COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN (CW/QAPP)

for

DETAILED EFFLUENT CHARACTERIZATION: 1993-1994

Task 18
MWRA Harbor and Outfall Monitoring Project

submitted to

MASSACHUSETTS WATER RESOURCES AUTHORITY
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June 23, 1993

AMENDMENT TO
COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN (CW/QAPP)

for

DETAILED EFFLUENT CHARACTERIZATION: 1993-1994
NUTRIENTS, MOLYBDENUM, AND SULFUR ISOTOPES

Task 20 — Task Order 13
MWRA Harbor and Outfall Monitoring Project

submitted to

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MWRA Harbor and Outfall Monitoring Project — Amendment to the Detailed Effluent Characterization — Nutrients, Molybdenum, and Sulfur Isotopes

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Massachusetts Water Resources Authority (MWRA)

3. DATE OF REQUEST

November 1, 1993

4. DATE OF PROJECT INITIATION

December 1, 1993

5. PROJECT MANAGEMENT

Dr. Michael Connor, MWRA Director of Environmental Quality Department

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Mr. Ken Keay, MWRA Detailed Effluent Characterization Task Manager

Dr. Carlton Hunt, Battelle Project Manager for Harbor and Outfall Monitoring

Dr. Allen Uhler, Battelle Detailed Effluent Characterization Task Leader

6. QUALITY ASSURANCE MANAGEMENT

Ms. Rosanna Buhl, Battelle Project QA Officer

7. PROJECT DESCRIPTION

This document amends the Combined Work/Quality Assurance Project Plan (CW/QAPP) for Detailed Effluent Characterization (Shea, 1993). It will guide the collection and analysis of effluent samples collected from Deer Island and the Pilot Secondary Treatment Plant for nutrients and other selected parameters. All analyses will be conducted at the direction of MWRA. The information in this amendment supplements that found in Shea (1993).

7.1 Objective and Scope

This amendment expands the objectives and scope listed in Shea (1993) to include:

- monthly measurements of concentrations of total molybdenum, nutrients, and stable sulfur in the MWRA effluent.
- measurements of total molybdenum, nutrients, *Clostridium perfringens*, and the stable isotopes of nitrogen and sulfur from the Pilot Secondary Treatment Plant at the influent, control effluent, and Chemical Enhanced Pilot Treatment (CEPT).

7.2 Data Usage

The data usage will be the same as defined in Section 7.2 of Shea (1993) except that the words contaminant and toxics are replaced with nutrients. Further more, the various nutrient phases and species will contribute to refined water quality models evaluating effects of nutrient discharge in Massachusetts Bay.

7.3 Technical Approach

To accomplish the objectives defined for this task order:

- the composite effluent sample collected as part of the metals composite sample defined in Section 7.3 of Shea (1993) will be analyzed for molybdenum.
- nutrient and stable isotope samples will be collected as grab samples and processed immediately.
- measurement of the above parameters in a number of Pilot Secondary Treatment Plant samples will occur at the request of MWRA.

Nutrient analyses for both the effluent and pilot treatment plant samples will include dissolved inorganic nutrients (ammonia (NH_4), nitrate (NO_3), nitrite (NO_2), phosphate (PO_4), silicate (SiO_4)), dissolved organic carbon (DOC), dissolved organic nitrogen (DON), dissolved organic phosphorus (DOP), particulate organic carbon (POC), particulate organic nitrogen (PON), particulate organic phosphorus (POP), and biogenic silica (BioSi).

Isotope analyses will include δ^{15}Nitrogen and δ^{34}Sulfur ratios in particulate matter.

7.4 Monitoring Parameters and Collection Frequency

The types of samples, sample containers, and sample preservation requirements for the analysis included in this amendment are summarized in Table 1.

Table 1. Sample Containers and Preservation

Parameter	*Sample Volume and Container*	*Immediate Sample Processing/Preservation*
Molybdenum	1 1-L polyethylene bottle in double plastic bag[1]	5 mL HNO_3, refrigerate
Stable isotope — sulfur	4 1-L polyethylene bottles	Filter onto glass fiber filters (0.7 μm nominal pore size), freeze[2]
— nitrogen	1 1-L polyethylene bottle	Filter onto glass fiber filters (0.7 μm nominal pore size), freeze[2]
C. perfringens	1 250-mL polypropylene bottle	Sodium thiosulfate[3], refrigerate, ship immediately
Nutrients	1 1-L polyethylene bottle	Filter; retain filtrate for dissolved inorganic nutrients[4], TDN[5], TDP[5], DOC[6] analysis; retain filter for biogenic silica, POP, POC and PON analysis; ship immediately

[1]This is the same bottle as used for the metals listed in Table 1 of Shea (1993).
[2]This processing and preservation modifies that listed in Table 1 of Shea (1993).
[3]Neutralizes chlorine.
[4]Preserved with chloroform.
[5]Preserved with potassium persulfate.
[6]Preserved with phosphoric acid.

7.5 Parameter Table

The analytes that will be measured and the analytical methods are summarized in Table 2. This table modifies Table 2 of Shea (1993) for this work. The analytical methods used to measure DOC, POC, DOP, DON, PON, NH_4, NO_3, NO_2, PO_4, and SiO_4 in seawater (Table 2 of Albro *et al.* (1993)) will be used for the effluent samples. Section 12.2 describes modifications necessary to measure these at high concentrations in sewage effluent.

Table 2. Laboratory Analyses and Methods

Parameter	***Units***	***Methodology[1] (EPA Method No.)***	***Storage (Holding Time[2])***
Clostridium perfringens	#/100 mL	incubation/ spore counting (Bisson and Cabelli, 1979)	Refrigeration (24 hours)
Trace Metals			
Mo	µg/L	GFAAS (modified EPA 246.2)	Room temperature[2] (6 months)
Stable Isotopes			
$\delta^{15}N$, $\delta^{34}S$	%	mass spectrometry	Thaw and dry at 60°C prior to shipment for analysis (6 months)
Nutrients			
Particulate Organic Phosphorus	µM	Solorzano and Sharp (1980)	Dry over desiccant. (3 months)
Biogenic Silica	µM	Knauss *et al.* (1983)	Dry over desiccant. (3 months)

[1]No EPA-published methods exist with the required detection limits. See Section 12 for discussion of modified EPA methods and literature references.
[2]Storage temperature once sample has been acidified.

Methods for biogenic silica, particulate organic phosphorus, and molybdenum are described in Section 12.

8. PROJECT FISCAL INFORMATION

This project is being carried out under the Harbor and Outfall Monitoring contract (Contract No. S138) between MWRA and Battelle Ocean Sciences.

9. SCHEDULE OF ACTIVITIES AND DELIVERABLES

Detailed effluent characterization for the parameters included in this amended CW/QAPP will be conducted from December 1993 through December 1994 (13 months). Pilot treatment plant studies will be conducted on a schedule to be determined by MWRA. Up to three studies are planned.

10. PROJECT ORGANIZATION AND RESPONSIBILITIES

The organization of this task is the same as described in Figure 1 of Shea (1993), with the following exceptions. Biological Analytical Laboratories, Inc., North Kingstown, RI, will analyze effluent and pilot secondary treatment plant samples for *Clostridium perfringens* spores. The University of Rhode Island (URI) will perform all the nutrient analyses. Dr. Peter Doering will oversee all nutrient analysis of effluent samples.

11. DATA QUALITY REQUIREMENTS AND ASSESSMENTS

Table 3 adds to Table 5 of Shea (1993).

Data quality objectives, other than MDLs, are presented in Table 6 of Shea (1993).

11.1 Nutrients

The data quality objectives for laboratory measurements defined in Table 7 of Albro *et al.* (1993) are appropriate to the measurement of nutrient effluent. However, high concentrations are expected which may require additional dilution to ensure accuracy and precision. These data quality objectives are amended to include the information in Table 4 below.

Table 3. Method Detection Limit (MDL) Goals

Parameter	MDL Goal[1]	NPDES MDL[2]	Water Quality Criteria
Metals	(μg/L)	(μg/L)	(μg/L)
Molybdenum	0.50	80	NA[3]
Nutrients	(μM)	(μM)	(μM)
Dissolved Ammonia	0.04	NA	NA
Dissolved Nitrate	0.02	NA	NA
Dissolved Nitrite	0.02	NA	NA
Dissolved Phosphate	0.02	NA	NA
Dissolved Silicate	0.04	NA	NA
Dissolved Organic Nitrogen	2	NA	NA
Dissolved Organic Phosphorus	0.6	NA	NA
Dissolved Organic Carbon	30	NA	NA
Particulate Organic Carbon	4	NA	NA
Particulate Organic Nitrogen	3	NA	NA
Particulate Organic Phosphorus	0.02	NA	NA
Biogenic Silica	0.04	NA	NA

[1]MDL goals are based on past performance at Battelle (metals) and URI (nutrients) and the goal of detecting concentrations at least 5 times less than the corresponding lowest salt water aquatic life criteria.
[2]NPDES MDLs are typical MDLs reported by MWRA in their NPDES monitoring reports; the listed MDLs meet the EPA Contract Laboratory Program (CLP) requirements.
[3]Not available.

Table 4. Objectives for Laboratory Measurement

Parameter	*Units*	*Method by which Analytical Accuracy is Assessed*	*Precision[1] (Better than)*
Particulate Organic Phosphate	μM	Potassium phosphate monobasic Standard	± 10%
Biogenic Silica	μM	Pure Silica Standard	± 10%

12. SAMPLING AND ANALYTICAL PROCEDURES

12.1 Effluent Sample Collection

All effluent samples will be collected by MWRA staff. Detailed instructions for sample collection and processing are attached (Appendix A).

12.2 Laboratory Analytical Procedures

The analytical methods to be employed on this task for *Clostridium perfringens* and stable isotopes $\delta^{15}N$ and $\delta^{34}S$ are described in Sections 12.2.3 and 12.2.4 of Shea (1993) respectively. Analytical procedures for molybdenum and nutrients are described below.

12.2.1 Molybdenum

In addition to the metals listed in Shea (1993), all effluent samples will be analyzed for total-recoverable molybdenum. Samples will be prepared for total-recoverable molybdenum analysis in conjunction with the rest of the metals samples. Preparation procedures for determining total-recoverable metals will follow those listed in Section 12.2.2 of Shea (1993). Digested samples will be analyzed directly (no preconcentration) by graphite furnace atomic absorption spectroscopy (GFAAS).

