Assessing Contaminant Concentrations and Trends in Deer Island Treatment Plant Effluent Using Survival Analysis Techniques

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Assessing Contaminant Concentrations and Trends in Deer Island Treatment Plant Effluent Using Survival Analysis Techniques

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EXECUTIVE SUMMARY

The Massachusetts Water Resources Authority (MWRA) operates the Deer Island Treatment Plant, which began discharging secondary-treated wastewater into Massachusetts Bay (the bay) on September 6, 2000. MWRA's National Pollutant Discharge Elimination (NPDES) permit requires that it monitors the discharge, or final effluent, and complies with limits on certain parameters to reduce the likelihood of degrading the bay's ecosystem. Monitoring results for a wide range of pollutants are reported each month to the US Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection, and all monitoring data are available to the public.

Effluent monitoring is designed to find out (1) the concentrations of contaminants entering and leaving the treatment plant; and (2) whether the effluent quality consistently meets permit limits. The permit also requires MWRA to periodically test the toxicity of the effluent on sensitive marine organisms. Many tested contaminants are on the EPA's priority pollutants list; that is, a set of regulated pollutants for which the agency has established analytical methods. MWRA monitors the final effluent before it enters the outfall tunnel and is diffused into the bay, for contaminants including metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pesticides.

What We Analyze in the Effluent and Why

CONTAMINANT	DESCRIPTION	WHY WE MONITOR
Metals	Priority pollutant metals	Absorbed easily by living organisms. Can be toxic at high levels.
Polycyclic Aromatic Hydrocarbons (PAHs)	Trace components of fossil fuels, especially oils. Also combustion byproducts produced when coal, oil, gas, wood, garbage, and tobacco are burned	Can linger in small particles in the air. Evidence of increased cancer risk.
Polychlorinated Biphenyls (PCBs)	Banned in the U.S. in 1979. Non-flammable, chemically stable, used to create many products including motor oil, paint, caulking, and plastics.	Linked to cancer, neurological, and reproductive problems. Remain in some products manufactured before 1979.
Pesticide: DDT, DDE	Banned in the U.S. in 1972, but used in some countries.	DDE is a DDT breakdown product. Harmful to wildlife.
Pesticide: Chlordane	Banned in the U.S. in 1988. Allowed for termite control until 1988. Persists in the environment.	Suspected carcinogen. Used on crops like corn and citrus, and on lawns and domestic gardens.

Effluent data contain many contaminant levels that fall below detection limits

After 21 years of monitoring, MWRA's dataset includes a large number of samples with nondetects, meaning the analyte was in such low concentrations it fell below the detection limit (DL) of the particular analytical method used. For example, lead had 79% nondetects out of more than 1,500 samples for which it was analyzed, and the DDT breakdown product 4,4'-DDE showed as nondetects in nearly half the samples.

Analyzing datasets that include high frequencies of nondetects can be challenging. Commonly, a nondetect is either deleted, replaced by zero, or by part or all of the detection limit, distorting the results. Instead, using a special statistical method called survival analysis which accounts for high frequencies of nondetects, we estimated "average" contaminant concentrations and their projected ranges for nondetects, and discovered the following:

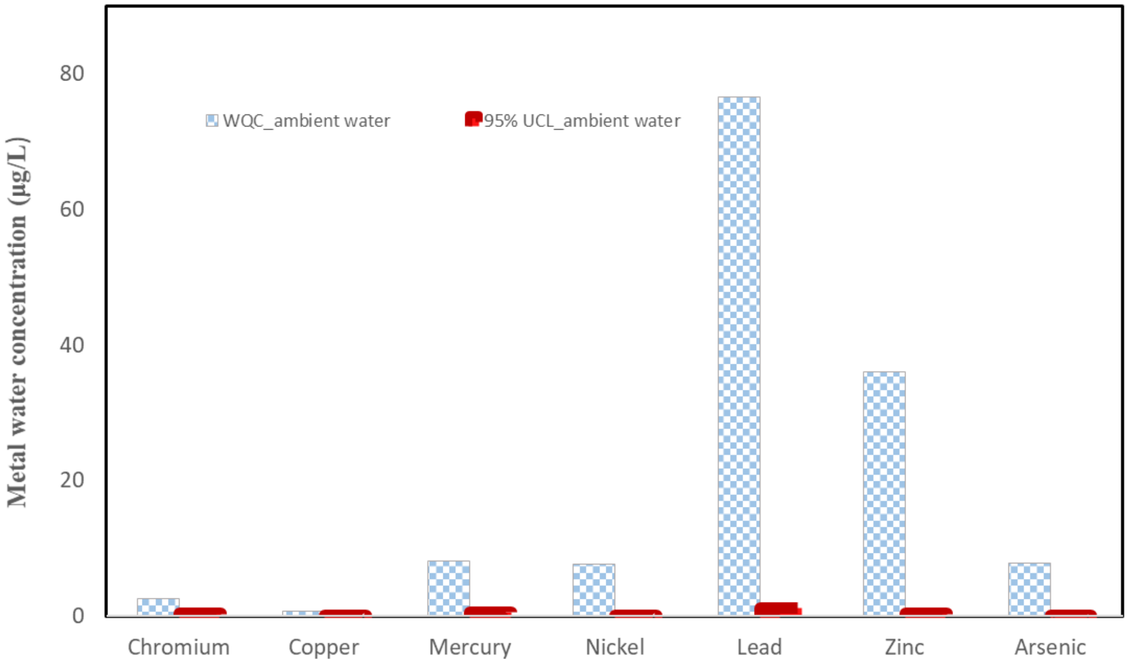
Some metals have never or seldom been detected in the effluent

Metal	Time Period	Detected in Effluent
Antimony	2010-2019	Once
Arsenic	2018-2019	Never
Beryllium	2010-2019	Never
Selenium	2010-2019	Twice

Many contaminants have concentrations in the final effluent that are significantly lower than the water quality criteria even *before discharge* and dilution in Massachusetts Bay. These are:

- Metals: Arsenic, cadmium, chromium, lead, mercury, nickel, and zinc
- PAHs: Acenaphthene, anthracene, benzo[k]fluoranthene, fluorene, fluoranthene, chrysene, and pyrene
- Pesticides: Alpha-chlordane

In Massachusetts Bay, estimated mean metal concentrations (UCL: 95% upper confidence limits) near the outfall discharge were much lower than the EPA's water quality criteria (WQC)



The concentrations of some contaminants not in the EPA's priority pollutant list remained steady or decreased significantly over time. These include:

- PAHs: 1-methylphenanthrene, 2,3,5-trimethylnaphthalene, biphenyl, benzo(e)pyrene, benzo(g,h,i)perylene, acenaphthylene, and perylene.
- PCBs: BZ 52 Tetrachlorobiphenyl, BZ 101 Pentachlorobiphenyl, BZ 118 Pentachlorobiphenyl, BZ 138 Hexachlorobiphenyl, BZ 153 Hexachlorobiphenyl, BZ 180 Heptachlorobiphenyl, and BZ 187 Heptachlorobiphenyl
- Pesticides: Trans-nonachlor

There was a slight upward trend in effluent concentrations of some individual contaminants such as iron, molybdenum, and the PAH phenanthrene. However, their environmental impacts are expected to be negligible after discharge and dilution in the bay.

The results of the evaluations in this report suggest that the concentrations of targeted contaminants are all low compared to relevant water quality criteria, and are stable or decreasing over time. Therefore, we conclude that the current effluent contaminant monitoring is sufficient, and in some cases more than enough to protect the bay's environment. This may justify reducing or ending monitoring for these contaminants in the receiving waters of Massachusetts Bay.

INTRODUCTION

Ever since the development of MWRA's ambient monitoring plan in the early 1990s by MWRA and the Outfall Monitoring Task Force, environmental monitoring in Massachusetts Bay has been guided by concerns expressed by the public and government regulators that people can continue to safely eat fish and go swimming and boating, and the ecosystem would not be degraded.

The effluent monitoring program is designed to answer these two questions:

- Do effluent contaminant concentrations exceed permit limits?
- What are the concentrations of contaminants in the influent and effluent and their associated variability?

The Deer Island Treatment Plant began discharging into Massachusetts Bay on September 6, 2000. The outfall is regulated under a National Pollutant Discharge Elimination System (NPDES) permit from the U.S. Environmental Protection Agency (EPA) and Massachusetts Department of Environmental Protection (MADEP). MWRA began monitoring under the permit-attached ambient monitoring plan with the aim of (among other things) testing for compliance with permit requirements and the MWRA's 2001 Contingency Plan (MWRA, 2001). The effluent monitoring questions and analytes, and a summary of the evaluations of effluent monitoring through 2009, can be found in Chapter 2 of the current monitoring Plan (MWRA 2010).

Evaluations conducted in support of revisions to the monitoring plan in 2004 and 2009-2010 have determined that effluent quality, water quality, sediment and biological parameters were within the bounds projected by the EPA's 1988 supplemental environmental impact statement (SEIS) and that there is no concern for acute or short-term environmental changes. These findings were incorporated into the current (2010) monitoring plan, which has been endorsed by OMSAP and approved by EPA and MADEP (MWRA, 2019).

Effluent monitoring results for the concentrations of potentially toxic contaminants since 2000 have been reported in three standalone reports (Delaney and Rex, 2007; Delaney, 2009, 2010) and are summarized in annual *Outfall Monitoring Overview* reports (e.g. Werme et al., 2018). These reports consistently documented concentrations of monitored contaminants well below SEIS estimates.

In 2018, OMSAP, MWRA, and other stakeholders started a process of monitoring review to identify questions not currently addressed, and to discuss possible changes in strategy and priorities. All agreed that MWRA should review the current monitoring program and identify changes that might free up resources for special studies about new environmental challenges, such as emerging contaminants of concern.

In this report, we analyzed effluent monitoring data for metals, PAHs, PCBs, and to determine long-term compliance with water quality regulations and temporal trends in concentration. The objective was to evaluate concentrations of the studied chemicals in the DITP effluent over the last 20 years and determine any potential to adversely impact the environment in Massachusetts Bay. This would document whether the effluent monitoring of these contaminants is environmentally protective, justifying the end of monitoring for these parameters in sediments and potentially in fish and shellfish tissues.

2.0 METHODS

2.1. Data Source

The analysis focuses on most of the contaminants measured in sampling conducted as part of MWRA's ambient monitoring program which include 50 chemicals grouped in three categories: metals, PAHs, PCBs and pesticides. The analyses in this report were originally performed with data extracted from MWRA's database for final effluent samples collected from 1999 to 2017 for metals and from 2006–2017 for PAHs, PCBs and pesticides. As more data became available through October 2019, the 2018-2019 data were analyzed separately with descriptive and inferential statistics focused on those chemicals for which water quality criteria (WQC) are provided by the EPA. The dataset is characterized by large sample sizes for each chemical (varying from 44 to 2035 samples), high frequency of nondetects (NDs) or "censored" values, and multiple detection limits (DLs) below which the analyte could not be detected or identified (Table 1). The presence of those NDs will determine the types of statistical analysis performed on the data as described below.

2.2. Data Analysis

Common procedures within the environmental chemistry field to deal with censored observations include:

- Deleting or ignoring the nondetects in the calculation of summary statistics
- Substituting a fraction of the reporting limit for censored observations. Substitution consists in replacing non-detected measurements by one of the following:
  - detection limit (DL)
  - half of the DL
  - zero

Substitution can lead to loss of important signal in the data, resulting, for example, in inaccurate summary statistics and the failure to detect the correlation or linear relationship between two variables. Substituting values for NDs can lead to false differences (between variables) that are not there or failure to detect differences that are there (Helsel, 2012). Helsel and Hirsch (2002) pointed out that the simple substitution methods have no theoretical basis and generate distributions with large gaps. For example, Figures 1a and b show gaps in the distribution of silver and dichlorodiphenyldichloroethylene (4,4’-DDE) concentrations in MWRA’s final effluent created by substituting half of the detection limit to non-detected values.

It can be seen from Figures 1a and b that substituting one half of detection limits for nondetects results in gaps in the frequency distribution of the data for silver and 4,4’-DDE (see right tails of distributions), suggesting that substitution is a poor method for computing descriptive statistics. Also, it distorts estimates of the standard deviation, and therefore all parametric hypothesis using that statistic. Thus there is a need to use statistical methods designed for handling data with NDs. Scientists have recommended that survival analysis techniques used in medical and industrial studies (which often contain a high frequency of nondetects) be applied to environmental data (Millard and Deverel, 1988; Helsel and Hirsch, 2002; Helsel, 2012).

Table 1. Count and frequency of detection of parameters measured in the final effluent of the Deer Island Wastewater Treatment Plant

Metals	Data years	Number of samples	Detects (%)	Number of DLs [a]
Aluminum	2010 – 2017	619	58.8	1+ [b]
Antimony	2010 – 2017	193	0.51	1+
Arsenic	2010 – 2017	191	7.32	1+
Beryllium	2010 – 2017	193	0	— [c]
Boron	2010 – 2017	193	21.7	1
Cadmium	2010 – 2017	442	48.4	1+
Chromium	1999 – 2017	1407	67.1	1+
Copper	1999 – 2017	2035	74.7	1+
Iron	2010 – 2017	193	100	—
Lead	1999 – 2017	1518	20.8	1+
Mercury	1999 – 2017	1527	67	1+
Molybdenum	2010 – 2017	408	99.7	1
Nickel	1999 – 2017	1471	96.9	1+
Selenium	2010 – 2017	193	0	—
Silver	1999 – 2017	1398	54.4	1+
Zinc	1999 – 2017	1415	99.5	1

a. DL: Detection limit.
b. 1+: More than one detection limit reported.
c. Not applicable because percentage of detection = 0 or 100.

