Contaminant Monitoring of Deer Island Treatment Plant Effluent:

2000 - 2005

Massachusetts Water Resources Authority

Environmental Quality and Laboratory Services
Departments
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EXECUTIVE SUMMARY

This report reviews the results of five years of detailed monitoring of the Massachusetts Water Resources Authority (MWRA)'s Deer Island Treatment Plant (DITP) final effluent. Intensive, low-detection-method monitoring of toxic contaminants in the effluent is required in the Ambient Monitoring Plan, which is attached to DITP's National Pollutant Discharge Elimination System (NPDES) Permit. The time-frame covered was August 2000 through July 2005, which is the time frame for the first DITP NPDES permit. Constituents studied included trace metals, cyanide, pesticides, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), volatile organic chemicals, and semivolatile organic chemicals. For pesticides, PCBs, and PAHs, higher sensitivity methods were employed than the standard NPDES-approved methods. This allowed the trace concentrations of these constituents to be detected at levels at which the NPDES-approved methods would only produce non-detects.

All laboratory results judged to be valid were included in this study. This includes all properly collected and tested samples collected for the monthly NPDES Discharge Monitoring Report (DMR) and all high sensitivity samples collected as part of the Ambient Monitoring Plan (AMP) attached to the NPDES permit.

Despite the use of specialized low-detection methods, there were many tests which yielded "non-detects" due to the low concentrations in DITP final effluent. To fully use the non-detect results, the statistical approaches described by Helsel (1990, 2005, 2005a) were used. Using statistically rigorous methods it was possible to estimate median and upper 95th percentile concentrations and produce valid trend plots and regressions that take into account the non-detect results.

Effluent concentrations and loadings were compared to previous, historical estimates and were found to generally be comparable to, or lower than, predicted. None of the contaminants were found to be present in DITP effluent at concentrations that would exceed water quality criteria after the permitted dilutions. Moreover, most of the contaminants met water quality criteria in the effluent **before** the 70:1 initial dilution that occurs at the end of the outfall tunnel where effluent is diffused into Massachusetts Bay. (The 70-fold dilution is the most conservative dilution value, the actual available dilution is usually higher.) After dilution, contaminant concentrations were well below the water quality criteria.

One group of effluent contaminants of concern during the development of MWRA's permit in the mid 1990's was PCBs, which are banned from use but can enter the sewer system via runoff. MWRA's NPDES permit has a limitation on discharges of PCBs as Aroclors; the detailed AMP effluent monitoring requires measurement of Total PCBs. Using EPA-approved methods, Aroclor mixtures were never detected in DITP effluent. However, using the most sensitive methods, a few PCB congeners were frequently detected at low parts per trillion concentrations (nanograms per Liter, ng/L), with a median Total PCB concentration of 1.4 ng/L. The current EPA national recommended water quality criterion for PCBs is 0.064 ng/L for human health consumption of water and organisms or organisms only (EPA, 2006). Assuming an available ambient dilution of 364:1 (the dilution used for human health criteria), the median Total PCB concentration in the diluted effluent would be 0.0038 ng/L—well below the water quality criterion. The average effluent Total PCB loading was less than 1 kg/year, far lower than the 50 kg/year predicted by the environmental impact studies used for planning DITP.

It is important to note that MWRA can detect relatively subtle changes in contaminant levels in its effluent because of its use of specialized, very sensitive, low-detection methods. For most contaminants, even the highest concentrations detected would meet water quality criteria in the receiving water.

TABLE OF CONTENTS

APPENDIX B. ADDENDUM TO CONTAMINANT MONITORING OF DEER ISLAND TREATMENT PLANT EFFLUENT 2000-2005: EFFLUENT DATA FOR 2005-2008

APPENDIX C. ADDENDUM TO CONTAMINANT MONITORING OF DEER ISLAND TREATMENT PLANT EFFLUENT 2000-2005: EFFLUENT DATA FOR 2005-2009

LIST OF TABLES

LIST OF FIGURES

1.0 INTRODUCTION

The Massachusetts Water Resources Authority (MWRA) was issued a permit under the National Pollutant Discharge Elimination System (NPDES) for its Deer Island Treatment Plant (DITP) to allow it to discharge treated wastewater into Massachusetts Bay beginning in August 2000. MWRA began discharge into Massachusetts Bay on September 9, 2000. In addition to the typical NPDES permit requirements, the DITP permit included an extensive Ambient Monitoring Plan (AMP) and a companion Contingency Plan (CP) that require MWRA to perform monitoring activities in Massachusetts Bay. The AMP also includes sampling and testing of the DITP effluent for contaminants that goes beyond the normal NPDES permit requirements. This report presents and interprets the results for nearly five years of detailed effluent monitoring.

This report includes results for metals, cyanide, polychlorinated biphenyls (PCBs), pesticides, polycyclic aromatic hydrocarbons (PAHs), other semivolatile organic compounds, and volatile organic compounds (VOCs).

2.0 METHODS

2.1 Sampling

When the DITP ocean outfall went on line in September 2000, the new components of the treatment plant included the outfall tunnel diffuser system, the dechlorination capability located 850 feet into the outfall tunnel, and the final effluent sampling location, designated FEFF. Because it is not physically possible to collect samples after the last treatment step, which is dechlorination, a sampling system was designed to reflect the last steps of treatment. The FEFF sampling location includes a sample loop, dechlorination process, and a permanent composite sampler. The final effluent enters the sample loop at the head end of the hypochlorite contact basin, after the treated plant effluent has been dosed with sodium hypochlorite and mixed. The sample loop runs a total of 1500 feet along the walls of the contact basin, keeping the effluent temperature the same as the wastewater in the contact basin. The flow through the sample loop is controlled by the plant flow rate so that the traverse time in the loop is the same as the plant effluent experiences as it travels through the contact basin and into the outfall tunnel to the point at which dechlorination takes place. At the end of the sample loop, the loop's effluent is dosed with bisulfite at a dosage matched to the actual plant effluent bisulfite dose. Then the dechlorinated sample loop effluent passes through the permanent composite samplers. Portable composite samplers were also used at this location when additional sample volume was needed.

All results included in this report are for 24-hour composite samples of final plant effluent, except for cyanide and VOCs, which were grab samples. The 24-hour composite samples were collected nominally from 8:00 AM until 8:00 AM the next day. These composite samples were all time-based. The permanent sampler was programmed to collect a 75-mL sample using a dipper arm every 15 minutes, which is 96 samples/day. The portable samplers were also programmed to collect a 75-mL sample every 15 minutes. The trade-offs between time-based and flow-based compositing are discussed in Appendix B.

All composite samplers were collected in pre-cleaned 10-L glass jars. All composite samples were aliquoted by mixing the composite sample and pouring into pre-cleaned glass or plastic sample containers. The grab samples were collected from the well of the permanent composite sampler directly into pre-cleaned sample containers.

A field quality control (QC) program was used to demonstrate the cleanliness of the sampling procedures. This included collecting a field equipment blank in which laboratory reagent water is passed through the composite sampler, into the sample jar, and aliquoted into the sample containers. About 150 field equipment blank samples were collected and tested for metals, pesticides/PCBs (as Aroclors) and semivolatile organic compounds using the NPDES-approved methods from August 2000 through July 2005. Most of the results were non-detects. Detected analytes in field equipment blanks are summarized in Table 1. No PAHs or PCBs (as Aroclors) were detected in field equipment blanks. The pesticides methoxychlor and 4,4'-DDT were each detected once. The semivolatiles benzoic acid and benzyl alcohol were each detected once, 2,6-dinitrotoluene was detected twice, and benzidine was detected three times. A few metals were detected a few times: chromium and silver were each detected once, copper was detected twice, iron was detected three times, and mercury was detected 8 times. Nickel was detected in nine field equipment blanks at an average of 6 µg/L. As shown in Section 3.1, nickel had a median concentration of 2.9 µg/L in DITP effluent, so it is likely that the effluent results are biased slightly high from contamination during sampling. Zinc was detected in nearly two thirds of the field equipment blanks with an average concentration in detected samples of 11 µg/L and a maximum concentration of 29 µg/L. As shown in Section 3.1, zinc had a median concentration of 27 µg/L in DITP effluent, so it is likely that the zinc effluent results are biased slightly high from contamination during sampling.

Table 1. Summary of Detected Analytes in Field Equipment Blanks.

Analyte	Number of Times Detected	Maximum Detection	Average Detection
4,4'-DDT	1	6 ng/L	
Methoxyclor	1	215 ng/L	
2,6-Dinitrotoluene	2	13 µg/L	12 µg/L
Benzidine	3	161 µg/L	74 µg/L
Benzoic Acid	1	29 µg/L	
Benzyl Alcohol	1	8 µg/L	
n-Decane	1	215 µg/L	
Chromium	1	4 µg/L	
Copper	2	15 µg/L	15 µg/L
Iron	3	43 µg/L	40 µg/L
Mercury	8	66 ng/L	24 ng/L
Nickel	9	14 µg/L	6 µg/L
Silver	1	3 µg/L	
Zinc	91	29 µg/L	11 µg/L

2.2 Quality Assurance/Quality Control

MWRA's Central Laboratory is certified for wastewater (and drinking water) testing by the Massachusetts Department of Environmental Protection (DEP). All field sampling and laboratory testing was conducted by trained and certified staff from the MWRA Department of Laboratory Services (DLS) located at the Central Laboratory at DITP. The quality assurance/quality control (QA/QC) program is described in a Quality Assurance Management Plan (MWRA 2003) and all sampling and testing procedures are described in Standard Operating Procedures (SOPs) available at the Central Laboratory.

All laboratory tests include batch QC indicators, consisting generally of a method blank, laboratory control sample, a matrix spike, and either a matrix spike duplicate, or a duplicate sample. All test results, including QC results, are entered into a Laboratory Information Management System (LIMS), either manually or electronically from the laboratory instrument's data system. Manually entered results are verified for transcription by the analyst. Then all test results are validated by a supervisor and final sample results are approved by a manager.

The current QC objectives for the effluent analytes are included in Table 2. Method Detection Limits (MDLs) were determined using the EPA procedure (40 CFR 136 App. B). The methods used in this study are based on EPA methods approved for NPDES testing, but we have pushed the detection limits as low as possible to try to avoid getting non-detects. Metals and cyanide tests were quantified down to the MDL, unless the sample required dilution. Organic tests were quantified down to a reporting limit approximately equivalent to the lowest calibration standard. However, organic test results were quantified below the reporting limit if the detection criteria were met (*e.g.* adequate signal to noise ratio, within retention time window, *etc.*).

In this report procedures were used to include non-detect results in a statistically valid way based on the work of Helsel (1990, 2005, 2005a). This avoids having to leave out non-detects or make an arbitrary decision on what numerical value to substitute for a non-detect. This is discussed in more detail in Section 3.0.

Table 2. Quality Control Objectives

Parameter	Lab Precision	Accuracy	Blank Cleanliness	MDL	MDL (revised)
Metals					
Aluminum (ICP- axial)	0-13%	88-115%	≤15 µg/L	9.4 µg/L	
Antimony (ICP- radial)	0-20%	82-128%	≤ 25 µg/L	11 µg/L	
Arsenic (GFA)	0-13%	91-120%	≤ 0.8 µg/L	0.3 µg/L	
Beryllium (ICP- radial)	0-5%	91-106%	≤ 0.5 µg/L	0.5 µg/L	
Boron (ICP- radial)	0-30%	93-110%	≤ 250 µg/L	7.0 µg/L	
Cadmium (GFA)	0-10%	76-124%	≤ 0.03 µg/L	0.03 µg/L	
Chromium (GFA)	0-14%	82-126%	≤ 0.7 µg/L	0.1 µg/L	
Copper (ICP- radial)	0-5%	82-111%	≤ 10 µg/L	1.0 µg/L	
Copper (GFA)	0-20%	82-114%	≤ 1.0 µg/L	0.4 µg/L	
Copper (ICP/MS)	0-20%	80-120%	≤ 10 µg/L	0.10 µg/L	
Iron (ICP- radial)	0-5%	86-105%	≤ 30 µg/L	0.8 µg/L	
Lead (ICP/MS)	0-20%	80-120%	≤ 2.0 µg/L	0.05 µg/L	
Lead (GFA)	0-24%	93-126%	≤ 2.4 µg/L	0.3 µg/L	
Mercury (CVAA)	0-9%	83-118%	≤ 0.01 µg/L	0.01 µg/L	
Mercury (CVAF)	0-24%	85-115%	≤ 0.50 ng/L	0.10 ng/L	
Molybdenum (GFA)	0-10%	68-117%	≤1.0 µg/L	0.4 µg/L	
Nickel (GFA)	0-8%	90-127%	≤ 0.7 µg/L	0.8 µg/L	
Selenium (GFA)	0-16%	88-122%	≤ 0.9 µg/L	0.2 µg/L	
Silver (GFA)	0-16%	82-116%	≤ 0.09 µg/L	0.02 µg/L	
Thallium (GFA)	0-15%	89-125%	≤ 1.0 µg/L	0.6 µg/L	
Zinc (ICP- axial)	0-6%	89-107%	≤ 1.5 µg/L	0.2 µg/L	
Inorganics					
Cyanide	0-62%	78-118%	≤ 0.01 mg/L	0.004 mg/L	

