Full Size, isco.com) was placed at Site 10, selected based on a narrow stream width that facilitated mixing. On August 21-22 before 11.5 mm of rain fell overnight, the autosampler was manually triggered and programmed to collect 24 samples in 1L HDPE bottles at variable intervals of time ranging from 20 minutes in the middle to 1 hour intervals at the beginning and end of collection, with prior automatic rinsing of the intake tube. The bottles were transported to the laboratory the next morning where they were subsampled for immediate microbial analysis, and subsequent TSS and metals analysis. At the time of autosampler sample retrieval, two other 1L samples were manually collected from Site 4 and Site 5 upstream of the autosampler site.

Laboratory Analytical Methods. All water samples were analyzed for major cations (Ca, K, Mg, Na) and trace metals (Al, Ba, Cd, Cr, Cu, Fe, Mn, Pb, Zn) by inductively-coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optima 5300DV instrument. Mixed metal standards were prepared and analyzed at wavelengths to minimize spectral interferences with other constituent metals. For major cations, samples were diluted by a factor of 10-100 using 2% HNO_3 to ensure that elemental concentrations were within the linear dynamic range of the instrument. Trace metal samples were analyzed without dilution. Only metals above detection are reported.

For microbial and total suspended solids analyses, water samples were stored in a dark cooler, on ice, during collection and transport to the laboratory. Samples for microbial enumeration were processed as quickly as possible upon arrival in the laboratory and, including those collected via the autosampler, within 18 hours of collection. Ideally samples would be processed within 6 hours of collection, but storm event sampling via an autosampler did not allow such rapid processing for some samples in this study. However, negligible decay of pathogens has been measured in similar water samples within the first 24 hours following collection when samples are stored in the dark and on ice [15].

Immediately before sample processing, each bottle was gently mixed to resuspend particles. The concentration of the fecal indicator bacterium (FIB), *Enterococcus*, was measured in unfiltered water samples using the IDEXX Enterolert system (www.Idexx.com) with standard dilution (10 mL sample, in 90 mL sterile water), incubation (24 hours at 41°C), and the Most Probable Number (MPN) enumeration procedures described by Suter et al.[16].

For determination of Total Suspended Solids, 500 mL of water from each sample was filtered, using vacuum, through a pre-combusted and preweighed glass fiber filter. The filter was transferred to a preweighed tin, dried for 24 hours at 105°C and then reweighed. The difference in filter weight over the volume of water filtered was calculated as the total suspended solid concentration in the sample (mg/L).

Statistical Analyses. Statistical analyses were conducted using the CoStat package (CoHort Software, cohort.com). Descriptive data for the April sampling under dry and wet conditions were tabulated, and polynomial regressions were plotted for analytes as a function of log-normally transformed *Enterococci* values - only significant coefficient values of multiple determination are considered. Correlation matrices of Pearson product moment coefficient r values were compiled for dry and wet weather at all sites, and August single-site storm event data. For the temporal, storm-event dataset, regression coefficients of multiple determination and non-parametric Spearman Rank Correlation r values were obtained and tabulated between various combinations of parameters such as stream stage, TSS and *Enterococci* vs selected analytes.

3. RESULTS

3.1. Hydrology

Flow from the concrete CSO structure (Site 5) was estimated as less than 0.008 m^3/s under dry conditions, discharging upward from the center of the creekbed to create an irregularly-shaped pool (Site 6) approximately 15 m in diameter and 0.6 m deep. However, the abundance of stormwater debris (plastic bags/garbage) and sediments ranging from clay to cobble-size in the surrounding area suggests large discharges during wet weather, when the pool attains water depths of 1.4 to 1.7 m measured at the weir (Site 4). Observations of flow velocity and direction were made under varying tidal and weather conditions as context for the collected creek water quality samples. While dry-weather discharge at Site 10, the most downstream site, was measured at 0.036 m^3/s at low tide, backwater effects of high tide reduce downstream creek velocity to zero and sometimes cause reverse flow at flood tide, backing up water from the creek and CSO discharge in the pool at Site 6. However, specific conductance data (not shown) provides no evidence of brackish water intrusion from Little Neck Bay into the studied creek segment.

3.2. Confirmation of Sewage Discharge and Spatial Water Quality Patterns: Chemistry and Bacteria

April spatial sampling results (Table 1) demonstrate contamination of Alley Creek from a malfunctioning CSO (Site 5) observed to flow continuously during both dry and wet weather. Water samples collected directly from the CSO discharge into the creek (Site 5) contained levels of *Enterococci* as high as 8,700 MPN/100 mL (Table 1) even during dry weather, confirming fecal pollution from the malfunctioning CSO. At the time of collection, the applicable EPA *Enterococci* guideline for primary contact recreation was 61 or fewer *Enterococci* cells per 100 mL of water [17] and the CSO discharge into the creek at Site 5 exceeded that EPA guideline by more than two orders of magnitude.

The fecal indicator bacteria *Enterococci*, as well as major cations (Na), and trace metals (Ba, Fe, Mn, Zn, Cu, Cr), vary both spatially along the tidal creek and in response to minor precipitation (Table 1, Figures 2,3 and 4ab). In both dry and wet conditions, upstream of the CSO (Sites 1-4) where the creek flow is dominated by groundwater input, *Enterococci* levels are low (MPN/100mL of 10 or less) and acceptable in comparison to the EPA guideline [17] for primary contact recreation. The peak *Enterococci* concentrations from the spatial survey occurred at Site 5, where the CSO discharged into the creek (Table 1; Figure 2ab). Compared to the source at Site 5, there is a significant decrease (by 18x in dry weather and 1.7x in wet weather) in concentrations of *Enterococci* downstream (Sites 6,7,10). In contrast, Sites 8 and 9 on a side branch, representing the non-CSO impacted part of the creek, have relatively low concentrations following both dry and wet weather.

The concentrations of Na and Fe (Figure 2ab) peak at or near the CSO outflow (Sites 5,6) in both dry and wet weather, but the concentrations are lower in wet weather, especially for Fe. Mn shows a similar pattern in dry weather, but reaches a minimum at the CSO in wet weather (Figure 3ab). Ba concentrations at the upstream sites (Sites 1-4) do not vary significantly between dry and wet weather (Figure 4ab), but concentrations in wet weather are considerably lower beginning at the CSO (Site 5,6) and extending downstream (Site 10). Ba concentrations at the spring site (Site 8) and just downstream (Site 9) were largely unaffected by wet vs. dry weather, consistent with the low levels of fecal indicator bacteria.