12.2.2 Nutrients

The analytical methods for nutrient analysis are described in Albro *et al.* (1993). Dissolved inorganic nutrient analysis methods are described in Section 12.4.1; particulate carbon and nitrogen in Section 12.4.3; dissolved organic nitrogen and phosphorus in Section 12.4.4; and dissolved organic carbon in Section 12.4.5. Analytical methods for particulate phosphorus and biogenic silica are described below. Due to the high concentrations of dissolved nutrients in the effluent, dilution of samples will undoubtedly be required to produce concentrations which fall within the linear range of the autoanalyzer. Dilution of the following samples is anticipated: dissolved inorganic nutrients and total dissolved nitrogen and phosphorus.

The response of the autoanalyzer is linear over the concentration range of 0-40 μmolar for dissolved inorganic nitrite, nitrate, ammonia, and silicon. The linear

range is 0-25 μmolar for soluble reactive phosphorus. Typical concentration ranges for sewage effluent are 1-10 μmolar for nitrite, 2-50 for nitrate, ~1000 μmolar for ammonia, 100-200 μmolar for silicate, and 30-50 μmolar for phosphate. Ordinarily, ammonia requires a 100% dilution while other analytes require a 4x dilution. Dilutions of 20x or less are accomplished in the autoanalyzer sample cup (5 ml) using calibrated volumetric pipettes.

Dilutions greater than 20x are accomplished in acid-cleaned containers of larger volume using volumetric pipettes. Samples are diluted with deionized water (Mega Pure).

Samples for total dissolved nitrogen and phosphorus are first oxidized converting all N and P to inorganic form. The digested sample is then diluted appropriately as above before analysis on the autoanalyzer.

Samples for particulate carbon, nitrogen, phosphorus and biogenic silica are not diluted. Amounts sufficient for analysis are obtained by filtering appropriate volumes of effluent. Thus, for a seawater sample, 60 mls may have to be filtered, whereas only 5 mls of effluent would be required to obtain sufficient particulate carbon and nitrogen for analysis.

Particulate Phosphorus. The method used to determine particulate phosphorus will be a modification of Solorzano and Sharp (1980). The filter with retained particulates will be placed into a scintillation vial, 2 mL of 0.017 M $MgSO_4$ added, and dried. The dried filter is then baked at 450°C. After addition of 0.2 M HCl, particulate phosphorus is determined calorimetrically using a Technicon II Autoanalyzer as described for inorganic phosphate in Section 12.4.1 of Albro *et al.* (1993).

Biogenic Silica. Particulate matter for determination of biogenic silica will be extracted using a wet alkaline digestion (Knauss *et al.*, 1983). Particulates retained on a 0.4 Poretics membrane filter are digested with 0.2 N NaOH, and neutralized with 0.2 N HCl. Dissolved silica is measured colorimetrically using a Technicon II Autoanalyzer and biogenic silica is calculated.

13. SAMPLE CUSTODY

See Section 13 of Shea (1993). The MWRA personnel collecting the samples will initiate the Chain-of-Custody (COC) form. An example COC form is presented in Figure 2 of Shea (1993). Table 5 adds to the protocols listed in

Table 7 of Shea (1993) with the exception of CP, *Clostridium perfringens*, which corrects the name of the analytical laboratory.

Table 5. Protocol Codes and Related Samples

Protocol	*Lab*	*Description*
CP	BAL	*Clostridium perfringens*
POC/PON	URI	Particulate organic carbon/particulate organic nitrogen
DOC	URI	Dissolved organic carbon
POP	URI	Particulate organic phosphorus
DON/DOP	URI	Dissolved organic nitrogen/dissolved organic phosphorus
BioSi	URI	Biogenic silica
DIS NUT	URI	Dissolved nutrients
MET	BOS	Metals (Ag, Cd, Cu, Mo, Ni, Pb, Zn)

14. CALIBRATION PROCEDURES AND PREVENTIVE MAINTENANCE

14.1 Calibration Procedures and Response Factor Stability

Section 14.1 of Shea (1993) and Section 14.3 of Albro *et al.* (1993) describe the calibration procedures that will be employed. Particulate organic phosphorus and biogenic silica are analyzed on a Technicon II Autoanalyzer. Calibration procedures for the Technicon II Autoanalyzer are outlined in Section 14.3 of Albro *et al.* (1993). However, calibration standards for the nutrients will be prepared in deionized water, not seawater, for the effluent samples.

14.2 Instrument Maintenance

See Section 14.2 of Shea (1993) and Section 14.3 of Albro *et al.* (1993).

15. DOCUMENTATION, DATA REDUCTION, AND REPORTING

See Section 15 of Shea (1993).

16. DATA VALIDATION

See Section 16 of Shea (1993).

17. PERFORMANCE AND SYSTEM AUDITS

Performance and system audits will follow the guidelines described in Section 17 of Shea (1993) as well as those described in Section 11 of this document.

18. CORRECTIVE ACTION

See Section 18 of Shea (1993).

19. REPORTS

The reports to be prepared under this task order are listed in Table 6.

Table 6. Schedule of Reports.

Revised Scope of Work	December 31, 1993
Quality Assurance Project Plan Modifications	January 15, 1994
1994 Effluent Characterization Data Report for Nutrients[1]	February 1995
Draft 1994 Annual Effluent Characterization Report: Methods, Results, and Interpretation Sections	February 1995
Final 1994 Annual Effluent Characterization Report: Methods, Results, and Interpretation Sections	April 1995
Pilot Treatment Plant Data Report	To be determined
Draft 1994 Pilot Treatment Plant Synthesis Report: Methods, Results, and Interpretation Sections	To be determined
Final 1994 Pilot Treatment Plant Synthesis Report: Methods, Results, and Interpretation Sections	To be determined

[1]Will be included with the 1994 Effluent Characterization Data Report developed under Task 18.

20. REFERENCES

Albro, C., J. Kelly, J. Hennessy, P. Doering, J. Turner. 1993. Combined Work/Quality Assurance Project Plan (CW/QAPP) for Baseline Water Quality Monitoring: 1993-1994. Submitted to the Massachusetts Water Resources Authority, Boston, MA. May 21, 1993.

Bisson, J.W. and V.J. Cabelli. 1979. Membrane filter enumeration method for *Clostridium perfringens*. *Appl. Environ. Microbiol.* 37:5-66.

Knauss, G.L., C.L. Shelske, and C.O. Davis. 1983. Comparisons of three wet-alkaline methods of digestion of biogenic silica in water. *Freshwater Biol.* 13:73-81.

Shea, D. 1993. Combined Work/Quality Assurance Project Plan (CW/QAPP) for Detailed Effluent Characterization: 1993-1994. Submitted to the Massachusetts Water Resources Authority, Boston, MA. June 23, 1994.

Solorzano, L. and J.H. Sharp. 1980. Determination of total dissolved phosphorus and particulate phosphorus in natural waters. *Limnol. and Oceanogr.* 25:754-758.

APPENDIX A

INSTRUCTIONS FOR SAMPLE COLLECTION AND PROCESSING

Clostridium Sample Collection. *Clostridium perfringens* samples will be collected in 250-mL polypropylene bottles. The bottles contain sodium thiosulfate, a chlorine neutralizer. The bottles should be filled to the bend in the neck of the bottle leaving 1/2 inch of air space. The samples should be shipped on blue ice the same night of the date of collection and marked for next day delivery. Ship samples to:

Gerri Miceli
Biological Analytical Laboratories, Inc.
610 Ten Rod Road
North Kingstown, RI 02852

In addition, please call Gerri Miceli at (401) 294-6677 with the shipping number so that coolers may be tracked if the need arises.

Metals and Mercury Sample Collection Metals samples will be collected in 500-mL polyethylene bottles and the mercury samples in 500-mL Teflon bottles. Each of the bottles will contain 5 mL of 50% nitric acid; handle with caution. Fill the bottles with sample up to the shoulder of the bottle, cap tightly, and invert the bottle at least twice to mix the acid with the sample, double bag, and refrigerate.

Note: To avoid contamination of the bottle or sample:

- Handle the bottles with clean gloves (supplied with bottles).
- While wearing the gloves avoid touching objects other than the bottle and cap, especially metal objects.
- While sampling, hold the cap with clean gloves, avoiding the inner surface. If it is not possible to hold the cap, place it in a clean bag.
- Leave the bottle uncovered for as little time as possible.

Organic Sample Collection. Organic samples will be collected in 2-L amber glass bottles. Fill the bottles with sample up to the handle on the neck, cap, and refrigerate.

Stable Isotope Sample Collection. The stable isotope samples will be initially collected in 5 1-L polyethylene bottles and then filtered immediately. Four of the bottles will be marked for sulfur and one will be marked for nitrogen. Fill each of the bottles to the base of the neck.

Setting up the filtering apparatus

(1) Connect the vacuum hose from the manifold to the waste receiving chamber, from the waste chamber to the water trap, and from the trap to the vacuum pump.

(2) Place the bottom half of the glass filter unit with the rubber stopper in the manifold.

(3) With gloved hands open the foil packet containing the filters. Using the forceps provided pick up a filter by the edge (avoid touching the middle of the filter) and place it on the filter unit.

(4) Place the top half of the filter unit on the bottom half and clamp.

(5) The manifold has on/off valves to control vacuum. When the valve stem is parallel to the manifold tube it is in the off position; when perpendicular it is on. Make sure only the two valves with the filter units are on.

Filtering for sulfur isotope analysis

(1) All four bottles labeled for sulfur are to be filtered. Several filters may be used and all are to be combined to make one sample. Filter approximately 200 mL of sample through the filter at a time (or less depending on the particulate load). Filter as much sample through each filter as possible. (Please note on the sample label and custody sheet the total volume filtered through all of the filters for sulfur; do the same for the nitrogen filtration.)

(2) When a bottle is emptied of sample, rinse it twice with approximately 20 mL of deionized water to remove any particles adhering to the walls of the bottle.

(3) Once the filter starts to clog and the sample only dribbles through, stop adding sample to the filter unit.

(4) Let the filter go to near dryness, then rinse the filter three times with approximately 10 mL of deionized water. This gets rid of any dissolved sulfur.

(5) After the rinses and the filter has gone dry, shut the vacuum off, and remove the top of the filter unit. With the forceps, touching only the edges of the filter, fold the filter in half. It is important to fold the filter exactly in half to avoid the loss of sample.

(6) Make a pouch from a piece of aluminum foil by folding it in half and folding over two of the sides. Place the filter in the middle of the foil.

(7) Repeat the above steps until all 4 L of sample have been filtered, placing all filters on the same foil pouch.

(8) Fold the remaining side of the foil pouch, label the sample, place in a zip lock bag, and freeze.