Parameter	Lab Precision	Accuracy	Blank Cleanliness	MDL	MDL (revised)
PCBs [1]				**Previous MDL**	**New MDL**
2,4-Cl_2(8)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.5 ng/L	0.2 ng/L
2,2’,5-Cl_3(18)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.2 ng/L
2,4,4'-Cl_3(28)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.7 ng/L	0.3 ng/L
2,2',3,5'-Cl_4(44)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.8 ng/L	0.3 ng/L
2,2',5,5'-Cl_4(52)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.7 ng/L	0.2 ng/L
2,3',4,4'-Cl_4(66)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.8 ng/L	0.3 ng/L
3,3',4,4'-Cl_4(77)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.8 ng/L	0.3 ng/L
2,2'4,5,5'-Cl_5(101)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.8 ng/L	0.2 ng/L
2,3,3',4,4'-Cl_5(105)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.7 ng/L	0.2 ng/L
2,3',4,4'5-Cl_5(118)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.7 ng/L	0.2 ng/L
3,3',4,4',5-Cl_5(126)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.1 ng/L
2,2',3,3,4,4'-Cl_6(128)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.5 ng/L	0.1 ng/L
2,2',3,4,4',5-Cl_6(138)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.2 ng/L
2,2'4,4',5,5'-Cl_6(153)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.2 ng/L
2,2'3,3,4,4',5-Cl_7(170)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.9 ng/L	0.2 ng/L
2,2',3,4,4',5,5'-Cl_7(180)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.5 ng/L	0.3 ng/L
2,2',3,4,5,5',6-Cl_7(187)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.2 ng/L
2,2',3,3',4,4',5,6-Cl_8(195)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.9 ng/L	0.2 ng/L
2,2',3,3'4,4',5,5',6-Cl_9(206)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.3 ng/L
Decachlorobiphenyl-Cl_{10}(209)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.3 ng/L
PAH [2]					
Naphthalene	≤ 30% RPD	50-150%	≤ 5 ng/L	2.4 ng/L	3.8 ng/L
C_1-naphthalenes	≤ 30% RPD	50-150%	≤ 5 ng/L	2.4 ng/L	3.8 ng/L
C_2-naphthalenes	≤ 30% RPD	50-150%	≤ 5 ng/L	2.4 ng/L	3.8 ng/L
C_3-naphthalenes	≤ 30% RPD	50-150%	≤ 5 ng/L	2.4 ng/L	3.8 ng/L
Acenaphthylene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.3 ng/L	0.7 ng/L
Acenaphthene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.7 ng/L	0.7 ng/L
Fluorene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.3 ng/L	0.4 ng/L
C_1-fluorenes	≤ 30% RPD	50-150%	≤ 5 ng/L	4.3 ng/L	0.4 ng/L
C_2-fluorenes	≤ 30% RPD	50-150%	≤ 5 ng/L	4.3 ng/L	0.4 ng/L
C_3-fluorenes	≤ 30% RPD	50-150%	≤ 5 ng/L	4.3 ng/L	0.4 ng/L
Anthracene	≤ 30% RPD	50-150%	≤ 5 ng/L	3.1 ng/L	0.6 ng/L
Phenanthrene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.3 ng/L	0.8 ng/L
C_1-phenanthrenes/anthracene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.3 ng/L	0.8 ng/L
C_2-phenanthrenes/anthracene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.3 ng/L	0.8 ng/L
C_3-phenanthrenes/anthracene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.3 ng/L	0.8 ng/L
C_4-phenanthrenes/anthracene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.3 ng/L	0.8 ng/L
Dibenzothiophene	≤ 30% RPD	50-150%	≤ 5 ng/L	1.5 ng/L	0.2 ng/L
C_1-dibenzothiophenes	≤ 30% RPD	50-150%	≤ 5 ng/L	1.5 ng/L	0.2 ng/L
C_2-dibenzothiophenes	≤ 30% RPD	50-150%	≤ 5 ng/L	1.5 ng/L	0.2 ng/L
C_3-dibenzothiophenes	≤ 30% RPD	50-150%	≤ 5 ng/L	1.5 ng/L	0.2 ng/L
Fluoranthene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.0 ng/L	0.2 ng/L
Pyrene	≤ 30% RPD	50-150%	≤ 5 ng/L	3.6 ng/L	0.5 ng/L
C_1-fluoranthenes/pyrenes	≤ 30% RPD	50-150%	≤ 5 ng/L	3.6 ng/L	0.5 ng/L

Parameter	Lab Precision	Accuracy	Blank Cleanliness	MDL	MDL (revised)
(PAHs cont) benzo(a)anthracene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.2 ng/L	0.2 ng/L
Chrysene	≤ 30% RPD	50-150%	≤ 5 ng/L	5.0 ng/L	0.2 ng/L
C_1-chrysene	≤ 30% RPD	50-150%	≤ 5 ng/L	5.0 ng/L	0.2 ng/L
C_2-chrysene	≤ 30% RPD	50-150%	≤ 5 ng/L	5.0 ng/L	0.2 ng/L
C_3-chrysene	≤ 30% RPD	50-150%	≤ 5 ng/L	5.0 ng/L	0.2 ng/L
C_4-chrysene	≤ 30% RPD	50-150%	≤ 5 ng/L	5.0 ng/L	0.2 ng/L
benzo(b)fluoranthene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.8 ng/L	0.4 ng/L
benzo(k)fluoranthene	≤ 30% RPD	50-150%	≤ 5 ng/L	2.8 ng/L	0.2 ng/L
benzo(a)pyrene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.7 ng/L	0.4 ng/L
dibenzo(a,h)anthracene	≤ 30% RPD	50-150%	≤ 5 ng/L	2.9 ng/L	0.2 ng/L
benzo(g,h,i)perylene	≤ 30% RPD	50-150%	≤ 5 ng/L	3.8 ng/L	0.2 ng/L
Indeno(1,2,3-c,d)pyrene	≤ 30% RPD	50-150%	≤ 5 ng/L	4.7 ng/L	0.3 ng/L
Perylene	≤ 30% RPD	50-150%	≤ 5 ng/L	1.7 ng/L	0.3 ng/L
Biphenyl	≤ 30% RPD	50-150%	≤ 5 ng/L	1.9 ng/L	0.2 ng/L
benzo(e)pyrene	≤ 30% RPD	50-150%	≤ 5 ng/L	0.6 ng/L	0.3 ng/L
Dibenzofuran	≤ 30% RPD	50-150%	≤ 5 ng/L	4.5 ng/L	0.3 ng/L
Benzothiazole	≤ 30% RPD	50-150%	≤ 5 ng/L	5.8 ng/L	1.9 ng/L
Pesticides [1]					
Hexachlorobenzene	≤ 30% RPD	50-150%	≤1.0 ng/L	0.5 ng/L	0.3 ng/L
Lindane (gamma- BHC)	≤ 30% RPD	50-150%	≤1.0 ng/L	0.5 ng/L	0.3 ng/L
Heptachlor	≤ 30% RPD	50-150%	≤1.0 ng/L	0.4 ng/L	0.4 ng/L
Aldrin	≤ 30% RPD	50-150%	≤1.0 ng/L	0.5 ng/L	0.3 ng/L
Heptachlorepoxide	≤ 30% RPD	50-150%	≤1.0 ng/L	0.4 ng/L	0.1 ng/L
Alpha-chlordane	≤ 30% RPD	50-150%	≤1.0 ng/L	0.4 ng/L	0.2 ng/L
Trans-Nonachlor	≤ 30% RPD	50-150%	≤1.0 ng/L	0.8 ng/L	0.3 ng/L
Dieldrin	≤ 30% RPD	50-150%	≤1.0 ng/L	0.4 ng/L	0.3 ng/L
Endrin	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.2 ng/L
Mirex	≤ 30% RPD	50-150%	≤1.0 ng/L	1.0 ng/L	0.2 ng/L
2,4’-DDD	≤ 30% RPD	50-150%	≤1.0 ng/L	0.8 ng/L	0.2 ng/L
4,4’-DDD	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.3 ng/L
2,4’-DDE	≤ 30% RPD	50-150%	≤1.0 ng/L	0.7 ng/L	0.2 ng/L
4,4’-DDE	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.3 ng/L
2,4’-DDT	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.2 ng/L
4,4’-DDT	≤ 30% RPD	50-150%	≤1.0 ng/L	0.7 ng/L	0.3 ng/L
DDMU	≤ 30% RPD	50-150%	≤1.0 ng/L	0.7 ng/L	0.3 ng/L
Gamma-Chlordane	≤ 30% RPD	50-150%	≤1.0 ng/L	0.5 ng/L	0.2 ng/L
Cis-Nonachlor	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.2 ng/L
Oxychlordane	≤ 30% RPD	50-150%	≤1.0 ng/L	0.6 ng/L	0.4 ng/L

1. New MDLs from ADOC #2005-31
2. New MDLs from ADOC #2004-32

2.3 Analytical Procedures

2.3.1 Metals

Several methods were used for metals testing, depending on the concentration in the samples and the sensitivity of the method, following EPA series 200 methods (EPA 1983) except as noted. Inductively Coupled Plasma Optical Emission Spectrometry (ICP) was used for aluminum, antimony, boron, beryllium, copper, iron, and zinc (Method 200.7). Graphite Furnace Atomic Absorption Spectrometry (GFAA) was used for arsenic, cadmium, chromium, copper, molybdenum, nickel, selenium, silver, and thallium (EPA Method 200 series). To meet a requirement in the DITP NPDES permit to use "an EPA approved method with the lowest minimum detection level possible" (EPA 2000, p. 4), a monthly sample was sent out to a contract laboratory for ICP/Mass Spectrometry testing for copper and lead by EPA Method 200.8. Cold vapor atomic absorption (CVAA) spectrometry by EPA Method 245.2, or cold vapor atomic fluorescence (CVAF) spectrometry by EPA Method 1631 was used for mercury. EPA Methods 200.8 and 1631 were performed by contract laboratories.

Metals digestion. Acid-preserved, unfiltered samples are digested for total metals other than mercury according to the EPA 200 Series method (EPA 1983) by heating at approximately 85°C with concentrated acids. The samples are refluxed until all elements have been freed from any complexing organic molecules and sample volume reduced. The samples are then filtered to remove any insoluble material and brought up to volume using deionized water.

Graphite Furnace Atomic Absorption Spectrometry. In GFAA a controlled temperature program dries, ashes, then atomizes a sample within a graphite tube. A light beam from a hollow cathode or electrode-less discharge lamp is directed through the tube into a monochromator. A detector measures the amount of light absorbed by the sample as it is atomized. The light energy absorbed is a measure of the analyte concentration.

Inductively Coupled Plasma Atomic Emission Spectrometry. In ICP analysis an aerosol generated in a nebulizer and spray chamber from an acidified solution is carried into an inductively coupled argon plasma. The high temperature of the plasma (6000-8000 K) excites elements to emit light of characteristic wavelength. The emitted light is dispersed by a grating spectrometer and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive detector. Background and spectral interferences are corrected mathematically. ICP/MS analysis uses a similar nebulizer and plasma torch, but the ions generated by the plasma are introduced into a low-resolution quadrupole mass spectrometer.

Cold Vapor Atomic Absorption and Atomic Fluorescence Spectrometry. Aqueous samples for mercury are tested according to EPA method 245.2. An acid-preserved aqueous sample is prepared for cold vapor atomic absorption spectrometry by acidifying, then oxidizing using potassium permanganate and potassium persulfate. The sample is then heated in a water bath for two hours at 95 C to accelerate the oxidation of all mercury to the inorganic form. The digested sample, with mercury in the divalent form (Hg^{++}), enters the CVAA instrument and is mixed with a reducing agent ($SnCl_2$) to form elemental mercury vapor. The mixture flows into a liquid-gas separator where argon is introduced to carry the mercury vapor through a drying tube for water vapor removal. The dry vapor then enters one path of a double path optical cell, which has been optimized for fast response time (small diameter) and sensitivity (long length). A mercury source, powered by a constant current power supply, delivers a stable source of emission at 254 nm. Absorbance by the mercury cold vapor is measured using a solid state detector with a wide dynamic range. The resulting signal is referenced to the simultaneous absorbance of the pure carrier gas flowing through the second optical path under ideal conditions. The CVAF method uses a similar approach except that mercury is oxidized during digestion with BrCl and the instrumental measurement is made by atomic fluorescence instead of atomic absorption. A gold trap is used to preconcentrate the mercury vapors which give Method 1631 very high sensitivity.

2.3.2 Cyanide

Grab samples are tested for total cyanide by midi-distillation and semi-automated colorimetry (autoanalyzer) using a modification of EPA Method 335.2. Samples are collected in plastic containers. Samples are tested for oxidizing substances (chlorine) and sulfides at the time of collection. If oxidizing substances or hydrogen sulfide, are present, the sample is pretreated. Then samples are preserved with sodium hydroxide (NaOH) to pH >12. Cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a manual reflux-distillation operation with mineral acid in the presence of magnesium ion and absorbed in a scrubber containing sodium hydroxide solution. In a colorimetric measurement using an autoanalyzer, cyanide is converted to cyanogen chloride (CNCl) by reaction of cyanide with chloramine-T at pH 8. After reaction is complete, a colored complex is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 570 nm for the complex formed with pyridine-barbituric acid reagent and CNCl.

2.3.3 Polychlorinated Biphenyls

Polychlorinated Biphenyls (PCBs) consist of a biphenyl backbone (two benzene rings linked by a single bond between one carbon atom on each benzene ring) with one to ten chlorines substituting for the hydrogen atoms on the two benzene rings. There are a total of 209 possible PCB congeners (isomers) ranging from mono-chloro-biphenyl to deca-chloro-biphenyl. The congeners are enumerated systematically from 1 to 209 with increasing level of chlorination from mono-chloro- to deca-chloro-biphenyls (Ballschmiter and Zell 1980).

Since 1929, mixtures of PCB congeners were prepared and sold for a variety of uses, including in plasticizers, surface coatings, inks, adhesives, flame retardants, pesticide extenders, and paints (World Health Organization 2003). PCBs are persistent in the environment. EPA banned most uses of PCBs in 1979.

Each month, three types of PCB analysis were performed on composite samples for DITP effluent:

- Aroclors by Method 608 (EPA 1984)
- Twenty PCB congeners by modified Method 608 or 8270
- “Total PCBs” using sixty seven PCB congeners by modified Method 608

In addition, each month samples of the fertilizer pellets prepared from DITP biosolids (digested sludge) were tested by Method 8080.

Aroclors by Methods 608 and 8080. For the monthly Discharge Monitoring Report, one effluent composite sample is tested each month for Aroclors using the NPDES approved Method 608 (40 CFR Part 136). A measured portion of the aqueous sample is serially extracted at a neutral pH with methylene chloride. The collected extract is then concentrated and solvent exchanged into hexane. The extract may then undergo one or more cleanup procedures to remove various interferences, depending on the nature of the sample. After concentration and any cleanup procedure, the extract is spiked with a retention time internal standard and injected onto the gas chromatograph (GC). The analytes are separated by the GC and detected by an electron capture detector (ECD). Qualitative determination of Aroclors is based on retention time matching of several peaks on two dissimilar high resolution GC columns. Quantitative determination of the Aroclors is based on the area of the GC/ECD peaks, by comparison of the area response against an injected standard for that Aroclor.

Fertilizer pellet samples are tested for Aroclors using EPA Method 8080 (SW-846, see www.epa.gov/epaoswer/hazwaste/test/sw846.htm). This method is similar to Method 608 except that it was specifically developed for soils and other solid samples. A nominal aliquot (3.0 g) of soil/sediment sample is spiked with the surrogate solution and then mixed with anhydrous sodium sulfate and serially extracted (3x) with 1:1 acetone/methylene chloride solvent mixture by sonication. The extract is then filtered, concentrated, solvent exchanged into hexane, adjusted to 10 mL final volume and cleaned up. The extract is analyzed by GC/ECD as discussed above.

