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Baseline

Caffeine in Boston Harbor past and present, assessing its utility as a tracer of wastewater contamination in an urban estuary

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ABSTRACT

Sites throughout Boston Harbor were analyzed for caffeine to assess its utility as a tracer in identifying sources of sanitary wastewater. Caffeine ranged from 15 ng/L in the outer harbor to a high of 185 ng/L in the inner harbor. Inner harbor concentrations were a result of combined sewage overflow (CSO) events as well as illicit discharge of sanitary sewage into municipal storm drains. Comparing current results to data from 1998 to 1999 shows reductions in caffeine levels. Reductions are attributed to termination of effluent discharge to the harbor, declines in the number of CSOs and discharge volume along with efforts to eliminate illicit discharges. Spatial distributions of caffeine identified CSOs as major contemporary sources to the inner harbor. The findings further establish the utility of caffeine as a tracer for sanitary wastewater contamination in urban estuaries and demonstrate the efficacy of pollution reduction strategies undertaken in recent decades in Boston Harbor.

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Boston Harbor, Massachusetts, is located on the eastern coast of the United States, with the metropolitan Boston area having a population of 1.96 million people (USCB, 2014). Boston Harbor is an urbanized estuary, 125 km^2 in area with a mean water depth of 4.7 m and tidal range of 2.7 m (Signell et al., 2000). It is located adjacent to the city and has a long history as a center of commerce with numerous industrial facilities and a major shipping port. The dense human population combined with activities in and around the harbor has resulted in long-term sustained, anthropogenic inputs to and degradation of the estuary. Major contributors have been the discharge of wastewater treatment plant (WWTP) effluents and combined sewage overflows (CSO) to the harbor, which have been occurring for decades and have negatively influenced water quality (Taylor, 2010). To address this problem, the Massachusetts Water Resources Authority (MWRA) was created in 1985, and started capital improvements and expansion to wastewater treatment systems. In 2000, a 14 km long tunnel opened, effectively ending long-term effluent releases within the harbor by relocating wastewater discharges to Massachusetts Bay. Infrastructure upgrades have reduced CSO discharge volume from 1.25×10^7 m^3 per year to approximately 1.7×10^6 m^3 per year, of which 89% is processed at CSO treatment facilities, representing an overall reduction of over 86% over the past 27 years. Improvements to WWTP infrastructure continue with the goal of ending CSO discharge to the harbor, which still occurs episodically during wet weather events. In addition, communities in and around the harbor have been eliminating illicit discharges of sanitary sewage through their respective municipal stormwater outfalls over the same time frame. For example, the Boston Water and Sewer Commission (BWSC, 2015) has eliminated discharge of over 9.73×10^5 m^3 per year of sanitary sewage that was discharged to BWSC storm drains.

One approach to measuring the source and magnitude of sanitary wastewater contamination in aquatic ecosystems is through the use of appropriate chemical markers (Sidhu et al., 2013). Caffeine is a distinct indicator of anthropogenic inputs to natural waters, particularly of sewage treatment outflows (Chen et al., 2002; Sauvé et al., 2012). It also correlates well with wastewater loadings and CSO discharges (Buerge et al., 2003, 2006). Widely consumed and present in many food products and beverages, caffeine is also used in the formulation of numerous pharmaceutical compounds (Graham, 1978). Consumption of caffeine in the United States averages approximately 300 mg per person daily (FDA, 2010) and during conventional secondary WWTP processes, caffeine removal is generally 90% or more (Stamatis and Konstantinou, 2013). With a half-life estimated of up to 100 days in estuarine waters (Benotti and Brownawell, 2009), caffeine shows potential as a sensitive tracer of untreated sanitary wastewaters (e.g., CSOs).

As part of a larger national effort to understand the fate and behavior of emerging contaminants in estuarine systems, we measured caffeine in June 2015 throughout Boston Harbor. The objectives here were to: identify temporal trends, comparing current caffeine concentrations in

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the harbor to data previously collected in 1998–1999 by Siegener and Chen (2002); evaluate the utility of caffeine as a tracer for untreated sanitary wastewater (e.g., CSO and non-point discharges) in an urban estuary; and assess the efficacy of recent infrastructure improvements by the MWRA.

Field sampling was conducted on June 2–3, 2015, at 24 sites throughout Boston Harbor. Water was collected 1 m below the surface with an all Teflon pump system, passed through a 1 μm spiral wound glass fiber filter and stored in amber glass bottles. Samples were kept on ice until returned to the laboratory, and stored in the dark at 4 °C. An extraction protocol using Oasis HLB solid phase extraction (SPE) cartridges (6 cm^3, 500 mg, Waters Corp., Milford, MA) was adapted from EPA Method 1694. Briefly, a 500 mL sample was adjusted to pH 2 using hydrochloric acid (6 N) and spiked with 100 ng of caffeine-d_3 (CDN Isotopes). The cartridges were conditioned with 6 mL of methanol (MeOH), followed by 6 mL of Milli-Q water, 6 mL of pH 2 Milli-Q, and equilibrated with 6 mL of pH 2 artificial seawater. Samples were loaded onto SPEs using vacuum at a rate of 5–10 mL/min. SPEs were washed with 12 mL of pH 2 Milli-Q water, dried for 15 min under vacuum and eluted with 12 mL of MeOH. Extracts were evaporated to dryness, reconstituted to 1 mL using a 80:20 mixture of Milli-Q water:MeOH, vortexed, transferred to LC vials and stored at 4 °C until analysis. All blanks, field duplicates and matrix samples were prepared in the same manner.