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Table 1 Water quality data from all sites - Dry and Wet conditions in April 2011

	pH(-)	Na (mg/L)	Ba (µg/L)	Entero. (MPN/ 100mL)	Fe (µg/L)	Mn (µg/L)	Zn (µg/L)	Cu (µg/L)	Cr (µg/L)
	Dry/*	**Dry/Wet**	**Dry/Wet**	**Dry /Wet**	**Dry/Wet**	**Dry/Wet**	**Dry/Wet**	**Dry/Wet**	**Dry/Wet**
1	7.09	13.1/12.7	19.2/19.3	0/0	- / -	- / -	41.4/38.9	0.7/0.7	7.1/7.1
2	7.21	44.9/ 45.9	25.2/25	0/0	46.5/1.5	15/10.8	24.4/31.2	- / -	3.8/3.4
3	7.46	44.3/ 46.2	26.2/25.2	10/0	376/44.5	31.2/29.7	41.7/122.6	0.7/0.7	4.1/0.7
4	7.53	44.6 / 42.3	26.9/26	0/10	295.6/52.4	33.1/37	102/89.4	0.8/ -	2.6/0.3
5	7.38	153.2/118.6	41.1/12.1	8664/5172	876.3/56.5	125/4.7	54.5/29.6	4.3/1.7	1.1/0.6
6	7.46	104.7/116.8	33.6/12.6	3873/3609	518.5/82.4	71.2/11.6	58/43.6	2.8/1.1	1.0/0.1
7	7.33	87.9/104.7	35.3/16.7	1418/2465	501.9/95.4	67.1/23.9	51.8/44.9	1.5/2.0	1.7/0.2
8	6.94	8.7/8.3	16.5/15.5	0/0	- / -	- /0.2	54.6/39.9	3.1/0.9	1.5/1.2
9	7.00	45.2/54.8	34.5/38.8	0/10	144.3/20.7	20.2/27.2	34.3/32.8	0.3/0.3	0/0.4
10	7.45	70.0/104	35.9/16.8	482 / 2987	426.4/87.9	58.4/18.1	39.6/29.8	0.1/0.6	0.8/0.3

*not collected in wet conditions

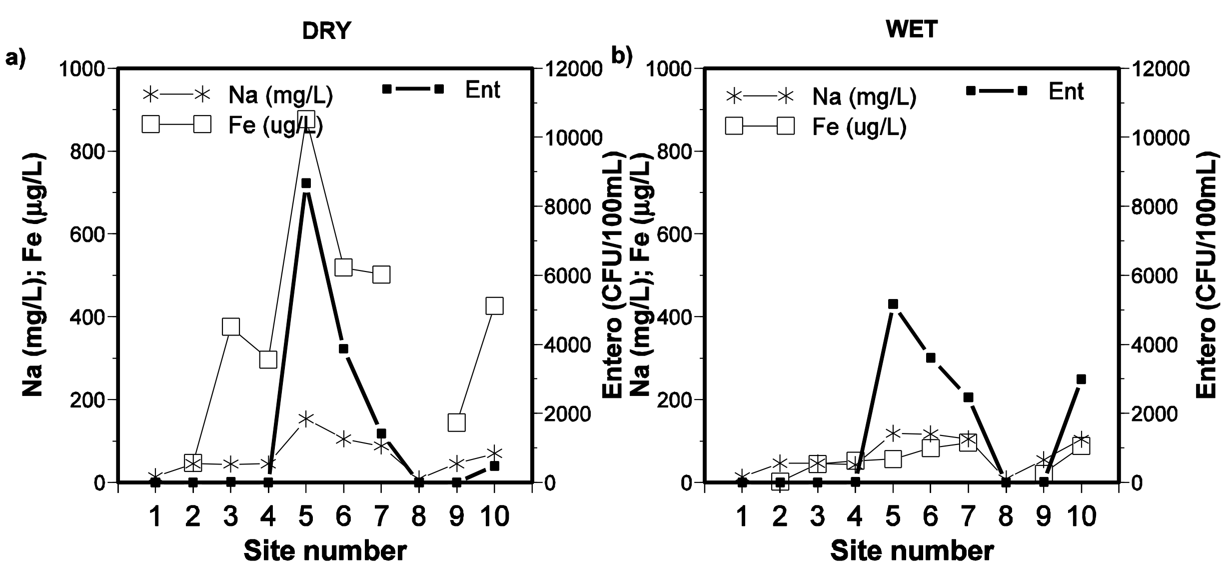

Figure 2 Selected metal ion concentrations (Na, Fe) compared to *Enterococci* at Alley Creek field sites: a) shows dry conditions and b) shows wet conditions. Sites 8 and 9 represent water quality unaffected by CSO contamination.

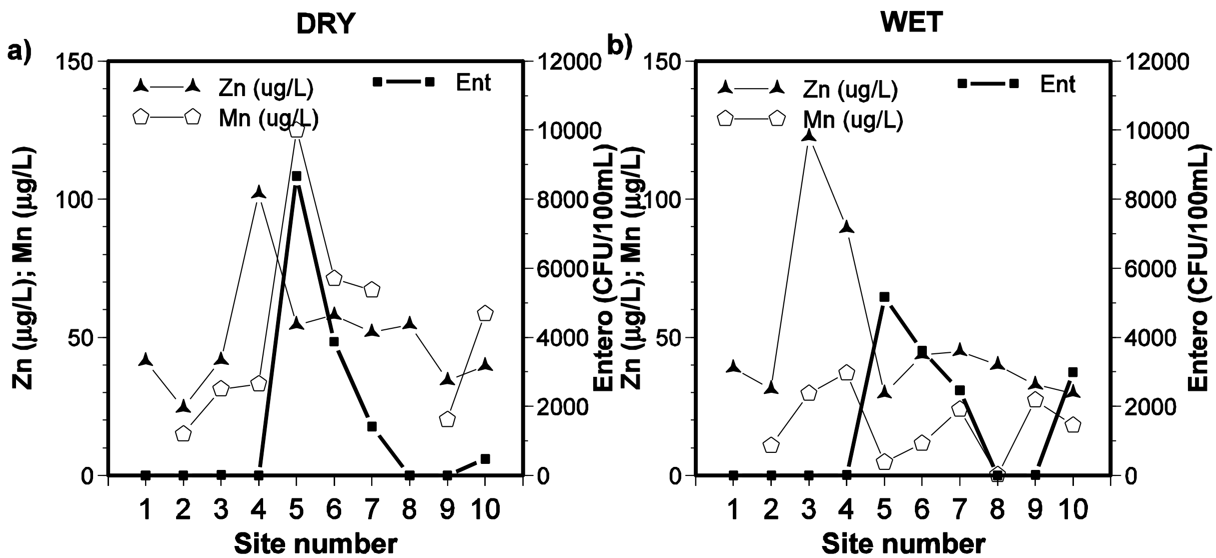

Figure 3 Selected metal ion concentrations (Zn, Mn) compared to *Enterococci* at Alley Creek field sites: a) shows dry conditions and b) shows wet conditions. Sites 8 and 9 represent water quality unaffected by CSO contamination.