Twenty PCB congeners by modified Method 608 or 8270. For the AMP, each week one effluent composite sample is tested for 20 PCB congeners. The 20 PCB congeners are known as the “NOAA list” because these are the congeners that have been monitored for years in the National Oceanic and Atmospheric Administration’s (NOAA) “Mussel Watch” program (Lauenstein 1993). They are also the same congeners that are monitored in the fish and shellfish and the benthic sediments part of the AMP.

A 2-L sample is extracted by passing the sample through a C-18 bonded solid phase extraction disk. The extract is eluted from the disk with methylene chloride. The solvent is evaporated and exchanged to hexane. The sample extract is cleaned up by back extraction with sulfuric acid and a neutral bicarbonate solution. The extract is dried over sodium sulfate and concentrated to a final volume of 1 mL, or 2mL if sample matrix has heavy matrix background.

In modified Method 608, the extract is spiked with a retention time internal standard and injected onto the gas chromatograph (GC). The analytes are separated by the GC and detected by an electron capture detector (ECD). Qualitative determination of individual congeners is based on retention time matching on two dissimilar high resolution GC columns. Quantitative determination of the individual congeners is based on the area of the GC/ECD peak, by comparison of the area response against a series of injected standards for that congener.

In modified method 8270, methylene chloride sample extracts are analyzed by GC/Mass Spectrometry (MS) operating in the Selected Ion Monitoring (SIM) mode. For increased sensitivity the SIM mode monitors a set of specific masses that are typical of the PCB congeners, rather than scanning complete mass spectra. Two GC runs are performed for each sample, one analysis to determine the congener compounds and one analysis for the pesticide compounds. The target analytes are identified by their characteristic primary and secondary (confirmation) ions, and by their retention times as compared to the analytical standards. Quantitation is performed using the internal standard technique.

In both of these methods the “Total PCBs” result is computed as the arithmetic total of all detected congeners. If no congeners are detected, the Total PCB result is the normal single congener reporting limit.

“Total PCBs” using sixty seven PCB congeners by modified Method 608. The DITP NPDES permit requires that the effluent be tested each month for “Total PCBs”, but at present there isn’t a NPDES-approved method for Total PCBs. So, MWRA developed a dual-column high resolution GC-ECD based on EPA Methods 608 that measures 67 of the 209 possible PCB congeners. MWRA carefully selected the 67 congeners to cover the major constituents of each Aroclor mixture. These 67 congeners cover over 80% of each Aroclor mixture with the exception of Aroclor 1232 where the coverage is only 58% (Frame *et al.* 1996).

The coverage from the 67 congeners is skewed toward the heavier Aroclors, because these tend to show up more frequently in MWRA wastewater compared to lighter Aroclors. But even for the lightest Aroclors, the 67 congeners gives 87% coverage for 1016 and 58% for 1232, so any significant amounts of even the lighter Aroclors in the effluent would be detected. Weathering, or other processes, will distort the Aroclor patterns, but the congener-specific analysis will still detect the presence of these congeners, so the Total PCB result should be independent of the degree of weathering.

MWRA believes that 67 congeners is adequate because the remaining 142 congeners each make only a fraction of one percent contribution to the coverage. Additionally the list of 67 congeners includes 11 of the 12 congeners listed by the World Health Organization (EPA, 1999b) as "toxic" congeners. These 12 dioxin-like congeners are also included in the proposed EPA rule for monitoring dioxin-like compounds in sewage sludge (EPA 1999a). One congener, BZ-81 (3,4,4',5-tetrachlorobiphenyl), is not included in MWRA's 67-congener list. This congener is reported by Frame *et al.* (1996) to have no higher than 0.02 weight percent abundance in any Aroclor mixture, so its absence will not affect MWRA's Total PCB results.

MWRA determined the performance characteristics of this method and submitted it to EPA-Region I for review in 2000. In this method the "Total PCBs" result is computed as the arithmetic total of all detected congeners. If no congeners are detected, the Total PCB result is the normal single congener reporting limit. In May, 2006, EPA-Region I completed its review of this method and approved it.

Subsequent to the issuing of the DITP NPDES permit, USEPA has redefined Total PCBs to be "the sum of all homolog, all isomer, all congener, or all Aroclor analyses" (EPA 2002). However, at present USEPA only has a NPDES-approved test method for Aroclors and it is unclear how this definition would be used to derive a numeric criterion for Total PCBs in a future NPDES permit. At some point USEPA may approve for NPDES use a congener-based Total PCB method (*e.g.* Method 1668A).

2.3.4 Pesticides

Selected pesticides are determined using the same methods as for PCBs as described in the previous section.

2.3.5 Polycyclic Aromatic Hydrocarbons (PAH)

Polycyclic aromatic hydrocarbons (PAH) consist of fused aromatic rings. In addition to the individual target PAH compounds, the analysis estimates concentrations of certain alkyl-substituted PAH homologues. Aqueous samples for PAH are prepared and analyzed by modified EPA method 625 (EPA 1984). Samples are phase-extracted with methylene chloride without performing any pH adjustment to the sample. Methylene chloride sample extracts are analyzed by GC/MS operating in the Selected Ion Monitoring (SIM) mode. Target compounds are identified by their characteristic primary and secondary ions and by their retention times. Quantitation is performed using the internal standard technique. Alkyl-substituted PAH homologues concentrations are determined using the response factors of the parent PAH compound.

2.3.6 Other Semivolatile Organic Compounds

EPA Method 625 (EPA 1984) is used to test composite samples for extractable semivolatile organic compounds (or chemicals). This is also referred to as the Acid Base Neutral (ABN) test. The aqueous sample is phase-extracted serially with methylene chloride, first at a pH>11 for all base/neutral compounds, and again at a pH<2 for all acidic (phenolic) compounds. Adjustment of the sample pH ensures the solubility of the different compound classes in the organic solvent. The collected extract is dried, concentrated and analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) operating in the full scan mode. Target compounds are identified by comparison of the retention times and mass spectra with those in analytical standards run on the same GC/MS. Quantitation of compounds is conducted using the internal standard method.

2.3.7 Volatile Organic Compounds

EPA method 624 (EPA 1984) is used to test grab samples for volatile organic compounds (or chemicals) (VOCs) by gas chromatography/mass spectrometry (GC/MS). Standards and samples are purged with helium at ambient temperature and the volatile organic purgeable compounds are displaced and collected on a trap. The trap is then heated and back flushed with helium to desorb the purgeables onto a GC column. The GC is temperature-programmed to separate the purgeable organics. Individual compounds are detected by a mass spectrometer.

2.4 Treatment Plant Information

Information included in this report was provided by the DITP Process Control unit. Plant flows are measured by flow meters, and electronic readings are recorded by the Process Information and Control System (PICS). These results are reviewed by the Process Control unit to remove any spurious readings and the reviewed results are stored in an electronic database.

In particular for this report, the daily DITP plant flow was recorded in million gallons per day (MGD). Measured concentrations are multiplied by plant flow to compute loadings. For most contaminants the concentration will be from a 24-hour composite sample, thus representing the average effluent concentration for that time period. This average concentration is multiplied by the plant flow for the same 24-hour period, resulting in the effluent loading for that 24-hour period.

Metric units for loadings are in kilograms (kg) per day or per year. English units are in pounds (lbs) per day or per year. Pounds per day can be converted to kilograms per day by dividing by 2.2, or to kilograms per year by multiplying by 165 (since 365 / 2.2 = 165).[1]

2.5 NPDES Permit Effluent Discharge Limits: Dilution Factors

Before the effluent monitoring results are presented, it is instructive to discuss the process for setting NPDES permit effluent discharge limits, because these limits are the threshold that determines whether the effluent will contribute to an exceedance of an ambient water quality criterion.

EPA proposes, and States adopt, water quality criteria that set ambient levels of individual pollutants that will generally protect the designated use of the receiving water (e.g. fishable, swimmable) (EPA 1996). EPA's efforts on criteria development have been focused on the list of 126 "priority toxic pollutants". The NPDES permit writer needs to determine "whether a discharge causes, has the "reasonable potential" to cause, or "contributes to an excursion above an applicable narrative or numerical water quality criterion" (EPA 1996). This is best accomplished by using actual effluent and ambient monitoring data and a water quality model of the receiving water system.

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[1] To convert to metric tons (1000 Kg) or English tons (2000 lbs), use the formulas: 1 kg = 2.2046 lbs, 1 gal = 3.785 L, Therefore, if the density of water is 1.000 kg/L, a gallon of water weighs 8.344 pounds.

For the 2000 DITP NPDES permit, EPA and the Massachusetts Department of Environmental Protection (MA-DEP) used the Roberts physical scale model of the DITP ocean outfall (Roberts and Snyder 1993). This was a simulation of the outfall in a large tank under carefully controlled conditions.

Attachment S of the 2000 permit shows a sample permit limit calculation using the dilution factors derived from the Roberts model and using the following mathematical equation:

$$C_l = C_a + [(C_c - C_a)/(1/S_n + 1/S_b - 1/(S_n)(S_b))]$$

where:

C_l = water quality limitation
= the level of a pollutant that is acceptable to meet water quality criteria. (i.e. the NPDES permit limit)

C_a = maximum ambient data sample
= level of a pollutant that is sampled from the water column, within fairly close distance to the outfall discharge area.

C_c = water quality criterion
= level set as the criterion to meet without dilution.

S_n = nearfield initial dilution
= 70:1

S_b = background farfield dilution
= 150:1 (occurs at a 990 MGD flow rate);
= 256:1 (occurs at a 690 MGD flow rate); and
= 364:1 (occurs at the long-term average flow rate).

The dilution factors were selected by EPA to be the worst-case situation—that is, when dilution was at the lowest. Nearfield initial dilution of at least 70:1 was predicted to occur when Massachusetts Bay was highly stratified and when there were no currents. Roberts and Snyder (1993) showed that this initial dilution varies with effluent flow rate and this was taken into account in Attachment S of the NPDES permit: 71.3: 1 at 990 MGD and 79.5:1 at 690 MGD.

Background farfield dilution takes into account "background build-up entrainment"—that is, effluent discharged from the outfall moves back and forth with the tides, building up the concentration of pollutants somewhat. Farfield dilution factor estimates came from the Signell/HydroQual mathematical hydrodynamic model of Massachusetts Bay (Signell *et. al,* 1996).

There were three background farfield dilution factors that were used with the three kinds of water quality criteria:

- Acute Criteria—90th percentile of the hourly average flow (990 MGD) gives a farfield dilution of 150:1.
- Chronic Criteria—90th percentile of the 4-day running average flow (690 MGD) gives a farfield dilution of 256:1.
- Human Health Criteria—50th percentile of the 4-day running average flow (long-term average flow rate) gives a farfield dilution of 364:1.

A dye-dilution plume-tracking field study (Hunt *et al*. 2002) showed that the outfall was performing as expected with measured dilutions consistent with results from the original physical model studies and the mathematical model used to design the outfall:

> *"Dilution of ~85 was observed in the field data within ~50 meters of the diffuser line which slowly increased to ~105 three hundred meters from the diffusers. Oceanographic mixing and dispersion further increased the dilution after the dye had exited the outfall system. Dilutions of 200 to 400 were measured 24 hours following discharge. It is concluded that the outfall is behaving as expected and that acceptable water quality is being achieved at the outfall."*

The ambient, or background concentration, used in this calculation is also a worst-case situation. It is the highest reported concentration in the receiving water that is collected within the closest distance to the outfall discharge area. For most pollutants, the ambient concentration is much less than the water quality criterion, that is, $C_a << C_c$. In this case C_a is negligible in the calculation. So, if the ambient concentration of a contaminant is low in Massachusetts Bay, as is generally the case, the effluent gets diluted by at least 70:1 as it comes out of the outfall and is diluted much further after that.

EPA's NPDES Permit Writer's Manual (EPA 1996) describes a statistically-based approach for taking into account variability in effluent monitoring data to estimate a maximum concentration for the effluent for a given parameter. The statistical tables included in this manual only go up to a sample size of n=20 and the text does not address how to handle non-detects. The approach uses observed maximum effluent concentration, the assumption of a log-normal distribution, and an estimate of the coefficient of variation (CV = mean/standard deviation) to estimate the upper confidence bound (95th or 99th) on an upper percentile (95th or 99th) of the effluent concentration distribution for a specified sample size. A recent WERF report (Warren-Hicks *et al*. 2006) examined this "double-bounded" statistical approach and found it to be statistically "inefficient" (more variable than necessary and less precise than possible) and advocates for a Maximum Likelihood Estimator (MLE) approach. For example, they showed by computer simulation that even for a sample size as large as n=100 the EPA approach has a 40% probability of estimating a 99th percentile that is more than twice the true 99th percentile. This overly conservative inefficient approach tends to find "reasonable potential" when it truly is not (e.g. false positive).

In this report we compiled tens to hundreds of results for each trace contaminant collected over the five years of the NPDES permit and report the observed median, maximum, and 95th percentile concentrations. These can be compared to the applicable water quality criteria after taking into account a suitable dilution factor.

3.0 RESULTS AND DISCUSSION

Detection Limits and Numerical Results. How best to handle laboratory results below or near the method detection limit (MDL) has long been an active area of research in environmental science. D. R. Helsel (1990) has been a leader in this area. He refers to "non-detects," or "less than" values, as "censored" results. Environmental results are often "left censored" since there are often censored results at low concentrations. Right-censored, or "greater than" values are less common.

Helsel (2005, 2005a) examined the three approaches to handling non-detects. The first approach, substitution, consists of "fabricating" values for the non-detects, such as zero, the detection limit, half the detection limit, etc. This approach is easy and widely used, but has "no theoretical basis" (Helsel, 2005a). It is arbitrary and yields biased and highly variable estimates of population parameters (Helsel 2005). The second approach, maximum likelihood estimation, has only been used sporadically in environmental studies (Helsel 2005a). By assuming a mathematical form, or shape, for the distribution of results, the detected values are used to estimate numerical values for the non-detected values. Helsel (2005a) feels this is the method of choice when there are at least 50 observations and either the proportion of non-detects is small or the form of the distribution is well known. Implementing this approach requires fairly sophisticated mathematical manipulations.

The third approach, nonparametric methods, offers a middle ground, because it avoids making assumptions about the distribution and does not require sophisticated calculations. Instead of computing parameters of the data, such as mean and standard deviation, in this approach the relative positions (ranks) of the data are used. For example, the median of a set of results is the value that is in the middle when the results are placed in order. The median (the 50th percentile) can be computed without making assumptions about the distribution of the data as long as fewer than half the results are non-detect. Nonparametric methods are now commonly used in environmental studies (Helsel 2005).