Filtering for nitrogen isotope analysis

Follow the same steps for sulfur isotope analysis as above with the 1-L sample and place the filter(s) in a different foil pouch.

Dissolved Inorganic Nutrients (Keep water\no replicates\no blanks)

1. Shake sample so it is well mixed.
2. Rinse 60 mL syringe three times with 10 mL of sample. Use Teflon® tip to draw up sample.
3. Fill syringe with sample.
4. Remove Teflon tip and attach filter cartridge to syringe.
5. Nutrient sample bottle contains chloroform preservative. **DO NOT RINSE BOTTLE WITH SAMPLE.**
6. Filter at least 20 mL of sample into nutrient sample bottle.
7. Use as many filter cartridges as necessary to obtain 20 mL.
8. <u>To reuse filter cartridge:</u> Unscrew and lift off top two pieces, discard spent filter, rinse all three pieces with deionized water, put new filter on to cover rubber gasket (these filters tear easily, try dragging the filter across base into position). Match teeth in top to teeth in base, press down, screw down outer unit <u>tight.</u> It shouldn't wobble. Discard if filter doesn't seal or filter blows out; if this occurs redo sample.
9. Wipe lip of sample bottle.
10. Dry out cap, cap bottle, return to kit.

TDN and TDP (Keep water\two reps\two blanks)

1. Follow steps 1-4 of dissolved inorganic nutrient.
2. Filter sample into glass tubes.
3. Glass tubes contain potassium persulfate preservative.
   DO NOT RINSE.
4. Bottom of sample meniscus should be filled to reach the etched line on the glass tube.
5. Return tube to kit.
6. Repeat for second glass tube.
7. Do nothing with the third and fourth tubes, they will serve as blanks.

Biogenic Silica (Keep filter\two reps\two blanks)

1. Shake sample so it is well mixed.
2. Continue using same 60 mL syringe and Teflon tip used for TDN and TDP.
3. Draw up exactly 20 mL of sample.
4. Remove Teflon tip and attach filter cartridge from bag labeled BS#1. Note: The filter is a different type than used for nitrogen and phosphorus dissolved and particulate samples.
5. Filter all 20 mL.
6. If you feel positive that you can get more sample through the filter; remove filter cartridge, replace Teflon tip, draw up the amount that will pass through the filter, remove Teflon tip, replace filter cartridge and resume filtering. It is important that you completely empty the syringe.
7. Remove filter cartridge, draw 10 mL of air into the syringe, reattach cartridge, push air through cartridge to dry out filter. Repeat until all sample has passed through filter.
8. Keep track of the total volume of sample filtered and record on storage bag labeled BS#1.
9. Return filter cartridge to bag labeled BS#1 and return bag to kit.
10. Repeat steps 1-9 for filter cartridge in bag marked BS#2.
11. Blanks: a. Get a clean 60 mL syringe.
    b. Draw up 10 mL of air (no Teflon tip).
    c. Attach filter cartridge from bag marked BS Blank 1.
    d. Push air through it and return to bag.
    e. Repeat for BS Blank 2.

DOC (Keep water\no reps\no blanks)

1. Shake sample.
2. Continue using same 60 mL syringe and Teflon tip used for biogenic silica.

3. Fill syringe with sample.
4. Remove Teflon tip and attach filter cartridge.
5. Filter at least 40 mL into amber bottle.
6. Amber bottle contains phosphoric acid preservative. DO NOT RINSE.
7. Use as many filter cartridges as necessary to obtain 40 mL.
8. Return amber bottle to kit.

POP (Keep filter\2 reps\2 blanks)

1. Shake sample.
2. Continue using same 60 mL syringe and Teflon tip used for DOC
3. Draw up exactly 35 mL of sample.
4. Remove Teflon tip and attach filter cartridge from bag labeled POP#1.
5. Filter all 35 mL of sample.
6. If you feel that you can get more sample through the filter, follow step 6 of the biogenic silica procedure.
7. Dry out filter as in step 7 of the biogenic silica procedure.
8. Keep track of the total amount filtered and record on storage bag labeled POP#1.
9. Return filter cartridge to bag labeled POP#1 and return to kit.
10. Repeat steps 1-9 for filter cartridge in bag marked POP#2.
11. Blanks - Follow step 11 of the biogenic silica method but use filter cartridges labeled POP Blank 1 and Blank 2.

POC AND PON (Keep filter\2 reps\2 blanks)

1. Shake sample.
2. Attach Teflon tip to 10 mL syringe and rinse three times with 5 mL of sample.
3. Fill syringe with exactly 10 mL of sample.
4. Attach filter cartridge from bag marked PCN#1.
5. Push <u>all</u> 10 mL through filter.
6. If you feel that you can get more water through the filter, follow step 6 of the biogenic silica procedure.
7. Dry out the filter as in step 7 of the biogenic silica procedure.
8. Keep track of the total amount filtered and record on storage bag marked PCN#1.
9. Repeat procedure for filter cartridge labeled PCN#2.
   Return bags to kit.
10. Blanks — Follow step 11 of biogenic silica procedure but use filter cartridges labeled PCN Blank 1 and Blank 2.

All nutrient samples should be shipped on the same day they are collected. Ship for overnight delivery.

COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN (CW/QAPP)

for

DETAILED EFFLUENT CHARACTERIZATION: 1993-1994

Task 18
MWRA Harbor and Outfall Monitoring Project

CONCURRENCES AND APPROVALS:

Battelle Project Manager	Carlton D. Hunt Dr. Carlton Hunt	6-23-93 Date
Battelle Project QA Officer	Rosanna J. Buhl Ms. Rosanna Buhl	6-23-93 Date
MWRA Project Manager	Michael J. Mickelson Dr. Michael Mickelson	6/28/93 Date

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1. PROJECT NAME

MWRA Harbor and Outfall Monitoring Project

2. PROJECT REQUESTED BY

Massachusetts Water Resources Authority (MWRA)

3. DATE OF REQUEST

December 6, 1992

4. DATE OF PROJECT INITIATION

December 6, 1992

5. PROJECT MANAGEMENT

Dr. Michael Connor, MWRA Director of Environmental Quality Department
Dr. Michael Mickelson, MWRA Harbor and Outfall Monitoring Project Manager
Mr. Ken Keay, MWRA Detailed Effluent Characterization Task Manager

Dr. Carlton Hunt, Battelle Project Manager for Harbor and Outfall Monitoring
Dr. Allen Uhler, Battelle Detailed Effluent Characterization Task Leader

6. QUALITY ASSURANCE MANAGEMENT

Ms. Rosanna Buhl, Battelle Project QA Officer

7. PROJECT DESCRIPTION

7.1 Objective and Scope

The overall objective of the Detailed Effluent Characterization Task is to measure the concentrations of trace metals and organic contaminants in the MWRA effluent to obtain an accurate estimate of discharge loads and a chemical "fingerprint" to help trace the discharge in the environment. This work is intended to supplement routine measurements of effluent constituents conducted as part of the National Pollutant Discharge Elimination System (NPDES) permit compliance monitoring and other effluent monitoring conducted to evaluate treatment plant performance, and to set local limits for industrial dischargers. These regular routine monitoring analyses do not include many contaminants that are important for assessing the transport, fate, and effects of the effluent discharge. In addition, the analytical detection limits reported for the NPDES monitoring are too high to detect many of the contaminants of concern and are often higher than the water quality criteria that might be used to assess potential adverse effects of the effluent discharge. The analytical methods employed under this task will provide significantly lower detection limits than those used for NPDES monitoring, and will provide measurements of additional contaminants and sewage tracers that are important for source identification and contaminant transport modeling.

A secondary objective of this task is provide data on the concentrations of selected trace metals and organic contaminants in the influent and effluent of the Pilot Secondary Treatment Plant to assess the performance of this treatment process in removing toxic contaminants from the effluent discharge.

The scope of this task includes transporting effluent samples collected by MWRA staff to the Battelle Ocean Sciences laboratory, measuring the concentrations of selected analytes in the effluent, and reporting the data for interpretation under Task 25.2.4 (Detailed Effluent Characterization). Per direction of MWRA and the Outfall Monitoring Task Force, only the total concentrations of contaminants will be measured; dissolved, particulate, and colloidal fractions will not be measured. In addition, stable isotopes, sterols/sterones, and *Clostridium perfringens* will only be measured in effluent samples if specifically requested by MWRA.

7.2 Data Usage

The Detailed Effluent Characterization Task will provide data on effluent contaminant concentrations at very low levels that will be used to

- Obtain more accurate estimates of contaminant discharge loads.
- Estimate short-term (day to week) and long-term (month to year) variability and temporal patterns in discharge loads.
- Estimate the annual mean discharge load of toxic contaminants and effluent tracers.
- Compare to NPDES monitoring data collected each month.
- Establish an effluent source "fingerprint" based on the distribution of contaminants and chemical tracers that are unique to this source.
- Assess the performance of the Pilot Secondary Treatment Plant in removing toxic contaminants from the effluent discharge.

Data from this task and other tasks of the Harbor and Outfall Monitoring Project will be integrated and used to produce, under Task 25, synthesis reports describing the relation between contaminant discharge loads and measured contaminant distributions in the environment. Concentrations of toxic contaminants will be compared to water-quality criteria to evaluate the potential impact of discharging effluent into Massachusetts Bay.

7.3 Technical Approach

To accomplish the objectives, effluent samples will be collected by MWRA staff using their regular procedures for collecting 24-h composite samples and aliquots of these samples will be poured into sample containers supplied by Battelle. Samples will be collected twice each month during the regular NPDES monitoring sample collection: once at the beginning of the seven-day NPDES collection period and once at the end of the seven-day NPDES collection period. This will provide data for comparison to NPDES monitoring data for two of the three NPDES samples analyzed each month and will provide information on the short-term variability of discharge loads. These procedures are similar to procedures used in a previous study of organic contaminants in the MWRA effluent (Shea, 1992a and 1992b) and in a study of trace metals in the effluents of municipal discharges in the metropolitan New York area (Battelle, 1991).

The analytical methods to be employed on this task are modifications of existing EPA methods that are comparable to those used in previous studies (Shea, 1992a and 1992b; Battelle, 1991) and will provide data that are comparable to related studies of the same contaminants in water, sediment, and animal tissue.

The study of pilot plant treatment efficiency has not been designed. When requested by MWRA, Battelle will transport samples from MWRA to Battelle Ocean Sciences laboratory and perform the requested analyses. Laboratory techniques described for the monthly effluent monitoring will be employed as needed for the pilot plant study. Any specific deviations from this CW/QAPP (e.g., measuring a subset of parameters, changing the number of sample replicates, or other sample design changes) will be discussed with MWRA and documented in a letter to the MWRA Project Manager. The pilot plant study will not be discussed further in this CW/QAPP.