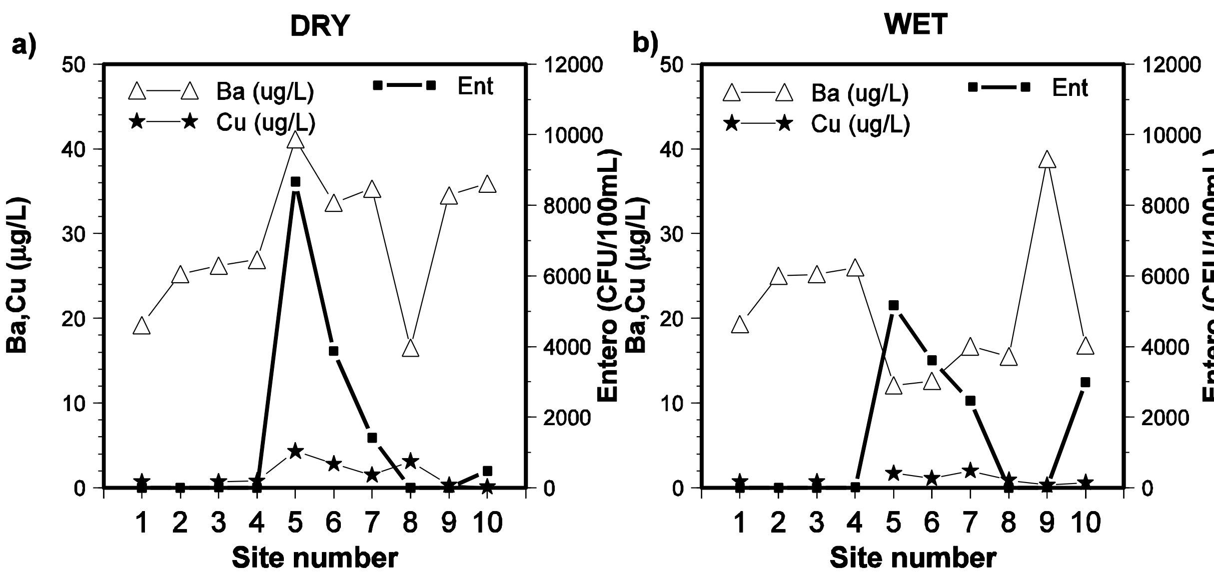

Figure 4 Selected metal ion concentrations (Ba, Cu) compared to *Enterococci* at Alley Creek field sites: a) shows dry conditions and b) shows wet conditions. Sites 8 and 9 represent water quality unaffected by CSO contamination.

In contrast, the trace metals Cu and Zn have their highest concentration peaks at different locations, Cu showing relatively little variation peaking at Sites 5 or 7 (Figure 4ab). However, the highest Zn peaks occurred upstream of the CSO in both dry weather and in wet weather (Figure 3ab). These Zn concentrations approach (Site 4 in dry weather) and exceed (Site 3 in wet weather) the US EPA National Recommended Water Quality Criterion of 120 µg/L [18]. Except for these peaks, Cu and Zn do not show unusual concentrations for natural waters in a moderately urbanized area [19,20].

3.3. Storm-Event Time-Series Sampling: Chemistry and Bacteria

The August time-series samples (Table 2) demonstrate how *Enterococci* counts, total suspended solids (TSS) and metals concentrations change at a site downstream (Site 10) from the CSO discharge during a storm event (Figure 5a-d). This particular storm event occurred between high and low tides, so the peak in the water height corresponds entirely to flow from the CSO resulting from the precipitation shown (Figure 5a). Temporal sampling during the rain event shows TSS, and Zn exhibiting maximum concentrations coinciding with maximum creek water level, and an *Enterococci* peak that was slightly delayed with respect to creek level. *Enterococci* concentrations rise to a maximum near 20,000 MPN/100 mL after the hydrograph peak, then fluctuate, declining to approximately 6,000 MPN/100ml over the next 12 hrs (Figure 5b), a concentration that was still substantially elevated relative to the dry weather condition at Site 10 (Table 1; Figure 2a).

Ba and Na (and other major ions - not shown) concentrations decrease with rain, reaching a minimum with the hydrograph peak and not quite recovering over the next 12 hours (Figure 5c). Variations in metals concentrations are more complex, with Fe and Cu maxima just preceding the maximum rainfall and creek water level. They then both decrease as the hydrograph reaches its peak, with Fe reaching a minimum then rising more than 5-fold over the next 6 hours, well above pre-rainfall values. Cu concentrations do not rise above their pre-hydrograph peak but fluctuate near 5 µg/L. Cr, at extremely low levels during the rainfall, rises to reach a peak about six hours after the storm event (Figure 5d). Mn, previously detected in spatial samples, was below detection for the storm-event sampling.

3.4. Statistical Analyses and Interactions

In dry weather, Fe, Na, Mn, Al and Ba are always significantly correlated with log-transformed *Enterococci* ($p<=0.05$), but in wet weather, only Fe and Na retain significant correlation with *Enterococci* and each other (Table 3). Ba is moderately positively correlated ($r=0.76$, $p<=0.05$) with *Enterococci* in dry weather and inversely correlated in wet weather ($r=-0.56$, ns), also indicated by a negative Spearman Rank Correlation value (Table 2). Fe, Mn, Cu and Al are correlated significantly with each other ($p<=0.01$) in dry weather, and are not significantly correlated in wet weather. During the storm event, time-series samples show that Zn and TSS are highly correlated with each other and water level ($r=0.88$, $p<=0.01$, Table 4).