We have pushed all of the analytical methods in this study as low as possible using standard environmental laboratory methods (e.g. GC/MS, ICP, GFAA, etc.) to minimize non-detects, but for many variables most of the results are still non-detect. Generally, results above the MDL, or a reporting limit (RL) as in the case of the multi-component organics tests, have been recorded in our Laboratory Information Management System as a numerical result. Below this, results are recorded as <MDL or <RL. For GC/MS selected ion monitoring (SIM) tests, we have reported numerical results below the MDL when all identification criteria were met (correct retention time and mass peaks).

In this report we used graphical and statistical procedures that can appropriately handle non-detect results, as discussed by Helsel (2005a). The procedures are included in the Minitab (Version 14 from www.minitab.com) software package supplemented by additional macros from Helsel (www.practicalstats.com/nada). To use these procedures two simple encoding procedures are used. In the first, a non-detect flag is used: "0" for a detect, and "1" for a non-detect. In the second approach results are represented as an interval: from START to END. A non-detect has an interval from 0 to the detection or reporting limit. A detect value has the same START and END value. A simple example is given in Table 3 for two results: <2.4 and 4.17:

Table 3. Example of Encoding for Non-Detects.

RESULT	ND	START	END
<2.4	1	0	2.4
4.17	0	4.17	4.17

This encoding is simple to perform in an EXCEL spreadsheet and it is used with ease in Minitab.

When a parameter had less than 50% non-detects, the non-parametric Turnbull approach was used. (In Minitab: Stat > Reliability/Survival > Distribution Analysis – Arbitrary Censoring > Nonparametric Distribution Analysis). This is similar to the non-parametric Kaplan-Meier approach (In Minitab: Stat > Reliability/Survival > Distribution Analysis – Right Censoring > Nonparametric Distribution Analysis), but to use K-M, the data must be “flipped” to transform it into right-censored data (instead of left-censored). This means subtracting each data point from an arbitrary number that is larger than every data point. For example, if a concentration result is <250 µg/L, and a flipping constant of 1000 is used, instead of representing this result as START=0, END=250, it is represented as START=1000, END=750. These two approaches give similar, but not identical results.

When there was 50 – 80% non-detects, logarithmic transformation was used to approximate a normal distribution. Then either a robust Maximum Likelihood Estimation (MLE) or robust ROS (“regression on order statistics”) was used. If there are more than 50 observations, regular MLE was used. (In Minitab: Stat > Reliability/Survival > Parametric Distribution Analysis – Arbitrary Censoring with MLE Estimation Method.)

When there was greater than 80% non-detects, only high sample percentiles were estimated (e.g. 95th percentile).

Censored scatter plots were generated in Minitab using Helsel’s CPlot routine (Helsel 2005a) in which non-detects are represented by a bar (“|”). Censored box plots were generated in Minitab using Helsel’s CBox routine (Helsel, 2005a). Regressions were performed in Minitab using three of Helsel’s routines: ATS, CKend, and CRos (Helsel 2005a).

Surrogate Recoveries and Organic Parameters. In trace organics analysis, surrogate standards, or “surrogate internal standards” are non-target organic chemicals routinely spiked into environmental samples before sample preparation begins. Surrogate recoveries are intended to mimic the recovery of target organic compounds, and thus are measures of method precision and accuracy. In some environmental programs, notably the NOAA National Status and Trends program, target compound concentrations are adjusted, or “corrected”, using the surrogate recoveries to adjust for method biases. However, this is not routinely practiced in most EPA methods for trace organics. Appendix A is a discussion of the advantages and disadvantages of “surrogate correction” and our decision not to surrogate adjust the trace organics results presented in this report.

For the trace organic analyses presented in this report, MWRA used low concentrations to spike the surrogates, consistent with the levels expected in real samples. The resulting surrogate recoveries are indicative of the precision of the target analytes at these low concentrations. Since the surrogates are at low concentrations, they are not appropriate for recovery adjustment of the target analytes.

It should be noted that MWRA reports on organic constituents in benthic sediments, fish, and shellfish prepared by the Harbor and Outfall Monitoring contractors are always surrogate recovery corrected. The surrogates are spiked at significantly higher concentrations than used for the aqueous samples in this report, which is more appropriate for recovery “correction”.

Summary of Results. Ambient Monitoring Plan requirements include intensive, low-detection-method monitoring of toxic contaminants in final effluent from the Deer Island Treatment Plant, beyond what is normally required for effluent monitoring. Constituents studied included trace metals, cyanide, pesticides, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), volatile organic chemicals, and semivolatile organic chemicals. For pesticides, PCBs, and PAHs higher sensitivity methods were employed than the standard NPDES-approved methods. This allowed the trace concentrations of these constituents to be detected at levels at which the NPDES-approved methods would only produce non-detects.

Results of effluent chemistry data collected from August 2000 through July 2005 (the first five years of the DITP permit) show that none of the contaminants, with the possible exception of PCBs as described below, were found to be present in DITP effluent at concentrations that would exceed water quality criteria after initial dilution. Most of the contaminants met water quality criteria in the effluent even before the 70:1 initial dilution[2] that occurs at the end of the outfall tunnel where effluent is diffused into Massachusetts Bay. After dilution, contaminant concentrations were well below the water quality criteria. Table 4 summarizes the results of metals analyses, and Table 5 summarizes the results of representative pesticides, PAHs, and PCBs. Both tables include the lowest, most-stringent recommended EPA water quality criterion for each parameter.

Table 4. Metals Detections and Concentrations in DITP Final Effluent.

Metal	Method	Samples	Non-Detects	Detects (%)	Range (µg/L)	Median (µg/L)	Upper 95% Percentile (µg/L)	Lowest EPA Water Quality Criterion (µg/L)*
Aluminum	ICP	352	118	234 (66%)	24 – 860	78	191	None
Antimony	ICP	121	121	0 (0%)	<15 - <25			5.6 (HHC)
Arsenic	GFAA	124	120	6 (5%)	<0.8 – 1.2	<0.8		0.018 (HHC)
Beryllium	ICP	121	121	0 (0%)	<0.5			None
Boron	ICP	121	57	64 (53%)	<250 – 432	252	369	None
Cadmium	GFAA	417	56	361 (86%)	<0.03 – 0.39	0.089	0.198	8.8 (CCC)
Chromium	GFAA	417	51	366 (88%)	<0.70 – 8.1	1.0	1.96	50 (CCC) as Cr^{+6}
Copper	GFAA	161	1	160(99%)	<1 – 25	8.4	14.9	3.1 (CCC)
	ICP	458	142	316 (69%)	5.6 – 39.6	11.3	21.4	3.1 (CCC)
	ICP/MS	56	0	56 (100%)	5.6 – 21	10.2	16.3	3.1 (CCC)
Iron	ICP	144	0	144 (100%)	120 – 1090	355	618	None
Lead	GFAA	421	374	47 (11%)	<2.4 – 14.8	<2.4	3.52	8.1 (CCC)
	ICP/MS	31	1	30 (97%)	0.33 – 4.2	1.3	3.1	8.1 (CCC)
Mercury	CVAA	418	57	361 (86%)	<0.01 – 0.22	0.018	0.051	0.94 (CCC)
	CVAF	54	0	54 (100%)	0.0048 – 0.062	0.018	0.062	0.94 (CCC)
Molybdenum	GFAA	310	0	310 (100%)	2.1 – 28	7.2	13.8	None
Nickel	GFAA	421	1	429 (100%)	<0.7 – 7.3	2.9	4.9	8.2 (CCC)
Selenium	GFAA	121	121	0 (0%)	<0.9			71 (CCC)
Silver	GFAA	413	8	405 (98%)	<0.09 – 4.2	0.34	0.72	1.9 (CMC)
Thallium	GFAA	121	121	0 (0%)	<1			0.24 (HHC)
Zinc	ICP	428	0	428 (100%)	12 – 99	27.2	49.7	81 (CCC)

* From EPA, 2004. Based on Saltwater or Human Health Criteria.
CCC: Criterion Continuous Concentration is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

CMC: Criteria Maximum Concentration is an estimate of the highest concentration of a material in surface water to which an aquatic community can exposed briefly without resulting in an unacceptable effect.

HHC: Human Health Criterion is based on a carcinogenicity of 10^{-6} risk

PCBs were never detected in DITP effluent as Aroclor mixtures, which are the only PCBs limited in MWRA's NPDES permit, but a few PCB congeners were frequently detected at low parts per trillion

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[2] 70:1 is the initial dilution used in MWRA's NPDES permit. This dilution was derived by assuming near worst-case conditions of maximum effluent flow and strong stratification in the receiving waters. Actual effluent dilution will nearly always exceed 70:1.

concentrations (nanograms per Liter, ng/L), with a median Total PCB concentration of 1.4 ng/L. This would translate to a water concentration of 0.02 ng/L after the conservative 70-fold dilution, and 0.0038 ng/L after the applicable human health 364-fold dilution. The current EPA national recommended water quality criterion for PCBs is 0.064 ng/L for human health consumption of water and organisms or organisms only as listed in USEPA (2006).

Table 5. Pesticides, PAHs and PCBs Detections and Concentrations in DITP Final Effluent.

Compound	Sam ples	Non-Detects	Detects (%)	Range (ng/L)	Median (ng/L)	Upper 95% Percentile (ng/L)	Lowest EPA Water Quality Criterion (ng/L)*
Total Chlordane	522	32	490 (94%)	0.24 – 58	2.25	8.25	0.80 (HHC) for Chlordane only
Alpha-Chlordane (SIM only)	221	0	221 (100%)	0.34 – 7.9	1.04	3.7	0.80 (HHC) for Chlordane only
Total DDT	510	77	443 (87%)	0.17 – 13	0.78	2.54	0.22 (HHC) for 4,4'-DDT only
4,4'-DDE (SIM only)	199	0	199 (100%)	0.12 – 3.1	0.56	1.35	0.22 (HHC)
4,4'-DDT (SIM only)	220	188	32 (14%)	0.17 – 11	0.40	1.47	0.22 (HHC)
Gamma-BHC (Lindane)	638	386	252 (39%)	0.36 – 37	0.84	4.44	160 (CMC)
Gamma-BHC (Lindane) (SIM only)	221	175	46 (21%)	<0.5 – 37	0.51	4.54	160 (CMC)
Hexachlorobenzene (HCB)	638	495	143 (22%)	0.04 – 0.76	0.09	0.23	0.28 (HHC)
Hexachlorobenzene (HCB) (SIM only)	221	85	136 (62%)	0.04 – 0.63	0.09	0.17	0.28 (HHC)
Total PCB (SIM only)	268	0	268 (100%)	0.19 – 17.8	2.07	5.02	0.064 (HHC)
Chrysene	431	22	409 (95%)	3.18 – 334	13.5	52	3.8 (HHC)
Fluorene	431	74	357 (83%)	1.11 – 105	5.93	28	1,100,000 (HHC)
Total NOAA PAH	300	2	298 (99%)	10.8 – 3515	234	903	N/A

* From EPA, 2004. Based on Saltwater or Human Health Criteria.

CCC: Criterion Continuous Concentration is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

CMC: Criteria Maximum Concentration is an estimate of the highest concentration of a material in surface water to which an aquatic community can exposed briefly without resulting in an unacceptable effect.

HHC: Human Health Criterion is based on a carcinogenicity of 10^{-6} risk

3.1 Metals

From August 2000 until July 2005 hundreds of final effluent samples were tested for 17 trace metals. This ranged from 121 samples for antimony, beryllium, boron, selenium, and thallium to 619 samples for copper. Antimony, beryllium, selenium, and thallium were not detected in any sample. Arsenic was rarely detected. Lead was detected in only 17% of the samples. Virtually all of the samples had detected concentrations of iron, molybdenum, nickel, silver, and zinc. Most of the samples had detectable concentrations of cadmium, chromium, copper, and mercury. Hexavalent chromium, Cr^{6+}, was not detected in 118 effluent grab samples.

The trace metals results are summarized in Table 4. All results, including non-detects were taken into account to estimate the median and 95th percentile concentrations. For metals without non-detects, this was accomplished using a fit to a log-normal distribution. For metals with non-detects a non-parametric approach was used. For arsenic and lead there are so many non-detects that estimating a median or upper 95th percentile was highly uncertain.

The EPA approach to assessing "reasonable potential" to exceed a numerical water quality criterion (described in section 2.5 NPDES Permit Effluent Discharge Limits: Dilution Factors) can be used to gauge whether a NPDES permit limit is needed. All but five of the seventeen metals have maximum observed concentrations that are below the lowest water quality criteria, or have no water quality criteria.

Thus, the effluent meets the most stringent water quality criteria without dilution for these metals. Five of the metals, arsenic, copper, lead, silver, and zinc, had maximum detected concentrations that are above the lowest ambient water quality criterion for that metal. Therefore, these metals are given a closer examination in the rest of this section.

3.1.1 Arsenic

Arsenic was not detected in 95% of 124 DITP effluent samples. Its median concentration was <0.8 µg/L, but the 6 detected samples were above the Human Health Criterion of 0.018 µg/L. However, EPA's response to the draft NPDES permit comments for DITP discussed the need for a more appropriate ambient water quality criterion for arsenic in seawater even though the average arsenic concentration in seawater is about 1.7 µg/L (Neff 1997). Furthermore, EPA indicated that the effluent was expected to be lower than the concentrations measured in Massachusetts Bay and that the arsenic was in a chemical form, arsenate, which generally has "low toxicity and bioavailability to marine organisms." For these reasons EPA concluded that a numeric limit for arsenic in DITP effluent was not needed. Since the permit went into effect in 2000 this situation has not changed. EPA continues to work on a more appropriate marine arsenic water quality criterion (EPA 2003a).

3.1.2 Copper

Copper was observed to be present in DITP effluent at a median concentration of 10 µg/L. It was not detected in 33% of the 619 samples. The upper 95th percentile is estimated to be 21 µg/L and the maximum detected concentration was 40 µg/L. The maximum detected concentration is above the Criterion Continuous Concentration (CCC) of 3.1 µg/L by about a factor of thirteen. So, the initial dilution of 70:1 at the end of the DITP ocean outfall is sufficient to reduce the copper concentration below the ambient water quality criterion. These data support the present understanding that copper in the effluent does not have the potential to exceed water quality criteria, and that having no numeric discharge limit for copper is still appropriate.

3.1.3 Lead

Lead was observed to be present in DITP effluent at a median concentration of 1.3 µg/L, which is below the CCC of 8.1 µg/L. It was not detected in 83% of 452 samples at 2.4 µg/L. Most of the samples were tested by GFAA at MWRA, but 31 samples were tested by the more sensitive ICP/MS method at a contract laboratory. Of these, 29 were reported to have detectable lead concentrations between 0.3 and 2.4 µg/L. Two samples were above 2.4 µg/L, in agreement with the GFAA results. When all the lead results are used, even with 83% non-detects, a pattern of higher lead concentrations in effluent is seen when the plant flow is high (Figure 1).