Table 1. Count and frequency of detection of parameters measured in the final effluent of the Deer Island Wastewater Treatment Plant (continued)

PAHs	Data years	Number of samples	Detects (%) [c]	Number of DLs[a]
1-Methylnaphthalene	2006 – 2017	628	97.7	1+ [b]
1-Methylphenanthrene	2006 – 2017	624	89.6	1+
2-Methylnaphthalene	2006 – 2017	628	98.4	1+
2,3,5-Trimethylnaphthalene	2006 – 2017	624	90.6	1+
2,6-Dimethylnaphthalene	2006 – 2017	624	80	1+
Acenaphthene	2006 – 2017	624	91.2	1+
Acenaphthylene	2006 – 2017	624	40.3	1+
Anthracene	2006 – 2017	624	89.3	1+
Benzo[a]anthracene	2006 – 2017	635	99.8	1
Benzo[a]pyrene	2006 – 2017	625	98.1	1+
Benzo[b]fluoranthene	2006 – 2017	635	98.9	1+
Benzo[e]pyrene	2006 – 2017	635	97.2	1+
Benzo[g,h,i]perylene	2006 – 2017	635	97.2	1+
Benzo[k]fluoranthene	2006 – 2017	635	95.3	1+
Biphenyl	2006 – 2017	625	79.2	1+
Chrysene	2006 – 2017	635	99.8	1
Dibenzo[a,h]anthracene	2006 – 2017	635	45.9	1+
Fluoranthene	2006 – 2017	631	100	—
Fluorene	2006 – 2017	624	98	1+
Indeno[1,2,3-cd]pyrene	2006 – 2017	635	95	1+
Naphthalene	2006 – 2017	628	99.6	1+
Perylene	2006 – 2017	635	26	1+
Phenanthrene	2006 – 2017	624	100	— [d]
Pyrene	2006 – 2017	631	100	—

a. DL: detection limit.

b. 1+: More than one detection limit reported.

c. Percentages for non surrogate-corrected results reported here for comparison with the other groups of chemicals. All other statistical analyses were performed with surrogate-corrected data.

d. Percentage of detection = 0 or 100.

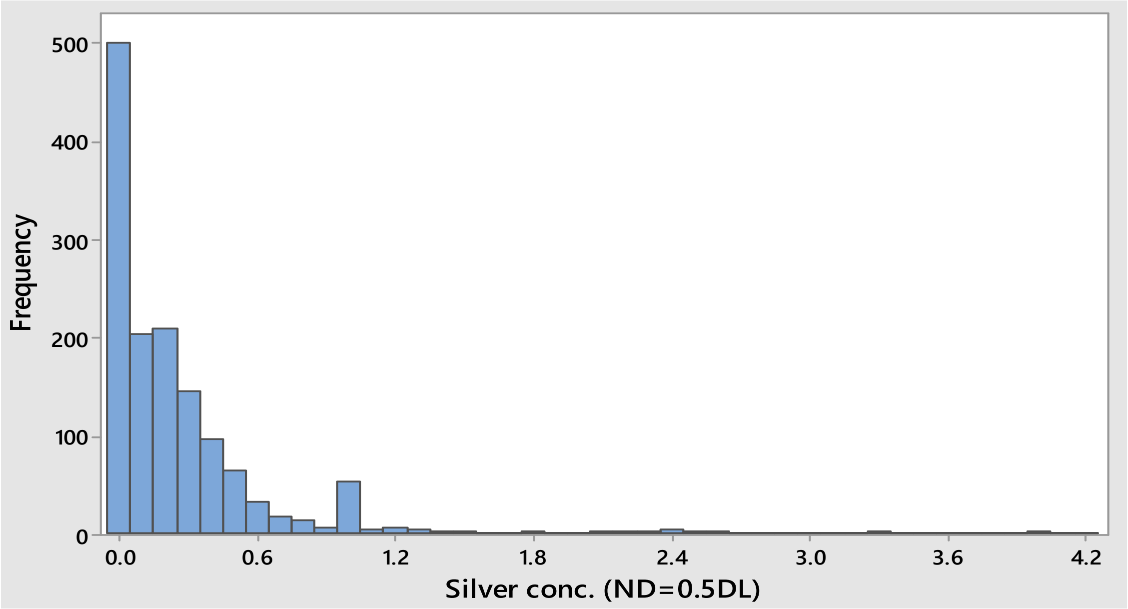
Table 1. Count and frequency of detection of parameters measured in the final effluent of the Deer Island Wastewater Treatment Plant (continued)

PCBs and pesticides	Data years	Number of samples	Detects (%)	Number of DLs [a]
4,4’-DDE	2006 – 2017	1068	53.5	1+ [b]
Alpha-chlordane	2006 – 2017	1068	80.1	1+
Trans-Nonachlor	2006 – 2017	863	93.2	1+
BZ 52 Tetrachlorobiphenyl	2006 – 2015	865	68.5	1+
BZ 101 Pentachlorobiphenyl	2006 – 2017	960	75	1+
BZ 118 Pentachlorobiphenyl	2006 – 2017	960	72.9	1+
BZ 138 Hexachlorobiphenyl	2006 – 2017	960	81.8	1+
BZ 153 Hexachlorobiphenyl	2006 – 2017	960	90.4	1+
BZ 180 Heptachlorobiphenyl	2006 – 2017	960	41.2	1+
BZ 187 Heptachlorobiphenyl	2006 – 2017	960	24.9	1+
Total PCBs[c]	2006 – 2017	648	—	—

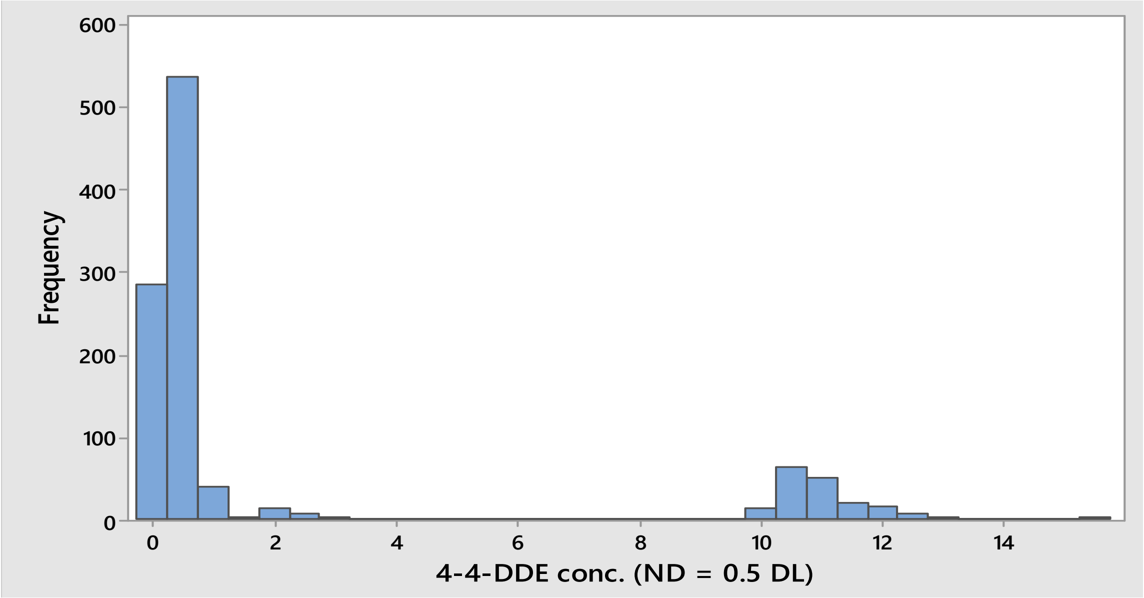
a. DL: Detection limit.
b. 1+: More than one detection limits reported.
c: Sum of all congeners in a daily sample.

Figure 1. Effect of simple substitution of nondetects on the distribution of silver (a) and 4,4'-DDE (b) concentrations at DITP's final effluent (1999 – 2017)

(a) Silver



(b) 4,4'-DDE



2.2.1. Applying Survival Analysis Methods to Environmental Data

Survival analysis is generally defined as a set of methods for analyzing data where the outcome variable is the time until the occurrence of an event of interest. In the medical field, for example, if the event of interest is cancer, then the time origin could be the time point of cancer diagnosis and the endpoint (or event of interest) could be death due to the cancer studied (Kartsonaki, 2016; https://www.cscu.cornell.edu/news /statnews/stnews78.pdf). Observations are called "censored" when the information about their survival time is incomplete. In the above example if patients are followed in the study for 24 weeks, the following scenarios may happen:

- *Right censoring*. A patient does not experience the event of interest (i.e., death) for the duration of the study (survival time > 24)
- *Left censoring*: An individual has died any time before the 24 weeks (survival time < 24)
- *Interval censoring*: A patient has died sometime before 24 weeks and the exact time of the event is not observed (survival time: 0 – 24)

The statistical methods developed to address survival analysis are directly applicable to the analysis of environmental results. Environmental data are often left-censored, where low concentrations are known only to be below one or multiple detection limits (i.e., < DL), the "event of interest" in this case. As mentioned, the presence of those <DLs or NDs provides valuable information about an environmental population and should not be omitted. Several parametric and nonparametric survival analysis methods have been proposed in the literature for handling nondetects. In this work, the following methods were used:

2.2.1.1. Summary statistics

1. *The Kaplan-Meier method.* The Kaplan-Meier (KM) technique constructs a partial ranking of the data by determining the number of data points below each detected concentration and uses that information to generate a probability distribution function (or censored probability plot) that adequately fits the joint sample of detects and nondetects. The fitted distribution model is then used to estimate the population mean and standard deviation. Kaplan-Meier is non parametric and so does not require that the data follow a known distribution. However, the dataset must be multiply censored (more than one detection limit) and no more than 50 –70% nondetects. In this study, basic statistics for all chemicals with less than 50% nondetects and more than one detection limits (Table 1) were calculated using the KM method.

2. *Maximum Likelihood Estimation*. Maximum likelihood estimation (MLE) is a parametric method that requires the underlying distribution of the data to be known or assessed. In most environmental applications, the interest is to show that the original or transformed data follow a normal distribution with the aim to estimate population parameters (such as the mean and variance) from sample data such that the probability (likelihood) of obtaining the observed data is maximized. MLE was used in this work to estimate summary statistics for chemicals that do not meet the assumptions of the KM method (especially chemicals with NDs > 50%; Table 1) after verifying that the data are log-normally distributed.

2.2.1.2. Comparison of Chemical Concentrations in Final Effluent and expected in Ambient Water with Water Quality Criteria

The comparison of contaminant concentrations in the effluent with water quality standards is intended to determine whether there is any potential impact of contaminants on ecological heath. The EPA recommends aquatic life criteria for toxic chemicals in ambient waters, and these have been adopted into applicable state water quality standards (314 CMR 4.00.). Aquatic life criteria are "the highest concentration of specific pollutants in water that are not expected to pose a significant risk to the majority of species in a given environment or a narrative description of the desired conditions of a water body being 'free from' certain negative conditions" (https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table). The water quality criteria provided includes the criterion maximum concentration (CMC or acute toxicity) and the criterion continuous concentration (CCC or chronic toxicity), mostly for metals and pesticides. Hence, in this report the chronic toxicities were compared with metal and pesticide concentrations in the effluent and dissolved in Massachusetts Bay estimated using a dilution factor of 70:1 projected by Roberts and Snyder (1993) and documented in the field (Hunt et al., 2002; Roberts et al. 2011).[1]

There are no criteria for acute or chronic concentrations recommended for polycyclic aromatic hydrocarbons (PAHs). For these groups of compounds, the EPA recommends human health criteria that "represent the specific levels of chemicals or conditions in a water body that are not expected to cause adverse effects to human health" (https://www.epa.gov/wqc/national-recommended-water-quality-criteria-human-health-criteria-table). Thus the human health criteria were used to assess historical compliance for these chemicals and total PCBs. For discharges to marine waters, the applicable criteria are those relating to "Human Health for the consumption of Organism Only", since there is no exposure from consumption of water in this case as there would be for discharges to a drinking water source.

Two statistical methods were used to compare mean concentrations of chemicals with water quality standards (i.e., CCCs and human health criteria): the one-sample test and bootstrapping (Helsel, 2012; http://www.practicalstats.com/news/archive.html).

1. *One-sample test and bootstrapping*. The one-sample test is a parametric method that tests the hypothesis that the mean of a sample equals a prespecified value (e.g., WQC). The test p-value can then be divided in half to test whether the mean exceeds – or is less than – the standard (Dennis Helsel in https://www.practicalstats.com/resources/Newsletters/18Aug_Compare2Stds-withNDs.pdf). The one-sample test requires that the data follow a normal distribution. Even though that condition was not satisfied for the majority of chemicals in the dataset, the results of the comparisons are validated by the following considerations:

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[1] The current discharge permit (permit MA0103284, August 2000, Attachment S) incorporates background build-up, so the assumed effective dilution applicable to the potential to exceed chronic water quality criteria varies by contaminant, but is slightly less than 70:1. For human health criteria, only the farfield concentrations are considered to have the potential to exceed these criteria, so the effective dilution is 364:1.

(i) The Central Limit Theorem (CLT) can be invoked to assume that chemical concentration means follow a normal distribution. This theorem states that when a sample size (*n*) is sufficiently large, the sampling distribution of the mean is approximately normal, even when the population distribution (or underlying data) is not itself normal (Devore and Peck, 2005). How "large" must *n* be remains debatable but based on considerations about skewness coefficients in environmental data (coefficients ≥ 1), many statisticians suggest that the CLT can be safely applied if *n* exceeds 30 (Devore and Peck, 2005; Helsel, 2012). The large sample sizes for chemicals in our data set ($n = 44 – 2{,}035$; Table 1 and Appendix A) amply satisfy the assumptions of the Central Limit Theorem and thus support the use of the one-sample test.

(ii) The appropriateness of the one-sample test was further evaluated by comparing the means and confidence limits so obtained with bootstrapped means and intervals for some chemicals. The bootstrap method consists in computing statistics from repeated random samples selected from the observed sample data with replacement (Neter et al., 1996). The repeated samples have the equal number of observations as the original sample and may contain both censored and uncensored observations (Helsel, 2012). Bootstrapping in this study involves 1000 repeated computations of lognormal means using the BootMLE macro for Minitab provided from http://practicalstats.com/nada/downloads.html. The results show that bootstrapped two-sided 95% confidence intervals are symmetric around the means, reflecting that the distribution of the means approaches normality (Figure 2a and b). Therefore, the Central Limit Theorem can be assumed for the large sample sizes in this study as borne out by the close agreement between parameters calculated by the one-sample test and bootstrapping (Figure 2c).