Analysis was performed on a Waters Xevo TQD MS/MS in electrospray ionization (ESI) mode. A 10 μL aliquot was injected onto the column (Acquity BEH C18, 2.1 mm × 50 mm, 1.7 μm pore size, Waters Corp). Caffeine was measured by MS/MS with ionization conditions of the source set to 0.5 kV in ESI+. Other MS/MS parameters were: source temperature 150 °C, desolvation temperature 500 °C, desolvation flow 900 L/h, and cone flow 20 L/h. A 10 point calibration curve was constructed ranging from 0.25 ng/mL to 300 ng/mL, with a minimum $r^2 = 0.99$ or better. Calibration verification standards were run every 10 samples and were within 10% of the stated value. Blank values for caffeine were <1 ng/L, while the matrix spike recovery was 107%. Relative percent difference (RPD) between duplicate samples was 7%.

Inverse Distance Weighting (IDW) was employed to develop a response surface for the spatial distribution of caffeine within Boston Harbor. This deterministic technique provides a simple and robust framework for spatial predictions. This type of analysis uses the inverse of the distance to each known point when assigning weights at unknown points. The IDW analyses were performed with ArcGIS Geostatistical Analyst (Esri, Redlands, CA, USA).

Caffeine concentrations in Boston Harbor ranged from 15 to 185 ng/L during June 2–3, 2015 (Table 1, Fig. 1). Four locations in the inner harbor exceeded 100 ng/L (Pleasure Bay, Fort Point Channel, and the Mystic and Charles Rivers), while sites by Winthrop Point and the mouth of the harbor were much lower. In the outer harbor, concentrations declined rapidly as a function of distance from the inner harbor and the shoreline. Prior to sampling, 2.3 cm of rain fell on 5/31/2015 with an additional 2.8 cm of rain on 6/2/2015, totaling more than 5.1 (NOAA, 2015). This rainfall resulted in episodic discharges from 2 CSO facilities (Somerville and Prison Point) within the inner harbor from 5/31/2015–6/02/2015, totaling 4.13×10^4 m^3 (Fig. 1). Using influent caffeine concentrations supplied by MWRA (Table 1), an estimated 0.28 kg of caffeine was released to the inner harbor during this CSO event. Based on the timing of the CSO releases and our sampling, this possibly explains the elevated concentrations throughout the inner harbor. Weather conditions during the May 1998 sampling event were very similar (NOAA, 2015), with heavy rain falling during the sampling period (~5.1 cm). Despite the similarity in weather conditions, caffeine levels from this period (5/8/1998) were higher by more than a factor of 2 in the inner harbor (Fig. 1, Table 1). This is almost certainly due to CSO discharges that have since been reduced or eliminated. Conversely, the 4/7/1999 sampling period occurred during dry weather with no recorded precipitation 4 days prior to sampling. The dry conditions yielded only slightly lower levels at most locations, with the exception of sites at Island End and Logan Airport, which were higher (Table 1). The elevated levels during this period are attributed to the Deer Island outfall (Siegener and Chen, 2002), which was active at this time, with concentrations in the vicinity of the outfall ranging from 960 to 1600 ng/L (Fig. 1). Overall, the sustained discharge from the Deer Island outfall and large number of active CSOs explain the higher caffeine levels recorded during sampling events in 1998–1999.

Data in the outer harbor during 1998–1999 is limited, but two sites near the mouth of the Neponset River had the highest concentrations: Commercial Point (410 ng/L) and Savin Hill Cove (295 ng/L). These levels were due to CSO discharges that were eliminated in 2000 (MWRA, 2015). In contrast, during the 2015 sampling, concentrations in the outer harbor exhibited a decreasing caffeine gradient with distance from the inner harbor and the shoreline. Commercial Point

Table 1
Concentrations of caffeine in Boston Harbor from current study and 1998–1999 (Siegener and Chen, 2002). Inner harbor sites *, outer harbor +.

Site name	Date	Caffeine ng/L	Site name	Date	Caffeine ng/L
Commercial Pt +	May-98	220	Commercial Point +	Jun-15	75
Deer Island Outfall *	May-98	960	Old Harbor 1 +	Jun-15	40
Logan Airport *	May-98	180	Old Harbor 2 +	Jun-15	33
Charles River Basin *	May-98	370	Winthrop *	Jun-15	26
Charles River Dam *	May-98	340	Logan Airport *	Jun-15	25
Island End *	May-98	340	Old Outfall *	Jun-15	45
Lower Harbor +	May-98	140	Long Island +	Jun-15	48
Savin Hill Cove +	May-98	295	Thompson Island +	Jun-15	54
			Pleasure Bay +	Jun-15	185
Commercial Point +	Apr-99	410	Mystic River *	Jun-15	127
Lower Harbor +	Apr-99	180	Charles River *	Jun-15	119
Deer Island Outfall +	Apr-99	1600	Ft. Point Channel *	Jun-15	133
Logan Airport *	Apr-99	240	Quincy 5 +	Jun-15	36
Ft. Point Channel *	Apr-99	230	Quincy 4 +	Jun-15	61
Charles River Basin *	Apr-99	130	Quincy 3 +	Jun-15	28
Charles River Dam *	Apr-99	160	Quincy 2 +	Jun-15	25
Mystic River *	Apr-99	220	Quincy 1 +	Jun-15	28
Island End Marina *	Apr-99	1600	Quincy 6 +	Jun-15	30
			Hingham 1 +	Jun-15	19
			Hingham 2 +	Jun-15	24
Deer Island Influent	May-98	20,000	Hingham 3 +	Jun-15	18
Deer Island Effluent	May-98	6700	Hingham 4 +	Jun-15	26
MWRA Influent	2007	6700	Fort Adam +	Jun-15	15
			Weymouth +	Jun-15	37

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