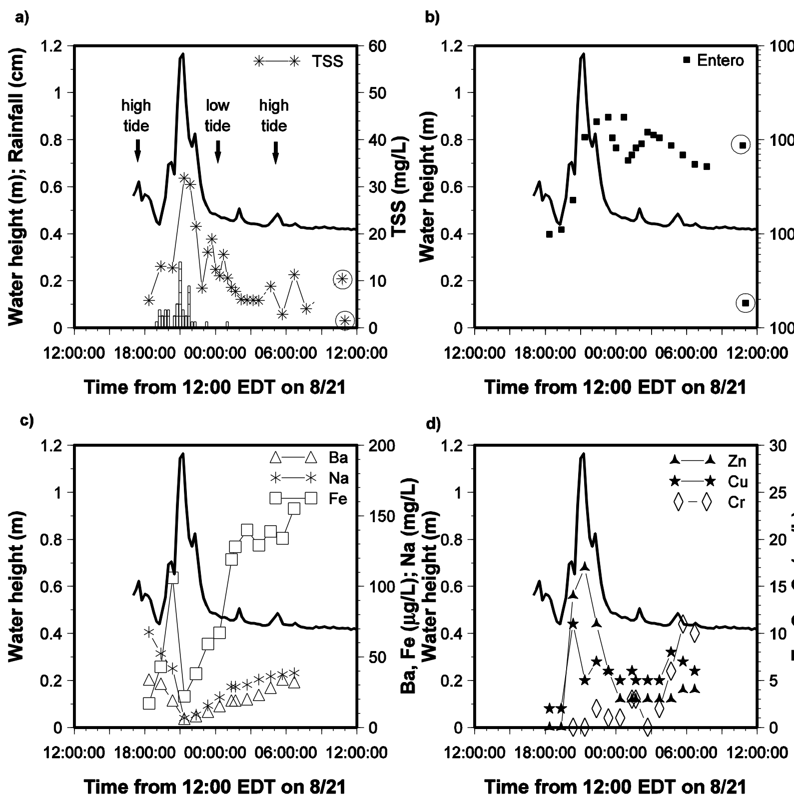

Figure 5 Alley Creek stage hydrographs with corresponding August storm pollutographs at Site 10. Circled TSS and *Enterococci* datapoints indicate samples collected at Site 4 upstream (low values) and Site 5 (high values) on 8/22/11. Note tidal extremes shown in a).

Table 2 Water quality data and measures of statistical correlation from Site 10 during August storm event (n=14)

		Concentration			Water level	ENT	TSS	Water height	ENT	TSS
Parameter	Units	Max.	Mean/ Median	Min.	Coeff. multiple determ. R^2	Coeff. multiple determ. R^2	Coeff. multiple determ. R^2	Spearman Rank Corr. r	Spearman Rank Corr. r	Spearman Rank Corr. r
ENT	MPN/ 100mL	17329	8414†	183	0.05 ^{ns}	--	0.12 ^{ns}	0.22 ^{ns}	--	0.30 ^{ns}
TSS	mg/L	31.8	11.6	2.84	0.78***	0.12 ^{ns}	--	0.62*	0.30 ^{ns}	--
Ba	μg/L	34	21.4	6.0	0.41*	0.50**	0.52**	-0.68**	-0.65*	-0.66*
Ca	mg/L	37.9	23.1	5.9	0.48**	0.54**	0.53**	-0.70**	-0.68*	-0.56*
Mg	mg/L	18.8	9.3	1.1	0.42*	0.46*	0.45**	-0.68**	-0.69**	-0.60*
Na	mg/L	67.6	32.0	6.6	0.25 ^{ns}	0.71***	0.41*	-0.45 ^{ns}	-0.85***	-0.43 ^{ns}
Fe	μg/L	155	92.6	17.0	0.35*	0 ^{ns}	0.37*	-0.69**	0.08 ^{ns}	-0.48 ^{ns}
Zn	μg/L	17.0	5.3	0	0.78***	0.09 ^{ns}	0.61***	0.50 ^{ns}	0.46 ^{ns}	0.56*
Pb	μg/L	5.9	2.4	0	0.12 ^{ns}	0.03 ^{ns}	0.05 ^{ns}	-0.22 ^{ns}	0.10 ^{ns}	-0.13 ^{ns}
Cu	μg/L	11.0	5.7	2.0	0.02 ^{ns}	0.03 ^{ns}	0 ^{ns}	0.13 ^{ns}	0.20 ^{ns}	0.18 ^{ns}
Cr‡	μg/L	11.0	3.3	0	0.18 ^{ns}	0.14 ^{ns}	0.18 ^{ns}	-0.59*	-0.40 ^{ns}	-0.42 ^{ns}

***significant at p<=0.001; **significant at p<=0.01; *significant at p<=0.05; ^{ns}not significant; ‡n for Cr = 12**;** † median for ENT due to non-normal distribution

Table 3 Correlation (Pearson product moment coefficient r) matrix of spatial water quality data: lower left triangle contains values for dry weather data at all sites and the upper right triangle contains values for wet weather data at all sites

WET DRY\	Log ENT	Fe	Na	Mn	Al	Ba	Cu	Zn	Cr
Log ENT	__	0.82*	0.95***	-0.18 ^{ns}	-0.15 ^{ns}	-0.56 ^{ns}	0.60 ^{ns}	-0.36 ^{ns}	-0.51 ^{ns}
Fe	0.87**	__	0.75*	-0.02 ^{ns}	0.34 ^{ns}	-0.70 ^{ns}	0.56 ^{ns}	-0.04 ^{ns}	-0.73*
Na	0.88***	0.91**	__	-0.10 ^{ns}	0.20 ^{ns}	-0.42 ^{ns}	0.54 ^{ns}	-0.26 ^{ns}	-0.57 ^{ns}
Mn	0.87**	0.97***	0.98***	__	0.01 ^{ns}	0.62 ^{ns}	-0.28 ^{ns}	0.64 ^{ns}	-0.36 ^{ns}
Al	0.79*	0.90**	0.93***	0.97***	__	-0.22 ^{ns}	-0.48 ^{ns}	0.52 ^{ns}	-0.79 ^{ns}
Ba	0.76*	0.74*	0.87***	0.81*	0.82**	__	-0.63 ^{ns}	0.24 ^{ns}	0.01 ^{ns}
Cu	0.44 ^{ns}	0.88**	0.55 ^{ns}	0.89**	0.64 ^{ns}	0.15 ^{ns}	__	-0.14 ^{ns}	-0.23 ^{ns}
Zn	0.02 ^{ns}	0.26 ^{ns}	0.07 ^{ns}	0.18 ^{ns}	0.04 ^{ns}	-0.07 ^{ns}	0.16 ^{ns}	__	-0.20 ^{ns}
Cr	-0.43 ^{ns}	-0.32 ^{ns}	0.49 ^{ns}	-0.41 ^{ns}	-0.48 ^{ns}	-0.63*	-0.27 ^{ns}	-0.48 ^{ns}	__