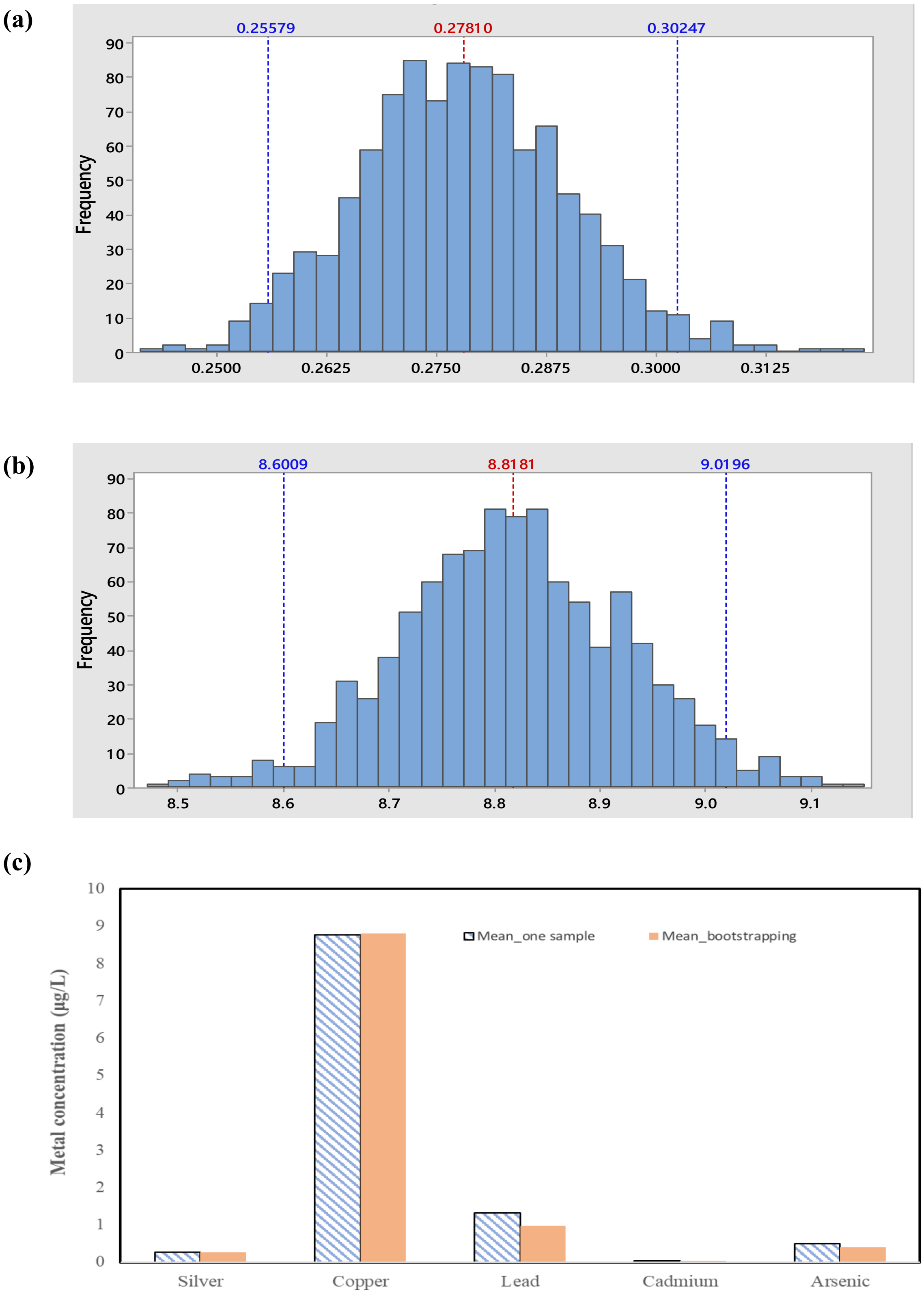
2. One-sample modified sign test. For data pairs (x_i,y_i ; i = 1,...n) comparing two samples (or a sample with a standard), the sign test determines whether x is generally larger or smaller than y, or equal (tied) (Helsel and Hirch, 2002). While the standard sign test deals with ties by deleting them from all calculations, Fong et al. (2003) provide methods to correct for ties in the calculation of test p-values. The EPA does not specify which parameter (mean or median) should be compared with contaminant human health criteria. For these chemicals, we used the one-sample modified sign test to estimate the population medians and compare them to the targets or reference values (i.e., Human Health Criteria).

We use a one-sided alternative hypothesis (also known as a directional hypothesis) to determine whether the population mean/median concentration of a given contaminant (μ) is less than the CCC/HHC (μ_0). The decision rule was (at a 0.05 alpha level):

$$H_0: \mu = \mu_0$$

$$H_a: \mu < \mu_0$$

Figure 2. Bootstrapped mean concentrations for silver (a) and copper (b) and comparison with means obtained from one-sample test (c)



This one-sided test has greater power than a two-sided test to detect differences between the parameter and the pre-specified value. For the one-sample test, the statistical software used (Minitab) tests for the equality of the mean to the CCC (i.e., two-sided test). The outputted p-value was then divided in half to test whether the mean was lower than the Water Quality Criteria.

3. Generalized Wilcoxon (GW) test. The GW test is a nonparametric score test that determines whether distribution functions (edfs) differ among groups of censored data without assuming normality (Helsel, 2012). The test is designed to handle data censored at multiple reporting limits by assigning estimated percentiles (or scores) to uncensored observations falling between the censoring thresholds. The GW test was used to determine differences in annual concentrations of individual PCBs using a u-score or Gehan test statistics (h).

2.2.1.3. Assessment of Non-regulated Contaminants

Many of the chemicals studied do not have water quality/human health criteria to use as a benchmark for compliance. These were evaluated by testing if the means, medians or probabilities of observing a detected value remain steadily low over time. Various methods for group comparisons proposed by Helsel (2012) were used to compare sampling years as explained below.

1. *Likelihood-ratio test*. The likelihood-ratio test is a Maximum Likelihood Estimation method equivalent to an ANOVA F-test that determines whether data classified by groups differs significantly from unclassified data (Helsel, 2012). The null hypothesis of equality of means is rejected when the log-likelihood statistic with classification (*Lgroups*) is significantly greater than that for no classification (*Lnull*). The test statistic is the "-2 log-likelihood"

$$-2 \text{ log– likelihood} = -2\,(Lnull - Lgroups) \qquad \text{(eq. 1)}$$

Where L is the log-likelihood of each situation. The resulting statistic is compared to a chi-square distribution with k-1 degrees of freedom (k= number of variables) to calculate the p-value of the test. Annual differences in aluminum concentrations were analyzed with this method.

2. *Analysis of Variance (ANOVA)*. Analysis of variance was used to compare annual concentrations of contaminants for which there are no water quality criteria that have 100 % detection (Table 1), as well as surrogate-corrected PAHs. Although the dataset consists of repeated observational data collected at one sampling point (i.e., DITP effluent), the appropriateness of using ANOVA is supported by the following:

- Because the test was used for chemicals with no nondetects, there was no need for simple substitution that would introduce bias in the annual means and the significance of the test
- According to the Minitab software website (https://support.minitab.com/en-us/minitab/18/help-and-how-to/statistics/nonparametrics/how-to), the test performs very well with skewed and nonnormal distributions if the sample size is greater than 15 or 20. Moreover, in keeping with the Central Limit Theorem described above, normal

distribution of the means can be assumed because of the large sample sizes of the contaminants involved (n = 193 – 635).

3.0 RESULTS AND DISCUSSION

Section 3.1 presents the concentrations for the compounds in the effluent, how frequently they were detected, and summary statistics for each. Then in section 3.2 we compare contaminant levels in the DITP effluent, and estimated resulting concentrations in ambient water near the effluent outfall, with water quality criteria.

3.1. Patterns of Detection and Concentration

Tables 2 to 5 present detection frequencies and concentrations for metals (1999 – 2017), PAHs and PCBs (2006 – 2017). A summary of descriptive statistics for each group of compounds is provided below.

3.1.1. Metals

Some of the metals considered in this analysis are included in the *EPA Guidance Manual (2004)* list of mandatory pollutants of concern because of their widespread occurrence in wastewater. These are: arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver and zinc. From 1999 to 2017, the highest detection frequencies were found for iron (100%), molybdenum (99.7%), zinc (99.5%) and nickel (96.9%). High detection for molybdenum and zinc were in keeping with the high frequency of detection reported for both metals (82% and 95%, respectively) in the MWRA (2000) local limits development for data collected from 1997 – 1999. Also, percent detections of lead (20.8%) and arsenic (24%) remained relatively low as in the 1997 – 1999 survey (24% and 15%, respectively). Antimony was virtually undetected (1/193 samples) while beryllium and selenium have never been detected in the effluent since 2010 (Table 2). Highest mean concentrations were calculated for iron (274.5 µg/L), boron (217 µg/L), aluminum (40.8 µg/L) and zinc (24.6 µg/L). The percent detections were higher for some chemicals in 2018 – 2019 and lower for others compared to the results from 1999-2017. However, reported concentrations in 2018 and 2019 were comparable to earlier results and maximum concentrations were overall lower (Appendix A).

Metal loadings in the influent can be attributed to one of the following sources: water supply, corrosion, residential, industrial, known commercial, infiltration and inflow, septage and unknown/other commercial sources. The EPA guidance manual (EPA, 2004) assumes that industries are the major source of metals to wastewater and that pollutant reductions should focus only on permitted industries. However, the MWRA's local limit development report (2000) reveals that industrial discharges make up a very low percentage (less than 5%) of DITP influent loadings of the targeted pollutants (copper, lead, mercury, and molybdenum). For example, major contributors to copper loading in DITP influent are unknown commercial (30% of loading sources,) sewer line corrosion (27%) and infiltration (22%).

Table 2. Basic statistics for metal concentrations (µg/L) in the final effluent of the Deer Island Wastewater Treatment Plant

Metal	Data years	Samples (Count)	Detects (%)	Range	Mean	25th percentile	Median	75th percentile	Statistical Method [a]
Aluminum	2010 – 2017	619	58.8	<15 – 559	40.80	21.80	29.90	45.90	KM
Antimony	2010 – 2017	193	0.51	N/A [b]	N/A	N/A	N/A	N/A	N/A
Arsenic	2010 – 2017	191	7.32	<0.8 – 2.01	0.50	0.20	0.31	0.48	MLE
Beryllium	2010 – 2017	193	0	N/A[c]	N/A	N/A	N/A	N/A	N/A
Boron	2010 – 2017	193	21.7	<250 – 351	217.07	183.74	212.18	245.03	MLE
Cadmium	2010 – 2017	442	48.4	<0.03 – 0.26	0.04	0.01	0.03	0.05	MLE
Chromium	1999 – 2017	1407	67.1	<0.7 – 10.3	1.06	— [c]	0.90	1.22	KM
Copper	1999 – 2017	2035	74.7	<1 – 70.8	8.81	6.38	10	10.80	KM
Iron	2010 – 2017	193	100	124 – 1090	274.53	204	252	322	MLE
Lead	1999 – 2017	1518	20.8	<1.2 – 21.4	1.33	0.35	0.65	1.19	MLE
Mercury	1999 – 2017	1527	67	<0.0018 – 0.242	0.01	0.003	0.008	0.01	KM
Molybdenum	2010 – 2017	408	99.7	<1 – 12.1	4.09	2.88	3.77	4.95	MLE
Nickel	1999 – 2017	1471	96.9	0.7 – 17.3	2.75	2.10	2.59	3.16	KM
Selenium	2010 – 2017	193	0	N/A	N/A	N/A	N/A	N/A	N/A
Silver	1999 – 2017	1398	54.4	<0.09 – 4.21	0.27	—	0.13	0.31	KM
Zinc	1999 – 2017	1415	99.5	6 – 116	24.75	16.93	22.54	30.02	MLE

a: Method used for summary statistics. KM: Kaplan-Meier; MLE: Maximum Likelihood Estimation

b: Non applicable. The chemical was not detected in any sample. Antimony is virtually in that category with only one detection

c: The KMSTATS macro des not calculate a percentile whose value is below the lowest in the dataset. The 25th percentile can thus be taken as the lowest <DL

3.1.2. Polycyclic Aromatic Hydrocarbons (PAHs)

Descriptive and inferential statistics for PAHs were performed with data corrected for surrogate recovery. Most of the 24 PAH compounds included in this analysis were detected more than 90 percent of the time. Only acenaphthylene, perylene and dibenzo[a,h]anthracene were detected less than 50 % of the time (Table 3). The high detection frequency of PAHs in wastewater is not surprising because of the ubiquity of these compounds in the environment. PAHs are compounds with two or more fused aromatic rings that occur in the environment from petrogenic and pyrogenic sources. Petrogenic sources include freshwater oil spills, underground and above ground storage tank leaks, and the accumulation of petroleum products associated with transportation (e.g., asphalt). Pyrogenic PAHs result from pyrolysis, *i.e.*, when organic substances (oil, coal and wood) are exposed to high temperature under low oxygen or non oxygen conditions (Mastral and Callen, 2000; Jiao et al, 2012). Other anthropogenic sources of PAHs include incineration of industrial and domestic wastes and chemical manufacturing (Onojake et al., 2014; Abdel-Shafy and Mansour, 2016).

PAHs emitted into the atmosphere are deposited onto terrestrial and aquatic ecosystems by dry and wet depositions. Some of these PAHs are from nearby sources, such as automotive exhaust from adjacent roadways while others are from more distant sources and have been carried various distances through the atmosphere (Abdel-Shafy and Mansour, 2016). PAHs can enter sewage systems from all compartments of the physical environment and from human waste, thus their high detection frequencies in the DITP effluent.

To reduce PAHs in the sewerage system, it is important to identify their origin. Diagnostic ratios of specific PAH congeners were used to identify possible sources of PAHs in the DITP effluent. These ratios are considered to be accurate and reliable tools for source identification of PAHs (Zhang et al., 2006; Edokpayi et al, 20016; Adeniji et al, 2019). In most cases, pyrolytic origin is concluded if the ratio of individual congeners is higher than a certain threshold or the ratio of the sum of low molecular weight PAHs (LMWs) over high molecular weight PAHs (HMWs) is less than one (i.e., $\sum$LMW/HMW < 1; Table 4). The ratio $\sum$LMW/HMW in the DITP effluent is practically equal to one, meaning that LMWs and HMWs were present at equal concentrations in the wastewater and that petrogenic and pyrogenic contributions to the system were similar. However, most of the other diagnostic ratios point to the fact that the PAHs measured in the effluent had a predominant pyrolytic sources such as biomass and coal combustion and vehicular emissions (Table 4).