The upper 95th percentile is estimated to be 3.5 µg/L and the maximum lead concentration observed was 15 µg/L. This is above the CCC, however, the initial dilution of 70:1 at the end of the DITP ocean outfall is sufficient to reduce the lead concentration to below the ambient water quality criterion. These data support the present understanding that lead in the effluent does not have the potential to exceed water quality criteria, and that having no numeric discharge limit for lead is still appropriate.

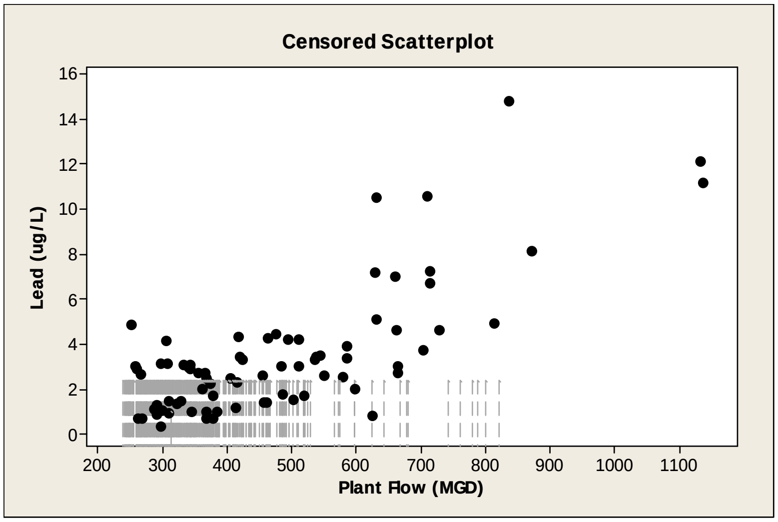

Figure 1. Censored scatter plot for Lead (µg/L) versus Total Plant Flow (MGD).

3.1.4 Silver

Silver was observed to be present in DITP effluent at a median concentration of 0.34 µg/L. The upper 95th percentile was estimated to be 0.72 µg/L. The maximum concentration of 4.2 µg/L is above the Criteria Maximum Concentration (CMC) of 1.9 µg/L by about a factor of two. The highest result occurred in August 2002 during a plant upset caused by an "experiment" with a slug of industrial wastewater. It is not representative of the typical DITP effluent. The initial dilution of 70:1 at the end of the DITP ocean outfall is sufficient to reduce the silver concentration to below the ambient water quality criterion. These data support the present understanding that silver in the effluent does not have the potential to exceed water quality criteria, and that having no numeric discharge limit for silver is still appropriate.

3.1.5 Zinc

Zinc was observed to be present in DITP effluent at a median concentration of 27 µg/L, which is below the CCC of 81 µg/L. The upper 95th percentile is estimated to be 50 µg/L. The maximum zinc concentration observed, 99 µg/L, was slightly above the CCC of 81 µg/L. However, the initial dilution of 70:1 DITP ocean outfall diffuser is sufficient to reduce the zinc concentration to below the ambient water quality criterion. These data support the present understanding that zinc in the effluent does not have the potential to exceed water quality criteria, and that having no numeric discharge limit for zinc is still appropriate.

3.2 Cyanide

From August 2000 until July 2005, 115 samples were tested for cyanide. All were non-detect with a reporting limit of <10 µg/L.

The lowest EPA water quality criterion for cyanide is a 1 µg/L Criteria Maximum Concentration (CMC) and Criterion Continuous Concentration (CCC) in saltwater. With all samples non-detect at 10 µg/L, the DITP effluent does not exceed either criterion after initial dilution. Also, these criteria are for free cyanide, but it is likely that any cyanide in treatment plant effluent is probably complexed by heavy metals, thus lowering the free cyanide concentration even further.

All but three influent samples over the course of this monitoring had undetectable cyanide concentrations. The three detected influent samples had 12 – 16 µg/L cyanide. This indicates that cyanide concentrations are very low in the DITP influent, indicating good success of the MWRA industrial pretreatment program.

We would be remiss if we did not mention some of the subtleties of testing for cyanide in wastewater treatment plant samples. In a Water Environment Federation conference presentation in 1997, we discussed our two observations (Delaney *et al.* 1997): (1) that thiocyanate (SCN^-) present in wastewater was being converted to cyanide in the EPA-approved test procedure and (2) that the ascorbic acid that is required to dechlorinated NPDES samples was also contributing to cyanide formation. Based on our work, we were included in a multi-year Water Environment Research Foundation study on cyanide formation and fate in complex effluents (Kavanaugh *et al.* 2003). This study, and the resulting publications by Zheng *et al.* (2003, 2004, 2004a, 2204b) confirmed and elaborated our observations.

These concerns are now reflected in the *Standard Methods* compendium (APHA 2004):

"In some instances, particularly with industrial wastes, it may be susceptible to interferences such as those from conversion of thiocyanate to cyanide in the presence of an oxidant, e.g., nitrate." (page 4-38);

"Ascorbic acid is no longer being recommended for preservation of samples for cyanide analysis. Ascorbic acid functions as a carbon donor in the presence of nitrite or nitrate, and generates cyanide during the distillation." (page 4-37).

Fortunately, the levels of cyanide, if any, potential interferences, and the limited need to dechlorinated final effluent samples, are such that cyanide was not detected in any effluent samples over the course of this monitoring.

3.3 Polychlorinated Biphenyls (PCBs)

Aroclors in effluent and fertilizer pellets. For the monthly Discharge Monitoring Report (DMR), one effluent composite sample is tested each month for Aroclors. All effluent samples for Aroclors have been non-detect. PCBs are present at only very low concentrations (low parts per trillion, ng/L) and there is no obvious Aroclor pattern. We frequently see detectable amounts of Aroclors in the fertilizer pellets formed from the biosolids removed from DITP wastewater, and only occasionally see detectable amounts of Aroclors in DITP influent samples.

Each week a composite of fertilizer pellets from the Fore River Pelletizing Plant is tested for Aroclors. In 283 samples from August 2000 through July 2005, Aroclors were detected in fertilizer pellets with the following frequency:

- Aroclor 1260: 98%
- Aroclor 1254: 41%
- Aroclor 1016: 11%

Aroclor 1260 had a median concentration of 300 µg/kg and an upper 95th percentile of 900 µg/kg. Aroclor 1254 had a median concentration of 247 µg/kg and an upper 95th percentile of 475 µg/kg. Aroclor 1016 had a median concentration of about 90 µg/kg and an upper 95th percentile of about 216 µg/kg. The nominal reporting limit was about 260 µg/kg for most Aroclors by this method. No other Aroclors were detected.

Twenty PCB congeners in effluent. Each week one effluent composite sample is tested for 20 PCB congeners. The 20 PCB congeners are known as the “NOAA list” because these are the congeners that have been monitored for years in the National Oceanic and Atmospheric Administration’s (NOAA) “Mussel Watch” program (Lauenstein 1993). They are also the same congeners that are monitored in the fish and shellfish and the benthic sediments part of the AMP, and so are also called the “AMP PCBs”.

From 2000 until June 2004, the samples were tested by dual-column high resolution gas chromatography with electronic capture detection (GC-ECD). From July 2003 to the present, the samples were tested by a SIM GC-MS modified version of EPA Method 8270. The performance characteristics of this method were demonstrated by side-by-side testing from July 2003 until June 2004. Once EPA Region-I approval of the SIM method was obtained, the GC-ECD method was curtailed. A total of 515 tests were performed on samples from 296 different days. Fifty tests were non-detect. The median concentration for all samples was estimated to be 1.4 ng/L and the upper 95th percentile was estimated to be 4.6 ng/L.

“Total PCBs” using sixty seven PCB congeners by modified Method 608. The DITP NPDES permit requires that the effluent be tested each month for “Total PCBs”, but at present there is not a NPDES-approved method for Total PCBs. So, MWRA developed a dual-column high resolution GC-ECD based on EPA Methods 608 that measures 67 of the 209 possible PCB congeners. MWRA carefully selected the 67 congeners to cover the major constituents of each Aroclor mixture. These 67 congeners cover over 80% of each Aroclor mixture with the exception of Aroclor 1232 where the coverage is only 58%. In 2000 MWRA submitted performance characteristics of this method to EPA-Region I for review. They approved our use of this method in 2005. In this method the “Total PCBs” result is computed as the arithmetic total of all detected congeners. A total of 63 tests were performed on samples from 62 different days. Fifteen tests were non-detects. The median concentration for all samples was estimated to be 1.1 ng/L and the upper 95th percentile was estimated to be 3.2 ng/L.

When all the Total PCB results are pooled, the median is estimated to be 1.4 ng/L and the upper 95th percentile is estimated to be 4.5 ng/L. At an average DITP plant flow of 392 MGD and a median Total PCB concentration of 1.4 ng/L, the typical PCB loading is only 2 grams per day.

PCB Method Comparison. The three PCB methods can be compared using samples with detectable PCB concentrations that were tested by more than one method. No significant correlation was observed between the 20 congener SIM method and the 67 congener ECD method ($r=0.30$, $p=0.18$, $n=21$). A weak correlation was observed between the 20 congener ECD method and the 67 congener ECD method ($r=0.39$, $p=0.009$, $n=27$). Fairly good correlation was observed between the 20 congener SIM method and the 20 congener ECD method ($r=0.62$, $p<0.001$, $n=47$). A scatter plot for these two methods is shown in Figure 2, but it is observed that the SIM method gives higher concentration results than the ECD method, suggesting that it is better able to detect congeners at low concentrations in DITP effluent. The ECD method may be prone to interferences causing false negatives for individual congeners. Even so, the high amount of scatter in these data suggests that the quantitative results are fairly imprecise at these concentrations.

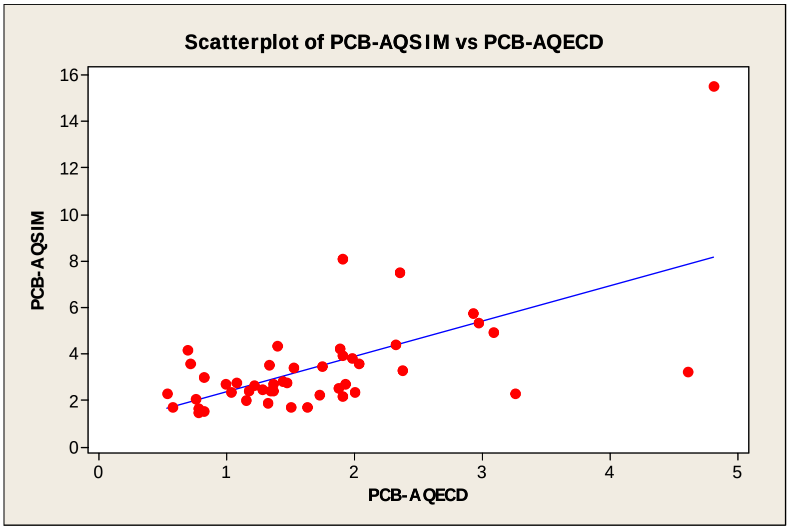

Figure 2. Scatter Plot of Detected Total AMP PCBs (ng/L) by SIM versus ECD.

The distribution of Total AMP PCB and Total PCB results are compared using Censored Box Plots in Figure 3. It can be seen that the heart of the distributions are at comparable concentrations. The AMP PCB distribution extends to higher concentrations, but this may be due to the much larger number of Total AMP PCB samples compared to Total PCB samples.

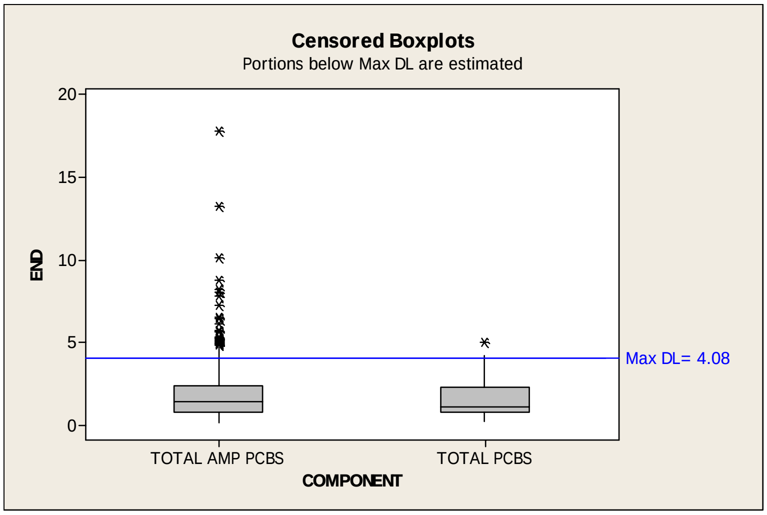

Figure 3. Censored Box Plots of Total AMP PCBs and Total PCBs.

Total PCB trends by all methods. Figure 4 shows a censored scatter plot of Total PCBs by all methods since the new NPDES permit went into effect in August 2000 until July 2005. Non-detect samples are represented by “|”. It is notable that there is a higher frequency of non-detect results in the first half of this time period. However, it isn’t possible to distinguish between improvement in the PCB test method to detect low-level congeners and changes in the low-level congener concentrations.

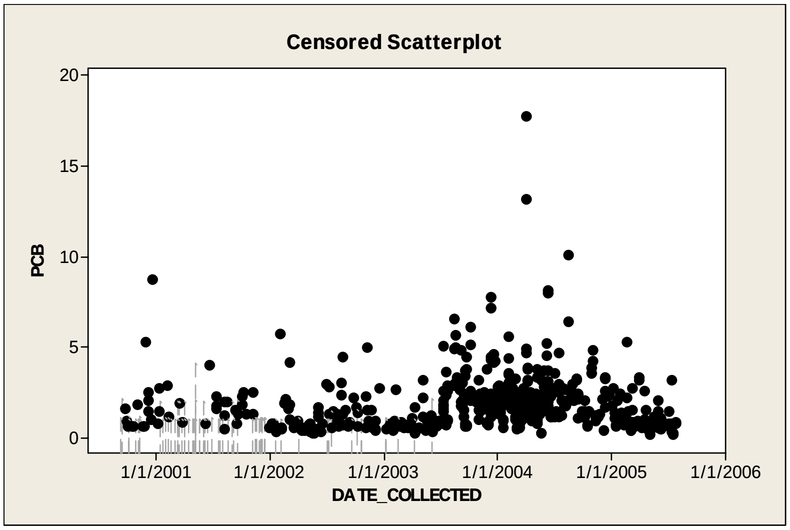

Figure 4. Censored Scatter Plot of all Total PCB (ng/L) results from August 2000 until July 2005.