Details of the sampling and analytical procedures to be used in this task are provided in Section 12.

7.4 Monitoring Parameters and Collection Frequency

The types of samples, sample containers, and sample preservation requirements are summarized in Table 1. The frequency of sample collection will be two sets

Table 1. Sample Containers and Preservation

Parameter	*Sample Volume and Container*	*Immediate Sample Processing/Preservation*
Organic Contaminants	2 2-L amber glass bottles	Refrigerate
Metals (Ag, As, Cd, Cu, Ni, Pb, Zn)	1 1-L polyethylene bottle in double plastic bag	5 mL HNO_3, refrigerate
Mercury	1 1-L Teflon bottle in double plastic bag	5 mL HNO_3, refrigerate
C. perfringens	1 250-mL amber glass bottle	Refrigerate
Stable isotopes	1 1-L polyethylene bottle	Refrigerate

of samples collected every month, one set at the beginning of the NPDES seven-day sampling period and one set at the end of the seven-day NPDES sampling

period. Sampling will begin in June 1993 and end in November 1994. The sampling frequency may be altered by MWRA to meet the study objectives (e.g., the frequency of stable isotope measurements will likely be less frequent than the other measurements). Additional effluent samples from the pilot plant study will be analyzed by Battelle at the request of MWRA.

7.5 Parameter Table

The chemical parameters to be analyzed in the laboratory and the methods to be used are summarized in Table 2. A more detailed list of the organic analytes is presented in Table 3. Effluent samples will be refrigerated as soon as possible after sampling, remaining at 4 °C until sample processing begins.

8. PROJECT FISCAL INFORMATION

This project is being carried out under the Harbor and Outfall Monitoring contract (Contract No. S138) between MWRA and Battelle Ocean Sciences. Some of the analyses described in this CW/QAPP are not within the present scope of this contract (i.e., sterone analyses and some stable isotope analyses). If these analyses are requested by MWRA, the contract will be amended to include this additional scope of work.

9. SCHEDULE OF ACTIVITIES AND DELIVERABLES

Detailed effluent characterization monitoring activities will span the period from the date of project initiation (see Section 4.0) until February 1995, when the last annual synthesis report is due. Activities include effluent sampling and laboratory analyses, with deliverables consisting of associated data reports and synthesis reports. Effluent sampling will be conducted every month beginning June 1993 and continuing through November 1994 (Table 4). MWRA staff are responsible for scheduling sample collection and for notifying Battelle when samples are available. Draft data reports are due in December 1993 and December 1994; schedules may need to be modified depending on the date of the November 1993 and 1994 sampling, this will be at the direction of MWRA. Final data reports are due 2 weeks after receiving comments from MWRA. The Draft Detailed Effluent Characterization Synthesis Reports, prepared under Task 25, are due in February 1994 and February 1995; final synthesis reports are due 2 weeks after receiving comments from MWRA.

Table 2. Laboratory Analyses and Methods

Parameter	*Units*	*Methodology[1] (EPA Method No.)*	*Storage (Holding Time[2])*
Clostridium perfringens	#/100 mL	incubation/ spore counting	Refrigerate (6 months)
Stable Isotopes $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$	%	mass spectrometry	Refrigerate (6 months)
Organics			
Polychlorinated biphenyls	ng/L	GC/ECD (modified 8080)	Refrigerate (7 days/40 days)
Polynuclear Aromatic Hydrocarbons	ng/L	GC/MS (SIM) (modified 8270)	Refrigerate (7 days/40 days)
Pesticides	ng/L	GC/ECD (modified 8080)	Refrigerate (7 days/40 days)
Linear alkyl benzenes	ng/L	GC/MS (SIM) (modified 8270)	Refrigerate (7 days/40 days)
Trace Metals			
Ag	µg/L	GFAAS (modified 272.2)	Refrigerate (6 months)
Cd	µg/L	GFAAS (modified 213.2)	Refrigerate (6 months)
Cu	µg/L	GFAAS (modified 220.2)	Refrigerate (6 months)
Cr	µg/L	GFAAS (modified 218.2)	Refrigerate (6 months)
Hg	µg/L	CVAAS (modified 245.1)	Refrigerate (28 days)
Ni	µg/L	GFAAS (modified 249.2)	Refrigerate (6 months)
Pb	µg/L	GFAAS (modified 239.2)	Refrigerate (6 months)
Zn	µg/L	GFAAS (modified 289.2)	Refrigerate (6 months)

[1] No EPA-published methods exist with the required detection limits (see Table 5). See Section 12 for discussion of modified EPA methods and literature references.

[2] Where two times are given, the first refers to the maximum time prior to extraction of sample; the second refers to the maximum time prior to instrumental analysis.

Table 3. Effluent Chemistry Analytes

Metals
- Ag silver
- Cd cadmium
- Cu copper
- Cr chromium
- Hg mercury
- Ni nickel
- Pb lead
- Zn zinc

Polychlorinated biphenyls
- 2,4,-Cl_2(8)
- 2,2′,5-Cl_3(18)
- 2,4,4′-Cl_3(28)
- 2,2′,3,5′-Cl_4(44)
- 2,2′,5,5′-Cl_4(52)
- 2,3′,4,4′-Cl_4(66)
- 3,3′,4,4′-Cl_4(77)
- 2,2′4,5,5′-Cl_5(101)
- 2,3,3′,4,4′-Cl_5(105)
- 2,3′,4,4′5-Cl_5(118)
- 3,3′,4,4′,5-Cl_5(126)
- 2,2′,3,3,4,4′-Cl_6(128)
- 2,2′,3,4,4′,5-Cl_6(138)
- 2,2′4,4′,5,5′-Cl_6(153)
- 2,2′3,3,4,4′,5-Cl_7(170)
- 2,2′,3,4,4′,5,5′-Cl_7(180)
- 2,2′,3,4,5,5′,6-Cl_7(187)
- 2,2′,3,3′,4,4′,5,6-Cl_8(195)
- 2,2′,3,3′4,4′,5,5′,6-Cl_9(206)
- Decachlorobiphenyl-Cl_{10}(209)

Linear alkyl benzenes (LAB)
- phenyl decanes
- phenyl undecanes
- phenyl dodecanes
- phenyl tridecanes
- phenyl tetradecanes

Polynuclear aromatic hydrocarbons (PAH)
- naphthalene
- C_1-naphthalenes
- C_2-naphthalenes
- C_3-naphthalenes
- acenaphthylene
- acenaphthene
- fluorene
- C_1-fluorenes
- C_2-fluorenes
- C_3-fluorenes
- anthracene
- phenanthrene
- C_1-phenanthrenes/anthracene
- C_2-phenanthrenes/anthracene
- C_3-phenanthrenes/anthracene
- C_4-phenanthrenes/anthracene

PAH (continued)
- dibenzothiophene
- C_1-dibenzothiophenes
- C_2-dibenzothiophenes
- C_3-dibenzothiophenes
- fluoranthene
- pyrene
- C_1-fluoranthenes/pyrenes
- benzo[*a*]anthracene
- chrysene
- C_1-chrysene
- C_2-chrysene
- C_3-chrysene
- C_4-chrysene
- benzo[*b*]fluoranthene
- benzo[*k*]fluoranthene
- benzo[*a*]pyrene
- dibenzo[*a,h*]anthracene
- benzo[*g,h,i*]perylene
- indeno[1,2,3-*c,d*]pyrene
- perylene
- biphenyl
- benzo[*e*]pyrene
- dibenzofuran

Pesticides
- hexachlorobenzene
- lindane
- heptachlor
- aldrin
- endrin
- heptachlorepoxide
- alpha-chlordane
- trans-Nonachlor
- dieldrin
- mirex
- o,p′-DDD
- p,p′-DDD
- o,p′-DDE
- p,p′-DDE
- o,p′-DDT
- p,p′-DDT

Sterols/Sterones
- 5β-cholestan-3β-ol
- 5β-cholestan-3α-ol
- cholest-5-en-3β-ol
- 5α-cholestan-3β-ol
- 5β-cholestan-3-one
- 5α-cholestan-3-one

Table 4. Schedule of Effluent Sampling. Two Samples per month will be generated that are separated in time by 3-5 days.

Sampling Date	*Event_ID*
June 1993	E9301
July 1993	E9302
August 1993	E9303
September 1993	E9304
October 1993	E9305
November 1993	E9306
December 1993	E9307
January 1994	E9401
February 1994	E9402
March 1994	E9403
April 1994	E9404
May 1994	E9405
June 1994	E9406
July 1994	E9407
August 1994	E9408
September 1994	E9409
October 1994	E9410
November 1994	E9411

10. PROJECT ORGANIZATION

The project organization is shown in Figure 1. Dr. Michael Mickelson is the MWRA Project Manager. He will be informed of all matters pertaining to work described in this CW/QAPP. Mr. Ken Keay is the MWRA Task Manager. The MWRA contact for sample collection and transfer is Mr. Maury Hall. Dr. Carlton Hunt is the Battelle Project Manager responsible for the overall performance of this project. Dr. Allen Uhler will be the Task Leader and will have overall responsibility for the Task. Mr. Dion Lewis will oversee trace metal analysis for Battelle; Ms. Carole Peven will oversee organic contaminant analysis for Battelle. Ms. Rosanna Buhl, Project QA Officer, will oversee the QA activities for all technical work conducted by Battelle.

Battelle's subcontractor, MTH Environmental Associates (MTH), Marstons Mills, Massachusetts, will analyze effluent samples for *Clostridium perfringens* spores. Battelle's subcontractor, Marine Biological Laboratory, Woods Hole, Massachusetts, will analyze samples for stable isotopes. Analysis of samples for organic analytes and metals will be performed by Battelle.

11. DATA QUALITY REQUIREMENTS AND ASSESSMENTS

The quality of the data produced for the detailed effluent characterization depends on the accuracy, precision, representativeness, comparability, and completeness of the data. In addition, method detection limits (MDLs) must be sufficiently low to measure the organic analytes at ng/L concentrations or lower and the metals at μg/L concentrations or lower. The MDL goals for chemical contaminants are listed in Table 5, along with typical MDLs from the MWRA NPDES monitoring program using standard EPA methods and some water quality criteria for comparison. Data quality objectives, other than MDLs, are presented in Table 6 for the chemical contaminants.

There is very little precedence for establishing data quality requirements and assessments for stable isotope and *C. perfringens* analyses because they are non-routine analyses that have rarely been measured in effluent samples and the data are intended for qualitative use. Data quality requirements and assessments for these analyses are discussed below.