Table 3. Basic statistics for PAH concentrations (ng/L) in the final effluent of the Deer Island Wastewater Treatment Plant (low detection level methods)

PAH	Data years	Samples (Count)	Detects (%)	Range[a]	Mean	25th percentile	Median	75th percentile
1-Methylnaphthalene	2006 – 2017	628	97.7	0.40 – 596.59	10.48	4.31	5.81	8.22
1-Methylphenanthrene	2006 – 2017	624	89.6	0.26 – 129.19	5.92	2.94	4.40	7.05
2,3,5-Trimethylnaphthalene	2006 – 2017	624	90.6	0.30 – 397.06	11.11	5.41	8.39	12.64
2,6-Dimethylnaphthalene	2006 – 2017	624	80	0.17 – 273.82	8.58	3.11	6.37	9.86
2-Methylnaphthalene	2006 – 2017	628	98.4	0.64 – 691.83	19.34	5.37	8.86	18.56
Acenaphthene	2006 – 2017	624	91.2	0.42 – 90.16	11	5.19	8.39	13.75
Anthracene	2006 – 2017	624	89.3	0.37 – 38.48	5.52	2.88	4.13	6.74
Benzo[a]pyrene	2006 – 2017	625	98.1	0.30 – 113.48	6.69	31.14	4.46	6.83
Benzo[b]fluoranthene	2006 – 2017	635	98.9	0.31 – 196.89	11.15	5.18	7.32	11.30
Benzo[e]pyrene	2006 – 2017	635	97.2	0.27 – 107.75	5.68	2.76	3.71	5.67
Benzo[g,h,i]perylene	2006 – 2017	635	97.2	0.23 – 84.03	6.40	2.64	4.13	6.76
Benzo[k]fluoranthene	2006 – 2017	635	95.3	0.33 – 72.24	5.72	2.59	3.87	6.39
Biphenyl	2006 – 2017	625	79.2	0.28 – 71.06	6.96	2.36	4.28	9.28
Fluorene	2006 – 2017	624	98	0.69 – 152.06	10.34	5.40	8.38	12.42
Indeno[1,2,3-cd]pyrene	2006 – 2017	635	95	0.18 – 89.14	7.16	0.18	4.73	7.72

a: Surrogate-corrected data in the original dataset. Used for PAH here and in other statistical calculations because of the importance of recovery standards in the chemical analysis of PAHs and the large differences between corrected and non-corrected concentrations.

Table 4. Molecular ratios (mean ± SD) and possible sources of PAHs in the DITP effluent (2006 - 2017) [a]

PAHs	Petrogenic	Pyrolitic	DITP effluent
LMW/HMW [b]	> 1.0	< 1.0	1.08
Anthracene/178	< 0.1	≥ 0.1	0.03 ± 0.02
Anthracene/(Anthracene+Phenanthrene)	< 0.1	> 0.1	0.25 ± 0.14
Benzo[a]anthracene/228	< 0.2	0.2–0.35	0.03 ± 0.03
Benzo[a]anthracene/(Benzo[a]anthracene+Chrysene)	< 0.2	0.2–0.35	0.41 ± 0.04
Chrysene/Benzo[a]anthracene	< 0.4	> 0.9	1.44 ± 0.30
Fluoranthene/Pyrene	< 1.0	> 1.0	0.94 ± 0.21
Fluoranthene/(Fluoranthene+Pyrene)	< 0.4	> 0.4	0.47 ± 0.06
Indeno(123,cd)pyrene /(Indeno(123,cd)pyrene +Benzo[g,h,i]perylene)	< 0.2	> 0.2	0.53 ± 0.11
Phenanthrene/Anthracene	> 15	< 10	3.93 ± 2.14

a: The 2018 – 2019 data have similar characteristics with Benzo[a]anthracene/(Benzo[a] anthracene + Chrysene) = 0.42 ± 0.02; Benzo[a]anthracene/228 = 0.02 ± 0.01; Fluoranthene/(Fluoranthene + Pyrene) = 0.39 ± 0.08

b: *LMW* low molecular weight, *HMW* high molecular weight.

3.1.3. Polychlorinated Biphenyls (PCBs) and Pesticides

Although long since banned, and not detected with EPA standard methods, most of the pesticides and PCBs measured in the outfall monitoring program are usually detected using the very low detection limits used for this study. BZ 187 Heptachlorobiphenyl and BZ 180 Heptachlorobiphenyl had the lowest percents of detection (25 and 41 % respectively; Table 5). PCBs are mixtures of synthetic organic chemicals that were used for different applications in the United States. They were produced and marketed under the trade names of Aroclor until Mosanto Chemical Company discontinued manufacturing in 1977 and the importation ban (in the U.S.) took effect in 1979 (ATSDR, 2000). Some manufacturing processes such as processing of paper products or asphalt roofing materials, production of chlorinated solvents, paints and plastics may inadvertently generate PCBs (https://www.govinfo.gov/content/pkg/CFR-2011-title40-vol31/pdf/CFR-2011-title40-vol31-sec761-3.pdf). Thus despite the ban of PCB manufacturing and restriction in commercial use, these contaminants are ubiquitous in the environment because of their chemical stability. PCBs can enter wastewater system through atmospheric deposition and stormwater, water supply systems, leaks, leaching from coatings and plastics containing PCBs and human waste. The analysis of PCBs entering wastewater treatment plants in China and the U.S. indicates that industrial sources include processing of pharmaceuticals, pigments and dyes, textile dyeing and finishing, biochemical, and inorganic chemicals (Litten et al., 2002; Yao et al., 2014)

Table 5. Basic statistics for pesticide and PCB concentrations (ng/L) in the final effluent of the Deer Island Wastewater Treatment Plant

Chemical	*Data years*	Samples (Count)	Detects (%)	Range	Mean	25th percentile	Median	75th percentile	Stats method[a]
4,4’-DDE	2006 –2017	1068	53.5	<1.02 – 3.08	0.33	0.18	0.24	0.33	KM
Alpha-chlordane	2006 – 2017	1068	80.1	<1.02 – 4.55	0.71	0.40	0.54	0.82	KM
Trans-Nonachlor	2006 – 2017	863	93.2	<1.02 – 2.57	0.30	0.17	0.23	0.33	KM
BZ 52 Tetrachlorobiphenyl	2006 – 2015	865	68.5	<0.25 – 0.68	0.18	0.12	0.16	0.21	KM
BZ 101 Pentachlorobiphenyl	2006 – 2017	960	75	<0.25 – 0.88	0.18	0.11	0.16	0.21	KM
BZ 118 Pentachlorobiphenyl	2006 – 2017	960	72.9	<0.50 – 0.64	0.15	0.10	0.13	0.18	KM
BZ 138 Hexachlorobiphenyl	2006 – 2017	960	81.8	<0.25 – 0.88	0.18	0.11	0.16	0.22	KM
BZ 153 Hexachlorobiphenyl	2006 – 2017	960	90.4	<0.25 – 1.08	0.14	0.08	0.11	0.15	KM
BZ 180 Heptachlorobiphenyl	2006 – 2017	960	41.2	<0.25 – 7.03	0.14	0.08	0.12	0.17	MLE
BZ 187 Heptachlorobiphenyl	2006 – 2017	960	24.9	<0.25 – 0.57	0.10	0.06	0.09	0.12	MLE
Total PCBs[b]	2006 – 2017	648	—	0.54 – 17.53	4.89	2.63	4.75	6.44	MLE

a: Method used for summary statistics. KM: Kaplan-Meier; MLE: Maximum Likelihood Estimation
b: Sum of all congeners in a sample

3.2. Comparing Contaminant Levels in the DITP Effluent and Estimated in Ambient Water with WQC

The rationale for this methodology is that if the level of a chemical has been significantly lower than water quality criteria (WQC) or remains consistently low over almost two decades of water quality monitoring, it may be appropriate to reevaluate the frequency or even the necessity of monitoring that chemical. Since the state of Massachusetts generally adopts[2] EPA recommended criteria into its water quality standards, the EPA's criteria continuous concentrations (CCCs) were compared with metal and pesticide concentrations in the effluent and estimated in Massachusetts Bay. The CCC is the highest concentration of a chemical in water that aquatic organisms can be *chronically* exposed to without resulting in an adverse effect.

The statistical test reveals that many metals have mean concentrations in the final effluent significantly lower than the CCCs even before accounting for dilution in Massachusetts Bay ($p < 0.001$). These are: arsenic, cadmium, chromium, lead, mercury, nickel, zinc (Table 6). Copper was the only metal whose concentration the effluent was higher than the CCC, but as shown later, the concentration was much lower than the WQC after dilution in the Bay. Other metals were not considered in the analysis because they were either not detected or do not have saltwater CCCs. These include: aluminum (CCC determined through site-specific biotic ligand model), antimony, beryllium, boron, iron, molybdenum, selenium and silver. The following organic compounds had effluent concentrations significantly lower than their respective HHC ($p < 0.001$): Alpha-Chlordane, acenaphthene, anthracene, benzo[k]fluoranthene, fluorene, fluoranthene, chrysene, and pyrene (Table 7). Other chemicals such as 4,4'-DDE, benzo[a]pyrene, benzo[b]fluoranthene, benzo[a]anthracene, dibenzo[a,h]anthracene, indeno [1,2,3-cd]pyrene, and total PCBs, had concentrations in the effluent higher than their HHCs. However, as discussed later, ambient concentrations of these compounds will be negligible after dilution in Massachusetts Bay.

To better assess the effect of contaminants on ecological health, the CCCs (HHCs for PAHs) were compared with the upper 95 % confidence limit (UCL) of mean concentrations (medians for PAHs) estimated in Massachusetts Bay for the sampling years reported in Tables 2 and 3. The 95% confidence limit means that an interval estimate with different samples would capture the "contaminant population" mean concentration 95% of the time. Thus comparing the WQC with the upper endpoint of the interval (i.e., ratio WQC/UCL) is a good indicator of whether or not contaminant concentrations in ambient water may ever exceed the standards.

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[2] Current Massachusetts Surface Water Quality Standards, 314 CMR 4.00, generally adopt EPA recommended criteria as of 2002. Proposed revisions to the Water Quality Standards will update these to current EPA criteria with just a few exceptions.

Table 6. Comparison of metal concentrations (µg/L) in the DITP final effluent with water quality criteria

Chemical	Mean ± 95 % CI [a]	WQC (CCC) [b]	*P (α = 0.05)*
Arsenic	0.50 ± 0.05	36	0.000
Cadmium	0.04 ± 0.01	7.9	0.000
Chromium	1.06 ± 0.03	50	0.000
Copper	8.81 ± 0.02	3.1	0.000 [c]
Lead	1.33 ± 0.02	5.6	0.000
Mercury	0.01 ± 0.00	0.94	0.000
Nickel	2.75 ± 0.05	8.2	0.000
Zinc	24.75 ± 0.52	81	0.000

a: 95 % CI: 95 % confidence limit of samples means.

b: EPA's national recommended water quality criteria (criteria continuous concentration or chronic criteria).

c: The MLE one-sample is a two-sided test. The alternative hypothesis is: population mean ≠ WQC. Thus the *p*-value is still zero (i.e., $p < \alpha$) when the mean is > WQC.

Table 7. Comparing concentrations of organic compounds (ng/L) in the DITP final effluent with water quality criteria

Compound	Median ± 95 % CI [a]	WQC [b]	*P (α = 0.05)*
Alpha-Chlordane	0.24 ± 0.01	0.32	0.000
4,4'-DDE	0.54 ± 0.04	0.018	1.000
Acenaphthene	8.39 ± 0.60	90,000	0.000
Anthracene	4.13 ± 0.21	40,000	0.000
Benzo[a]pyrene	4.46 ± 0.34	0.13	1.000
Benzo[b]fluoranthene	7.32 ± 0.32	1.3	1.000
Benzo[k]fluoranthene	3.87 ± 0.29	13	0.000
Fluorene	8.38 ± 0.50	70,000	0.000
Benzo[a]anthracene	6.20 ± 0.23	1.3	1.000
Fluoranthene	22.89 ± 1.04	20,000	0.000
Chrysene	8.52 ± 0.24	130	0.000
Dibenzo[a,h]anthracene	4.29 ± 0.24	0.13	1.000
Pyrene	25.96 ± 1.04	30,000	0.000
Indeno[1,2,3-cd]pyrene	4.73 ± 0.48	1.3	1.000
Total PCBs	4.74 ± 0.31	0.064	1.000

a: 95 % confidence limit of samples medians.

b: EPA's human heath criteria (HHCs) for the consumption of "organisms only".

Ambient water concentrations of pollutants (C_w) were estimated as described in equation 2 using effluent concentrations and a dilution factor of 70:1 projected in Roberts and Snyder (1993) and verified by dye dilution studies after the outfall discharge began (Roberts et al., 2011).

$$C_W = \frac{C_{eff.}}{70} + C_B \qquad \text{(eq. 2)}$$

Where $C_{eff.}$ is contaminant concentration in the DITP effluent and C_B is the background concentration measured at a site uninfluenced by the outfall. To our knowledge, there are no updated background water concentrations available for the studied contaminants.

Baseline data are reported in the Supplemental Environmental Impact Statement (SEIS; USEPA, 1988) for arsenic, cadmium, chromium, copper, lead, mercury and nickel. These were used as C_Bs in equation 2, except for copper where a more recent value (0.38 µg/L) reported by Hunt et al., 2002 was used. Contaminants for which background concentrations are not available were considered as zero. This may introduce some uncertainty in estimated ambient water concentrations (and comparison with WQC) but this effect is mitigated by the fact that, for most chemicals, effluent concentrations are much lower than EPA's standards even before considering dilution in Massachusetts Bay (see Table 6 and 7). Therefore, the contribution of the effluent to ambient water toxicity will be minimal to negligible.

The results show that estimated metal concentrations in ambient water (i.e., UCLs for 2010 – 2017) were much lower than WQC with Criteria Continuous Concentration/Upper Confidence Limit ratios varying from 13 to 1,317 (Figure 3, Table 8, and Appendix B). Upper confidence limits of median PAH concentrations estimated in water were orders of magnitude lower than the HHCs for almost all chemicals, with HHC/ambient water ratios ranging from 2 to over 700,000 (Figure 4, Table 8, and Appendix B). Of the 671 samples collected from DITP's effluent from 2006 – 2019, after 70:1 dilution with receiving water, the highest effluent contribution to total PCBs in Massachusetts Bay would be about 0.013 ng/L, in average, which is much lower than the EPA's human health criteria of 0.064 ng/L (Figure 5 and Appendix B).

