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Certified Mail

August 31, 2010
In reply refer to SHEA-110315

Regional Water Quality Control Board
Los Angeles Region
320 West 4th Street, Suite 200
Los Angeles, CA 90013

Attention: Mr. Peter Raftery

Subject: Environmental Sampling of Dioxins and Other Low Solubility Pollutants at Parts-per-Billion and Lower Concentrations Report for the Final Interim Source Removal Action (ISRA) submitted in Response to California Water Code Section 13304 Order (NPDES NO. CA0001309, CI NO. 6027, SCP NO. 1111, SITE ID NO. 2040109)

Dear Mr. Raftery:

The Boeing Company (Boeing), on behalf of Boeing and the National Aeronautics and Space Administration (NASA), wishes to provide the attached Environmental Sampling of Dioxins and Other Low Solubility Pollutants at Parts-per-Billion and Lower Concentrations Report for the Final Interim Source Removal Action (ISRA) currently being conducted in Outfalls 008 and 009 in response to California Water Code Section 13304 Order. The attached report was prepared on behalf of and in collaboration with the Boeing Surface Water Expert Panel.

If you have any questions or require anything further, please contact Lori Blair at 818-466-8741.

Sincerely,

Tom Gallacher
Director, Santa Susana Field Laboratory
Environment, Health, and Safety

Attachment: Environmental Sampling of Dioxins and Other Low Solubility Pollutants at Parts-per-Billion and Lower Concentrations Report

cc: Ms. Cassandra Owens, RWQCB
Mr. Buck King, DTSC
Mr. Allen Elliott, NASA
Mr. Jon Jones, Boeing Surface Water Expert Panel

Environmental Sampling of Dioxins and Other Low Solubility Pollutants at Parts-per-Billion and Lower Concentrations:

Field Protocols for Collecting SSFL ISRA Performance Samples and Obtaining Replicate Splits Using a Dekaport Cone Splitter

Including Field Blanks and Laboratory Reporting Requirements for Identifying QA/QC Problems

Eugene R. Weiner

This report was prepared on behalf of and in collaboration with the Boeing Surface Water Expert Panel.

Wright Water Engineers, Inc.

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1. INTRODUCTION

Special sampling and analytical procedures are needed for measuring environmental pollutants quantitatively at parts-per-billion concentrations or lower. Even slight accidental sample contamination, which might not be significant in more routine sampling programs, can cause serious errors when sampling for very low concentrations of pollutants. It is important to use sampling protocols that minimize such errors, follow the protocols carefully and consistently, and always include field quality control blanks designed to help detect and quantify accidental contamination when it occurs.

Pollutants with low aqueous solubility, such as dioxins[1], require additional special attention because they tend to partition preferentially from the dissolved state to a sorbed state on solid surfaces such as sediments and container walls. For low-solubility pollutants, any sampling step that requires transferring a sample from the original collection container to other containers has the potential for introducing quantitation errors because sorbed pollutants are seldom transferred in a consistent manner. Sample transfer difficulties are minimized by pre-rinsing collection and transfer containers and by always using a cone splitter, Figure 1, for splitting a single sample containing sediment into two or more replicate samples.

Figure 1: Dekaport Cone Splitter for making replicate water samples. The device, including legs, weighs 8 pounds and is 26.1 inches tall. The splitter without legs is 13.4 inches in height and is constructed entirely of Teflon®. The legs and supporting frame are anodized aluminum. From top to bottom, the cone splitter consists of a 4-inch diameter upper reservoir, stand pipe to deliver a uniform flow to the splitter cone, splitter cone chamber, and 10 exit ports to which 3/8-inch O.D, Teflon® tubing can be attached for collecting split samples.

[1]There are 17 related tetra- through octa-chlorinated dioxin and furan compounds that are analyzed to establish compliance with the SSFL Dioxin TEQ limit. In this document, the entire set of 17 dioxin/furan COCs are referred to generically as "dioxins."

2. SUMMARY OF FIELD PERFORMANCE SAMPLING PROCEDURES

2a. Objectives

The field performance sampling protocol has three main objectives:

1. To collect stormwater runoff samples that are acceptable representations of environmental conditions at the place and time of sampling.

2. To store and transport these samples in a manner that maintains the important physical and chemical properties of the sample. This generally requires that samples are properly cooled and, if necessary, preservatives added and pH adjusted as soon as possible after collection.

3. To prevent contamination of samples that can result in false analytical results.

In order to accomplish these objectives, all procedures that involve sample-handling must be consistently controlled. This includes selecting, cleaning, and properly using equipment such as sample splitters, sample containers, tubing, gloves, and other materials that may come in contact with the sample, both in the field and during transport to the laboratory.

Quality control checks (equipment and field blanks) are designed to test how well the sampling procedures are executed. But even if all sampling procedures are performed correctly, stormwater runoff is inherently heterogeneous and successive samples collected from the same location will generally have some degree of variability in composition. For this reason, when certain comparisons are required, such as comparing analyses of the same sample by different laboratories or seeking correlations among different water quality parameters (e.g., association of dioxins with sediments), it is important to make all comparisons from splits of a single sample and not from different samples, even if collected within a short time from the same location.

The greatest source of stormwater heterogeneity comes from spatial and temporal fluctuations in total solids. This is because low solubility pollutants, like dioxins and many metals, tend to concentrate in sediments by sorption. Replicate samples that vary significantly in solids concentration will also have less agreement in chemical pollutant concentrations. Using a cone splitter to obtain replicate samples by splitting a single sample has been shown to improve reproducibility among replicate samples split from a single sample containing sediment. The care and use of a cone splitter is described in this report.

2b. Field Quality Control (QC)

Equipment and field QC blanks should be obtained to determine if positive detects have been influenced by field sampling and sample splitting activities. Since contaminant of concern (COC) detects for metals and dioxins are expected, one equipment rinsate (equipment blank) per event should be analyzed to represent the decontamination

process. Additional equipment rinsates should be collected and placed on hold, to be analyzed if unusual detects are noted in the site samples.

These equipment and field QC procedures apply to sampling for all COCs. QC blanks generated during sampling activities are necessary to provide assurance that positive detects for COCs are not from accidental contamination during sampling.

- Equipment Blanks: Obtain from the laboratory a sample of reference laboratory blank-grade water known to be initially free of contaminant analytes (e.g., dioxins and metal COCs). Use this clean water as a final rinse when cleaning sampling equipment. The equipment blank is used to check the effectiveness of decontamination procedures or to verify that new materials (containers, tubing, etc.) in contact with environmental samples do not contribute COCs. For example, one equipment blank should be poured through the cleaned cone splitter, collected from each outlet tube, and composited into a normal sample container for laboratory analysis.