***significant at p<=0.001; **significant at p<=0.01; *significant at p<=0.05; ^{ns}not significant

Table 4: Time series correlation (Pearson product moment coefficient r) matrix for storm event Site 10 samples

	ENT	Water Level	TSS	Fe	Ba	Na	Zn	Cu	Cr
ENT	—								
Water Level	0.22^{ns}	—							
TSS	0.35^{ns}	0.88***	—						
Fe	-0.01^{ns}	-0.59*	-0.61*	—					
Ba	-0.71**	-0.64*	-0.72**	0.37^{ns}	—				
Na	-0.85***	-0.50^{ns}	-0.64*	0.09^{ns}	0.88***	—			
Zn	0.29^{ns}	0.88***	0.78***	-0.28^{ns}	-0.68**	-0.59*	—		
Cu	0.18^{ns}	0.15^{ns}	0.07^{ns}	0.43^{ns}	-0.23^{ns}	-0.30^{ns}	0.55*	—	
Cr	-0.37^{ns}	-0.42^{ns}	-0.42^{ns}	0.56^{ns}	0.82**	0.50^{ns}	-0.40^{ns}	0.08^{ns}	—

***significant at p<=0.001; **significant at p<=0.01; *significant at p<=0.05; ^{ns}not significant

The dominant hydrologic variation is the change in creek water level occurring during the storm event (Table 2). Total suspended solids and Zn, with synchronous concentration peaks, are well predicted by water height (R^2=0.78, p<=0.001). The Spearman's Rank Correlation r indicates significant inverse correlations between water height and Ba, Ca, Mg and Fe. Likewise, Ba, Ca, Mg and, in addition, Na are significantly inversely correlated with *Enterococci*. Ba, Ca and Mg as well as Zn are weakly inversely correlated with TSS, but other parameters are non-correlated.

Enterococci values are elevated (5000-8000 MPN/100 mL) at the CSO outfall (Figure 2ab, Site 5) under wet and dry conditions in April, but those concentrations are far exceeded by values near 20,000 CFU/100 mL during the storm event sampling at Site 10 further downstream in August (Figure 5b), even though the CSO discharge was for a relatively small rainstorm. In contrast to data values from the spatial samples (Table 1), no Mn or Al at all was detected during the temporal sampling of the storm event. Storm-event concentrations of Fe, despite the post-storm rise noted earlier, are still considerably lower (Figure 5c) than they were at most sites, even upstream of the CSO (Figure 2a, Sites 3-5) during the dry weather spatial sampling. Likewise, the peak values of Zn during the spatial sampling (Figure 3ab, Table 1) are 6-7 times those of the peak of the storm event data (Figure 5d). In contrast, the peak value of Cu (Figure 5d) during the storm event is more than twice the maximum value measured during the earlier spatial sampling (Figure 3ab, Table 1). Finally, Cr at the end of the storm sampling at Site 10 (Figure 5d), rises to a value 30% higher than the highest value measured during the spatial sampling, at the overflowing well (Table 1, Site 1).

4. DISCUSSION

4.1. Confirmation of Dry Weather Sewage Discharge

Although properly functioning CSOs are intended to discharge only during wet weather, sampling of continuous flow at a CSO, during both dry and wet weather (Table 1), clearly indicate that the discharge always contains high levels of fecal pathogens. Since CSOs are designed to discharge sewage, and dry weather excludes stormwater, dry-weather flow implies some fraction of raw sewage in the sampled discharge likely accompanied by groundwater seepage into the pipe infrastructure. However, other sources of pathogens could include wildlife in the wetland area, accumulated sewage sediments or stormwater contaminants previously washed into the CSO pipe infrastructure. Because reports of continuously malfunctioning CSOs in dry weather are rare, this provides an unusual opportunity to assess the impact of such a pollution source on a tidal stream.

Comprehensive determination of the first flush phenomenon requires flow-weighted sampling and cumulative mass and volume analyses [8,21], which were not possible here. The unsteady, non-uniform hydraulic regime in a tidal wetland makes examination of water quality data one of the only approaches to understanding pollution dynamics and sources. Locations upstream of the CSO outfall (Site 5) are not affected by the microbiological contamination yet show metals variations that imply other non-sewage sources of contamination. Locations directly downstream from the CSO outfall (excluding Sites 8 and 9) demonstrate significant degradation of water quality (Table 1) from the contribution of CSO pollution to groundwater and surface water flow, mediated by changes in weather and hydrologic conditions.

4.2. Contaminant Sources: Spatial And Temporal Data

The major natural source of water to the Alley Creek tributary is groundwater, represented primarily by results obtained at Site 1, the flowing well, and Site 8, the bubbling spring. The data values at these sites are indicative of shallow groundwater quality unaffected by CSO discharge or other contamination (Table 1, Figures 2-4ab). Cr is at its highest concentrations (typical for local groundwater) at the flowing well (Site 1) in both dry and wet conditions, steadily decreasing downstream (Table 1), with lower Cr concentrations at Site 8, likely because the spring discharges from shallower groundwater than discharged by the well at Site 1.

The three order-of-magnitude increase in *Enterococci* at Site 5 in both dry and wet weather provides convincing evidence of fecal bacteria contamination, consistent with a malfunctioning CSO. In other studies, elevated TDS has been found to indicate sewage discharge [22-24]. Similarly, in this study, major ions such as Na have maximum concentrations at Site 5 (Figure 2a). It is possible that non-human contamination, such as avian or other wildlife feces, or even pet waste, washed from urban streets, could enter the storm sewer system and contribute to this microbiological contamination, especially in wet weather. Resuspended sediment that was previously deposited by sewage in the pipe infrastructure [11,25] can also be an important source of FIB from CSO discharges. Additional human-specific fingerprinting analyses [26], would be needed to be 100% certain of a human source of microbiological contamination. However, compared to other documented human fecal contamination from sewage effluent [11,14,25], our findings of over 10^3 MPN/100 mL concentrations of FIB even under dry conditions, strongly suggest a human source from raw sewage. This key finding of CSO malfunction in dry weather was subsequently confirmed by the NYC Department of Environmental Protection, which in July 2011 notified 11 homeowners southeast of the study area that they were required to reroute their sewage connections (Sapienza, pers. comm. 2011).