Deviations from the analytical scheme and data quality requirements presented in this CW/QAPP will be noted in the laboratory records associated with the analytical batch and in project files. All quality control (QC) data will be reported with the sample data. All corrective actions will be documented.

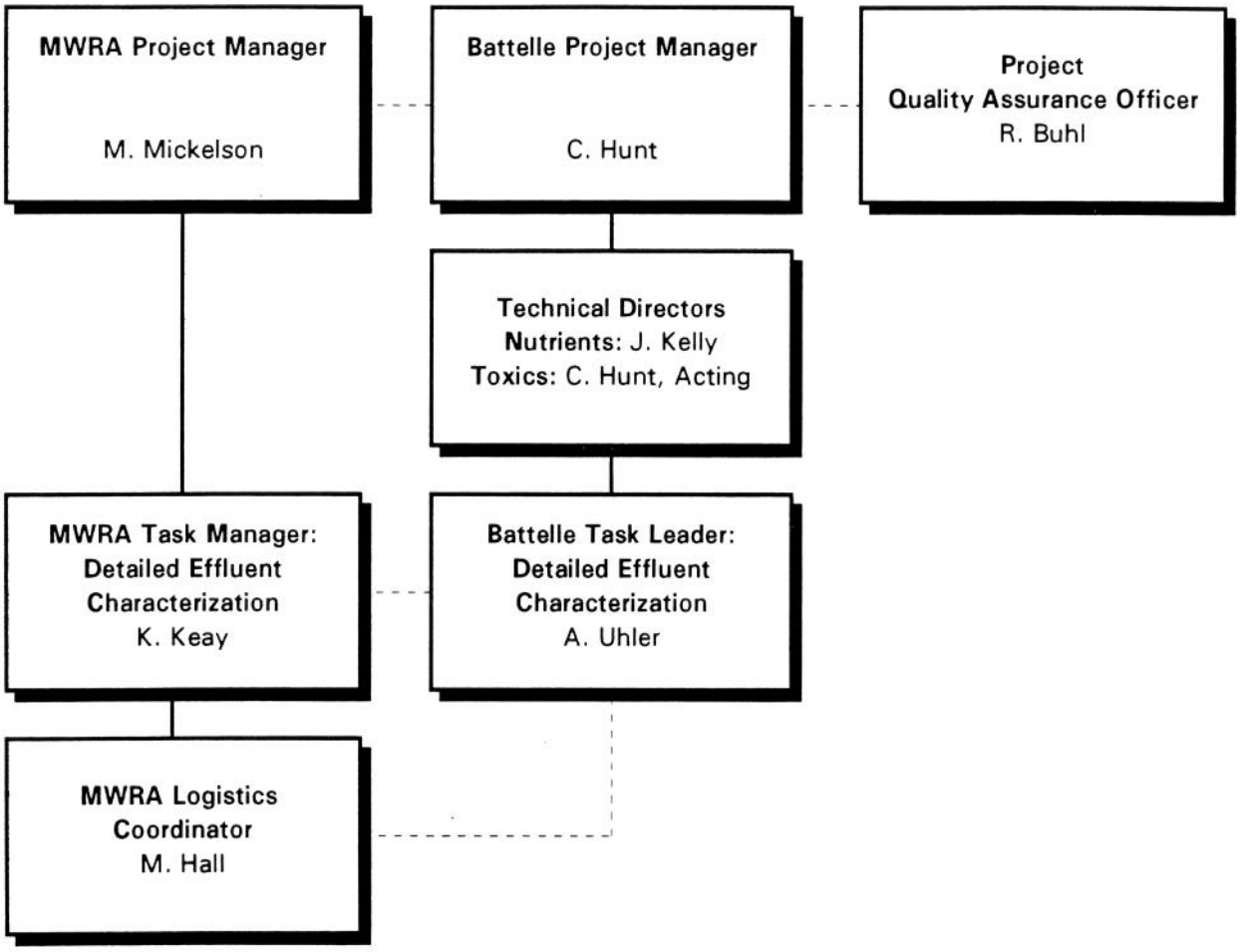

Figure 1. Organization Chart for Detailed Effluent Characterization.

Table 5. Method Detection Limit (MDL) Goals

Parameter	MDL Goal[1]	NPDES MDL[2]	Water Quality Criteria[3]
Metals	(μg/L)	(μg/L)	(μg/L)
Ag silver	0.50	10.0	2.3
Cd cadmium	0.50	4.0	9.3
Cu copper	0.50	10.0	2.9
Cr chromium	1.0	10.0	50.0[4]
Hg mercury	0.005	0.2	0.025
Ni nickel	1.00	10.0	8.3
Pb lead	0.50	1.0	5.6
Zn zinc	2.00	6.0	86
Organic Analytes	(ng/L)	(ng/L)	(ng/L)
Polychlorinated biphenyls (PCB) (as congeners)	1	500	30
Linear alkyl benzenes (LAB)	50	NA	NA
Polynuclear aromatic hydrocarbons (PAH)	10	10,000	16-710
Pesticides	1	50-100	1-30
Sterols/sterones	10	NA	NA

[1] MDL goals are based on past performance at Battelle and the goal of detecting concentrations at least 5 times less than the corresponding lowest salt water aquatic life criteria.

[2] NPDES MDLs are typical MDLs reported by MWRA in their NPDES monitoring reports; the listed MDLs meet the EPA Contract Laboratory Program (CLP) requirements.

[3] Water quality criteria listed are the lowest salt water aquatic life criteria published by EPA. Criteria listed for PAH and pesticides are the range of individual values; PAH criteria are lowest observed effects levels. Human health criteria are generally lower than the aquatic life criteria.

[4] As chromium VI.

Table 6. Data Quality Objectives for Effluent Samples[1]

Quality Control Sample Type and Frequency	*Data Quality Objective*	*Corrective Action*
Procedural Blank Organics: 1/20 samples Metals: 1/20 samples	< 5 × MDL < 5 × MDL	Reextraction, reanalysis, and/or blank subtraction — determined by Task Leader; all corrective actions documented
EPA Performance Sample Organics: 1/year Metals: 1/year	± 30% difference vs. known values ± 30% difference vs. known values	Performance documented
Matrix Spike (MS/MSD) Organics: 1 set/20 samples Metals: 1 set/20 samples	50-150% recovery ≤ 30% RPD Average % CV: ± 35% individual analyte ± 30% average of all analytes	Document deviations
Surrogate Internal Standards (SIS) Every organics sample	50-150% recovery (one PAH SIS may exceed)	Results examined by project management or task leader. Corrective action (reextraction, reanalysis) or justification documented.
Calibrations: Initial	Organics: ± 25% RSD individual analyte ± 10% RSD average of all analytes Metals: Calibration regression coeff (r) > 0.99	Reanalyze or document and justify
Check	Organics: ± 25% RSD individual analyte ± 10% RSD average of all analytes Metals: ± 15% of true value	Remedial maintenance, new initial calibration, reanalyze samples at discretion of analyst and task leader. Decision documented and/or justified.

[1] See text in Section 11.0 for explanation.

When a sample does not meet the data quality objective and is not reanalyzed, the justification for this decision will be documented

11.1 Chemical Contaminants

11.1.1 Precision

Analytical precision will be determined using the concentrations of matrix spike (MS) and matrix spike duplicate (MSD) samples, with the relative percent difference (RPD) between duplicate analyses serving as the measure of precision. The RPD goal for MS/MSD samples is 30%. The RPD is calculated by

$$RPD = [\, 2\,(D_1 - D_2) \,/\, (D_1 + D_2)] \times 100$$

where D_1 = concentration of the first duplicate sample and
D_2 = concentration of the second duplicate sample.

11.1.2 Accuracy

Analytical accuracy will be evaluated based on percent recoveries of analytes in MS and MSD samples (one set of MS/MSD samples with every twenty effluent samples), the recovery of surrogate internal standards (SIS) that are added to every sample (organics only), as well as the results of the procedural blanks which will be analyzed with every twenty samples.

The data quality objective for accuracy is $\leq$30% difference between the measured concentrations and the calculated values in the matrix spikes for each individual analyte. Procedural blanks are to contain less than five times the method detection limit (MDL) of any target analyte.

All effluent samples and associated QC samples processed for organic analysis will be spiked with the appropriate SIS before extraction. Quantification of the SIS will be based on the recovery internal standards (RIS) added to the final extract just before instrumental analysis. The acceptable SIS recovery range is 50%-150%; one of the PAH surrogate internal standards can be outside this range as long as the others are within the acceptable range. Because samples are quantified relative to the recovery of the SIS which is added before extraction, any loss of analytes during processing is corrected by a comparable loss of the SIS. Therefore, recoveries of less than 50% may be considered acceptable. Each sample showing low recoveries will be individually examined by the laboratory manager and/or task leader to determine the necessity of reextraction or reanalysis.

No standard reference materials (SRM) will be analyzed for this task because no effluent SRMs exist. However, Battelle will participate in three annual interlaboratory comparison exercises: (1) National Oceanic and Atmospheric Administration National Status and Trends Program (NOAA NS&T Program), (2) EPA Performance Evaluation Program, and (3) Massachusetts Department of Environmental Protection contract laboratory evaluation.

11.1.3 Completeness

The completeness of chemical analyses will be ensured by comparing the chain-of-custody forms received by the laboratory with the list of samples analyzed. All samples will be analyzed for the parameters listed in Table 3, and these analyses will be documented in the Chemistry Department project files. The data quality objective is 100% completion.

11.1.4 Comparability

All data developed for this project must be demonstrated to be comparable to similar data generated by other laboratories or by other similar studies. To accomplish this, Battelle will employ methods that are modifications of EPA methods and that are comparable to those used on previous effluent characterization studies (Shea, 1992a and 1992b; Battelle, 1991). In addition, these methods are comparable to those being used in other related studies of water, sediment, and animal tissue [e.g., for the MWRA, Massachusetts Bays Program (MBP), and NOAA NS&T Program]. In addition, Battelle participates in a series of interlaboratory calibration exercises for analysis of PAHs, PCBs, pesticides, and metals in water, sediment, and tissue using methods that are similar to those proposed for this task (see Section 11.2).

11.1.5 Representativeness

Representativeness has been addressed primarily in the sample collection design through the use of 24-h composite sampling, twice each month. Representativeness will also be ensured by proper handling, storage, and analysis of samples so that the material analyzed reflects the material collected as accurately as possible.