- Field Blanks: These blanks are prepared during sampling by filling a clean container with COC-free laboratory blank-grade water and treating it in a manner that allows ambient sources of COCs other than storm runoff to be detected. For example, one field blank should be exposed to the atmosphere at the sampling site for at least as long as collected samples are exposed, so that airborne contaminants can be detected. If it is raining, protect the airborne blank from the rain during atmospheric exposure.

- If the "COC-free" laboratory blank-grade water or preservative becomes suspect, an unopened QC blank containing only laboratory blank-grade water and preservative (if used) should be tested.

Equipment and field blanks should be retained and analyzed only if there are positive detects in the samples. Should there be positive detections for COCs, the contract laboratory should be able to eliminate itself as a source of contamination by providing its laboratory method blank and instrument background checks. The combination of equipment blanks, field blanks, occasional laboratory verification blanks, and the laboratory's background checks can be used to identify whether positive detections are field-related, laboratory-related, or sample-related.

2c. Grab Sampling When Using a Cone Splitter

Single grab samples represent the conditions that exist in the source at the moment the sample is collected and do not necessarily represent conditions at any other time. However, since more than one sample is normally required from a given site for each sampling event, it is best to always use a cone splitter for filling sample bottles. This is because all COCs will sorb to some extent to sediments and using the cone splitter assures the maximum uniformity of sediment distribution among the samples.

The cone splitter has a 4-liter reservoir and works best with water sample volumes of 3-4 liters because:

1. It is important to pour the entire collected water sample through the splitter at one time. Some sediment settles quickly and may remain behind. When the entire collected water sample is poured through the splitter at one time, with care to completely empty the pouring container, problems with rapid settling of particles during pouring are minimized.

2. It also is important to maintain, during most of the pour, a substantial water pressure head above the standpipe to the splitter cone. This helps to maintain a uniform pressure drop in all of the pathways to the sample containers, prevents air from entering the splitting block while transferring the sample, and facilitates an even division of the sample.

Thus, it generally will be necessary to repetitively collect a number of smaller grab samples from the source and transfer them to a compositing container (approximately 1-gallon or larger) in order to obtain a sufficient volume for pouring through the cone splitter. A side benefit of this procedure is that the repeated collection and compositing of smaller samples provides a degree of time and flow integration that helps smooth small temporal and spatial variations in the source sediment composition.

Bottles for different analyses (e.g., metals and dioxins) and different sized sample containers with or without preservatives can be connected to the splitter at the same time (see Figure 2).

Figure 2: Cone splitter with different kinds of collection containers attached. The three plastic containers are each connected to two outlet ports for collecting larger sample volumes.

3. STEP-BY-STEP FIELD PROCEDURES

3a. Types of Sample Containers

Three different kinds of sample containers are used in the field. A single collection container is used to collective successive samples from the source to be added to a compositing container. When the compositing container is filled to the correct volume, it is poured into the cone splitter and the sample is subdivided into smaller volumes in laboratory containers correctly designed for their designated analyses (amber glass for dioxin and polyethylene with preservative for metals). To avoid confusion, the following definitions are used throughout:

- The collection container is a pre-cleaned amber glass container (generally 1-liter or 40-mL VOAs, depending on the size of the source flow) used to collect surface water samples from the source flows and to transfer the sample to the compositing container.
    - The collection container is always pre-rinsed with source water before its initial use and discarded (or saved for cleaning) when the compositing container has been filled.
- The compositing container is a pre-cleaned glass container (approximately 1-gallon or larger) into which successive source water samples are transferred and composited until a sufficient volume (generally 3-4 liters) has been collected for pouring through the cone splitter.
    - The compositing container is always pre-rinsed with source water before its initial use and discarded (or saved for cleaning) when the composited sample has been poured through the cone splitter.
    - The collected sample in the compositing container must be protected from exposure to light. If an amber glass container of sufficient size (at least 3-4 liters) is not available, wrap the compositing container with a light shield (e.g., aluminum foil or a clean black plastic bag).
- Laboratory containers are pre-cleaned and labeled amber glass (for dioxin) or polyethylene (for metals) containers positioned at the tubing outlets of the cone splitter. They receive the split portions (subsamples) of the composited sample as they exit from the splitter.
    - Laboratory containers are never pre-rinsed before use.
    - They may contain acid or preservative as required for their particular sample analysis.
    - When the split is complete, laboratory containers are capped, sealed and stored in a cooler for transport to the laboratory.

3b. Field and Equipment QA/QC Blanks

Field Blank

At each sampling location:

- One bottle of clean laboratory blank-grade water should be opened and remain open in a location protected from precipitation during the entire sampling event. This sample is exposed to the atmosphere in the same manner as the collected environmental samples. When sampling is finished, this bottle is closed, sealed, labeled, and stored with the environmental samples for transport to a laboratory.

- For a given sampling episode, if no COCs are detected, the field blanks do not need to be analyzed.

Equipment Blank

- After rinsing the cone splitter with deionized water and before the pre-rinse with source water, pass 1-liter of laboratory blank-grade water through the splitter as an equipment rinse blank and collect all of it using all of the outlet tubes. Composite the entire collected equipment rinse blank from the 10 outlet tubes into a 1-liter laboratory container. This equipment blank container is capped, sealed, labeled, and stored with the environmental samples.

- For a given sampling episode, if no COCs are detected, the equipment blank does not need to be analyzed.

3c. Setting Up and Preparing the Cone Splitter for Use

Using a cone splitter adds several complications to collecting performance samples, such as keeping the splitter clean, leveling it, pre-rinsing it, attaching tubing and laboratory containers, etc. The difficulties of dealing with these requirements are related to where the splitter must be set up in relation the sampling location. In addition, the performance of a new cone splitter must be tested and confirmed to be adequate before use, see Appendix C.

Each field sampling event entails filling a single composite container to be split later into different laboratory containers destined for various COC analyses. Although some of the laboratory containers on the splitter may require preservative, none can be added to the total composited sample. Therefore, when some preservative is required (e.g., acid in metal samples; dioxin samples are not preserved), splitting should be performed as soon as possible after sample collection.

EPA guidelines state that composited samples may be preserved initially without chemical preservatives by holding them at 4 ºC until compositing and splitting is completed. However, this general requirement may be moderated somewhat for stormwater performance sampling (but not for compliance sampling) without compromising analytical accuracy.

In surface water runoff, the more rapid metal chemical and biological changes (hydrolysis, redox change, sorption to sediment, dissolution, and precipitation), that preservation is intended to minimize, have mostly already occurred by the time the samples are collected. Adding acid to unfiltered metal stormwater samples is more a matter of converting all samples to the same state of dissolved metals, than it is of preserving the state of the sample at the time of collection. Therefore, adding preservative to metal stormwater samples may be delayed a few hours to allow multiple sites to be sampled before composite samples are transported to a "clean area" not subject to contamination for splitting.