Figure 3. Comparison of upper confidence limits (UCL) of estimated mean metal concentrations in Massachusetts Bay with EPA's water quality criteria (WQC)

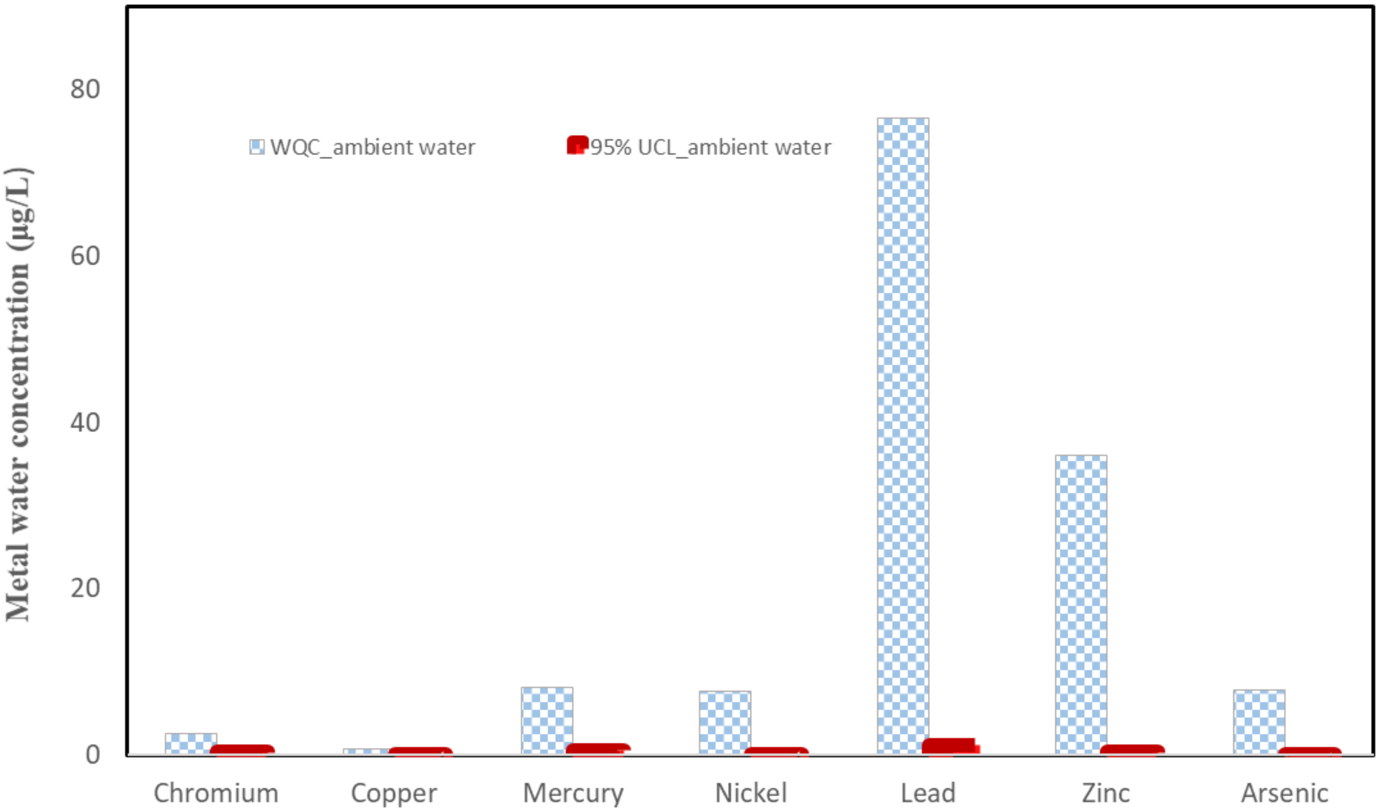


Table 8. Comparing concentrations of chemicals in DITP effluent and estimated in ambient water with water quality Criteria (1999/2006 – 2017)

Chemical	Unit	95 % UCL (effluent) (“UCL_{eff}”) [a]	Estimated ambient water concentration (“UCL_{amb}”)	WQC [c]	Ratio WQC/UCL_{eff}	Ratio WQC/UCL_{amb}
Arsenic	µg/L	0.550	0.478	36	65	75
Cadmium	µg/L	0.050	0.006	7.9	158	1,317
Chromium	µg/L	1.090	0.326	50	46	153
Copper	µg/L	8.830	0.478	3.1	0.35	6
Lead	µg/L	1.350	0.071	8.1	6	114
Mercury	µg/L	0.010	0.004	0.94	94	235
Nickel	µg/L	2.800	0.643	8.2	3	13
Zinc	µg/L	25.270	1.171	81	3	69
Acenaphthene	ng/L	*8.990*	0.128	90,000 *	10,011	703,125
Anthracene	ng/L	*4.340*	0.062	40,000 *	9,217	645,161
Benzo[a]anthracene	ng/L	*6.430*	0.091	1.3*	0.20	14
Benzo[a]pyrene	ng/L	*4.760*	0.067	0.13*	0.03	2
Benzo[b]fluoranthene	ng/L	*7.640*	0.110	1.3*	0.17	12
Benzo[k]fluoranthene	ng/L	*4.140*	4.146	13*	3	3
Chrysene	ng/L	*8.760*	0.125	130*	15	1,040
Dibenzo[a,h]anthracene	ng/L	*4.530*	0.066	0.13*	0.03	2
Fluoranthene	ng/L	*23.930*	0.341	20,000*	836	58,651
Fluorene	ng/L	*8.880*	1.127	70,000*	7,883	62,112
Indeno[1,2,3-cd]pyrene	ng/L	*5.180*	0.074	1.3*	0.25	18
Pyrene	ng/L	*27.000*	0.385	30,000*	1,111	77,922
Total PCBs	ng/L	*5.050*	0.003	0.064*	0.01	21

a: 95% a: upper confidence limit (UCL) of sample mean or median. Italicized values are UCLs of medians.

b: Conservatively estimated using an average dilution factor of 70:1 in Massachusetts Bay (Roberts and Snyder, 1993, Roberts et al. 2011)

c: EPA’s criterion continuous concentration (CCC) and human heath criteria (HHC) for the consumption of organisms. Asterisks indicate HHCs.

Figure 4. Comparison of upper confidence limits of estimated median PAH concentrations in Massachusetts Bay with EPA's human health criteria (HHC)

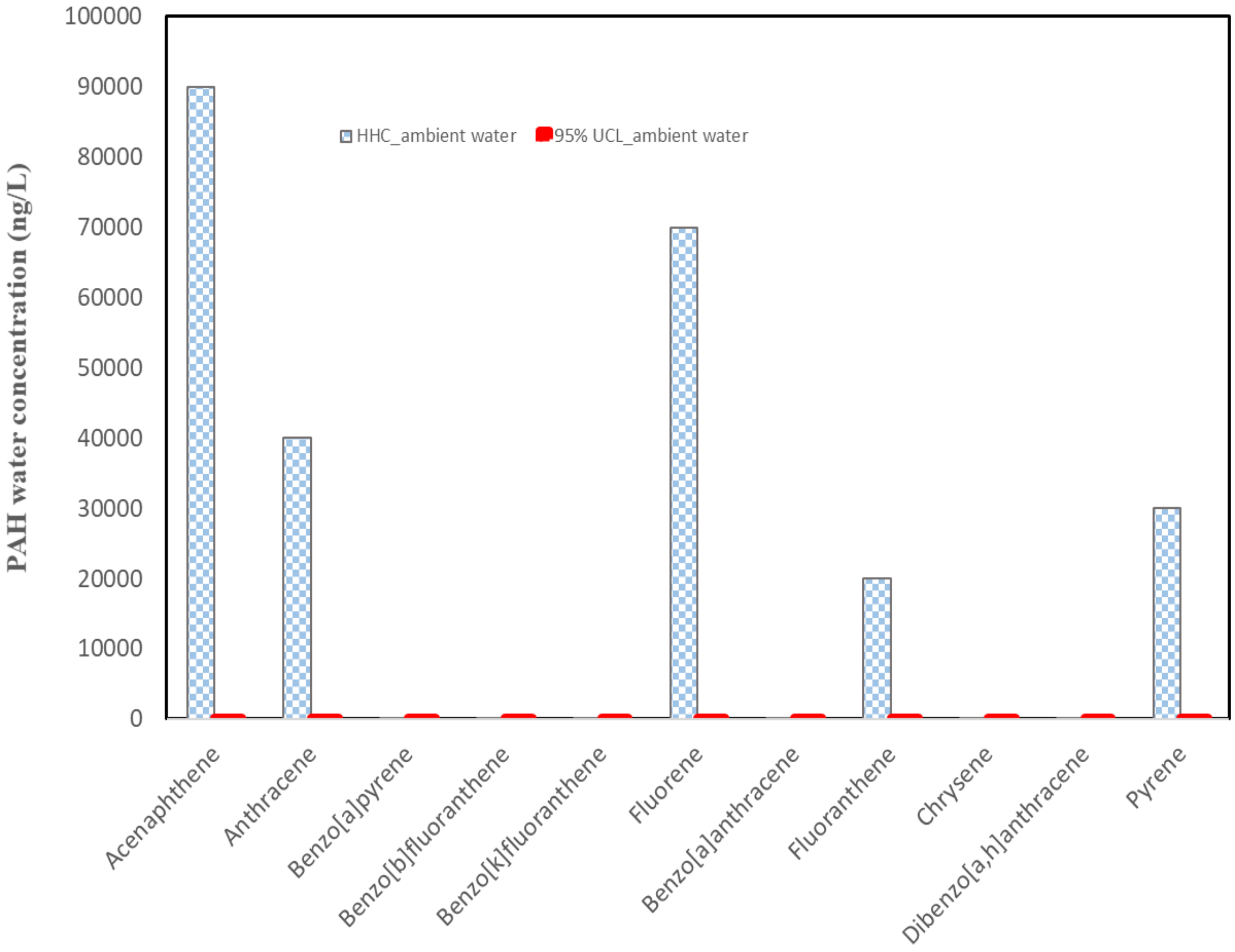
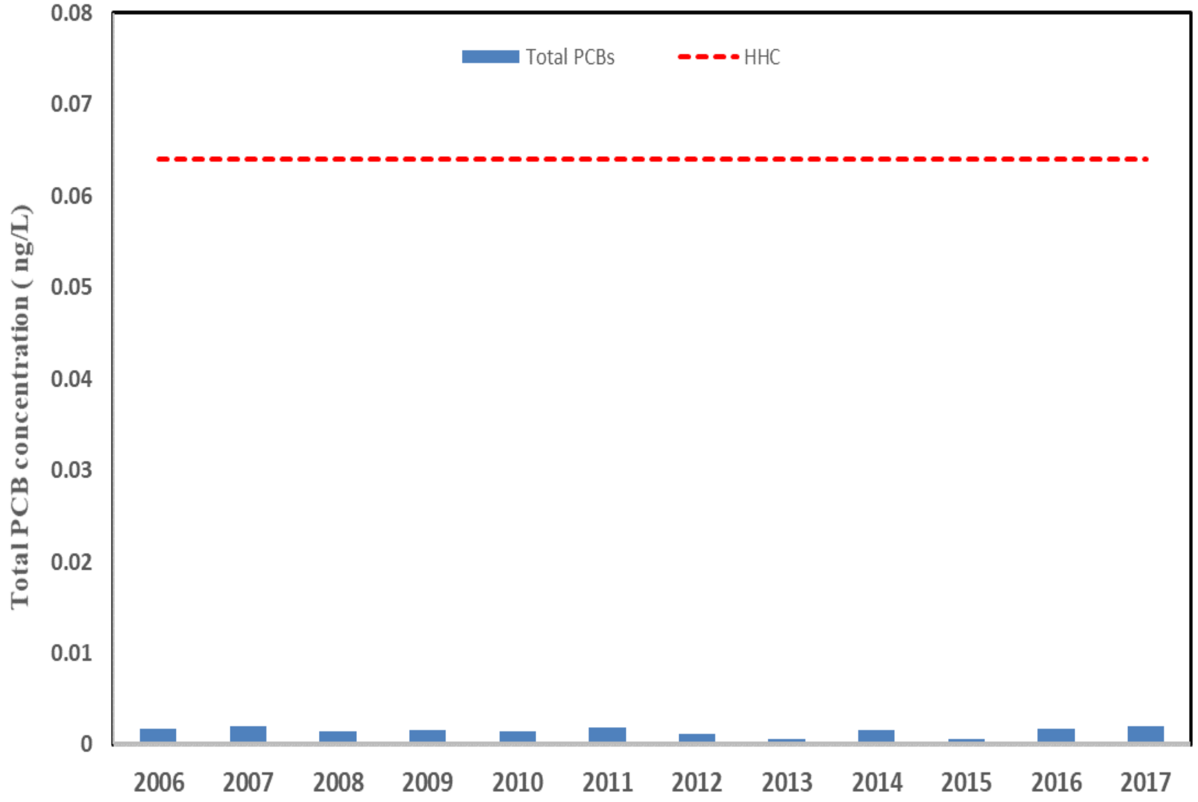