11.2 Stable Isotopes

The precision of stable isotope analyses will be measured through replicate analysis of samples that are split in the laboratory. Precision for particulate samples generally ranges from 0.1 to 1.0% with sulfur analysis usually being less precise than carbon or nitrogen. Accuracy will be assumed to be similar to that of published values of absolute error for stable isotope measurements (e.g., $\pm$0.3% for carbon). Comparability will be ensured by using the same methods

and laboratory that has performed similar measurements on MWRA sludge samples and on samples for other sewage disposal studies. Measures of accuracy and precision will be reported in the annual data reports.

11.3 *Clostridium perfringens*

The precision of *C. perfringens* analyses will be measured through replicate analysis of samples that are split in the laboratory. Precision for particulate and sediment samples generally ranges from 5 to 25%. A direct measure of accuracy is not possible because of a lack of standards, but results from a recent interlaboratory comparison indicate that agreement between two laboratories can range from 25 to 55%, or possibly higher if the sample is unusually heterogeneous (Parmenter and Bothner, 1993). Comparability will be ensured by using methods used previously to measure *C. perfringens* in MWRA effluent and sludge samples, sediment samples from Boston Harbor and Massachusetts Bay, and on samples for other sewage disposal studies. Measures of precision will be reported in the annual data reports.

12. SAMPLING AND ANALYTICAL PROCEDURES

12.1 Effluent Sample Collection

Effluent samples will be collected by MWRA staff using their regular procedures for collecting 24-h composite samples and aliquots of these samples will be poured into sample containers (Table 1) supplied by Battelle. Samples will be collected twice each month during the regular NPDES monitoring sample collection: once at the beginning of the seven-day NPDES collection period and once at the end of the seven-day NPDES collection period. These procedures are similar to procedures used in a previous study of organic contaminants in the MWRA effluent (Shea, 1992a and 1992b) and in a study of trace metals in the effluents of municipal discharges in the metropolitan New York area (Battelle, 1991).

All sample containers supplied by Battelle will be cleaned as appropriate to the measurement parameter. Metals sample containers will be cleaned in hot acid, using trace metal cleaning methods. Bottles for organic samples will be precleaned I-Chem bottles.

Battelle will pick up the effluent samples at the MWRA's Alewife Brook Pumping Station, 329 Alewife Brook Parkway, Somerville, MA. Each month, MWRA will inform Battelle when sampling has begun and when samples will be

available for pickup. Battelle will pick up samples upon notification of availability of the second set of samples collected by MWRA each month.

12.2 Laboratory Analytical Procedures

The analytical methods to be employed on this task are modifications of existing EPA methods that are comparable to those used on previous effluent characterization studies (see Section 11.0). The analytical methods are listed in Table 2; chemical analytes of interest are listed in Table 3. Brief descriptions of the analytical methods are given below.

12.2.1 Organic Analysis

Effluent samples will be serially extracted for PAH, LAB, chlorinated pesticides, and PCB following a modification to EPA Method 3510. This is the same extraction method used previously for characterization of the MWRA effluent (Shea, 1992a and 1992b). Each 2-L effluent sample will be transferred to a 3-L separatory funnel (measuring the volume with a graduated cylinder). The sample bottle will be rinsed with dichloromethane (DCM) and the rinseate added to the separatory funnel. The appropriate surrogate internal standards will be added to the sample and the sample will be serially extracted three times with 120 mL of DCM. The extract will be passed through a 20-g alumina column, eluting with 50 mL of DCM. The filtrate will be reduced in volume to about 1 mL using Kuderna-Danish and nitrogen concentration techniques. The concentrated extract will be further cleaned using size-exclusion (gel permeation) high-performance liquid chromatography (HPLC), which is a modification of EPA Method 3640. This procedure will remove common contaminants (including elemental sulfur) that interfere with instrumental analysis. The post-HPLC extract will be concentrated to approximately 0.5 mL under nitrogen and the recovery internal standards will be added to quantify extraction efficiency. The final extract will be split for analysis, one half remaining in DCM for PAH and LAB analysis, and the other half solvent-exchanged with isooctane for PCB and pesticide analysis.

This preparation scheme will be slightly modified when extracting effluent samples for sterol/sterone analysis in addition to PAH, LAB, PCB, and pesticides (see Grimalt *et al.*, 1990). Once the effluent sample is extracted three times and the extracts combined, these combined extracts will be concentrated to approximately 1 mL using Kuderna-Danish and nitrogen concentration techniques. This 1-mL extract will be chromatographed through a 20-g F-20 alumina column and separated into fractions for analysis. A combined fraction containing saturated, aromatic, and chlorinated hydrocarbons, including PAH, LAB, PCB, and chlorinated pesticides will be eluted with 100 mL DCM (F_1

fraction). Two polar fractions (F_2 and F_3) containing the sterones and sterols, respectively, will be eluted with a two-step process using 25 mL of 10% methanol in DCM, and 50 mL of 20% methanol in DCM. The F_2 and F_3 fractions will be kept separate and concentrated under nitrogen to approximately 1 mL, and spiked with the appropriate recovery internal standard. The F_1 fraction will be concentrated to 900 μL, and introduced to the HPLC for further cleanup and final preparation as described in the first paragraph of this section.

Sample extracts will be analyzed for PAH and LAB compounds by gas chromatography mass spectrometry (GC/MS) using a modification of EPA Method 8270. The modifications are (1) operating the mass spectrometer in the selected-ion-monitoring (SIM) mode and (2) tuning the mass spectrometer with PFTBA. Concentrations of LAB compounds will be determined as five separate LAB groups (those with alkyl chains containing 10, 11, 12, 13, and 14 carbon atoms) by monitoring the m/z 91 molecular ion during the GC/MS analysis following the method of Eganhouse *et al.* (1983). LAB will be quantified versus the surrogate internal standard 1-phenylnonane. Pesticides and PCB congeners will be analyzed by gas chromatography/electron capture detection (GC/ECD) using EPA Method 8080, modified to include additional analytes and a second column for qualitative confirmation. Sterone concentrations will be determined by direct analysis with gas chromatography/flame ionization detection (GC/FID). Sterols will analyzed as their trimethyl silane derivatives using GC/FID. All analytes will be quantified using the internal standard method.

12.2.2 Metal Analysis

The sample preparation procedures for determining total recoverable metals are defined by EPA (Section 4.1.4 of 600-01-79-020, March, 1983). For all metals except mercury, 100 mL of the sample is spiked with 5 mL of hydrochloric acid and the sample is reduced in volume to about 10-20 mL by evaporation. The solution is then filtered through a Nuclepore 0.4 μm membrane. To increase sensitivity, the filtrate will not be diluted back to 100 mL. To reduce sample contamination, all sample preparation will be performed in a Class 100 clean room and all sample containers and sample preparation equipment will be rigorously cleaned according to the procedures of Patterson and Settle (1976). All effluent samples are directly analyzed by graphite furnace atomic absorption spectroscopy (GFAAS) for silver, cadmium, copper, nickel, lead, and zinc.

The EPA method for total recoverable mercury (EPA Method 245.1) will be modified because of its unacceptably high detection limit of 0.2 μg/L. A 500-mL aliquot of the unfiltered, acidified sample will be processed by using a two-step analytical scheme that uses $NaBH_4$ to cleave the carbon-mercury bonds that exist in the effluent samples and to reduce and vaporize the mercury. The liberated mercury is then collected on a gilded-sand column and subsequently

heated from the gold column for detection by cold vapor atomic absorption spectroscopy (CVAAS). This mercury method is described in greater detail in Gill and Fitzgerald (1987) and Gill and Bruland (1990).

12.2.3 Clostridium perfringens

The enumeration of *C. perfringens* spore densities will be performed on selected effluent samples by membrane filtration, using serial half-log dilutions of the effluent according to the procedure developed by Bisson and Cabelli (1979). The effluent will be filtered using sterile filtration apparatus and membrane filters that have been rinsed with sterile phosphate-buffered saline (PBS). The filters will be incubated for 18 to 24 h at 44.5 °C, exposed to ammonium hydroxide, and the *C. perfringens* colonies will be counted and recorded. All final data will be reported in units of spores per 100 mL of filtered effluent.

12.2.4 Stable Isotopes

The analysis of stable isotopes of carbon (^{13}C) and nitrogen (^{15}N) will be performed sequentially on the same sample by mass spectrometry. Sulfur isotope (^{34}S) measurements will be made on a separate sample using a different sample preparation method and mass spectrometer. All effluent samples will be filtered with 0.4-μm membranes prior to analysis; stable isotope analysis will be performed on the retained particulate material. Additional fractionation of the samples may be requested by MWRA to determine ^{15}N in dissolved nitrogen species (e.g., ammonia, nitrate, organic nitrogen). If MWRA requests these analyses, the fractionation procedures will be submitted as an addendum to this CW/QAPP.

Prior to analysis of carbon and nitrogen isotopes, samples will be acidified to remove carbonate and dried in scintillation vials at 60 °C. The samples are then flash-combusted at 1800 °C in an evacuated gas manifold and the resulting gases are routed via a helium carrier flow to a cryogenic trap to separate the water, carbon dioxide, and nitrogen gases. Carbon dioxide and nitrogen are analyzed sequentially for ^{13}C and ^{15}N using a Finnigan Delta S mass spectrometer. The excess ^{13}C in each sample is detected by comparing $^{13}C/^{12}C$ against a PeeDee Belemnite limestone reference. The excess ^{15}N in each sample is detected by comparing the $^{15}N/^{14}N$ against an air reference.

The separate sample aliquot for sulfur isotope measurement will be rinsed in deionized water to remove any isotopic signal from seawater sulfate. Samples will be dried and combusted in a sealed tube with potassium nitrate to oxidize sulfur species to sulfate salts. These sulfate salts will be digested in an acid solution, the solution is filtered, and 10% barium chloride solution is added to precipitate sulfate as barium sulfate. The barium sulfate is recovered by filtering the solution through ashless filters, which are then combusted in crucibles.

Finally, the residual barium sulfate ash is mixed with vanadium pentoxide and elemental copper, and transferred to a vacuum apparatus. Upon heating, sulfur dioxide is released and then cryogenically trapped on the vacuum line and analyzed for ^{34}S using a Finnigan MAT 251 isotope ratio mass spectrometer. The excess ^{34}S in each sample is determined by comparing the $^{34}S/^{32}S$ against a Canyon Diablo Triolite meteorite reference.

13. SAMPLE CUSTODY

Battelle's standard procedures for sample tracking and custody will be used on all detailed effluent characterization sample collections. Effluent samples are identified by an unique sample ID which is a concatenation of *event_id* (5-character ID unique to each monthly sampling; see Table 4) and *marker_no* (which is a non-repeating number for each sample). To identify the subsamples removed from each composite sample, a protocol coding system has been developed for this project (Table 7). A set of chain-of-custody (COC) forms (Figure 2) will be generated for each set of samples. Each completed COC will be signed and dated by the staff member entering the information.