Every step in the detailed procedures below should be performed in the same way every time to help assure unbiased results. For example, one should always wet the cone splitter first with deionized water and then with source water before a split and always tap the splitter at the end of a split to release adhering droplets.

1. If it can be done within about 5 hours, it is acceptable to transport the composited samples a short distance within the SSFL from the sampling site to the splitter.

    a) Each composited sample should be split as soon as possible, up to about 5 hours.

        i) The 5 hour limit is a guideline, not a firm rule. It was selected by "best professional judgment" to allow time for sampling multiple sites before having to perform the splitting procedure. If it is found to be insufficient, tests should be performed to determine whether longer delays before splitting will affect analytical results.

    b) During filling at the site, the composite container should be wrapped with aluminum foil or a clean, black plastic bag to protect against light exposure, and kept in a cooler at no more than 4 ºC.

    c) After filling, the composite container should be securely capped, labeled with pertinent information, and stored in a cooler at no more than 4 ºC until splitting is completed.

2. If possible, it is best to set the splitter up in an enclosed building space near the sampling sites that can be used as an ad-hoc laboratory. A space should be chosen that can be maintained in a clean condition and, ideally, can be reserved for sampling-related activities only.

    a) Next best would be to set the splitter up in an enclosed van or truck.

    b) If necessary, set the splitter up in the field at the sampling site.

        i) Try to select a field location close to the sample collection point and as level as feasible. If it is raining, protect the splitter from precipitation with some appropriate cover, such as a plastic tent.

3. Visually inspect the pre-cleaned cone splitter (see Appendix D) for any problems, such as broken or dirty parts, misalignment, or foreign material, especially in threaded parts such as tubing connectors.

4. Use a bullseye bubble level, as in Figure 3, to level the splitter.

    a) The cone splitter does not have adjustable legs for leveling. Some possibilities for leveling it are:

        i) Make a platform from a plywood square or circle with three leveling screws threaded through it that can be screwdriver adjusted.

        ii) Attach a wooden platform to an adjustable tripod head.

        iii) Modifying the legs of the apparatus so they are adjustable, like a camera tripod, could be a valuable permanent modification of the splitter.

        iv) A quick fix is to have a small collection of carpenter's shims available for shimming the legs.

    b) Excessive care in leveling is not necessary, but the bubble should be reasonably centered.

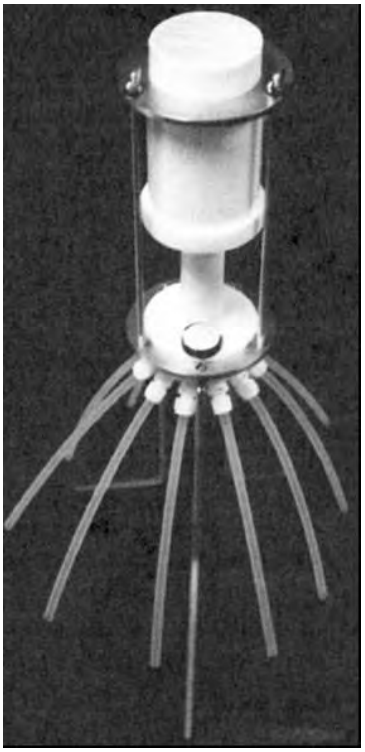

Figure 3: Cone Splitter with bubble level on lower flat surface.

5. Securely connect pre-cleaned fluorocarbon (Teflon®) tubing to each outlet.

    a) Every outlet must have an identical tube (equal diameters and lengths) attached to assure uniform flow conditions at each outlet. No outlets should be closed to flow.

    b) When pre-rinsing the splitter, outlet tubes can empty rinse water to a waste container.

    c) When collecting split samples, outlet tubes are inserted into the laboratory containers that receive the splits for analyses. Tubes not used for split samples can empty to a waste container.

    d) Containers will generally have to be supported so their openings are at the same level and to assure they cannot accidentally be tipped over during splitting.

        i) If the same container arrangement is always used, the wooden platform used for leveling can be fitted with wooden blocks predrilled to hold the containers securely at the correct heights.

        ii) For greater flexibility, short lengths of 2-inch aluminum angle stock can be mounted vertically at each container position on the leveling platform. Containers can be attached securely to the open side of the angle with small bungee cords and with wooden blocks beneath the containers to adjust their heights.

        iii) Aluminum rods, with three-finger laboratory clamps and clamp holders can be substituted for the setup in ii.

6. Wet the splitter and attached tubing by pouring through 1 or 2 liters of deionized water. Lightly tap the system to dislodge adhering water drops and discard all the water.

7. Rinse again, this time using 2 to 4 liters of the source water to be sampled. Lightly tap the system to dislodge adhering water drops and discard all the water. Place laboratory containers under the outlet tubes.

    a) Laboratory containers are never pre-rinsed before use.

    b) Outlet tubes should enter the container opening to avoid spilling, but should not become submerged below the sample surface. This insures that different back pressures at the tubing exits do not influence flow rates.

    c) Laboratory containers used for dioxin analysis should be protected from light exposure. Use amber glass containers or wrap containers with a light shield such as aluminum foil.

d) Two or more outlet tubes can be combined into a single container to collect different volumes of the original sample, see Figure 2 and Appendix B.

   i) If combining multiple outlet tubes into a single container, make sure all tubes permit free flow so that no unequal back pressures can develop.

e) Direct sample discharge from unused outlet tubes to a waste container.

3d. Collecting Grab Samples To Be Used with the Cone Splitter

Use only pre-cleaned glass sample collection and compositing containers. The collection container should be a wide-mouth amber glass bottle of convenient size for immersing into the source flow (up to 1-liter) and the compositing container should be a clean, minimum of 1-gallon glass bottle, either amber colored or wrapped with a light shield, which is filled repeatedly as necessary from the collection container. Both containers should have clean closure caps with Teflon® seals.

1. Wear disposable powder-free nitrile gloves when sampling or handling sampling equipment, including the cone splitter.

   a) When holding any sample container for collecting, pouring, labeling, or any other activity, keep your gloved hands away from the region of the container opening, even if it is capped, in order to prevent contaminating the sample. Contamination of a sample is still possible when a capped container that was contaminated near its opening in the field is re-opened in the laboratory.