However, the peak FIB concentration at the CSO was lower following wet weather (5172 MPN/100mL, Table 1) compared to dry weather (8664 MPN/100mL, Table 1), and wet weather concentrations immediately downstream are higher (Site 10: 2987 MPN/100mL, Table 1) than dry weather concentrations. This is because the wet weather inflow contributes a larger total sewage load but the greater volume of inflow dilutes and transports the fecal microbes farther downstream. The FIB peak concentrations downstream of the CSO in both wet and dry weather are far in excess of the U.S. EPA guideline of 61 MPN/100 mL for *Enterococci* at freshwater swimming beaches [17], and steadily decline downstream, indicating no other sources. It is not known how much farther such high concentrations of FIB are transported downstream into Little Neck Bay within several days of major storm events, but sewage following rain events clearly impairs water quality over a much larger stream reach than during dry weather.

In dry weather, metals such as Fe, Mn and Ba generally show a progressive increase in concentrations downstream at Sites 2-5, a peak at Site 5 then Fe and Mn decrease downstream (Figures 2-4a, Table 1), suggesting the major source is again the CSO, but that secondary sources are present in the wetland upstream. Fe is well known to occur at elevated concentrations in sewage [22], in combination with Mn with which it is highly correlated (Table 3), explaining the similar patterns of these metals in dry-weather discharges at Site 5 (Figures 2a,3a). Ba has often been used as a tracer of terrestrial particulates [27] released from wetlands and sediments into rivers [19] with maximum concentrations observed farther downstream in estuaries [28]. Unlike Fe, which is present in lower concentrations everywhere in wet weather, Mn is unaffected upstream, but reaches a minimum at the CSO location (Site 5). Compared to dry conditions, Ba in wet weather also shows an inverted concentration profile at the central field sites, with a minimum at Site 5 (Figure 4ab). Mn, Ba and to a certain extent Fe (see below) are therefore inferred to be diluted by stormflow entering at the CSO.

Cu, Zn and Cr are well-known anthropogenic contaminants occurring within sewage [22,24], as well as urban stormwater runoff [29]. Zn shows maxima along Alley Creek under wet and dry conditions (Figure

3ab) at densely vegetated sites, and peaks during the storm event, but storm event concentrations are relatively low compared to the dry and wet-weather spatial data. In contrast, Cu has a larger event peak (Figure 5d) due to stormwater [30] at the CSO compared to the modest dry- and wet-weather concentrations at the other field sites (Figure 4ab, Table 1). These results confirm earlier work [31] showing that the major Cu and Zn source is stormwater runoff via different pathways and over different (historical) timeframes, from the surrounding major highways (Figure 1). However, from its lowest values during the storm event, Cr increases well above previously observed groundwater concentrations (Figure 5d). This temporal data pattern is not consistent with stormwater sources because the increase is up to six hours after the peak runoff times expected from the storm event.

4.3. Hydrologic Processes: Remobilization and Tidal Backwater

Field observation of sediments provides evidence of remobilization: cobbles and coarse sand and gravel are apparent in temporally variable sediment bars at the CSO pool (Site 6). A fine clay-like sediment is also deposited in bars farther downstream near Site 7, but never upstream of the CSO. Sediments and vegetation roots [32] could form a long-term reservoir for adsorbed metals and a source for newly desorbed metals with relatively fresh stormwater inflow. The hydrodynamics of sediment resuspension are known to cause rebounds in concentrations from particulate-bound metals [33]. Solids may accumulate within the sewer pipeline infrastructure, only to be remobilized over time. Dry weather flow here could account for some mobilization, but most solids are probably discharged during storm events [25]. Such storm event remobilization would certainly account for an initial desorption-driven Fe and Cu pulse, then the rise in TSS coinciding with the peak of the water-level hydrograph.

The combination of hydrologic processes and contaminant sources leads to unusual dynamics. Flow downstream from the CSO pool along the tidal creek is modulated by the tide such that the maximum streamflow (0.036 m^3/s) at low tide is reduced to almost no measurable streamflow at Site 10 at high tide. However, the groundwater, sewage and sediment sources continue to supply FIB and metals to the stream upstream of Site 10, even as the stormwater level recedes and there is no export of these contaminants downstream. The result is to maintain, and even increase in some cases, dissolved concentrations of selected contaminants. The elevated FIB counts and limited tailing off 12 hours after the storm event are likely due in part to this tidal backwater effect. Hence, the rise in Zn, Cu and especially Cr in the early hours of 8/22 as high tide is reached, suggests that tidal backwater reduces creek flow and retains high concentrations near the central sampling sites (sites 4-7,10).

4.4. Chemical and Bacteriological Fate And Transport

Dilution appears to be the major factor in the variation of constituents representative of both groundwater, such as Cr, and sewage, such as *Enterococci*, Na and Mn. Dilution decreases concentrations of Cr downstream as additional surface water is added, and this effect is enhanced by wet weather (Table 1). In the April dataset, wet weather conditions generating increased stormwater cause a paradoxical lowering of the peak *Enterococci* values and Mn at the CSO outfall (Figure 2b) compared to dry conditions because of stormwater dilution of the continual sewage outflow from this malfunctioning CSO. It is important to note that the wet weather comparison on April 20th, was conducted the day after minor rainfall and did not capture the first flush. Dilution also seems to be the principal mechanism affecting concentrations of Na and Ba during the storm event (Figure 5c), and the dramatic difference in Fe between dry and wet-weather conditions.

However, not all of the data trends can be explained by dilution, and chemical processes may affect such variation. Further investigation, both laboratory and in-situ, would be needed to fully confirm such interpretation, however plausible mechanisms can be identified. Changes in pH can cause release of metals in wetlands [34], however abrupt spatial differences in pH were not measured in this study (Table 1) and rapid temporal changes are not considered likely. Contaminated sediments that accumulate over time [35,36] at such an urban CSO provide the matrix for interactions with particulates that can affect concentrations as stormwater and sewage solids settle out. Weather conditions or variations in source water [16] disturb the chemical equilibrium between water column concentrations and sediment-sorbed metal complexes and ions.