Also, there also doesn't appear to be an obvious difference in the "Total PCB" concentration between the 20- and 67-congener methods. Beyond the 20 NOAA congeners, just 15 other congeners were detected a total of only 38 times. Therefore, it appears that the "20 congener" method should be adequate to characterize the PCB content of the DITP effluent. Congener #110, the most frequently detected non-NOAA congener, was detected 12 times.

It should be noted that it is unlikely that we would see subtle temporal trends in Total PCB results due to the expected variability in the results. The Horwitz curve predicts that inter-laboratory measurements of chemicals at the ng/L (parts per trillion) levels will have variability on the order of ±100% (Albert and Horwitz 1997).

The MDLs for individual PCB congeners are in the range of 0.2 to 1.0 ng/L. Most of the PCB hits are close to the MDL, and the Total PCB result is a summation of these low-levels hits. Also, the PCBs are presumably from multiple sources. This high level of measurement and source variability apparently washes out any subtle trends in the results.

The Total PCB results grouped by calendar year are shown in Table 6. The average median concentration ranged from 0.7 to 2.0 ng/L. The variability, as evidenced by the 5th and 95th percentiles, obscures any temporal trends although there is an indication that Total PCB concentration may have been highest in 2004, but has dropped since then.

Table 6. Annual median Total PCB concentration (ng/L) and 5th and 95th percentiles.

Year	Number	Non-Detects	5th Percentile	Median	95th Percentile
2000	22	8	<0.6	0.7	>2.5
2001	68	42	<0.5	0.8	2.5
2002	79	10	0.3	0.8	3.1
2003	135	5	0.5	1.7	5.0
2004	199	0	0.7	2.0	4.7
2005	71	0	0.3	0.8	2.8

PCBs may increase in DITP influent during periods of high runoff. Further analysis and study of influent PCBs would be needed to address this question.

Detected congeners are characteristic of Aroclors 1254 and 1260. A tabulation of the frequency of detection of congeners since August 2000 shows that two congeners (BZ 138 and 153) were detected in about 80% or more of the samples. These two congeners are both significant constituents of Aroclors 1254 and 1260. Seven other congeners were detected in 19 to 58% of the samples. These congeners are also indicative of Aroclors 1254 and 1260, though some of them are also found in other Aroclors (1016, 1232, and 1248). The fertilizer pellets produced from DITP biosolids (digested sludge) show a similar pattern with all samples over the pertinent timeframe always showing characteristics of Aroclor 1260, often showing 1254, and sometimes showing 1016, when detectable concentrations of Aroclors were present. The average Aroclor concentration in fertilizer pellets was 323 µg/kg.

Caged mussels exposed to DITP effluent show a similar pattern. For example the 2003 mussel bioaccumulation study detected the following congeners in decreasing concentration in the caged mussels deployed at the outfall location: 180 > 153 > 138 > 101 > 187 > 118, though the results for congener 180 may be biased high due to an interference (Lefkovitz *et al.* 2004).

Table 7. Frequency of Detection of the Prevalent Congeners.

	AMP PCB-AQECD	AMP PCB-AQSIM	67 Congeners PCBT AQECD	All Tests	Frequency	Occurrence in Aroclor Mixtures *
BZ 153 HEXACHLOROBIPHENYL	221	220	41	482	83%	9% in 1260, 4% in 1254
BZ 138 HEXACHLOROBIPHENYL	205	215	38	458	79%	6% in 1254, 6% in 1260
BZ 118 PENTACHLOROBIPHENYL	121	191	23	335	58%	7% in 1254, 2% in 1248
BZ 180 HEPTACHLOROBIPHENYL	102	164	20	286	49%	11% in 1260
BZ 101 PENTACHLOROBIPHENYL	36	207	9	252	44%	8% in 1254, 3% in 1260, 2% in 1248
BZ 187 HEPTACHLOROBIPHENYL	75	154	10	239	41%	5% in 1260
BZ 52 TETRACHLOROBIPHENYL	10	127	2	139	24%	7% in 1248, 5% in 1260, 5% in 1016, 3% in 1242, 2% in 1232
BZ 105 PENTACHLOROBIPHENYL	84	17	13	114	20%	3% in 1254, 2% in 1254
BZ 44 TETRACHLOROBIPHENYL	15	91	4	110	19%	6% in 1248, 4% in 1016, 2% in 1254, 2% in 1232

* Based on Frame *et al.*, 1996.

Sung and Higgins (1998) reported on trace contaminants in DITP effluent from samples collected in 1996 and 1997. During this time DITP either had only primary treatment, or had just started secondary treatment. Twenty PCB congeners (the AMP PCB congeners) were monitored by dual-column GC-ECD, though two congeners (18 and 180) were believed to be impacted by interferences. "Total PCB" concentrations for these 20 congeners were observed to range from 0 to 33 ng/L. In addition to congeners

18 and 180, the most common congeners detected were: 101, 118, 128, 138, 153, and 187. All of these six congeners, except 128 are reported as being detected with fairly high frequency in Table 7. Congener 128 has only been detected 10 times during the time frame of this report, and all of these were below 0.5 ng/L. Overall, the congener pattern has remained fairly consistent.

Three detected congeners are co-planar. Of the detected congeners listed in Table 7, three are among the 13 co-planar dioxin-like congeners included on the World Health Organization list (Van den Berg *et al.* 1998). These three congeners (BZ-105, 118, and 180) have Toxicity Equivalency Factors (TEF) of 0.001, 0.001, and 0.0001, respectively, compared to 2,3,7,8-tetrachloro-dibenzo-dioxin (2,3,7,8-TCDD), which has a TEF of 1 (van den Berg *et al.* 1998), and as such would be the drivers of a toxic equivalency (TEQ) calculation based on PCBs.

The groupings developed by McFarland and Clarke (1989) can be used to characterize the level of environmental concern of the congeners detected in DITP effluent. None of the frequently detected congeners listed in Table 7 are in the highest concern group (highest potential for toxicity and presence in commercial PCB formulations) (1A), three are in Group 1B (moderate potential for toxicity and frequently reported in environmental and tissue samples) (BZ-105, 118, and 138), three are in Group 2 (moderate potential for toxicity with high relative abundance in mammalian tissue) (BZ-101, 153, and 180), and three are in Group 3 (low potential for toxicity but occur frequently (BZ-44, 52, and 187).

3.4 Pesticides

Pesticide concentrations are determined in the same samples and using the same methods as for PCBs. From August 2000 through July 2005 there were 12,354 individual pesticide results from 421 samples. Some samples were tested in duplicate or by two methods (NPDES-approved method and/or a higher sensitivity GC-ECD or GC-MS-SIM method). Of these there were 2,831 detects (23%). Three pesticides were never detected: DDMU, Mirex, and Oxychlordane. Twenty eight different pesticides were detected at least once. Seventeen of these pesticides were detected less than 10 times each: 2,4'-DDE, 2,4'-DDT, Aldrin, Alpha-BHC, Beta-BHC, Chlordane (Technical), Delta-BHC, Dieldrin, Endosulfan I, Endosulfan II, Endosulfan Sulfate, Endrin, Endrin Ketone, Endrin Aldehyde, Heptachlor Epoxide, Methoxychlor, and Toxaphene. Three additional pesticides were detected less than 100 times: 2,4'-DDD, CIS-Nonachlor, and Heptachlor. The other eight pesticides were detected between 100 and 500 times: 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, Alpha-Chlordane, Gamma-BHC (Lindane), Gamma-Chlordane, Hexachlorobenzene, and Trans-Nonachlor.

Given this pattern of detections, it makes sense to examine the results as Gamma-BHC (Lindane), Hexachlorobenzene, Total DDT and Total Chlordane. Total DDT is the sum of the detected concentrations of: 2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT. For historical consistency on this project, Total Chlordane is defined as the sum of the detected concentration of: Alpha-Chlordane, Heptachlor, Heptachlor Epoxide, and Trans-Nonachlor. It doesn't include Gamma-Chlordane, although it is frequently detected.

Gamma-BHC (Lindane) had a median concentration of 0.8 ng/L, an upper 95th percentile of about 6 ng/L and a maximum detected concentration of 37 ng/L. Overall it was detected in 40% of 638 tests. It was detected regularly in 2000 to 2003 but was detected less frequently in 2004 when the GC/MS SIM method was adopted. This suggests the SIM method is either less prone to false positives or less sensitive than GC-ECD, or possibly the concentrations have gone down over time. Figure 5 is a censored scatter plot of Gamma-BHC effluent concentrations over the time frame of this report. The higher concentration non-detects of about 20 ng/L are from the lower sensitivity NPDES-approved method.

Gamma-BHC (Lindane) has a saltwater Criteria Maximum Concentration (CMC) of 0.16 µg/L (160 ng/L), which is lower than its HHC. With a maximum observed concentration of 37 ng/L, and assuming an ambient receiving water concentration of zero, the undiluted DITP effluent has a lower Gamma-BHC concentration than the CMC, so there is no reasonable potential to exceed the water quality criterion.

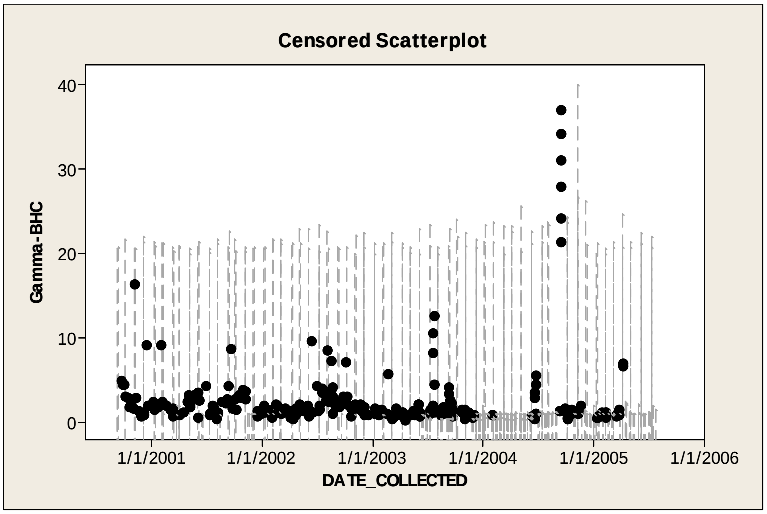

Figure 5. Gamma-BHC (ng/L) from August 2000 through July 2005.

Hexachlorobenzene had a median concentration of 0.1 ng/L, a 95th percentile of about 0.3 ng/L and a maximum detected concentration of 0.8 ng/L. Overall it was detected in 22% of 638 tests. It was detected infrequently in 2000 to 2003. In 2004, when the SIM method was adopted, it was detected fairly regularly, usually in the range of 0.05 to 0.2 ng/L. Figure 6 is a censored scatter plot of Hexachlorobenzene effluent concentrations over the time frame of this report. The higher concentration non-detects of about 20 ng/L are from the lower sensitivity NPDES-approved method.

Hexachlorobenzene has a human health water (plus organism) criterion (HHC) of 0.00028 ug/L (0.28 ng/L). Assuming an ambient concentration of zero, the calculated effluent limit is 40 ng/L. The maximum observed concentration has been 0.8 ng/L, so there is no reasonable potential to exceed the water quality criterion since the diluted DITP effluent is not expected to exceed the HHC.

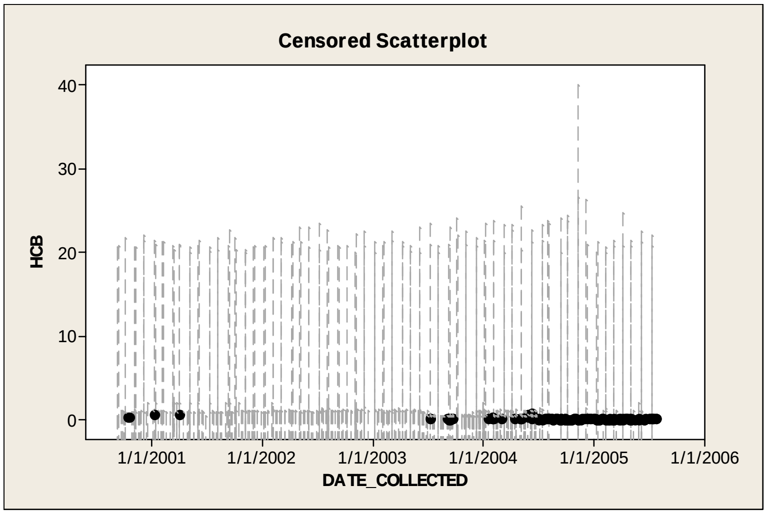

Figure 6. Hexachlorobenzene (ng/L) from August 2000 through July 2005.

Total Chlordane, as defined above, had a median concentration of 1.1 ng/L, an upper 95th percentile of about 11 ng/L and a maximum detected concentration of 37 ng/L. Overall Total Chlordane components were detected in 82% of 307 sampling days. Most hits were below 10 ng/L, but there were a few hits from 10 to 37 ng/L suggesting episodic inputs to the sewer system. Figure 7 is a censored scatter plot of Total Chlordane effluent concentrations over the time frame of this report.

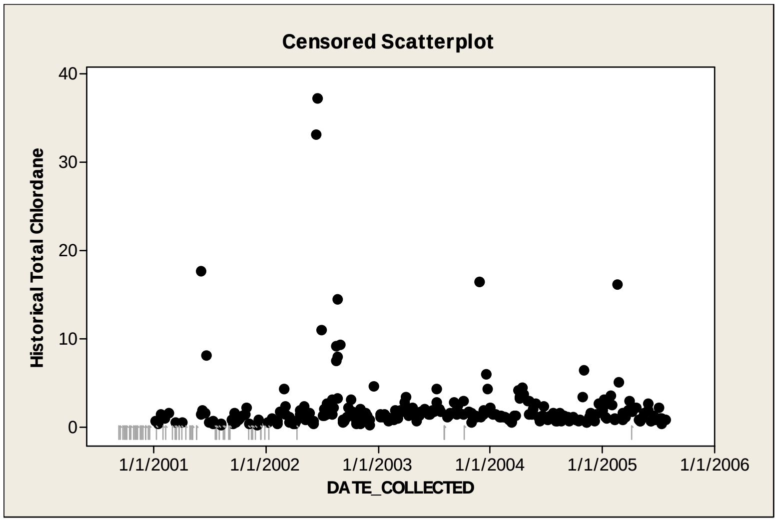

Figure 7. Total Chlordane (ng/L) from August 2000 through July 2005.