2. Prepare both the pre-cleaned collection and compositing containers by pre-rinsing each at least 3 times with the water being sampled. Exposing sorption sites on the container walls to COCs in the rinse water will minimize additional sorption from the samples.

   a) Pre-rinsing needs to be done only once for both containers, prior to collecting the first sample from the source and starting to fill the compositing container for pouring through the splitter.

   b) When pre-rinsing the collection and compositing containers, cap and shake them to also expose the inside surface of the cap to the rinse water.

   c) For flows too small to collect into a 1-liter collection container, use a sample-rinsed standard 40-mL amber glass VOA vial. Do not collect from small flows into a container with a small entrance opening (such as a syringe), as this preferentially biases the sample against large sediment particle sizes.

   d) Keep the compositing container capped except when pouring collected samples into it.

3. Collect an environmental sample by submerging the collection container in a central portion of the flow, opening first.

    a) While in the flow, position the collection container so its opening is pointing into the flow to fill it.

    b) Hold the collection container on its body away from its opening.

    c) Avoid stirring up settled sediments. If necessary, use a smaller container.

    d) Return the filled container quickly to the surface.

4. Pour the sample from the filled collection container into the compositing container and recap the compositing container until the next grab sample is added.

5. Repeat steps 3 and 4 (without additional pre-rinsing of the collection bottle) until 3 to 4 liters of sample have been transferred to the compositing container.

    a) It is important that the entire sample in the compositing container is poured through the splitter to avoid leaving any sediment behind.

    b) For this reason, it is best to try to collect just enough total sample in the compositing container to fill all the laboratory containers with the desired volumes for laboratory analyses. Too little is better than too much because any sediment left in the compositing container after pouring will be biased toward larger sediment sizes.

    c) Appendix B describes a procedure for filling the compositing and laboratory containers with the correct volumes.

6. After each sampling event, discard the sample collection containers (or return them to the laboratory for cleaning). Do not reuse them for another sampling event. Simple rinsing of the containers with deionized or distilled water is not acceptable.

    a) The most common source of field-related COC contamination is from re-use of sampling equipment and containers (grab samplers, tubing, buckets, containers, etc.) because COCs, especially dioxins, can concentrate into low solubility organic layers that build-up on the container wall with re-use.

3e. Adding the Composited Sample to the Cone Splitter

1. Shake the sample in the capped compositing container for 10 to 15 seconds.

2. Quickly uncap the compositing container and invert it over the cone splitter top reservoir, allowing it to fully empty into the splitter. You are trying to prevent significant settling of sediments while pouring.

a) Position the splitter low enough so the compositing container does not have to be lifted too high into an awkward position for easy pouring.

b) When smaller containers are used, they may be rested it on the reservoir top.

c) It may be necessary to place a filter screen over the reservoir opening to capture debris from sediment, plants or insects that could potentially clog the splitter.

    i) If required, captured debris can be removed from the screen and analyzed separately.

    ii) Carefully cleaned (and tested by analyzing equipment blanks) fiberglass window screening may be used.

3. After the flow has stopped, tap the compositing container and splitter assembly to dislodge adhering drops into the attached laboratory containers.

    a) Visually examine all attached laboratory containers. Water levels should be the same in identical containers. If not, examine the splitter and outlet tubing for partial clogging, out-of-level positioning, or misaligned components.

    b) If any problems are found, correct them, pour all subsamples back into the composite container (if no preservatives were in the sample bottles), and split again.

        i) Such problems are expected to be rare, but the possibility might be a good reason to wait until laboratory samples are removed from the splitter before adding preservative (unless containers are routinely obtained from the laboratory with preservatives already added).

4. Remove laboratory containers from the splitter, cap them securely, attach identifying labels, and place containers into the storage cooler for transport, concluding the sample splitting event.

    a) Sample containers can be placed in separate Ziploc bags to prevent labels from blurring by moisture or falling off and getting lost.

5. After each splitting event, discard the sample compositing containers (or return them to the laboratory for cleaning). Do not reuse them for another splitting event. Simple rinsing of the containers with deionized or distilled water is not acceptable.

    a) The most common source of field-related COC contamination is from re-use of sampling equipment and containers (grab samplers, tubing, buckets, containers, etc) because COCs, especially dioxins, can concentrate into low solubility organic layers that build-up on the container wall with re-use.

6. The cone splitter must be rinsed with at least 3-liters of deionized water after each composite split from the same site and runoff event.

    a) The splitter must be Level 1-cleaned after each composite split from different sites on the same day, and Level 2-cleaned after all samples collected on the same day have been split, see Appendix D.

4. REFERENCES CONSULTED

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8. “Cleaning a Cone Splitter” Office of Water Quality Technical Memorandum 97.03, Subject: Protocols for Cleaning a Teflon Cone Splitter to Produce Contaminant-Free Subsamples for Subsequent Determinations of Trace Elements, http://water.usgs.gov/admin/memo/QW/qw97.03.html

APPENDIX A
Laboratory Reporting Requirements for Identifying Laboratory QA/QC Problems

(Elizabeth Wessling)

In order to accurately compare sample results from different laboratories, it is necessary to evaluate all aspects of the sample preparation and analysis. To accomplish this evaluation, all laboratory documentation from time of receipt to reporting of the sample results for each analytical method along with the associated QC information must supplied by the laboratories. The following outlines the documentation that must be provided for each general type of analysis.

All sample receiving information including the executed chain-of-custody, airbills, sample receipt checklists, sample delivery group (SDG) assignment sheet, and any other correspondence relevant to the SDG will be provided.

Organics

Case Narrative inclusive of each analytical method:

- Sample Result Forms (one complete sample result form for each analysis, reanalysis, or dilution analysis)
- Surrogate Recovery Forms (may be included on the sample result form)
- MS/MSD Summary Forms
- LCS/LCSD Summary Forms
- Method Blank Summary Forms
- Tuning and Mass Calibration (GCMS methods)
- Initial Calibration
- Continuing Calibration
- Sample Run Logs GC
- Internal Standard (Isotope Dilution) Recovery Summary
- Intercolumn Comparison for GC

In addition to the summary information, all supporting raw data (chromatograms, quantitation sheets, and spectra) for all samples, standards, tunes, QC samples, percent solid calculations, benchsheets, and run logs must be included in the data package.

Inorganics

Case Narrative inclusive of each analytical method:

- Sample Result Forms
- Part 1 Initial and Continuing Calibration Verification
- Part 2 CRDL Standard
- Blanks
- ICP Interference Check Sample
- ICPMS Tune for ICPMS methods
- Internal Standards for ICPMS
- Spike Sample Recovery

- Post Digestion Spike Sample Recovery (if performed)
- Duplicates
- Laboratory Control Sample
- Standard Addition Results (if performed)
- ICP Serial Dilutions
- ICP Interelement Correction Factors
- ICP Linear Range
- Preparation Logs
- Analysis Run Logs

In addition to the summary information all supporting raw data for all samples, standards, QC samples, percent solid calculations, distillation logs, digestion logs, benchsheets, and run logs will be included in the data package. All sample receiving information including the executed chain-of-custody, airbills, sample receipt checklist, SDG assignment sheet, and any other correspondence relevant to the SDG will be provided.