Concentrations of *Enterococci* are influenced by FIB sorption onto particulates [37], and the sediments at the CSO may harbor such pathogen refuges over temporal scales of hours to weeks [38-40]. Resuspension of previously deposited sorbed FIB can explain the delayed peak and continued high concentrations of *Enterococci* for the 12 hours following the storm (Figure 5b) which may not be directly related to the peak of stream discharge or total suspended solids [26]. Metals such as Fe and Mn are diagenetically mobile and their concentrations are affected by adsorption and desorption processes, leading to their accumulation at sediment surfaces at Alley Pond Park [31]. Data for dry-weather conditions (Figures 2a, 3a) indicate that although there are upstream sources (presumably from natural sediments), the largest concentrations are associated with fecal pathogen contamination at Site 5, the CSO.

5. CONCLUSIONS AND IMPLICATIONS

This study has shown a clear case of continuous flow at a malfunctioning CSO, strongly suggesting sewage discharge. The major impact of this finding is that the continuous concentrated pathogen and metal contamination from often-overlooked dry weather discharge is spread out over a much larger spatial range by increased flow during storm events, as hypothesized. Although the spatial area affected increases during wet weather, the dilution of this pathogen source with stormwater decreases some contaminant concentrations. The temporal variation of contaminant concentrations is complex, with some contaminants exhibiting maxima due to first flush mechanisms and others being diluted by greater fresh stormwater flows. As found in another recent study [10], pathogen and metals loading is highly dependent on relative flows that change unpredictably at this site. Larger storms, with higher overall contaminant loading, often do not result in higher *concentrations* of contaminants in surface water.

Separate sources of discharge are indicated by different contaminants. Fe and Mn, with high concentrations under dry conditions, and maxima at the CSO outfall, are supplied by both sewage and natural (soil) sources in the wetland, and concentrations of both metals are controlled by dilution, and likely by precipitation/dissolution and adsorption/desorption. In both wet and dry weather, Zn appears to have a significant non-sewage-related source in the wetlands upstream of the CSO. In contrast, Cu is supplied in part by sewage but is also a major constituent of stormwater, which dominates during storm events.

The delay in pathogen peak, continued high levels of FIB, and rise in Fe and Cr following the storm event suggest that the tidal backwater is important to understanding pollutant distribution in coastal marsh systems. Additional work will be needed to confirm the presence of human sewage and quantify the relative importance of these different sources of flow and contaminants to the tidal wetland environment surrounding the CSO. While these levels of pathogens and metals potentially present a serious health hazard to humans, the nearest likely exposure pathway would be via water transported downstream to Little Neck Bay, a popular boating venue. Further work is also needed to evaluate how far downstream contaminants may be transported given adsorption/deposition processes and limited long-term viability of fecal organisms. The discovery and required remediation of the overlooked dry-weather discharge from this CSO also presents an opportunity to monitor the transition to a future scenario in which the CSO no longer discharges under dry weather conditions.

REFERENCES

[1] US EPA. Report to Congress: Impacts and control of CSOs and SSOs. *EPA 833-R-04-001*: Washington DC, 2004. cfpub.epa.gov/npdes/cso/cpolicy_report2004.cfm Accessed 29 November, 2011.

[2] Gasperi J, Garnaud S, Rocher V, Moilleron R. Priority substances in combined sewer overflows: case study of the Paris sewer network. *Water Science and Technology*, 2011, (63)5: 853-858, doi: 10.2166/wst.2011.122.

[3] Ham Y-S, Kobori H, Takasago M. Effects of combined sewer overflow and stormwater on indicator bacteria concentrations in the Tama River due to the high population density of Tokyo Metropolitan area. *Environmental Monitoring and Assessment,* 2009, 152: 459-468. DOI 10.1007/s10661-008-0330-6

[4] Wayrauch P, Matzinger A, Pawlowsky-Reusing E, Plume S, von Seggern D, Heinzmann B, Schroeder K, Rouault P. Contribution of combined sewer overflows to trace contaminant loads in urban streams. *Water Research,* 2010, 44(15): 4451-4462.

[5] Eganhouse RP, Sherblom, PM. Anthropogenic organic contaminants in the effluent of a combined sewer overflow: impact on Boston Harbor. *Marine Environmental Research,* 2001, 51: 51-74.

[6] Welker A. Occurrence and fate of organic pollutants in combined sewer systems and possible impacts on receiving waters. *Water*

Science and Technology, 2007, 56(10): 141-148, doi: 10.21 66/wst.2007.755

[7] Casadio A, Maglionico M, Bolognesi A, Artina S. Toxicity and pollutant impact analysis in an urban river due to combined sewer overflows loads. *Water Science and Technology,* 2010, 61(1): 207-215.

[8] Barco J, Papiri S, Stenstrom MK. First flush in a combined sewer system. *Chemosphere*, 2008, 71:827-833.

[9] He JX, Valeo C, Chu A, Neumann NF. Characteristics of suspended solids, microorganisms and chemical water quality in event-based stormwater runoff from an urban residential area. *Water Environment Research,* 2010, 82(12): 2333-2345.

[10] Phillips PJ, Chalmers AT, Gray JL, Kolpin DW, Foreman WT, Wall GR. Combined sewer overflows: an environmental source of hormones and wastewater pollutants. *Environmental Science and Technology,* 2012, 46: 5336-5343, dx.doi.org/10.1021/es3001294.

[11] Mallin MA, Cahoon LB, Toothman BR, Parsons DC, McIver MR, Ortwine ML, Harrington RN. Impacts of a raw sewage spill on water and sediment quality in an urbanized estuary. *Marine Pollution Bulletin,* 2007, 54: 81-88.

[12] Arnone RD, Walling JP. Waterborne pathogens in urban watersheds. *Journal of Water and Health*, 2007, 5(1):149-162.

[13] Roslev P, Bastholm S, Iversen N. Relationship between fecal indicators in sediment and recreational waters in a Danish estuary. *Water, Air, Soil Pollution,* 2008, 194: 13-21.

[14] Izbicki JA, Swarzenski PW, Burton CA, Van DeWerfhorst LC, Holden PA, Dubinsky EA. Sources of fecal indicator bacteria to groundwater, Malibu lagoon and the near-shore ocean, Malibu, California, USA. *Annals of Environmental Science*, 2012, 6: 35-86.