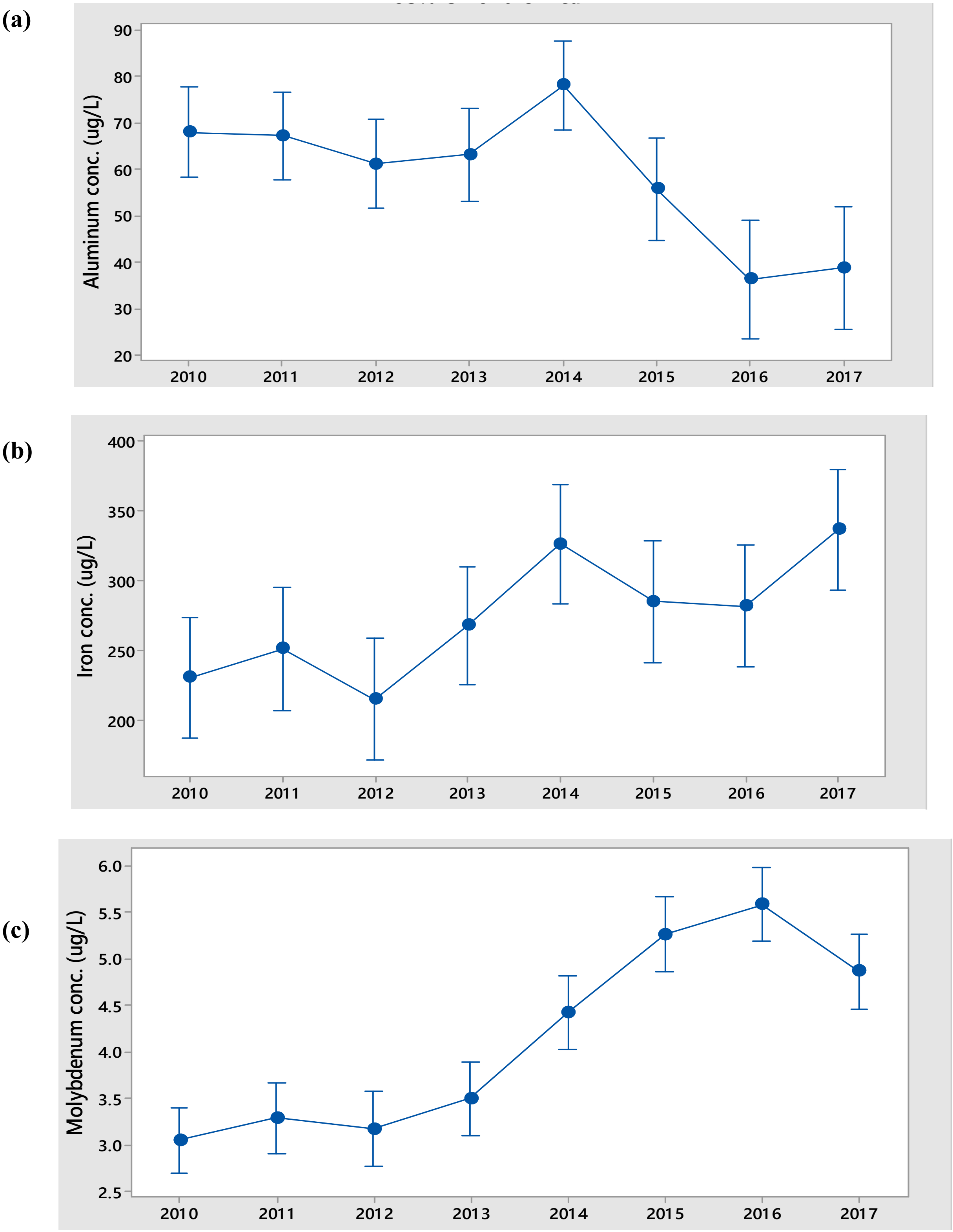
Figure 5. Comparison of total PCB concentration estimates in Massachusetts Bay with the EPA's human health criteria (HHC)



3.3. Temporal Trends in Contaminants without WQC

Some contaminants tested in the effluent are not in the EPA's priority list; that is, a set of regulated chemical pollutants for which analytical test methods have been developed. Since there are no WQC for these chemicals, their evaluation focuses on observation of temporal trends combined with statistical tests (likelihood-ratio test and ANOVA) to determine if there were significant changes in concentration over time. Aluminum is included in this category because CMCs and CCCs must be calculated for specific sites by the EPA's biotic ligand model that was not considered in this study. The results show that aluminum concentration remained steady from 2010 to 2013. The concentration increases in 2014 before decreasing significantly from 2015 to 2017. The likelihood-ratio test shows that aluminum concentrations in 2012, 2014 and 2017 were significantly lower than 2010 (Figure 6a). On the other hand, iron and molybdenum concentrations have increased from 2012 to 2017 (Figures 6b and c). Iron prevalence is probably due to the substantial contribution of domestic sources (along with industrial loads) to wastewater. For example, certain household products such as toilet paper, toothpaste and aerosol deodorant contain average iron concentrations of 215, 136.1 and 136.2 mg/kg product, respectively (Tjandraatmadja et al., 2008).

Figure 6. Temporal trend in DITP final effluent concentrations (µg/L) of aluminum (a), iron (b) and molybdenum (c). Error bars represent 95% CI



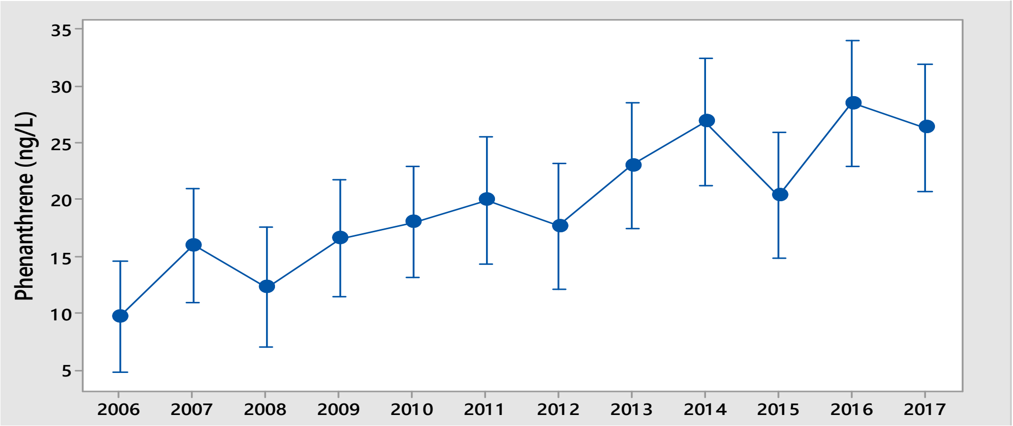
Typical molybdenum effluent concentrations are in the low parts per billion, averaging between 3 and 5.5 micrograms per liter between 2010 and 2017. Molybdenum enters wastewater through typical commercial and industrial sources including pigments, lubricants and corrosion control chemicals. In addition, research suggest that about 80 to 90 percent of the molybdenum detected in the influent passes through the treatment process into the effluent (https://www.kingcounty.gov/~/media/services/environment/wastewater /industrial-waste/docs/ TechAssistance/Molybdenum _Report_2011_Final.ashx?la=en). No CCC is provided for silver in the EPA's aquatic life criteria table. Average silver concentration in the effluent was low at 0.28 µg/L (Table 2). The highest concentration of this chemical measured in the effluent was 4.21 µg/L in August 2004. Nevertheless, the estimated concentration in Massachusetts Bay would be very low (0.06 µg/L) after applying the 70:1 dilution factor.

Time series and ANOVA for the PAHs with no WQC show that all are present only in the low parts per trillion range. There was an increase in phenanthrene concentrations from 2010 to 2017. Phenanthrene average concentration (19 ng/L) was the second highest among the low molecular weight PAHs after anthracene (32 ng/L). Sources of phenanthrene include diesel fuel exhaust, coal tar pitch, particle emissions from natural gas combustion, municipal incinerator waste (Fang et al., 2006). Hence this compound is a significant contributor to pyrolytic PAH mixture in the effluent. On the other hand, from 2013 to 2017, there was an overall downward trend or steadiness in concentrations of the following compounds:

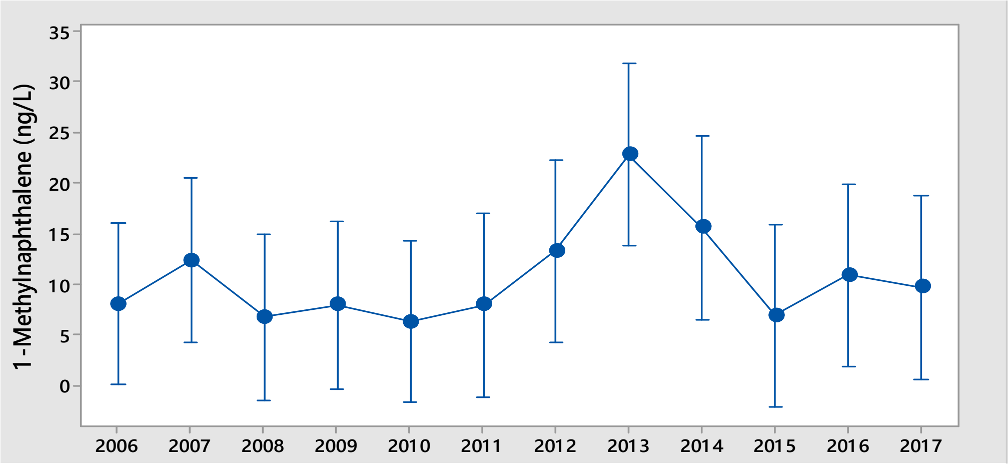
- PAHs: 1-methylnaphthalene, 1-methylphenanthrene, biphenyl, benzo(e)pyrene, benzo(g,h,i)perylene, acenaphthylene, and perylene (Figure 7).
- PCBs and pesticides: BZ 52 Tetrachlorobiphenyl, BZ 101 Pentachlorobiphenyl, BZ 118 Pentachlorobiphenyl, BZ 138 Hexachlorobiphenyl, BZ 153 Hexachlorobiphenyl, BZ 180 Heptachlorobiphenyl, BZ 187 Heptachlorobiphenyl, and trans-nonachlor (Figure 8).

Figure 7. Temporal variation in DITP final effluent concentrations (ng/L) of phenanthrene (a), 1-methylnaphthalene (b), 1-methylphenanthrene (c), 2,3,5-trimethylnaphthalene (d), 2,6-dimethylnaphthalene (e), 2-methylnaphthalene (f), biphenyl (g), benzo(e)pyrene (h), benzo(g,h,i)perylene (i), acenaphthylene (j), naphthalene (k), and perylene (l). Error bars represent 95% CI

(a)



(b)



(c)

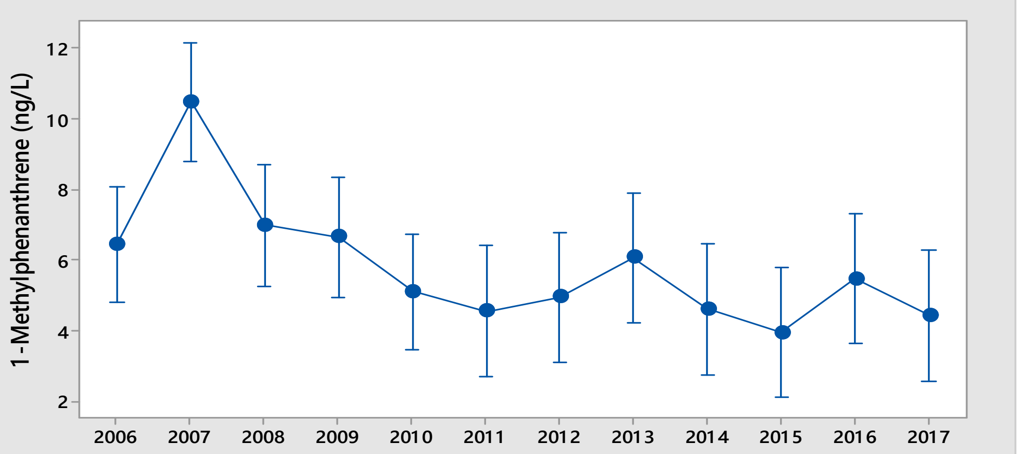
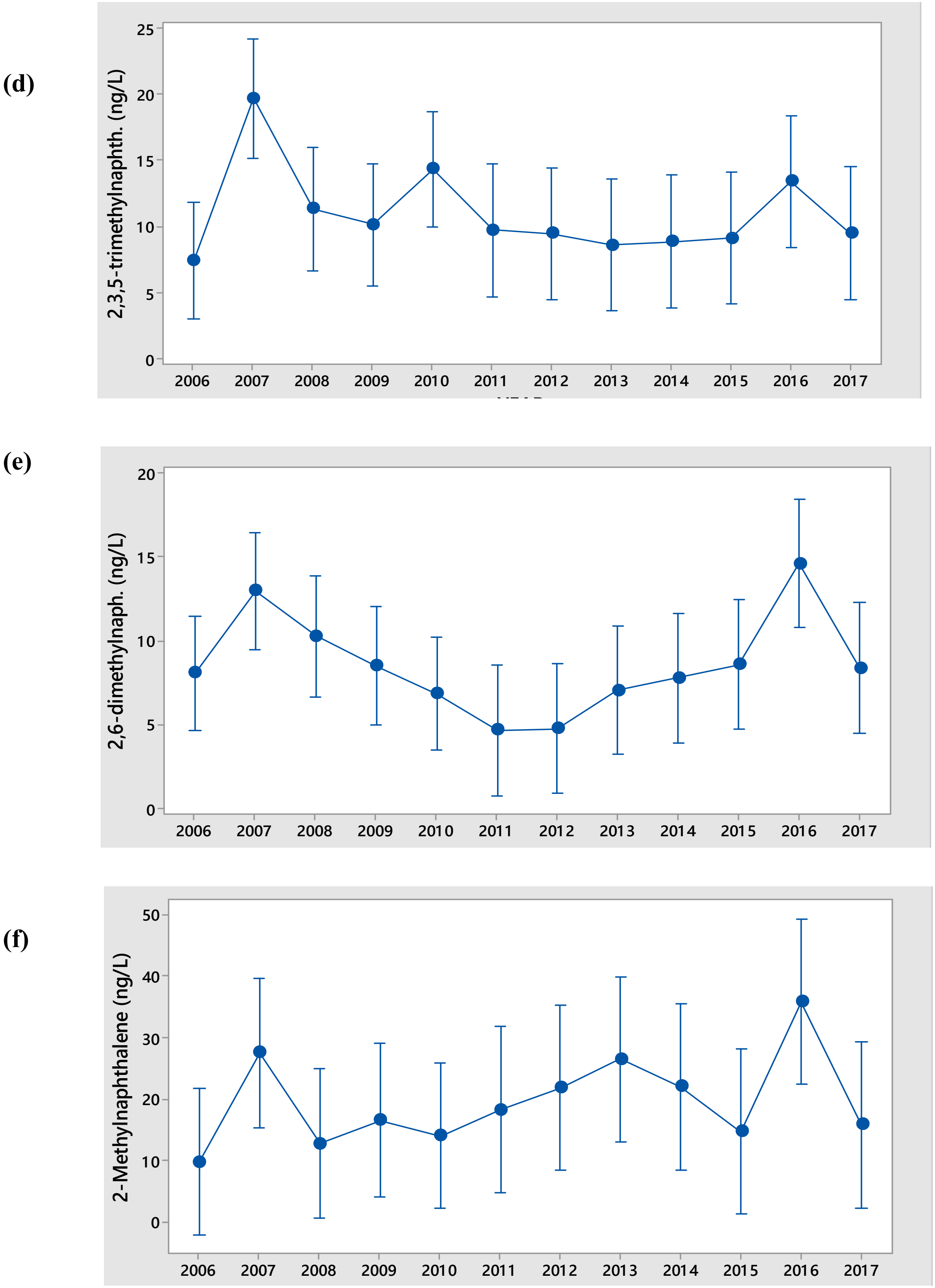
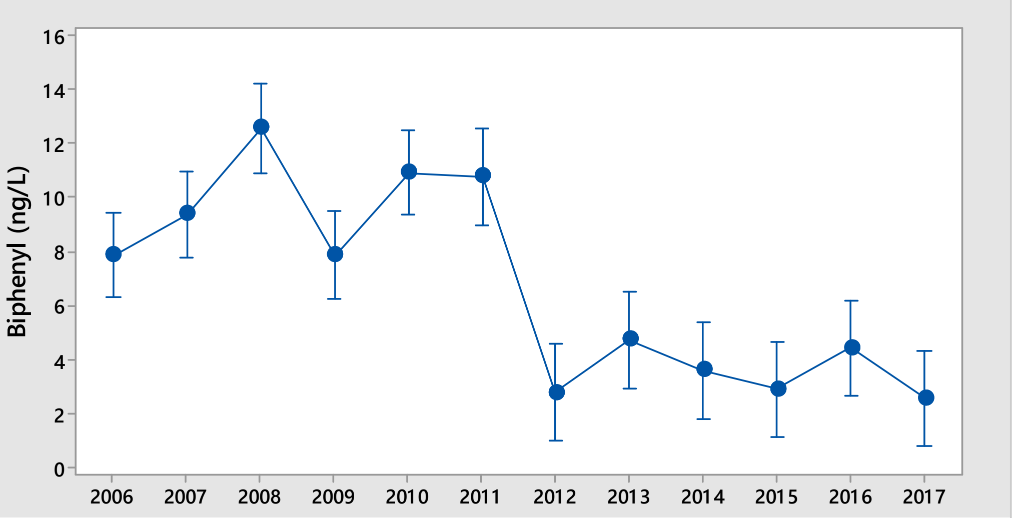