APPENDIX B
Filling the Compositing and Laboratory Containers with the Correct Volumes

Outlet tubes can be combined into a single container to collect various volume combinations of the original composited sample. Care must be taken however, when combining outlet tubes into one container, to make sure there is no backpressure resulting from bending the tubing in ways that restrict their flow.

Since the composited sample is always split into 10 equal parts, it is convenient to choose a total composited volume such that required laboratory sample volumes are close to a simple multiple of 1/10 of the composited volume.

Suppose that the following laboratory samples are required from a particular site: two 1-L splits for dioxin analysis and four 250-mL splits for metal analyses. A convenient collection scenario would be:

- Collect a composite volume of 4.5-L, which the splitter will divide into ten 450-mL portions.

- Connect each of the two 1-L laboratory containers to two adjacent outlet tubes. After splitting, each 1-L container will contain 900-mL of sample, which is probably close enough to the needed 1-L.

- Connect each of four 500-mL containers to one outlet tube. After splitting, each 500-mL container will contain 450-mL, with enough room to add acid for pH adjustment.

- Only 8 of the outlet tubes have been used, collecting a total of 3600 mL. Since no splitter outlet must ever be closed off, the two unneeded outlet tubes must be allowed to discharge the excess 900 mL to a waste container.

APPENDIX C
Initial Preparation and Performance Test of a New Cone Splitter

(Adapted from Reference 1)

1. Prepare a Splitter Performance Test Notebook (SCN) in which to record and save data from the inspection and Performance Test procedures below. Prepare the pages so that relevant observations can be conveniently checked off or notations made concerning the steps below. Date and initial each entry page as it is used.

2. Visually inspect the cone splitter and all of its parts for cleanliness and clean if necessary. Note relevant observations in the SCN.

3. Inspect the cone splitter housing and outlet ports. They should be smooth and symmetrical without any burrs or machining defects visible. Note relevant observations in the SCN.

4. Place the splitter on a stable platform or bench in a level position. Level it, preferably with a bulls-eye bubble level as in Figure 3, by shimming its legs. Note relevant observations in the SCN.

5. Connect 10 Teflon® outlet tubes to the outlet ports and mark the tubes 1 to 10, as in Figure 4.

    a) All tubes must be approximately the same length, long enough to enter the mouths of the receiving containers but not long enough to be submerged in the collected samples.

    b) Be sure all tubes are pushed as far as possible into the Swagelok fittings at the outlet ports. The tubing end should be flush with the flat surface on the inside of the port.

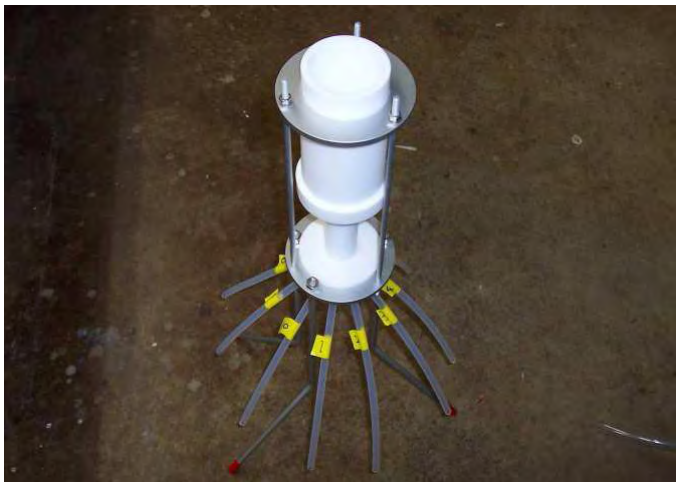

Figure 4: Cone splitter with outlet tubes attached and labeled 1-10.

6. Place receiving containers under the tubes.

    a) Outlet tubes should enter the container opening to avoid spilling, but should not become submerged below the sample surface. This insures that different back pressures at the tubing exits do not influence flow rates.

7. Wet and superficially clean the cone splitter by rinsing 2-3 liters of deionized water through it and discard the water.

    a) After rinsing, tap the apparatus to dislodge adhering water drops

8. Replace empty containers under each outlet.

9. Accurately measure approximately 3-4 liters of tap water into a l-gallon plastic bottle.

    a) Record the value in the SCN.

10. Rapidly invert the 1-gallon bottle over the reservoir, letting it flow as fast as possible. Rest the inverted bottle on top of the reservoir if desired.

    a) For proper operation, the splitter stand-pipe must be full and discharging at its full flowing capacity.

11. After all water has passed through the splitter, tap the assembly several times to dislodge adhering water drops.

    a) Check for spills and leaks. If any are observed, discard the test, correct the problem, and repeat the test.

12. Accurately measure the volumes of the 10 subsamples within ±1 mL (e.g., use a graduated cylinder). Record the volumes for each outlet in the SCN.

13. Repeat the test five more times for a total of six tests. Use approximately the same initial volume for each test.

Calculating Cone Splitter Performance Test Statistics

A Microsoft Excel spreadsheet application is provided to make all the necessary performance test statistical calculations from entered data. When data from the SCN is entered, the spreadsheet calculates:

For each of the 6 tests:

1. Total recovered sample volume.

2. Sample volume loss in splitter.

3. Average of outlet volumes.

4. Error (deviation from the average) for each subsample volume.
5. Standard deviation of all subsamples
6. Percent standard deviation

For the set of 6 tests:

1. Average total recovered volume.
2. Average outlet volume over all tests for each outlet.
3. Average percent error over all tests for each outlet.
4. Average standard deviation over all tests.
5. Average percent deviation over all tests.

Note the error patterns for individual outlets into the SCN, to determine which outlets show consistent bias. If significant, mark them with their average percent bias error.

The cone splitter is considered acceptable for sample processing if the average percent deviation for all 6 tests is 3.0 percent or less, and no individual outlet error exceeds ± 5.0 percent.

Table 1 is an example cone splitter performance test using the Excel spreadsheet.

Table 1: Sample cone splitter performance test calculations using MS Excel spreadsheet. Performance test data are entered into the highlighted cells.