Table 7. Protocol Codes and Related Samples

Protocol	*Lab*	*Description*
ORG	BOS	Organic contaminants (PAH, LAB, PCB, and pesticides)
MET	BOS	Metals (Ag, Cd, Cu, Ni, Pb, and Zn)
HG	BOS	Mercury
CP	MTH	*C. perfringens*
ISO	MBL	Stable isotopes (^{13}C, ^{15}N, ^{34}S)

The COC includes fields for entering pertinent information about each sample collection and general comments (see Figure 2). This same information will be printed on barcoded labels. The barcode contains the sample ID. One label will be attached to the sample log form, one label will be attached to each sample container, and another label will be attached to the sample's accompanying COC form.

CHAIN-OF-CUSTODY RECORD	
For MWRA Effluent Samples	
Project Name: Harbor and Outfall Monitoring — MWRA Contract No. S138	
Treatment Plant: Deer Island	Weather: Recorded By:
Plant: Deer Island Date: Time:	Sampler Type:
MWRA Sample No.:	Effluent Volume:
Event_ID: E9301	Comment:
Position: Effluent	
Protocol: Lab: Sampled By:	
Plant: Deer Island Date: Time:	Sampler Type:
MWRA Sample No.:	Effluent Volume:
Event_ID: E9301	Comment:
Position: Effluent	
Protocol: Lab: Sampled By:	
Plant: Deer Island Date: Time:	Sampler Type:
MWRA Sample No.:	Effluent Volume:
Event_ID: E9301	Comment:
Position: Effluent	
Protocol: Lab: Sampled By:	
Plant: Deer Island Date: Time:	Sampler Type:
MWRA Sample No.:	Effluent Volume:
Event_ID: E9301	Comment:
Position: Effluent	
Protocol: Lab: Sampled By:	

Released By/Date/Time/Company	Transporter/Airbill #	Received By/Date/Time/Company

PLEASE RETURN THE ORIGINAL OF THIS COMPLETED CHAIN-OF-CUSTODY FORM TO ALLEN UHLER-BATTELLE

Figure 2. Chain-of-Custody Form for Effluent Samples.

The COC set will have a form for each month and will be used by the Battelle staff transporting the samples. The COC form will accompany samples to their final destination. If the custody of samples is transferred between laboratories, the COC form will be signed by both the staff member that relinquishes custody and the staff member assuming custody of the samples. Copies of all COC forms will be returned to Battelle's Task Leader and put into the task notebook. Battelle will assume custody of samples immediately upon sample transfer. Field documentation will consist of COC forms containing the project name, sample location, sample type designation, alphanumeric sample codes, and other pertinent information on the sample (see Figure 2). During sample collection, COC forms will be completed by MWRA staff and labels will be affixed to the sample containers, thereby creating a link between the sample and data recorded on the COC form. The COC forms will have a duplicate label that also contains the same alphanumeric code as the corresponding label on the sample container, ensuring the tracking of sample location and the status. Battelle will keep a copy of the COC form, and will ensure that a copy accompanies the samples during transport. The original COC form will be submitted to Battelle's database manager and maintained in the data sources notebook.

Upon completion of the monthly sampling, custody of samples will be transferred to the appropriate laboratory (Table 7). Laboratory custody of all samples will be the responsibility of the appropriate Battelle department or subcontractor. Upon receipt of samples at the laboratory, the recipient will examine the samples received, verify that the information recorded on the copy of the COC forms is accurate, and log the samples into the laboratory by signing the COC form on the *Received By* line, and by entering the date and time of sample receipt. Any inconsistencies between samples listed as having been released and samples that were actually received, or any damage to containers, labels, etc., will be noted in the laboratory sample log book and immediately communicated to the Task Leader. Sample numbers that include the complete field ID number will be used to track the samples through the laboratory. All archived samples will remain in the custody of the appropriate Battelle or subcontractor laboratory for a period of 1 y after sample collection, at which time the MWRA will be contacted about their disposition. All data generated for this study will be maintained for 3 years, after which time MWRA will be contacted.

14. CALIBRATION PROCEDURES AND PREVENTIVE MAINTENANCE

14.1 Calibration Procedures and Response Factor Stability

14.1.1 Organic Analysis

Analytical instruments will be calibrated before sample analysis. Response factors (RF) will be generated for each target analyte using the following equation:

$$RF = \frac{A_x}{A_{IS}} \times \frac{C_{IS}}{C_x}$$

where: A_x = peak area of the analyte in the calibration standard
A_{is} = peak area of the appropriate internal standard in the calibration standard
C_x = concentration of the analyte in the calibration standard
C_{is} = concentration of the appropriate internal standard in the calibration standard.

Three concentrations of standard solutions that encompass the expected range in sample concentrations will be analyzed. Initial calibrations will be acceptable if the relative standard deviations (RSD) are within 25% of the mean for each individual analyte, and the mean of all analyte RSDs is 10%. Any exceptions will be documented and justified by the Task Leader.

The system calibration will be verified a minimum of once every 24 h using a mid-range calibration check. Using the mean RF of each analyte from the initial calibration, the percent difference between those mean values and the RFs from the midrange calibration checks will be calculated. The percent difference is calculated by

$$\% \text{ Difference} = [(RF_i - RF_r) / RF_i] \times 100$$

where RF_i = average response factor from the initial calibration, and
RF_r = response factor from the midrange calibration check.

The calibration checks will be acceptable under the same criteria as the initial calibration (i.e., 25% for individual analytes, 10% for the means). If the percent difference between the RFs is greater than the acceptability criteria, remedial maintenance will be performed on the instrument, a new initial calibration will be performed, and the affected batch of samples will be

reanalyzed, at the discretion of the analyst and project management. Because GC/ECD and GC/MS analyses are multicomponent analyses, it may not be necessary to reanalyze all samples. For example, if only certain analytes are detected in a sample, and the calibration is acceptable for those particular analytes, the sample should not require reanalysis. Reanalyses will be performed at the discretion of the analyst and program management. Deviations from calibration or data objectives will be documented in the project files.

Samples analyzed by GC/ECD and GC/MS will be bracketed by two acceptable calibrations, initial or check. Analytes will be quantified by using the average RFs for that individual analyte generated from the initial calibration unless otherwise stated.

14.1.2 Metal Analysis

The atomic absorption instrumentation will be calibrated daily before samples are analyzed. Calibration standards will be prepared each day and effluent sample digestion solutions will be quantified by GFAAS for all metals except mercury using the method of additions to avoid inaccuracies resulting from chemical interferences. Calibration standard check samples (as NIST-certified aqueous sample 1643c or EPA Performance Evaluation samples) will be analyzed every 10 samples to ensure continued accuracy. Measurements that are not bracketed by an accuracy check standard within 15% of its true value will be rejected and reanalyzed after corrective action is taken (as needed). GFAAS measurements will be made in duplicate for each sample; if the relative percent difference (RPD) between duplicate injections is greater than 10%, then the sample measurement will be rejected unless the absorbance values are very low and small differences (<0.004 abs units) result in high RPD values. Sample quantitations will only be accepted if the standard additions quantitation curve has a correlation coefficient of 0.99 or better.

The CVAAS measurements of mercury will be quantified by standard comparisons; mercury calibration standards will be prepared the day of analysis, and samples will be quantified within the linear range of the instrument and below the highest calibration standard. Instrument performance will be monitored using continuing accuracy check standards (with a 15% acceptance criteria), prepared by an analyst other than the analyst that prepares the calibration standards. Samples will be analyzed once for quantitation; all duplication exercises will be laboratory or field duplicates. Sample quantitations will proceed only if the calibration standard curve is linear with a correlation coefficient of 0.99 or better.

If the target correlation coefficient for the calibration curve is not obtained for the atomic absorption instrumentation, then the instrument operation and

instrument integrity will be assessed and analytical standards evaluated. Necessary remedial action will be taken, and the calibration procedure repeated until a satisfactory calibration for each trace metal can be obtained. Any sample concentrations that are above the highest calibration atomic absorption standard will be reanalyzed (after appropriate dilution if necessary). All instrumental maintenance will be documented in instrument logbooks.

14.2 Instrument Maintenance

Analytical instrumentation will be properly calibrated and maintained in accordance with SOPs or manufacturer's instructions as specified in operations manuals. Procedures for calibration and maintenance of the more complex analytical equipment are described below.

14.2.1 Gas Chromatograph Mass Spectrometer

Detector response (electron-capture detectors and mass spectrometer) and capillary column performance will be monitored/calibrated daily by injection of GC standards containing known amounts of targeted compounds (e.g., PAH mixture, pesticides, PCB mixtures, and LAB calibrations). Both the responses per unit amount and the resolution of specific components will be monitored. If any evidence of chromatographic column performance deterioration is observed, the column will be replaced. In addition, a maintenance log containing a detailed record of all maintenance performed will be maintained for each instrument.

14.2.2 Atomic Absorption Spectrophotometer

Maintenance of the GFAAS instrumentation includes complete furnace and furnace window cleaning, graphite tube and stabilized temperature platform observation and replacement. The associated maintenance log forms are filled out each day for each parameter and include the above actions and the hollow cathode or electrodeless discharge lamp energy for continued monitoring of elemental lamp performance.

15. DOCUMENTATION, DATA REDUCTION, AND REPORTING

15.1 Documentation

Initially, all data will be recorded either (1) electronically onto computer storage media from laboratory data systems or (2) manually into laboratory notebooks or on established data forms. All notes will be written in ink. Corrections to hand-entered data will be initialed, dated, and justified. Completed forms, laboratory

notebooks, or other forms of hand-entered data will be signed and dated by the individual entering the data. It will be the responsibility of the laboratory managers to ensure that all data entries and hand calculations are verified. Laboratory records of sample preparation will be maintained in sample batch books. In addition to these documentation procedures, sample logs associated with field and laboratory custody and tracking will be maintained in project files. Manually recorded data from subcontractor laboratories will be entered by the subcontractor into PC-based spreadsheets and submitted to Battelle.

15.2 Data Reduction

Data reduction involves the process of converting raw numbers into data that have direct chemical meaning or can be compared statistically for differences between mean values.

GC/MS data will be acquired and reduced on Hewlett-Packard A-series minicomputers with dedicated chromatography software. GC/ECD data will be acquired and reduced by the Hewlett Packard 3350A Laboratory Automation System. Data generated during metals analyses will be transferred from the instruments to PC, where analyte concentrations will be calculated. Organic analyte data will be reported in units of ng/L; metals concentrations will be reported in μg/L; stable isotope data will be reported as % for $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$; *C. perfringens* data will be reported as spores/100 mL.