Figure 7. Temporal variation in DITP final effluent concentrations (continued)

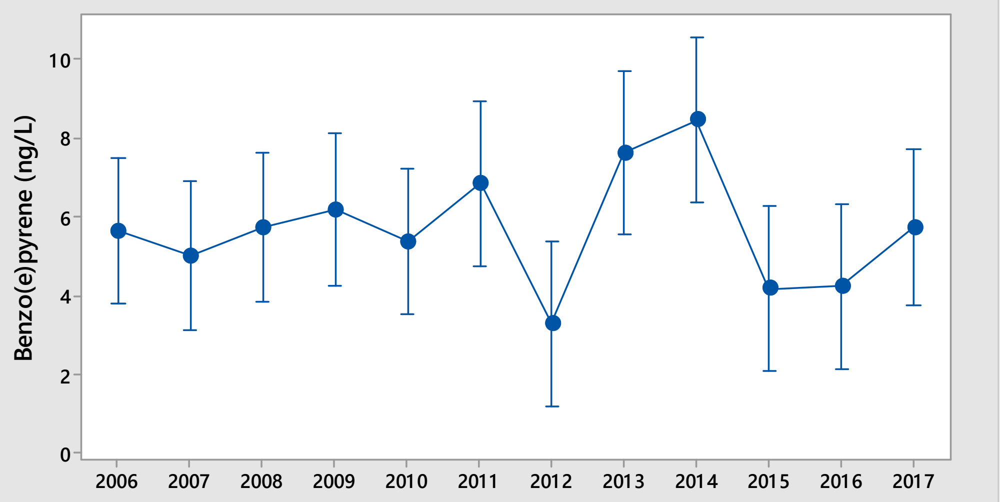


Figuree 7. Temporal variation in DITP final effluent concentrations (continued)

(g)



(h)



(i)

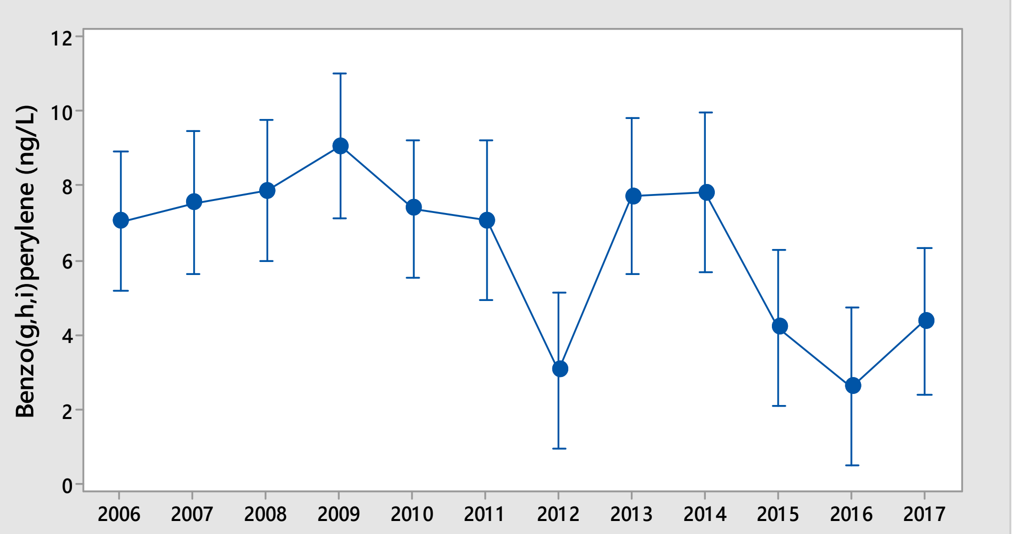
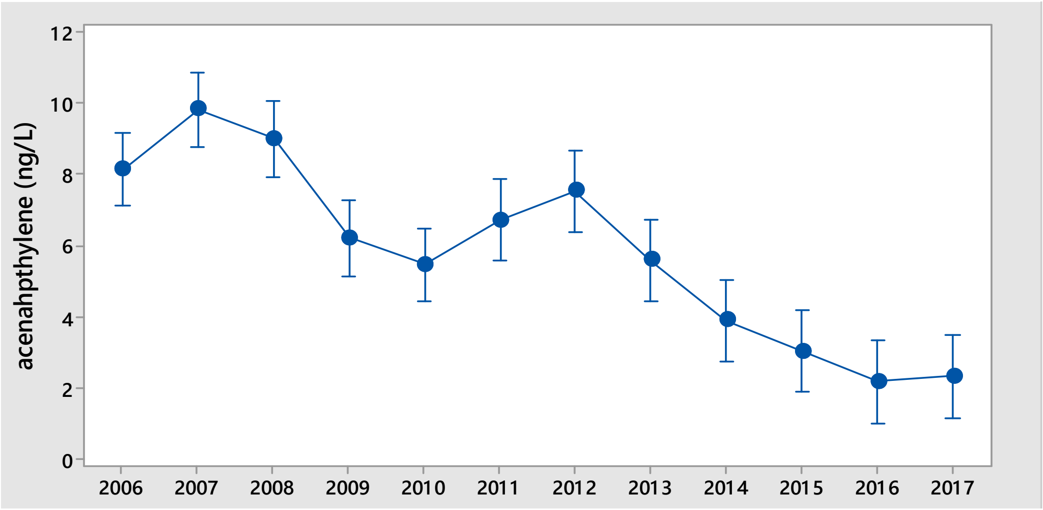
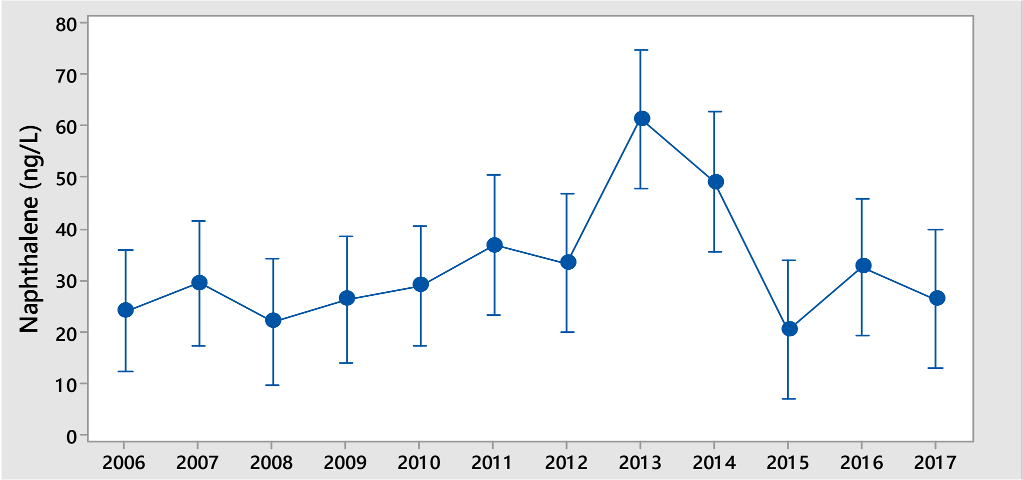


Figure 7. Temporal variation in DITP final effluent concentrations (continued)

(j)



(k)



(l)

.

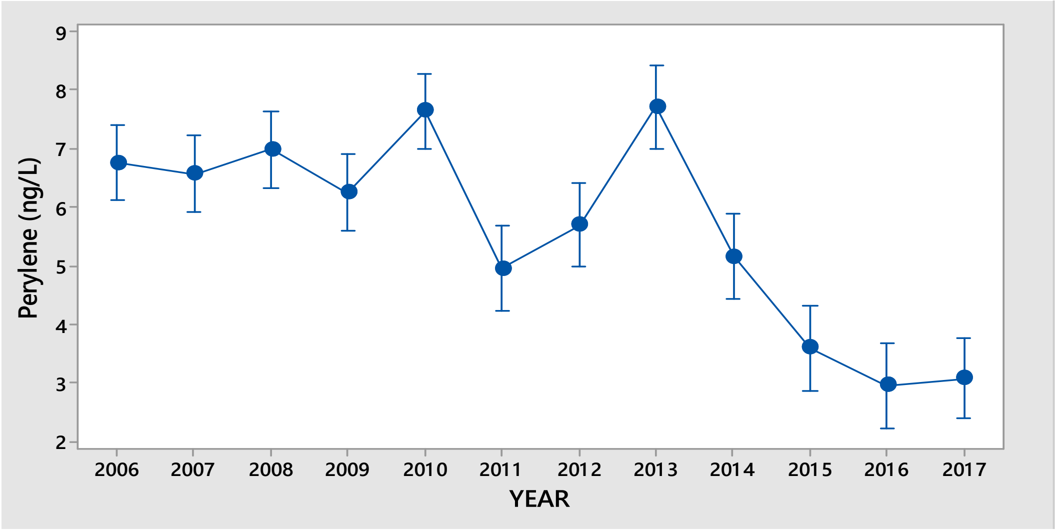
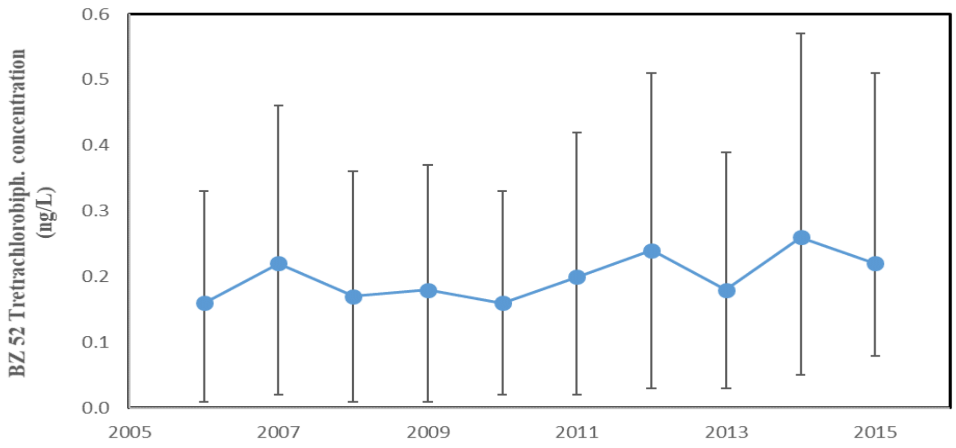
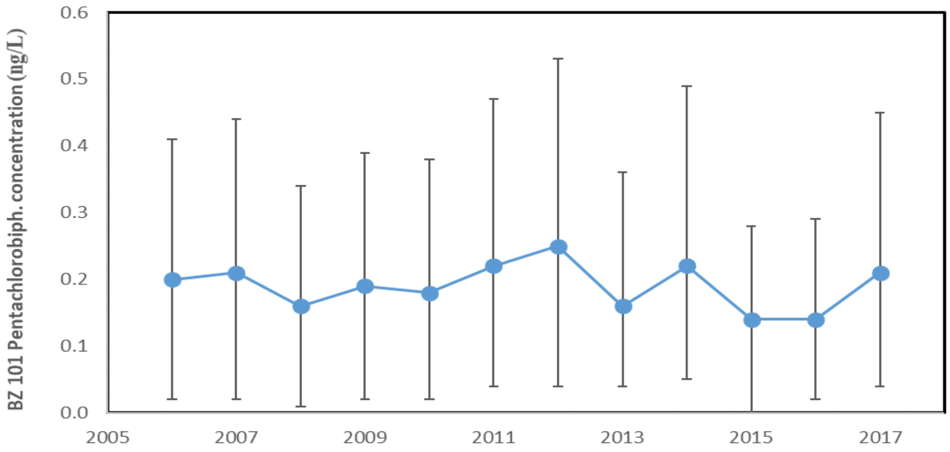


Figure 8. Temporal variation in DITP final effluent concentrations (ng/L) of PCBs and pesticides: BZ 52 Tetrachlorobiphenyl (a), BZ 101 Pentachlorobiphenyl (b), BZ 118 Pentachlorobiphenyl (c), BZ 138 Hexachlorobiphenyl (d), BZ 153 Hexachlorobiphenyl (e), BZ 180 Heptachlorobiphenyl (f), BZ 187 Heptachlorobiphenyl (g), and trans-nonachlor (h). Error bars represent 95% CI

(a)



(b)



(c)