Chlordane has a human health water (plus organism) criterion (HHC) of 0.00080 µg/L (0.80 ng/L). Assuming an ambient concentration of zero, the calculated effluent limit is 290 ng/L. The maximum observed concentration has been 37 ng/L, so there is no reasonable potential to exceed a water quality criterion since the diluted DITP effluent is not expected to exceed the HHC.

Total DDT had a median concentration of 0.90 ng/L, a 95th percentile of about 3 ng/L and a maximum detected concentration of 13 ng/L. Overall it was detected in 85% of 520 tests. Figure 8 is a censored scatter plot of Total DDT effluent concentrations over the time frame of this report.

4,4'-DDT has a human health water (plus organism) criterion (HHC) of 0.00022 µg/L (0.22 ng/L). Assuming an ambient concentration of zero, the calculated effluent limit is 80 ng/L. The maximum observed Total DDT concentration has been 13 ng/L, so there is no reasonable potential to exceed a water quality criterion since the diluted DITP effluent is not expected to exceed the HHC.

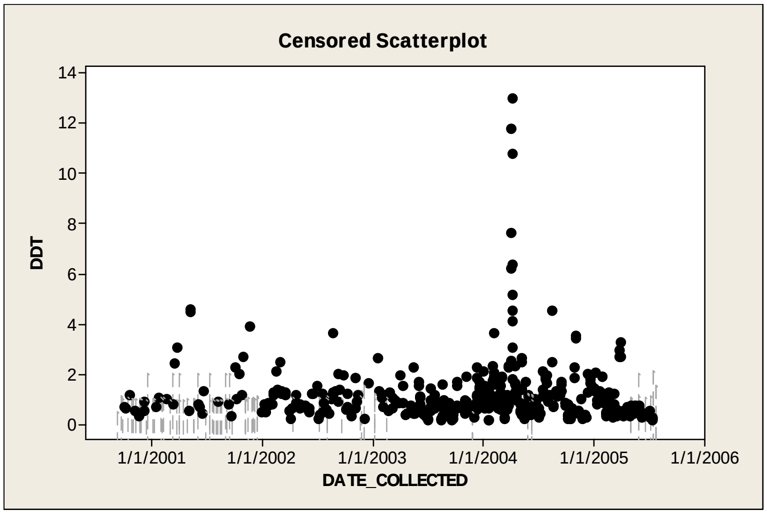

Figure 8. Total DDT (ng/L) from August 2000 through July 2005.

It is important to note that the NPDES-approved pesticide methods (608 and 612) have method detection limits ranging from 4 ng/L for Gamma-BHC to 50 ng/L for Hexachlorobenzene. Only a few Gamma-BHC and Chlordane results would even be detected above the NPDES detection limits using NPDES-approved method. So, the higher sensitivity methods were needed to detect the actual concentration of these pesticides. The NPDES-approved methods were not sensitive enough for this use.

3.5 Polycyclic Aromatic Hydrocarbons

Testing for PAH was performed on 299 samples during the timeframe of this report. Many samples were tested in duplicate and the results of these tests have been averaged. For the 24 NOAA individual PAH compounds, the median concentration was 9 ng/L, which is less than twice the nominal reporting limit of 5 ng/L. The upper 95th percentile of all NOAA PAH compounds was about 52 ng/L. About 18% of the individual PAH results were non-detect.

The NOAA PAH compounds appear to be generally log-normally distributed.

For example, Chrysene had detectable concentrations in 95% of 431 tests. It had a median concentration of 13 ng/L and an upper 95th percentile of about 52 ng/L. The data were log-normally distributed with some skewing towards higher concentrations.

Non-detects are problematic in computing the composite parameter Total NOAA PAH. For graphical presentation of trends, non-detects were equated to zero in computing Total NOAA PAH.

In 299 samples, only 2 were non-detect for all NOAA PAH components. The Total NOAA PAH concentration followed a log-normal distribution with some minor skewing at both high and low concentrations. It has a mean of 333 ng/L, a median of 234 ng/L and an upper 95th percentile of 903 ng/L.

The trend of the Total “Historical” NOAA PAH concentration is shown in Figure 9. At an average DITP plant flow of 392 MGD and a median Total NOAA PAH concentration of 234 ng/L, the average PAH loading is about 350 grams per day (0.76 pounds/day).

Most of the PAH compounds on the NOAA list have Human Health water quality criteria of 0.0038 µg/L (3.8 ng/L) (EPA 2004). With a 364x dilution factor for chronic contaminants, a limit for individual PAH compounds would be 1.38 µg/L. The highest individual PAH concentration detected was 0.5 µg/L (513 ng/L for Fluoranthene on 3/22/01), which is well below this. Therefore there is no need for any PAH NPDES limits because there is no reasonable potential to exceed a water quality criterion.

Fluorene was the only PAH included in the DP-29 report (Camp Dresser and McKee 1994). DP-29 predicted a dry weather load of 0.1 lbs/day and a wet weather load of 0.4 lbs/day.

In 431 tests Fluorene was not detected in 17% of the samples It had a median concentration of 5.9 ng/L and an upper 95th percentile of 27 ng/L. We observed a typical loading of 0.004 lbs/day and a maximum loading of 0.08 lb/day. This indicates that the effluent is substantially cleaner than predicted.

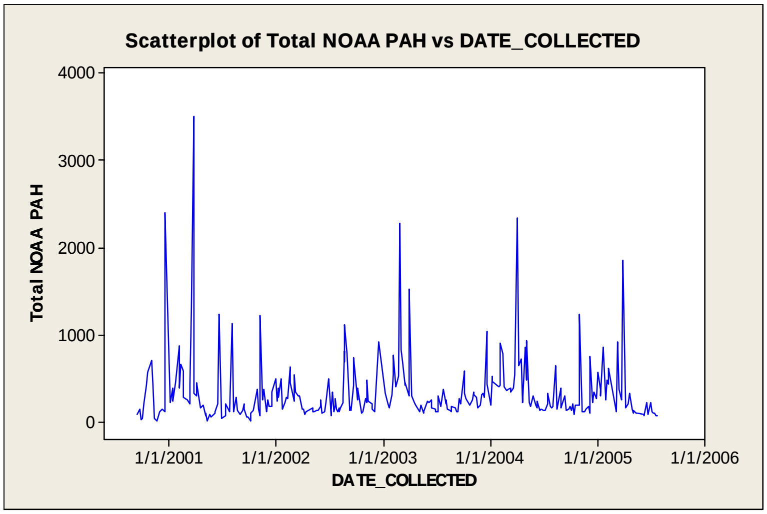

Figure 9. Total NOAA PAH Trend Plot.

3.6 Other Semivolatile Organic Compounds

A total of 113 DITP effluent composite samples were tested for 72 semivolatile organic compounds using the NPDES approved Method 625. Generally, results were quantified down to a reporting limit of 10 µg/L.

Only two chemicals were detected, each in only one sample. Bis(2-ethylhexyl)phthalate was detected at 14 µg/L on September 13 2001. With 364:1 dilution, its concentration would be well below the HHC criterion of 1.2 µg/L. The other chemical, n-decane, was detected at 3 µg/L. This chemical does not have an EPA water quality criterion. Based on this lack of detectable concentrations semivolatile organic compounds are at too low a concentration to be detected in DITP effluent using the NPDES approved method.

3.7 Volatile Organic Compounds

A total of 115 DITP effluent grab samples were tested for 43 volatile organic compounds using the NPDES approved Method 624. Generally, results were quantified down to a reporting limit of 5 µg/L.

Six chemicals were detected less than five times each: 1,3-dichlorobenzene, 1,4-dichlorobenzene, 2-butanone, carbon disulfide, toluene, and trichloroethylene. Five of these chemicals either have no water quality criterion, or were detected well below the lowest water quality criterion. The one exception is trichloroethylene. It was detected one time at 6 µg/L, compared to the human health criterion of 2.5 µg/L. With 364:1 dilution, its concentration would be well below the HHC criterion.

Acetone was detected in 81% of the samples. It had a median concentration of 8 µg/L, and an upper 95th percentile of 26 µg/L, but acetone does not have an EPA water quality criterion.

Chloroform was detected in all but one sample, primarily because it is a common chlorine disinfection by-product. It had a median concentration of 6 µg/L, and an upper 95th percentile of 10 µg/L. With 364:1 dilution, its concentration would be well below the HHC criterion of 5.7 µg/L.

Methylene chloride was detected in about 28% of the samples. It had a median concentration of 3 µg/L, and an upper 95th percentile of 4 µg/L. With 364:1 dilution, its concentration would be well below the HHC criterion of 4.6 µg/L.

Tetrachloroethene was detected in about 75% of the samples. It had a median concentration of 3.7 µg/L, and an upper 95th percentile of 10 µg/L. With 364:1 dilution, its concentration would be well below the HHC criterion of 0.69 µg/L.

3.8 Comparison of Effluent Quality to Historical Estimates.

Since 1988, there have been a series of estimates of loadings from DITP. These estimates have been based on progressively more complete and accurate data. Table 8 updates loadings estimates, which are compared to estimates used in the SEIS (EPA 1988) and by Sung and Higgins (1998). SEIS loadings estimates were based on a plant flow of 390 MGD and 100% secondary treatment. Sung and Higgins (1998) estimates were based on a limited number of early secondary treatment results. Data used in our report correspond to an average flow of 359 MGD and 93% secondary treatment. Most of the new loadings estimates are comparable to, or lower than, Sung and Higgins estimates, and far below original planning estimates for the treatment plant. These reductions are likely due to good removal efficiencies being obtained in primary and secondary treatment, coupled with reductions in influent loadings, as well as more frequent sampling and more sensitive analytical chemistry.

Mean loadings estimates for this report were based on taking the “best” (lowest detected concentration or most sensitive method) metals results for each day that was sampled, multiplying it by the daily plant flow for that day. For parameters with no (or exceedingly few) non-detects (Zn, Total PCB, Total PAH, Total DDT, and Total Chlordane), a simple arithmetic average was used. For the other parameters, Helsel’s robust Regression on Order Statistics (ROS) was used. In this approach, a robust regression is used to fit log transformed data with their normal scores. Then normal scores for the nondetects are fit to this distribution. Then the fitted points are back transformed to the original scale and descriptive statistics are computed (*e.g.* mean). This approach only assumes that the data fit a log-normal distribution and purportedly avoids transformation bias.

Table 8. Annual Effluent Loadings Estimates

Parameter	Projected for Secondary (Kg/yr) (SEIS)	Projected for Secondary (Kg/yr) (Sung and Higgins 1998)	Mean Loading Kg/yr (this report)
Cadmium	697	21	55
Chromium	3,517	490	648
Copper	11,945	14,000	6,588
Lead	4,961	2,400	850
Mercury	216	50	12
Molybdenum		6,800	3,743
Nickel	8,926	2,400	1,534
Silver	299	620	207
Zinc		14,000	16,318
Total PCB	50	4.8	0.91
Total PAH		1,400*	112+
Total DDT		0.67	0.46
4,4'-DDT (only)	28		0.37
Total Chlordanes		0.48	0.86
Heptachlor (only)	10		0.20

* 40 PAH compound classes

\+ Total NOAA PAH, 24 compounds

Copper and lead loadings have gone down significantly, coincident with marked improvements in corrosion control in the MWRA drinking water treatment system. Molybdenum loadings have dropped, probably as a result of the voluntary MWRA industrial pretreatment program to encourage facilities with cooling towers to use alternatives to molybdenum-based corrosion control chemicals.

Mercury, silver, nickel, and to a lesser extent zinc have decreased, presumably due to MWRA industrial source reduction efforts and changes in usage patterns. The apparent increase in cadmium annual loading is due to Higgins and Sung (1998) setting their non-detect values to zero.

Reductions in Total PCB and Total DDT loadings are presumably due to these substances being banned and, over time, a generally cleansing of the sewer system infrastructure.

The Total PAH loading in Sung and Higgins (1998) was based on 40 PAH compound classes, which included alkyl-substituted PAH homologues, so these results are not directly comparable to the Total NOAA PAH results presented here, based on a subset of 24 of the 40 compound classes. It appears that on average about half of the PAH concentration in Sung and Higgins is from alkyl-substituted homologues that are not included in the Total NOAA PAH results, this would lower the Sung and Higgins PAH loading to approximately 700 Kg/y, which is still a factor of six higher than observed in this study. The main cause of this difference is that the effluent samples used by Sung and Higgins only received up to 80% secondary treatment. However, lower influent PAH loadings and higher removal efficiency are also likely to have contributed to the lower PAH loadings observed in this report.

Annual loadings for Total Chlordanes are about the same as in Sung and Higgins. The slight increase is probably not statistically significant and is probably due to using a method with greater sensitivity, allowing lower concentrations to be detected.

PCB congener concentrations in effluent are always very low. The lowest method detection limit (MDL) in the NPDES-approved Method 608 is 3 ng/L for heptachlor. The Method 608 MDLs range up to 240 ng/L for toxaphene. Aroclor 1242 is listed as having an MDL of 65 ng/L; it is the only Aroclor with an MDL listed in Method 608. We are routinely reporting PCB congeners (and pesticides) down to 0.5 to 1 ng/L. Most congener results are non-detect and the median "Total PCB" concentration was only 1.4

ng/L. Expressed as a loading, this is only about 2 grams per day. The single highest single congener detection was 5.72 ng/L, but the median detected concentration was about 0.3 ng/L.

Effluent loadings for PCBs are lower than predicted. In 1994, MWRA and its consultant prepared estimates of contaminant loadings based on Deer and Nut Island Treatment Plant influent data from samples collected on various days from 1991 to 1994. The influent sample results were used with anticipated removal efficiencies from primary and secondary treatment to estimate future effluent loadings. These loadings were compared to the 1988 Supplemental Environmental Impact Statement (EPA 1988). The loadings examined were for average dry-weather conditions and wet-weather conditions. The 1994 loadings estimates were significantly lower than the SEIS estimates, but it is important to note that the current measured loadings are lower still. In fact, even the largest loadings for the 2000 to 2004 timeframe are lower than the average dry-weather loadings estimates from 1994. Presumably this is a combination of lower PCB levels in the MWRA sewer system and better removal rates than predicted.