[15] Pope ML, Bussen M, Feige MA, Shadiz L, Gonder S, Rodgers C., Chambers Y, Pulz J, Miller K, Connell K, Standridge J. Assessment of the effects of holding time and temperature on *Escherichia coli* densities in surface water samples. *Appl. Environ. Microbiol*, 2003, 69: 6201-6207.

[16] Suter E, Juhl A, O'Mullan G. Particle association of Enterococcus and total bacteria in the lower Hudson River Estuary, USA. *Journal of Water Resources and Protection,* 2011, 3(10): 715-725.

[17] US EPA. *Ambient Water Quality Criteria for Bacteria.* EPA 440/5-84-002, Washington DC, 1986.

[18] US EPA, *United States Environmental Protection Agency National Recommended Water Quality Criteria.* Washington DC, 2012. http://water.epa.gov/scitech/swguidance/standards/current/index.cfm#altable, accessed 4 March 2012.

[19] Neal C, Robson AJ, Harrow M, Hill L, Wickham H, Bhardwaj CL, Tindall CI, Ryland GP, Leach DV, Johnson RC, Bronsdon RK, Cranston M. Major, minor, trace element and suspended sediment variation in the River Tweed: results from the LOIS core monitoring programme. *Science of the Total Environment,* 1997, 194/195: 193-205.

[20] Neal C, Neal M, Hill L, Wickham H. The water quality of the River Thame in the Thames Basin of south/southeastern England. *Science of the Total Environment*, 2006, 360: 254-271.

[21] Hathaway JM, Hunt WF. Evaluation of first flush for indicator bacteria and total suspended solids in urban stormwater runoff. *Water, Air, Soil Pollution,* 2011, 217: 135-147.

[22] Wilkie PJ, Hatzimihalis G, Koutoufides P, Connor MA. The contribution of domestic sources to levels of key organic and inorganic pollutants in sewage: the case of Melbourne, Australia. *Water Science and Technology,* 1996, 34(3-4): 63-70.

[23] Pantsar-Kallio M, Mujunen S-P, Hatzimihalis G, Koutoufides P, Minkkinen P, Wilkie PJ, Connor MA. Multivariate data analysis of key pollutants in sewage samples: a case study. *Analytica Chimica Acta,* 1999, 393: 181-191.

[24] Rule KL, Comber SDW, Ross D, Thornton A, Makropoulos CK, Rautiu R. Survey of priority substances entering English wastewater treatment works. *Water and Environment Journal,* 2006, 20: 177-184.

[25] Passerat J, Ouattara NK, Mouchel JM, Rocher V, Servais P. Impact of an intense combined sewer overflow event on the microbiological water quality of the Seine River. *Water Research*, 2011, 45(2): 893-903, doi:10.1016/j.watres.2010.09.024

[26] Surbeck CQ, Jiang SC, Ahn JH, Grant SB. Flow fingerprinting fecal pollution and suspended solids in stormwater runoff from an urban coastal watershed. *Environmental Science and Technology,* 2006, 40: 4435-4441.

[27] Colbert D, McManus J. Importance of seasonal variability and coastal processes on estuarine

manganese and barium cycling in a Pacific Northwest estuary. *Continental Shelf Research,* 2005, 25:1395-1414.

[28] Coffey M, Dehairs F, Collette O, Luther G, Church T, Jickells T. The behavior of dissolved barium in estuaries. *Estuarine, Coastal and Shelf Science*, 1997. 45: 113-121.

[29] Kayhanian M, Singh A, Suverkropp C, Borroum S. Impact of annual average daily traffic on highway runoff pullutant concentrations. *Journal of Environmental Engineering,* 2003, 129 (11): 975-990.

[30] Camponelli KM, Lev SM, Snodgrass JW, Landa ER, Casey RE. Chemical fractionation of Cu and Zn in stormwater, roadway dust and stormwater pond sediments. *Environmental Pollution,* 2010, 158(6): 2143-2149, doi:10.1016/j.envpol.2010.02.024

[31] Cochran JK, Hirschberg DJ, Wang J, Dere C. Atmospheric deposition of metals to coastal waters (Long Island Sound, New York U.S.A.): Evidence from saltmarsh deposits. *Estuarine, Coastal and Shelf Science*, 1998, 46: 503-522.

[32] Rouff AA, Eaton TT, Lanzirotti A. Heavy metal distribution in an urban wetland impacted by combined sewer overflow. *Chemosphere*, 2013, 93: 2159-2164 doi:10.1016/j.chemosphere.2013.07.077

[33] Estebe A, Mouchel J-M, Thevenot DR. Urban runoff impacts on particulate metal concentrations in river Seine. *Water, Air and Soil Pollution,* 1998, 108: 83-105.

[34] Gambrell RP. Trace and toxic metals in wetlands - a review. *Journal of Environmental Quality,* 1994, 23: 883-891.

[35] Rozan TF, Benoit G. Mass balance of heavy metals in New Haven Harbor, Connecticut: predominance of nonpoint sources. *Limnology and Oceanography,* 2001, 46 (8): 2032-2049.

[36] Fugate D, Chant B. Aggregate settling velocity of combined sewage overflow. *Marine Pollution Bulletin,* 2006, 52: 427-432.

[37] Characklis GW, Dilts MJ, Simmons III OD, Likirdopulos CA, Krometis LH, Sobsey MD. Microbial partitioning to settleable particles in stormwater. *Water Research*, 2005, 39 (9): 1773-1782 , doi:10.1016/jwatres.2005.03.004.

[38] Lee CM, Lin TY, Lin CC, Kohbodi GA, Bhattl A. Persistence of fecal indicator bacteria in Santa Monica Bay beach sediments. *Water Research,* 2006, 40(14): 2593-2602, doi:10.1016/j.watres.2006.04.032.

[39] Hartz A, Cuvelier M, Nowosielski K, Bonilla TD, Green M, Esiobu N, McCorquodale DS, Rogerson A. Survival potential of Escherichiacoli and Enterococci in subtropical beach sand: implication for water quality managers. *Journal of Environmental Quality,* 2008, 37 (3): 898-905, doi:10.2134/jeq2007.0312.

[40] Fries JS, Characklis GW, Noble RT. Sediment-water exchange of Vibrio sp. and fecal indicator bacteria: implications for persistence and transport in the Neuse River Estuary, North Carolina, USA. *Water Research,* 2008, 42(4-5): 941-950, doi:10.1016/j.watres.2007.09.006.

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