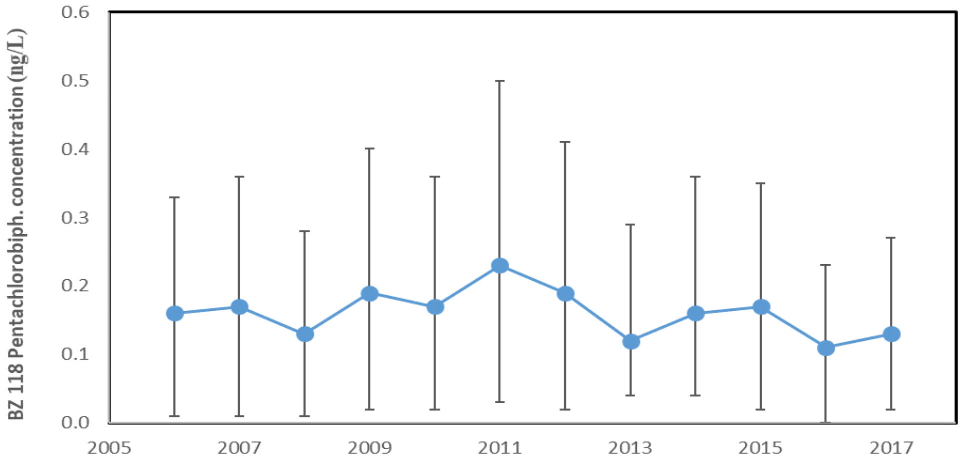


Figure 8. Temporal variation in DITP final effluent concentrations of PCBs and pesticides (continued)

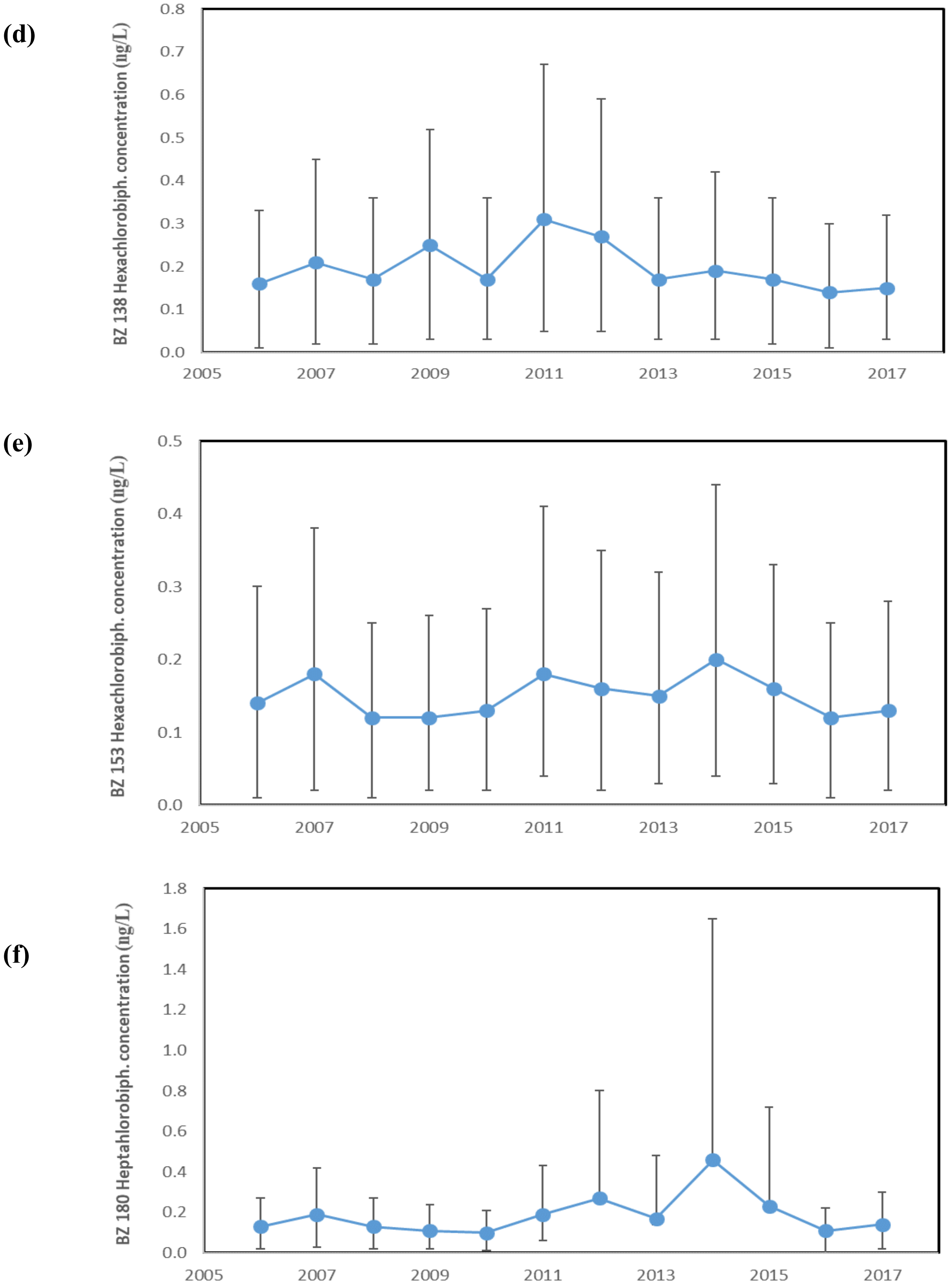
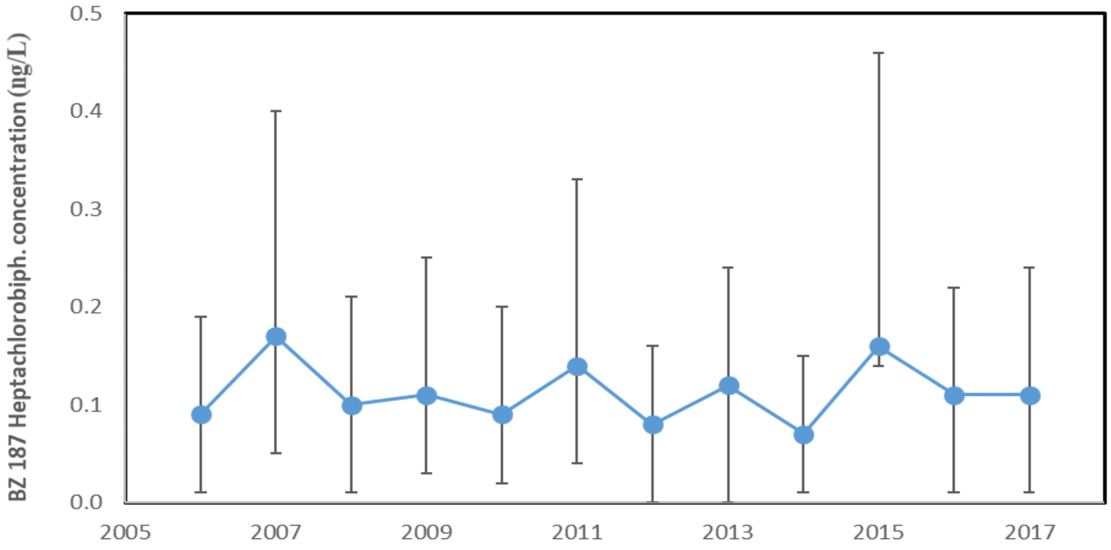
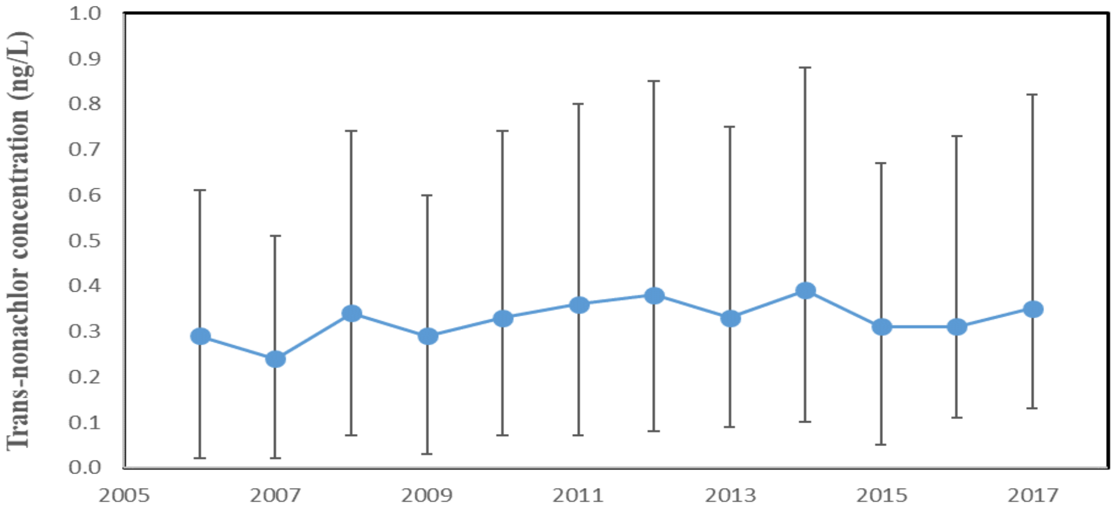


Figure 8. Temporal variation in DITP final effluent concentrations of PCBs and pesticides (continued)

(g)



(h)



4.0 CONCLUSIONS

This study analyzes more than 15 years of monitoring data for metals, PAHs, PCBs and pesticides to determine the possibility of dropping or phasing out sampling for some of these contaminants in the eventual change in the MWRA's monitoring program. The dataset is characterized by significant amounts of non-detected values for many chemicals. Survival analysis techniques were used for descriptive statistics and comparison with water quality criteria. The appropriateness of those techniques for the data at hand warrants high confidence in the outcome of the analysis. The results show that, over almost two-decade monitoring period, some contaminants were never detected in the effluent while others were at concentrations orders of magnitude lower than the EPA's water quality criteria even before accounting for dilution in Massachusetts Bay.

These results document conclusively that ongoing effluent monitoring for contaminants of concern during the development of the Ambient Monitoring Plan is environmentally protective, supporting the cessation of monitoring for these contaminants in sediments and animal tissues in the environment. Additionally, the results suggest that for some contaminants, effluent concentrations are consistently so low that the current monitoring frequency could be reviewed.

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APPENDIX A

Table A.1. Characteristics of metal data measured in the final effluent of the Deer Island Wastewater Treatment Plant in 2018 – 2019

Metal	Data years	Samples count	Detects (%)	Concentration range (ng/L)
Arsenic	2018 – 2019	44	0	—
Cadmium	2018 – 2019	92	32.6	<0.03 – 0.13
Chromium	2018 – 2019	92	26	<0.7 – 4.62
Copper	2018 – 2019	93	100	2.1 – 11.4
Lead	2018 – 2019	93	31.1	<0.28 – 3.09
Mercury	2018 – 2019	94	100	0.002 – 0.013
Nickel	2018 – 2019	92	95.6	<0.7 – 4.15
Silver	2018 – 2019	89	3.37	<0.09 – 0.10
Zinc	2018 – 2019	92	100	9.79 – 57

Table A.2. Characteristics of organics data measured in the final effluent of the Deer Island Wastewater Treatment Plant in 2018 – 2019

PAH	Data years	Samples count	Concentration range (ng/L) [a]
Acenaphthene	2018 – 2019	94	2.04 – 33.26
Anthracene	2018 – 2019	94	0.43 – 14.93
Benzo[a]anthracene	2018 – 2019	94	2.60 –27.64
Benzo[a]pyrene	2018 – 2019	94	1.26 – 18.48
Benzo[b]fluoranthene	2018 – 2019	94	2.42 – 36.09
Benzo[k]fluoranthene	2018 – 2019	94	0.92 – 12.39
Fluoranthene	2018 – 2019	94	4.79 –72.52
Fluorene	2018 – 2019	94	1.53 – 30.45
Chrysene	2018 – 2019	94	3.39 –34.85
Dibenzo[a,h]anthracene	2018 – 2019	94	0.64 –5.94
Pyrene	2018 – 2019	94	6.58 –66.77
4,4’-DDE	2018 – 2019	112	0.09 – 2.38
Alpha-chlordane	2018 – 2019	112	0.20 – 1.70
Trans-Nonachlor	2018 – 2019	90	0.08 – 0.81

a: Surrogate-corrected data. Used here and in other statistical calculations because of the importance of recovery standards in the chemical analysis of PAHs and the large differences between corrected and non-corrected concentrations.

APPENDIX B

Table B.1. Comparing concentrations of chemicals estimated in ambient water with water quality criteria (2018 – 2019)

Chemical	Unit	UCL_ambient water concentration [a]	Standard (WQC or *HHC)* [b]	Ratio Standard/ambient water
Cadmium	µg/L	0.005	7.9	1,580
Chromium	µg/L	0.306	50	163
Copper	µg/L	0.465	3.1	7
Lead	µg/L	0.071	8.1	114
Mercury	µg/L	0.004	0.94	235
Nickel	µg/L	0.643	8.2	13
Zinc	µg/L	1.170	81	69
Alpha-Chlordane	ng/L	0.010	4	400
Acenaphthene	ng/L	*0.163*	90,000 *	552,147
Anthracene	ng/L	*0.062*	40,000*	645,161
Benzo[a]anthracene	ng/L	*0.084*	1.3*	15
Benzo[a]pyrene	ng/L	*0.054*	0.13*	2
Benzo[b]fluoranthene	ng/L	*0.098*	1.3*	13
Benzo[k]fluoranthene	ng/L	*0.033*	13*	394
Chrysene	ng/L	*0.107*	130*	1,215
Dibenzo[a,h]anthracene	ng/L	*0.006*	0.13*	22
Fluoranthene	ng/L	*0.296*	20,000*	67,568
Fluorene	ng/L	*0.174*	70,000*	402,299
Indeno{1,2,3-cd]pyrene	ng/L	*0.120*	1.3*	11
Pyrene	ng/L	*0.259*	30,000*	115,830
Total PCBs	ng/L	*0.013*	0.064*	5

a: 95% upper confidence limit (UCL) of sample mean or median conservatively estimated using an average dilution factor of 70:1 in Massachusetts Bay (Roberts and Snyder, 1993, Roberts et al. 2011). Italicized values are UCLs of medians.

b: EPA's criterion continuous concentration (CCC) and human heath criteria (HHC) for the consumption of "organisms only". Values with asterisks are HHCs.

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