CONE SPLITTER PERFORMANCE TEST CALCULATOR

(All volumes in mL)

Test 1			Test 2			Test 3		
Initial volume added =		2499.4	Initial volume added =		2499.5	Initial volume added =		2499.5
Outlet #	**Outlet vol.**	**% error**	**Outlet #**	**Outlet vol.**	**% error**	**Outlet #**	**Outlet vol.**	**% error**
1.0	248.4	-0.5	1.0	249.5	-0.1	1.0	247.4	-0.9
2.0	246.8	-1.1	2.0	246.8	-1.2	2.0	245.6	-1.6
3.0	249.4	-0.1	3.0	251.0	0.5	3.0	250.6	0.4
4.0	250.7	0.4	4.0	252.6	1.1	4.0	252.5	1.1
5.0	248.1	-0.6	5.0	248.3	-0.6	5.0	249.8	0.0
6.0	252.2	1.0	6.0	250.3	0.2	6.0	252.7	1.2
7.0	245.7	-1.6	7.0	246.2	-1.5	7.0	246.0	-1.5
8.0	252.7	1.2	8.0	254.2	1.7	8.0	252.9	1.3
9.0	248.7	-0.4	9.0	247.3	-1.0	9.0	247.5	-0.9
10.0	253.9	1.7	10.0	252.1	0.9	10.0	251.8	0.8
total recovered volume =		2496.6	total recovered volume =		2498.3	total recovered volume =		2496.8
sample loss =		2.8	sample loss =		1.2	sample loss =		2.7
average outlet volume =		249.7	average outlet volume =		249.8	average outlet volume =		249.7
standard deviation =		2.7	standard deviation =		2.7	standard deviation =		2.8
% standard deviation =		1.1	% standard deviation =		1.1	% standard deviation =		1.1

For each test run, enter performance data into shaded cells. The spread sheet will calculate the performance test statistics.

The cone splitter is acceptable if the average percent standard deviation is 3% or less and no individual outlet error exceeds ±5%.

Test 4			Test 5			Test 6		
Initial volume added =		2499.5	Initial volume added =		2499.5	Initial volume added =		2499.4
Outlet #	**Outlet vol.**	**% error**	**Outlet #**	**Outlet vol.**	**% error**	**Outlet #**	**Outlet vol.**	**% error**
1.0	248.1	-0.7	1.0	247.8	-0.8	1.0	247.8	-0.8
2.0	248.4	-0.5	2.0	246.3	-1.4	2.0	246.3	-1.4
3.0	251.1	0.5	3.0	249.8	0.0	3.0	249.8	0.0
4.0	251.3	0.6	4.0	251.8	0.8	4.0	251.8	0.8
5.0	249.3	-0.2	5.0	250.2	0.2	5.0	250.2	0.2
6.0	252.0	0.9	6.0	252.7	1.2	6.0	252.7	1.2
7.0	246.3	-1.4	7.0	246.6	-1.3	7.0	246.6	-1.3
8.0	253.3	1.4	8.0	253.1	1.3	8.0	253.1	1.3
9.0	247.1	-1.1	9.0	248.2	-0.6	9.0	248.2	-0.6
10.0	250.6	0.3	10.0	251.7	0.8	10.0	251.7	0.8
total recovered volume =		2497.5	total recovered volume =		2498.2	total recovered volume =		2498.2
sample loss =		2.0	sample loss =		1.3	sample loss =		1.2
average outlet volume =		249.8	average outlet volume =		249.8	average outlet volume =		249.8
standard deviation =		2.3	standard deviation =		2.5	standard deviation =		2.5
% standard deviation =		0.9	% standard deviation =		1.0	% standard deviation =		1.0

AVERAGES		
Outlet #	**Av. vol.**	**% error**
1.0	248.2	-0.6
2.0	246.7	-1.2
3.0	250.3	0.2
4.0	251.8	0.8
5.0	249.3	-0.2
6.0	252.1	0.9
7.0	246.2	-1.4
8.0	253.2	1.4
9.0	247.8	-0.8
10.0	252.0	0.9
av. recovered volume =		2497.6
average outlet volume =		249.8
av. standard deviation =		2.5
average % std. dev. =		1.0

APPENDIX D
Cleaning the Cone Splitter

(Adapted from References 2 and 8)

Table 2: Cleaning Supplies Required

Item	Comments
Acid solution	Either one of the solutions below is required. Hydrochloric, ACS trace element grade – 5% by volume in deionized water. Nitric, ACS trace element grade - 10% by volume in deionized water.
Methanol	ACS pesticide-grade. Methanol is toxic, flammable, volatile and absorbed through the skin. Wear gloves and observe safety precautions when handling.
Detergent	Non-phosphate laboratory detergent, such as Liquinox™ or Alconox™.
Aluminum Foil	For wrapping non-amber sample containers to exclude light.
Plastic sheeting	Non-colored, used for providing clean work surfaces.
Sealable bags	Polyethylene in various sizes for storing and protecting splitter parts. Larger trash bags can be used for storing the assembled cone splitter.
Brushes and sponges	Assorted sizes, non-colored, soft bristle, non-metallic; toothbrushes or small test tube brushes can be used to clean the splitter outlet ports.
Deionized or distilled water	Maximum specific conductance of 1 micro-Siemen/cm. Must not be used as a substitute for QA/QC blank water.
Gloves, disposable	Nitrile, powder-free, assorted sizes.
Laboratory blank-grade water	Blank water certified by a laboratory to be suitable for collecting inorganic and organic blank samples.
Jerricans or carboys	Suitable for waste and acid neutralization containers.
Acid neutralization materials	Marble (limestone) landscaping chips (1-2 cm chips recommended). Pour used HCL or HNO_3 solution into a neutralization container with marble chips covering the bottom. The solution can be discarded when narrow range pH indicator strips show a reading greater than 6.0.
Tap water	If tap water is available, use it for initial rinsing of detergent washed parts and for initial removal if encrusted soils. Otherwise, substitute deionized water.
Tissues	Laboratory grade, lint free (e.g., Kimwipes™.
Washbasins	One dedicated washbasin per cleaning solution (i.e., acid, methanol, detergent, etc.). May be plastic; stainless steel is recommended for methanol.
Squeeze wash bottles	Polyethylene for general use, Teflon© required for methanol bottle and any bottles used for QA/QC blank water.
Safety equipment	Material Safety Data Sheets (MSDS), safety glasses, chemical spill kit, laboratory coat or apron, emergency phone numbers, etc.

Introduction

For parts-per-billion (ppb) analyses, it is as important to carefully follow the cone splitter cleaning protocol as to follow the sampling and splitting protocols. The cleaning protocol below has been demonstrated to be adequate for trace metals and organics at the ppb level. However, NPDES dioxin limits at SSFL require sampling at the parts-per-trillion (ppt) level, which is uncharted territory for equipment cleaning protocols. For splitting surface runoff samples in which COCs are closely associated with sediments, as at SSFL, it has been shown that, at ppb levels, using a cone splitter produces more reliable analytical results than alternative methods. For ppt levels, using a cone splitter appears to be even more necessary. If equipment blanks should show that the cleaning protocol is not adequate for ppt dioxin sampling, improvements will have to be sought.