Menzie *et al.* (1991) estimated that the MWRA POTW discharges contained <250 kg/yr of PCBs. Menzie-Cura & Assoc. (1991) estimated that PCB loadings to Massachusetts Bay were about 2,600 kg/yr and that atmospheric deposition contributed 85% of the PCB loading, with the MWA discharge contributing about 400 kg/yr. However, they note that these estimates are probably too high since PCB usage had been decreasing and since "no individual PCB compound is present in [MWRA] effluent greater than 10 ng/L." Hunt *et al.* (1995) observed the MWRA POTW effluent loading to be 26 kg/year in 1993/1994 from the old MWRA primary treatment plants, compared to 36 kg/year estimated by Shea (1994). Based on DITP Pilot Plant data, Hunt *et al.* predicted that full secondary effluent would result in a loading of 1 kg/year. Butler *et al.* (1997) revised the PCB loading estimate to 9 kg/year using 1995 DITP primary treatment plant and pilot plant results. Sung and Higgins (1998) used the first secondary treatment samples from the new DITP in 1997 to revise this estimate to 4.8 kg/year. This report has found that the average PCB loading from DITP is 0.69 kg/yr.

Using an annual PCB atmospheric deposition flux for the Chesapeake Bay (EPA 1999) of 16.3 $\mu g/m^2$ and an area of 3,670 km^2 for Massachusetts Bay (Alber and Chan 1994), the atmospheric source of PCB is estimated to be 59 kg/yr—significantly greater than the DITP effluent loading.

4.0 SUMMARY AND CONCLUSIONS

The study has enabled MWRA to thoroughly characterize trace contaminant levels in DITP effluent through the first five years of permitted operation, including during a range of weather and operational conditions. More than 600 samples were analyzed for some contaminants; the least number of samples for a given contaminant was more than 100.

Trace contaminants are at very low levels in DITP effluent, and, as expected, for all contaminants measured there is no reasonable potential to exceed water quality criteria. The abundant operational data has enabled us to update annual loading estimates with a high degree of confidence. These estimates showed that most contaminants are significantly lower than were predicted by the planning studies, including EPA's Supplemental Environmental Impact Study which provided the foundation for the design of DITP. These results are consistent with ambient monitoring data that show virtually no change in fish tissue chemistry or sediment quality in areas that could be affected by MWRA's discharge (Hunt *et al.* 2006).

PCBs as Aroclors are never detected in the effluent using EPA-approved methods. For Total PCBs, levels are extremely low as would be expected for banned contaminants. Assuming a dilution in Massachusetts Bay of 364:1, average Total PCB concentration in the effluent of 1.4 ng/L would be 0.0038 ng/L, far below the water quality criterion of 0.064 ng/L.

For trace contaminants, many samples have concentrations below method detection limits. We show that it is practical to replace the customary, but arbitrary and mathematically non-defensible methods (of using a fraction of the detection limit for example, or zero) for handling non-detect results with statistically valid approaches to estimating the central tendency of the data, and we recommended that such statistically valid methods be used.

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APPENDIX A

DISCUSSION OF SURROGATE RECOVERY CORRECTION

In trace organics analysis, surrogate standards, or “surrogate internal standards” are routinely spiked into environmental samples before sample preparation begins. Surrogate recoveries are intended to mimic the recovery of target organic compounds, and thus are measures of method precision and accuracy. In some environmental programs, notably the NOAA National Status and Trends program, target compound concentrations are “corrected” using the surrogate recoveries to adjust for method biases. However, this is not routinely practiced in most EPA methods for trace organics. This section examines our decision not to surrogate adjust the trace organics results presented in this report.

How does variability change with concentration?

Before we discuss surrogate recoveries, we should remind ourselves that the variability of chemical measurements depends on the concentration of the target compounds. This is elegantly expressed in the Horwitz relationship. Using a wide variety of interlaboratory studies, Horwitz et al. (1980) showed that there is an inverse relationship between sensitivity and precision that is independent of the nature of the target compound or the analytical technique. In fact, the interlaboratory variability, as expressed by the coefficient of variation (relative standard deviation) increases by a factor of two for every two orders of magnitude decrease in concentration. They also showed that the intralaboratory variability is usually about a half or a third of the interlaboratory variability.

The Horwitz relationship captures the analytical chemist’s intuition that measurement variability increases with decreasing concentration.

What is a surrogate?

In trace organics analysis, surrogates (“surrogate standards”, or “recovery internal standards”) are added to every field and Quality Control sample at the beginning of the sample preparation process. They are carried through the sample preparation and analysis process and are meant to mimic the target compounds. They are chosen to have chemical and physical properties similar to the target compounds but are not expected to be present in the samples. Because they are similar to the target compounds, and because they go through the sample analytical process, the recovery of the surrogates is expected to be similar to the precision and accuracy of the target compounds.

The ideal surrogate is an isotopically labeled version of the target compound (e.g. naphthalene-d8 for naphthalene) because in this case the chemical and physical properties are almost identical. Isotopically labeled surrogate can only be used when the chromatographic detector can distinguish between the labeled and unlabeled compound. This is the case with Mass Spectrometry (MS), but not, for example, with Electron Capture Detectors (ECD). However, you would need an isotopically labeled version of every target compound to fully take advance of this special relationship between isotopic isomers.

Even in this ideal situation the recovery of a target compound and its isotopically labeled surrogate do not agree perfectly. Figure shows a plot of naphthalene versus naphthalene-d8 recoveries in Laboratory Control Samples (no sample matrix) for the SIM-GC-MS test over almost four years. Although there is a high degree of correlation (r=0.93, n=136), there is still noticeable variability.

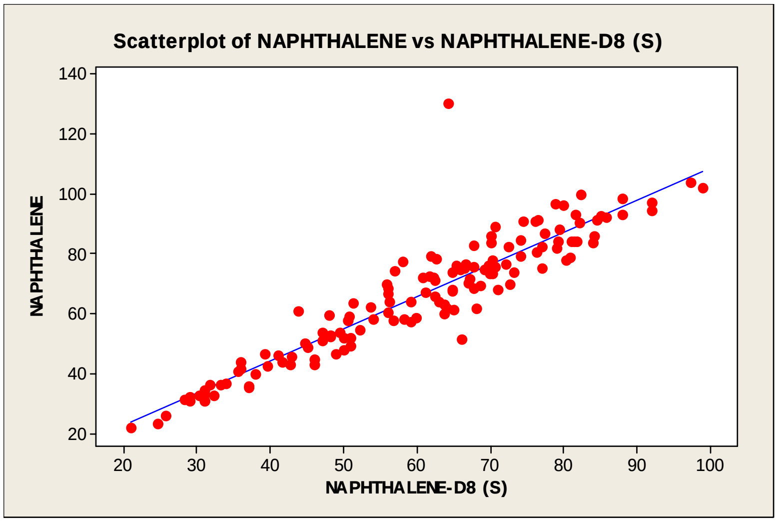

Figure 10. Naphthalene versus Naphthalene-d8 % recovery in Laboratory Control Samples.

When sample matrix is present, for example in matrix spike samples, this correlation degrades (Figure , r=0.78, n=109). When you compare different surrogates in real samples, this correlation degrades further. Figure shows a scatter plot of phenanthrene-d12 versus naphthalene-d8 in real samples. While there is still a statistically significant correlation, the correlation only accounts for about half of the scatter in the data (r=0.48, n=349).

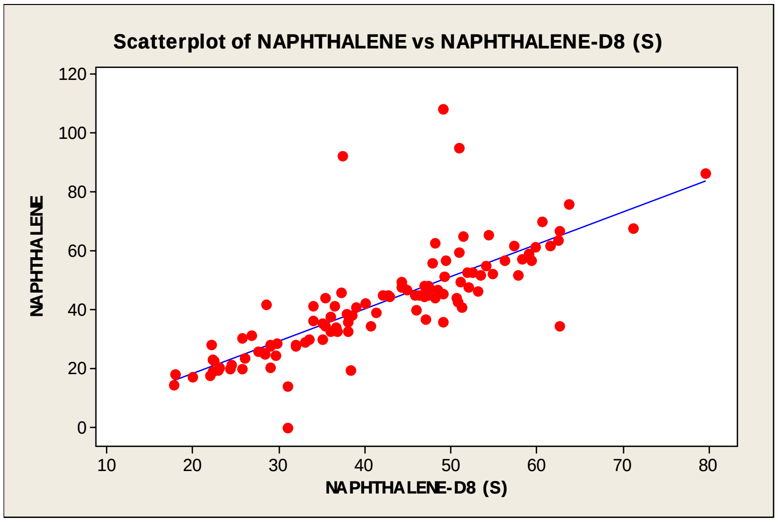

Figure 11. Naphthalene versus Naphthalene-d8 % recovery in Matrix Spike Control Samples.

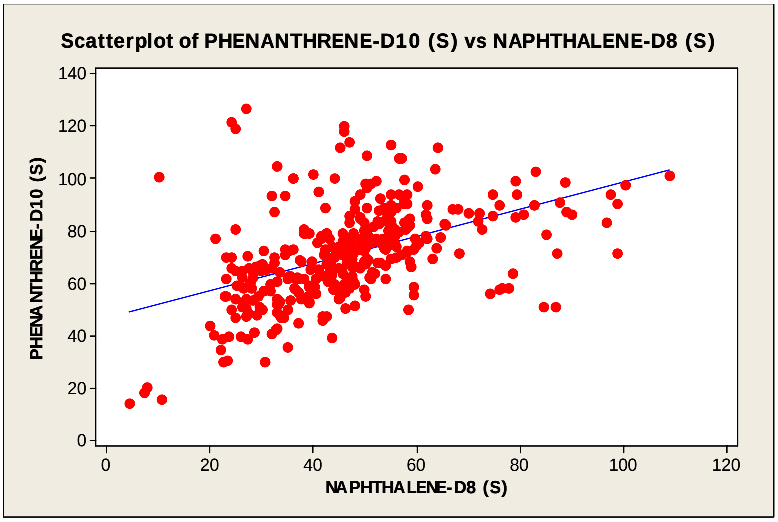

Figure 12. Phenanthrene-d10 versus Naphthalene-d8 % recovery in Real Samples.

Why use surrogates?

There are two basic reasons for using surrogates: monitoring method performance (precision and accuracy) and recovery correction. Matrix spikes and matrix duplicate/sample duplicates monitor method performance for all spiked target compounds, but generally at a frequency of one set per batch. Surrogates monitoring method performance on every sample, but only for the surrogate compounds, not the target compounds.

Most methods used for measuring organic compounds include sample preparation steps (extraction, concentration, and cleanup) that are not 100% quantitative. Due to incomplete extraction and losses during concentration and cleanup, the recovery for target compounds is often less than 100%. Also, due to the effect of the sample matrix (e.g. emulsions), the recovery is reduced and is variable.

In principle, the recovery of the surrogates should be similar to the recovery of the target compounds, and therefore the surrogate recovery could be used to "correct" the target compound concentration. To be effective, the surrogates must behave very similarly to the target compounds and the surrogate recovery should be stable from sample to sample. If the surrogate recovery varies, then the "corrected" target compound concentrations will be even more variable than the "un-corrected" concentrations.

What are the two schools of thought on surrogates?

As noted in the previous section, the two schools of thought on surrogates are "monitoring method performance" and "recovery correction". To monitor method performance, the surrogates should be spiked at concentrations comparable to the concentration of the target compounds. In particular, to shed light on low-level "hits", the surrogates should be spiked at low concentrations, approach the reporting/quantitation limits.

For recovery “correction”, surrogates should be spiked at high concentrations so that the surrogate recovery reflects the actual recovery of the analytical procedure, rather than the random variability that is prevalent at low concentrations.

What is common practice for surrogates?

EPA methods for semivolatile organics in the NPDES, RCRA, and CERCLA programs do NOT allow surrogate recovery “correction”. A recent EPA guidance document (EPA 2003) on detection and quantitation says, “EPA believes that recovery correction may be appropriate if (1) the recovery is consistent across laboratories, matrices, and conditions, and (2) the relative variability (as relative standard deviation) remains constant as the recovery decreases. These two requirements are rarely met; therefore, recovery correction would be appropriate only in rare circumstances.”

EPA guidance on fish sampling and analysis (EPA 2000a) says, “Reported data should not be corrected for percent recoveries of surrogate recovery standards. Recovery data should be reported for each sample to facilitate proper evaluation and use of the analytical results.”

“Standard Methods for the Examination of Water and Wastewater” (APHA 2004) does not appear to advocate the use of surrogate recovery correction (e.g., Method 6410B). Neither does the National Environmental Laboratory Accreditation Program (NELAP) nor the EPA drinking water laboratory certification manual.

The counter argument is the methods used for the NOAA National Status and Trends Mussel Watch program. Surrogate recovery correction is used routinely in this program, and has been for many years (see for instance Lauenstein and Cantillo, 1993 and 1998). It is not clear what surrogate standard recovery QC goals are used or what performance is actually achieved. However, it should be noted that this program is for measuring trace chemicals in mussel tissue samples, which is a more difficult matrix than wastewater.

Thompson, *et al.* (1999) succinctly summarized the arguments for and against surrogate recovery correction as follow:

Arguments for correction

- *The purpose of analytical science is to obtain an estimate of the true concentration of the native analyte with an uncertainty that is fit for purpose.*
- *The true concentration can be estimated only if significantly low recoveries of analyte are corrected.*
- *An uncorrected bias due to low recovery means that results will not be universally comparable, not transferable and therefore unfit to support mutual recognition.*
- *Methods of correction advocated are isomorphic with perfectly acceptable analytical techniques such as internal standardization and isotope dilution and therefore not suspect in principle.*
- *Although some uncertainty is inevitably associated with correction factors, that uncertainty can be estimated and incorporated into a combined uncertainty for the final result.*

Arguments against correction

- *Estimated recoveries based on a surrogate may be higher than the corresponding value for the native analyte. The resultant corrected result would still have a negative bias.*
- *Estimated correction factors may be of doubtful applicability because they may vary among different matrices and for different concentrations of analyte.*

- *Estimated correction factors often have a high relative uncertainty, whereas uncorrected results usually have the smaller relative uncertainty associated with volumetric and instrumental measurement alone. (However, the uncertainty is small only if no contribution from the bias is included). Therefore corrected results will have a high relative uncertainty, sufficiently high if made explicit to create an unfavorable impression among those unfamiliar with the problems of analysis. This in turn might affect the credibility of science in the enforcement of legislation.*
- *Relatively small deviations from unity in correction factors could arise largely through random errors rather than a systematic loss of analyte. In that circumstance correction could make the absolute uncertainty of the result greater.*
- *Some legislation imposing maximum limits on contaminants is framed on the understanding that uncorrected results will be used for enforcement purposes.*

For the trace organic analyses presented in this report, MWRA used low concentrations to spike the surrogates, consistent with the levels expected in real samples. The resulting surrogate recoveries are indicative of the precision of the target analytes at these low concentrations. Since the surrogates are at low concentrations, they are not appropriate for recovery adjustment of the target analytes.

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