In addition to analyte concentrations in field samples, statistical evaluations will be performed on all quality control samples. Percent recoveries of the spiked analytes will be calculated for all matrix spike and matrix spike duplicate samples. Additionally, the relative percent difference (RPD) between the MS and MSD samples will be calculated:

$$RPD = \frac{2 \times (A_{MS} - A_{MSD})}{A_{MS} + A_{MSD}} \times 100$$

where A_{MS} = amount of analyte detected in MS sample
A_{MSD} = amount of analyte detected in MSD sample.

The RPD between sample duplicates will also be calculated:

$$RPD = \frac{2 \times (C_1 - C_2)}{(C_1 + C_2)} \times 100$$

where C_1 = concentration (ng/g) of analyte detected in sample 1
C_2 = concentration (ng/g) of analyte detected in sample 2

Quality control objectives for these calculations are presented in Table 6.

15.3 Reporting

Three formats will be used to report the effluent chemistry data to MWRA

(1) Data submitted for inclusion in the Harbor Studies Database
(2) Data presented in annual data reports
(3) Data summarized and interpreted in annual synthesis reports.

15.3.1 Harbor Studies Database

Only data that have been designated as final by the Task Leader will be loaded into Battelle's copy of the Harbor Studies Database. All data will be loaded into the database by Battelle data management staff following the formats described below. Data provided by Battelle and subcontractors will be loaded into the database by Battelle data management staff. Upon receipt, each diskette will be logged in and assigned an unique login identifier. Any changes or additions to data, necessary for loading into the database, will be made using well-documented SQL scripts that indicate the original values. The original diskette, SQL scripts, and data-loading documentation will be filed at Battelle according to login identifier. The data sources notebook will contain the COC forms and data entry information.

Sample Collection Data

Sample collection data contained in the sample COC form will be provided as Lotus spreadsheet files. Columns will include sample_id, stat_id, ddate, ttime, and protocol code.

Analytical Data

Effluent chemistry data generated by Battelle will be electronically transferred from the instrument to a PC-based spreadsheet and then transferred into Oracle, from which the final report tables will be generated. Data in laboratory

notebooks or on data sheets will be manually entered into a PC-based spreadsheet.

All data generated by Battelle subcontractors will be either electronically transferred from the instrument to a PC-based spreadsheet or read from the instrument display (or optical field of a microscope) and manually entered into laboratory notebooks or data sheets. Data in laboratory notebooks or on data sheets will be manually entered into a PC-based spreadsheet.

Data resulting from the stable isotope and *Clostridium perfringens* analyses will be submitted by the appropriate subcontractor (Section 10) as PC-based spreadsheets.

15.3.2 Data Reports

Data reports will be submitted to MWRA in both hard-copy and electronic forms. Data will be presented in tables containing the results of individual sample analysis plus QC data.

15.3.3 Annual Synthesis Reports

Annual synthesis reports for the detailed effluent characterization task will include tables and graphics presenting summaries of results. These presentations may show temporal trends in effluent constituent concentrations and distribution. The objective of these data presentations will be to communicate our understanding of the relevance of measured effluent constituents to the task objectives and data usage discussed above.

16. DATA VALIDATION

All data reported for this project will be reviewed to check for errors in transcription, calculation, or computer input by the technical staff of the appropriate laboratory. The validation procedures that will be performed are

- 100% of data that are hand-entered into a database or spreadsheet will be verified for accuracy either by (1) printing the spreadsheet and proofreading against the original hand entry or by (2) duplicate entry into the database and comparison of the entries to detect any differences. These tasks will be carried out by two people and documented for each data set.

- All manual calculations will be checked for accuracy by a second staff member.

- Calculations performed by software will be checked by the technical staff member at a frequency sufficient to ensure the accuracy of the calculations. All data-reduction algorithms will be verified prior to final data submission.

- Analytical results and supporting data will be reviewed by the analytical supervisor to ensure that the data are complete, accurate, and technically correct prior to submission to the database.

- Database staff will check the received data and associated documentation for completeness, freedom from errors, and technical reasonableness.

- All new software developed for this task will be validated before entry of data.

The Battelle Task Leader will be responsible for validation of all data generated by Battelle to ensure that the data are accurate, complete, and scientifically reasonable. Subcontractors will be responsible for conducting similar data validations to ensure that the data provided to Battelle are accurate, complete, and scientifically reasonable. As an additional data validation step, Battelle Task Leaders will review all subcontractor data for technical reasonableness. The entire process will be fully documented in the Data Sources Notebook.

A primary component of data validation is verification that the documented procedures are in control. Validation of data includes a review of QC sample versus the data quality requirements (Section 11). This review will be conducted at a frequency sufficient to implement corrective action (Section 18). QC samples that do not meet the data quality requirements will be documented as deviations. The Task Leader will determine whether out-of-control QC results will invalidate or qualify data reported for field samples.

17. PERFORMANCE AND SYSTEM AUDITS

This project will be monitored by the project QA officer. All tabular and graphic data reported in deliverables and associated raw data generated by Battelle will be audited by the task QA office. Raw data will be reviewed for traceability, accuracy, completeness, and proper documentation. For laboratory data, statistical random audits of reported values will be conducted to ensure that the data are accurate, traceable, and within the QC specifications of this CW/QAPP.

All deliverables generated during the course of this project will be submitted to an internal review prior to delivery of drafts to MWRA. This three-part process consists of technical, editorial, and QA reviews.

Audits of the subcontractor laboratory data-collection programs will be the responsibility of the subcontractor. During the time work is in progress, an audit will be conducted by the subcontractor QA officer to evaluate the laboratory data-production process. All data must be audited by the QA officer prior to submission to the Task Leader and must be accompanied by a signed QA statement that describes the types of audits and reviews conducted and any outstanding issues that could affect data quality.

Performance reviews, procedures used to quantitatively determine the accuracy of the total measurement system or its components, will be the responsibility of technical personnel. Performance reviews will include assessment of QC samples, such as blanks, spikes, standards, and replicates, all of which are discussed in detail in Section 11.

18. CORRECTIVE ACTION

Identification of problems regarding technical performance is the responsibility of all staff members working on this project. Responsibility for overall conduct of the project, including schedule, costs, and technical performance lies with the Battelle Project Manager. He is responsible for identifying and resolving problems that (1) have not been addressed promptly or successfully at a lower level, (2) influence other components of the project, (3) require changes in this CW/QAPP, or (4) require consultation with Battelle management or with MWRA.

Technical problems relating to sample collection (schedule changes, modifications to the sampling plan, etc.) will be resolved through discussion with the MWRA Task Manager and Battelle Task Leader. Problems relating to the overall successful completion of the project will be reported to the MWRA Task Manager in a timely manner for discussion and resolution between the Battelle and MWRA managers.

Identification of problems and corrective action at the laboratory level will be resolved by the laboratory staff. Issues that affect schedule, cost, technical performance, or data quality will be reported to the Battelle Task Leader or the Battelle Project Manager. They will be responsible for evaluating the overall

impact to the project and for discussing corrective actions with the MWRA Task Manager.

A QA/QC Corrective Action Log will be maintained by the Task QA Officer and submitted to MWRA at quarterly intervals. The log will include documentation of QA/QC activities as they occur, descriptions of the methods and procedures recommended to prevent the problem from reoccurring, and verification that these actions have corrected the problem.

19. REPORTS

Reports related to the detailed effluent characterization task include data reports and annual synthesis reports.

19.1 Data Reports

Following complete laboratory analysis of samples from each year, a data report that provides a tabular summary of results of the analyses will be submitted to MWRA. The due dates for the draft and final data reports are listed in Section 9.

19.2 Annual Synthesis Reports

After each monitoring year, an annual synthesis report will be submitted. The synthesis report will analyze, interpret, and synthesize the effluent data, and will allow MWRA to (1) describe baseline effluent characterization, (2) use the effluent data for purposes discussed in Section 7.2, and (3) make modifications to the Harbor and Outfall Monitoring Plan. Contents of the synthesis reports may include

- Introduction/Objectives
- Sampling Design
- Chemical Characterization Results
- Integration of Study Results/Synthesis

The due dates for the draft and final annual synthesis reports are listed in Section 9.

20. REFERENCES

Battelle. 1991. Results of the ambient and municipal sample interlaboratory comparison study in ambient waters and discharges to New York/New Jersey Harbor. Final Report submitted to the Environmental Protection Agency under Work Assignment 2-202, Contract No. 68-C8-0105.

Bisson, J.W. and V.J. Cabelli. 1979. Membrane filter enumeration method for *Clostridium perfringens*. *Appl. Environ. Microbiol.* 37:55-66.

Eganhouse, R.P., E.C. Ruth, and I.R. Kaplan. 1983. Determination of long-chain alkylbenzenes in environmental samples by argentation thin-layer chromatography/high resolution gas chromatography and gas chromatography mass spectrometry. *Anal. Chem.* 55:2120-2126.

Gill, G.A., and W.F. Fitzgerald. 1987. Picomolar mercury measurements in seawater and other materials using stannous chloride reduction and two-stage gold amalgamation with gas phase detection. *Mar. Chem.* 20:227-243.

Gill, G. A., and K. W. Bruland. 1990. Mercury speciation in surface freshwater systems in California and other areas. *Environ. Sci. Technol.* 24:1392-1400.

Grimalt, J.O., P. Fernandez, J.M. Bayona, J. Albaiges. 1990. Assessment of fecal sterols and ketones as indicators of urban sewage inputs to coastal waters. *Environ. Sci. Technol.* 24:357-363.

Parmenter, C.M. and M.H. Bothner. 1993. The distribution of *Clostridium perfringens,* a sewage indicator, in sediments of coastal Massachusetts. US Geological Survey Open File Report 93-8 (draft).

Patterson, C.C. and D.M. Settle. 1976. The reduction in orders of magnitude errors in lead analysis of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collecting and processing. In La Fleur, P.D. (ed.), *Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis.* National Bureau of Standards Spec. Publ. 422. U.S. Government Printing Office, Washington, DC.

Shea, D. 1992a. Data report on organic contaminants in Deer Island and Nut Island influents and effluents. Submitted to the Massachusetts Water Resources Authority, Boston, MA. January 22, 1992.

Shea, D. 1992b. Data report on organic contaminants in Deer Island and Nut Island influents and effluents. Submitted to the Massachusetts Water Resources Authority, Boston, MA. July 15, 1992.