If the cleaning requirements of dioxin ppt sampling are found to be beyond present capabilities, it might be necessary to adopt statistical sampling procedures, similar to those used for microbiological COCs such as *E. coli*, where single grab samples are never assumed to be representative of the source.

The cone splitter must be cleaned each time before being used for splitting any new composited samples. A new composited sample is one collected from a different site on the same day or from the same site on a different day or the same site for a different sampling event on the same day.

1. Before using a previously cleaned splitter for the first time, always start by pouring 2 or 3 liters of deionized water through the splitter. Then collect an equipment blank.

    a) Collect the equipment blank by pouring 1-liter of laboratory blank-grade water through the splitter and collect all of it using all of the outlet tubes. Composite the entire collected equipment blank from the 10 outlet tubes into one 1-liter laboratory container. This equipment blank container is capped, sealed, labeled, and stored with the environmental samples.

    b) If no COCs are detected in samples collected before the next cleaning, the equipment blank does not need to be analyzed.

2. When splitting a series of samples collected from the same location and runoff event, rinse the splitter between samples with at least 3-liters of deionized water.

3. When splitting samples collected from different sites on the same sampling day, follow the Level 1 cleaning protocol (simpler than Level 2) between each split.

4. After all samples collected on the same day have been split, follow the Level 2 cleaning protocol (more thorough than Level 1) as soon as possible and store the cone splitter under clean conditions (see below) until the next sampling day.

5. Differences between the Level 1 and Level 2 cleaning protocols are:

    a) Level 2 requires complete disassembly of the cone splitter, whereas Level 1 does not.

    b) Level 2 includes a detergent soak-and-scrubbing step, whereas no detergent is used to clean the cone splitter in Level 1.

    c) Level 2 includes a 30-minute acid soak, whereas a single acid rinse is used in Level 1.

Level 1 Cleaning Protocol

- Level 1 cleaning is used each time before the splitter is used for processing samples collected from different sites on the same day.

- The cone splitter need not be cleaned between processing successive multiple samples collected from the same site.

- The splitter must not be allowed to dry between Level 1 cleanings.

- A Level 2 cleaning is required if the splitter has dried before being cleaned or was used for splitting samples with known or suspected high concentrations of trace elements.

Inspect the cone splitter. If it appears dirty, is suspected of being contaminated, or has been allowed to dry, then it should be fully disassembled and cleaned using the Level 2 cleaning protocol described below. Otherwise, proceed with the Level 1 protocol.

<u>Level 1 Cleaning Steps</u>

1. Discard any used plastic bags from storing the cone splitter.

2. Rinse the splitter with at least 3-liters of deionized water.

3. Wearing disposable gloves, rinse with one liter of 5-percent by volume HCL to remove any adsorbed metals.

    a) The used acid/water solution should be placed in a neutralization container for proper disposal.

4. Change gloves and rinse the cone splitter with at least three 1-liter aliquots of deionized water.

5. If the next subsamples to be collected are to be analyzed for metals only and not for organics (including dioxins), omit steps 6-9.

6. Using a Teflon® wash bottle, rinse splitter reservoir interior with 250-500 mL of pesticide-grade methanol (methyl alcohol) to remove adsorbed organic contaminants. Allow the liquid to drain through all the outlet tubes to waste containers and disposed of properly.

    a) Methanol is flammable, volatile, a skin and lung irritant and poisonous if ingested. Read its attached Material Safety Data Sheet before using. Use methanol sparingly in a well ventilated area, away from open flames or sparks. When possible, performing this rinsing step in a hood is preferred.

    b) A methanol rinsed cone splitter may not be used for obtaining subsamples to be analyzed for total particulate carbon (TPC), particulate organic carbon (POC) or dissolved and suspended organic carbon (DOC) analyses. Omit the methanol rinse if these analyses are needed.

7. Dispose of gloves used in the methanol rinse.

8. Wearing new gloves, rinse methanol from the splitter with laboratory blank-grade water from a wash bottle, paying special attention to the upper part of the reservoir. Collect the rinse water through all outlet tubes to waste containers.

9. Follow the wash bottle rinse by pouring 3-liters of laboratory blank-grade water through the splitter, collecting the rinse water through all outlet tubes to the same waste containers.

10. The splitter is ready to process a new composited sample from another site or sampling event.

11. When all samples collected on the same day have been processed, clean the cone splitter using the Level 2 protocol prior to storage.

Level 2 Cleaning Protocol

Level 2 cleaning is used:

- Before using a new splitter the first time.
- After all samples from a given sampling day have been processed.
- Any time the splitter has been allowed to dry before being cleaned.
- Any time the splitter has been used with samples with known or suspected high concentrations of trace elements.

Level 2 Cleaning Steps

1. Prepare a contaminant-free space for working.

    a) Gather the cleaning supplies, the equipment to be cleaned and plastic bags with which to double-bag and seal bag the cleaned equipment. Check Table 2 for the cleaning supplies needed.

    b) Place clean plastic sheeting over the work surface.

2. Put on disposable, powder-free nitrile gloves, a laboratory coat or apron, and safety glasses.

3. Clean the items used to clean the equipment.

    a) Fill superficially clean washbasins with the non-phosphate detergent solution. Put wash bottles, scrub brushes, and other small items used for cleaning into a washbasin. **Soak for 30 minutes.**

    b) Scrub interior and exterior sides of basins with soft scrub brushes. Fill wash bottles with a soapy solution and shake vigorously.

    c) Rinse all items thoroughly with tap water to remove detergent residue. No detergent bubbles should appear when fresh tap water is agitated in the basin or wash bottle.

    d) Rinse washbasins with deionized water.

    e) Pour 5-percent HCl (or 10-percent HNO_3) solution into washbasins, standpipes, and wash bottles. Soak for 30 minutes.

    f) Discard used acid solution into a neutralization container containing a bottom layer of marble chips.

    g) Rinse washbasins and wash bottles with deionized water.

4. Unwrap the equipment to be cleaned and discard the storage bags. Change gloves.

5. Fully disassemble the cone splitter, carefully safeguarding all of the small parts.

6. Soak the splitter parts and Teflon® outlet tubing for 30 minutes in a 2-percent (for hard water) or less solution of phosphate-free laboratory detergent. Use a cleaned basin for soaking.

7. Wearing disposable nitrile gloves, scrub all surfaces with a nonmetallic brush.

    a) A clean tooth brush or small soft-bristle test tube brush can be used to clean the small splitter parts.

b) Pay particular attention to removing foreign material from threaded and hard-to-access parts.

8. Rinse all splitter parts thoroughly with deionized water.

9. Soak non-metal parts for 30 minutes in a 5-percent, by volume, solution of HCl. Carefully swirl the acid solution several times during the 30-minutes soak to enhance desorption of trace elements not removed during the detergent washing process.

    a) Discard used acid solution into a neutralization container.

10. Change gloves and rinse all splitter parts three times with 1-liter aliquots of deionized water.

    a) Allow all parts to air-dry.

    b) Discard the rinse water in a neutralization container.

11. Reassemble the cone splitter and double-bag and seal it in plastic bags for storage.

Storage of Level 2-Cleaned Cone Splitter

1. Before reassembling and storing, cone splitters always should be visually inspected for damage especially the cone splitting chamber. Units that show damage or wear should be recalibrated to check their serviceability. Check discharge tubing frequently for proper length and cleanliness. Replace tubes as conditions warrant.

2. Allow the cone splitter to dry. If the splitter will be used again within 3 days, it need not be dry when stored providing it is kept chilled to prevent bacterial growth.

3. Double-bag the cone splitter into new clean plastic bags. Seal each bag separately.

APPENDIX E
Inherent Variability in Parts-Per-Billion Analyses of Low Solubility Pollutants

This appendix contains a very brief description of certain statistical and technical limitations inherent in the sampling and chemical analysis of parts-per-billion (ppb) concentrations of low solubility pollutants such as dioxins and certain metals. Although the following discussion contains information about dioxins, the same issues apply to any low solubility pollutant that must be analyzed at ppb concentrations.

Analytical Variability

Analytical limitations introduce a significant and unavoidable degree of variability in the reported results. As a current example, the expected variability of repeat measurements on a single sample containing 2,3,7,8-TCDD at $3x10^{-8}$ mg/L (30 pg/L)[2] seems to be between ±25% to ±10% (measured as %- relative standard deviation, RSD), depending on the amount of interfering substances in the sample.[3] This is a laboratory-induced variability that must be added to the field sampling variability, which has been reported to be as large as ±30% for particulate sample types.[4]

No data could be found for the expected variability at lower concentrations comparable to SSFL NPDES limits. However, as sample concentration decreases for the same analytical method, precision inevitably decreases and expected variability increases. Achieving acceptable analytical results for SSFL NPDES samples requires extreme rigor and consistency in all the separate analytical steps of sample extraction, concentration, calibration, and instrumental operation.

The two main reasons for this variability in dioxin measurements are:

- The very low water solubility of dioxins in general.
    - The water solubility of 2,3,7,8-TCDD (TCDD) is 19x10-6 mg/L. In general, all of the dioxin congeners containing 4 or more chlorine atoms have similar low water solubilities.
    - Low solubility causes dioxins in environmental water samples to be largely associated with sediments. Although the TCDD solubility of 19x10-6 mg/L is greater than the EPA drinking water MCL for TCDD (3x10-8 mg/L), it is small enough to result in most water-borne dioxin molecules being bound to sediments.

[2] 30 pg/L ($30x10^{-12}$ g/L) is the EPA drinking water standard and is a common requirement for analytical samples. It is about 1000-times larger than the SSFL NPDES limits.

[3] This value is estimated from information in the EPA Method 1613 document, some reported values from the literature, and a telephone discussion with the Chief Analyst at Pace Laboratories.

[4] "Femtograms or phantomgrams? An analytical view of the organochlorine issue", Ray Clement, Ontario Ministry of Environment and Energy, Laboratory Services Branch, Chemical Institute of Canada, 1997, http://www.thefreelibrary.com/Femtograms+or+phantomgrams%3F+an+analytical+view+of+the+organochlorine...-a020029520.

- Because of suspended sediment (TSS) inhomogenieties, TSS samples from the same source tend to have higher variability in their measured concentrations than would be the case for dissolved analytes. Standard Methods[5] reports an analytical precision (standard deviation) of 21.20 mg/L for TSS analyses of water samples containing 293 mg/L of a TSS standard. This is equivalent to an RSD of ±7.2%.

- When dioxins are distributed between dissolved and solid phases, extra analytical processing steps are required for filtration, drying the solids, different extraction procedures to separate the analyte from the solid and from water, and recombining the extracted analytes into a single sample; all before concentrating the sample to increase analytical sensitivity.

- The necessity to quantitatively measure the analyte at a very low concentration.

  - This requires that at least 1 liter of collected sample be extracted and concentrated. At least 5% of the concentrate must be injected into the GC/MS instrument to assure that there is enough dioxin present in the injected sample to obtain the required sensitivity. To analyze for 30 pg/L of dioxin, the lab calibrates with 10 pg/L spikes and adjusts instruments for a 1 pg/L detection limit. Measurement errors can be introduced in every step. The laboratory reporting requirements listed in Appendix A illustrate the many potential sources of error inherent in part-per-billion laboratory analyses.

Sampling Variability

Sampling procedures introduce additional measurement variability, which must be added to the analytical variability. Dioxins in stormwater tend to concentrate on suspended solids carried in the flow and it is essentially impossible to collect sequential samples from the same source in which the solids and, consequently, the dioxins are equally distributed.

The greatest source of stormwater sampling variability comes from fluctuations in the suspended solids content of different samples collected at the same time from the same source. Replicate samples collected sequentially, whose percent solids levels vary significantly between replicates, will have poor agreement in dioxin concentrations between replicates. The percent standard deviation of dioxin concentrations for samples of equal sediment concentrations depends on the sample size, increasing as sample size decreases.

Thermal mixing assures that the dissolved portion of dioxin is uniformly distributed, but the sediment-sorbed portion will be spatially variable for several reasons:

[5] Single-laboratory analyses of 77 samples containing a known TSS of 293 mg/L. "Standard Methods for the Examination of Water and Wastewater", 19th edition, 1995, A.D. Eaton, et al., Eds., American Public Health Assoc., Washington, DC.

- Particles with different masses are transported in flowing water at different velocities and settle vertically at different rates.

- Different sediment particles can have different surface areas because they may be of different sizes, have different porosities, and have different weathering histories.

- Dioxins will sorb differently to particles of different chemical origins. In general, for equal weights, organic sediments will contain more dioxin than inorganic sediments.

- Particles from different sources may have different densities and will not be homogeneously distributed throughout the sample volume.

Even if a single large sample were theoretically split precisely into smaller replicates, each containing exactly the same sediment concentrations, there still would be variability in their dioxin concentrations because different sediment particles will contain different numbers of sorbed dioxin molecules. The smallest dioxin variability would only be achieved if all replicates contained identical particle size distributions, identical particle density distributions, identical particle surface area distribution, and identical distributions of organic and mineral sediments, a presently impossible goal.

At the present time, the cone-splitter appears to be one of the best methods for splitting stormwater samples. It is simple to use and has been shown to more reliably split aqueous samples with significant solids or sediment content than the more commonly used tilt and pour method, which has poor repeatability and yields split samples with widely varying solids concentrations and particle size distributions.